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Technological gaps inhibiting the exploitation of CRMs primary resources

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DELIVERABLE 6.1:

TECHNOLOGICAL GAPS AND BARRIERS ON PRIMARY RESOURCES

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ABOUT THE SCRREEN PROJECT

Since the publication of the first list of Critical Raw Materials (CRM) in 2010 by the Ad-hoc Working Group on CRM, numerous European projects have addressed (part of) the CRMs value and several initiatives have contributed to gather (part of) the related community into clusters and associations. This led to the production of important knowledge, unfortunately disseminated. Numerous databases have also been developed, sometimes as duplicates.

The SCRREEN project aims at gathering European initiatives, associations, clusters, and projects working on CRMs into a long-lasting Expert Network on Critical Raw Materials, including stakeholders, public authorities and civil society representatives.

SCRREEN will contribute to improve CRM strategy in Europe by:

- (i) mapping primary and secondary resources as well as substitutes of CRMs,
- (ii) estimating the expected demand of various CRMs in the future and identifying major trends,
- (iii) providing policy and technology recommendations for actions improving the production and the potential substitution of CRM,
- (iv) addressing specifically WEEE and other End-of-Life (EoL) products issues related to their mapping and treatment standardization, and
- (v) identifying the knowledge gained over the last years and easing the access to these data beyond the project.

The project consortium also acknowledges the challenges posed by the disruptions require the development of new CRM strategies. For this reason, stakeholder dialogue is at the core of the SCRREEN project: policy, society, R&D and industrial representatives are involved to facilitate strategic knowledge-based decision-making to be carried out by these groups. Specific attention will also be brought on informing the general public on our strong dependence on imported raw materials, on the need to replace rare materials with substitutes and on the need to set up innovative and clean actions for exploration, extraction, processing and recycling.

Introduction

This task capitalizes on the outputs of WP4 and the mapping of primary resources of CRM conducted in WP3. The main goal is to identify the technological gaps and barriers for the development and uptake of technologies for primary resources' mining, processing, recovery and recycling activities. This analysis will contribute to determining the needs for policy instruments, market-related settings, training and technological development to promote a robust display of new technologies that broadens CRM's supply within Europe. To do so, for every selected primary CRM, a description of the reserves of EU countries is presented, followed by the identification and analysis of the technological gaps and barriers of the mining, processing and recycling processes. Finally, an assessment of the environmental impacts of alternative technologies and waste treatment processes is carried out for those CRM in which relevant information has been found.

TECHNOLOGICAL GAPS AND BARRIERS IN PRIMARY RESOURCES

ANTIMONY

1. THE PRIMARY RESOURCES

The most important antimony minerals present in exploited ore deposits are: stibnite (Sb_2S_3), berthierite (FeSb_2S_4), boulangerite ($\text{Pb}_5\text{Sb}_4\text{O}_{11}$), stephanite (Ag_5SbS_4), jamesonite ($\text{Pb}_4\text{FeSb}_6\text{S}_{14}$), bournonite (PbCuSbS_3), tetrahedrite ($(\text{Cu,Fe})_{12}\text{Sb}_4\text{S}_{13}$), freibergite ($(\text{Ag,Cu,Fe})_{12}(\text{Sb,As})_4\text{S}_{13}$), gudmundite (FeSbS), ullmannite (NiSbS), dyscrasite (Ag_3S), breithauptite (NiSb), kermesite ($\text{Sb}_2\text{S}_2\text{O}$), valentinite/senarmontite (Sb_2O_3). Stibnite is the principal source of mined antimony. However, despite this mineral being widely distributed, it is not common to find economically valuable deposits [1].

Generally mined antimony bearing deposits contain from 0.1 to 2 wt.% Sb, and antimony is a by-product of gold, silver, lead or zinc sulphidic ores. The presence of precious metals is often a deciding incentive for parallel antimony recovery.

The list of major world antimony mining companies comprises [1]:

- China: Hsikwanghan Twinkling Star, Hunan Cheznu Min., China Tin Group, Shenyang Huacheng Antimony.
- Australia: Mandalay Resources.
- Russia: GeoProMining.
- South Africa: Murchison Consolidated.
- Tajikistan: Anzob.
- Turkey: Cengiz & Ozdemir Antimuan Madenleri.

According to the resource-mapping results of WP3, during the period 1996-2000 no mine production of antimony or of antimony metals or powders within the EU-28 was undertaken. Some antimony oxides are believed to have been produced but no robust data are available in literature.

2. GAPS & BARRIERS – PROPOSED PROCESSING ROUTES

The mineral processing of mined ores is a rather tedious activity, comprising crushing, sorting (including sometimes hand sorting, e.g. in Chinese mining companies), grinding and physical separation techniques, such as gravity upgrading and flotation. This latter produces upgraded

concentrates with different value (from above 5 wt.% Sb to about 60 wt.%Sb), leaving behind gangues and tailings with Sb content of about 0.2 wt.%, that should be landfilled according to local environmental law.

The other primary source for antimony recovery consists of the by-products from refining of crude lead recovered from processing of primary copper and lead-zinc concentrates. In this case the usual route of action is smelting of antimonial lead, with Sb content up to 20%, suitable for manufacturing of different Pb-Sb alloys according to market demand.

The upgraded antimony concentrates from primary source (ore mining and mineral processing) contain different Sb concentrations, what determine the methods applied for their processing- either pyrometallurgical or hydrometallurgical [2].

Pyrometallurgical Methods

Generally, the concentrates of the lowest grade of sulphidic type (with 5-25% Sb content) are volatilized to raw Sb_2O_3 ; the medium grade (with 25-40% Sb content) are smelted in blast furnace; and the high-grade concentrates (with 45-60% Sb content) are processed by liquation or reduction with iron (so-called iron precipitation). These methods are characterized in more detail below [2].

- Oxide volatilization
- Sulphide liquation
- Oxide reduction
- Iron precipitation
- Blast furnace smelting

Hydrometallurgical Methods

Hydrometallurgical methods are useful for processing all kinds of antimony concentrates. Generally, these methods comprise two-stage leaching followed by electrowinning. Only two lixiviant systems are currently available to be used for leaching of antimonial charges: alkaline sulphide system and acid chloride system, whereas the former predominates.

- The alkaline sulphide system
- The acidic chloride system

MINING

There is no current reported Antimony mining activity in EU, although it took place in the past. Besides the absent production, several deposits have been reported and countified. WP3 highlights known occurrences and/or deposits for each of the CRM within the EU28. However,

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for any material to be produced within a country its production must be economic and it must be competitive with other countries of the world.

BENEFICIATION

Some beneficiation techniques that have been studied in order to improve flotation are briefly hereto described:

At the Russian Skalnog, for antimony-arsenic ores, several new agents have proved their efficiency in antimony recovery through flotation. OKSAFOR 43 and PEMISOL show very good collecting properties: OKSAFOR 43 provides the highest efficiency for antimonite, to 3 mg/l concentration of the agent corresponds 98.9 % yield of the mineral. A 15 mg/l concentration of agent O-1107 and PEMISOL allowed 87-89% antimony recovery. Other composites which presented good efficiency are Dibutyldithiophosphate ammonium and Ethylaminoxanthate. Such processes are considered potentially useful for deposits in Austria where polymetallic ores can be found [3].

At the Sarylakhsy and Sentachansky Deposits (Russia) hydrazine $N_2H_{21}/2H_2SO_4$ as an activator was studied for Au-Sb ores. Hydrazine addition at rate of 8 g/t improves flotation parameters and reduce loss of antimony by 0.4 % and gold by 30 %. A recovery rate of Sb-63.01%, Au-12.8 g/t (ppm) was obtained. The results show that the described method could be suitable for Bulgarian explored Au-Sb ores [4].

The following method, involving the application of sulfate-reducing bacteria *Desulfovibrio Desulfuricans*, has been used for antimony concentration at the Tyrny-Auz (Russia) tungsten-molybdenum deposit. Such bacteria have been used for mercury and antimony separation and extraction of oxidized antimony minerals. The reported method is potentially useful in Austrian deposits where polymetallic Sb ores can be found. A mixture of sodium hydroxide and sulphate-reducing bacteria was used as solvent, reaching a 96-98% antimony extraction rate [5].

METALLURGY

The upgraded antimony concentrates from primary sources (ore mining and mineral processing) contain different Sb concentrations, which determine the methods applied for their processing, being either pyrometallurgical or hydrometallurgical methods.

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- Oxide volatilization
- Sulphide liquation
- Oxide reduction
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- Blast furnace smelting

Hydrometallurgical Methods

Hydrometallurgical methods are useful for processing all types of antimony concentrates. Generally, these methods comprise two-stage leaching followed by electrowinning. Only two lixiviant systems used for leaching of antimonial charges are currently available: alkaline sulphide system and acid chloride system, whereas the former predominates.

- The alkaline sulphide system
- The acidic chloride system

Some innovative technics are described in detail in [7]. Sulfide alkaline leaching of gold antimony concentrates after electrolytic recovery of antimony from solutions enabled extraction of 98 % gold and 96.5 % antimony to marketable products. Ferric chloride leaching of Au-concentrates, proceeding from a Au – Sb concentrates with the content of 62 % Sb, 25 % S, 14 g/t Au, produced 99.1 – 99.3 % antimony passing to solution; 95 – 96.0 % gold was left in cake, which is 11 g/t; and antimony content in the cake was 3.3 – 4.0 %.

BARYTE

1. THE PRIMARY RESOURCES

Baryte or barite (BaSO_4) is a naturally occurring barium sulphate mineral. It can contain strontium and forms a complete solid solution series to the mineral celestite (SrSO_4). It is generally white or colourless, depending on the presence of impurities. Baryte deposits are found throughout the world in a variety of geological environments. Three major types of baryte deposits are stratiform, vein and residual. Most baryte is now produced from stratiform deposits [8].

According to the outputs of WP3 and WP4, baryte deposits are limited in EU member countries (minor deposits still exist in Germany, Romania and Greece). Major deposits of the mineral occur in Brazil, Nigeria, Canada, Chile, China, India, Pakistan, Guatemala, Iran, Mexico, Morocco, Peru, Turkey, South Africa and US. Small vein type barite deposits occur throughout

In 2015, production in the EU28 amounted to 178,811 tonnes from Bulgaria, Germany, Italy, Slovakia and the United Kingdom. This was, however, a significant decline compared to production in the recent past when output was also recorded in Belgium, France, Greece, Poland, Portugal, Romania and Spain. The barite market is significantly high in oil-producer countries. For example, in US more than the 97% of 2.4 million tons of barite concentrate are consumed by the crude oil industry [8].

Baryte occurrences are identified in several EU countries. In Belgium the Fleurus deposit was intermittently in production during the 20th century and has a remaining resource of 0.3 Mt of ore according to the Minerals4EU database [9]. In Bulgaria, resource information is available for the Divlya baryte deposit, which has an inferred mineral resource of 124,000 t of ore and the Kremikovtsi iron deposit, where baryte is present as a possible by-product in the probable mineral reserve of 68.2 Mt of ore. On the other hand, the ProMine database [10] suggests more than 12 Mt of baryte for Kremikovtsi.

France has historically been an important baryte producer with numerous small deposits and some larger ones having been in production. The most common mineral associations are baryte-fluorspar-lead-zinc, with baryte being either the main commodity or a possible by-product. Currently, the most important deposits are in Chaillac (Les Redoutières, Raillier), which have a proved mineral reserve of 900,000 t of baryte ore and a measured mineral reserve of 200,000 t. In Germany two deposits are currently mined for baryte obtaintion: Grube Klara in the SW of Germany and Niederschlag in the SE. In 2016, 95,345 t of baryte ore was mined at Grube Klara [9].

In Poland five baryte deposits are listed from Poland both at the ProMine database and by the Polish Geological Institute. Some of the deposits have been in production and there have been plans for re-opening some of them according to the Polish Geological Institute. Baryte resources in Poland are estimated to be 5.67 Mt [11].

Three baryte deposits are listed in Sweden [9]. The largest is the giant Aitik copper-gold deposit in northern Sweden that contains an unexploited baryte resource. Two small deposits (Hartung-Pottäng and Strömnäs Västra) are also mentioned but there is no resource information available for any of the deposits.

In the UK, currently the only operating mine where baryte is the primary product, is the Foss Mine, near Aberfeldy in Scotland, operated by M-I Swaco, a subsidiary of Schlumberger. This stratabound, sedimentary exhalative deposit was discovered in 1973 and is of late Proterozoic age. The high-grade mineralisation occurs in the Ben Eagach Schist formation, with the mineralised zone extending intermittently over a 7 km strike length and up to 110 metres in thickness [12]. The Foss Mine has been operated since 1985 and personal communication in August 2014 indicated there was approximately 0.9 million tonnes of resource remaining. Production is expected to cease once the new extraction begins at the nearby Duntanlich deposit.

Aside from the resources remaining in the Foss mine, the UK's resources include the Duntanlich deposit, also near Aberfeldy in Scotland. This deposit is very similar to that at the Foss mine, being of the same type, age and within the same strike length. It received planning permission in September 2016 and the company, M-I Swaco, expect to begin extraction towards the end of 2018 [13]. Duntanlich contains a measured resource of 7 million tonnes, with an additional inferred resource of 13 million tonnes.

2. GAPS & BARRIERS – PROPOSED PROCESSING ROUTES

MINING

Mining methods vary according to the type of deposit. Major stratiform deposits are exploited by open pit where possible. The ore is drilled and blasted and then trucked to the mill for pressing. Conventional underground methods are used as appropriated to the shape and altitude of the deposit [8].

Following initial crushing, some amount of baryte is sold as 'direct shipping ore' if it is sufficiently pure. If there are contaminants such as fluorite, quartz, galena or pyrite, **gravity separation and flotation** are used to separate them after grinding. Then the concentrate is either dried and sold as a powder or further processed for specific applications.

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In **gravity separation** the techniques of washing, desliming, screening, jigging and shaking tabling are used.

Flotation is used when sulphides (galena, sphalerite, pyrite) and fluorite, calcite associated. Anionic surfactants such as fatty acids, alkyl sulfates, alkyl sulfonates are usually used as the collectors for flotation of baryte from other minerals. Cationic amine collectors are also used. Sodium silicate is used as the modifier.

BENEFICIATION

Barite occurrences are commonly associated with fluorite (CaF_2) concentrations while in most of cases contains a variety of impurities such as a silicates, calcite, and iron as. Several processes have been developed for the beneficiation of barite concentrate prior to its use as a drilling mud. The most widely used process for barite beneficiation and enrichment consists of a combination of gravity separation and flotation techniques (Figure 1) [14].

Using this flowsheet, a chemical grade and drilling mud grade barite concentrate are produced. Flotation, which is more efficient in case of fine sized barite concentrate, can be either reverse or direct. Reverse flotation generally involves removals of base metals sulphides or pyrite leaving a concentrated barite in the tailing, which is recovered using flotation. Direct flotation of barite is performed from the ores that contain fluorspar, silicates, and Rare Earth Oxides (REO) [14]. Various agents are used at the flotation processing in relation to specific impurities. Sodium silicate is an important reagent acting as a dispersant and silicate depressant. Aluminum depresses calcite while citric acid is a fluorspar depressant and is used during barite flotation from the ores that contain fluorspar.

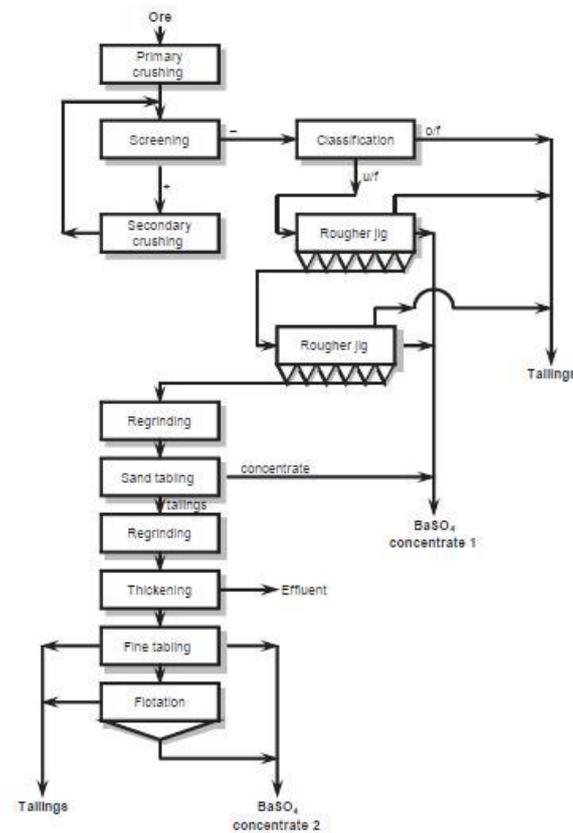


Figure 1 – Beneficiation of barite ore using gravity separation and flotation [14].

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

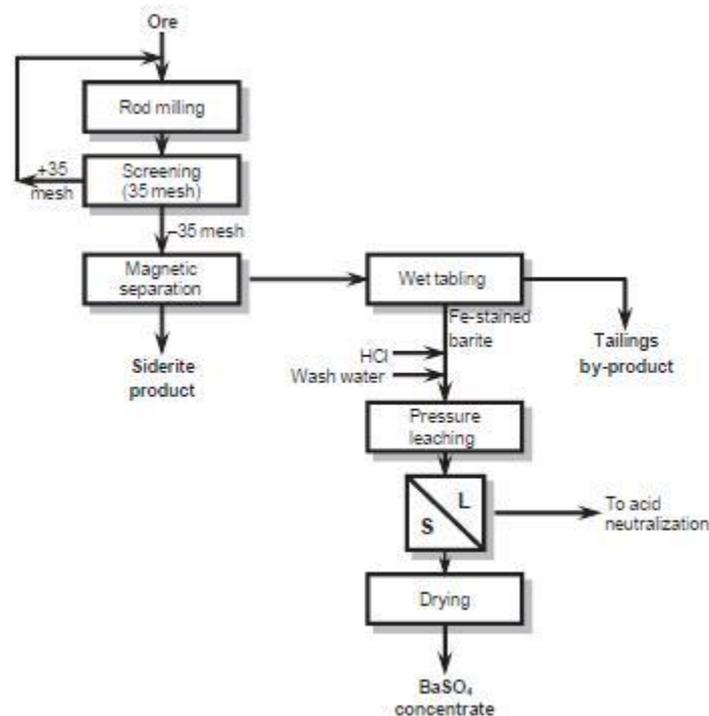


Figure 2 - Beneficiation of barite concentrate via magnetic separation method [14]

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

Table 1 – Specifications of different baryte grades [14]

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

Research on the optimization of the flotation stage have been developed by different authors which are briefly described below:

In [15] it is shown that Nigerian baryte could be floated effectively using locally available raw materials such as the burnt empty palm bunch to prepare a palmitate collector. Palmitic acid is also a major component of palm oil. The results obtained agreed with previous research

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works on baryte flotation using different commercial collectors which are not readily available in most countries. However, the use of locally available palm bunch as raw material to prepare the collector reagent in this work has made a difference, as the grade of baryte obtained shows an upgrade from 75.4 % to 91.9 % in the concentrate. The final baryte recovery meets the requirement for petroleum-related applications and other allied industries. The article also advocates that other beneficiation methods e.g. jigging and magnetic separation should be carried out prior to flotation to add excellent value to the mineral [15].

In [16] it is reported that crude Nigerian baryte was floated with sodium oleate as collector at varying oleate concentrations, pulp pH, and temperatures. Using “pure” baryte selected from the crude baryte, oleate adsorption densities at the baryte–water interface were determined as well at varying oleate concentrations, pulp pH, and temperatures, by using electrical conductivity measurements. Flotation recovery augmented with increasing adsorption density to about 100% recovery at maximum oleate adsorption density at pH 9.0 to 10.0 in the region of the zero point of charge (zpc) of the Nigerian baryte, and to about 100% recovery and maximum oleate adsorption density at the temperature range 30 to 40°C.

[17] examined the optimization of a beneficiation plant for recovering marketable barytes from crude ores of different characteristics. The plant, which was part of a mining complex in Sardinia, consisted of a jig section integrated with a flotation line. The problem was studied using a suitable model of the process, based upon experimental and field data pertaining to both the characteristics of the feed material and the performance of machinery. Data were automatically processed with the aid of a computer to find the optimum setting of each section, in order to maximize profit for each kind of ore separately fed to the plant. Moreover, the advantages of blending the various concentrates - not all of them individually marketable - were also demonstrated. The study shows that the overall economic result might be improved provided suitable proportions of each kind of ore are fed to the plant. Such information is fundamental for the long-term planning of exploitation of available reserves and provides guidelines for further prospecting.

Recently, Innovation Metals Corp. (IMC), a private Ontario-based company that develops cost-effective separation and purification processes for the critical-materials industry, has developed a processing technology for the production of high-purity barium sulfate (“barite”). The IMC technology will be used by Voyageur Minerals Ltd (VM) to produce consistent high-grade baryte suitable for multiple industrial grades, including the pharmaceutical market and high-end filler markets, such as reagents, paints and plastics [18].

Moreover, on completion of pilot-scale testing, a commercial-scale demonstration plant with a production capacity of 2,000 tonnes per year of high-purity barite will be built. The production will initially begin from a 10,000-tonne bulk sample. After the Demo Plant is

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completed and tested, VM plans to increase production to 6,000 – 10,000 tonnes per year. The Company has been working with IMC to test the technology and initial results indicate that pharmaceutical grade baryte (99.5%+ purity) can consistently be achieved. Pharmaceutical-grade baryte is currently sold for a range between US\$2,800 – US\$7,500 per tonne [18].

3. ENVIRONMENTAL IMPACT OF ALTERNATIVE TECHNOLOGIES AND RESIDUE TREATMENT

Environmental impact of alternative technologies on baryte mining and beneficiation processes has hardly been studied.

Specific attention has been given to the environmental impact of baryte when used as a weighting agent to drilling muds to counteract pressure in the geologic formations being drilled. It was found out that barite muds contain elevated (compared to marine sediments) concentrations of several metals. Some of these metals are bioavailable, may harm the local marine ecosystem [17].

SUMMARY

In 2015, production in the EU28 amounted to 178,811 tonnes from Bulgaria, Germany, Italy, Slovakia and the United Kingdom. This was, however, a significant decline compared to production in the recent past when output was also recorded in Belgium, France, Greece, Poland, Portugal, Romania and Spain.

Mining methods vary according to the type of deposit. Major stratiform deposits are exploited by open pit where feasible. The ore is drilled and blasted and then trucked to the mill for pressing. Conventional underground methods are used considering the shape and altitude of the deposit.

Following initial crushing some baryte is sold as ‘direct shipping ore’ if it is sufficiently pure. If there are contaminants such as fluorite, quartz, galena or pyrite, **gravity separation and flotation** are used to separate them after grinding. Then the concentrate is either dried and sold as a powder or processed further for specific applications.

Research on the optimization of the flotation stage has been developed by different authors. However, the environmental impact of such alternative processes has hardly been studied.

BERYLLIUM

1. THE PRIMARY RESOURCES

Beryllium is primarily produced from two minerals: bertrandite, which contain about 15%wt ($\text{Be}_4\text{Si}_2\text{O}_7(\text{OH})_2$) and beryl, which contains up to 5% wt ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$). According to the resource-mapping results of WP3 there is no mine production of beryllium in the EU and no known production of beryllium oxides, hydroxides, unwrought metal or powders.

However, there are several Beryllium occurrences in the EU: Austria, Czech Republic, Germany, Finland, France, Norway, Italy, Portugal, Spain and Sweden, scarce information about them is available.

- Known unexploited resources (tonnage data exists): Finland, France, Norway, Portugal.
- Assumed unexploited resources only (no tonnage data): Denmark, Greenland, Germany, Sweden.

Main occurrences with known unexploited resources are described as follows:

In Finland Beryllium contents are reported from four deposits in Finland. resource estimate available is for the Rosendal deposit in SW Finland, which has 206.85 t of beryllium [19]. In Norway the only beryllium deposit known in Norway is found in Høgtuva, where several small deposits occur in an area of 8 km² [19]. The largest is the Bordvedåga deposit, which can be followed in outcrop in an area of 400 m x 20 m. With a cut-off grade of 0.1 % Be and the thickness of 1.5 m of the mineralized zone, a resource of 350,000 t with 0.18 % Be is identified (equals to 630 t Be). The main beryllium mineral is phenakite, whereas høgtuvaite, genthelvite and gadolinite are subordinate beryllium phases.

At present the only country with the capacity to host a fully integrated beryllium production, from mining to recycling, is USA. According to [20] in 2014 USA and Japan were the main Be processors, representing 75% and 25%, respectively, of the world processing industry.

2. GAPS & BARRIERS – PROPOSED PROCESSING ROUTES

Given the small size of Beryllium deposits, it is improbable that most of the occurrences will now or in the future be of economic significance.

According to what is presented in Deliverable 4.1., no active beryllium mining, beneficiation or metallurgy processes have been identified within the EU. There is a gap of available data concerning potential mining processing routes for beryllium.

Finding a potential ore deposit and investigating it to the knowledge level that is required for the mining decision is a time and money-consuming process that may take even decades. In addition to the financial and technical obstacles, the establishment of new mines is hindered by prolonged permitting procedures, increasing social resistance, and NIMBY attitudes in most EU28 countries. These are issues that also need to be addressed when discussing exploration and mining issues.

3. ENVIRONMENTAL IMPACT OF ALTERNATIVE TECHNOLOGIES AND RESIDUE TREATMENT

No information available regarding environmental impact of alternative technologies and residue treatment has been identified.

BISMUTH

1. THE PRIMARY RESOURCES

In earth crust bismuth is twice as abundant as gold and the most important ores of bismuth are bismuthinite and bismite. Native bismuth is known from Australia, Bolivia and China. In China and Vietnam, bismuth is a by-product or coproduct of tungsten and other metal ore processing.

According to the resource-mapping results of there is no mine production of bismuth within the EU. There may be a small quantity of refined bismuth metal production, but this would be from imported materials.

In Finland bismuth is reported as a minor commodity in the Petrovaara Cu-Au occurrence, which has a noncompliant resource estimate of 0.15 Mt of ore at 1.31 % Cu. In addition to Cu, there is 0.1-4 ppm Au, up to 2.8 % Pb and up to 88 ppm Bi [19]. As bismuth is not routinely analyzed, there are other Cu, Cu-Au and Au occurrences that contain potentially recoverable bismuth, at grades in several tens of ppm Bi, but Bi is not included into the mineral resources estimated.

In Sweden, bismuth is reported as a by-product in the small historic Ädelfors gruvor Au deposit, which was in production in 1890–1916 [19]. The bismuth content of the ore is unknown. In the same way that in Finland, bismuth is not routinely analyzed and there may be other Cu, Cu-Au and Au occurrences that contain it.

2. GAPS & BARRIERS – PROPOSED PROCESSING ROUTES

As mentioned in Deliverable D4.3, bismuth production is highly dependent on the production of the main metals such as Au.

3. ENVIRONMENTAL IMPACT OF ALTERNATIVE TECHNOLOGIES AND RESIDUE TREATMENT

Due to its rather benign properties, no special environmental harms are posed by bismuth itself, however it can be seriously affected by the main metals' extraction methods.

BORATES

1. THE PRIMARY RESOURCES

Elemental boron is a metalloid which is not found in pure form in nature. Often boron combines with oxygen or other elements to form boric acid or other compounds known as borates. Four borate minerals: colemanite, kernite, tincal and ulexite make up to 90% of the borate minerals used by industry. Boron compounds are bought and sold based on their boric oxide compounds (B_2O_3) [21] [22].

The borate deposits are associated with volcanic activity and arid, dry climates, with the largest viable deposits located in the Mojave Desert in the US, the Alpidic belt in southern Asia and the Andean belt of South America. The US deposits consists primarily of tical, kernite and borates contained in brines and small amounts of ulexite and colemanite. About 70% of all deposits in turkey are colemanite [21] [22].

According to the resource-mapping results of WP3, there is currently no production of borates within the EU. Borate deposits are known in southern and southwestern Europe, but there is no information available in the databases used in this study. An excellent example is the Jadar deposit in Serbia. The Jadar deposit is a sedimentary deposit with a previously unknown mineral jadarite as main commercial component. The deposit was identified while drilling Miocene lake sediments in search for sodium borates and is owned and developed by Rio Tinto. The resources are estimated at 136 million tonnes grading 1.9% Li_2O , which places it among the largest lithium deposits in the world. The deposit also contains a borates resource of 21 million tonnes of B_2O_3 . According to the company, if developed, the deposit could supply more than 10% of global lithium demand. It could also supply a significant proportion of global demand for borates [23].

The project is currently in the pre-feasibility stage. Significant investment is necessary to continue the technical analysis and planning, which is required to move from pre-feasibility to feasibility, then to construction and operation. A team of international experts in various disciplines, from mining to processing to communities, is completing studies as part of the pre-feasibility stage to further assess the technical and economic viability of the project [24].

2. GAPS & BARRIERS – PROPOSED PROCESSING ROUTES

Rio Tinto is developing innovative technologies for the extraction of lithium carbonate and boric acid from the Jadar deposit. Such technology is being tested at small scale in Australia. No detailed information is available relatively to such technology [21].

No further information is available regarding the proposed processing routes for Jadar deposit or other potential deposits within the EU28.

Although quite a few of such deposits have been in production at some time, most of them are currently considered as mined out, uneconomic, or not just explored at such detail that a feasibility study can be performed [22].

3. ENVIRONMENTAL IMPACT OF ALTERNATIVE TECHNOLOGIES AND RESIDUE TREATMENT

No information has been gathered regarding environmental impact of alternative technologies and residue treatment.

CERIUM

1. THE PRIMARY RESOURCES

According to the review study of Goodenough et al. (2016), the most important European resources are associated with alkaline igneous rocks and carbonatites [25]. Within Europe, several REE metallogenetic belts are identified on the grounds of age, tectonic setting, lithological association and known REE enrichments. The most well-known REE belts are those belonging to the Precambrian to Palaeozoic age, which occur in Greenland and in the Fennoscandian Shield. The Gardar Province of SW Greenland, the Svecofennian Belt and the subsequent Mesoproterozoic rifts in Sweden are relevant given their REE potential. In regard to their REO grade and ore size, the European REEs deposits are comparable with some of the most significant deposits worldwide (Figure 3). The most important European multi-metallic deposits – including cerium – are quoted in Table 2. The major deposits are Kvanefjeld and Norra Kärr, and the main barriers for their exploitation are described in HEAVY RARE EARTH ELEMENTS and YTTRIUM sections.

The current section focuses on Olserum (Sweden) and Sokli (Finland) deposits, in which elevated concentrations of cerium have been reported. In the Olserum area, close to the placer localities in the Västervik region, there are several vein-hosted, REE-rich mineralisations associated with iron ore. These relatively unstudied deposits are apparently epigenetic, and contain abundant monazite-(Ce) and xenotime-(Y), and a relatively high proportion of HREE [26]. Olserum hosts an indicated mineral resource of 4.5 million tonnes with a 0.6 %wt concentration in REO. The Sokli carbonatite (approximately 360 – 380 Ma) in north eastern Finland, hosts an unexploited deeply weathered phosphate deposit enriched in niobium (Nb), tantalum (Ta), zirconium (Zr), REE and uranium (U). The carbonatite intrusion consists of a magmatic phoscorite-carbonatite core that measures approximately 9 km in diameter. Late-stage carbonatite veins in the magmatic core and in the fenite outer zone have high potential for REE mineralisation. Chemical analyses from drill cores showed a high total REE content of 0.5 – 1.8 %wt. The mineral assemblage includes REE-bearing ancylite-(Ce) and bastnäsite-(Ce), Sr-apatite, monazite, strontianite, baryte and brabantite, rich in LREE, P, fluorine (F), Sr and Ba [26].

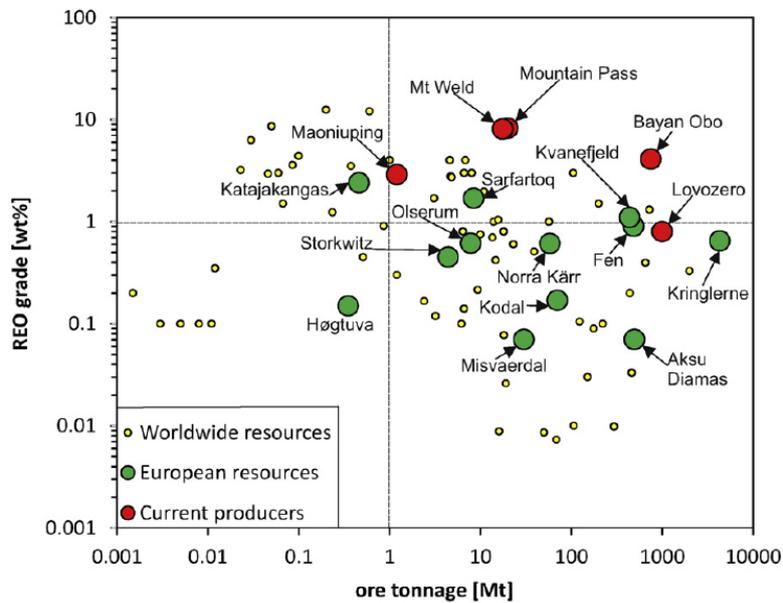


Figure 3 – Grade and tonnage plot comparing European REE deposits with those worldwide [26]

Table 2 - The main primary unexploited resources of cerium in EU and their main processing barriers [25] [26]

Type of ore	Cerium form	Major deposits	Gaps and barriers			
			Mining	Beneficiation	Metallurgy	Residues
High temperature hydrothermal	Phosphate minerals (xenotime, allanite, monazite)	Olserum, Sweden		x		
Carbonatite	Ancylite-(Ce) and bastnäsité-(Ce)	Sokli, Finland		x		
Alkaline intrusions	Steenstrupine phase	Kvanefjeld, Greenland, Denmark				x

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Agpaitic nepheline syenites	Eudyalite and other phases	Kringlerne, Greenland, Denmark				
Agpaitic rocksand syenites in gneiss	Eudyalite and other phases	Norra Kärr, Sweden				

2. GAPS & BARRIERS – PROPOSED PROCESSING ROUTES

MINING

REEs containing ores are mined underground or superficially (open pits) following the hydrothermal or pegmatite veins (in case of non-altered rocks). Mining techniques are well developed and no gaps and barriers at the mining step have been reported.

BENEFICIATION

Olserum deposit

The beneficiation of Olserum ore has been tested at laboratory scale within the framework of the EU research project EURARE. A sample with an average content of 0.6 wt.% in REO was used. This was provided by the Tasman company (Currently Leading Edge Materials). The target mineral phases were monazite and xenotime. Flotation was selected as the most appropriate beneficiation technique for medium grain size ore. A concentrate with 20 wt.% in REO content was received under the optimum conditions, while the recovery approached 70% [27]. **The results showed that the ore is enriched in REO at a satisfactory level, however a further optimization of the process at pilot scale is necessary.** The mineralogical investigation of Olserum ore [28] revealed a complex structure dominated by monazite-(Ce), xenotime-(Y), and fluorapatite hosted by veins that contain biotite + quartz + magnetite as the main gangue minerals, either occurring within quartz + biotite + plagioclase ± cordierite metasedimentary rocks (Figure 4). **A complex magnetic separation-flotation process could potentially be tested for the enrichment of the ore, considering the presence of magnetite and ilmenite, which dispose a high magnetic susceptibility value.**

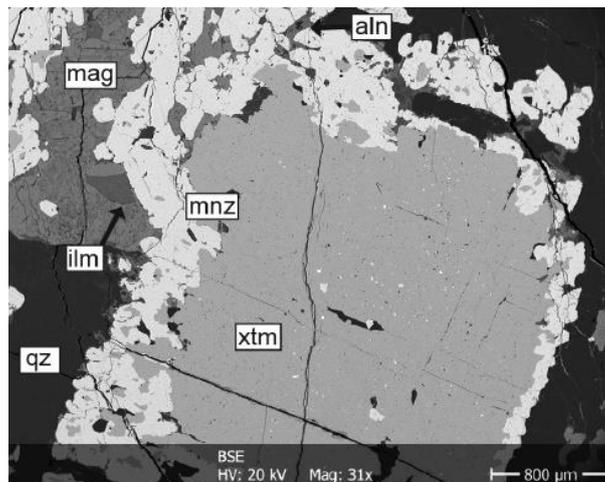


Figure 4 – SEM polished micrograph of ore from Olserum [27].

Sokli deposit

La, Ce, Pr, Nd are the main REEs in the Sokli ore. REEs content is distributed in several mineral phases rendering the beneficiation of the ore to be challenging. At least 7 minerals containing REE, Sr and/or Ba as major elements have been identified in the Sokli carbonatite veins. The drill core samples indicated that carbonatitic rocks consist of silicate minerals, such as biotite or phlogopite and albite, with calcite-dolomite and the accessory minerals aegirine, and apatite. Alkaline rocks contain a variety of pyroxene-group minerals, but only aegirine is exclusive to these rocks. Typical accessory REE-bearing minerals are monazite, REE-rich Sr-apatite, strontianite, ancylite-Ce, and baryte. They are strongly enriched in LREE, P, F, Sr and Ba [29].

No published data concerning beneficiation tests of Sokli REE-containing carbonatites has been found. REE enrichment of carbonatite ores is challenging because of their complex mineralogy and the complicated and costly processing. **Prior to the development of the beneficiation process, a detailed geochemical study of Sokli ore using several core drill samples is necessary so that the distribution of REEs in various phases is able to be quantified.** REE-bearing minerals are incorporated into various silicate and carbonate phases. Carbonatite ores are usually beneficiated using a combination of magnetic separation and flotation techniques (Figure 5). According to the study of Ni et al. 2012 [30], a rich pyrochlore concentrate (95% Nb₂O₅ recovery) was obtained by a carbonatite, while the gang silicate and carbonate phases were efficiently removed. **A similar magnetic separation/flotation complex process could potentially be tested in the case of Sokli ore.**

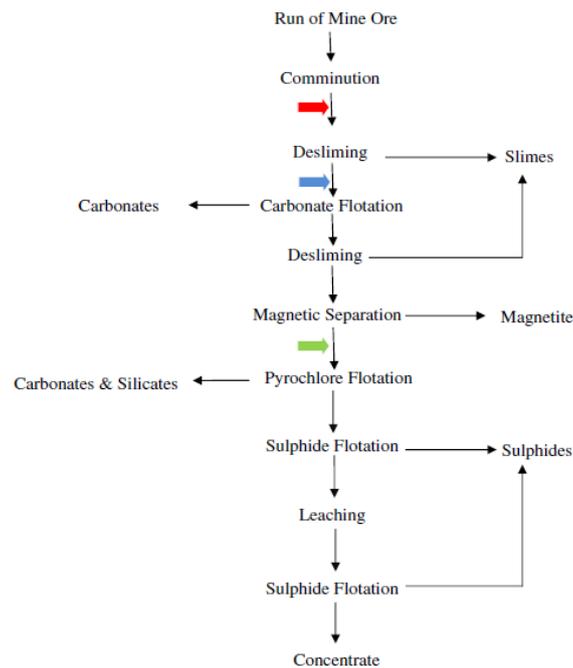


Figure 5 – Beneficiation of a carbonatite aiming to pyrochlore recovery. A similar methodology could potentially be tested in case of Sokli ore [30]

METALLURGY

Olserum deposit

There is no available published data concerning the metallurgical processing (leaching and REEs recovery) of Olserum concentrate after its flotation. Tasman Metals Ltd. proposes the caustic leaching of the concentrate using a dense 70% NaOH solution. The REEs will be then recovered via solvent extraction, possibly by using two different agents; one for light REEs, among them Ce, and a second for the heavy REE [31].

Sokli deposit

There is no available data related to the metallurgical processing of Sokli ore. The optimization of the ore's beneficiation consists of a required/preceded step.

3. ENVIRONMENTAL IMPACT OF ALTERNATIVE TECHNOLOGIES AND RESIDUE TREATMENT

The processing methodologies of Olserum and Sokli ores have not yet been established, and therefore a speculation concerning the environmental impact of the applied processes should be avoided. **Nevertheless, it should be stressed out that radiological studies indicate a**

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significant content in NORMs (natural occurring radionuclide materials) in case of Sokli ore. According to these studies, an average U-238 activity concentration of 310 Bq/kg, ranging between 100-1000 Bq/kg (most U bounded to pyrochlore-group minerals), was measured. Additionally, an average Th-232 activity concentration of 533 Bq/kg, ranging between 200-1700 Bq/kg Th (mostly incorporated in pyrochlore-group and monazite-group minerals) was detected [32]. The quantification of NORMs in the ore should be further investigated, while a safety and health plan, initially for the mining process, should be prepared.

COBALT

1. THE PRIMARY RESOURCES

According to the resource-mapping results of WP3, the main primary Co reserves in the EU territory exist in Finland, where the metal is currently successfully recovered by using polymetallic Ni-Co-Cu sulphides through various metallurgical routes including bioleaching (Freeport-McMoRan Company) and hydrometallurgy-pyrometallurgy combination (Outokumpu Company). Table 3 presents the most significant unexploited cobalt deposits in EU and the classification of the gaps and barriers for their potential exploitation. Polymetallic nickel sulphides deposits in Scandinavia and nickeliferous laterites in Greece are the major unexploited primary Co reserves in EU.

Table 3 - The main primary unexploited resources of cobalt in EU.

Type of ore	Cobalt form	Major deposits	Gaps and barriers		
			Mining	Beneficiation	Metallurgy
Sulphide nickel ores	Co-petlandite	Rönnbäcken Ni-Co deposit, Sweden		x	
	Pyrrhotite, pentlandite, chalcopyrite, pyrite	Stormyra Ni-Cu-PGE Deposit, Norway		x	
Nickeliferous laterites	Ni-Co ions or oxide impurities in various mineral phases	Greece (various limonitic and serpentinitic deposits)			x

2. GAPS & BARRIERS – PROPOSED PROCESSING ROUTES

MINING

Nickel sulphide ores are mined underground or superficially (open pits) following the metalliferous veins, while laterite ores generally occur near the surface and they are mined

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relatively easily by surface-mining methods. Mining techniques for both types of ores are well developed and there is little room for innovation.

BENEFICIATION

Greek laterite deposits

The beneficiation of greek laterite ores (serpentinitic and limonitic) is practically impossible in most of cases. The mineral phases in laterites are composed by micro and sub micro particles creating a colloidal-like mixture. Furthermore, the separation of the different phases in greek laterites is ineffective as Co is distributed in various minerals (phyllosilicates and iron and chromium oxides as well) [33]. In any case the beneficiation of garnieritic laterites from Nea Caledonia and Indonesia using sodium oleate present poor results [34].

Co-sulphide deposits in Scandinavia

The effective beneficiation of Ni-Co rich sulphides consists a major issue, specifically in case of the relatively medium-small deposits or large deposits with low Co grade in Scandinavia (Sweden and Norway).

Rönnbäcken is a major (>200 Mt) Fe-Ni-Co-Cu deposit in Sweden that has been mineralogically studied in detail. The ore, which is hosted in ultramafic serpentinitic rocks, is composed by high grade primary Ni-sulphides rich in cobalt such as heazlewoodite (70% Ni), Pentlandite (20-40% Ni+Co) and millerite (60-70% Ni). The ore is hosted in ultramafic serpentinitic rocks. Pentlandite is very rich in Co (concentrations 18-36% w/w) [35]. Several relatively small Co deposits (<5 Mt) exist in Norway. The Stormyra Ni-Cu-Co deposit with the ore containing 1.09% w/w Ni, 0.48% w/w Cu, and 0.04% Co w/w; and the Dalen deposit with ore containing 0.29% Ni w/w, 0.12% w/w Cu, and 0.02% w/w Co are the most exhaustively studied deposits [36]. A key factor for the exploitation of both Swedish and Norwegian Co deposits is their efficient beneficiation. Flotation tests under various conditions have already been designed in case of Rönnbäcken deposit.

Flotation is the most appropriate technique for the beneficiation of polymetallic cobalt rich sulphide ores. However, **two major barriers** are identified for low grade ores [34]:

- A clean and satisfactory separation of pentlandite (which is the main phase rich in Co) from pyrrhotite and other sulphides is difficult to obtain in practice since pyrrhotite typically contains intergrown inclusions of pentlandite, as well as nickel is present in solid solution.
- Talc and other naturally hydrophobic magnesia-bearing minerals, which are the host rock of polymetallic ores, have a tendency to aggregate with sulfides, resulting in a

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exceptionally high concentrate in magnesia. The presence of magnesia causes viscosity problems in the slag during smelting. Magnesia also triggers conditions favourable to hetero-coagulation of minerals, thus leading to nickel and cobalt loss.

Recent improvements have been reported in the flotation of Ni sulphides (which also contain Co) from several deposits in Finland (similar to Swedish and Norwegian deposits). The results show that chalcopyrite and pyrrhotite can be effectively floated without collectors at electrode potentials of +400 mV and +50 mV respectively, and pyrite does not float even at +700 mV. Collectorless flotation studies have also proved that optimum Ni recovery is obtained when pH is adjusted between 3 and 5 and polypropylene is used as a frother.

METALLURGY

Greek laterite deposits

High-pressure acid leaching in sulfuric acid (HPAL) is the most efficient method for Co recovery by laterites (yield>90%). The limonitic laterite slurry feed (45% in solid) is mixed with H₂SO₄ in autoclave operating at 250 °C and 40 bar. The leachate, contacting 55% Ni and 5% Co v/v is processed via sulphide precipitation, re-dissolution and solvent extraction. Then, it can be recovered by either electrowinning or hydrogen reduction. The method is industrially applied in case of Ravensthorpe, Australia (1% Ni and 0.04% Co), Ambatovy, Madagascar (1.2% Ni and 0.12% Co); and Goro, New Caledonia (1.5% Ni and 0.1% Co) laterites. An industrial leach autoclave is typically 4.5 m diameter 30 m long with six stirred compartments. It treats about 2000 tonnes of solid feed per day [37], [38].

Significant limonitic and serpentinitic nickeliferous laterite deposits exist in Greece, with an average content in cobalt ranging between 0.05 and 0.08 w/w%. The above percentages render technically feasible the cobalt extraction [39].

The major barrier for the recovery of Co from greek nickeliferous laterites is mainly related to techno-economic data. Greek laterites are processed via pyrometallurgy for the production of FeNi through a reductive roasting in kilns, followed by reductive smelting in electric furnaces and refining in OBM type converters. The process, which is applied since the 1960s, does not allow the recovery of the laterites cobalt content, which is lost in the metallurgical slag. Therefore, the cobalt exploitation from greek nickeliferous laterites requires a total modification of the currently followed metallurgical route (adjusted to a hydrometallurgical route), which inevitably will be accompanied by large capital investment.

The heap-leaching process has been proposed as a hydrometallurgical process for the simultaneous recovery of nickel and cobalt by greek laterites due to its low capital and operating cost. Additionally, heap-leaching boosts the processing of low Ni content ores such

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as greek laterites (Ni<1%w/w). Laboratory tests have been performed using sulfuric acid as a leaching reagent while in columns with 10 cm diameter and various heights. The results in case of serpentinitic laterite with 0.05 %w/w cobalt content (1.05 nickel %w/w) is presented in Figure 6. A recovery rate of nickel and cobalt of 60% and 45%, respectively, was achieved within 10 days. The sulphuric acid consumption amounted to 40 kg H₂SO₄/kg Ni. It was found that the effectiveness of leaching depended on the calcite content of the ore as this adversely affected the permeability of the heap.

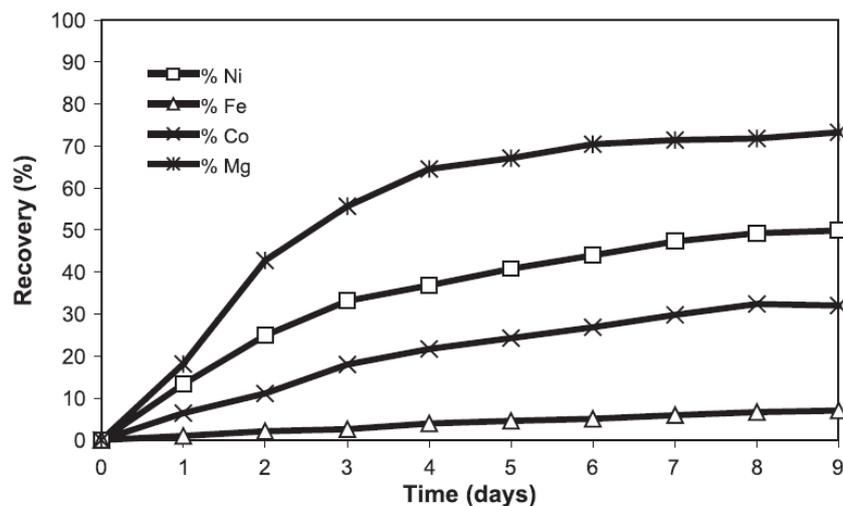


Figure 6 - Recovery yields of Ni and Co by greek serpentinitic laterites through heap leaching process using sulfuric acid [39].

Subsequently, cobalt, manganese and magnesium are simultaneously extracted by Cyanex 272, leaving nickel in solution, which is easily concentrated by solvent extraction using Cyanex 272. Cobalt content can be almost totally precipitated as Co(OH)₂ through the addition of NaOH in the leaching liquor. However, the precipitation of Mn(OH)₂ impurities can not be avoided [40]. Thus, all or most of the manganese must be removed before cobalt electrowinning, so that the purified barren solution is recycled to the heap leaching stage. The separation from manganese is successfully achieved by the leaching of the cobalt-manganese hydroxide by ammonia–ammonium carbonate. The cobalt obtained in the solution can be obtained by electrowinning, while manganese remains in the residue. The optimum leaching conditions are found to be: NH₃/(NH₄)₂CO₃ /solid hydroxide 1:1 w/w and solid to liquid ratio = 10%. At those conditions, cobalt recovery reaches 93% whereas manganese leaching does not exceeds 0.05% [40].

The above described cobalt recovery process is well designed and successfully applied at laboratory scale. **However, the most important technological barrier to overcome is the low yield extraction of the cobalt (about 40%) during the heap leaching process.** Mineralogical studies [33] have shown that the cobalt distribution is wide in almost all mineral phases in

greek laterites (including iron oxides and chromite), while on the other hand the heap leaching with sulfuric acid is efficient (dissolving) mainly in case of phyllosilicates. Therefore, studies on the selective leaching of greek laterites targeting on Co extraction should be performed using various leaching agents under various conditions. The most appropriate technologies that should be tested are; (a) the bioleaching, which has been applied in case of limonitic laterites presenting Co recovery yield >90% [41]; and (b) the selective chlorination within the temperature range of 300–500 °C using aluminum chloride after the laterite ore reduction (Co recovery yield >80%) [42].

Co-sulphide deposits in Scandinavia

The metallurgical processing of polymetallics rich in Co sulphide ores is well established via different routes.

3. ENVIRONMENTAL IMPACT OF ALTERNATIVE TECHNOLOGIES AND RESIDUE TREATMENT

Greek laterite deposits

A rough comparison between the current processing of greek laterites and the alternative hydrometallurgical processing, aiming to Co-Ni production, concerning the environmental impact of both methods can be attempted.

Figure 7 and Figure 8 comparatively present the energy consumption and the CO₂ equivalent emissions between the pyrometallurgical and the hydrometallurgical processing of laterites from Australia and Indonesia (high pressure acid leaching) [43]. It is indicated that the CO₂ emissions are significantly lower in case of hydrometallurgical processing. The energy consumption between HPAL and pyrometallurgy is comparable given that significant quantities of natural gas are consumed for the operation of the high HPAL reactors. Furthermore, it should be stressed out that the energy consumption in case of hydrometallurgy can be dramatically lowered by applying heap leaching in atmospheric pressure instead of HPAL.

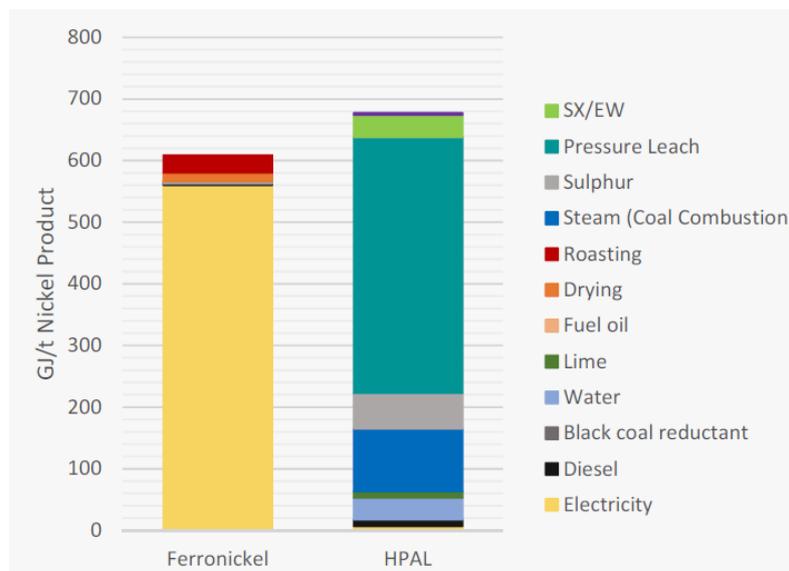


Figure 7 - Energy consumption comparison for the production of nickel through FeNi pyrometallurgy and HPAL[43].

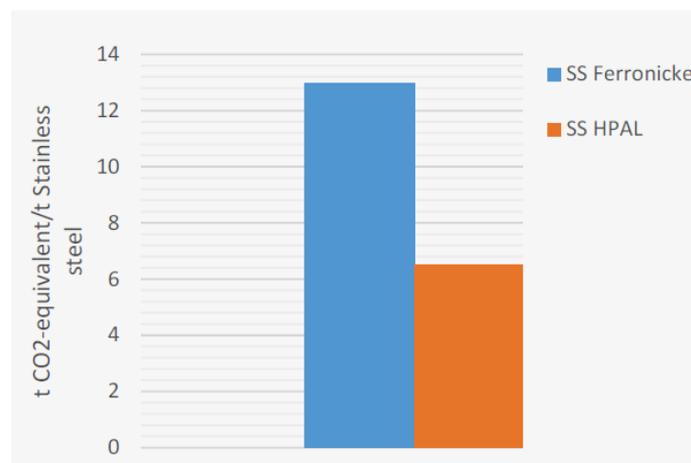


Figure 8 - CO₂ equivalent emissions comparison for nickel production through FeNi pyrometallurgy and HPAL [43].

The main environmental impact of the laterites hydrometallurgical processing should be focused on the management of liquid wastes. However, environmentally friendly technologies have been developed during the last decades, including acid drainage prevention using high density polyethylene layers, while the solid wastes can be used as a constitute of ceramic materials.

SUMMARY

The unexploited cobalt resources in EU are relatively limited. However, two different ore types might be potentially processed aiming at the recovery of Co among other valuable metals: (a)

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the polymetallic Ni-Co-Cu deposits exist in Sweden and Norway and (b) the nickeliferous (limonitic and serpentinitic) in Greece. The technological barrier in the processing of the first ore-type is mainly related to its beneficiation effectiveness. However, new improved flotation results have been reported in case of Ni-Co-Cu ores. On the other hand, Co extraction by nickeliferous laterites present important techno-economical and metallurgical gaps and barriers that should be overcome including the required capital investment and the improvement of the leaching yield. Specific pilot scale leaching tests at various conditions should be performed in advance. The environmental impact of the hydrometallurgical processing of greek laterites aiming to Co-Ni recovery is expected to be lower in comparison to the current applied FeNi pyrometallurgical route.

COKING COAL

1. THE PRIMARY RESOURCES

According to the resource-mapping results of WP3, the coking coal used in Europe has its origin mainly in Russia (32.5%), Colombia (23.2%), Australia (15.8%) and USA (14.3%). In EU the production of hard coals takes place principally in Poland and Ukraine, though there is also some minor production in UK, Germany, Czech Republic, Spain and Turkey [44]. The production of coking coal in EU-28 represents less than 4.2% of the worldwide production, while the consumption of this raw material is 8.7% [45].

2. GAPS & BARRIERS – PROPOSED PROCESSING ROUTES

MINING

Coal mining may be conducted either through surface or underground mining. Underground mining is undertaken via long wall or room-and-pillar mining. There is a high potential for improved mining in terms of securing the safety of people and of the supply during periods of difficult weather conditions. During the last decades a significant number of coking coal mines in Europe have been closed.

BENEFICIATION

In general, crushing reduces the overall top size of the coal so that it can be more easily handled. The processed and crushed material is classified using screening, cyclone etc. as described in more detail in D4.1. The coal is washed and often some flotation method is used. After the separation step for heavy gangue and light coal the material is dewatered. Washing water is collected and reused. Wash coal for delivery to customer is prepared by mixing coarser and finer fractions [46]. The beneficiation process is well established, but by implementing recovery improvements a larger part of mined coal with minimum ash content can be achieved. Higher ash content in coking coal results in lower carbon content and higher contents of SiO_2 and Al_2O_3 as well as other oxides, contributing to higher slag volumes. Thus, the consumption of coke and coal must be avoided.

METALLURGICAL PROCESSING

The metallurgical processing of coking coal includes pyrolysis, transferring the coking coal to metallurgical coke. The coking coal to be used varies depending on quality requirements related to the application, as well as the coke production technology.

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The coking coal blend is charged into the furnace and is heated up in absence of air up to a maximum temperature of approximately 1000-1100°C [46]. In many plants coking coal density charging is practised, while in others stamp charging is used. The later means that the coking coal blend is packed before being placed into the coke oven. There is potential for developments of the coking process both for coke production via density charging and stamp charging.

A modified coke production procedure can improve the coke quality, also with less optimum coal blend, and thereby enabling flexibility in coking coal selection. For example, the thermoplastic behaviour during coking, which is important for the coke quality, has been shown to be potentially influenced by the temperature profile, as well as by particle size and proportions of coals with different properties in the coal blend [47]. Further, additives with binding properties as e.g. hypercoal can also increase the flexibility and enhance the coke quality achieved for different raw material blends and also allow a larger proportion of coals with lower coking properties [48]–[50].

Further, the development of functional coke by additions to minimise or eliminate attack from alkalis in the blast furnace are an interesting area for innovation. It has e.g. been found that some alkali aluminates reduce the catalytic effect from alkalis on the reaction of CO₂ with C in coke.

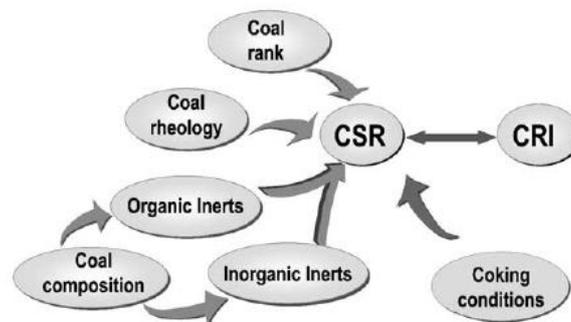


Figure 9 - Parameters influencing the coke quality measured as CRI (coke reactivity index) and CSR (strength after reaction) by subjecting the coke to CO₂ at 1100 °C [51].

When using stamp charging, lower quality of the coking coal blend can be accepted and coke with high cold strength still can be produced. However, these additional developments require further improvements in the quality of the coke. In case of density charging, it is of special importance that the wall pressure is kept below critical values to avoid harming the coke oven. This must be taken into account in the development. Parameters influencing the coke quality and the existent correlations are schematically shown in Figure 9.

Alternative coking processes, some being part of D4.1 and D4.2, enable the use of lower rank coking coals and are less sensitive for wall pressure. By allowing lower rank coals the costs for coke processing will be reduced. The advanced development of the Jewell–Thompson non-recovery ovens have been put into operation at Inland Steel Chicago (Figure 10).

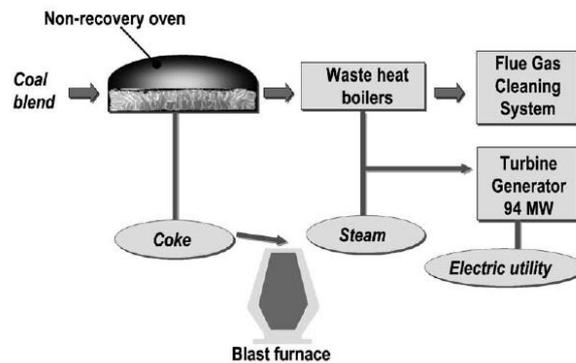


Figure 10 - Exmple of alternative coking method using longer time, being less sensitive to high wall pressures [51].

SUMMARY

Coking coal is mainly mined and produced outside EU. EU-28 consume more than double compared to the contribution to world production. Barriers exist mainly in the metallurgical step by optimised coking procedure and development of functional additives to the coking coal blend. The innovation lies mainly in the development of the processing of coking coal to coke. However, to reduce the amount of coal ash is of paramount importance. Further, the issuance of licences to operate coking coal mines in Europe should increase the availability of coking coals in Europe.

HAFNIUM

1. THE PRIMARY RESOURCES

Generally, hafnium occurrence do not exist per se, but it is usually associated with zircon mineral and baddeleyite [52]. This material is extracted as a residue from the purification process of zirconium metal. Both minerals are present in a wide variety of rocks, but rarely in economic concentrations. Hafnium containing deposits are majorly formed in the sedimentary zones, whose minerals have been separated from their primary rock by erosion [53].

Historically, zircon was recovered as a byproduct from the titanium minerals, but in recent years the higher demand and price for zircon have shifted the balance, and new mining projects hold zircon as their primary economical mineral [54]. Prices are established through negotiations between primary producers and processors or users. According to the metal bulletin in-warehouse Rotterdam, the average price at the beginning of 2018 for hafnium metal 99% (max 1% Zr) was 887 US\$/kg [52].

There is no standard calculation of hafnium resources and reserves. Based on the USGS estimate of zirconium reserves (74.4 Mt ZrO₂ or 55 Mt Zr) and the average ratio Zr: Hf = 50: 1, the estimated order of magnitude of the reserves of hafnium are at 1.1 Mt. Worldwide metallurgical production of zirconium was about 1.38Mt in 2016, and 70-80t since 2010 for hafnium powder called sponges [52]. The different countries containing reserves and producing hafnium are shown in Figure 11 and Figure 12:

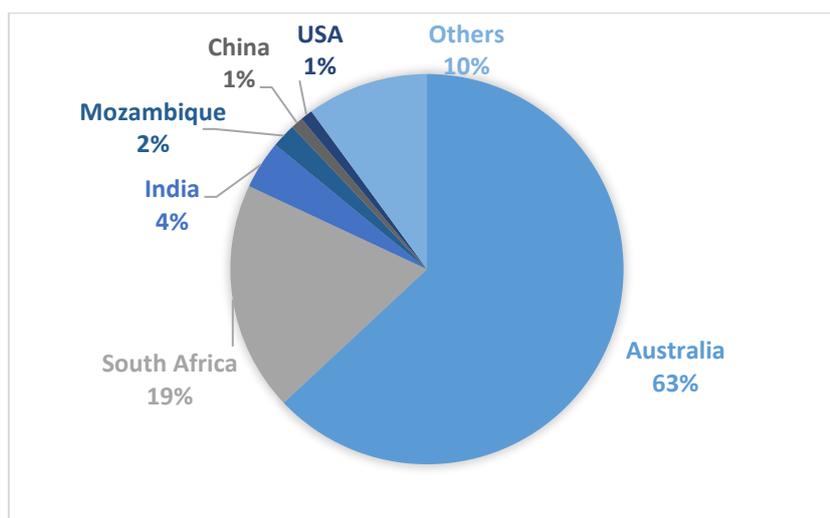


Figure 11 - Estimated reserves of hafnium in 2017 [55].

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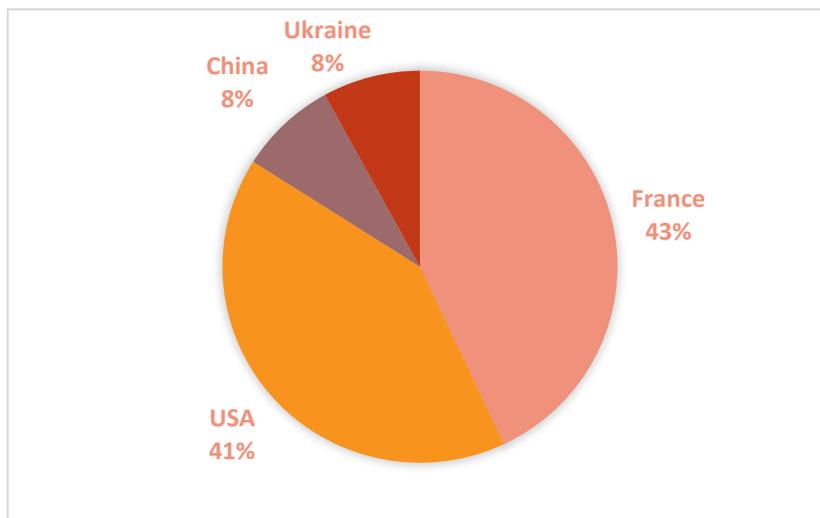


Figure 12 : Worldwide hafnium sponges production [55]

2. GAPS & BARRIERS – PROPOSED PROCESSING ROUTES

MINING

As previously said, there are no hafnium mines. Zirconium mineral comes from heavy mineral concentrates, which have been extracted dry or dredged, depending on the geological structure.

BENEFICIATION

The zircon beneficiation consists of sieving to remove any remaining rock or roots, before separating the heavy minerals from the lighter clays and slits into a bank of hydro-cyclones. Then magnetic, electrostatic and gravitational separations allow to separate zircon from other minerals like ilmenite, rutile or quartz. Hafnium is a byproduct, and it is extracted from zirconium concentrates by metallurgical processes.

METALLURGY

Hafnium is extracted from zirconium refining in metallurgical process for nuclear grade because of their almost opposite physical properties in nuclear reactor environment (<100ppm of hafnium). There is no need to remove the hafnium from zirconium in the chemical process industry applications, because of their similar chemical properties.

Several commercial techniques are in place for the separation of zirconium and hafnium. The major techniques can be divided into liquid-liquid solvent extraction, extractive distillation,

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ion-exchange separation and multiple crystallization of potassium zirconium fluoride (Figure 13) [56]. Extractive distillation uses a counter flow technique with a column of molten salt for the separation. This technique is currently used only in France (Framatome, Cezus plant) [57]. Liquid-liquid solvent extraction have two main techniques, the tributyl phosphate (TBP) nitric acid process, currently used in India, and the methyl isobutyl ketone (MIBK) process, which is used in USA. The MIBK process allows for extraction of both zirconium and hafnium, but the TBP process only allows extraction of zirconium [53]. This explains why USA and France abandoned the TBP process in the 1950s and 1970s, respectively. The crystallization process is easier, but it is a batch process.

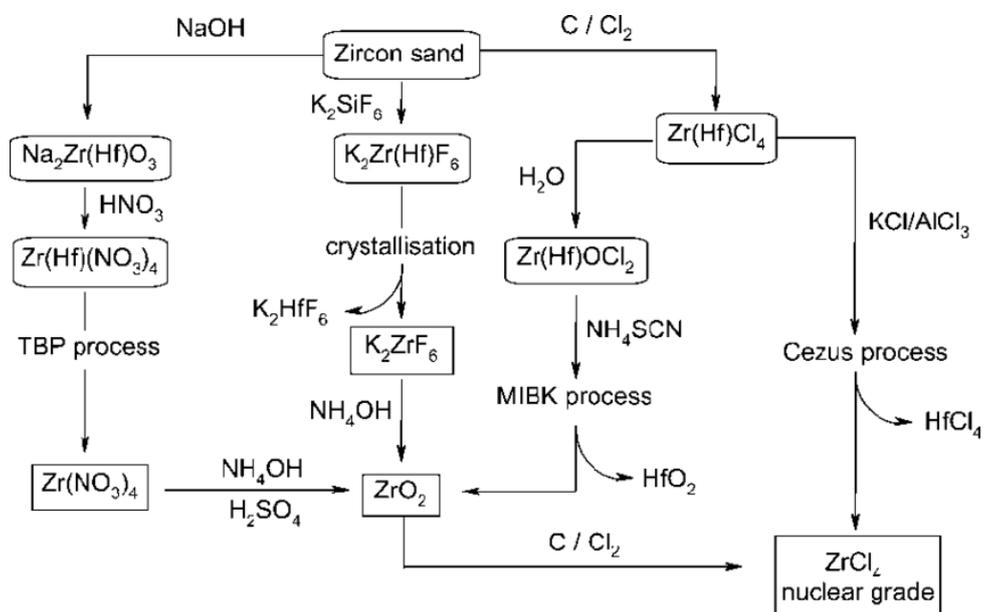


Figure 13 : Example of zirconium / Hafnium separation for nuclear grade [56]

Given the increasing environmental concerns surrounding CRM processing, other processes are in development to reduce the extractive distillation, which consume a significant amount of energy, as well as to diminish the use of MIBK reagent, which produce thiocyanate complexation and therefore toxic gases like hydrogen sulphide (H₂S) and hydrogen cyanide (HCN) [56]. For example, some studies show that when using magnetic resin with phosphoric acid functionality [58], or flotation [59] or nano filtration [56], and for solvent extraction, Cyanex 925 constitutes a viable alternative to MIBK [60]. Another example of alternative solvent extraction process is the Dubbo project to recover zirconium, hafnium and rare earth elements. This project was in development since 1995, and currently a pilotplant is being built

in Australia in consultation with the market to refine product specifications. This is the most advanced poly-metallic project outside China [61].

3. ENVIRONMENTAL IMPACT OF ALTERNATIVE TECHNOLOGIES AND RESIDUE TREATMENT

Because of hafnium and zirconium's limited solubility and reactivity in the environment, ecological health concerns in the aquatic environment or in soils are minimal. Furthermore, these elements do not accumulate in the food chain and they are not essential for human health. The sources of zirconium and hafnium only originate in the industrial system. They are considered elements of low toxicity to humans, and therefore the risk of exposure for the general population is considered low [54].

Within the mining industry, a temporary land use issue from the landscape distribution by surface mining is identified. The major direct emissions are related of the use of fossil fuels in machinery, acids and reagents like MIBK. Other associated elements might impact the environment, like thorium or uranium in baddeleyite, especially if they appear concentrated in waste streams [53].

SUMMARY

There is not a specific mining activity focused on hafnium. That explains the low rates of hafnium production. Hafnium is extracted from zirconium refining in metallurgical process for nuclear grade (similar chemical properties but almost opposite physical properties). These two elements are present in a wide variety of rocks, but rarely in economic concentrations.

Several commercial techniques for the separation of zirconium and hafnium exist, as well as studies to reduce extractive distillation and use of MIBK process. Apart from the fuel consumption, the radioelement concentration and the use of MIBK, there is no environmental impact specific to hafnium.

HEAVY RARE EARTH ELEMENTS

1. THE PRIMARY RESOURCES

The current section is referred to the assemblage of heavy rare earth elements (HREEs) including europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium, due to their common occurrence in the ore deposits. The main notable deposits of HREEs are presented in Table 4.

The Norra Kärr ore consist a grennaite rock which is composed by nepheline syenite with phenocrysts of eudialyte in a fine-grained groundmass rich in aegirine. It is subdivided into three distinct units: fine grained grennaite (GTC), pegmatitic grennaite (PGT) and migmatitic grennaite (GTM). The chondrite-normalized REE distribution of the ore can be seen in Figure 14 [62]. It is obvious that the ore is enriched in HREEs, except europium. The Norra Kärr reserves are estimated at 41.6 Mt with an average 0.57% concentration in HREOs.

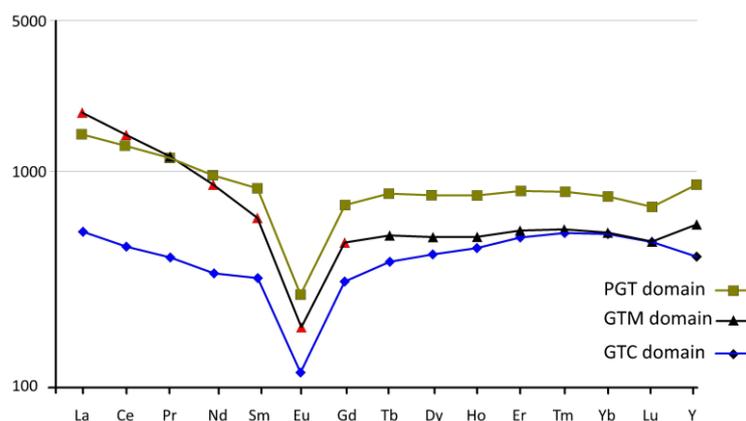


Figure 14 - Chondrite-normalized REE distribution for mineralized domains in Norra Kärr ore [62]

Kvanefjeld in Greenland is one of the largest HREEs-uranium deposits in the world containing 10.33 Mt of HREEs. The metallic values distribution of the ore can be seen in Figure 15. The main HREEs contained in Kvanefjeld deposit are praseodymium, dysprosium and terbium [63].

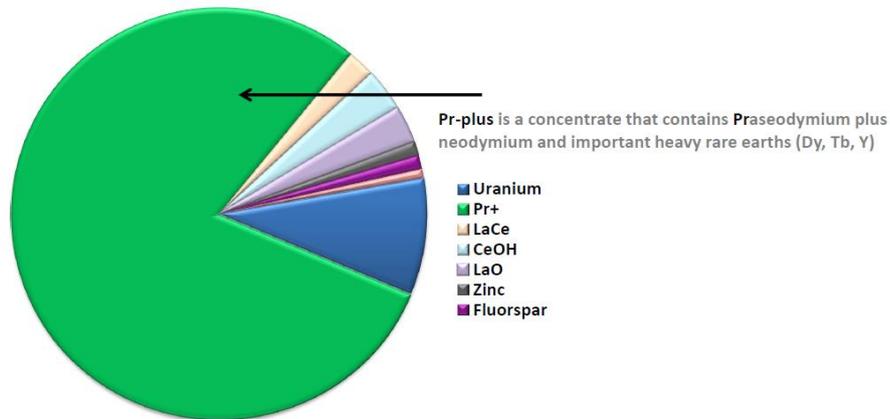


Figure 15 - Distribution of various metallic values in Kvanefjeld ore [63]

As mentioned in previous WP, several REEs occurrences have been reported in Finland. In southern Finland several localities with NYF (niobium–yttrium–fluorine) pegmatite types haven been described. The pegmatite veins occur into the Paleoproterozoic (1.85–1.80 Ga) Late Svecofennian granite–migmatite zone [64]. Furthermore, syentites intrusions occur within Svecofennian (ca. 1.92 Ga) gneisses in Lamujärvi. However, it should be noted that Lamujärvi occurrence is relatively poor in HREEs and the wt.% ratio between light (LREE) and heavy REE (HREE) is 91/9 [65].

Table 4 - The main primary unexploited resources of HREEs in EU [62], [63] [64], [65]

Type of ore	Yttrium form	Major deposits	Gaps and barriers			
			Mining	Beneficiation	Metallurgy	Residues
Alkaline intrusions	Eudyalite grennaite, kaxtorpите, lakarpите phases	Norra Kärr, Sweden			x	
Alkaline intrusions	Steenstrupine phase	Kvanefjeld, Greenland, Denmark	x			x

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Granitic pegmatites and syenites in gneiss	Allanite, gadolinite, fergusonite, monazite and xenotime	southern Finland, Lamujärvi				
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The technological barriers concerning the treatment of the residues generated by the processing of Kvanefjeld ore are described in detail in the YTTRIUM section. The current paragraph is focused on the expected problems related to the radiation exposure during the mining of Kvanefjeld deposit. Furthermore, the main technological barriers concerning the metallurgical processing of the European HREEs deposits are described.

2. GAPS & BARRIERS – PROPOSED PROCESSING ROUTES

MINING

No technological barriers have been reported concerning the planned mining process of European HREEs deposits. For example, Norra Kärr could be exploited by open pit mining. The deposit crops lie only under a thin soil cover, and is typically greater than 100 m wide, such that risk of dilution or loss is extremely low [62]. The most significant challenges are related to the exposure of radionuclides during the mining of Kvanefjeld ore in Greenland and the ensuring of workers safety. The most common area in mining operations in which elevated radioactivity is measured is the crushing circuit located in the mineral concentrator. In this installation, the ore is crushed to fine pebbles in the dry conditioning before wet grinding. As the coarse rocks from the mine are reduced in size, the trapped radon gas is released in the environment.

Assuming that 3 million tonnes of Kvanefjeld ore are treated annually with an average radon concentration in the crushing building of about 3000 Bq/m³, a dose rate due to inhalation of radon decay products of 8 µSv/h has been estimated. The average radon concentration is well above the reference concentration of 1000 Bq/m³ recommended for workplaces [66], which is also reflected in the estimated dose rate that in 1000 h would result in a dose of 8 mSv. However, the potential thoron release during the crushing has not been still precisely calculated. It has been assumed that the average thoron concentration in air will be about 400 Bq/m³ resulting in a dose rate contribution of 5 µSv/h [67].

The additional dose rate contribution from thoron in the mining area should be limited and monitored carefully to ensure that the dose rate will be below the respective reference established by the IAEA. As a solution for the decreasing of the radiation exposure during the

mining process, the wetting of the extracted ore has been proposed [67]. After its crushing, the ore will be contacted with water to produce slurry inside a grinding mill. The dry fine rocks will be converted to a mixture of water and powdered ore. The produced solids/ore will not be allowed to dry out (i.e. maintained in a water suspension or cover). The water cover will dramatically reduce the emissions of radon, alpha and beta radiation. Gamma radiation however will be still emitted through the water layer at acceptable doses.

BENEFICIATION

Norra Kärr, Sweden

The beneficiation of Norra Kärr ore has been optimized through various techniques. The most efficient complex flotation-magnetic separations process is described in the YTTRIUM section. The beneficiation tests are based on the principle that eudyalite is paramagnetic and can be separated by the other phases with higher magnetic susceptibility. The degree of eudyalite liberation was satisfactory for particle sizes of 60 µm to 80 µm [62].

Kvanefjeld, Greenland

Detailed beneficiation tests of Kvanefjeld ore through a simple froth flotation process have recently been performed at pilot scale [63]. The results showed that the ore is enriched x10 wt.% in REEs. No significant beneficiation barriers have been reported.

METALLURGY

Norra Kärr, Sweden

The metallurgical processing of the Norra Kärr has been established in detail. The method involves the leaching of the ore with sulphuric acid and subsequently the neutralization of the leachate with magnesium oxide. REEs are separated via solvent extraction using organic solvents. Eudyalite can effectively be dissolved with a mild acid concentration at 30 °C, while the REE extraction yield approaches 90%. The main technological barrier of the leaching process is related to the high concentration of the leachate, which decreases the efficiency of the followed solvent extraction step. In order to remove the silica, the pH is increased from the leach condition to a value in excess of pH 3 to destabilize the silica, causing it to precipitate. According to the published reports [68], the neutralization and the precipitation of silica is performed by the addition of MgO, however no detailed data is available in the literature.

Several techniques have been proposed for the removal of silica in leaching solutions and could be potentially examined as an alternative route in case of Norra Kärr ore. The use of a high temperature acid bake, usually with H₂SO₄, in order to carry out the desired reaction with

concomitant dehydration of any silica gel formed has been successfully applied. This technique increases the reaction rate and avoids the formation of gelatinous silica. A second technique is related to the changing of the character of the gelatinous silica residue from acid leaching such using incremental digestion. This approach can be achieved by utilizing stage wise addition of the ore to the leaching acid [69].

Kvanefjeld, Greenland

The metallurgical feasibility of Kvanefjeld ore has been tested at satisfactory level and no insurmountable gaps and barriers have been reported. The main parameters that still should be optimized concern: (a) the selection of the most effective leaching agent and (b) the preventing of zinc co-precipitation as impurity in HREEs precipitate [70].

The laboratory leaching testwork has demonstrated that atmospheric acid leaching at 95 °C of the flotation concentrate is the most cost effective and efficient method for the extraction of HREEs. However, the leach extractions for LREEs are relatively lower but consistent with industry standards. High pressure acid leaching provides no extraction benefit over atmospheric leaching.

The Kvanefjeld ore is rich in zinc, therefore the Zn content should be removed from the leaching liquor before the HREEs precipitation. The selective precipitation of Zn as zinc sulphide has been achieved using sodium sulphide solution. Subsequently, HREEs are precipitated by raising the pH with dilute sodium carbonate solution. There are no detailed available data in the literature concerning the Zn impurity content in the HREEs carbonate precipitate.

LANTHANUM

1. THE PRIMARY RESOURCES

According to the review study of Goodenough et al. (2016), the most important European resources are associated with alkaline igneous rocks and carbonatites [25]. Ilímaussaq Kringlerne deposit in Greenland, Fen carbonatite complex in Norway and Norra Kärr in Sweden consist the most significant EU deposits enriched in LREEs, and especially lanthanum. The technological gaps and barriers for the exploitation of Norra Kärr ore are described in Cerium D6.1 chapter.

Ilímaussaq Kringlerne in Greenland consist a large REEs deposit with a 0.68 wt.% average concentration in TREO. It is located neighbouring to Kvanefjeld deposit. Its mineralogical/geochemical characteristics are similar to the respective of Norra Karr ore. The HREE/LREE content ratio is 31/69 (Figure 16) [71]. REEs are hosted in eudyalite coarse grains (500 µm). The most significant advantage of the Kringlerne ore is that no radiological issues have been reported. The deposit is planned to be exploited by TANBREEZ Company group which is activated for over 20 years in the identification and development of mining projects in Greenland. According to the company, it is expected that a rate of 500,000 tonnes/year is going to be extracted the first years with an increase to 1.5m/t – 5 m/t. The ore will be mined and hauled to the treatment plant located on the adjacent fjord [71].

The Fen carbonatite complex located in south Norway is an enriched REE/Th deposit. It is reported to contain 486 million tonnes, of søvite rock type, with an average content of about 0.9% TREO, and is therefore considered among the largest REE deposits in the world. REEs of the Fen Carbonatite Complex deposit are found in synchysite-parasite minerals and in low-thorium monazite minerals [72]. Rödberg ore is a specific hematite-calcite-dolomite carbonatite rock type inside Fen complex deposit, that has been formed from ferrocarnatite transformation occurred by the action of groundwater oxidizing hydrothermal solutions. Comparing to other rock formations present in Fen complex, Rödberg ore is enriched in light REE (La to Eu in the lanthanide series) consisting a well exploited REE carbonatite deposit. LREE enrichment is caused by fine-grained dissemination of monazite, bastnäsite, parasite and/or synchysite minerals [73].

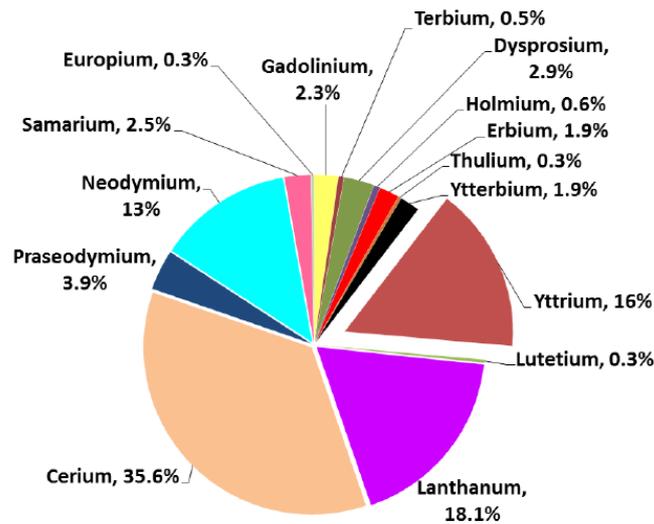


Figure 16 - REE elements distribution in Kringlerne ore [71]

Table 5 - The main primary unexploited resources of lanthanum in EU and their main processing barriers [25] [71] [72] [73].

Type of ore	cerium form	Major deposits	Gaps and barriers			
			mining	beneficiation	metallurgy	Residues
High temperature hydrothermal	Phosphate minerals (xenotime, allanite, monazite)	Olserum, Sweden		x		
Carbonatite	Ancylite-(Ce) and bastnäsite-(Ce)	Sokli, Finland		x		
Igneous alkaline intrusions	Steenstrupine phase	Kvanefjeld, Greenland, Denmark				x

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Igneous alkaline intrusions	Eudyalite and other phases	Ilímaussaq Kringlerne Greenland, Denmark (neighbouring to Kvanefjeld)			x	
Carbonatite	Distributed in monazite, bastnäsite, parasite and/or synchysite phases	Fen, Norway			x	x
Agpaitic rocks and syenites in gneiss	Eudyalite and other phases	Norra Kärr, Sweden			x	

2. GAPS & BARRIERS – PROPOSED PROCESSING ROUTES

MINING

The mining of Kringlerne and Fen ores have been well described and no gaps and barriers have been reported [73], [74]. Kringlerne ore is planned to be extracted from two open pits; Hill site on the plateau of the Killavaat Alannuat mountain and Fjord site at the shore of the Kangerluarsuk Fjord South-west of the port. It is expected that the production will start at the Fjord site and shift to the Hill site after approximately 5 years. Haul roads will connect the two mining areas with the processing plant which will be located at the shore of the fjord. The concentrates will be stored in buildings next to the processing plant. Tailings will be pumped through a 7 km pipeline to Fostersø for deposition. Fen deposit consist of a pipe with a depth at least 2 km. The mining of the deposit will initially take place with open pit excavation.

BENEFICIATION

Kringlerne deposit

The crushed and sized Kringlerne ore in the fine ore storage bin will be transferred by vibrating feeders to the magnetic separation plant where it is passed through a number of phases of magnetic separation. The three products from the magnetic separation consist of [73], [75]:

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- highly magnetic mafic minerals (arfvedsonite)
- weakly magnetic eudialite
- non-magnetic feldspar

The eudialite and feldspar will be transported onto separate stockpile buildings prior to export shipment, while the mafic minerals are tailings.

It should be stressed out that there is not enough published data concerning the chemistry and the mineralogy of the concentrate produced by the magnetic separation pilot tests. The exact metallurgical processing of the ore will be determined according to the mineralogical characteristics of the produced concentrate. Furthermore, the magnetic separation process should be upscaled at semi-industrial level in order the efficiency of the method be ensured.

Fen deposit (in respect to Rödberg ore)

Rödberg ore beneficiations was examined in the framework of Eurare project, however the results showed a low REEs liberation due to the fine gran size of the REEs-host mineral phases [76]. Unfortunately, there is not enough published data available.

METALLURGY

Kringlerne deposit

Kringlerne ore (eudyalite ore) was hydrometallurgically processed at pilot scale in the University of Aachen [77]. The route that was followed is described in the flowsheet of Figure 17 [77]. HCl and H₂SO₄ acids were used for the leaching tests, while the produced liquor was neutralized with CaCO₃. REEs were precipitated with Na₂CO₃. A 2 kg REE-carbonate (12.1% REE) mixture from 30 kg of Tanbreez concentrate was finally produced. More than 95% of REEs were precipitated producing the REE-carbonate. **The main problems that reported are:**

- **The formation of silica gel through the polymerization of silicic acid ($\equiv\text{Si-OH} + \text{HO-Si}\equiv \rightarrow \equiv\text{Si-O-Si}\equiv + \text{H}_2\text{O}$).**
- **Difficulties in leached material transport due to agglomeration in the fuming reactor (blockage of pump and valves with material)**

The formation of silica gel was limited by the addition of concentrate first and then the acid in appropriate ratio (max. 6 kg per charging in one reactor).

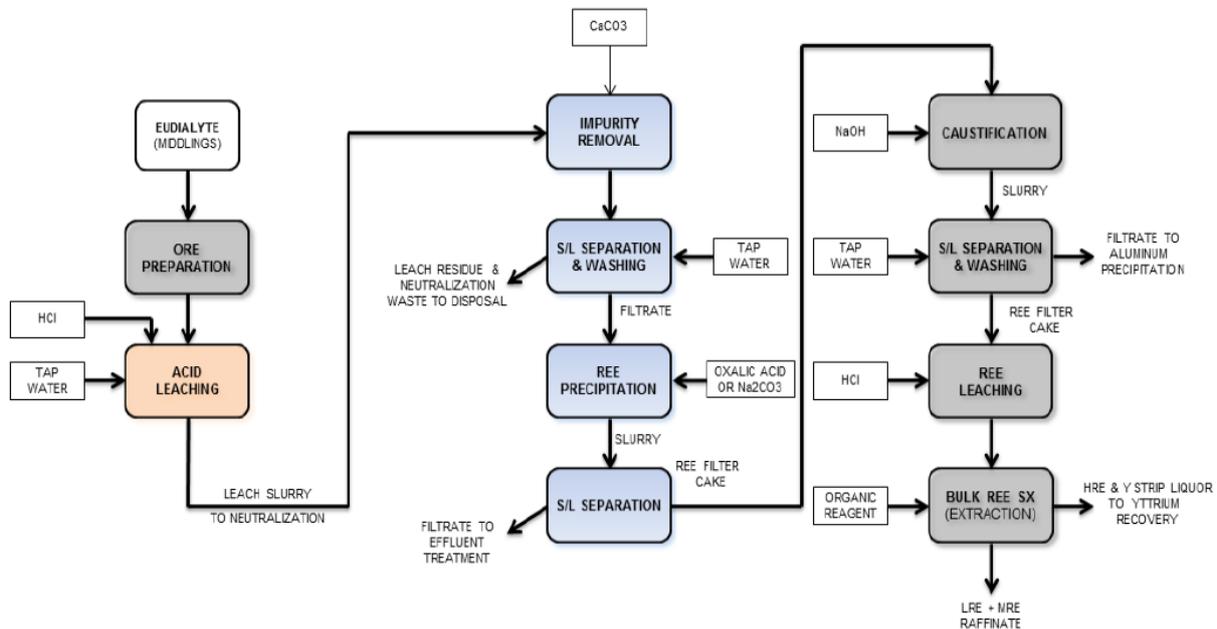


Figure 17 - Hydrometallurgical processing of Kringlerne ore according to the method developed in Aachen University [8]

As an alternative process for the eudyalite Kringlerne ore, the molecular recognition technology has been recently proposed [78]. The method is based on the sequestration of REEs ions on hybrid nanoparticles. The ore was leached with nitric acid and subsequently neutralized with NH_4OH at $\text{pH} \approx 6.5$. Silica-organic ligand nanoadsorbents were introduced in the neutralized solution. After the sequestration, centrifugation and drying of the nanoparticles, a final material containing wt.% 37.9 Ce, 8.7 Nd, 6.2 Y and 5.1 La was received. The results showed that a richer REEs product is obtained in comparison to the conventional leaching-precipitation method. However, the method should be upscaled.

Fen deposit (in respect to Rödberg ore)

REE hydrometallurgical extraction from bastnäsite (the dominant phase in Rödberg ore) is industrially applied through different hydrometallurgical routes depending on purity. Caustic soda cracking, sulfuric acid baking or a combination of roasting and HCl leaching are the main industrial methods for bastnäsite treatment.

The sulfuric acid leaching of Rodberg bastnasite ore from Norway containing an average of 1.36 % REEs has been in the direct leaching process [79]. The results showed that filtering difficulties do not happen for all parameter combinations. The optimum leaching conditions were: 2M concentration of sulfuric acid, 35°C heating, 80min, 150g/l slurry and 70rpm stirring. The maximum REEs recovery that achieved was around 75%. As second option, a combination of hydro and pyro metallurgy is proposed.

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As an alternative approach for Rödberg ore processing, the reductive smelting followed by leaching is proposed. The bastnaesite ore will be submitted to carbothermic reductive smelting producing metallic iron for steel industry and a slag. The slag should contain a high fraction of rare earth elements together with other compounds that normally appear in slags. Therefore, the slag can be considered a rare earth concentrate suitable for leaching operations in acid and for subsequent recovery of REEs [79].

According to a recently described route, the ionic liquid betainium bis(trifluoromethylsulfonyl)imide (HbetTf₂N) has been applied directly as a leaching agent on a low-grade rare earth element (REE) Rödberg ore [80]. Leaching tests were performed at laboratory scale, while REE load was received using HCl acid (Figure 18). The factors that were studied during leaching were water ratio into ionic liquid, leaching temperature, pulp density (%w/v) and retention time. Leaching of Rödberg ore with HbetTf₂N resulted to 65–100% recovery of light REE and 40–60% recovery of heavy REE. Additionally, 80–90% of Ca and Mg content dissolves, whereas the HbetTf₂N is selective against iron and silicon resulting in a Fe/Si rich residue.

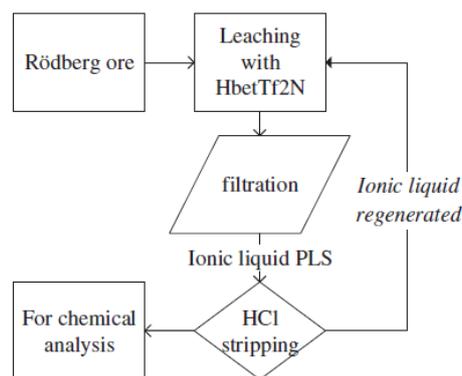


Figure 18 - Processing of Rödberg ore using ionic liquids [80]

The above quoted methods indicate that the hydrometallurgical processing of Rödberg ore should be upscaled either using the conventional method with sulfuric acid leaching or using ionic liquids. The purity of the received REE mixture (in respect to Ca and Mg content) should be examined in relation to various parameters.

3. ENVIRONMENTAL IMPACT OF ALTERNATIVE TECHNOLOGIES AND RESIDUE TREATMENT

A significant reserve of ²³²Th (675.000 tonnes) occurs in the Fen Central Complex. The extraction of thorium is not a priority, however natural occurring radionuclides (NORMs) are

in association with REEs phases in Fen district. Thorium occurs in several minerals, such as thorite ((Th, U)SiO₄), thorianite (ThO₂), allanite ((Ce,Ca,La,Y,Th)₂(Al,Fe²⁺, Fe³⁺)₃(SiO₄)₃(OH)), but the most common is the rare earth-thorium-phosphate mineral, monazite ((Ce, La, Nd, Th, Y)PO₄), which contains up to about 1-15 % thorium oxide (ThO₂). The NORMS total concentration was measured in several localities in Fen (Figure 19) [81]. It was found out that hot spot exists with high levels of radionuclides (up to about 7000 Bq/kg ²³²Th and 150 Bq/kg ²³⁸U) and elevated gamma dose rates (up to 10 µGy/h) were identified. “Hot spots” were observed within legacy NORM (former mining) sites, and also in some undisturbed surrounding ²³²Th-rich site. The above data should be taken into consideration as during the mining process solid residues with high concentrations in NORMs will be generated.

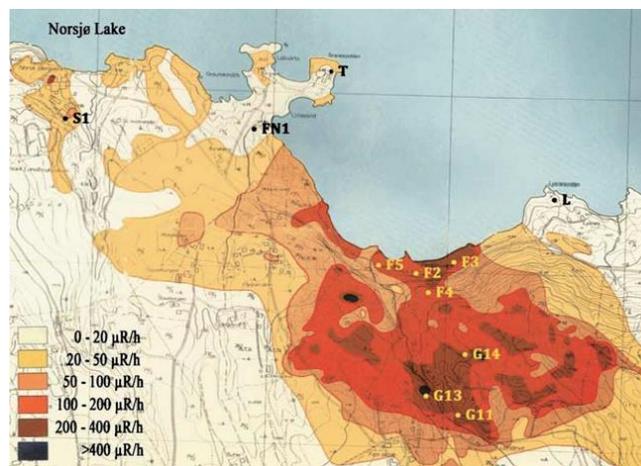


Figure 19 - Radiation map of Fen Central Complex in southern Norway [81]

NATURAL GRAPHITE

1. THE PRIMARY RESOURCES

Natural graphite is a crystalline mineral of pure carbon, which exists in the form of amorphous graphite, flake graphite and crystalline graphite. Natural graphite has important properties, such as chemical inertness, low thermal expansion and lubricity, which make it perfect material for certain uses such as refractories and steelmaking [21]. In 2016 the global mine production of natural graphite amounts to 1.2 million tons and the production is dominated by China (61%), India (14%) and Brazil (7%). In general, natural graphite is mainly used for refractories, batteries, friction products, lubricants and the other miscellaneous, as shown in Figure 20.

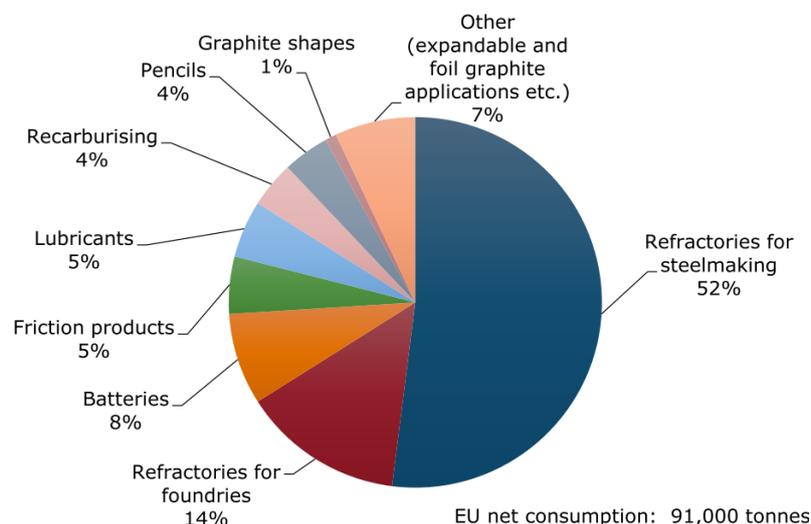


Figure 20 – Global uses of natural graphite in 2014 [21]

The only graphite mine currently (2018) in production in Europe is the Trælen flake graphite deposit, which is located in northern Norway, in the island of Senja. The graphite grade in the Trælen deposit is 31 % Cg and proven reserves are 1.8 Mt [82]. Both in 2016 and 2017, 8,000 tonnes of graphite were produced from the Trælen mine [55]. Graphite producers in the EU28 have clearly experienced difficult times in recent years, with production ceasing but restarting in Austria, Germany and Sweden, stopping completely in Czech Republic and ceasing, restarting and then ending again in Romania (Figure 21). In 2015 production amounted to 22,351 tonnes in the EU28 (mostly from Austria) compared to a global total of 2.2 million tonnes [83].

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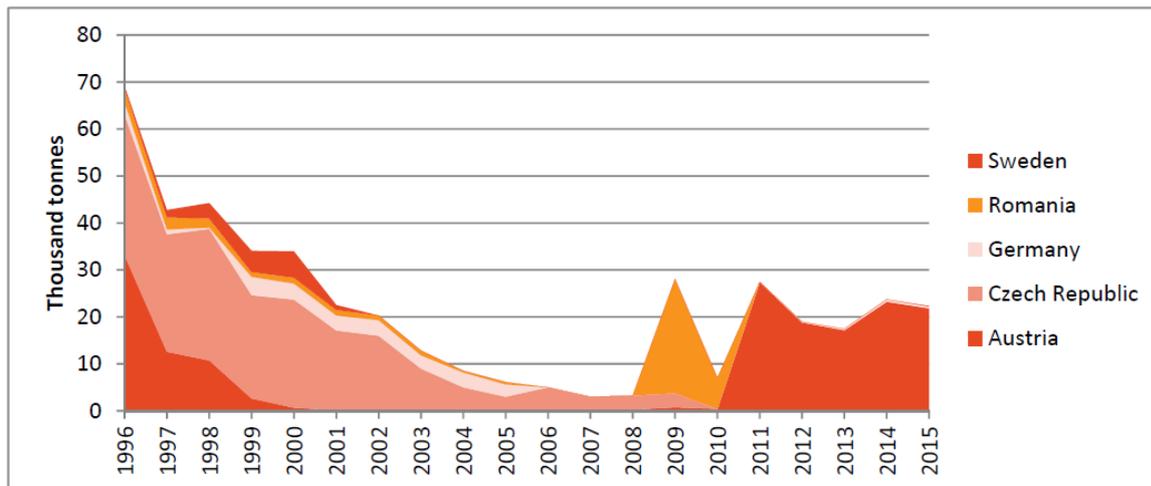


Figure 21 – Natural graphite production in the current EU28 countries during the period 1996-2015 [83].

2. GAPS & BARRIERS – PROPOSED PROCESSING ROUTES

MINING

Natural graphite can be mined by both open pit and underground mining methods. Open pit mining involves extracting rock or minerals from an open pit or burrow. Drilling and blasting methods are common methods used to liberate large-sized graphite flakes. Underground mining is done when the ore is present at a greater depth. Drift mining, hard rock mining, shaft mining and slope mining are methods used for underground mining [84].

BENEFICIATION

The mineral processing of natural graphite may vary from a complex four-stage flotation (e.g. mills at Europe and United States) to simple hand sorting and screening of high-grade graphite ore at Sri Lanka. A typical processing flowsheet of processing natural graphite is shown in Figure 22. The key steps for the processing include comminution (crushing, grinding, etc.) and flotation [85].

- **Comminution.** Size and grade are two important parameters of graphite products for commercial considerations. On one hand it is the best to maximize the number of large particles (flakes) and minimize the comminution steps. On the other hand, proper comminution is required to liberate the gangue minerals and impurities. Therefore, the comminution of natural graphite varies with the type of the ore to be processed.
- **Flotation.** Graphite is naturally hydrophobic; thus, it can be upgraded by flotation. As for natural graphite, surfactants and depressants are normally added to improve the

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flotation process. In general, graphite flotation is carried out by combining a simple rougher flotation stage with several stages of cleaning flotation. Fine graphite can be upgraded to about 95% carbon by flotation.

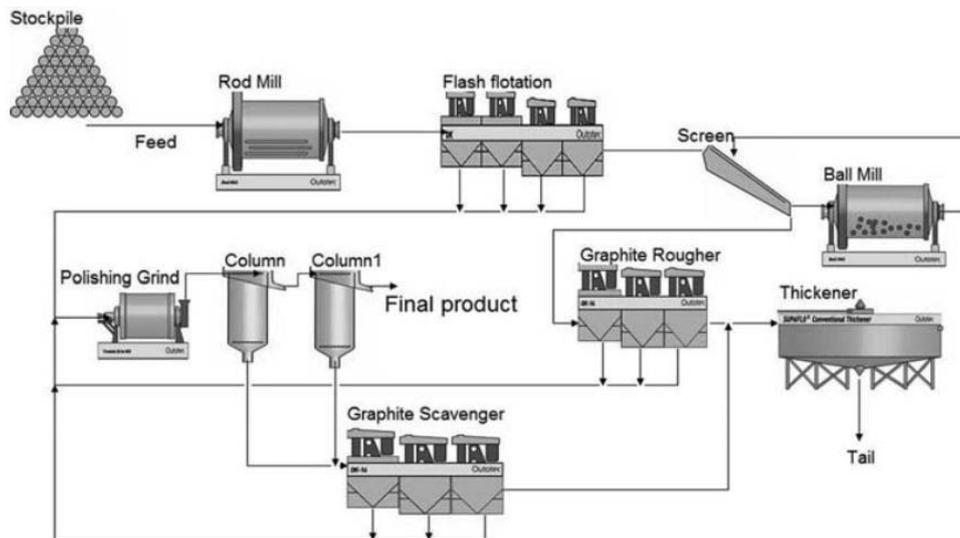


Figure 22 – Typical flowsheet of processing natural graphite [85]

Dense media separation (DMS) is considered the most efficient of the gravity separation processes. The graphite with less gangue content and higher carbon content is less dense, thus easier to float in DMS. Using ZnCl₂ solutions, DMS, allowed a 92% upgrading of microcrystalline graphite [85].

Processing ultra-fine graphite is very complicated, nevertheless there is some demand for fine graphite flakes. Recent studies demonstrated that it is possible to selectively separate very fine graphite from a mixture of minerals by film flotation. In this method the graphite particles cluster at the air-water interface. It has been estimated that about 60% of very fine graphite particles can be recovered at the water surface [85].

Another technic for fine graphite purification is the two-liquid separation. Such method uses differences in surface wettability of minerals in water and oil. At the end of the process, impurities are left in the aqueous phase while fine graphite particles are transferred into the oils phase and collected, allowing to agglomerate, adding acetone. Experimental results showed an impurity reduction from 8 to 2 wt%. Ash content can be reduced from 16 to less than 1.8 wt% [85].

REFINING

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To produce high purity graphite two processes are commonly used to refine graphite: acid leaching and roasting [85].

- Acid leaching is the most common technique to refine the natural graphite after flotation. The commonly used acids include HCl, HF, H₂SO₄, HNO₃ or even mixtures of them. The type of the acid to be used is dependent on the type of the impurities in the graphite. Sometimes, acid leaching is also taken as a pretreatment before floatation, as the leaching process reduce the contents of impurities in the graphite and thus increase the hydrophobicity of the graphite. Acid leaching is an effective way to remove silicate impurities, while the products usually contain too much sulfidic sulfur, which needs to be removed by additional refining process.
- Roasting-leaching is an effective way to eliminate both silicates and sulfides from the graphite concentrates. The roasting-leaching process normally consists of roasting, water washing and then acid leaching. According to the literature, treatment of 1 Mt graphite concentrate needs 450-500 kg NaOH and requires numerous steps of digestion, washing and drying of the graphite. The roasting-leaching process can produce graphite with 99.99% carbon. The main drawbacks of this process are the generation of a large quantity of acidic and alkaline wastewater.

Microwave treatment [85]: to avoid the residues of the roasting-leaching process an alternative method has been tested, such method uses a microwave heating technic. The different matter bonded to graphite absorbs in different ways the microwave radiation, thanks to such property pyrite may be selectively heated and decomposed into pyrrhotite or iron sulfate. Furthermore, the bonds of sulfur-carbon in organic sulfur compounds can be broken. Microwave treatment can be considered an efficient pretreatment of natural graphite before comminution or chemical leaching. A leaching experiment with HCl and HNO₃ and microwave radiation proved the effectiveness of the describe technic increasing graphite grade from 95 to 99.43%.

3. ENVIRONMENTAL IMPACT OF ALTERNATIVE TECHNOLOGIES AND RESIDUE TREATMENT

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

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SUMMARY

The global demand of graphite is increasing, leading to the necessity to exploit lower grade resources. To maintain the required purity of graphite it is necessary to develop efficient beneficiation and refining techniques. The main beneficiation techniques used nowadays are comminution and flotation, nevertheless new promising methods are being studied to increase separation efficiency and allowing an effective recovery of finer graphite. High purity graphite is particularly important for current demand. The main refining techniques used to obtain high purity degrees are acid leaching and roasting leaching, but an alternative method, microwave treatment, may allow to obtain higher purity degrees and reduce the dangerous residues produced during leaching processes.

NEODYMIUM PRASEODYMIUM DYSPROSIUM SAMARIUM

1. THE PRIMARY RESOURCES

According to the resource-mapping results of WP3, the main primary neodymium, praseodymium, dysprosium (heavy REEs) and samarium, which consist the base components for the construction of permanent magnets occur in Scandinavian countries (including Greenland) and Finland [25]. The petrology of the main Nd-Dy-Pr and Sm containing ores in Europe is characterized by alkaline or agpaitic intrusions (Table 6). The Norra Kärr deposit is located in southern Sweden approximately 300km SW of Stockholm consisting the only heavy REE deposit of note within the European Union (except Greenland) and can provide the EU with a long term REEs capacity. The Norra Kärr reserves are estimated at 41.6 Mt with an average 0.57% concentrations in REOs [62]. As it can be seen in Table 7, Norra Kärr ore, in addition to LREEs and yttrium, contains also elevated concentrations of Nd-Dy-Pr and Sm. Kvanefjeld and Kringlerne in Greenland consist two major deposits rich in heavy REEs (neodymium, dysprosium and praseodymium).

Öko-Institut (2011) estimated that the annual produced amount of neodymium and dysprosium in Greenland can reach 33.000 and 2.000 tons respectively. This amount represents the 5-8% of the global neodymium supply and 10-16% of the global dysprosium supply [86], [87]. Kvanefjeld ore has been characterized as a premium rare earth oxide concentrate ('Premium REE') containing primarily terbium, dysprosium, neodymium and praseodymium, and as well as LREEs (lanthanum and cerium). The average concentration of Kvanefjeld ore in REOs is about 1.09 wt.%, while the specific HREEs concentration has been estimated at 12% of total REOs content. In addition to REEs, uranium, zinc concentrate, fluorspar and sodium hypochlorite (NaClO) is planned to be extracted according to the metallurgical process.

The Kringlerne deposit comprises the layered kakortokites in the southern part of the Ilímaussaq Complex, with eudialyte-group minerals and their alteration products (notably catapleiite and nacareniobsite-(Ce)) as the main economic minerals. It is estimated that its average REOs content is about 0.65% wt.% including a high ratio of HREEs (0.31% of the total REOs). The absence of containing radionuclides consists the main advantage for the processing of Kringlerne ore. In addition to Kvanefjeld and Kringlerne, several other smaller deposits containing HREEs have been discovered and geologically described in Greenland (Table 8).

Table 6 - The main primary unexploited resources of Nd, Dy, Pr and Sm in EU [25], [62], [86], [87].

Type of ore	Yttrium form	Major deposits	Gaps and barriers			
			mining	beneficiation	metallurgy	Residues
Alkaline intrusions	eudyalite grennaite, kaxtorpite, lakarpite phases	Norra Kärr, Sweden			x	
Alkaline intrusions	Steenstrupine phase	Kvanefjeld, Greenland, Denmark				x
Agpaitic nepheline syenites	Eudyalite and other phases	Kringlerne, Greenland, Denmark				

Table 7 - Chemical analysis and REEs recovery from Norra Kärr ore according to the study of Saxon et al. 2015 [87].

Element	Overall Recovery [%]	Weight [%]	Relative % Distribution
La	77.84	4.935	10.9
Ce	78.02	10.750	23.6
Pr	78.82	1.458	3.2
Nd	79.01	6.763	14.9
Sm	79.42	1.650	3.6
Eu	79.44	0.269	0.6
Gd	79.32	1.657	3.6
Tb	79.13	0.351	0.8
Dy	78.78	2.191	4.8
Ho	78.00	0.491	1.1
Er	77.40	1.288	2.8
Tm	76.89	0.182	0.4
Yb	76.10	1.138	2.5
Lu	75.48	0.149	0.3
Y	72.92	12.210	26.8

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Table 8 – Greenland deposits containing HREEs according to European Commission reports [86].

Locality	Metallogenetic type	Type of resource estimate	Exploration status	Tonnage (Mt)	Tonnage TREO (Mt)	Grade (%) TREO	HREE (%)	Grade Co-/by products
Kvanefjeld	Alkaline igneous	JORC-Indicated	Feasibility	437	4.77	1.09	12	U: 274 ppm Zn: 0.22% F: n.a.
Sørensen	Alkaline igneous	JORC - Inferred	Feasibility	242	2.67	1.1	13	U: 304 ppm Zn: 0.26% F: n.a.
Zone 3	Alkaline igneous	JORC – Inferred	Feasibility	95	1.11	1.16	12	U:300 ppm Zn: n.a. F: n.a.
Kringlerne	Alkaline igneous	JORC - Inferred	Feasibility	4,300	28	0.65	31	Zr ₃ O ₈ : 1.8% Nb ₂ O ₃ : 0.2%
Motzfeldt	Alkaline igneous	n.a.- Inferred	Exploration	340	0.9	0.26	19	Ta ₂ O ₃ :120 ppm Nb ₂ O ₃ :1850 ppm ZrO ₂ :4600 ppm
NIAQ Karrat	Carbonatite associated?	n.a.	Exploration	26	0.3	1	13	n.a.
Sarfartoq (ST1)	Carbonatite associated	NI 43-101 - Inferred	Scoping	14.1	0.2	1.53	2	n.a.
Qeqertaasaq	Carbonatite/Vein associated	n.a.	Exploration	45	0.5	1	1	Nb ₂ O ₃
Milne Land	Fossil placer	n.a.	Exploration	5	0.1	1	13	2% ZrO ₂

2. GAPS & BARRIERS – PROPOSED PROCESSING ROUTES

MINING

REEs containing ores worldwide ores are mined underground or superficially (open pits) following the hydrothermal or pegmatite veins (in case of non-altered rocks). Mining techniques are well developed and no gaps and barriers at the mining step have been reported.

BENEFICIATION

Norra Kärr, Sweden

Extensive beneficiation test work has been completed on representative samples from Norra Kärr aiming to the separation of eudialyte which is the most significant REEs-bearing phase. The beneficiation includes the crushing, grinding, magnetic separation of the ore. Eudialyte beneficiates efficiently using Metso's HGMS magnetic separation equipment, providing a clean and high recovery eudialyte-rich mineral concentrate. Beneficiation recovery higher than 90% is now expected and targeted [88]. The main parameter which should be optimized concerns the value of the magnetic separation intensity in order the low-magnetic eudyalite-

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aegirine be separated from the paramagnetic oxide phase. Otherwise, it has not been reported any significant technological barrier at the beneficiation step.

Kvanefjeld, Greenland

A pilot scale beneficiation plant for Kvanefjeld was designed and operated within the framework of Eurare EU research project. Froth flotation and Jameson cell technologies were used for the beneficiation tests [89]. An ore amount of 26 tonnes was successful treated in the pilot scale beneficiation circuit producing 2 tonnes of rare earth rich mineral concentrate. The results demonstrated the satisfactory effectiveness of the flotation methodology to generate a high-grade mineral concentrate from the extensive Kvanefjeld resources. The recovery of the REEs content exceeded 80%. Greenland Minerals Limited Company in a recent report supports that the flotation methodology for the processing of the Kvanefjeld ore has been further improved exceeding 95% of REEs extraction [89]. **Therefore, according to the available data, no important technological barriers are reported for the benefaction step.**

Kringlerne, Greenland

Kringlerne ore presents several mineralogical and geochemical similarities with Norra Karr ore. The HREE/LREE % ratio is about 31/69, while the majority of the REE amount is contained in eudyalite (33 wt% in the ore) which is average grain size is about 500 µm. The beneficiation through dry magnetic separation technique has been successfully tested. Over 1.5 tonnes of Kringlerne ore were processed at the TANBREEZ facilities in Australia using an Eriez 24" Salient Pole Rare Earth Drum magnetic separator, producing a 200 kg concentrate containing 1-2 wt% REEs. no major technological difficulties were reported [90].

METALLURGY

Norra Kärr, Sweden

The metallurgical processing of the Norra Kärr has been established in detail. The method involves the leaching of the ore with sulphuric acid and subsequently the neutralization of the leachate with magnesium oxide. REEs are separated via solvent extraction using organic solvents (for more details: D.6.1 Yttrium paragraph). The main technological barrier at the metallurgical processing is related with the formation of silica gel when leaching is performed operating at high pulp densities. The pregnant leach solution generated by the sulphuric acid dissolution of the eudialyte mineral concentrate has a characteristically high silica concentration that is in excess of that acceptable for metal recovery by traditional solvent extraction. To remove the silica, the pH is increased from the leach condition to a value in excess of pH 3 to destabilize the silica, causing it to precipitate. The neutralization residue, comprised largely of silica and minor contributions of Zr and aluminium (Al), is then separated

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from the PLS and washed to recover the entrained solution. Further leaching and precipitation test should be performed at pilot scale, in order the whole processes be optimized and the formation of silica gel be avoided [91].

Additionally, it has been observed that during the stirring in solvent extraction process, the oxalic acid was contacted with the loaded organic causing the formation of a rare earth oxalate precipitate at the interface of the two phases. Therefore, an additional centrifugation step is required for the collection of the interface precipitate. The stirring with alternative mechanical techniques could be examined.

Kvanefjeld, Greenland

Kvanefjeld ore has been submitted to extensive metallurgical test including bench scale and pilot plant tests, while the economic feasibility of its processing has been studied. The flow sheet, which utilises well developed technologies, comprises atmospheric leach circuit and selective precipitation circuit. The already performed test include [92], [93]:

- 60 bench-scale leach tests and several larger scale semi-continuous leach tests using a concentrate amount of 20-30 kg
- The leach discharge slurry produced from the semi-continuous leach test-work has been used to evaluate the performance of downstream units of the preferred flowsheet
- Samples of rare earth intermediate products have been produced and are currently under evaluation as feed for further processing in rare earth separation plants

The selected metallurgical process has been presented in the framework of Eurare project and it can be seen in Figure 23. The leaching is performed using sulphuric or hydrochloric acid at two stages: the first for the dissolution of the uranium rich phase and the second at more intense conditions aiming to the leaching of the REO phase. REEs are precipitated using caustic soda. The results showed:

- High rare earth recovery (over 90% yield)
- Good selectivity against impurities (Ca)
- No requirement to heat circuit and simple circuit operability based on pH

No significant processing barriers have been mentioned. However, the health and safety conditions should be more precisely described, especially concerning the management of the uranium-rich leachate and the U solvent extraction process.

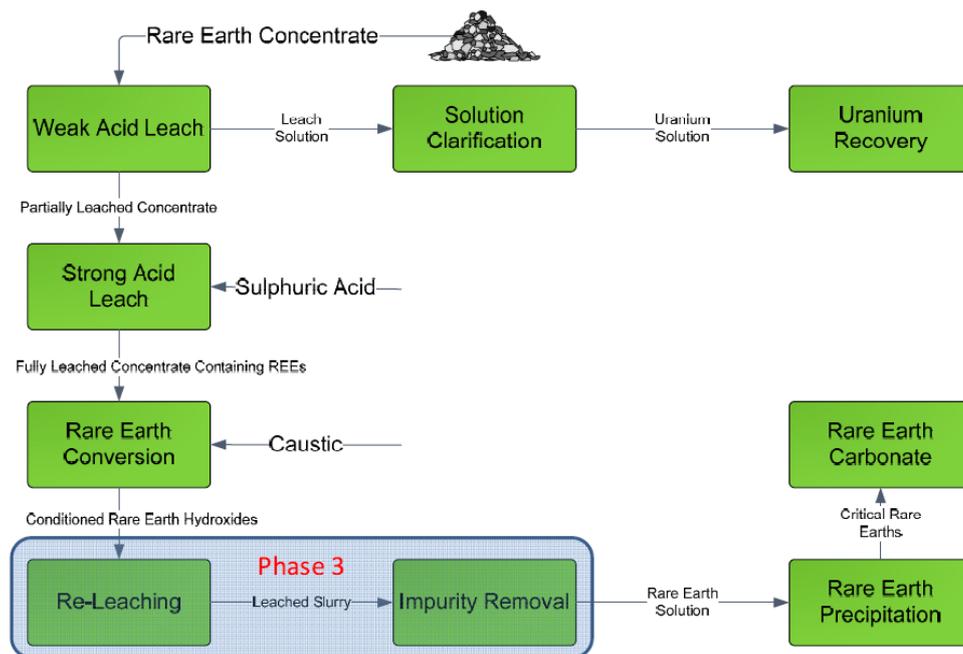


Figure 23 - Metallurgical processing of Kvanefjeld ore [64]

Kringlerne, Greenland

Eudyalite rich concentrate after magnetic separation process was hydrometallurgically processed via leaching and solvent extraction at Aachen University within the framework of EURARE project. Totally, 24kg of REE mixed concentrate was produced which again was separated into streams of La/Ce, Nd/Pr, Y and HREE chloride fractions. The high concentration of iron was faced with an additional precipitation test [90].

3. ENVIRONMENTAL IMPACT OF ALTERNATIVE TECHNOLOGIES AND RESIDUE TREATMENT

Kvanefjeld deposit – wastes treatment

Hazardous wastes generated during the metallurgical processing will be handled according to international standard regulations. In general, hazardous wastes will be shipped to Denmark and handled in compliance with a comprehensive EU initiated legal framework. Hazardous waste will be registered and traced using code standards. Wastes suitable for incineration is planned to be collected in Narsaq and transported to Qaqortoq for treatment at the incinerator. Qaqortoq will be the regional centre for receiving different waste types

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transported by ship and boat. Finally, all hazardous waste and scrap metal will be sent on to Denmark from Qaqortoq [94], [95].

Kvanefjeld deposit – radiation exposure

Radiation exposure is expected mainly during the mining process in the open pit locality. The expected annual gamma ray dose for the workers in the open pit has been calculated at 3.8 mSv which is significantly below the radiation limit for a worker according to the IAEA (20 mSv) [94], [95]. A second source of radiation exposure will be uranium oxide product during its transportation in solid form as the chemical uranium peroxide, UO_4 . It will be packaged into 200L steel drums and strapped into 20-foot sea containers, with handling and transportation consistent with IAEA guidelines. Given these conditions, the assessment concluded that doses to transport workers are well below dose limits. The radiation exposure to the local community (neighbouring villages) is a matter of low concern.

Arcadis Company has recently undertaken a detailed assessment of potential radiation exposure for both ecological and human receptors in relation to the Kvanefjeld project. The assessment considered exposure pathways for two categories of human receptors: town residents and visitors to the area, across three age groups: a toddler, a child and an adult. Exposure pathways which were considered included inhalation, consumption of water and food from local origins, radon and gamma exposure. The results showed that baseline exposure of town residents through food ingestion and radon is between 8-10 mSv/y, with radon exposure comprising 70% of this indicating a low-level radiation effect [94], [95].

NIOBIUM/TANTALUM

1. THE PRIMARY RESOURCES

Niobium and tantalum are transition metals. They have similar physical and chemical properties and are usually found as solid solutions in the same type of mineral deposits. In case of Columbite-tantalite, they are represented by the formula $(Fe, Mg, Mn)(Nb, Ta)_2O_6$, or minerals from the pyrochlore group.

The main economic resources exploited for tantalum are found in granite sections as well as in pegmatites that concentrate the following rare elements: Li, Nb, Rb, Cs, Be. It is often operated in co-product of niobium and lithium deposits. The main exploited tantalum minerals are, tantalite, Colombo-tantalite, Columbite, Wodginite, Struverite and Loparite (perovskite group). Addition of many pegmatites under evaluation in the northern regions of Europe and in Ireland, six main areas with Sn, Ta and Li were identified in the middle and southern Europe including the French district of Échassières (Allier).

Niobium and tantalum are enriched in alkali granites and syenites, carbonatites, granites on rare metals and pegmatite. Niobium and tantalum are present respectively in alkali carbonatites, and in granite and pegmatite of Sn Li.

The global production of tantalum was about 1200T in 2013 (44.5% Rwanda, 19.2% Congo, 13.5% Russia 7.7% Brazil, 4.7% Nigeria, 4.7% China and 3.1% Canada) see Figure 24. The worldwide production of Nb was about 58kT for Niobium in 2014 (89.6% in Brazil and 10.4% in Canada) see Figure 25. The worldwide reserve of deposits was estimated about 130-140 kt of tantalum. Australia represents about 49% of Ta reserve, and Brazil 26% (Figure 26). The worldwide reserve of Nb was more than 42MT in 2015, as shown by figure 4, 95% was in Brazil and 5% in Canada.

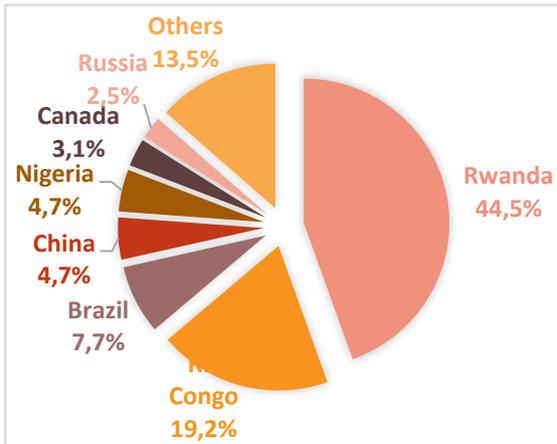


Figure 24 - Worldwide Ta production in 2013

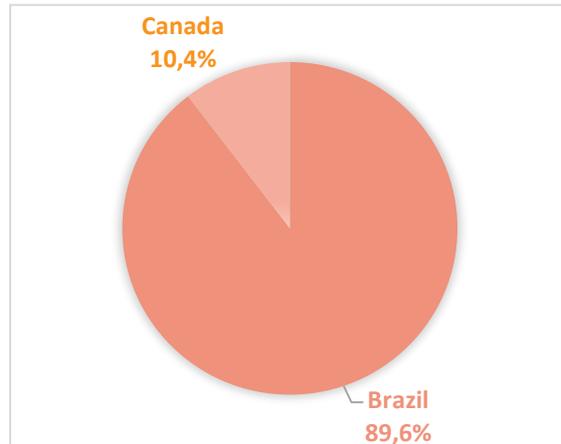


Figure 25 - Worldwide Nb production in 2014

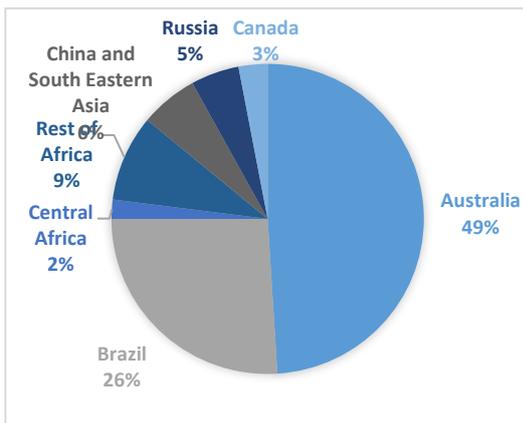


Figure 26 - Worldwide estimated reserves of Ta in 2015

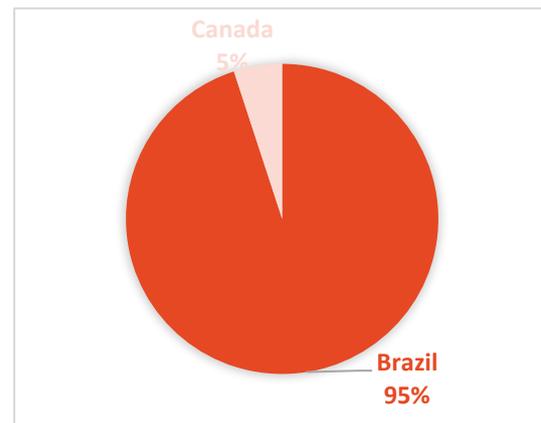


Figure 27 - Worldwide estimated reserves of Nb in 2015

2. GAPS & BARRIERS – PROPOSED PROCESSING ROUTES

According to the literature, the global Ta/Nb extraction process is very simple and easy. The main issues are as follow:

1. Low grade of Ta/Nb in deposits
2. The most important deposits of Ta/Nb are located in the conflict countries
3. The variation of Ta/Nb prices
4. The toxicity of reagents used in flotation and leaching technique

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MINING

Figure 28 shows the global distribution of Nb and Ta mines and deposits in overall the world. It is important to underline that the contribution of Europe in the world production of tantalum concentrate is very low. The only primary production of this metal is found in Echassières kaolin quarry (in France) which in 2011 produced 55 tons of Sn-Ta-Nb concentrate at 10% Ta₂O₅, i.e around 4.5 tons of Ta [96].

According to [97], there are five main known deposits of tantalum:

1. Deposits associated with granitic pegmatite (Lithium Cesium Tantalum)
2. Deposits associated with granites. These deposits (high reserve) contain low Ta such as (Abu Dabbab (Egypt), Ghurayyah (Saudi Arabia), Yichun (China) or Échassières.
3. Deposits associated with complexes carbonatites: These deposits are mainly exploited niobium (pyrochlore), tantalum is less concentrated such as in Niobec or Oka (Canada)
4. Deposits associated with hyper-alkaline complex (the capacity of deposits lower than 100 Mt with low content of Nb and Ta (0.1 à 1 % Nb₂O₅ and < 0.1 % Ta₂O₅). AZ fex exploitation of this type of deposits. Several projects are going on such in Gardar (Groenland).
5. Deposit alluvial (Placer) may have significant concentrations in tantalum. Ore, frequently consisting of Colombo-tantalite, is easily recoverable by a simple gravity process. These deposits are located mainly in Central Africa (Democratic Republic of the Congo, Rwanda, and Burundi) and in Russia (Urals).

Coltan extraction in Democratic Republic of the Congo (DRC)

Around 80% of Africa's tantalum reserves can be found in the DRC which is considered as conflict country. The tantalum is in the form of columbite-tantalite (coltan), which is easy to be extracted.

Niobium–tantalum

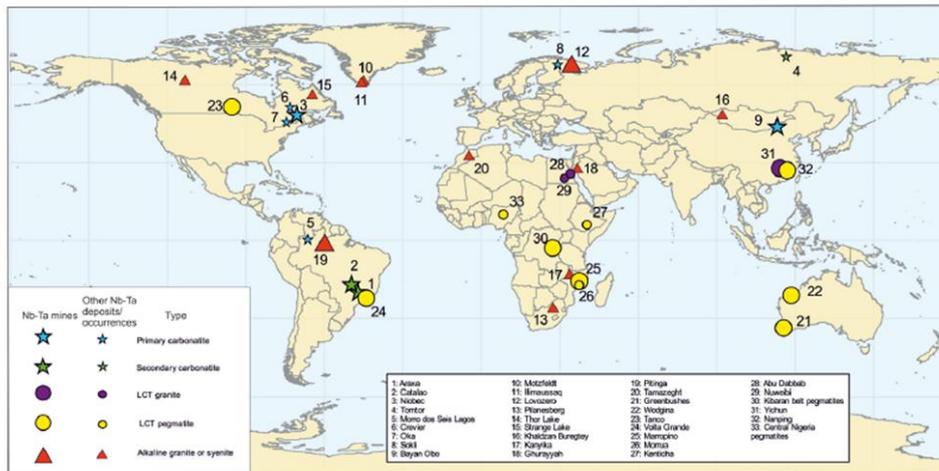


Figure 28 : Map showing the global distribution of Nb and Ta mines, deposits and major occurrences [96]

BENEFICIATION

Beneficiation of ores (from ores to concentrates)

As shown by Figure 29, tantalum oxide is concentrated from both minerals of Microlite and Colombo-tantalite. The process consists of the following operation units of mineral techniques [97]:

- Comminution and screening using conventional grinding, ball mill, and screens
- Fine and coarse de-sliming by using, screens and cyclones
- Conventional Low and High intensity magnetic separation to remove magnetic phases contained
- Flotation, by using diamine, xanthate as collectors in order to concentrate Ta/Nb
- Calcination to remove, antimony and sulphides. Using reagent for fine flotation is cost factor for the process and pollute the environment.
- Purification of concentrates of Ta₂O₅ (54%) in Microlite and 29-30% in Colombo-tantalite

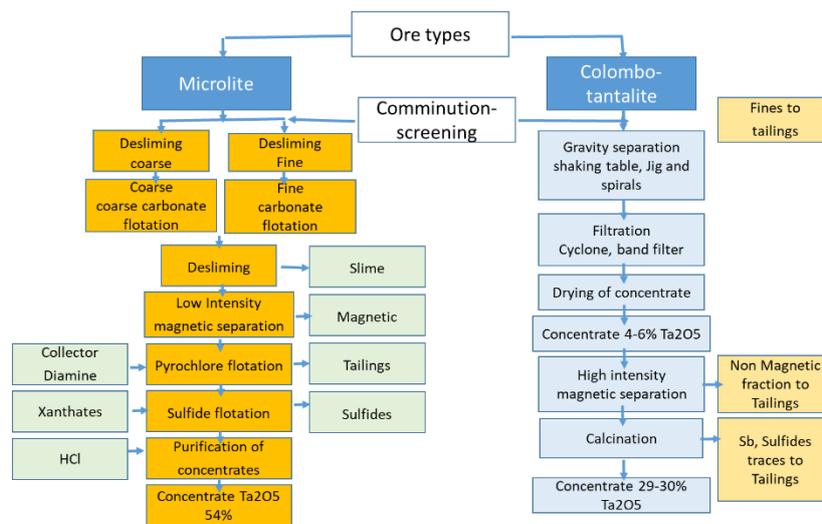


Figure 29 : Enrichment of Tantalum contained in Microlite (Pyrochlore) ore and Colombo-tantalite [97]

METALLURGY

Extractive metallurgy (From concentrates to marketable products)

In the literature, some tantalum extraction processes are identified from ore to two pure intermediates K_2TaF_7 and Ta_2O_5 by extractive metallurgy of tantalum starting from processing of its ore to two pure intermediates and their conversion to pure tantalum metal by various technically feasible processes. Though tantalum metal can be produced by several means only two processes – sodium reduction of K_2TaF_7 and fused salt electrolysis of K_2TaF_7 in the presence of oxide, have been successful on industrial scale

Fluorides, oxides and chlorides are the main compounds from which tantalum metal can be obtained. The concentrate of Ta/Nb is leached by mixture of HCl and H_2SO_4 to dissolve the metals contained. The metals in the solution obtained after filtration are separated by solvent extraction, allowing extraction of valuable metals from unwanted elements (Fe, Mn, Sn and Ti), by adding cyclohexane, de MIBK (methyl isobutyl ketone) or TPB (Tributyl phosphate). Ta-Nb solution is washed by H_2SO_4 (6-15N), then Ta and Nb are extracted by selective precipitation and after reduction and calcination, the products Ta_2O_5 and Ta-Nb carbide are obtained.

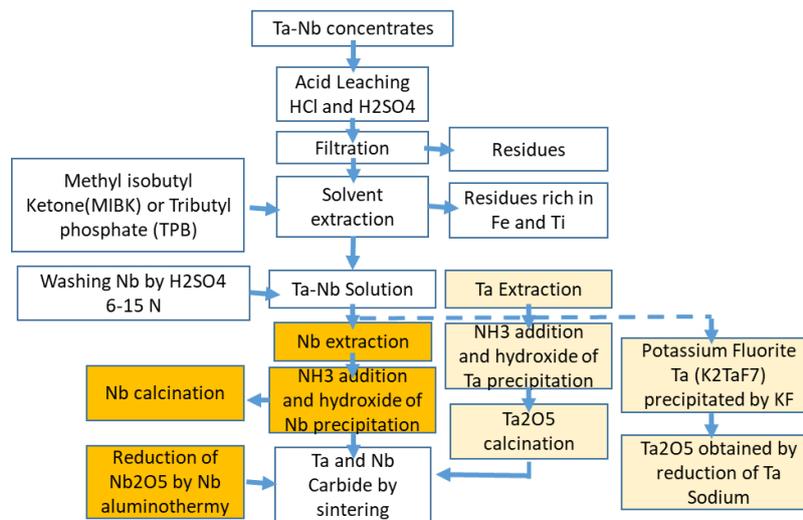


Figure 30 : Flowsheet of Recovery process of Ta and Nb from concentrates [97]

3. ENVIRONMENTAL IMPACT OF ALTERNATIVE TECHNOLOGIES AND RESIDUE TREATMENT

A few alternative technologies are reported in the literature. It seems that some investigation works are focalised on substitution of reagents used in the solvent extraction technique. For example: Substitution of HCl by ammonium he-fluoride (NH_4HF_2) allowing the selective precipitation.

The residues containing non recovered valuable metals and the effluents laden with organic matters of the processes may have an environmental impact.

SUMMARY

Niobium and tantalum are transition metals and have a similar physical and chemical properties. The main exploited tantalum minerals are, tantalite, Colombo-tantalite, Columbite, Wodginite, Struverite and Loparite, and the niobium is extracted as by product. The main economic resources exploited for tantalum are found in granite sections as well as in pegmatites. The contribution of Europe world production of tantalum concentrate is very low. The extraction process of Ta/Nb from ores is simple and easy. The technological barrier is mainly related with its beneficiation effectiveness and utilization of the toxic reagents applied in flotation and leaching technique. A few alternative processes are suggested to substitute the toxic reagents which may have an important environmental impact.

PGM

1. THE PRIMARY RESOURCES

Platinum Group Metals (PGM) consists of six neighboring metals in the periodic table: Ruthenium (Ru), Rhodium (Rh), Palladium (Pd), Osmium (Os), Iridium (Ir) and Platinum (Pt). These metals have a similar chemical property and are always associated with different concentration in the ores. Pt and Pd are the elements that are mainly present in the ores, and other metals are considered as by-products. PGM are used in a wide range of applications such as: electronic components, catalysts for chemical processes, vehicle catalytic converters, hydrogen fuel cells, and in the medical sector. The utilisation of Ru and Ir is very specific and limited.

The mines of PGM are associated to basic or ultrabasic magmatic rocks mantle origin, and to placers resulting from their erosion. The mines are classified as follow:

1. PGM mines rich and less sulfur, the platinum concentration is higher than Palladium. These mines can be found in Bushveld (South Africa), Great Dyke (Zimbabwe), Stillwater (USA).
2. Mines of sulfide of Nickel-Copper and PGM as by-products, in wherein the concentration of palladium is higher than Platinum. These mines are located in Norilsk-Talnakh and Pechenga (Russia), Sudbury (Canada), Jinchuan (China) and Kambalda (Australia).

The oxidized PGM ore estimates of the Great Dyke in Zimbabwe range from 160 to 250 Mt of material with average grades of 3–5 ppm Pt and more than 300 Mt estimated in the South African BIC [98]. This kind of ores are very difficult to process by conventional means.

The primary production of Pt and Pd, with 180 – 200t/y, has an economical and industrial importance. The primary production of Rhodium is about 25 t/y, however no significant production of Osmium is reported (<1 t/y) and less used. PGMs are classified in the European list of critical metals because of their unique applications in catalysts, fuel cells and electronics and medicine.

Figure 31 (right and left) shows respectively, the production and reserve repartition in Platine by countries. The total production of Pt in 2016 is around 190 t, where South Africa produced 72%, Russia 11.9%, Zimbabwe 8%, USA 2.1%, Finland 0.6% and other countries 1.1%. The reserve of this metal is estimated about 13 kt Pt, where 82% are in located in South Africa, 7.3% in Zimbabwe 5.9% in Russia, 1.6% in USA, 1.6% in Canada and 1.8% in other countries. It

is important to note that there are gaps in the present data, and therefore it must be addressed carefully, as some countries don't publish their data (for example, China).

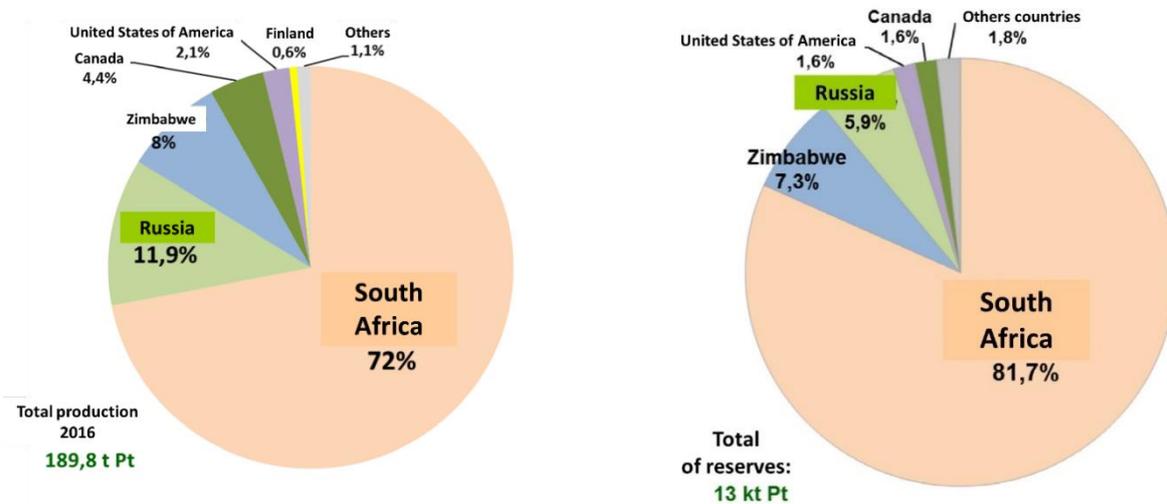


Figure 31 - Production and reserve repartition in Platine by countries [99]

According to the data published by BRGM [99] (Figure 32), the total production of Pd is around 210 t. Russia produced 41%, South Africa 38%, USA and Canada 13%, Zimbabwe 6% and others countries 2% (Figure 33). The total reserves of Pd is about 6 kt, out of which 52% are located in South Africa, 29% in Russia, 7.5% in USA, 6.2% in Zimbabwe, 4.7% in Canada and 0.5% in the others.

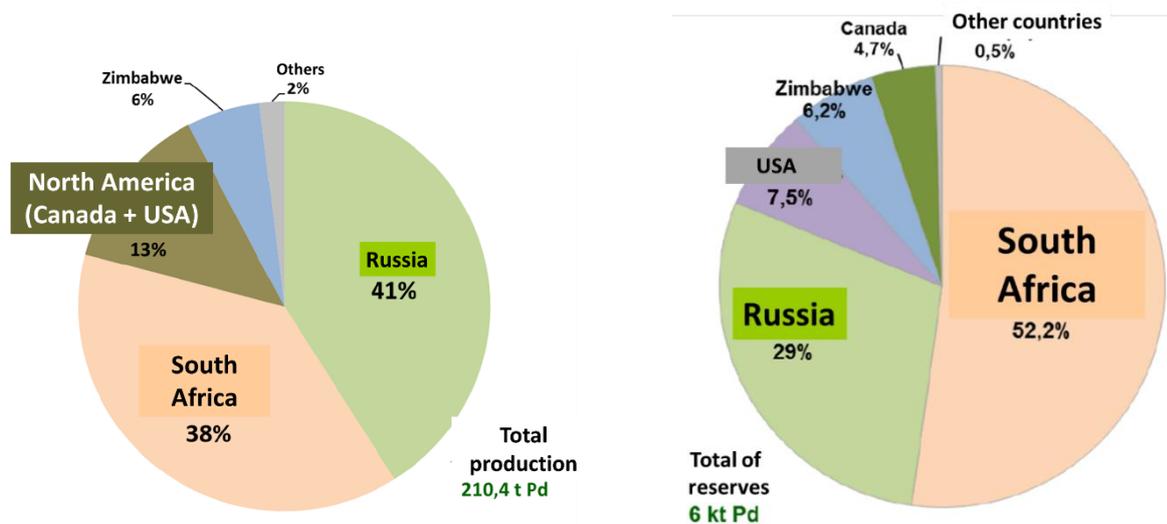


Figure 32 - Production and Reserve repartition in Palladium by countries [99]

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The worldwide production of primary was about 435 t of PGM in 2012, where 175.4 t of Pt, 196.6 t Pd and 224.4 t Rh. The production of other metals it is not published, but it is estimated to be between 20 and 30 t Ru, and 3 to 10 t Ir [100].

The mine production of Pt and Pd from 2012 – 2017 is reported by Statista and illustrated in Figure 33 and Figure 34. Figure 33 shows that the estimated Platinum production in South Africa ranged between 94 t and 140 t from 2012 to 2017, Russia (21-25 t), Zimbabwe (21 - 25 t), Canada (7 – 9 t), USA (3.6 – 4 t) and others (3.4 – 4 t). Regarding Palladium (Figure 34), Russia produced between 80 and 83 t, South Africa (58 -78 t), Canada (12 – 24 t), USA (12-13 t), Zimbabwe (9 – 12 t) and others (6 – 11.5 t).

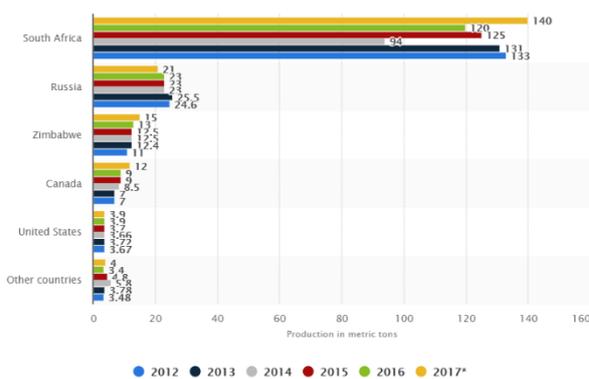


Figure 33 - Global mine production of Platinum from 2012 to 2017 by country (in metric tons) [101]

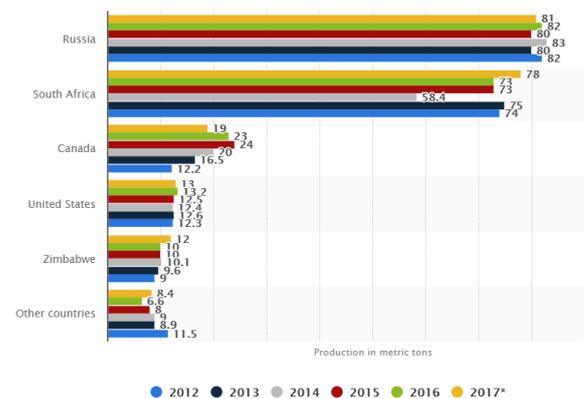


Figure 34 - Global mine production of Palladium from 2012 to 2017 by country (in metric tons) [102]

The given data must be more often considered with attention, because of the temporal evolutions and dynamics, that reflect best market and evolutions.

2. GAPS & BARRIERS – PROPOSED PROCESSING ROUTES

MINING

R. Sefako et al. 2017 [103] reviewed different routes of PGM recovery from oxide ores, which are chiefly focused on flotation and leaching methods. These methods are summarized in the following tables. According to them, the modified xanthate (PM230) and di-thiophosphate

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increase the recovery rate of PGM in the flotation of PGM oxide ores, followed by sulfurization pretreatment.

Table 9 - Flotation methods of oxidized PGM ores [103]

Recovery method	Method and process conditions	Recovery (%)	Salient aspects
Ore-pretreatment and flotation	(i) Leach with 0.5 M H ₂ SO ₄ for 20 min, Flotation with SIBX and Sendep depressant	70% (up from 50%)	Moderate recoveries High equipment cost—due to corrosiveness of H ₂ SO ₄
	(ii) Continuous bubbling of CO ₂ for 30–45 min. Flotation using SIBX, CuSO ₄ , NaOH at pH 9	50.4% (up from 40.6%)	Low recoveries Moderate equipment cost—less corrosive
Sulfidization and flotation	(i) Addition of base metal ions (Cu and Fe) at potential of –650 mV for 10 min, decantation and Flotation with SIBX, CuSO ₄ , NaOH at pH 9	80% (up from insignificant recovery)	High recoveries Poor reproducibility
	(ii) Sulfidization as above followed by flotation with SIBX and hydroxamate at pH 9, at depressant (CMC) dosage of 750 g/t	Increased overall recovery of four elements (Pt, Pd, Rh and Au) from 27 to 39%	Low recoveries Improved recovery mostly due to increased frothiness rather than the selectivity of the hydroxamate
Novel flotation reagent suites	Flotation with modified Xanthate (PM230) and dithiophosphate of a chromium-rich, highly oxidized ore	79.3% Pt and 79.2% Pd (up from approximately 50%)	High recoveries Promising process

Table 10 - Leaching methods of oxidized PGM ores [103]

Leaching method	Method and process conditions	Extraction (%)	Salient aspects
Ammonia preleaching + cyanide leaching	(i) Ammonia leaching and Cyanidation for 40 days with 0.5 M cyanide	40 and 73% total extraction Pt and Pd, respectively	Low-to-moderate extraction High reagent costs
	(ii) Heap and tank ammonia leaching + PGM recovery leaching	Approximately 100% Cu and Ni extraction in tank leaching 95% Cu and 60% Ni extraction in heap leaching	Promising base-metal recovery, development of a process for PGM recovery from oxidized ores still required
	(iii) Gravity separation for Au and Cyanidation at 125 °C for 6 h followed by CIP	80% Pt and 90–95% Pd	High extraction High reagent costs
Acid leaching	(i) Leaching with HCl at 25 °C for 72 h at pH 3	18.9% Pt and 18.5% Pd extraction	Low extractions High reagent costs High equipment cost due to corrosiveness of HCL
	(ii) Leaching with H ₂ SO ₄ at 25 °C for 72 h at pH 3	11.1% Pt and 13.8% Pd	Low extractions Low reagent costs High equipment cost due to corrosiveness of H ₂ SO ₄
	(iii) Leaching with 0.5 M HCl for 24 h, followed by Buffered siderophore (Desferrioxamine B) leaching for 70–120 h at ambient temperatures	Up to Pt 78% extraction	High extractions High reagent costs High equipment cost due to corrosiveness of HCL Highly sensitive to ore type
Bromide leaching	Roasting of the PGM ore then Bromine leaching	95% for gold, 85% for platinum and over 65% for rhodium	High extractions High equipment and operating costs due to a roasting stage

The extraction of PGM is mostly performed from underground mines. The exploitation costs are high because the work conditions are very difficult, where the social claims that, in the last

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decades, affect the mining sector of Platine in South Africa. This may affect the profitability of PGM extraction according to their actual prices.

The Platreef, one of the world's largest resources of platinum-group element (PGE) mineralization together with significant nickel and copper sulphides [104], [105] is found only in the northern lobe of the Bushveld Complex, in which the exploitation is conducted at the surface.

BENEFICIATION

The flotation technique is the typical commercial method used for the recovery of the Platinum Group Elements (PGE) from primary sulphide ores. After liberation the PGE-containing minerals from the rock matrix by crushing and grinding, the ore is then concentrated by using froth flotation circuits (wet process). The PGE containing minerals are removed as froth. The material is regrounded and refloated again to generate sulfide minerals of Ni-Fe-Cu-PGE for further treatment. It is important to note that the most important losses of PGE occur in the early processing steps, including crushing, milling, and froth flotation, owing to the diversity of PGE mineralogy. According to the literature, the different comminution devices may affect on flotation performance [106]. There is a number of flowsheets from various operations which have been previously published [107].

The high PGM recovery needs flotation of the sulphide mineralization, which is often done at natural pH of 8-9 to avoid depressing the PGM containing iron sulphides. For high activation of the sulphide minerals, CuSO_4 is added. The xanthate and dithiophosphate reagents are employed as collectors. It can be used soda instead of lime in the case of the association of PGM and iron sulphide minerals. Another benefit using soda ash is that it softens process water, controlling the hardness ions, which have an iron sulphide depressive effect when is at sufficient concentrations. It is reported that the high talc can negatively affect the concentration of PGM and their recoveries. CMC reagent is used to depress talc which hydrophobic and minimize its flotation.

To control the performance of the froth flotation recovery plants for PGM, Mintek's Mineralogy Division is currently developing PGM flotation prediction software that uses data from automated mineralogy systems to provide valuable information to the plant metallurgist [108].

METALLURGY

The copper and nickel sulfide minerals containing PGE can be melted in electric furnace and produce the matte containing base metals, and precious metals. This matte is then treated in

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converters to obtain nickel and copper (blister) melted then in anode and refined by electrolysis. The anodic slimes generated from electrowinning contained valuable metals (Se, Te, Au, PGE). After leaching some metals such as Se, Te, Cu, As, Sb, the residues separated contained precious metals, which can be melted in golden metal. To concentrate the PGE, the residues of refined nickel by carbonyl process containing PGE is melted by lead oxide or sodium carbonate.

The concentrated PGE is melted to recover the silicates in the slag and obtain alloys of base metals and PGE. These products are treated by different hydrometallurgical techniques [109]:

Leaching by aqua regia. This method is used for high grade product such as the residues obtained from lead smelting with 20% to 70% of PGE. The platinum is dissolved in the form of H_2PtCl_6 . Unfortunately this method generates toxic gas ($NOCl$).

Leaching halogenous dissolved in HCl: The chlorine solution in HCl dissolves the platinum in the form of chloroplatinic between 80° and 90° to recover palladium, it is possible to use bromine.

High pressure Leaching: The Platsol process allows to treat the sulfide concentrates of Cu-Ni-PGE containing Cr and Mg by hydrometallurgy. The concentrates are leached in autoclave by 5-20 g/l NaCl at $220^\circ C$ and 7 bars. Gold and PGE are precipitated by NaHS. The base metals are recovered by electrolysis. According to the concentrates, the recovery rates varied as follows: 83-99% Au, 50-98% Pt, 80-97% Pd, 77-95% Rh and 99% Cu and Ni.

[110] reviewed most recent literature of the predominantly hydrometallurgical approaches to PGM extraction, providing sixteen process flowsheet variants combining conventional and proprietary unit process technologies.

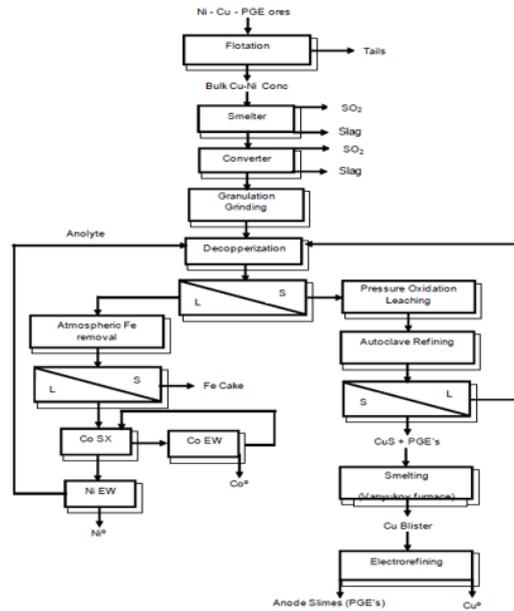


Figure 35 – Noril'sk Complex – New PGE Recovery Process Simplified [107]

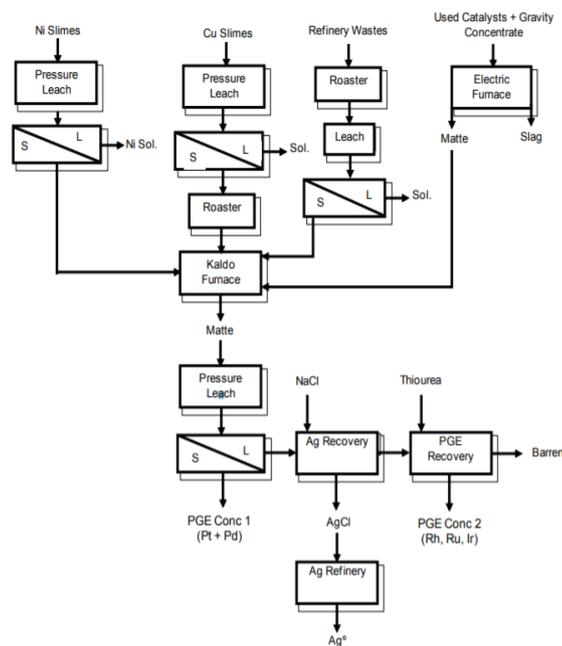


Figure 36 - New Treatment Process for Placer Platinum [107]

A typical example of beneficiation sequence of PGM can be identified at Western Platinum Ltd. [111]. The process consists of flotation to upgrade PGM from 3g/t to 200 g/t. The

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concentrate is then melted in the electric furnace to remove the rest of oxide/slugs from the matte. This technique may upgrade PGM from 240 g/t to 1500 g/t. To remove iron sulphides from the matte, a converter is used, where the PGM is upgraded from 1500 g/t to 6000g/t. The refining process is employed to remove Ni and Cu sulphides to concentrate PGM till 65% and refining precious metals to separate selectively (Pt, Pd, Rh, Ru, Ir and Au) to 99.9+% purity.

3. ENVIRONMENTAL IMPACT OF ALTERNATIVE TECHNOLOGIES AND RESIDUE TREATMENT

The Platinum Group Elements (PGE) emission from mining and production activities are less investigated in the literature, however, the main environmental impacts on the PGM mining are reported as follow:

1. The generated solid waste (tailings dams and waste rock dumps),
2. Water consumption: 273 to 544 m³/kg PGM (average about 400 m³/kg),
3. Energy consumption (mine, concentrator and smelter): 168 to 256 GJ/ kg PGM,
4. CO₂ emissions: 40 to 50 t/kg PGM → SO₂
5. Dust emissions,
6. Effluent pollution (acidic infiltration and runoff, and acid mine drainage (AMD)).

SUMMARY

The extraction of PGM is mostly performed from underground mines. The PGM mines are associated to basic or ultrabasic magmatic rocks mantle origin, and to placers resulting of their erosion. The PGM rich mines that contain less sulfur can be found in Bushveld (South Africa), Great Dyke (Zimbabwe), Stillwater (USA). The sulfide of Nickel-Copper mines containing PGM are located in Norilsk-Talnakh and Pechenga (Russia), Sudbury (Canada), Jinchuan (China) and Kambalda (Australia).

Several flowsheets of recovery process of PGM from ores are reported in the literature. The mineral process employed to concentrate PGM consists of crushing, grinding and flotation. Some PGM are lost in different stages of beneficiation process and must be optimized. Extractive metallurgy (pyro/hydrometallurgy) is mostly used to extraction PGM.

PHOSPHOROUS-PHOSPHATE ROCK

1. THE PRIMARY RESOURCES

According to the information stated in the WP3 and WP4, phosphate rock refers to unprocessed rocks containing about three hundred phosphate minerals, usually calcium phosphate as apatite with the formula $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl},\text{OH})$, and also to beneficiated concentrates. 80-85% of phosphate rock is mined from sedimentary deposits and the rest is mainly mined from igneous deposits. Large sedimentary deposits are located in China, the Middle East, northern Africa and the United States. Igneous deposits are mined in Brazil, Canada, Finland, Russia, South Africa and Zimbabwe [21] [112].

The only currently operating phosphate rock mine and phosphorus production plant in the EU is in Siilinjärvi, eastern Finland, where Yara International is mining the deposit hosted by the Siilinjärvi carbonatite intrusion. The apatite concentrate from the mine is used for phosphoric acid and fertilizer production in the adjacent plant. Full-scale mining of the Siilinjärvi deposit has taken place since 1979. Currently, about 10 Mt of ore is mined and 1 Mt of apatite concentrate produced annually to be further processed to 300,000 tons of phosphoric acid. The resource estimate (JORC) for the Siilinjärvi deposit is 1,617 Mt of ore with P_2O_5 content of 3.694 % [113].

2. GAPS & BARRIERS – PROPOSED PROCESSING ROUTES

MINING

Surface method is the most common way to mine phosphate rocks. In 2013, only one underground mine was active in the world [21]. Marine dredging has also been examined, for example off the coast of Mexico, the Eastern coast of the United States and currently off the Namibian coast [112].

BENEFICIATION

Phosphate ores may have a grade anywhere between 5 and 39 % of P_2O_5 . Beneficiation plants are commonly combined with the mine. After extraction, phosphate ore typically undergoes a process of concentration, which may include primary screening, wet or dry screening, washing, flotation, magnetic separation and drying to produce, in commercial terms, phosphate rock concentrate. The P_2O_5 level in the concentrate typically ranges in 28-40% [112]. Moroccan phosphate rock concentrate of 32%-33% P_2O_5 FOB is typically used as the benchmark for worldwide phosphate pricing [114].

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Phosphate rock may be transported to a port for export or a domestic plant for direct use or further downstream processing. However, only a limited amount of phosphate rock is sold or used without primary processing. Transportation of the ore, in the form of slurry, is usually managed by trucks, railways, conveyor belts, or pipelines [112].

There are several methods to beneficiate phosphate rock, and usually a combination of methods is used. In phosphate rock beneficiation, the availability of water is essential and may dictate the process or processes to be used. The total lack of freshwater availability may exclude deposits from development or restrict capacity. In areas where water availability is severely restricted, dry screening may be an effective way to produce concentrates or pre-concentrates if ore characteristics are suitable. Seawater can be used for washing, size classification, and flotation. Where other than freshwater is used for beneficiation, a freshwater final rinse is needed to remove as much chloride as possible from the final concentrate, since a high chloride content can lead to severe corrosion in further processing.

The study published by [115] describes new technologies based on the production of finer bubbles during the flotation process, this is made possible thanks to the advancement in air-sparging technologies. The first described technology is an air sparging system called CPT Cavitation-Tube, developed by Eriez Mineral Flotation Group-Canada, Inc. Such system takes advantage of hydrodynamic cavitation, which consists into the creation of gas bubbles due to the rupture of a liquid-liquid or liquid-solid interface due to the application of external forces. This method takes advantage of both normal-size bubbles and picobubbles. The latter acts as a secondary collector for particles. The CPT Cavitation-Tube system was applied to an ultrafine waste stream at a plant treating material from the Barreiro carbonate complex located in Araxá, Brazil. The application of this method allowed a 72% recovery of P_2O_5 , corresponding to an increase in plant yield of 3–5%.

The HydroFloat separator developed by Eriez Manufacturing combines the non-turbulent conditions of a teeter-bed separator with the selectivity of a flotation process. The teeter-bed is kept aerated by injecting compressed air and small amount of frothing agent into the fluidization water. The air bubbles become attached to hydrophobic particles reducing their density. Such regime produces a zone with high concentration of solids where adjacent particles collide, thus reducing overall particle velocity. A HydroFloat cell was installed for treating an intermediate grain size phosphate, nominally 0.425×0.106 mm achieving a phosphate recovery of 90%.

Siliceous sedimentary phosphate ores

Sedimentary phosphate ore is typically mined using draglines, made into a slurry, and transported by pipelines to the washing plant. Washing is often carried out using rotating

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drums (trommels), log washers, and sandwich screens. The washed slurry is then sized and deslimed in preparation for the Crago double float process, which is discussed below. The simplified process flow diagram of a washing plant is presented in Figure 37. As can be seen, the -16 mesh (-0.1 cm) size fractions from the vibratory screens are conveyed to the flotation circuit. The +16 mesh size fraction from the final vibratory screen is considered to be pebble product if it contains less than 1% of MgO. If the MgO content is greater than 1%, further processing is needed to remove dolomite [116].

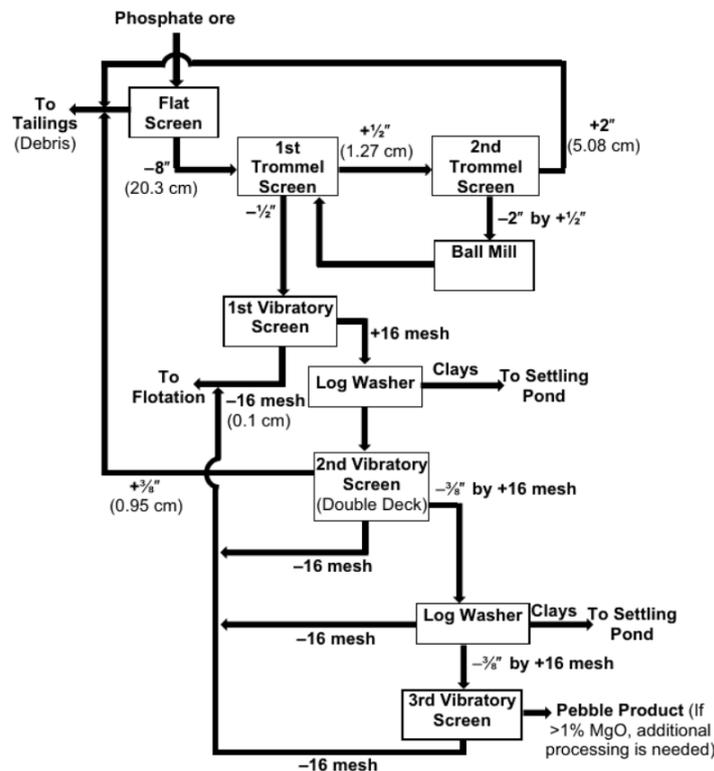


Figure 37 – Process flowsheet of a phosphate ore washing plant. The output of this process feeds the Crago double float process [116]

Since being patented in 1942, the Crago double float process has been the industry standard for the beneficiation of siliceous phosphate ores. The two floating processes of the Crago double float process are [117]:

1. Rougher flotation: Phosphate is floated from coarse silica using an anionic fatty acid collector, and
2. Cleaner flotation: fine silica is floated from phosphate concentrate using a cationic amine collector.

As the efficiency of this process depends heavily on a properly operated washing and conditioning steps, there are a few important process considerations [116]:

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- Desliming: Clays decrease the flotation efficiency and increase the reagent consumption.
- Sizing: Sizing allows for more efficient use of collector and better selectivity during anionic flotation.
- Conditioning: High percentage of solids increase phosphate grade and recovery during anionic flotation.

The necessity to mine and process lower grade phosphate deposits has led to the development of three alternative processes: the reverse Crago process [118], the all-anionic process, and the all-cationic process [119]. However, these processes are still at developmental stages and need further evaluation to determine whether they can be commercially exploited [116].

In [120], a study has been conducted to evaluate the performance of an innovative technology for dry beneficiation of phosphate, the rotary triboelectrostatic separator (RTS). Such new technology provides the following advantages:

1. Increases particle charge density;
2. An order of magnitude improving of the solid's throughput;
3. 70% efficiency enhancing;
4. More than 80% energy consumption.

Such technology has been tested on Florida phosphate samples obtaining the upgrading of a 10% P₂O₅ feed to a 30% P₂O₅ concentrate with a more than 85% P₂O₅ recovery and almost 90% acid insoluble rejection. Another result was the purification of a flotation concentrate with 31% P₂O₅ to nearly 35% P₂O₅. Furthermore, RTS, allowed a reducing the MgO content of a pulverized high dolomite pebble sample. The same technology was successfully applied for the beneficiation of Eshidiya (southern Jordan) phosphate minerals in the study [121].

In [121] a study is reported on the flotation concentration of sedimentary phosphorite from Sierra Espuña, in the province of Murcia, Spain, using a Denver D-12 mechanical subaeration cell. The mineral was first pretreated through grinding, sorting and discarding slimes. The results obtained showed that a neutral or slightly alkaline pH and short flotation times are beneficial for the concentration of sedimentary phosphorite.

Sedimentary phosphate ores with high magnesium oxide content

When treating sedimentary phosphate ores with high MgO content (MgO > 1%), resulting from significant levels of dolomite (CaMg(CO₃)₂) in the ore, the beneficiation process becomes

more complex because of the similar mineralogical properties between the phosphate and carbonate minerals. Several techniques have been developed for the beneficiation of high-MgO sedimentary phosphate ores, but viable technologies for processing such ores on an industrial scale do not exist [122]. Some of the most practical and advanced methods are presented in Table 11 [116]:

Process	Advantages	Disadvantages	Other remarks	Industrial examples
Organic acid leaching	<ul style="list-style-type: none"> • Good selectivity • Lower phosphate losses than with strong inorganic acids 	<ul style="list-style-type: none"> • Organic acids relatively expensive • Recovery of the organic acid may be challenging 	The smaller the particle size, the higher the efficiency. However, too fine sizes can impede the filtration of the phosphate concentrate.	No industrial examples available.
Thermal Decomposition (Calcination)	<ul style="list-style-type: none"> • Complete removal of carbonates • Low water demands 	<ul style="list-style-type: none"> • Energy intensive • Concentrate reactivity lower (in phosphoric acid production) • High capital costs 	Produces a phosphate concentrate suitable for the production of high-grade defluorinated phosphoric acid.	Mainly used for reducing the organic content of phosphate rock. However, in Djebel Onk, Algeria, the calciners are used for carbonate removal .
Heavy-media separation (HMS)	<ul style="list-style-type: none"> • Capable of processing coarse feed sizes • Relatively high throughput 	<ul style="list-style-type: none"> • Low selectivity 	HMS is usually proposed as a preconcentrating process that needs further processing to produce a saleable product.	A HMS plant was installed at Four Corners Phosphate Mine, U.S. in 1991, and by that time it was the only such plant in the phosphate mining industry. No recent information was available.

Table 11 – Processes developed for the beneficiation of high-MgO sedimentary phosphate ores [116].

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

Igneous phosphate ores

15%-20% of the world's phosphate production comes from igneous phosphate ores, which differ significantly from the more abundant sedimentary deposits. Finland's deposits are among the major igneous phosphate deposits in the world. Igneous phosphate rocks are typically of three types: carbonatite, nephelinic-syenite, and pyroxenite. Each of these types of deposits can vary notably in gangue minerals, but all of them are rich in fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) [116].

The types of impurities determine the needed beneficiation methods, which can therefore range from a relatively simple flow sheet to a more complicated one. However, the common process to all igneous phosphate concentrator flow sheets is the anionic fatty acid flotation of apatite. Other processing techniques such as magnetic separation (iron removal), copper flotation, calcite flotation, and barite flotation are implemented when needed. In some cases, these processes can generate valuable by-products [116].

In [115] several collectors for apatite in igneous ores have been reported: amphoteric sarcosine has been used in Finland to float apatite from calcite; for the same purpose amino-carboxylic acid reagent (Lilafлот OS-100) has been developed in Sweden; selectivity in floating apatite from dolomite of igneous ores has been given by a reagent of the immino bis methylene phosphoric acid class developed by Warren Springs Laboratories.

3. ENVIRONMENTAL IMPACT OF ALTERNATIVE TECHNOLOGIES AND RESIDUE TREATMENT

Especially in the U.S., public opposition to phosphorus mining is on the rise due to possible environmental and health effects related to phosphate mine tailings. In addition, heavy metals passing through to phosphorus fertilizers originating from some phosphate ores has raised concern. Therefore, phosphorus mining in Florida, where the largest deposits of phosphorus are found in the U.S., is being challenged about its effects on waterways and drinking water supplies. For example, the Florida South Fort Meade phosphorus mine has faced opposition to its expansion for this reason and is at risk to have to close if it cannot develop [117].

SUMMARY

The only operating mine in Europe is Siilinjärvi, in Finland. Generally, processing technics, depend on the gangue mineral associated with the mined rock, usually a combination of several methods is used. In the case of siliceous sedimentary phosphate ores, Crago double float process is used as industry standard. New technologies such as RTS, CPT Cavitation-Tube, HydroFloat separator, have been studied to improve the beneficiation process. In the case of sedimentary phosphate deposits with high magnesium oxide content beneficiation becomes

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more complex due to the similarities between phosphate and carbonate minerals. Several technics have been studied, but none of them works at industrial scale. For igneous phosphate ores several methods are used depending on the type, the most common is the anionic fatty acid flotation of apatite.

SCANDIUM

1. THE PRIMARY RESOURCES

According to the resource-mapping results of WP3, the primary Sc deposits in EU territory (plus Norway) are limited and mainly contained in mafic and hydrothermal-metasomatic intrusions in Northern Europe (Table 12). The main primary Sc reserve in the EU territory exist in Kiviniemi Scandium deposit, Eastern Finland (350 km NNE of Helsinki) [123], [124]. The deposit consists of a mafic intrusion surrounded by porphyritic granite. The Kiviniemi intrusion consists of five rock types: garnet-bearing fayalite ferrodiorite, leucoferrodiorite, ferrodiorite, diorite and granite. The main host rock for enriched scandium, yttrium and zirconium is the coarse-grained fayalite ferrodiorite. The surface extension of the main Sc-mineralized block is around 2.5 hectares and it's extending the vertical depth down to at least 167 meters. The deposit's size was recently identified by drilling in a depth up to 200 m. It has been estimated that the Sc-REE-Zr host rock reaches about 13.4 Mt of with an average 162.7 ppm average Sc concentration [123].

Biggejavri REE-Sc-U deposit in Norway can be mentioned as a second scandium primary source in EU. It consists of a hydrothermal-metasomatic REE albite U-REE containing mineralization. The deposit is small (0.05 Mt) with an average 0.013 % Sc concentration [125]. High concentrations of Sc have been measured in pegmatite dykes in several localities in Norway, such as in Iveland- Evje district North of Kristiansand and in Tørdal. In first case, Sc concentrations up to 10.000 ppm have been measured in beryls, while in second case a number of scandium minerals such as thortveitite (Sc_2SbO_7) has been reported. The scandium mineralization in Norway should be further investigated and quantified [125].

Nickeliferous laterite ores can be considered as a potential primary resource of scandium. However it should be stressed out that: (a) the Sc concentration in these ores is low (usually <100 ppm), (b) Sc distribution and reserves estimation has not been extensively studied [126].

Table 12 - The main primary unexploited resources of scandium in EU.

Type of ore	Scandium form	Major deposits	Gaps and barriers		
			mining	beneficiation	metallurgy

Mafic intrusions	Mainly in fayalite phase	Kiviniemi, Finland		x	x
Hydrothermal-metasomatic	In davidite phase hosted albite	Biggejavri, Norway		x	x
Laterite	In iron oxide phases	Greece			x

2. GAPS & BARRIERS – PROPOSED PROCESSING ROUTES

MINING

Nickel sulphide ores are mined underground or superficially (open pits) following the metalliferous veins while, laterite ores generally occur near the surface and they are mined relatively easily by surface-mining methods. Mining techniques for both types of ores are well developed and there is a little space for innovation.

BENEFICIATION

Biggejavri deposit, Norway

The beneficiation of a 150 kg sample from Biggejavri deposit has been examined at laboratory scale. The aim of the experimental test was the production of a concentrate rich in davidite [(La or Ce) (La,Ce,Ca)(Y,U)(Ti,Fe³⁺)₂₀O₃₈] which consists the main Sc phase [127]. Davidite is very fine sized and scattered among the host rock which composed mainly by albite (>90%), limestone, muscovite, chromite and rutile. The Sc concentration in the initial ore was 130 ppm. The ore was pulverized at the fraction of -90 µm, which was found necessary for reasonable liberation of the davidite and beneficiated via a complex magnetic separation-heavy liquids method. By wet high-intensity magnetic separation (HIWMS), a primary concentrate with 500-600 ppm Sc was obtained, while the yield was ranged from 75 to 70%. Subsequently, by separating the magnetic concentrate in heavy liquids, a final concentrate containing 1100-1200 ppm Sc is received with a yield around 40%. It is obvious that a significant quantity of scandium is being lost in non-magnetic fraction in the first step and light-weight fractions in the second step due to the fine scattered davidite inclusions in the initial ore.

The beneficiation of the ore with alternative separation methods could be potentially tested. The optical sorting could be a promising technique as davidite is a darkish-black colored mineral while albite is usually light white colored.

Kiviniemi deposit Finland

Similar enrichment difficulties can be arised in case of Kiviniemi concentrate in which the Sc concentration is low.

Nickeliferous laterites

Nickeliferous laterites are not submitted to enrichment (the beneficiation of laterites in Australia, aiming to Ni content enrichment, consists an exception).

METALLURGY

Biggejavri deposit, Norway

As it was previously described, Sc in Biggejavri deposit is contained in davidite phase which consist a rare oxide mineral with chemical end members La and Ce. Davidite is found in variable rock environment such as; albitites, syenite and carbonatite veins [128], however there are no available data concerning its processing for the extraction of REEs and scandium worldwide [129]. This fact generates an uncertainty regarding the leaching behaviour of this mineral. Therefore, it is proposed the performance of preliminary leaching experiments of Sc-containing concentrates from the Biggejavri deposit.

Kiviniemi deposit Finland

Scandium occurs mainly in the internal structure of iron-rich silicates, such as amphibole (40 %) and pyroxene (59 %). The metal can be recovered via leaching using specific acids. Preliminary tests showed that the most potential separation method of scandium was magnetic separation of a 346 ppm of Sc concentrate presenting a 72 % of recovery [130]. Acid solution of hydrogen fluoride and hydrochloric/sulphuric acid presented the optimum leaching results. Neither the quantity of acid nor recovery of scandium from acid solution has have been studied. The most important technological barrier is related with the consumption of large quantities of acids. This problem can be faced by the processing of the concentrate via the chelator method. The “wet chemistry group” at the University of Eastern Finland is recently working on this subject.

Nickeliferous laterites

Specific nickeliferous laterites contain Sc at concentrations near 100 ppm. The extraction of Sc by a limonitic laterite ore from Turkey has been studied at laboratory scale [131]. The results showed that under high-pressure sulphuric acid leaching, the Sc extraction reach 80.6%, while more valuable metals such as nickel, cobalt are also received in the liquor. Additionally, the separation of the Sc from the liquor has been studied via a pH-controlled precipitation process simulating the Sc recovery from a circuit into an already existing hydrometallurgical nickel-cobalt hydroxide processing plant [132]. Aiming to the selectively precipitate and concentrate scandium with minimum nickel and cobalt co-precipitation, the pH of the solution is adjusted by CaCO_3 , MgO , Na_2CO_3 and NaOH . It was found that precipitation with MgO or Na_2CO_3 is more maximize scandium with minimum nickel mass in comparison to the CaCO_3 route. Finally, a scandium-enriched residue by means of leaching, SX (solvent extraction), and precipitation, as an intermediate $(\text{NH}_4)_2\text{NaScF}_6$ product is received.

The production of scandium oxide by laterites leaching via the Neomet process has been performed at pilot scale. As it was proved, the Sc extraction is possible even in case of low concentrations in laterite (30g Sc/t), while the recovery degree approaches 100%. However, it should be mentioned that Neomet has not still been applied at industrial level [133].

The above experimental results are encouraging regarding the processing of a similar nickeliferous laterite ore in EU territory. Limonitic Sc containing laterites have been also found in Central Greece. Two major actions should be implemented aiming to recovery of Sc from greek laterites: (a) a detailed investigation and a quantification of the lateritic beds which contain Sc at relatively high concentrations (i.e. >80 ppm), (b) modification of the already existing metallurgical processing which is based on the reductive smelting.

3. ENVIRONMENTAL IMPACT OF ALTERNATIVE TECHNOLOGIES AND RESIDUE TREATMENT

The environmental impact that is generated by the processing of phosphate and silicate concentrates containing REEs and scandium has been described in detail in the Work Package 4.3. Similar environmental effect (generation of tailing and solid wastes after the leaching process) is expected by the leaching of fyalite (Finland) and davidite (Norway) concentrates. The recovery of scandium by laterites, in the framework of nickel production via the Neomet leaching process, is not going to generate a supplementary environmental impact. As it can be seen in Figure 38, scandium oxide is received through a precipitation process after to the leaching completion.

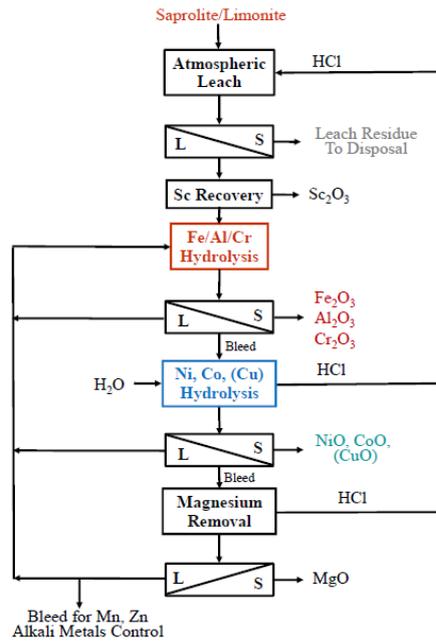


Figure 38 – Production of scandium oxide by laterites via the Neomet process [133]

SILICON

1. THE PRIMARY RESOURCES

Silicon is the second most abundant element in the Earth's crust. It is commonly found in rocks, sand, clays and soils, combined with either oxygen as silicon dioxide or with oxygen and other elements as silicates [21]. Quartz or quartzite is principally used for the extraction of silicon for ferrosilicon and silicon metal production. Despite that silica accounts for 66.62% of the mass of the upper crust, not all is viable for silicon metal production. This is due to the fact that silicon metal production requires high purity quartz or quartzite [21]. For silicon metal production, the quartz or quartzite must contain at least 99.5% silica (SiO_2), and the impurities must be low (Fe_2O_3 0.05-0.10%, Al_2O_3 0.10-0.20%, TiO_2 <0.006%, CaO <0.2%, MgO < 0.2% and P being avoided). The global mine production of silicon metal is dominated by China (61%), followed by other countries, such as Brazil, Norway, United states, France, etc [134].

In 2015, silicon metal was produced in Norway (150,000 t), France (100,000 t), Germany (29.953 t), and Spain (22,000 t). Except for Norway, which has local mine production, there is no information on where the mined raw material for this production comes from [19]. In Austria the ProMine database lists 21 deposits in which quartz is the main commodity. In Finland there are currently two active quartz mines in Finland, with a joint production of 92,813 t quartz in 2016, some of this may be categorized to medium to high-purity quartz [116].

In 2016 Norway produced 1.1 Mt quartz from five mines; most of this went into ferrosilicon and silicomanganese production in the same country. The Austertana mine annually produces 700,000-800,000 t quartz. At the Mårnes mine, annual production is 120,000-160,000 t quartz. Another highpurity quartz producer is the Nedre Øyvollen (Drag), pegmatite-hosted mine. The Kvinnherad quartz vein deposit is under development; it has a JORC-compliant resource of 4.29 Mt @ 65 % medium to high-purity quartz [135]. Another major deposit of vein quartz, Nasafjell in central North Norway with resources at >10 Mt quartz (open pit reserves estimated to 7–10 Mt), is also under exploration.

The Nesodden high-purity quartz deposit in south-western Norway has an inferred resource of 2.7 Mt quartz. In addition, there are tens of smaller vein quartz deposits containing 0.1-0.5 Mt of quartz across the country. Out of the unexploited pegmatite-hosted deposits entailing potentially high-purity quartz, the deposit Eiterelvdalen, in the Caledonides of the Nordland county, with an inferred resource of 0.425 Mt quartz is hereto addressed. Recent discoveries include several deposits of very high purity quartz in kyaniterich quartzites. Large tonnages

are available, especially near Solør in southern Norway. This type is considered as a target for future interest as progress in technology develops.

The FODD database [19] lists 52 quartz deposits in Sweden. These include three active mines in the Dal Group quartzites in central Sweden, with a joint annual production of 100,00 t of quartz concentrate used in the ferro-alloy industry. Of the known unexploited occurrences, at least the Lumivaara, Naakajärvi, Pajeb Munitjåure, and Långsjökullen vein occurrences in northern Sweden contain medium to high-purity quartz. The Långsjökullen and Naakajärvi deposits are estimated to contain 150,000-200,000 t and 8,400 t quartz, respectively.

2. GAPS & BARRIERS – PROPOSED PROCESSING ROUTES

MINING

Mining activity is present only in three countries. In Finland there are two active mines with a total production of 92813 t of quartz in 2016. In Norway, in 2015, five active mines produced 1.1 Mt of quartz. In Sweden three active mines produce 100 t per year [136]. Quartzite and quartz are usually used for the production of silicon metal. Quartzite is obtained by blasting operations in a quarry/mine while quartz is obtained by non-blasting operations through surface excavation of unconsolidated material (gravel quartz).

BENEFICIATION

The mineral processing of quartzite or quartz includes several fragmenting steps. The first step of the fragmenting is coarse crushing (primary crushing) by using e.g. a jaw crusher. Normally the crushing of quartzite requires less energy, since micro cracks in the rock's quartz are introduced during the blasting operation. However, crushing the gravel quartz demands more energy as the gravel quartz has gone through natural selection and only the strongest quartz boulders “survive” the size reduction during transportation in the river. For the first-step crushing, characteristic grain size (d80) for the feed is usually 300-1000 mm while the product d80 is 50-300 mm. After the first-step crushing the materials are screened, washed and the coarse fraction is further crushed to meet the market requirements (20-150 mm for the production of silicon metal in the submerged arc furnace). The fine materials that are generated through the mineral processing are usually regarded as residual materials, which can either be disposed or further screened to create fractions that can be sold or even given away, e.g. to the local community as filling material [137] [138].

METALLURGY

Reduction of the silica for the production of metallurgical grade silicon metal

Metallurgical-grade silicon metal is produced industrially by carbothermic reduction of silicon dioxide in submerged-arc electric furnaces. The input materials include silicon source (such as quartz) and reductant blend comprising coke, coal, charcoal and wood chips. To avoid introducing too many impurities into the final product high quality silicon source containing >99.5% SiO₂ and low-ash-bearing reductant are used. The produced metallurgical-grade silicon typically contains 98.5–99.5% silicon.

The common impurities in metallurgical-grade silicon include carbon, alkali-earth and transition metals, as well as boron and phosphorus. The by-product of this silicon metal production process is mainly condensed silica fume (0.2 to 0.4 ton of silica fume per ton of silicon metal). To have the process run properly, high operation temperature is needed (above 1800 °C), thus the process requires a lot of energy, which is supplied by the three electrodes deeply submerged in the charge mix. The specific electric energy consumption for the process is 11–13 MWh/ton of silicon metal [139].

Production of silicones and silanes

Silicone is produced from silicon metal. The production process includes a three-step synthesis, namely, chlorosilane synthesis, chlorosilane hydrolysis and polymerisation & polycondensation.

Silanes are a series of compounds made up of silicon and hydrogen. Among the silanes, silane (SiH₄) is widely used one. There are several routes to produce silane. The commonly used routes in the commercial scales include: (i) lithium hydride with silicon tetrachloride; (ii) lithium hydride with trichlorosilane; (iii) magnesium silicide with mineral acids and catalytic redistribution of chlorosilanes [139].

Production of silicon-containing aluminium alloys

Silicon-containing aluminum alloys are produced by adding metallurgical grade silicon metal into the melting furnace, such as induction furnace.

Production of solar-grade and electronic-grade silicon

Metallurgical-grade silicon is the precursor for the production of solar-grade silicon. The purity of the solar-grade silicon and electronic-grade silicon is very high. Therefore, the key of the process for the production of solar-grade and electronic-grade silicon is the refining step to

remove the impurities from the metallurgical-grade silicon. The process for the production of solar-grade silicon and electronic-grade silicon can be divided into the chemical route (known as Siemens process) and the metallurgical route. The descriptions of the two processes are shown as follows [140] [141].

Chemical route

The Siemens process is the dominant process for the production of polysilicon. The process contains the following steps:

1. The metallurgical-grade silicon particles are fluidized with hydrochloric acid in the presence of catalyst via the reaction $\text{Si} + 3\text{HCl} = \text{SiHCl}_3 + \text{H}_2$ to form trichlorosilane (SiHCl_3) gas;
2. The trichlorosilane undergoes multiple fractional distillation to produce high-grade trichlorosilane.
3. The purified trichlorosilane is reduced by hydrogen via reaction $\text{SiHCl}_3 + \text{H}_2 = \text{Si} + 3\text{HCl}$ in a Siemens reactor.
4. Silicon is deposited in a fine-grained polycrystalline form on an electrically heated inverse U-shape silicon rod ($T > 1100^\circ\text{C}$) in a cooled Siemens reactor.

The main disadvantages of the Siemens process include: (i) the production of chlorosilanes and reactions with hydrochloric acid which is toxic and corrosive; (ii) high energy consumption (200 kWh/kg Si).

Metallurgical route

The metallurgical route entails the refining of the metallurgical-grade silicon via several refining steps. Several examples of the refining steps are shown as follows:

1. Directional solidification and acid leaching to remove the elements (such as Fe, Al, Mg, Sb, Sn, Zn, Cu, Ni and Ti) that have low effective partition ratios in silicon. These elements are highly soluble in molten silicon but their solubility in solid silicon is relatively low. During the solidification the impurities are rejected in the grain boundaries. After crushing and acid leaching the impurities dissolve in the acid and thus the silicon is refined.
2. Vacuum refining to remove the phosphorus.
3. Slag refining or plasma refining to remove the boron, carbon and oxygen.

Since certain refining steps are only effective to remove specific impurities, the combination of the refining steps is required for the refining. Further, using the high-purity metallurgical-grade silicon is preferable for the process. The production share of solar-grade silicon by the

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metallurgical route was less than 8% in 2008. It is estimated that the production share of silicon by metallurgical route is likely to increase in the future.

Production of crystalline wafers

The crystalline wafers are produced from the high-purity silicon. The production can be achieved either by ribbon growth or a two-step process starting with ingot casting or crystallization followed by wafer manufacturing. At moment the production crystalline wafers is overwhelmingly by the latter process, which is described as follows [142].

Ingot casting

The product from the ingot casting process can be either a mono-crystalline silicon ingot or the poly-crystalline silicon ingot. Poly-crystalline silicon ingot has cost benefit over mono-crystalline silicon ingot; however, mono-crystalline silicon ingot has less defects and high quality, thus can be used for manufacturing electronics and high efficiency solar cells.

(a) The Czochralski process for single crystal ingot [142] [143]:

The Czochralski process is the common process for the production of crystal ingot. In this process the polysilicon together with boron (B) and phosphorous (P) is melted under vacuum in the quartz crucible at around 1420°C. The crystalline silicon seed rod is placed on the surface of the molten silicon in the crucible and is pulled up while rotating it to form a monocrystalline ingot, which has the same orientation of atoms as the seed crystal. The Czochralski process is a batch-based process and it takes about two days to complete a production cycle of an ingot.

(b) Bridgman process for polycrystalline silicon ingot [140], [142]:

In the case of the Bridgman process, a silicon nitride (Si_3N_4)-coated quartz crucible is usually employed for melting of the solar-grade or polycrystalline silicon material in a crucible and subsequent solidification of the multi-crystalline ingot. The Si_3N_4 coating serves as an anti-sticking layer preventing the adhesion of the silicon ingot to the quartz crucible walls. During this process the temperature gradient and growth rate are controlled to favour the growth of a high-quality crystal structure with low thermal stresses. During the solidification refining can also be achieved, as metal impurities are pushed to the top of the ingot. By applying this process, the high quality multicrystalline silicon ingots with mass of 250-300 kg, dimensions of up to $70 \times 70 \text{ cm}^2$ and heights of more than 30 cm can be obtained.

(2) Wafer manufacturing [142]

Prior to wafer manufacturing, the ingots undergo sectioning where the peripheral sections are cut. The monocrystalline cylindrical ingots undergo sectioning such that cubic ingots are produced, while multi-crystalline ingots are sectioned for the removal of highly contaminated peripheral regions. The ingots are then cut to blocks with a cross-sectional area (eg. 15.6 x 15.6 cm²) equal to the wafer size. About 25% and 15% of the material is lost from cutting of the mono-crystalline and multi-crystalline ingots respectively. Wafers are produced by cutting the silicon blocks into pieces with a thickness of less than 200 microns by using the multi-wire saw machines. During the cutting approximately 30% of the silicon is wasted as saw dust.

3. ENVIRONMENTAL IMPACT OF ALTERNATIVE TECHNOLOGIES AND RESIDUE TREATMENT

It is important to recycle the residue of the metallurgical phase, in fact, such residue still contains a significant amount of recoverable silicon metal powder. The energy consumed during the recycling process (<1 kWh/kg) is significantly lower than the conventional silicon metal production. Important parameters for recycling and upgrading of silicon metal powders are chemical purity (wt.% metallic silicon), chemical composition of impurities and particle size distribution. In the following part a recycling process of silicon metal powder from industrial powder waste stream is described. Such technic has been developed by ReSiTec.

Silicon metal powder, with a diameter ranging from 0-150 µm and purity < 50 wt.%, was collected. Different size distributions were considered and classified depending on the median of the distribution defined as D50. D50 splits the size distribution in half: 50% of the particles have a higher diameter and 50% a lower one. In the first step the coarser fraction of a D50 = 25 µm was recovered using chemical treatment and mechanical separation. The obtained product is a 99.5 wt.% recycled silicon metal powder. The finest portion removed from the first step is identified as D50= 5 µm. This finer fraction was again treated chemically and mechanically. The global two steps process permits obtaining a 99.9 wt.% pure silicon metal powder. A silicon metal powder with D50 = 50 µm was collected from a waste filter cake containing only 50% silicon metal powder. The recycling process consists of two steps: wet mechanical separation and dry mechanical separation (electrostatic separation). In the first step (wet separation) 85 wt.% purity was achieved, whereas in the second one a final 99.6% pure silicon metal powder was obtained [144].

TUNGSTEN

1. THE PRIMARY RESOURCES

Tungsten is a very resistant metal to acids, up to 400°C. With the highest melting point (3422°C), it belongs to the family of refractory metals with Molybdenum, Niobium, Rhenium and Tantalum. Combined with steels or carbon, it increases its hardness and resistance to heat. For these reasons, it is widely used in the following applications [145]:

- Cemented carbides (cutting, milling and turning tools): 55%
- Tungsten steels (high-speed steels for hot or cold working): 21%
- Tungsten metal (lighting, heating resistors, ammunition): 17%
- Specialist applications (super alloys, chemistry...): 7%

Tungsten can also be substituted in cemented carbides and alloys but at high cost and/or loss of performance.

Tungsten is not abundant in the Earth's crust (1.25ppm) but there are reserves in many countries (Figure 39; EU: UK (1.6%), Spain (1%), Austria (0.3%), and Portugal (0.1%)). The worldwide estimated reserves are about 3150kt in 2017 [146]. The three types of Tungsten deposits are classical vein deposits (0.5 - 5% WO₃) in Portugal, Spain and Bolivia for example, skarn deposits (0.3 - 1% WO₃) and bulk mineable deposits (greisen, porphyry, stockwork; 0.1 - 0.3% WO₃) in China and Austria for example [147]. The probability of finding other deposits is important. Worldwide Tungsten production was estimated at 80kt in 2015, and Figure 40 shows the repartition of tungsten production by countries [146]. It shows that more than 81% of worldwide production is performed by China.

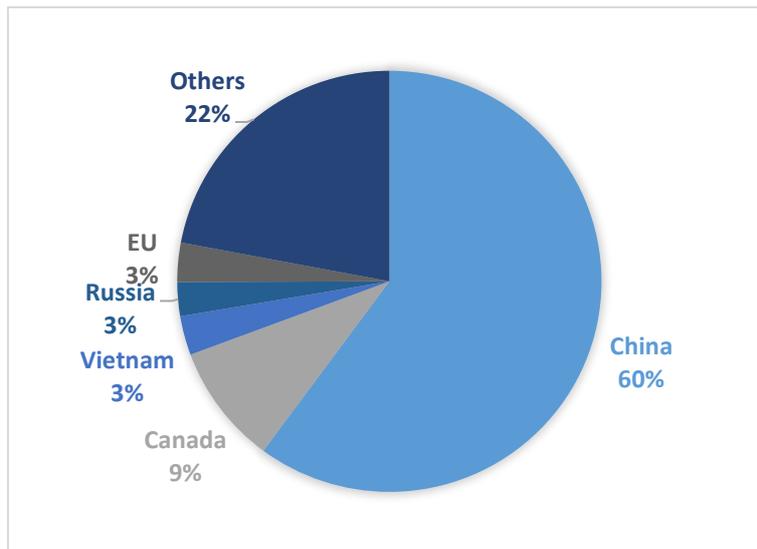


Figure 39: Worldwide estimated reserves of tungsten in 2017 [146]

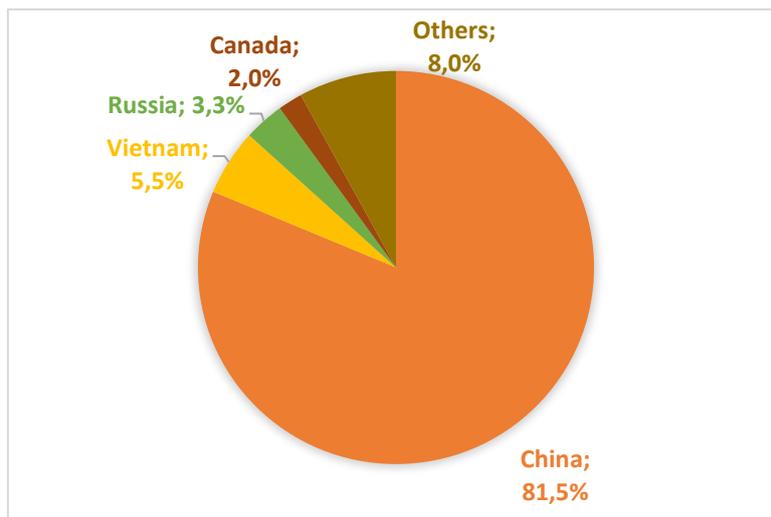


Figure 40: Worldwide tungsten production in 2015 [146]

Tungsten has been listed as one of the critical raw materials in Europe, both in terms of its high economic importance and its supply risk with market dominance by China. However, several projects are being assessed in order to open new producing centers in the coming years in Portugal and Spain, or around 2025 in France [147]. Twelve tungsten mines were exploited during the 20th century in France, and three deposits still have recognized resources of more than 10,000 t of WO₃ each: Montredon-Labessonié and Fumade (81), and Coat-an-Noz (22) [148].

The European MSP-REFRAM project (Multi-Stakeholder Platform for a Secure Supply of Refractory Metals in Europe) was realized from 2015 to 2017, aimed at constructing a network for securing supply of refractory metals in Europe [149].

2. GAPS & BARRIERS – PROPOSED PROCESSING ROUTES

MINING

Generally, underground mining methods are used in tungsten mine operations (China, Portugal, Bolivia, Canada, Peru, etc.), more rarely open pitting (Spain, Australia, etc.). Extraction is often of modest size, less than 2,000t of ore per day, or even artisanal, with manual sorting (China, Bolivia, etc.) [148].

BENEFICIATION

The majority of tungsten deposits contain less than 1.5% of WO_3 and ore concentrates international trading require 60-75% of WO_3 , which represents a large amount of gangue to be separated. That's why processing plants are generally located near the mine, to avoid transportation costs [150].

The ore is first crushed and milled to liberate the tungsten mineral crystals (comminution). Then, the liberated minerals are separated from gangue minerals by gravimetric methods (spirals, cones, shaking tables, jigs...) and cleaned from sulfide minerals by flotation or from magnetic minerals like pyrite by magnetic separation. Flotation is also used to enrich scheelite, and magnetic separation to concentrate wolframite. Some other methods are used like electrostatic to remove cassiterite from scheelite, or photometric to separate quartz from wolframite [151].

The beneficiation flowsheet depends on the nature of the mineralization in the ore body and on the liberation size of the Tungsten minerals. Figure 41 shows a simplified flowsheet of combined gravity-flotation procedure [151].

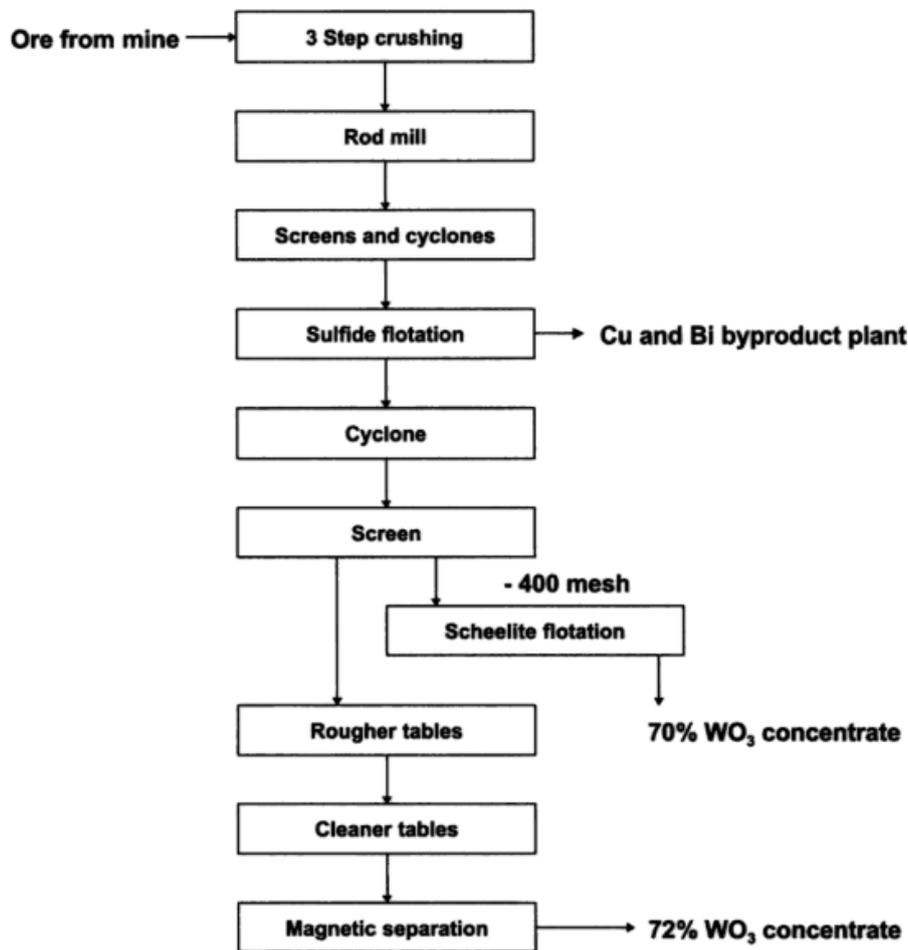


Figure 41 : Example of simplified flowsheet of combined gravity-flotation procedure [151]

There are several researches and innovations to improve the beneficiation process, because of the finer in grain size and the complex mineralogy. For example, the FAME European project works on economic and environmental challenges with increasing the range of yields of recovered raw materials with lower energy consumption and minimizing mine waste. The goal is to exploit European ore deposits that are often relatively small in tonnage terms. For instance, on a scheelite ore in Portugal, they study to liberate minerals without overgrinding, by a high voltage pulse (HVP) technology which are applied to the material immersed in water. Discontinuities in electrical properties of minerals generate cracks at the grain boundaries allowing full liberation of components. The results have showed an improvement of the scheelite liberation and a decrease in the grinding energy [152].

METALLURGY

Scheelite and wolframite concentrates are processed with several known hydrometallurgy (digestion, purification, solvent extraction, ion exchange, crystallization) and pyrometallurgy methods. Figure 42 shows the main processes used to obtain different intermediate and final products (framed in purple). It can process concentrates rich or poor in tungsten, and secondary deposits [152].

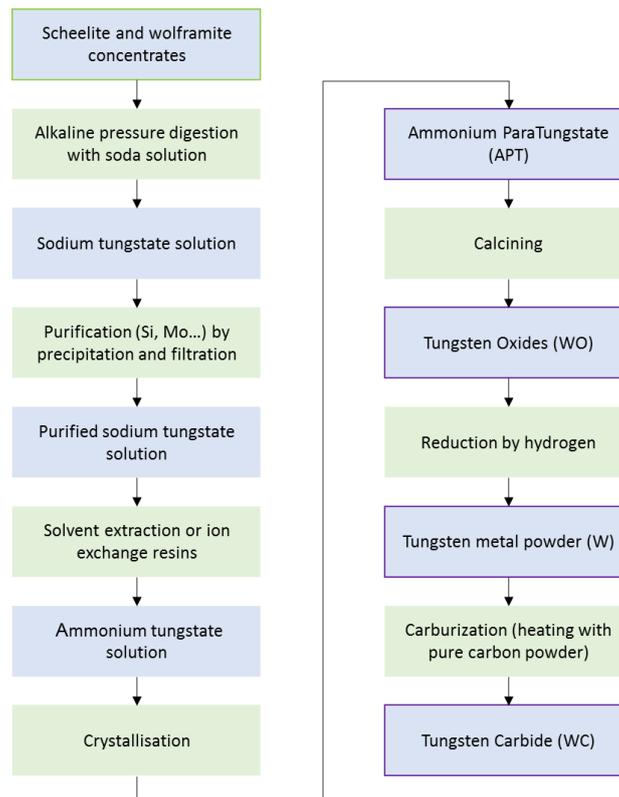


Figure 42: Main production processes [152]

Ammonium paratungstate (APT) is obtained by crystallisation and it is the main intermediate and the main tungsten raw material in the market. APT is calcined to yellow (WO_3) or blue oxide (WO_{3-x}), another intermediate.

If tungsten metal (W) is melted with tungsten monocarbide (WC), a eutectic composition of WC and W_2C is formed. This melt is cast and rapidly quenched to form extremely hard solid particles having a fine crystal structure. It is named cast carbide, another intermediate.

Scheelite and wolframite concentrates can also be smelted directly through aluminothermic and carbothermic reduction processes in an electric arc furnace to produce ferrotungsten (FeW up 75 to 85% W) [150].

Future challenges consist in decreasing tungsten losses in precipitation and purification, reducing chemical consumption and improving the efficiency of ion exchange and solvent extraction methods. As for pyrometallurgy methods, carburization is a one-step process, which is economical and energy efficient [147].

A European project named Optimore currently aimed at addressing these issues. Optimization of crushing, milling and separation used in tungsten and tantalum mineral processing, “by means of improved, faster and more flexible fine-tuning production process control based on new software models, advanced sensing and a more thorough examination of the physical process, which will result in a 7-12% yield increase and a 5% energy savings increase on the best production processes and best techniques available today” [153].

3. ENVIRONMENTAL IMPACT OF ALTERNATIVE TECHNOLOGIES AND RESIDUE TREATMENT

The most significant impacts of tungsten production are waste rock dumps and disposal of tailings. Most tungsten deposits contain less than 1.5% of WO_3 , which generate a lot of tailings, and blasted rock occupies more volume than in-situ material. Moreover, tailings do not contain chemical reagents or only in minor quantities, and low level of heavy metals. That is why they have been classified as “non-class A” facilities in accordance with the standards established in the EU Mining Waste Directive [147]. Tungsten has no known biological function, has no high toxicity and is not allergenic. Possible intoxications are exceptional and very strong occupational exposures [148].

SUMMARY

There is a strong demand of tungsten in the market, due to these specific characteristics (resistance to corrosion, acids and oxidation up to 400 °C, high melting point...). It can be substituted but at high cost and/or loss of performance. There is a supply risk with market dominance by China. That is why tungsten has been listed as one of the critical raw materials in Europe. It is not abundant in the Earth's crust and deposits contain less than 1.5% of WO_3 but there are reserves in many countries. Several projects are studied to open new producing centers in the coming years.

There are different intermediates of tungsten and metallurgical process is well known, but it can still be optimized by decreasing tungsten losses in precipitation and purification for example. The most significant impact of tungsten production is the volume of waste rock and tailings generated.

VANADIUM

1. THE PRIMARY RESOURCES

According to the resource-mapping results of WP4, vanadium is mainly mined and produced in China (53%), South Africa (24%), Russia (19%) and Brazil (3%) [154]. 85% of vanadium production is from the primary resource titaniferous magnetite and 15% from the other resources (such as catalyst and residuals from the power plant fired with heavy oils). Vanadium is listed as one of the Critical Raw Materials in 2017 in EU and EU import on vanadium is 84% [20].

2. GAPS & BARRIERS – PROPOSED PROCESSING ROUTES

MINING AND MINERAL PROCESSING

As mentioned earlier, vanadium is mainly produced from titaniferous magnetite, which is a type of iron ore. Therefore, the methods applied for mining iron ore in general apply for mining of titaniferous magnetite. Nowadays, the mining and mineral processing methods for iron ore have been well developed, and there is a little space for innovation. Nevertheless, titanomagnetite ore processing is a sophisticated large-scale process, during which a large volume of wastes or residual materials are generated. The barriers for mining and mineral processing of titaniferous magnetite lies in the ecological problems such as environmental pollution, land usage for mill tailing storage, the creation of sludge tanks for vanadium milling slimes, etc [155].

PYRO-METALLURGICAL PROCESSING OF TITANIFEROUS MAGNETITE

As shown in D4.1, 64% vanadium is produced by pyro-metallurgical process, during which iron is produced as the main product while vanadium as the by-product [156]. The barriers of the pyrometallurgical method mainly lie in large material and energy expenditures for the processing of titaniferous magnetite and that titanium contained in the raw material is not extracted and is lost with the waste at different stages of the process. Moreover, one of the most important barriers of this method is that titanium remains in the processed materials and significantly reduces the quality of the steels. Generally the concentration of titanium in raw materials should be less than 4%. [155] In one study it is demonstrated that low-grade titaniferous magnetite (containing up to 23% TiO_2) can be blended with hematite ore to produce pig iron, which could thereafter used to produce vanadium rich slag [157]. This may provide a method to use the low grade titaniferous magnetite.

HYDRO-METALLURGICAL PROCESSING OF TITANIFEROUS MAGNETITE

Hydro-metallurgical process is an important process for extracting vanadium from the titaniferous magnetite. Compared with the pyro-metallurgical process, the production capacity by this route is much smaller compared with the steel production. Further, hydro-metallurgical process relies much on the grades of the vanadium in the titaniferous magnetite or vanadium slag, as vanadium is the primary economic driver of the process. [156] Therefore, low vanadium in the primary ore and second materials could be the main barrier for applying a hydro-metallurgical process for vanadium extraction. Further, the yield of vanadium from the typical roast-leach process is around 82% [158], [159] and a lot of vanadium is lost in the leaching residuals. To improve the recovery of vanadium, various chemicals were tested in the roasting process; and it is demonstrated that vanadium extraction could reach 95%, 86%, and 64% by roasting-leaching process if sulphate, soda ash and salt, respectively, were used as the chemicals. Sulphate roasting could be more expensive than the established soda ash roasting process because of special material requirement for building a plant to process corrosive SO_3 by-product as well as to withstand higher temperatures and prolonged process time. The cost of Na_2SO_4 is also higher than that of Na_2CO_3 . However, the economics of sulphate roasting can be improved if the SO_3 by-product can be used to produce sulphuric acid [158].

Besides iron and vanadium, titaniferous magnetite is also regarded as an important source of titanium, especially considering the shortage of titanium raw materials. In the future a comprehensive utilization of iron, vanadium and titanium from the titaniferous magnetite ore could be the trend. In one study it is demonstrated (as shown in Figure 43) that titanium concentrate and iron concentrate could be produced by applying a hydro-metallurgical process. The produced titanium concentrate could be used for titanium production and iron concentrate could be used for iron and vanadium production by following, for example, a pyro-metallurgical process [155]. The comprehensive recovery of all the valuable materials could improve the raw material efficiency of titaniferous magnetite and increase the economic value.

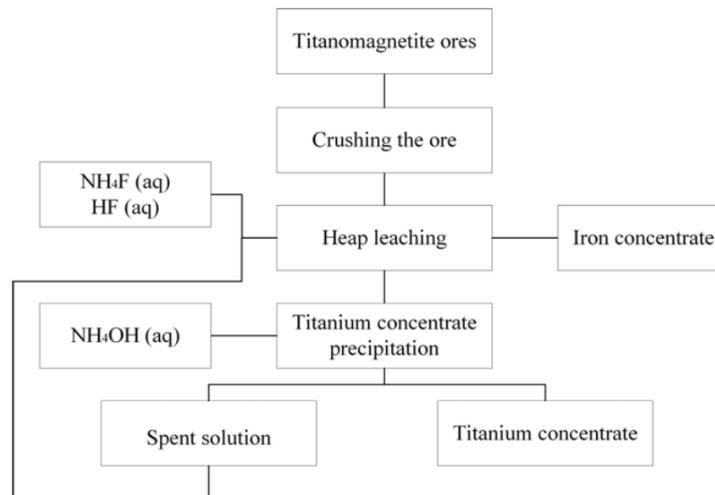


Figure 43 - Processing schematic diagram for titaniferous magnetite [155]

SUMMARY

Vanadium is listed as one of the Critical Raw Materials in EU and EU has high import-dependence on vanadium. Barriers exist in the mining/mineral processing steps and vanadium production steps. The mining and mineral processing of titaniferous magnetite could potentially cause various environmental problems due to the creation of secondary/waste materials during processing. The main barrier for the vanadium extraction in the pyro-metallurgical process lies in the presence of titanium in the titaniferous magnetite, which could on one hand affect the ironmaking process in the blast furnace and on the other hand deteriorate the steel quality due to the involvement of titanium in the steel. The main barrier for the vanadium extraction in the hydro-metallurgical process lies in the low vanadium content and low recovery of vanadium from the materials, which decrease the economic value of the extraction process. In the future developing a comprehensive process to concentrate the iron, vanadium and titanium in the ore in different fractions by either mineral processing and/or metallurgical processing is favored, as this will improve the raw materials efficiency and the economic value of the production process.

YTTRIUM

1. THE PRIMARY RESOURCES

According to the resource-mapping results of WP3, the main primary yttrium deposits in EU territory occur in Scandinavian countries and Finland. The petrology of yttrium deposits is characterized by alkaline pegmatite intrusions (Table 13). The Norra Kärr deposit is located in southern Sweden, approximately 300 km SW of Stockholm consisting the only heavy REE deposit of note within the EU (except Greenland) with a high potential to provide the EU with a long term REEs capacity. The Norra Kärr reserves are estimated at 41.6 Mt with an average 0.57% concentrations in REOs. Yttrium is mainly contained in eudyalite, grennaite, kaxtorpите and lakarpite phases with a maximum reported concentration of 3590 ppm [160].

Kvanefjeld in Greenland is one of the largest REEs-uranium deposits in the world with a total reserve of 619 Mt and 0.84 Mt of yttrium oxide. Mineralisation is hosted by lujavrite, with the mineral steenstrupine the dominant host to both uranium and REEs [161]. In southern Finland several localities with NYF (niobium–yttrium–fluorine) pegmatite types haven been reported. The veins occur into the Paleoproterozoic (1.85–1.80 Ga) Late Svecofennian granite–migmatite zone [64]. Furthermore, syentites intrusions occur within Svecofennian (ca. 1.92 Ga) gneisses in Lamujärvi. The exploitation of yttrium-rich ores from Norra Kärr and Kvanefjeld is expected to be performed in the close future by Leading Edge Materials and Greenland Minerals and Energy Ltd. Companies respectively. The feasibility study for various beneficiation and metallurgical steps has already been completed.

Table 13. The main primary unexploited resources of yttrium in EU [160] [161] [64]

Type of ore	Yttrium form	Major deposits	Gaps and barriers			
			mining	beneficiation	metallurgy	Residues
Alkaline intrusions	eudyalite grennaite, kaxtorpите, lakarpite phases	Norra Kärr, Sweden				
Alkaline intrusions	Steenstrupine phase	Kvanefjeld, Greenland, Denmark				x

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Granitic pegmatites and syenites in gneiss	allanite, gadolinite, fergusonite, monazite and xenotime	southern Finland, Lamujärvi				
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2. GAPS & BARRIERS – PROPOSED PROCESSING ROUTES

MINING

REEs containing ores worldwide ores are mined underground or superficially (open pits) following the hydrothermal or pegmatite veins (in case of non-altered rocks). Mining techniques are well developed and no gaps and barriers at the mining step have been reported.

BENEFICIATION

Norra Kärr, Sweden

Extensive beneficiation test work has been completed on representative samples from Norra Kärr aiming to the separation of eudialyte which is the most significant REEs-bearing phase. The beneficiation includes the crushing, grinding, magnetic separation of the ore. Eudialyte beneficiates efficiently using Metso’s HGMS magnetic separation equipment, providing a clean and high recovery eudialyte-rich mineral concentrate. Beneficiation recovery higher than 90% is now expected and targeted [68]. The main parameter which should be optimized concerns the value of the magnetic separation intensity in order the low-magnetic eudyalite-aegirine be separated from the paramagnetic oxide phase. Otherwise, it has not been reported any significant technological barrier at the beneficiation step.

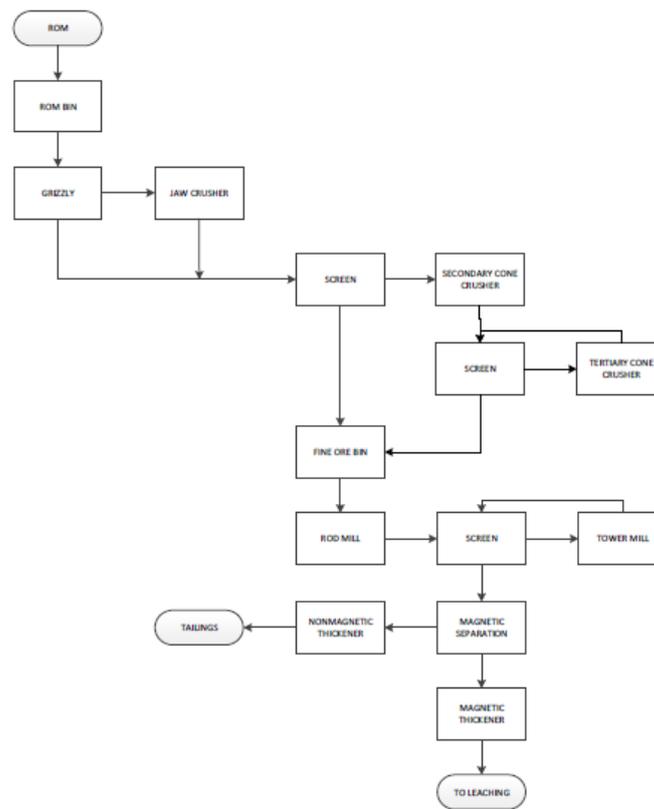


Figure 44 - Beneficiation process of Norra Kärr ore [68]

Kvanefjeld, Greenland

Detailed beneficiation tests of Kvanefjeld ore through a simple froth flotation process have recently been performed at pilot scale [161]. The results showed that the ore is enriched x10 wt.% in REEs. The high upgrade efficiency allows the shipping of the concentrate to a location where a hydrometallurgical plant can be more cost-effectively implemented. No significant beneficiation barriers have been reported.

Lamujärvi, Finland

The beneficiation of a syenite sample containing Zr (1587 ppm), Nb (up to 685 ppm), Ta (up to 82 ppm), REE (up to 5350 ppm) and Y (about 200 ppm) was attempted by GTK Mintec Company. The major REE-bearing minerals of the syenite are allanite, parisite, zircon, and apatite. The non-REEs bearing phases are titanite (15.4%), biotite (30.9%) and magnetite (8.2%). The proposed beneficiation process comprises a combination of magnetic separation and flotation (Figure 45) [65]. Under the optimum conditions, the produced REE-Ti concentrate contains: REE 23,000 ppm, Zr 5000 ppm, Nb 3400 ppm and TiO₂ 25.5% at REE. The REEs recovery was 57%. Additionally, high-value magnetic and non-magnetic fractions are

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produced such as: magnetic concentrate with the grade of FeO 86.6% and biotite concentrate with the grade of MgO 6.6%. The low REEs recovery consist the main disadvantage of the method. The possibility of the ore beneficiation using alternative techniques such as electrostatic separation it deserves to be examined.

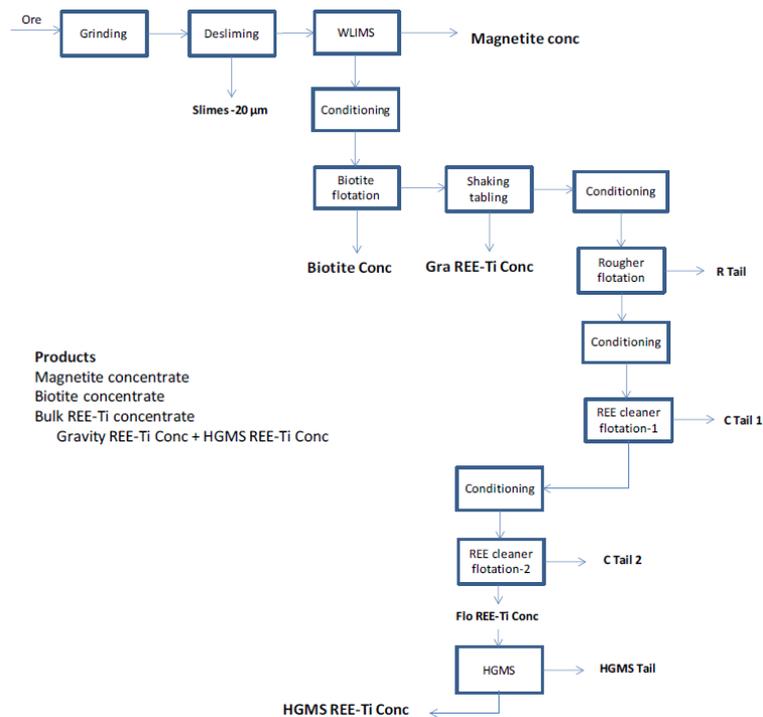


Figure 45 - Beneficiation process of the Lamujärvi REE-rich ore [65].

METALLURGY

Norra Kärr, Sweden

The metallurgical processing of the Norra Kärr has been established in detail. The method involves the leaching of the ore with sulphuric acid and subsequently the neutralization of the leachate with magnesium oxide. REEs are separated via solvent extraction using organic solvents. REEs are stripped from the pregnant solvent using oxalic acid. The precipitate is received with centrifugation and consist a mixture of various REEs and yttrium oxalates. The concentration of yttrium in the mixture exceeds 12 wt.%. The oxalate mixture is calcined and converted to oxide form. The impurities content in the final product is low (<0.2 wt.%).

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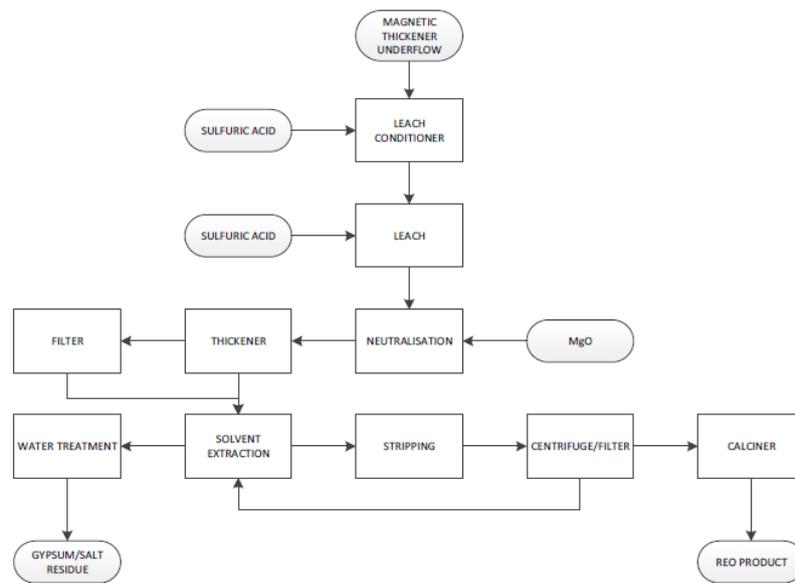


Figure 46 - Flowsheet of the metallurgical processing of the Norra Kärr ore [68]

Kvanefjeld, Greenland

Extensive metallurgical and infrastructure studies, including hydropower, for the step of the concentrate leaching have been performed the last decades. The sulphuric acid leaching at atmospheric conditions is proposed as the most efficient technique due to the following reasons [161]:

- The REEs and U recovery yield exceeds 90%
- No high-temperature acid bake or caustic crack is required
- The solvent extraction recovery of U and RE concentrates can be directly followed

The metallurgical processing of both Norra Kärr and Kvanefjeld Y-rich ores has been tested satisfactorily and notable gaps and barriers have not been mentioned.

3. ENVIRONMENTAL IMPACT OF ALTERNATIVE TECHNOLOGIES AND RESIDUE TREATMENT

The environmental impact of the future processing of Kvanefjeld ore should not be ignored as a significant number of radionuclides, mainly uranium and thorium, will be released during several processing steps. The removal of U(VI) from contaminated wastewater consists an important topic for the scientific community and it has been studied by various kinds of technologies, such as bioreduction, chemical precipitation and sorption. Conventional

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sorption techniques present several disadvantages such as poor sorption capacities and low efficiencies. Recent studies indicate the use of nanomaterials, especially carbon-based nanocomposites, as uranium sorbents. Amidoximated magnetite/graphene oxide nanocomposites have been successfully used for the adsorption of U(VI) in aqueous solutions [162]. The method deserves to be used for the purification of U-rich metallurgical wastes such the wastes that potentially be generated in case of Kvanefjeld ore.

BIBLIOGRAPHY

- [1] Ulrich Schwarz-Schampera, 'Antimony', in *Critical Metals Handbook*, 2014 John Wiley & Sons, Ltd., 2013, pp. 70–98.
- [2] W.C. Butterman and J.F. Carlin Jr, 'Mineral Commodity Profiles: Antimony', USGS Numbered Series 2003–19, 2004.
- [3] Dimitrios Filippou, Pascale St.Germain, and Tassos Grammatikopoulos, 'Recovery of metal values from copper-arsenic minerals and other related resources', *J. Miner. Process. Extr. Metall. Rev.*, vol. 28, no. 4, pp. 247–298, 2007.
- [4] P. M. Solozhenkin and A. N. Alekseev, 'Innovative processing and hydrometallurgical treatment methods for complex antimony ores and concentrates. Part I', *J. Min. Sci.*, vol. 46, no. 2, pp. 203–209, Mar. 2010.
- [5] Lyalikova-Medvedeva, 'Biotechnology of Concentrate and Antimony Ore Processing', *J. Min. Sci.*, vol. 37, pp. 534–541, 2001.
- [6] Corby G. Anderson, 'The metallurgy of antimony', *Chem. Erde*, vol. 72, no. S4, pp. 3–8, 2012.
- [7] Solozhenkin, P. M. and Alekseev, A. N., 'Innovative Processing and Hydrometallurgical Treatment Methods for Complex Antimony Ores and Concentrates. Part II: Hydrometallurgy of Complex Antimony Ores', *J. Min. Sci.*, vol. 46, no. 4, pp. 446–452, 2013.
- [8] Kevin A. Bonel, 'Barytes', BGS, Sep. 2005.
- [9] Minerals4EUDatabase, 'Mineral occurrence. Baryte', 2014. [Online]. Available: <http://minerals4eu.brgm-rec.fr/search/site/baryte>.
- [10] EGDI, 'ProMine Data Products', 2013. [Online]. Available: <http://www.europe-geology.eu/promine/>.
- [11] Polish Geological Institute, 'Baryte and Fluorspar', *Mineral Resources of Poland*, 2009. [Online]. Available: http://geoportal.pgi.gov.pl/surowce/chemiczne/baryt_fluoryt.
- [12] British Geological Survey, 'Baryte', 2000.
- [13] Duntanlich mine, 'Duntanlich mine', 2017. [Online]. Available: <https://duntanlich.com/about-duntanlich/>.
- [14] Srdjan M. Bulatovic, 'Chapter 34. Beneficiation of Barite Ores', in *Handbook of Flotation Reagents: Chemistry, Theory and Practice*, 1st ed., vol. Volume 3: Flotation of Industrial Minerals, Elsevier, 2014, p. 238.
- [15] Achusim-Udenko, A. C. Onyedika Gerald, Ogwuegbu Martins, and Ayuk Ausaji, 'Flotation recovery of barite from ore using palm bunch based collector', *Int. J. Chem. Sci.*, vol. 9, no. 3, pp. 1518–1524, 2011.
- [16] Ofor, O. and Nwoko, C., 'Oleate flotation of a Nigerian baryte : The relation between flotation recovery and adsorption density at varying oleate concentrations, pH, and temperatures', *J. Colloid Interface Sci.*, vol. 186, no. 2, pp. 225–233, 1997.
- [17] M. G. Ciccu, 'Optimization of an integrated flowsheet for barite processing', presented at the 20th International Symposium on the Application of Computers and Mathematics in the Mineral Industries, Johannesburg, 1987, vol. 2: Metallurgy, pp. 281–293.
- [18] Innovation Metals, 'Latest news', 2019. [Online]. Available: <http://www.innovationmetals.com/imc-latest-news/>.

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

- [19] Geological Survey of Finland, 'Fennoscandian Mineral Deposits application, Ore Deposits database and Maps', 2018. [Online]. Available: <http://en.gtk.fi/information-services/databases/fodd/index.html>.
- [20] European Commission, 'Study on the review of the list of critical raw materials', 2017.
- [21] European Commission, 'Study on the review of the list of critical raw materials. Critical raw materials factsheets', Luxembourg, Jun. 2017.
- [22] US Geological Service, 'Boron Statistics and Information', *National Minerals Information Center*, 2018. [Online]. Available: <https://www.usgs.gov/centers/nmic/boron-statistics-and-information>.
- [23] Río Tinto, 'Jadar', 2019. [Online]. Available: <https://www.riotinto.com/energyandminerals/jadar-4643.aspx>.
- [24] Rio Tinto, 'Annual Report. 2018'.
- [25] K.M. Goodenough *et al.*, 'Europe's rare earth element resource potential: An overview of REE metallogenetic provinces and their geodynamic setting', *Ore Geol. Rev.*, vol. 72, no. Part 1, pp. 838–856, 2016.
- [26] EURARE, 'Rare earth element deposits in Europe', *Eurare. Sustainable Exploitation*, 2017. [Online]. Available: <http://www.eurare.eu/countries/>.
- [27] Jason Yang and Damien Krebs, 'WP2: What Have We Learnt', Aachen, 04-Dec-2015.
- [28] Stefan S. Andersson, Thomas Wagner, Erik Jonsson, and Radoslaw M. Michallik, 'Mineralogy, paragenesis, and mineral chemistry of REEs in the Olserum-Djupedal REE-phosphate mineralization, SE Sweden', *Am. Mineral.*, vol. 103, no. 1, pp. 125–142, 2018.
- [29] Thair Al Ani and Olli Sarapää, 'Rare earth elements and their mineral phases in Jammi carbonatite veins and fenites on the south side of Sokli carbonatite complex, NE Finland', GTK, Aug. 2009.
- [30] Ni, X, Parrent, M, Cao, M, Huang, L., Bouajila, A., and Liu, Q., 'Developing flotation reagents for niobium oxide recovery from carbonatite Nb ores', *Miner. Eng.*, vol. 36–38, pp. 111–118, 2012.
- [31] Geoffrey Charles Reed, 'Amended and restated technical report for Olserum, REE deposit, southern Sweden', Tasman Metals Limited, Dural, 2013.
- [32] E. Pohjolainen, H. Tuovinen, P. Sorjonen-Ward, and R. Neitola, 'NORM related mineral developments in Finland', Vienna, 2018, pp. 287–292.
- [33] Maria Economou-Eliopoulos, 'Apatite and Mn, Zn, Co-enriched chromite in Ni-laterites of northern Greece and their genetic significance', *J. Geochem. Explor.*, vol. 80, pp. 41–54, 2003.
- [34] G. V. Rao, 'Nickel and cobalt ores : Flotation', *Metallurgist*, vol. 911, 2000.
- [35] SGU, 'Rönnebacken, a major nickel and iron project in Sweden', 2015.
- [36] Drake Resources, 'Significant nickel, copper, cobalt deposits acquired – Espedalen, Norway, ASX Announcement'. 31-Aug-2012.
- [37] Frank Crundwell, Michael Moats, Venkoba Ramachandran, Timothy Robinson, and W. G. Davenport, *Extractive Metallurgy of Nickel, Cobalt and Platinum Group Metals*, 1st Edition. Elsevier, 2011.
- [38] Dimitri Georgiou and Vladimiro G. Papangelakis, 'Behaviour of cobalt during sulphuric acid pressure leaching of a limonitic laterite', *Hydrometallurgy*, vol. 100, pp. 35–40, 2009.

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

- [39] Stella Agatzini-Leonardou and Ioannis G. Zafiratos, 'Beneficiation of a Greek serpentinitic nickeliferous ore Part II. Sulphuric acid heap and agitation leaching', vol. 74, no. Hydrometallurgy, pp. 267 – 275, 2004.
- [40] A. Katsiapi, P.E. Tsakiridis, P. Oustadakis, and S. Agatzini-Leonardou, 'Cobalt recovery from mixed Co–Mn hydroxide precipitates by ammonia–ammonium carbonate leaching', *Miner. Eng.*, vol. 23, no. 8, pp. 643–651, Jul. 2010.
- [41] Sarah L. Smith, Barry M. Grail, and D. Barrie Johnson, 'Reductive bioprocessing of cobalt-bearing limonitic laterites', *Miner. Eng.*, vol. 106, pp. 86–90, 2017.
- [42] Chuanlin Fan, Xiuqing Zhai, Yan Fu, Yongfeng Chang, Binchuan Li, and Ting-an Zhang, 'Extraction of nickel and cobalt from reduced limonitic laterite using a selective chlorination–water leaching process', *Hydrometallurgy*, vol. 105, no. 1–2, pp. 191–194, Dec. 2010.
- [43] J. Z. Khoo, N. Haque, G. Woodbridge, R. McDonald, and S. Bhattacharya, 'A life cycle assessment of a new laterite processing technology', *J. Clean. Prod.*, pp. 1765–1777, 2017.
- [44] Eurostat, 'Production and consumption of hard coal', *Eurostat. Coal consumption statistics*, 2018. [Online]. Available: http://ec.europa.eu/eurostat/statistics-explained/index.php/Coal_consumption_statistics#Consumption_and_production_of_hard_coal.
- [45] EURACOAL, 'Coal industry across Europe', 6th Edition with insights, 2017.
- [46] Manoj Kumar Sharma, Gohil Priyank, and Nikita Sharma, 'Coal Beneficiation Technology for Coking & Non-Coking Coal Meant For Steel and Thermal Power Plants', *Am. J. Eng. Res.*, vol. 4, no. 4, 2015.
- [47] R. Sakurovs, 'Some factors controlling the thermoplastic behaviour of coals', *Fuel*, vol. 79, no. 3–4, pp. 379–389, 2000.
- [48] Noriyuki Okuyama, Nobuyuki Komatsu, Takuo Shigehisa, Takao Kaneko, and Shigeru Tsuruya, 'Hyper-coal process to produce the ash-free coal', *Fuel Process. Technol.*, vol. 85, no. 8–10, pp. 947–967, Jul. 2004.
- [49] Okuyama, N., Furuya, A., Komatsu, N., and Shigehisa, T., 'International Conference of Coal Science and Technology Proceedings.', 2005.
- [50] Maki Hamaguchi, Naoki Kikuchi, Maria Lundgren, and Lena Sundqvist, 'Effects of non-coking coal and hypercoal addition on the properties of metallurgical coke', Luleå, Scanmet, Jun. 2016.
- [51] M.A Díez, R. Alvarez, and C. Barriocanal, 'Coal for metallurgical coke production: predictions of coke quality and future requirements for cokemaking', *Int. J. Coal Geol.*, vol. 50, no. 1–4, pp. 389–412, May 2002.
- [52] BRGM, 'Fiche de synthèse sur la criticité des métaux - L'hafnium', Jun. 2018.
- [53] Mikael Lundberg, 'Environmental analysis of zirconium alloy production', Uppsala Universitet, 2011.
- [54] James V. Jones III, Nadine M. Piatak, and George M. Bedinger, 'Zirconium and hafnium', Professional Paper 1802–V.
- [55] U.S. Geological Survey, 'Mineral commodity summaries 2019', 2019.
- [56] L. Poriel, A. Favre-Réguillon, S. Pellet-Rostaign, and M. Lemaire, 'Zirconium and Hafnium Separation, Part 1. Liquid/Liquid Extraction in Hydrochloric Acid Aqueous Solution with Aliquat 336', *Sep. Sci. Technol.*, vol. 41, no. 9, pp. 1927–1940, 2006.

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

- [57] Framatome, 'Business Unit Combustible (France)', *Business Unit Combustible (France)*. [Online]. Available: <https://www.framatome.com/FR/businessnews-142/areva-np-business-unit-combustible--usine-de-jarrie.html>.
- [58] A.M. Donia, A.A. Atia, A.M. Daher, and E.A. Elshehy, 'Extraction and Separation of Zirconium(IV) and Hafnium(IV) from Chloride Media Using Magnetic Resin with Phosphoric Acid Functionality', *J. Dispers. Sci. Technol.*, vol. 32, no. 2, pp. 193–202, 2011.
- [59] M. A. Kabili, M. A. Akl, A.M. Abdallah, and D.S. Ismail, 'Selective Separation-Flotation of Hafnium from Zirconium and Their Determination in Real Samples', *Anal. Sci.*, vol. 16, no. 7, pp. 713–718, 2000.
- [60] A. Da Silva, E. El Ammouri, and P.A. Distin, 'Hafnium/Zirconium Separation Using Cyanex 925', *Can. J. Metall. Mater. Sci.*, vol. 39, no. 1, pp. 37–42, 2000.
- [61] Alkane Resources, 'Dubbo Project', 2019. [Online]. Available: <http://www.alkane.com.au/projects/dubbo-project/>.
- [62] Mark Saxon, Magnus Leijd, Kurt Forrester, and Johan Berg, 'Geology, mineralogy, and metallurgical processing of the Norra Kärr heavy REE deposit, Sweden', presented at the Symposium on Strategic and Critical Materials Proceedings, Victoria, British Columbia, 2015, vol. 3, pp. 97–107.
- [63] Arctic Cluster for Raw Materials, 'The Kvanefjeld Project - Perspectives on Developing a World-Class Project in Greenland', Copenhagen, Oct-2015.
- [64] Olli Sarapää *et al.*, 'Rare earth exploration potential in Finland', *J. Geochem. Explor.*, vol. 133, pp. 25–41, 2013.
- [65] Xiaosheng Yang, Jukka Laukkanen, Akseli Torppa, and Neea Heino, 'Mineralogy and Beneficiation of Lamujärvi Syenites', *Nat. Resour.*, vol. 7, pp. 481–493, 2016.
- [66] IAEA, 'Radiation Protection and Safety of Radiation Sources: International Basic Safety Standards', Vienna, General Safety Requirements Part 3. No. GSR Part 3, 2014.
- [67] S. Nielsen, P. Roos, and K. Andersson, 'Predicted Radiation Exposure from Mining at Kvanefjeld Introduction to Radiation, Review of Baseline Information, and Predicted Radiation Exposures from Kvanefjeld Mining, Mineral Processing and Refining', *DTU Nutech*, Jun. 2015.
- [68] GBM, 'Amended & Restated Prefeasibility Study - NI 43-101 - Technical report for the Norra Kärr Rare Earth Element Deposit', Tasman Metals Ltd, Jul. 2015.
- [69] Paul B. Queneau and Cornelius E. Berthold, 'Silica in Hydrometallurgy: An Overview', *Can. Metall. Q.*, vol. 25, no. 3, pp. 201–209, 1986.
- [70] Greenland Minerals and Energy, 'Kvanefjeld Prefeasibility Study Confirms a Long-Life, Cost Competitive Rare Earth Element - Uranium Project', Company Announcement, 2012.
- [71] Greenland Minerals Authority, 'Greenland Minerals Authority', 2019. [Online]. Available: <https://govmin.gl/#>.
- [72] J. Schilling, 'Petrography, mineralogy and whole-rock data of the major lithologies of the Fen Complex', Geological Survey of Norway, 2013.
- [73] Peter M. Ihlen, Henrik Schiellerup, Håvard Gautneb, and Øyvind Skår, 'Characterization of apatite resources in Norway and their REE potential — A review', *Ore Geol. Rev.*, vol. 58, pp. 126–147, 2014.

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

- [74] Grontmij, 'Social Impact Assessment TANBREEZ Mining Greenland A/S. Social Impact Assessment Report', Aug. 2013.
- [75] Jason Yang, 'Studies on Mineralogy and Beneficiation of European REE Ores', presented at the 3rd PROMETIA Scientific Seminar, 14-15/12/2016, Berlin, 2016.
- [76] Efthymios Balomenos *et al.*, 'The EURARE Project: Development of a Sustainable Exploitation Scheme for Europe's Rare Earth Ore Deposits', *Johns. Matthey Technol. Rev.*, vol. 61, no. 2, pp. 142–153, 2017.
- [77] D. Voßenkaul, A. Birich, N. Müller, and N. Stoltz, 'Hydrometallurgical Processing of Eudialyte Bearing Concentrates to Recover Rare Earth Elements Via Low-Temperature Dry Digestion to Prevent the Silica Gel Formation', *J. Sustain. Metall.*, vol. 3, no. 1, pp. 79–89, 2017.
- [78] Polido Legaria, Elizabeth, 'Nanotechnology for hydrometallurgy extraction and separation of rare earth elements by hybrid nanoadsorbents.', Doctoral Thesis, thesis Swedish University of Agricultural Sciences, Uppsala, 2018.
- [79] Srećko R. Stopić and Bernd G. Friedrich, 'Leaching of rare earth elements with sulfuric acid from bastnasite ores', *Mil. Tech. Cour.*, vol. 66, no. 4, pp. 757–770, 2018.
- [80] Panagiotis Davris *et al.*, 'Leaching of rare earth elements from "Rödberg" ore of Fen carbonatite complex deposit, using the ionic liquid HbetTf₂N', *Hydrometallurgy*, vol. 175, pp. 20–27, 2018.
- [81] Jelena Mrdakovic Popic, Brit Salbu, Terje Strand, and Lindis Skipperud, 'Assessment of radionuclide and metal contamination in a thorium rich area in Norway', *J. Environ. Monit.*, vol. 13, no. 6, pp. 1730–8, Jun. 2011.
- [82] H. Gautneb, 'Natural graphite in Norway – Overview and latest exploration results', presented at the 5th Graphite and Graphene conference, London, United Kingdom, 2015.
- [83] T.J. Brown *et al.*, 'World Mineral Production 2011–2015', British Geological Survey, Keyworth, Nottingham, 2017.
- [84] US Geological Service, 'Graphite Statistics and Information', *National Minerals Information Center*, 2019. [Online]. Available: <https://www.usgs.gov/centers/nmic/graphite-statistics-and-information>.
- [85] Chehreh Chelgani, M. Rudolph, R. Kratzsch, D. Sandmann, and J. Gutzmer, 'A Review of Graphite Beneficiation Techniques', *Miner. Process. Extr. Metall. Rev.*, vol. 37, no. 1, pp. 58–68, 2016.
- [86] EU, 'Annex 1: Greenland mineral deposit descriptions', EU, Ref. Ares(2015)3227259-31/07/2015, Jul. 2015.
- [87] Damien Krebs, 'Greenland's Unique Kvanefjeld Multi-element Rare Earth Project. Producing a suite of rare earth products', *Johns. Matthey Technol. Rev.*, vol. 61, no. 2, pp. 154–155, 2017.
- [88] Kurt Forrester, Magnus Leijd, M. Oczlon, and H. Holmström, 'Beneficiation of rare earth element enriched eudialyte from the Norra Kärr peralkaline intrusion with wet high intensity magnetic separation', 2014.
- [89] Greenland Minerals Limited, 'A rare opportunity in Rare Earths', *Pitt Street Research*, 20-Sep-2018.
- [90] EURARE, 'Final Report Summary - EURARE (Development of a sustainable exploitation scheme for Europe's Rare Earth ore deposits)', 2018. [Online]. Available: <https://cordis.europa.eu/project/rcn/106537/reporting/en>.
- [91] B. Friedrich, D. Voßenkaul, and S. Stopic, 'Leaching of high silica containing ores - preventing gel-formation by dry digestion', presented at the ERES Conference, Santorini, Greece, 2017.

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

- [92] Greenland Minerals and Energy, 'EURARE Kvanefjeld Refinery Demo Plant Work Package 5', Oct-2015.
- [93] Greenland Minerals and Energy, 'Successful Pilot Plant Operation – Kvanefjeld Project', Company Announcement, Jun. 2015.
- [94] Greenland Minerals and Energy, 'Greenland Minerals Limited and Greenland Minerals & Energy A/S Kvanefjeld Project Social Impact Assessment', Jul. 2018.
- [95] Greenland Minerals and Energy, 'Kvanefjeld Feasibility Study Underway. Metallurgical Developments Continue to Advance and De-Risk Process Flow-Sheet', Company Announcement, Sep. 2012.
- [96] AS. Audion and P.Piantone, 'Panorama 2011 du marché du Ta', BRGM, Public report BRGM/RP-61343-FR, Jul. 2012.
- [97] BGS, 'Mineral profile Niobium-Tantalum', Apr. 2011.
- [98] T. Oberthür, F. Melcher, P. Buchholz, and M. Locmelis, 'The oxidized ores of the Main Sulphide Zone, Great Dyke, Zimbabwe: Turning resources into minable reserves-mineralogy is the key', *J. South. Afr. Inst. Min. Metall.*, vol. 103, no. 3, pp. 191–201, Mar. 2013.
- [99] J.F. Labbé and J.J. Dupuy, 'Panorama 2012 du marché des platinoïdes, report January 2014.', BRGM, Rapport Public, Jan. 2014.
- [100] BRGM, 'Fiche de synthèse sur la criticité des métaux - Le palladium', Version 2, Nov. 2017.
- [101] Statista, 'Major countries in global mine production of platinum', 2017. [Online]. Available: <https://www.statista.com/statistics/273645/global-mine-production-of-platinum/>.
- [102] Statista, 'Global mine production of palladium', 2017. [Online]. Available: <https://www.statista.com/statistics/273647/global-mine-production-of-palladium/>.
- [103] R. Sefako, K. Sekgarametso, and V. Sibanda, 'Potential Processing Routes for Recovery of Platinum Group Metals from Southern African Oxidized PGM Ores: A Review', *J. Sustain. Metall.*, vol. 3, no. 4, pp. 797–807, 2017.
- [104] Viljoen, M.J. and Schurmann, L.W, 'Platinum-Group Metals', in *The Mineral Res. of South Africa, Handbook*, vol. 16, 1998, pp. 532–568.
- [105] McDonald, I. and Holwell, D.A., 'Geology of the Northern Bushveld Complex & the setting and genesis of the Platreef Ni-Cu-PGE deposit', *Rev. Econ. Geol.*, vol. 17, pp. 297–327, 2011.
- [106] N. Solomon, M. Becker, A. Mainza, J. Petersen, and J.-P. Franzidis, 'Understanding the influence of HPGR on PGM flotation behavior using mineralogy', *Miner. Eng.*, vol. 24, no. 12, pp. 1370–1377, Oct. 2011.
- [107] Steve Cole, C. and Joe Ferron, *A review of the beneficiation and extractive metallurgy of the platinum group elements, highlight recent process innovations*. SGS, 2002.
- [108] Charles Bushell, 'The PGM flotation predictor: Predicting PGM ore flotation performance using results from automated mineralogy systems', *Miner. Eng.*, vol. 36–38, pp. 75–80, Oct. 2012.
- [109] Pierre Blazy and El-Aïd Jdid, 'Métallurgie des platinoïdes - Minerais et procédés', *Techniques de l'Ingénieur*, no. M2390 v1, 10-Dec-2003.
- [110] C.N. Mpinga, J.J. Eksteen, C. Aldrich, and L. Dyer, 'Direct leach approaches to Platinum Group Metal (PGM) ores and concentrates: A review', *Miner. Eng.*, vol. 78, pp. 93–113, Jul. 2015.

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

- [111] G. A. Bezuidenhout, J.J. Eksteen, G. Akdogan, and S.M. Bradshaw, 'Pyrometallurgical upgrading of PGM-rich leach residues from the Western Platinum base metals refinery through roasting', *Miner. Eng.*, vol. 53, pp. 228–240, Nov. 2013.
- [112] Steven J. Van Kauwenbergh, 'World Phosphate Rock Reserves and Resources', International Fertilizer Development Center, Alabama, United States, IFDC-G-I, Sep. 2010.
- [113] Stephen M. Jasinski, 'Mineral Resource of the Month: Phosphate Rock', *Earth*, 02-Dec-2013.
- [114] Scholz, R.W., Roy, A.H., Brand, F.S., Hellums, D., and Ulrich, A.E., *Sustainable Phosphorus Management. A Global Transdisciplinary Roadmap*. Springer, 2014.
- [115] Patrick Zhang, *Beneficiation of phosphates. Comprehensive extraction technology innovations advanced reagents*. Colorado, United States: Society for Mining, Metallurgy and Exploration, 2016.
- [116] Daniel Cassard *et al.*, *ProMine Mineral Databases: New Tools to Assess Primary and Secondary Mineral Resources in Europe*. Springer International Publishing Switzerland, 2015.
- [117] S. Komar Kawatra and J.T. Carlson, *Beneficiation of phosphate ore*. Colorado, United States: Society for Mining, Metallurgy and Exploration, 2014.
- [118] Decree Sophie, Peter Ihlen, Henrik Schiellerup, and Anders Hallberg, 'Potential of phosphate deposits in Europe', *SGA News*, vol. 41, Aug-2017.
- [119] MTÜ Eesti Mäselts, 'Ülevaade Eesti fosforiidist', 2019. [Online]. Available: <http://www.maeselts.ee/ulevaade-fosforiidist>.
- [120] Bo M. Stensgaard, Henrik Stendal, Per Kalvig, and Karen Hanghøj, 'Review of potential resources for critical minerals in Greenland', Center for Minerals and Materials. Geological Survey of Denmark and Greenland, 2016/3, 2016.
- [121] Bertil I. Pålsson, Olof Martinsson, Christina Wanhainen, and Andreas Fredriksson, 'Unlocking rare earth elements from European apatite-iron ores', presented at the ERES2014: 1st European Rare Earth Resources Conference, Milos, Greece, 2014.
- [122] S. M. Notholt, 'Phosphate resources of the European Economic Community', Report for the Commission of the European Communities, CREST Subcommittee on Raw Materials, Research and Development.
- [123] Janne Hokka and Tapio Halkoaho, '3D modelling and mineral resource estimation of the Kiviniemi Scandium deposit, Eastern Finland', *GTK*, 65/2015, May 2016.
- [124] EURARE, 'REE mineralisation in Norway', 2017. [Online]. Available: <http://www.eurare.eu/countries/norway.html>.
- [125] R. Kristiansen, 'A unique assemblage of Scandium-bearing minerals from the Heftetjern-pegmatite, Tørdal, south Norway', in *Norsk Bergverksmuseum Skrift*, 2009, vol. 41, pp. 75–104.
- [126] Demetrios Eliopoulos and Maria Economou-Eliopoulos, 'Geochemical and mineralogical characteristics of Fe–Ni and bauxitic-laterite deposits of Greece', *Ore Geol. Rev.*, vol. 16, no. 1, pp. 41–58, Mar. 2000.
- [127] T. Malvik, 'Preliminary beneficiation study of Biggejavre davidite ore', Trondheim, 1986.
- [128] T. Al-Ani and O. Sarapää, 'REE-minerals in carbonatite, alkaline and hydrothermal rocks, Northen and central Finland', presented at the ERES2014: 1st European Rare Earth Resources Conference, Milos, Greece, 2014.

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

- [129] C. K. Gupta and N. Krishnamurthy, *Extractive Metallurgy of Rare Earths*. CRC PRESS, 2005.
- [130] Ahven, M., 'Scandium deposits and potential in Finland', in *Abstracts of the 32nd Nordic Geological Winter Meeting*, Helsinki, Finland, 2016, vol. Special Volume, p. 111.
- [131] S. Kaya and Y.A. Topkaya, 'Extraction behaviour of scandium from a refractory nickel laterite ore during the pressure acid leaching process', in *Rare Earths Industry: Technological, Economic and Environmental Implications*, Amsterdam, The Netherlands: Elsevier, 2016, pp. 171–181.
- [132] Serif Kaya, Carsten Dittrich, Srecko Stopic, and Bernd Friedrich, 'Concentration and Separation of Scandium from Ni Laterite Ore Processing Streams', *Metals*, vol. 7, no. 557, pp. 1–7, 2017.
- [133] Bryn Harris and Carl White, 'Recent Developments in the Chloride Processing of Nickel Laterites', presented at the Conference: ALTA Ni-Co-Cu 2011, Perth, Australia, 2011.
- [134] Michel L. Bilodeau, Claude Duplessis, Valdiney Domingos de Oliveira, Caroline Lachance, Jean-Sébastien Tremblay, and Georgi Doundarov, 'Technical Report on Revised Preliminary Economic Assessment Langis', Canadian Metals Inc., Montreal, Sep. 2016.
- [135] Nordig Mining, 'Kvinnherad Quartz', 2017. [Online]. Available: <https://www.nordicmining.com/operations/kvinnherad-quartz/>.
- [136] Geological Survey of Sweden, 'Statistics of the Swedish Mining Industry 2016', *Periodiska publikationer* 2017:1, 2017.
- [137] Kurt Aasly, 'Properties and behavior of quartz for the silicon process', Thesis for the degree of philosophiae doctor, Norwegian University of Science and Technology, Trondheim, Norway, 2008.
- [138] Kurt Aasly, Terje Malvik, and Edin Myrhaug, 'Quartz for carbothermic production of silicon - effect of the process steps, handling and transport from mine to furnace', presented at the Silicon for the Chemical Industry VIII, Trondheim, Norway, 2006.
- [139] André Colas, 'Silicones: Preparation, Properties and Performance', Dow Corning, 2005.
- [140] Arjan Ciftja, Thorvald Engh, and Merete Tangstad, 'Refining and Recycling of Silicon: A Review', Norwegian University of Science and Technology, Trondheim, Norway, Feb. 2008.
- [141] S. Islam, 'New processes for the production of solar-grade polycrystalline silicon: A review', *Proc. Chemeca*, pp. 1826–1839, 2011.
- [142] M. Tangstad, 'Silicon processing: from quartz to crystalline silicon solar cells', presented at the South African Pyrometallurgy International Conference, 2011, p. 18.
- [143] SUMCO, 'Manufacturing of monocrystalline ingots used as the material of silicon wafers', *Monocrystalline pulling process*, 2017. [Online]. Available: https://www.sumcosi.com/english/products/process/step_01.html.
- [144] Monica Moen, Terje Halvorsen, Knut Mørk, and Sjur Velken, 'Recycling of silicon metal powder from industrial powder waste streams', Kristiansand, Norway, Special Feature, May 2016.
- [145] A.S. Audion and J.F. Labbé, 'Panorama 2011 du marché du tungstène', Public report BRGM/RP-61341-FR, Jul. 2012.
- [146] BRGM, 'Fiche de synthèse sur la criticité des métaux - Le tungstène', Version 2, Jul. 2017.

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

- [147] MSP-REFRAM, 'Towards a strong and sustainable European refractory metals supply-chain. MSP-REFRAM Final report', Final Report, 2017.
- [148] BRGM, 'Plaquette Mineral Info – Le tungstène', Sep. 2012.
- [149] Prometia, 'MSP-REFRAM. Multi-Stakeholder Platform for a Secure Supply of Refractory Metals', Prometia, 2017. [Online]. Available: <http://prometia.eu/msp-refram/>.
- [150] ITIA, 'Tungsten mining & beneficiation', *International Tungsten Industry Association. Information on tungsten: sources, properties and uses*, 2011. [Online]. Available: <https://www.itia.info/mining-beneficiation.html>.
- [151] Erik Lassner and Wolf-Dieter Schubert, *Tungsten. Properties, Chemistry, Technology of the Element, Alloys, and Chemical Compounds*. Springer, 1999.
- [152] Pr. Jason Yang *et al.*, 'Innovation potential in the recovery of refractory metals from primary resources', MSP-REFRAM, MSP-REFRAM-D2.3, Sep. 2016.
- [153] EC, 'OptimOre. Increasing yield on Tungsten and Tantalum ore production by means of advanced and flexible control on crushing, milling and separation process', *CORDIS*, 2018. [Online]. Available: <https://cordis.europa.eu/project/rcn/193894/reporting/es>.
- [154] U. National Minerals Information Center, 'Vanadium', *US Geol Surv Min. Commod Summ*, vol. 703, pp. 182–183, 2016.
- [155] V. Ivanovich, S. Id, R. A. Nefedov, V. V. Orlov, R. O. Medvedev, and A. S. Sachkova, 'Hydrometallurgical Processing Technology of Titanomagnetite Ores', pp. 1–12, 2018.
- [156] 'Reflections on the Vanadium Price'. [Online]. Available: <https://www.bushveldminerals.com/reflections-on-the-vanadium-price-2/>.
- [157] U. R. Q. E. R. I. Ohqghg, H. H. D. Q. Udgh, I. Klijk, J. Phwdprusklf, and W. Ri, 'Production of Pig Iron by Smelting of Blended Pre-Reduced Titaniferous Magnetite ore and Hematite Ore Using Lean Grade Coal', vol. 10, no. 8, pp. 1051–1058, 2016.
- [158] S. Nkosi, P. Dire, N. Nyambeni, and X. C. Goso, 'A comparative study of vanadium recovery from titaniferous magnetite using salt, sulphate, and soda ash roast-leach processes', in *3re Young Professionals COnference*, 2017, no. March, pp. 9–10.
- [159] X. C. Goso, H. Lagendijk, M. Erwee, and G. Khosa, 'Indicative Vanadium Department in the Processing of Titaniferous Magnetite by the Roast – Leach and Electric Furnace Smelting Processes', no. August, pp. 1–3, 2016.
- [160] Axel S.L. Sjöqvist, David H. Cornell, Tom Andersen, Muriel Erambert, Mattias Ek, and Magnus Leijd, 'Three Compositional Varieties of Rare-Earth Element Ore: Eudialyte-Group Minerals from the Norra Kärr Alkaline Complex, Southern Sweden', *Minerals*, vol. 3, no. 1, pp. 94–120, 2013.
- [161] Greenlands Minerals Authority, 'GOVMIN', 2019. [Online]. Available: https://govmin.gl/images/stories/minerals/events/perth_2012/company_pdf/13_gme.pdf.
- [162] Y. Zhao, J. Li, S. Zhang, H. Chena, and D. Shao, 'Efficient enrichment of uranium(VI) on amidoximated magnetite/graphene oxide composites', vol. 3, pp. 18952–18959, 2013.