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**Production technologies of CRM from secondary resources**

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Production technologies of CRM from secondary resources

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# Production Technologies of CRM from Secondary resources

SCRREEN D4.2

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## 01 PRODUCTION TECHNOLOGIES OF CRM FROM SECONDARY RESOURCES: ANTIMONY

### 1 OVERVIEW OF GLOBAL PRODUCTION OF ANTIMONY AND AVAILABLE SECONDARY SB RESOURCES

Antimony (Sb) is a metal, which is extracted as a main product in form of ores, as co-product or by-product of Au, Pb and Zn. The global primary production reaches on average 42,833 tones per year. Antimony ores and concentrates are not mined or processed in Europe; therefore EU is 100% reliant on their import. However, EU produces antimony trioxide (ATO) from unwrought metal, which also has to be imported. The biggest global producers of primary wrought Sb metal are China, with 87% share, Vietnam, with 11% share and small amounts by Russia, Kyrgyzstan and Bolivia. (European Commission, 2017).

The annual consumption of unwrought antimony in Europe is around 18,200 tones, which is mostly used for production of ATO, used for flame retardant manufacturing. Antimony is used in many industries, mainly in chemical products, electrical equipment, fabricated metal products and other non-metallic mineral products. The main applications of unwrought Sb (Figure 1) are synergist for flame retardants, in form of ATO (43%). Flame retardants are used in cable coatings, plastics, upholstered furniture, fabrics, car seats and household appliances. The second biggest share belongs to lead-acid batteries (32%), used in form of hard-lead alloys. The production of lead-alloys accounts for 14% of global Sb use. It can be also found as a component of catalysts used for production of polyethylene terephthalate (PET) and decolourizing agent in glass used in cameras, binoculars, photocopiers etc. (Dupont, Arnout, Tom, Koen, & Jones, 2016; European Commission, 2017).

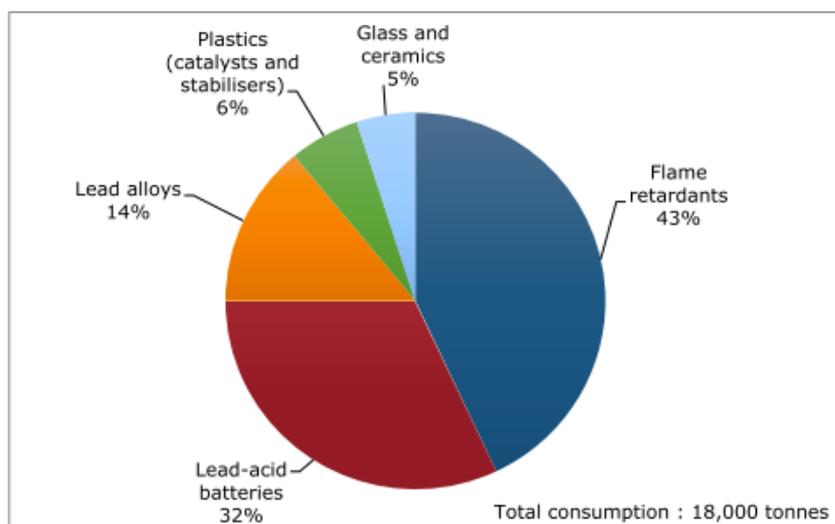


Figure 1 Global applications of antimony (European Commission, 2017)

Identification of secondary resources containing antimony is presented below.

- (1) Processing waste and historical waste
  - Mine tailings
  - Antimony processing slag

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- Copper processing residues
  - Lead processing residues
  - Flue dust
  - Municipal solid waste incineration ashes
- (2) Urban mines and manufacturing residues
- Lead-acid batteries
  - Spent catalysts
  - Sb-bearing flame retardants in plastics
  - Phosphor powders

## 2 PRODUCTION OF ANTIMONY FROM SECONDARY SB RESOURCES

Secondary antimony can be found in two main types of sources: in waste from processing the material containing antimony as well as in end of life products from urban mines and manufacturing residues.

### 2.1 PROCESSING WASTE AND HISTORICAL WASTE

#### 2.1.1 MINE TAILINGS

Antimony-containing mine tailings result from the production of lead, copper and gold. Antimony production generates many residues that can be potential secondary raw material sources. The composition of processing residues can vary substantially depending on the feed material and parameters of the process. For example, refining residues can contain 34.85-37.8 wt% Sb, oxidation residue about 63 wt%. In an antimony smelting plant in China, the residue of arsenic removal contained about 37.8 wt% Sb (Dupont et al., 2016).

#### 2.1.2 ANTIMONY PROCESSING SLAG

The amount of antimony trioxide contained in high-Sb slag from primary antimony processing can be up to 39.49 wt%, and in smelter slag about 1.11 wt% (Dupont et al., 2016).

A recovery of nanometer antimony trioxide from Sb-bearing slag with purity of 98.5% was achieved using a vacuum evaporation method. The sample used for the experiment contained 39.49 wt% Sb and was taken from an antimony refining plant in China. In this technique, the separation is possible due to differences in vapour pressure at a specific temperature for each of the constituents. The slag was heated in the vacuum chamber up to 893-1073 K to evaporate selectively  $Sb_2O_3$  from other components like PbO and  $SnO_2$ .  $Sb_2O_3$  has high vapour pressure and can evaporate into gas leaving remaining substances in the residue. The separation of Sb is relatively easy under vacuum conditions. It requires lower temperature comparing to separation at a normal pressure for the same evaporation rate (Keqiang & Rongliang, 2006).

The attempt to use a three-phase fluidized bed reactor was performed for arsenic removal from slag containing 20-40% Sb in form of sodium antimonite. The experiment resulted in removal 97% of arsenic and obtaining valuable antimony concentrate. The slag mixed with water was fluidized with air. The content of Sb slightly increased with higher temperature, however this negatively affects the separation of As and Sb, therefore leaching should be done at ambient temperature. The dissolution is purely physical, no chemical reaction takes

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place during leaching in fluidized bed. After removal of 97% arsenic, the high-grade Sb concentrate can be treated further for recovery of antimony (Fuxu, Hongjiu, Zhe, & Qingwen, 1989).

Another process used for recovery of antimony and gold is antimony smelting slag reduction in electric furnace. The slag comes from oxygen-enriched smelting of a bottom-blown furnace or Sb smelting of a blast furnace. The amount of Sb in the slag was reduced from 32% to less than 1% in the residual slag after processing. The slag was mixed together and homogenized with CaO and metallurgical coal and subsequently fed into the furnace at 1200°C. After 100 minutes of smelting a crucible was taken, naturally cooled and materials were separated and sampled. The content of gold, iron and antimony in the depleted slag and Sb alloy were detected using chemical analysis. The recovery of both gold and antimony from the slag is considered good and the process is feasible (Luo, Liu, & Qin, 2015).

### 2.1.3 COPPER PROCESSING RESIDUES

Antimony can be also found in copper ore, where it is treated as impurity that needs to be removed and therefore ends up in various residues. After ore smelting, the electro-refining process is applied by placing copper anodes in aqueous solution with  $\text{CuSO}_4$  and  $\text{H}_2\text{SO}_4$ . Subsequently, voltage is applied and copper and other less noble metals, including Sb, dissolve at the anode. The metals precipitate as hydrolysed species and can be found in the anode slime, which can be further processed for Sb recovery. Metals also accumulate in flue dust of smelter or converter. Examples of Sb content in the residue include 3-24.6 wt% in anode slime, 3.1wt% in flue dust and 1wt% in electrolyte. Yet, currently no recycling activities on industrial scale are conducted on Sb-bearing residues from copper processing. However, there are processes developed on laboratory scale to recover antimony from these waste flows (Dupont et al., 2016).

One of the techniques is alkaline sulphide leaching and subsequent electrodeposition for Sb metal extraction from copper ore (Figure 2). The process resulted in reduction of antimony content in the concentrate from 1.7% to less than 0.1% Sb. This outcome is desirable for copper and also improves Sb recovery (Awe, Sundkvist, Bolin, & Sandström, 2013).

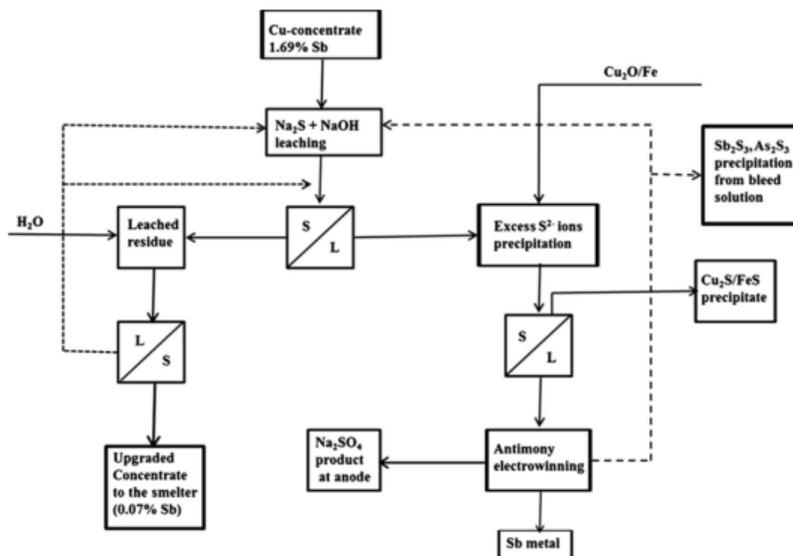


Figure 2 Flow chart of antimony removal and recovery from copper concentrate (Awe et al., 2013)

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Research has been done on Sb recovery from copper anode slime, which is a by-product of copper electrolytic recovery from spent printed circuit boards. The experiment used chloride leaching process of the tin-depleted residue in order to get  $SbCl_5$  acid solution. The residue contained over 24wt% of Sb. The antimony recovery in form of  $Sb_2O_5$  was obtained by applying hydrolysis and aging. The optimal conditions of 1.5 hydrolysis ratio and 7 days of aging time led to recovery rate of 97% Sb (Meng et al., 2015).

Alkaline fusion leaching was investigated to recover metals from copper anode slimes (Figure 3). In this process, the slime was fused in an electric muffle furnace with  $NaNO_3$  and  $NaOH$  and then water leached. The content of antimony in copper anode slime was estimated as 5.09wt%. As a result, some of the metals were leached out and the obtained product was valuable concentrate of Sb, Cu, Te and other precious metals, the antimony was recovered in form of  $NaSb(OH)_6$ , however the Sb concentration was only 3.5% (Li, Guo, Xu, Tian, & Feng, 2015).

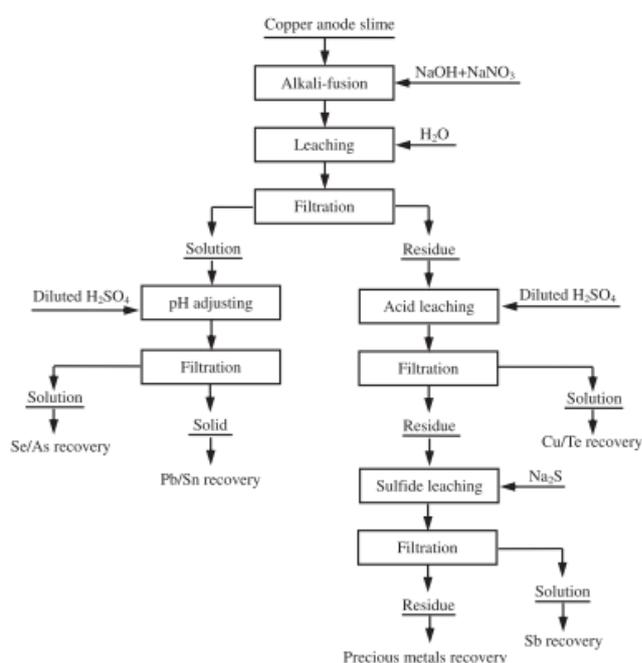


Figure 3 Flow chart of metals recovery from copper anode slime (Li et al., 2015)

Research has been carried out on antimony present in copper electrolyte solution. Sb can cause passivation of electrodes in electro-refining and should be removed. One method uses for this purpose selective desorption (Figure 4). Spent electrolyte from electro-refining of copper was pre-treated and passed through a column with C-467. After adsorption, the column was washed with dilute sulfuric acid and then water to remove soluble copper from resin. Subsequently, the resin was eluted, first to remove bismuth and then antimony. The two-step elution resulted in recovery rates of 92.6% Sb and 95.9 Bi. The electro-winning is therefore a suitable method for separation of Bi and Sb (Ando & Tsuchida, 1997).

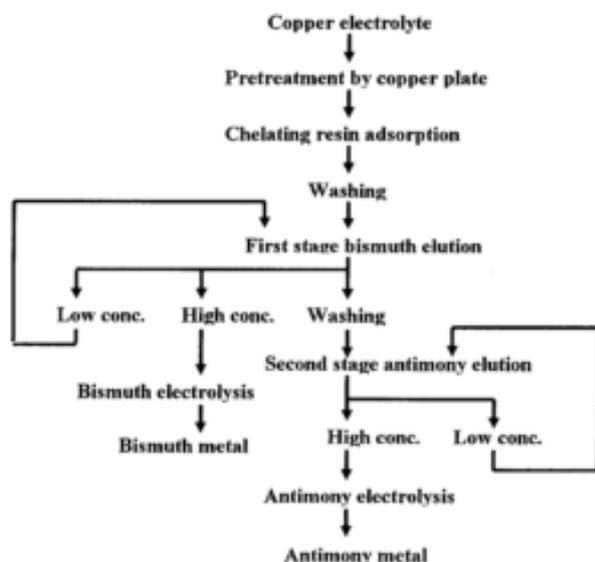


Figure 4 Flow chart for selective desorption (Ando & Tsuchida, 1997)

#### 2.1.4 LEAD PROCESSING RESIDUES

Due to the fact that antimony occurs in lead ores and the scale of lead production of 11,000,000 t/year in 2014, the residues from primary lead production are important source of secondary antimony. Examples in the literature show Sb content in lead processing residues of 63.6% in slime, 42.4% in Sb dust and 31.7% in softening skim (Dupont et al., 2016).

Alkaline sulphide leaching can be used to selectively remove Sb from lead smelting residues. Here, a mixture of NaOH and Na<sub>2</sub>S was used to solubilize Sb as Na<sub>3</sub>SbS<sub>3</sub>. The experiment resulted in recovery rates of 99.4% for smelter species, 89% for softening skims and 95% in flue dust (Anderson, 2001).

Recovery of antimony from lead anode slimes can be done by potential-controlled chloridization leaching and continuous distillation (Figure 5). The raw material for experiment contained 63.6% Sb and silver. The process is a closed-loop cycle and there is no waste generated. The process consists of two steps. First, the anode slime is leached in HCl solution and after 1 hour chlorine is added. Chloridization process ends when there are no Sb ions in the solution. Subsequently, solution is stirred and filtered. Second step is the concentration-distillation process and after than continuous distillation takes place. The recovery rate of Sb reached more than 95% and the final product was SbCl<sub>3</sub> (Cao, Chen, Yuan, & Zheng, 2010).

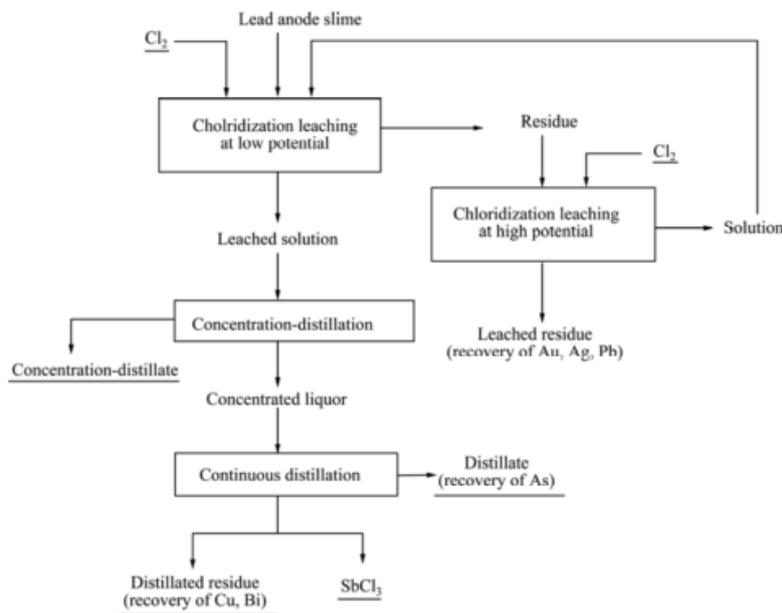


Figure 5 Flow chart for Sb recovery from anode slime. (Cao et al., 2010)

### 2.1.5 FLUE DUST

It is estimated that the flue dust from primary antimony production can contain 23.4 wt% of Sb. Flue dust from blast furnace in antimony smelting plant in China included 23.4 wt% (Dupont et al., 2016).

A study was carried out on Sb and Bi recovery from pressure-leached flue dust from copper smelting process. Pressure acid leaching is applied to arsenic-filter cake from copper concentrate smelting, which contains arsenic, bismuth, copper, antimony and other materials. The pressure leaching results in slag, which can be further processed. The antimony removal process is performed in three steps: kerosene desulphurization, chloride leaching and hydrolysis (Figure 6). The experiment has shown that contents of both metals are mostly enriched in kerosene desulphurization process. Under the optimal conditions, experiment resulted in 90.8% Sb and 95.8% Bi recovery from the flue dust (Zhang, Li, Shen, & Min, 2012).

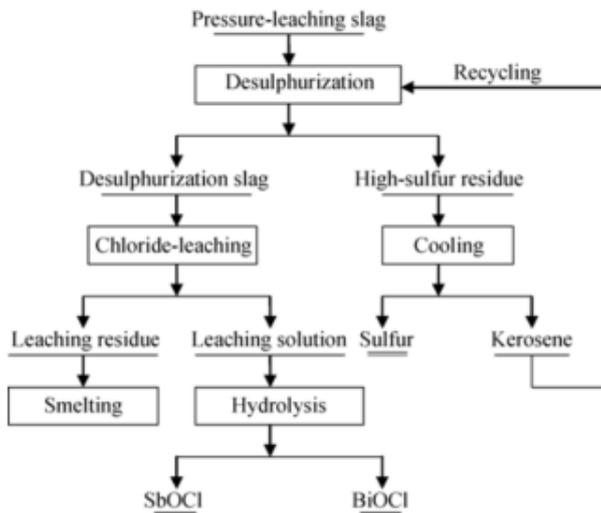


Figure 6 Flow chart of Sb recovery from flue dust (Zhang et al., 2012)

Antimonial dust from lead smelting also contains antimony, which can be recovered with pyrometallurgical process (Figure 7). The method includes 3 steps in order to extract Sb from the dust. First, reduction smelting in oxygen-rich bottom blow furnace is performed, which can reduce Sb content in slag to 2.8%. Then, alkaline refining is done to remove arsenic. Last step is blowing oxidation, after which the white antimony can be produced. The final product is  $Sb_2O_3$  with purity above 99.8% (Liu, Yang, Zhang, & Chen, 2014).

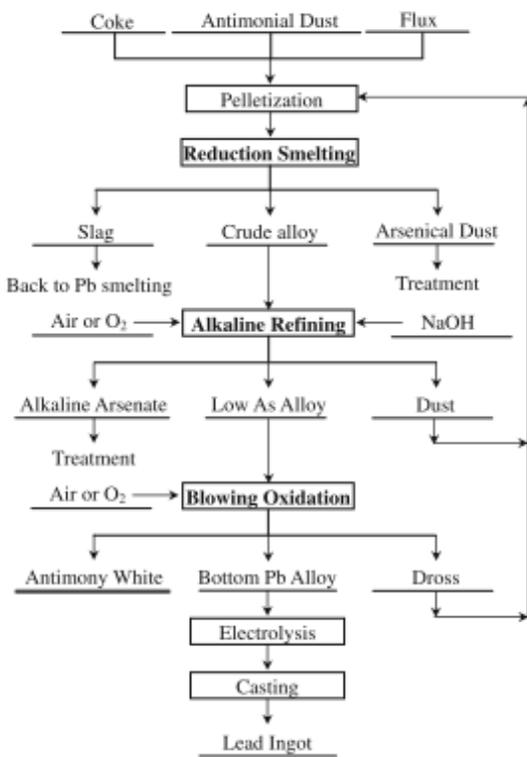


Figure 7 Recovery of antimony white from antimonial dust (Liu et al., 2014)

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## 2.1.6 MUNICIPAL SOLID WASTE INCINERATION (MSWI) ASHES

The MSWI plants create large amounts of residues, which can be potential sources of secondary materials. The presence of antimony in incineration waste comes mostly from antimony-bearing plastics, glass and textiles. Raw incineration waste can contain about 40-50 mg Sb per kg. One of the techniques to recover antimony from incineration fly ash used citrate solution for leaching out the antimony (Dupont et al., 2016).

## 2.2 URBAN MINES AND MANUFACTURING RESIDUES

### 2.2.1 LEAD-ACID BATTERIES

Antimony can be found in lead-acid batteries used as hard-lead alloy. The concentration can vary between 1-15% Sb in the alloy. The lead acid battery recycling process starts with removing the acid. Then, batteries are crushed in order to separate plastic elements, and lead can be separated into lead metal and lead oxide fractions using mechanical treatment. Lead metal can be directly re-melted and lead oxide is reduced in one of the of furnaces (Dupont et al., 2016).

An example is antimony recovery by smelting secondary lead from spent batteries. The smelting process comprises of two stages. First, reducing smelting of the raw material in reverberating furnace is applied, which produces lead bullion and slag containing almost all impurities, including antimony. The next step is the impoverishment of the slag in shaft and electric furnaces. The whole process produces low-Sb lead bullion which can be further refined to soft lead, using similar processes as primary lead production, for example in reverberating furnace. In the impoverishment furnace the slag rich in lead and the recycle dross from refining are processed and the impurities, mainly Sb, Sn, As, are used to produce lead-antimony alloy. This alloy can be transformed into other alloys and used in new batteries (Besser, Sorokina, Sokolov, & Paretskii, 2009). Figure 8 shows scheme of secondary lead production from spent lead-acid batteries, where antimony is recycled as well.

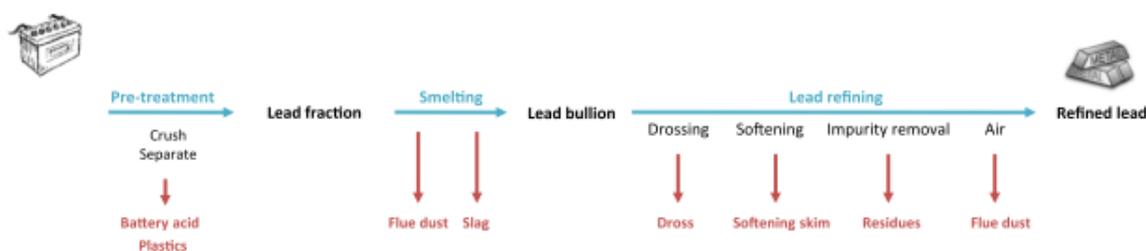


Figure 8 Scheme of secondary lead production from spent batteries (Dupont et al., 2016)

### 2.2.2 SPENT CATALYSTS

Antimony is also used in catalyst for PET production. After their end of life, the Sb can be recovered from those catalysts. One of the processes developed for this purpose is Sb recovery from spent ethylene glycol residues from production of PET polymers. This method involves combusting spent residues to obtain ash, from which Sb can be recovered. Another patent used chlorination of catalysts, followed by separation of  $SbCl_5$  from solution by distillation. The recovery rate is 80-95% of total antimony content in the solution. The product can be directly used as a catalyst (US 4005176 A, 1977).

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### 2.2.3 SB-BEARING FLAME RETARDANTS IN PLASTICS

Flame retardants used in polymers can contain 5-30 wt% of  $Sb_2O_3$ , although the exact quantity used depends on the type of polymer and application. Big share belongs to plastics used in waste electronic devices, which require large amounts of  $Sb_2O_3$  to assure safety during the use phase. Screening and sorting techniques are needed to identify high Sb content for its efficient recovery from plastics. One of those methods is X-ray fluorescence spectroscopy (XRF) for non-destructive screening. After sorting, the material can be put in special ovens to perform pyrolysis of polymer and leave antimony in the bottom ash or fly ash. Other method that can be used for flame retardants is named as alkaline reforming of high-impact polystyrene. Here, the spent polymer reacted in supercritical water and NaOH in a pressure reactor. In this process, 98% of antimony was removed (Dupont et al., 2016).

### 2.2.4 PHOSPHOR POWDERS

Antimony is used in halophosphate lamp phosphors that are applied in fluorescent lamps. The inside of the glass is coated with phosphors to enable emission of visible white light. Antimony is used in form of blue dopant to adjust the shade of white colour. The amount of halophosphate in lamp phosphor is estimated as 50%, from which 0.5-1 wt% is antimony that can be a source of secondary raw material. Currently, waste fluorescent lamps are recycled on industrial scale in France by the company Solvay, with capacity around 1000 tonnes per year. However, often the phosphor is still discarded without materials recovery, despite the high content of halophosphate (Dupont et al., 2016).

## 3 CURRENT RECOVERY RATES

The end of life recycling input rate for antimony is estimated as 28% (European Commission, 2017). Currently secondary antimony is obtained on a larger scale mostly from lead alloys found in scrap lead-acid batteries. According to the source, almost all antimony present in secondary lead streams is recycled (Dupont et al., 2016). Therefore, the secondary Sb availability highly depends on amounts and efficiency of lead and lead-acid batteries scrap recycling. Since primary Sb reserves are concentrated within very few countries, the secondary resources recovery becomes very important for assuring required supply in the EU (European Commission, 2017). On global scale, it was estimated, that in 2010 the secondary production of antimony accounted for about 20% of total Sb supply (Dupont et al., 2016).

## 4 KEY ACTORS IN ANTIMONY RECOVERY

Umicore is a company with facility in Belgium, which recycle spent batteries. The company recovers antimony from end of life batteries, mostly from electric cars. The batteries are first dismantled until cell or module level and then treated in UHT furnace. Pack materials are sent to certified recyclers and electronic components are treated for precious metals recovery. However the details on technologies used and recovery rates on Sb are not published (Umicore, n.d.)

Solvay in France is recycling halophosphate from spent fluorescent batteries, with capacity 1000 tones per year. In their process, glass plastic and metals are separated from spent lamps and recovered by other recyclers. Then, residual glass is separated at the Saint-Fons facility to obtain phosphor powder. The powder is suspended in aqueous solution, where is undergoes chemical treatment. Powders than retained after separation are dried, packaged and sent to second plant in La Rochelle. In the second facility, the powders are

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fed into a tunnel furnace, where they undergo thermal treatment. Next, powders are re-suspended, filtered and washed, after what they are treated with nitric acid. The powder go through batteries that separate six metals: La, Eu, Ce, Tb, Gd, Y. Last three steps are precipitation, filtration and calcination, after which metals are reused for phosphors production (Solvay, 2014). However, there is no mention of direct antimony recovery from fluorescent lamps.

## 5 CHALLENGES IN MATERIAL RECOVERY

The recovery of antimony from applications like flame retardants and plastics is very difficult due to the high dispersion. There is potential in Sb recovery from bottom ash after incineration of those products, yet the technology currently does not seem to be economically feasible (European Commission, 2017).

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## 02 PRODUCTION TECHNOLOGIES OF CRM FROM SECONDARY RESOURCES: BERYLLIUM

### 1 STATE OF THE ART ON PRODUCTION OF BE SECONDARY RAW MATERIALS

Figure 1 shows the value chain of the beryllium industry.

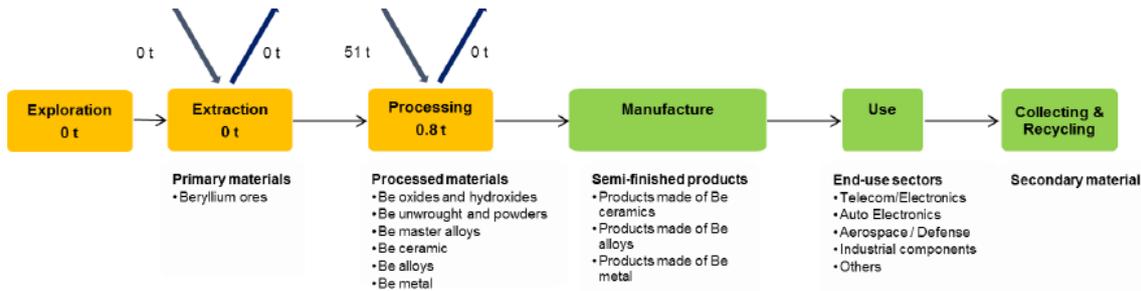


Figure 1 Simplified value chain for beryllium.[1]

Beryllium scrap is generated and recovered at various stages of production.

#### a) Post-consumer recycling (old scrap)

Beryllium is not recycled from end finished products (BeST [2]), therefore the end of life recycling input rate is set to 0%. The recuperation of pure metal of beryllium from end finished products is extremely difficult because of the small size of components and the tiny fraction of Beryllium contained in appliances (less than 40 ppm in appliance having the highest amount of Be) (BeST).

#### b) Industrial recycling (new scrap)

Beryllium can be recovered from new scrap generated during the manufacture of beryllium metals and alloys and during the fabrication of beryllium products.

### 1.1 END FINISHED PRODUCTS – END OF LIFE OF THE BERYLLIUM MATERIALS CONTAINED WITHIN PRODUCTS

The beryllium contained in the waste usually ends up in landfill. There is no post-consumer functional recycling of beryllium in Europe and in the world (no recovery of beryllium from old scrap displacing primary production of beryllium) (Bio Intelligence Service, 2015 [3]). The stock accumulated in landfill in the EU over the last 20 years is estimated around 610 t of beryllium content.

As a result, for old scrap the recycling flow value is quite high (~75%), but the recycled content and particularly the End-of Life Recycling Rate (EOL RR) material specific rate are very low.

#### 1.1.1 PURE BERYLLIUM METAL COMPONENTS

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

Much of the beryllium metal is contained in nuclear reactors and nuclear weapons, which are difficult to recycle and may have been contaminated. These applications are rarely dismantled, and the beryllium may have been lost during testing (Cunningham 2004 [4]).

### 1.1.2 BERYLLIUM ALLOYS COMPONENTS

Beryllium alloys are lost to the beryllium industry because they are recycled with the host metal or are lost to slag during smelting.

Recovery of beryllium metal from copper beryllium alloys that are included in components of post-consumer scrap (like electronics) is difficult because of the small size of the components, difficulty of separation, overall low beryllium content per device and the low beryllium content in the copper beryllium alloy (average 1.25 % beryllium).

The alloy makes up approximately 0.15% of the copper used in electrical equipment which, during pre-processing of end-of-life equipment, is collected together with other copper in the scrap and diluted to ~ 2 ppm in the copper recycling stream. In responsible copper recycling processes, the extremely small quantities of beryllium are immobilized in slags. Therefore, most of the scrap is recycled for its copper value, since beryllium recovery is not economically feasible (BeST).

## 1.2 MANUFACTURING – INDUSTRIAL SCRAP

The “new” Beryllium scrap is generated and recovered at various stages of production. Scrap generated during the manufacture of beryllium metals and alloys, and during the fabrication of beryllium products. The European industry generates a lot of “new scrap” (around the half of the beryllium input), during this manufacture step, which is totally sent back to producers outside Europe for reprocessing (European Commission 2017 [5]).

Practically all of the waste products generated as furnace drosses, slag, manufacturing process scrap is recovered and recycled through the arc furnace as a valuable source of beryllium. It required less than half the energy to recycle beryllium compared to mining it from the earth, and avoids the use of process chemicals such as sulfuric acid and ammonia.

Recycling, mostly from scrap generated during the manufacturing of beryllium products, may account for as much as 10% of apparent consumption (USGS 2009 [6]).

Beryllium scrap and beryllium alloy scrap are recycled from many different components. The main sources of beryllium scrap and beryllium alloy scrap are driven by the emphasis on technology and telecommunications. Electronic components, electrical components, and the aerospace industry are a few areas where beryllium scrap and beryllium alloy scrap can be found.

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With the main source of beryllium scrap and beryllium alloy scrap coming from automotive electronics, computers, optical-media product applications and other consumer driven products the main goal is returning scrap metal, such as beryllium scrap and beryllium alloy scrap, to the technological industry to be used again in the building process of technical equipment.

The European industry uses the Beryllium to manufacture various finished products. The main relevant industry sector that uses the Be are:

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

## 2 COMPANIES RECYCLING BERYLLIUM

- NGK Berylco France

NGK Berylco France, located in Couëron (France), near Nantes, positions itself undoubtedly since 1971, as a world leader in the field of processing high-precision strips, wires and bars in copper beryllium alloys responding to very specific requirements. Beryllium-copper alloy scrap can be directly recycled back to produce new alloy since it is attractive from both an economic and energy conservation point of view. The pure beryllium metal components used in technological applications can be easily recycled. [7]

- Monico Alloys

Founded in 1979, Monico Alloys is now over 100 employees strong and is one of the United States' leading importers and exporters of Titanium scrap. Monico Alloys facilities are among the best in the recycling industry. Combined, they Alloycover approximately 100,000 square feet of modern plant. Monico Alloys is a scrap industry leader. The ratio of the beryllium supply is said to be about 85/15 ratio between new beryllium scrap and beryllium alloy scrap and old beryllium scrap and beryllium alloy scrap.[8]

- Materion

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Materion. USA (Before Brush-Wellman). Brush Beryllium Company was founded in 1931 in Cleveland, Ohio. Clean scrap from manufacturing operations can be recycled directly as new copper beryllium alloy. [9]

### 3 DEFINITIONS

**Recycling-** Recycling is the collection and separation of materials that have reached the end of their useful life, and their reprocessing to create useable products. “Recycling is commonly used to include two fundamentally different kinds of scrap:

**Life cycle of manufactured product:[10]**

**New scrap.** Scrap produced during the manufacture of metals and articles for both intermediate and ultimate consumption, including all defective finished or semi-finished articles that must be reworked. Examples of new scrap are borings, castings, clippings, drosses, skims, and turnings. Its recovery minimises waste in the production and manufacturing process. It is also known as pre-consumer scraps.

**Old scrap** or obsolete scrap: Scrap including metal articles that have been discarded after serving a useful purpose. Typical examples of old scrap are electrical wiring, lead-acid batteries, silver from photographic materials, metals from shredded cars and appliances It is also known as post-consumer scrap or end of life scrap.

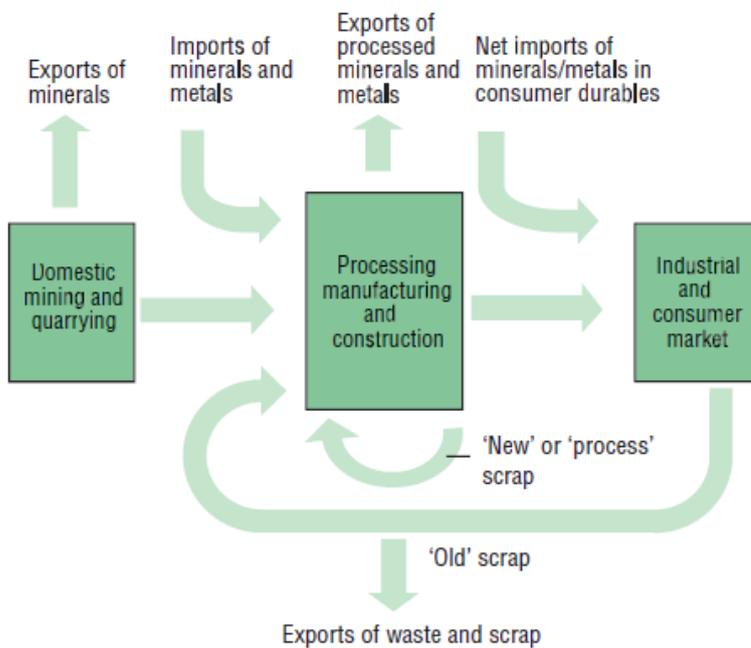


Figure 2 Life cycle of manufactured product.

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## 03 PRODUCTION TECHNOLOGIES OF CRM FROM SECONDARY RESOURCES: BORATES

### 1 STATE OF THE ART OF BORATES PRODUCTION

Figure 1 shows the value chain of borate:

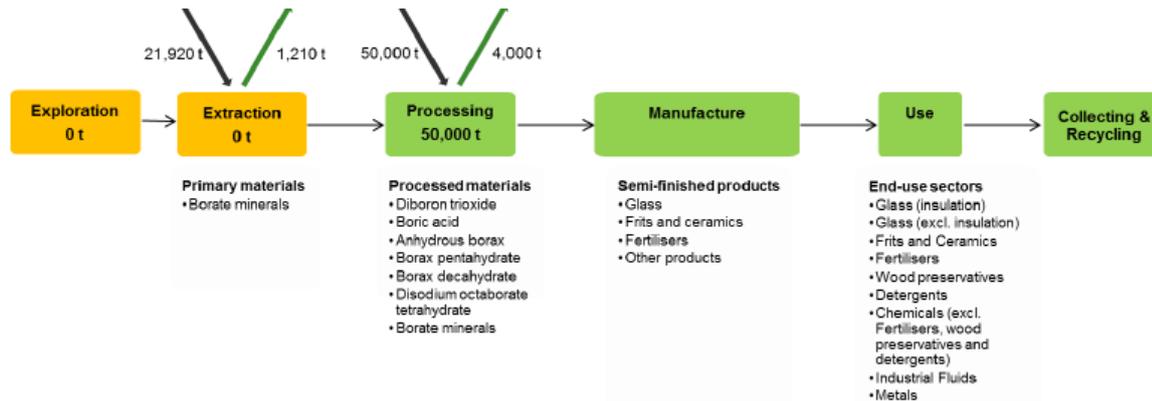


Figure 1 Simplified value Chain for Borates. [1]

EU end uses of borates area is shown in Figure 2. About half of all consumption globally of borates is used as an additive in glass. The next leading use is for frits and ceramics in the Ceramic Industries. The third use for boron compounds is as fertilizers in agriculture.

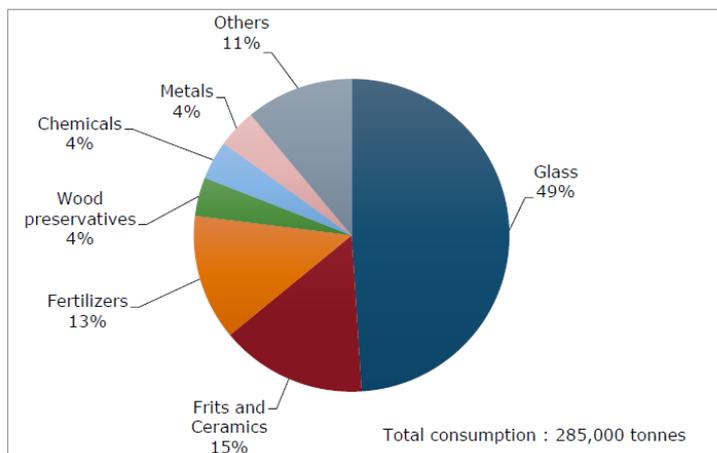


Figure 2 EU end uses of Borates Source: EU commission. [2]

### 2 RECYCLING

The EU stock of boron in use amounts 180 kt. The annual amount of boron in end of life products collected for treatment is about 66 kt: (respectively 45 kt for glass, 13 kt for frits and ceramics and 7 kt for other products,

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and only less than 1 kt of boron from fertilisers is collected for treatment, as most of it is dissipated into the environment).

More than half of boron in the collected products at end of life is sent for recycling – i.e. 34 kt. The annual amount of products heading for disposal is about 30 kt in boron content; therefore there is a significant stock of boron in landfill accumulated over years. [3]

There are two types of recycling: [4]

- Functional recycling, in which the metal is returned to raw material production.
- Non-functional recycling, which results in materials where specific mineral are not separated. It is beneficial for the environment but from a mineral perspective, it amounts to an open life-cycle, with the specific properties of the mineral being lost.

The functional recycling of boron is thus null. [5] Fertilisers, chemicals and detergents are not likely to be recycled considering these products are consumed with use. Borosilicate glass and ceramic cannot be recycled with normal glass because these materials have a higher heat resistance and therefore higher melting point compared to conventional glass. The presence of this kind of glass during recycling causes defects in the recycled glass.

Secondary materials result mostly from non-functional recycling. Borosilicate glass is currently not separated from boron-free container and flat glass. It means that boron in waste borosilicate glass is likely to end up in the manufacture of new glass containers or glass wool and it does not replace primary boron in the new production of borosilicate glass. Moreover, waste from ceramics is mostly used as a construction material. (Deloitte, European commission 2017 [6])

The annual amount of boron from non-functional recycling reach 21 kt from glass applications, 10 kt from frits and ceramics and 3 kt from other products. About 0.5 kt of boron is a result of recycling of biogenic waste flows such as food waste, manure and common sludge. This can be considered as functional recycling because such secondary material in fertiliser replaces boron from industrial fertilisers.

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## 04 PRODUCTION TECHNOLOGIES OF CRM FROM SECONDARY RESOURCES: COBALT

### 1 OVERVIEW OF GLOBAL COBALT PRODUCTION AND SECONDARY RESOURCES

Cobalt (Co) is mostly produced as a by-product or co-product with copper or nickel. Less than 6% of Co total primary production is mined as a main product. The average raw material production in form of ores and concentrates in the world is estimated as 135,497 tons on average in period 2010-2014, where in European Union (EU) it is 1,233 tonnes over the same period. The largest global mine producers of cobalt are: Democratic Republic of Congo with 64% share, China 5% and Canada 5%. In Europe cobalt is presently mined in New Caledonia (France, not part of EU) and Finland, with share of global total 2% and 1% respectively. In Finland, cobalt is mined in 4 plants and the production is around 1,200 tones. The EU reliance on import of cobalt ores and concentrates is estimated as 32%. About 642 tonnes of primary Co and 19,864 tons processed are imported to EU. Export values from the EU for the raw material and processed Co are 68 tonnes and 3,361 tonnes respectively. Processed materials include metals, oxides, hydroxides, sulphates, carbonates, chloride, acetate and other chemicals (European Commission, 2017).

Cobalt is used in a big range of end products, either in form of cobalt metal or in multiple cobalt bearing chemicals. The biggest share is assigned to production of battery chemicals, namely in Ni-Cd, NiMH and Li-ion types of batteries. Second highest consumer is super alloys used for jet engines. Cobalt is also used in hard materials for cutting tools, catalysts, pigments and ceramics, magnets, tyres adhesives and paint dryers and multiple other small applications, for instance in biotechnology, electrolysis (European Commission, 2017). Figure 1 shows main global application of cobalt in 2015.

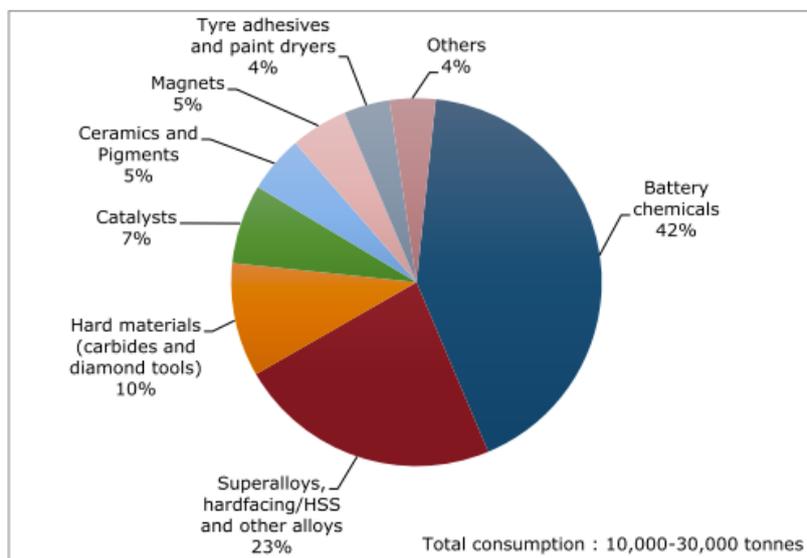


Figure 1 Global end use applications of cobalt in 2015 (European Commission, 2017)

The identified available secondary resources for Co recycling and recovery are listed below:

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- (1) Processing waste and historical waste
  - Smelting slag and sludge
  - Flotation tailings
- (2) Urban mines and manufacturing residues
  - Spent battery chemicals
  - Alloys scrap
  - Spent hard materials (cemented carbides, diamond tools)
  - Pigments
  - Spent catalysts
  - Tyre adhesive

## 2 PRODUCTION OF COBALT FROM SECONDARY RESOURCES

Secondary cobalt can be found in two main types of sources: in waste from processing the material containing niobium as well as in the end-of-life products from urban mines and manufacturing residues.

### 2.1 PROCESSING WASTE AND HISTORICAL WASTE

#### 2.1.1 SMELTING SLAG AND SLUDGE

Cobalt can be recovered from sludge generated in nickel refinery. The material fed to the process contained about 1.5% cobalt. After acid leaching, the spent electrolyte was precipitated and resulting in carbonate with about 14% cobalt (Wang, 2006).

Another source of secondary cobalt is low grade waste solution coming from copper open pit mine. Such resource in China consists of about 7.5 mg Co per litre. The process starts with neutralisation of waste solution, followed by precipitation of copper as a sulphide. Then, NiCo are extracted by ion exchange and precipitation into carbonite containing 10% Ni and 10% Co, which is sold in this form. It is estimated that recovery of cobalt can reach 33 tons per year.

Cobalt can be also recovered from zinc smelting waste/by-products. Hydrometal S.A., a subsidiary of Jean Goldschmidt Int. S.A. (JGI) processes such cobalt-containing cements at its plant in Engis (Belgium) is processing Co-containing cement from zinc electrolytes purification using cementation with zinc powder. Those cements, containing typically 5-7% of cobalt, can be further treated for metal recovery. Obtained cobalt concentrates that are sold to cobalt refineries contain over 65% Co. (Ferron, 2013). Fig. 2 is an illustration of the flowsheet. Typical obtained cobalt concentrates sold to cobalt refineries contain >65% Co, 3% Zn, 3% Fe and 3.8% Mn.

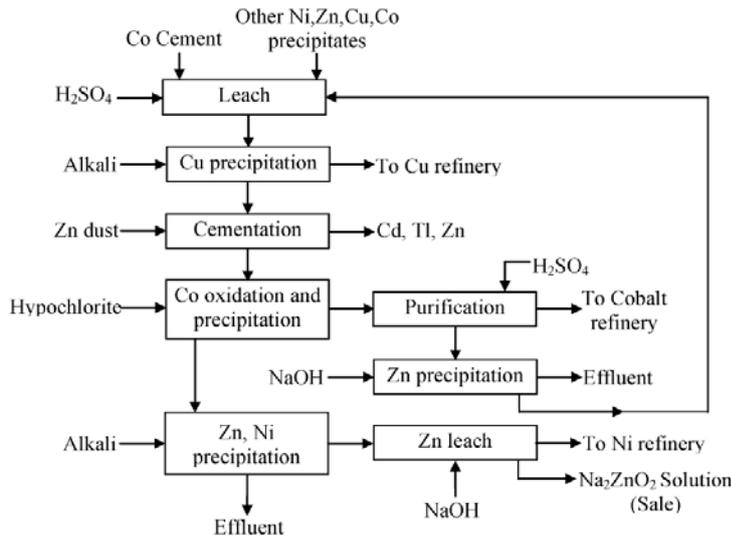


Figure 2 Process Flowsheet to Recovery Cobalt from Zinc Plant Cements.

### 2.1.2 FLOTATION TAILINGS

During the mineral processing of cobalt ores, the oxidised Co is processed using flotation technique, which takes place mostly in Democratic Republic of Congo. Part of cobalt ends up in flotation tailings, from where it is not recovered. The tailings are deposited on the site and become a historic waste potential source of cobalt. There were attempts to recover cobalt together with copper from those reserves. Interested companies have estimated recovery potential of 600 tonnes of Co per year from Kakanda tailings and 3000 tonnes from Kolwezi tailings. Yet, the outcome of those attempts is not known. A successful project took place in Reminex at their Bou Azzer operation in Morocco in 1997, with flotation tailings containing 0.4% Co. The process flowsheet illustrated in Figure 3 starts with leaching of flotation tailings with  $H_2SO_4$ , which is followed by purification and precipitation of Co. Obtained Co hydroxide is leached again and purified, which result in recovered Co metal. Research has shown that cobalt recovery from flotation can be improved by hydroxamate collectors (Ferron, 2013).

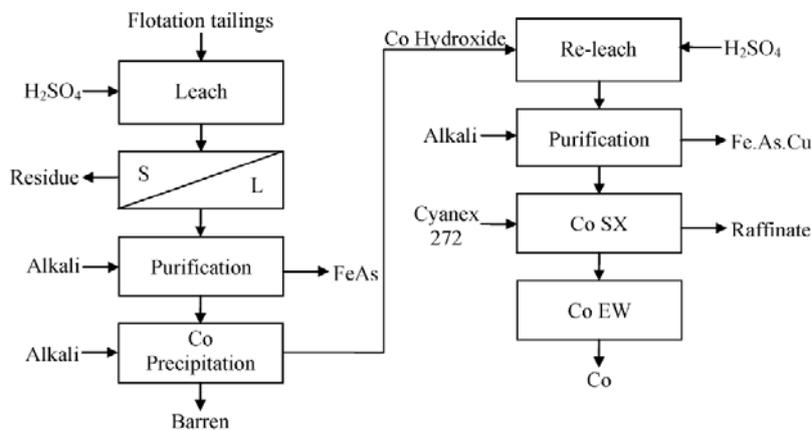


Figure 3 Process flow sheet to the treatment of flotation tailings at Bou Azzer. (Ferron, 2013)

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## 2.2 URBAN MINES AND MANUFACTURING RESIDUES

### 2.2.1 SPENT BATTERY CHEMICALS

Cobalt can be found in cathode of rechargeable NiCd and Li-ion batteries, and in both anode and cathode in NiMH battery. The amount of cobalt used in Li-ion electrodes depends on the exact composition, it can be up to 30% cobalt. According to Umicore Battery Recycling, a battery pack used in a small or medium notebook contains on average 13.8% of cobalt, which slightly less than 50 g of Co (Buchert et al., 2012). NiCd electrode contains 1% cobalt and NiMH 5% (European Commission, 2017; Zeng, Li, & Singh, 2014). Only in Germany in 2010, potential cobalt content in batteries of all sold notebooks was 461,305 kg and in smartphones 48,500 kg, which creates a substantial secondary resource of this metal (Buchert et al., 2012).

The process choice for cobalt recovery depends on the type of Co-bearing battery. Usually, large NiCo smelters are also prepared for recovery of cobalt from spent batteries. There are also plants dedicated for batteries recycling. For instance, Umicore from Belgium has a special division that has capacity to recycle 7000 tonnes of (Li-ion and NiMH) batteries per year (Umicore Battery Recycling, n.d.). The company is using smelting process with ultra-high temperature plasma torch, where previously separated NiMH and Li-ion batteries are fed. Obtained Fe, Co, Ni, Cu alloy is further refined and separated in hydrometallurgical processes to be used as new cathode material. Remaining components end up in slag, from where other valuable elements may be recovered as well.

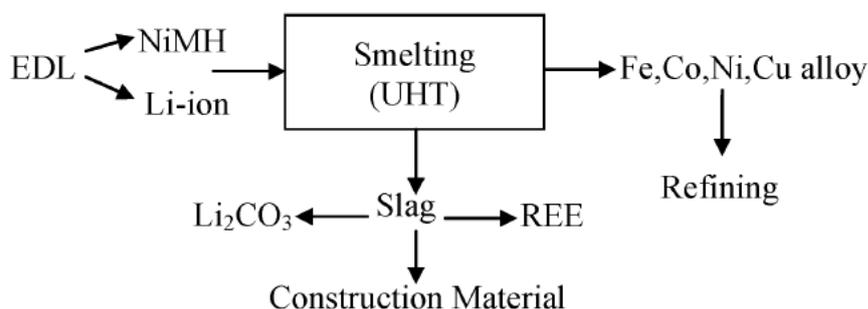


Figure 4 Process flow sheet of Umicore UBR process for recycling of rechargeable batteries.

Another hydrometallurgical method developed by TOXCO Inc. from Canada consists of crushing sorted batteries by hammer mill, then separation of mixed metals and plastic with paper on shaking table. Obtained slurry is filtered to get cobalt cake with composition up to 35% Co. Research has been focused also on electrochemical processing of spent batteries. In order to recover cobalt from cathode, it was dissolved in acid, where cobalt was separated together with nickel by solvent extraction and subsequently electrowon in specific conditions (Ferron, 2013).

Bioleaching is another way to recover cobalt from spent Li-ion batteries. A specific type of microorganism performs reactions that let them grow and reproduce, which is helpful in leaching of metals from waste. The bacteria are used to dissolve cathode from crushing Li-ion batteries with presence of additive substances. The leaching rate for cobalt can reach 98% (Zeng et al., 2014).

### 2.2.2 ALLOYS SCRAP

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Cobalt is very significant alloy component in many applications. For instance, Co-based super alloy can contain 39.2% Co, Ni-based and Fe-based super alloys have 15% Co each. Other types of alloys have even higher cobalt concentration: SmCo alloy with 66.2% Co, soft magnetic alloys 49% Co, prosthetic alloy with 62% Co, or wear-resistant alloy with 40.1% Co (Ferron, 2013).

There are few flows of cobalt bearing alloy scrap. It can be contained in residues from manufacturing, for instance rejects from casting operations, turnings waste from machining and in the end of life scrap (Ferron, 2013).

In some cases, cobalt bearing alloy scrap can be re-melted directly into the same application, for example in aero-engine elements, where the composition of alloys is certified (European Commission, 2017), or if the composition of alloy can be assured. This method is the easiest form of cobalt recycling, because it does not involve additional treatment or infrastructure.

Cobalt is often recycled industrially in sulphide smelter by mixing alloy scrap with primary cobalt sulphide concentrates, which is advantageous economy of scale activity. An example of such recycling technology is used by Xstrata smelter in Ontario (Figure 5). A variety of scrap alloys (large pieces, turnings, grindings, catalysts) are fed to the electric furnace together with roasted sulphide concentrates, which creates matte gas and slag. The matte goes into the Pierce-Smith converter, where another portion of scrap can be added. Here with supplied oxygen, products are matte, which is further processed in refinery, and slag. The slag is cleaned and converted to recover cobalt (Ferron, 2013).

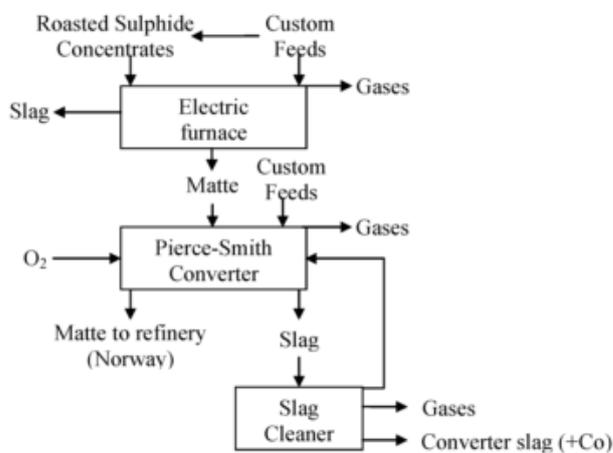


Figure 5 Simplified flow diagram of cobalt recovery in Xstrata smelter. (Ferron, 2013)

Alloy scrap is also recovered using hydrometallurgical methods. It usually concerns NiCo alloys for their separation and/or recovery of other valuable elements (W, Ta, Re) that would be lost otherwise. Complexity of recycling operations is depending on the composition of scrap alloys. The simple method to recover nickel and cobalt from alloy starts with leaching with acid HCl or H<sub>2</sub>SO<sub>4</sub>. The obtained material is further purified and next Co and Ni are separated (Ferron, 2013).

Research has shown a new method developed to recover cobalt from super alloy scrap, using double membrane electrolytic cells (DEMC) in order to get high-purity nickel and cobalt cathodes. In the end, the cathode had purity of more than 99.95% of cobalt (Wang, 2006). Figure 6 presents a flow chart of DEMC

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method for recovery of cobalt, but also Ni, Cu, Cr and Mo. Super alloy scrap is first melted, then carburized in order to turn them into anodes, which are brought to DEMC. Subsequently, anode is dissolved in anodic dissolution, from where anolyte is treated in several different steps to recover individual elements. Those steps include cementation, carbon treatment, cobalt solvent extraction. After the anolyte is purified, it goes to the cationic cobalt deposition compartment, from where pure cobalt is extracted. According to estimations, this process could be able to recover 1,535 kg of cobalt from 16,800 kg of treated super alloy per day (Kurylak, 2016).

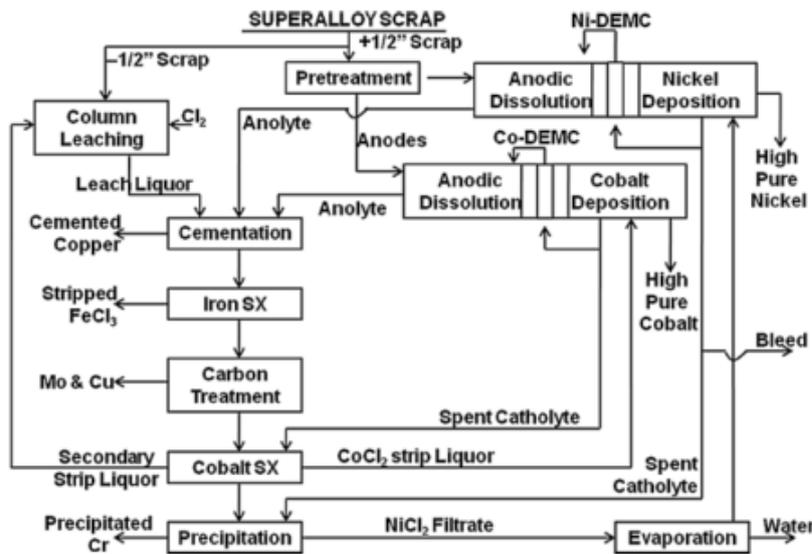


Figure 6 Flow chart for of super alloy scrap recycling using DEMC method. (Kurylak, 2016)

### 2.2.3 SPENT HARD MATERIALS (CEMENTED CARBIDE, DIAMOND TOOLS)

Cemented carbide is present in hard materials, which are used for production of tools. Carbide is produced from molybdenum or tungsten, where cobalt plays a role of binding material in form of metal powder (European Commission, 2017). Cemented carbide can contain 3-25% cobalt (Wang, 2006).

Another type of cobalt bearing hard material is diamond tools, in particular diamond grinding wheels and diamond saws. In those applications cobalt is used to assemble industrial diamonds on grinding wheel or as additive in segments of industrial diamond saw (European Commission, 2017).

In recycling of carbide scrap process (Figure 7), cleaned cemented carbide elements are melted with zinc metal in vacuum furnace, where cobalt dissolves in molten zinc. When zinc is distilled off, the material is crushed and milled and ready for screening for cobalt metal powder separation from hard carbide grains (Ferron, 2013).

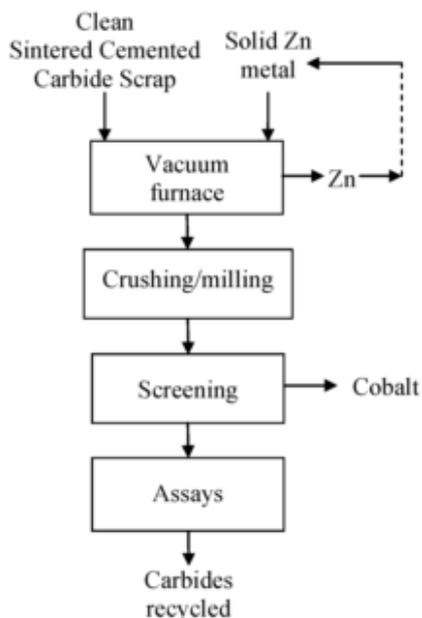


Figure 7 Simplified flow chart of cemented carbide recycling. (Ferron, 2013)

#### 2.2.4 PIGMENTS

Cobalt is used as an intensive blue pigment in paints, glass, ceramics (European Commission, 2017). However, the scrap bearing cobalt as a pigment is not suited for recycling, due to dilution of the metal and difficulties with its collection (Ferron, 2013).

#### 2.2.5 SPENT CATALYSTS

Cobalt can be found in desulphurisation catalysts for gas and oil refining processes. In chemical industry, Co acetate is combined with manganese bromide and used as catalyst in production of chemicals for plastics manufacturing (European Commission, 2017). Catalysts containing cobalt are also used in Fisher-Tropsch fuel synthesis from natural gas (Ferron, 2013).

Recycling technology for cobalt recovery from spent catalysts involve pyrometallurgical and hydrometallurgical processes. The recovery of cobalt in Gulf Chemical and Metallurgical Corporation, as shown in Figure 8, starts with processing of Co/Mo, Ni/Co/Mo/V or Ni/Mo catalyst in an electric arc furnace. After roasting and leaching the catalyst, alumina concentrate is formed, which is combined with a reductant and melted in the furnace. The product is an alloy with a composition of 37-43% nickel and 12-17% cobalt. Alloy is sold in this form to cobalt and nickel refineries (Wang, 2006). To treat specific cobalt catalysts simple hydrometallurgical methods can be used. Recovery process of CoMn catalyst starts with leaching using H<sub>2</sub>SO<sub>4</sub> and SO<sub>2</sub>. More than 95% of Co in the catalyst was dissolved and in the next step most of it was precipitated into high grade Co sulphide concentrate, ready for further treatment (Ferron, 2013).

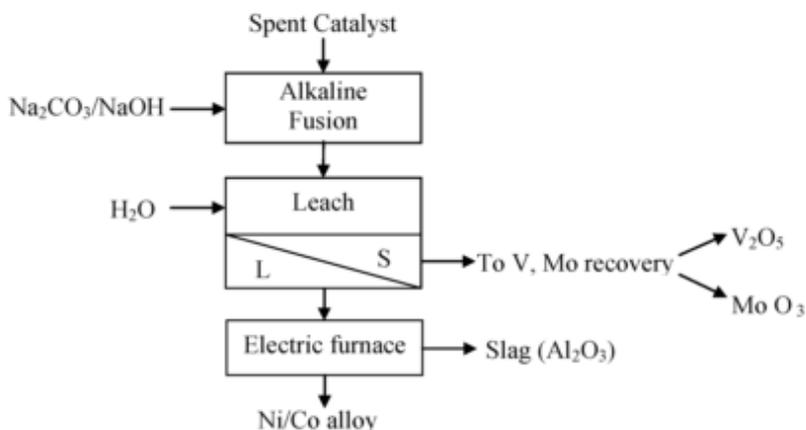


Figure 8 Simplified flow sheet for spent catalysts treatment. (Ferron, 2013)

## 2.2.6 TYRE ADHESIVE

Cobalt can be also found in a complex adhesive for bonding of rubber tyre with steel bracing (European Commission, 2017). However, no information was found on possible technologies or attempts of cobalt recycling from tyre adhesive.

## 3 CURRENT RECOVERY RATES

For US, there is data available for cobalt recovery rates. The end of life recycling rate for cobalt is estimated at 68%, while the recycled content of the fabricated metal is 32%, which includes also new scrap. The end of life recycling input rate, which is the amount of old scrap in the total material available for manufacturing including new scrap, is 0% (European Commission, 2017).

The exact recovery rates for EU are not always available. In EU the functional recycling of cobalt from secondary materials is estimated as 6,320 tones, however this data is highly estimative based on trade statistics, products average lifespan, collecting and recycling practices (BIO by Deloitte, 2015). End of life recycling input rate for cobalt in EU is estimated at 35% (European Commission, 2016). UNEP estimated the end of life recycling rate at 68%, which is a higher number than in case of other metals. Recycled content is estimated at 32%, which is a lower rate than most other metals (SETIS, 2016).

## 4 KEY ACTORS IN COBLAT RECOVERY

In Freeport Cobalt recycling facility Kokkola, Finland more than 50% of total feed is recycled material. The plant uses hydrometallurgical circuits, which can extract and purify cobalt to obtain high quality chemicals (Freeport Cobalt, 2015). In the EU one more cobalt recycling company was identified. Umicore, with their site in Hoboken, Belgium is recovering cobalt from spent batteries. This plant can recycle scrap battery cells, foils and powders. Umicore Cobalt & Specialty Materials (CSM) majors in recycling and refining of cobalt and nickel specialty chemicals, which find applications in rechargeable batteries, rubber tires, catalysts, pigments, hard materials. Umicore CSM has also several international business units, for example in China, Philippines, USA. Factory in Alabama, USA is focusing on acetate and nitrate salts production, but also offers recycling of spent catalysts (Umicore, n.d.).

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Globally, there are multiple companies that work on cobalt recovery from secondary resources, mostly in US. Globe Metal claims to be the biggest cobalt and nickel scrap recycler in Canada. The company recovers cobalt from all different sorts of scrap, from sludge, tailings to battery scrap (Globe Metal, 2016).

## 5 CHALLENGES IN MATERIAL RECOVERY

The major issue connected with cobalt recovery from spent batteries is sorting and identification of battery composition. Since the technology for batteries is still evolving, the recycling is more difficult than other better established products. A solution for those issues could be a universal recycling technology for mixed battery waste processing, that will consider differences between them (Zeng et al., 2014). It should be noted, that although there are many research activities in area of spent batteries, most of them are still in laboratory scale (Zeng et al., 2014). Another issue common in a number of critical metals is lack of proper collection system of end of life products, which hamper the cobalt recovery and can cause environmental issues if waste is not disposed properly.

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## 05 PRODUCTION TECHNOLOGIES OF CRM FROM SECONDARY RESOURCES: COKING COAL

### 1 OVERVIEW OF GLOBAL PRODUCTION OF COKING COAL AND SECONDARY RESOURCES

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

The main part of the coking coal is imported to Europe from North America and Australia and the selection of coal types depends both on the desired coke quality and the final metal product quality as some component in ash may dissolve in the metal, e.g. phosphorus. As can be seen from Table 1 both Australia and US has a net production while EU-28 and steel producing countries like Japan and North Korea without own coking coal sources have a large consumption. In fact, although the amount of coking coals produced are high in China there is a significant import of high quality coking coals. Also India has coking coal but this has in some cases undesired quality for use in ironmaking.

Table 1 Largest global coal producers and consumers with the amount and ratio of coking coal indicated, data collected from EURACOAL<sup>1</sup>

Largest coal producers				Largest coal consumers			
	Coking coal, Mt	Tot. coal prod Mt	Ratio of coking coal		Coking coal, Mt	Tot. coal prod Mt	Ratio of coking coal
China	611.1	3527.2	17.3%	China	658.1	3752.5	17.5%
United States	57.4	812.8	7.1%	India	105.6	912.3	11.6%
India	54.5	691.3	7.9%	United States	17.6	713.3	2.5%
Australia	191.1	508.7	37.6%	EU-28	59.9	686.9	8.7%
EU-28	20.9	498.9	4.2%	Russia	59.7	218.9	27.3%
Indonesia	2.7	469.3	0.6%	Japan	50.3	191.5	26.3%
Russia	78.0	349.3	22.3%	South Africa	4.0	176.0	2.3%
South Africa	3.2	252.1	1.3%	South Korea	38.9	139.3	27.9%
Kazakhstan	16	107.2	14.9%	Australia	3.9	122.2	3.2%
Colombia	4.7	90.3	5.2%	Turkey	6.2	87.3	7.1%
Others	50.3	401.6	12.5%	Others	67.3	705.7	9.5%
World	1089.9	7708.7	14.1%	World	1071.5	7705.9	13.9%

Secondary resources of coking coal can be found in terms of tailings in connection to mining and activities and production of coking coal. Moreover, alternative secondary materials judge to have potential as coking coal replacement has been investigated. This concerns e.g. waste plastics and by-products from the coking plant as tar, oils, etc.. However, as the coke quality is significantly influenced by less suitable coking materials already at a few percent such replacement.

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## 2 PRODUCTION OF COKING COAL FROM SECONDARY RESOURCES

As the requirements on metallurgical coke quality are high and quite well defined at the same time as the coking process and quality achieved are highly affected by the quality of coking coal, the most common coking process using density charging are not possible for secondary or low quality materials. At the same time several sources of coking coal are not suitable for production of metallurgical coke due to high ash, content of specific elements in the ash or because of giving to high reactivity of the coke produced..

### 2.1 PRE-TREATMENT METHODS FOR COALS

Potential coking coal resources in terms of mining tailings or low quality coal can be treated by flotation.<sup>4</sup> Such treatment is e.g. developed in India in order to make low quality and secondary resources suitable for cokemaking.

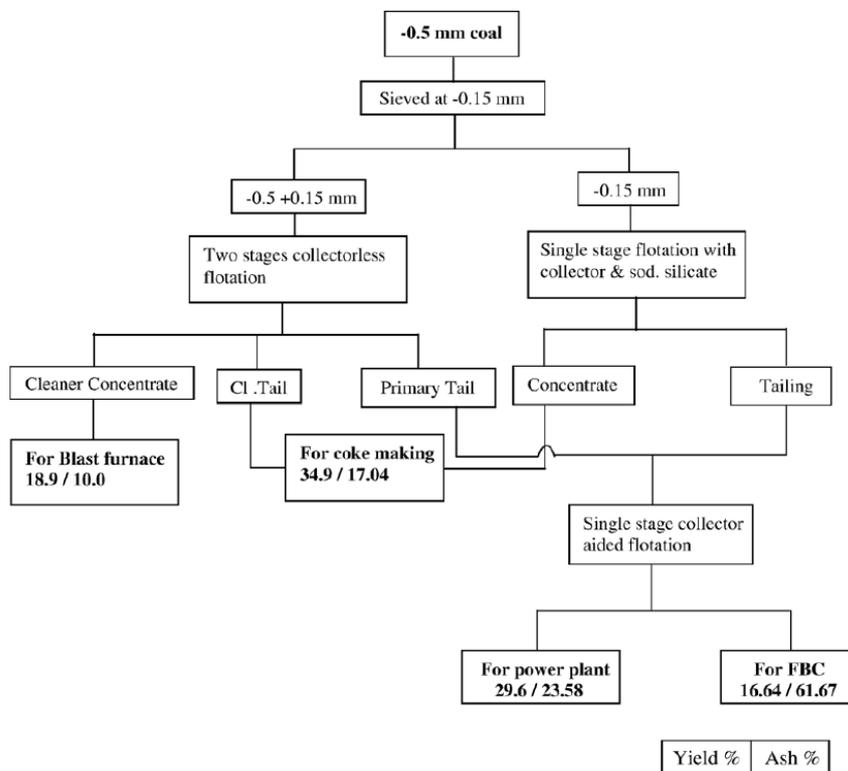


Figure 1 Process layout for floatation of low quality coal.

Conventionally, coarse coal is processed through gravity separation systems and fine coals through flotation although newer fine gravity systems are increasingly finding their applications. Due to a strong natural hydrophobicity and natural floatability pre-concentration of coals can be made by flotation. The floatability increases increased C content and higher-rank coal can usually be floated without the use of any collector, but not so with oxidized or weathered coal, sometimes extensive conditioning to minimize reagent consumption are needed. Natural floatability, according to them, depends also on the metamorphosis of the coal, its petrographic composition, degree of carbonification, surface oxidation, etc. and not necessarily on rank alone. As long as the surfaces of these solids remain uncontaminated (by oxidation or by embedded hydrophilic

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colloidal matter), the fines of such solids can easily be separated from associated hydrophilic particles. For such separation only the frother-acting surfactant is required but by the rate of aeration can be seen as the aeration as the bubble size increases increased air flow rate to the flotation. Higher air flow rate favors the stability of bubble-particle aggregate. As can be seen from the example in Figure 1 part of the low quality coal could be recovered for use in coke making, 34.09% having an ash content of 17.4%. However, with this comparably high ash content only a small amount can be used in the coking coal blend

Some coking coal with high S content are not efficiently floatated the conventional way, therefore, new scheme for upgrading this type of coals as well as of steam coals for energy production are under development.<sup>5</sup> In this process the low ash concentrate is first separated through reagent controlling measure, and then rough tailings is classified and thus the fine fraction is discarded. The coarse fraction of rough tailings so called middlings are further going through grinding-flotation process. The specific flowsheet is shown in Figure 2 and the method allows high recovery rate and quite low ash and S content of the coking coal at the same time. This method can followingly reduce the amount of tailings and increase the recovery of coking coal. Grinding middlings flotation process result shows that concentrate rate can reach to 68.35%, while ash content is only 11.51%, and the production efficiency is further considerably improved.

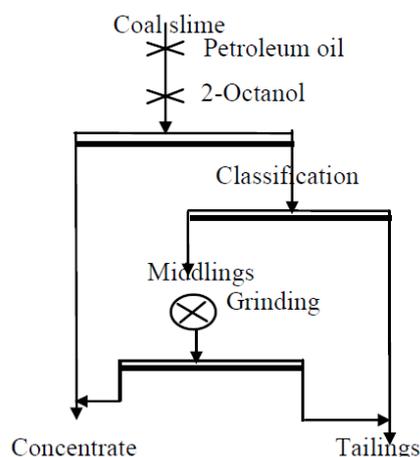


Figure 2 Scheme for improved recovery of « fat coal » or coking coal.

### 3 ALTERNATIVE COKEMAKING METHODS FOR INCREASED USE OF ALTERNATIVES TO COKING COALS

The enable the use of such materials to a larger extent alternative processes has been developed ase.g. stamp charging, scope 21 process and use of hypercoal.

#### 3.1 STAMP CHARGING

By stamp charging slightly less high qualitative coking coals can be used while still producing high quality coke. Higher density of the blend may cause more swelling and thereby be a risk for the coke ovens, especially in case of high oven batteries. Additives as e.g. oil can make it possible to give the blend higher density.

### 3.2 SCOPE 21 PROCESS

Research and development of new cokemaking process (SCOPE21) was conducted in Japan from 1994 to 2003 by the Japan Iron and Steel Federation (JISF)<sup>2,3</sup>. Pilot plant scale test was successful and a type new coke oven battery was constructed and started up in 2008 at Nippon Steel Oita works. The coke production capacity is 1 million ton per year. At present, high quality coke has been produced in this process using high blending ratio (over 50%) of non- or slightly-caking coal. Such process can also give open possibilities for use of secondary materials.

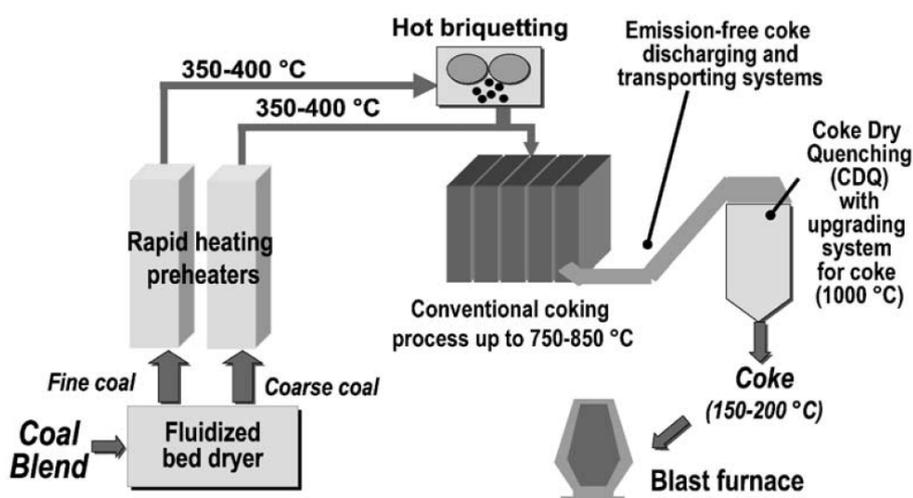


Figure 3 Scope 21 process for coke making developed in Japan.

As seen in schematic diagram in Figure 3 the coking process is divided into three stages: pretreatment of coal blend, a medium-temperature coking process, and upgrading of coke followed by dry quenching. The initial step consists of the separation of fine coal particles < 0.3 mm and coarse coal particles > 0.3 mm and the separated rapid heating to near to the temperature of thermal decomposition of coal (350–400 °C). The fine coal is agglomerated by hot briquetting and charged into a conventional coke oven together with the preheated coarse coal. The next stage is a coking process at a much lower temperature (750–850 °C) than in conventional process. The coke is finally discharged and subjected to a further heat treatment up to 1000 °C in the upper part of the CDQ facility.

### 3.3 CALDERON COKING REACTOR

This is a two-step process with the same aim as scope 21 process, including carbonization at low temperature followed by calcination of the coke in a separate device with complementary hot gas cleanup system<sup>2,4</sup>. This process shall also allow higher coking pressures than in conventional cokemaking.<sup>10</sup>

### 3.4 USE OF HYPERCOAL AS ADDITIVE TO COKING COAL BLEND

Research is on-going in order to increase the possible added amounts of thermal coals to the coal blend, in Japan this was enabled by addition of hypercoal<sup>6-10</sup> to the coal blend. Production of hypercoal involves a first step in which the carbon structure is dissolved into a solvent at elevated temperature and increased pressure.

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The solid ash is removed and solid carbon precipitated as the solvent is vaporized and collected for repeated use. In principle the hypercoal process can be used for producing material suitable in the coking coal blend using high ash containing coal that can be tailings from mining of thermal coals or coking coals.

### 3.5 PROCESS FOR RECYCLING OF WASTE PLASTICS IN COKING COAL BLEND

Waste plastics in coking coal blend has shown to be an alternative that can replace 1-2% of the coking coal and at the same time the coke quality is not lowered, see Figure 4 for the developed process. Only 20% of the plastic will remain in the coke and the rest will report to the coke oven gas or chemicals collected in the gas treatment plant.

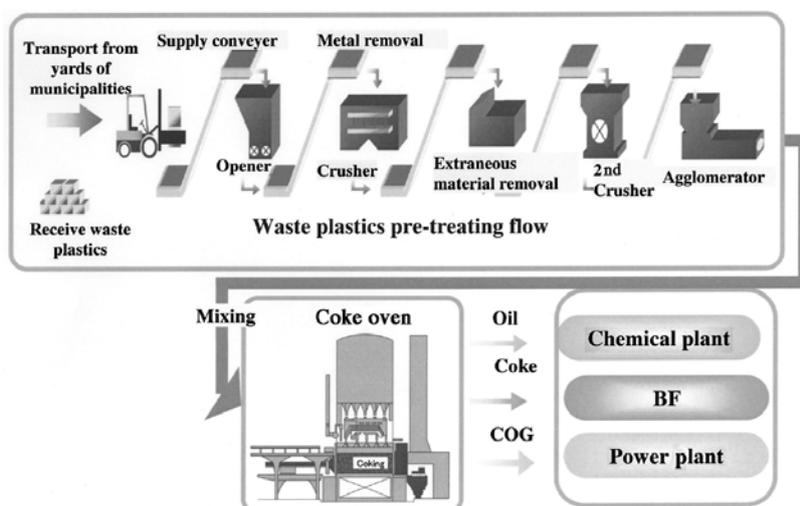


Figure 4 Process for using waste plastics in coking coal blend and achieving high recovery.

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## 06 PRODUCTION TECHNOLOGIES OF CRM FROM SECONDARY RESOURCES: FLUORSPAR

### 1 OVERVIEW OF GLOBAL PRODUCTION OF FLUORSPAR AND AVAILABLE SECONDARY CAF<sub>2</sub> RESOURCES

Fluorspar is the commercial name for fluorite (CaF<sub>2</sub>) and is mined as a by-product and transformed into acid grade (97% CaF<sub>2</sub>) or metallurgical grade (84% CaF<sub>2</sub>). The mineral is widely occurring in multiple locations. It is mostly produced in China, with 64% of global share, but can be found also in Mexico and Mongolia with 16% and 5% share respectively. Fluorspar is also produced in EU with about 290,000 tons in form of acid grade, mostly in United Kingdom, Spain and Germany. The EU import reliance is on level of 70% (European Commission 2017).

Globally, the fluorspar is consumed mainly by three industry fields, as described by Figure 1. First, the manufacture of hydrofluoric acid (HF), the main source of fluorine in industrial applications and a precursor to the production of most other fluorine-containing chemicals, notably fluorocarbons, accounts for approximately 40% of annual global fluorspar consumption. This field requires acid-grade fluorspar (acidspar). Secondly, 30% of global consumption of fluorspar is used as a steelmaking flux, in which metallurgical-grade fluorspar (metspar) is primarily destined. Thirdly, the manufacture of aluminum fluoride (AlF<sub>3</sub>) and cryolite (Na<sub>3</sub>AlF<sub>6</sub>) for aluminum smelting, which typically also require acid-grade fluorspar, account for approximately 18% of annual global fluorspar consumption. In the latter cases fluorspar, or fluorine it contains, is not incorporated in the final products, unlike in the manufacture of hydrofluoric acid and products derived from it. The remaining applications of fluorspar include use in the manufacture of cement, ceramics, enamel, glass, and welding rod coatings. (McRae 2017)

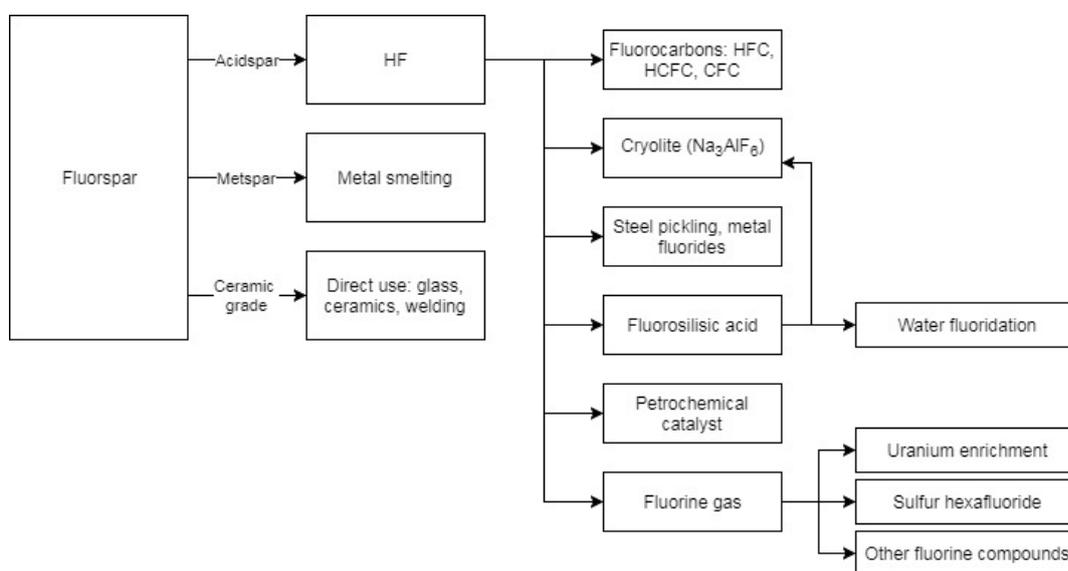


Figure 1 Processing routes of fluorspar. (British Geological Survey 2011; McRae 2017; Villalba et al. 2007).

The consumption of fluorspar in the EU is depicted in Figure 2. It also shows the detailed use of the hydrofluoric acid in various end applications.

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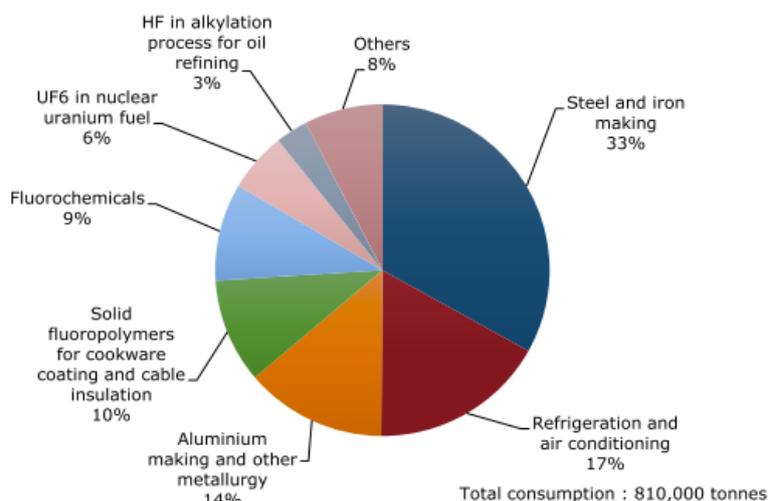


Figure 2 Fluorspar main applications in the EU. Derived from (European Commission 2017).

Fluorspar consumed in the production of HF and in subsequent chemical manufacturing processes is beyond recycling. There are however several alternative sources of HF, including calcium fluoride, depleted uranium hexafluoride, sodium fluoride and sodium fluorosilicate. The use of fluorosilicic acid is estimated to be the only one which could have a significant impact on global fluorspar production. (British Geological Survey 2010)

## 2 PRODUCTION OF FLUORSPAR FROM PROCESSING WASTE AND HISTORICAL WASTE AREAS

Fluorspar is recycled only in a small extent since it is essentially consumed in use, or recycling is not feasible. Some fluorspar is recycled internally by the manufacturing industry. (British Geological Survey 2010) Significant amount of fluorine bearing waste is generated by use of cryolite, HF and  $AlF_3$  in industrial processes, namely in pickling and etching of metals, aluminium production and alkylation in oil refining (BIO by Deloitte 2015). Also semiconductor industry produces significant amounts of HF-containing wastewaters (Van den Broeck et al. 2003).

It is estimated that, in the U.S., annually a few tons of synthetic fluorspar is recovered in uranium processing, petroleum alkylation and stainless steel pickling, in addition to some HF and fluorides being recovered during the smelting of aluminium and in the petroleum alkylation process. (McRae 2016)

### 2.1 URANIUM ENRICHMENT

Fluorspar is used as an inert bed in a fluidized bed reactor, where  $UF_4$  reacts with fluorine to form  $UF_6$ , as depicted in Figure 3. The only waste forming in the fluidized bed process is the spent fluorspar. This material is stored to allow for the decay of the short lived daughter products of  $^{238}U$ . After drying, it can either be consigned to a non-nuclear waste repository due to its low uranium content, or reused. (IAEA 1999)

Alternatively, a flame reactor is used for fluorination. In this process, the tail gases containing residual  $UF_6$ ,  $F_2$  and HF are recovered by treating the gases with KOH. The fluorides are precipitated as fluorspar, which is stored as non-radioactive waste. (IAEA 1999)

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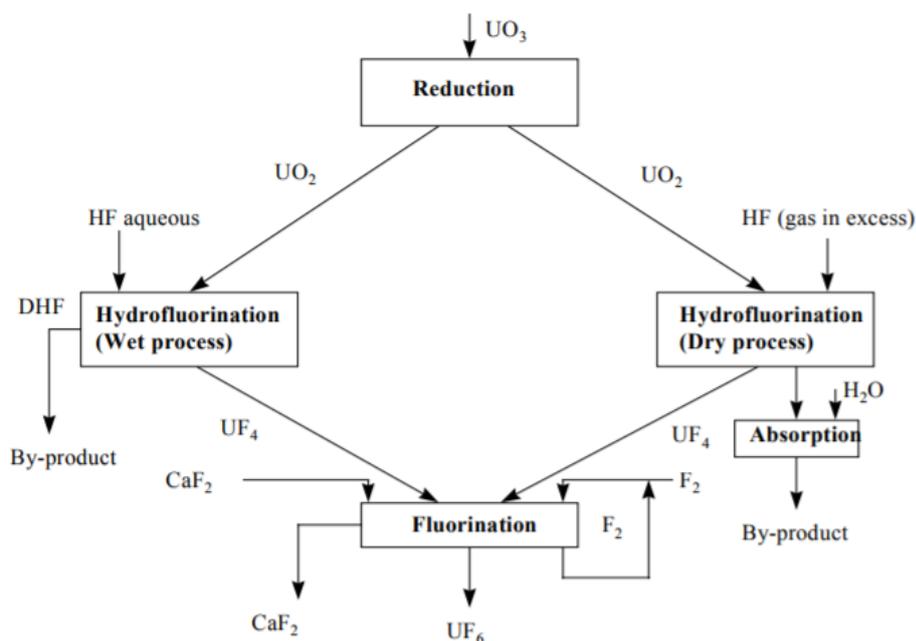


Figure 3 Fluorspar use in the fluorination step of the conversion of UO<sub>3</sub> to UF<sub>6</sub>. Derived from (IAEA 1999).

Secondary fluorspar can also be formed in the nuclear waste treatment, such as in the process Siemens has developed for the disposal of UF<sub>6</sub> enrichment waste. In this process, the final cleanup of the tail gas to remove the small amount of residual HF requires a caustic scrubber or a bed of calcium carbonate. In the latter option, a small quantity of fluorspar is formed when the calcium carbonate reacts with the residual HF. This synthetic fluorspar can be recycled to the steel industry. (Kogler et al. 1998)

## 2.2 WASTEWATERS

Both environmental regulations and efficient operation of wastewater treatment plants require fluoride removal from the effluent prior to discharge to the environment. The fluorides are commonly removed from industrial wastewaters by chemical precipitation, which is a cost-effective solution to several fluoride-bearing wastewaters. However, the low quality of the sludge, 40-60% of CaF<sub>2</sub>, prevents further use of the precipitated fluoride. (Aldaco et al. 2007)

A crystallization process in a fluidised bed reactor has been proposed as an alternative technology to achieve better quality of the sludge. (Aldaco et al. 2007) There is at least one commercial example of this technology, called Crystalactor, brought to market by Royal HaskoningDHV (Netherlands). The Crystalactor treatment plant employs a pellet reactor, partially filled with suitable carrier material. The water is pumped from bottom to top, maintaining the pellet bed in a fluidised state. A suitable reagent, usually an alkali, and dosage is needed in order to convert HF to fluoride. In addition, calcium is dosed to form fluorspar. After the pellets have grown enough, they settle at the reactor bottom. At regular intervals, a part of the largest pellets is discharged from the reactor and fresh carrier material is added. Essentially water-free pellets are obtained after an atmospheric drying. (Royal HaskoningDHV 2017a)

There are three locations where Crystalactor is used for chloride removal from wastewaters: polyisobutene production site in Nanjing (China), and solar panel manufacturing sites in Gelsenkirchen (Germany) and Seoul

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(South Korea). The fluorspar produced at the plant in China is sold to other industries. (Royal HaskoningDHV 2017b)

### 2.3 RECOVERY OF HF FROM PICKLING

Pickling of stainless steel is a process of treating the steel with HF and nitric acid. The acid can be regenerated after being used for pickling and recirculated back in the process. One technology to regenerate the acid is an ionic exchange process. Here, the spent acid is separated from metals and recirculated back to the pickling bath. The recycling rate for free HF acid reaches 80%, therefore the need for fresh acid is reduced to 30%. Due to reliability and low cost, the ion exchange method is commonly used for mixed acid purification. Another acid extraction method uses different steps to remove different complexes of HF, as shown in Figure 4. The third extraction step results in acid ions dissolved in water and ready to be recirculated in the pickling bath. The recycling rate of HF for this process is 70% (Dahlgren 2010).

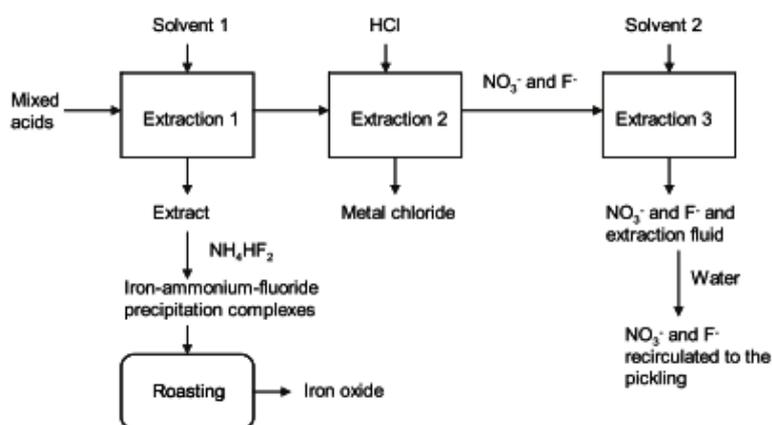


Figure 4 Scheme of mixed acid extraction. Derived from (Dahlgren 2010).

### 2.4 OTHER INDUSTRIAL WASTES

The fluorspar used in metallurgical industry is removed with slag waste, which is possibly recycled as low-level construction materials and fluorspar loses its original function. The literature doesn't acknowledge any functional recycling of fluorspar from slag waste.

Small amounts of fluorspar are recovered from the waste streams in HF production and recycled internally. In addition, some limited recycling of HF is feasible in downstream applications. (British Geological Survey 2010)

### 2.5 HISTORICAL WASTE AREAS

The elemental fluorine bearing waste mainly ends up in landfill. It is estimated that the accumulation of elemental fluorine in landfills within EU reached about 5.6 Mt over the last 20 years. (BIO by Deloitte 2015)

### 3 PRODUCTION OF FLUORSPAR FROM END-OF-LIFE PRODUCTS AND MANUFACTURING RESIDUES

Fluorspar is generally not recovered from manufactured products such as flint glass, enamels, and fibreglass insulation, since it is highly dispersed in those applications. Limited recycling of fluorspar from EoL products is theoretically feasible, yet there is no information of any recycling operations ongoing in the EU (Eunomia Research & Consulting Ltd 2015) and worldwide. Overall, only about 5 kt of elemental fluorine contained in the EoL waste is recycled. (BIO by Deloitte 2015). For example, about 60-70% of fluorochemicals from refrigerators and air-conditioners is recovered. (European Commission 2017)

In Japan, a decomposition of recovered fluorocarbons has been carried out at an industrial waste incinerator, where synthetic fluorspar is produced from the drainage with high fluorine content, which is generated in a flue gas scrubber attached to the decomposition process of CFCs/HCFE. The facility has been operated since 2004, and the quantity of the recovered fluorspar was 400 t in 2006, which is the most recent information found. The synthetic fluorspar has been supplied to steel makers and chemical producers. The process requires several problems of cost and impurities of the recovered fluorspar to be solved. (Yamatoya et al. 2007)

### 4 SUMMARISED DISCUSSION ON PRODUCTION OF FLUORSPAR FROM SECONDARY RESOURCES

Fluorspar, or calcium fluoride  $\text{CaF}_2$ , is essentially not recyclable, as it is mainly consumed in use. There are some application areas, such as metal smelting, glass and ceramics, where fluorspar is used in the raw, but no information was found of the recycling of fluorspar from these applications. There are however some processes where synthetic fluorspar is formed, such as in the uranium enrichment and wastewater treatment. This synthetic fluorspar is in some cases sold to the industry use.

The waste containing fluorine in other compounds, such as HF,  $\text{AlF}_3$  and fluorocarbons, is recycled more frequently. Especially HF is recovered during the pickling of stainless steel, smelting of aluminium, and in the petroleum alkylation process.

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## 07 PRODUCTION TECHNOLOGIES OF CRM FROM SECONDARY RESOURCES: GALLIUM

### 1 PRODUCTION OF GALLIUM FROM SECONDARY RESOURCES

Gallium as pure metal is silvery-white in appearance. It is relatively soft metal with a low melting point but with a relatively high boiling point. Gallium is magnetic and a good conductor of both electricity and heat. Due to its properties, its main use is in GaAs semiconductors in which GaAs acts as a substrate on which one, or more, very thin surface layers are deposited or grown. Depending on the end-uses, different quality substrate crystals are required, with integrated circuits (ICs) and microwave devices requiring the highest. (Butcher and Brown 2013)

Gallium production relies nearly entirely on by production from aluminium Bauxite processing. A schematic presentation of the global gallium flows in 2011 has been presented in Figure 1 and Figure 2. Largest gallium producer in 2014 was China with nearly 82 % share of production ending up to roughly 550 t. Other producing countries come way back, Germany with highest 40 t quantity. In overall, in 2014 around 675 t of gallium was produced globally. (Jaskula 2014)

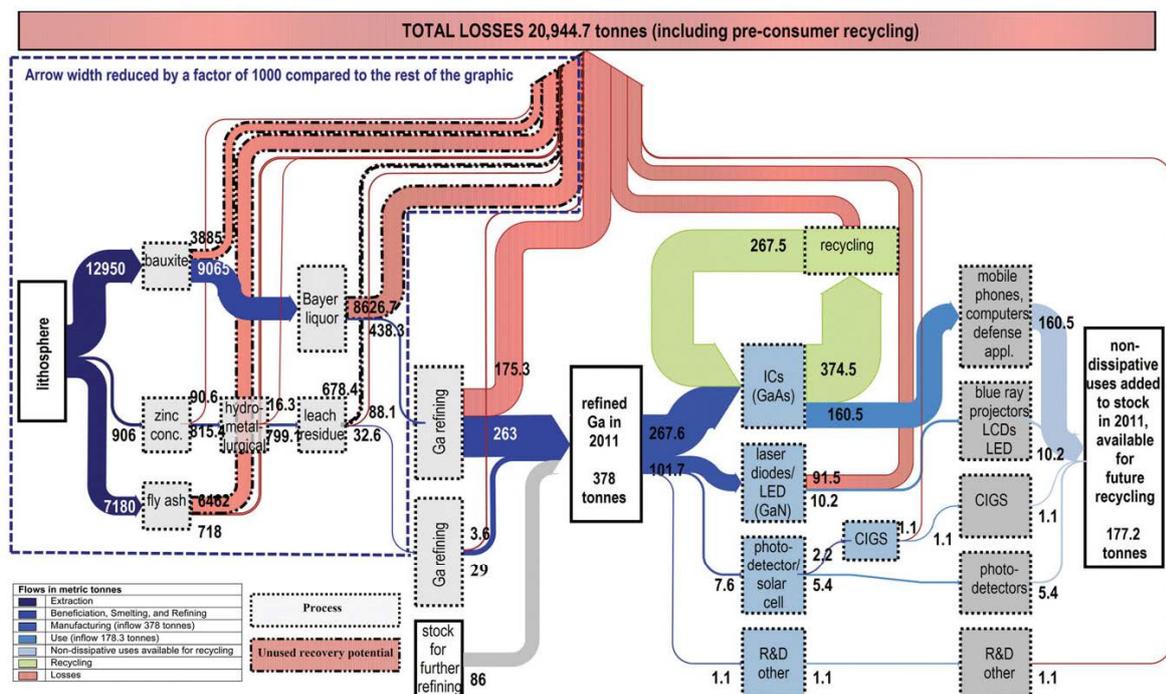


Figure 1 Global gallium flow analysis in 2011. zinc.con.=zinc concentration; Ga=gallium ; ICs=Integrated circuits ; GaAs=gallium arsenide ; LED=light-emitting diode ; GaN=gallium nitride ; R&D=research and development; GICS=copper indium gallium diselenide; LCDs= liquid crystal display. Note the scale difference in the box of dashed line. (Licht, Peiró, and Villalba 2015)

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**Global anthropogenic gallium system 2011 [tons/year]**

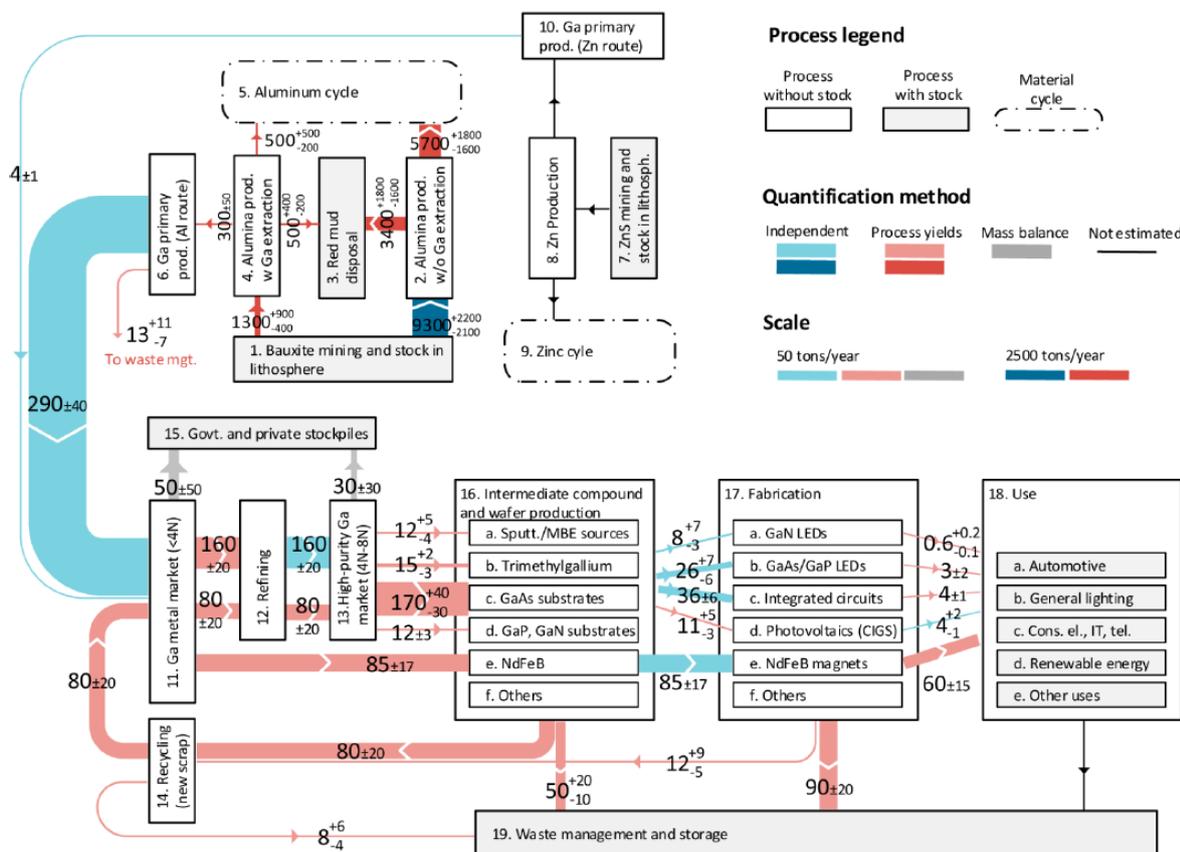


Figure 2 Global system of gallium production, refining, fabrication, use and recycling. Quantified flows are given as median  $\pm$ 84th and 16th percentile of Monte Carlo simulation. Colors indicate quantification method. Note that the flows in the upper part (dark colors) are shown in a different scale. (Løvik, Restrepo, and Müller 2015)

The gallium flow analysis reveals that recycling occurs only at the manufacturing stage from so called new scrap. The recycling in the manufacturing stage focuses especially on the GaAs wafer production. The fabrication of these semiconductor wafers generates about 60 % new scrap, with a gallium content ranging from 1 to 99.99 % (Butcher and Brown 2013). Bulk GaAs and clean wafers may be recycled internally at the crystal growth facilities by direct remelting. Recycled gallium metal may be further refined to obtain the same grades as from primary metal. (Licht, Peiró, and Villalba 2015)(Løvik, Restrepo, and Müller 2015) Worldwide secondary capacities are estimated at 200 t (Rongguo et al. 2016).

In the overall examination, fly ash has been identified as a potential source for gallium which however, at the moment is not utilized. Development actions and research within this field is taking a place (Blissett and Rowson 2012) (Fang and Gesser 1996) (GUTIERREZ 1997).

Gallium in the use phase dissipates to numerous end-applications such as notebooks, mobile phones, LEDs and photovoltaics from where the recycling is not at the moment economically feasible.(Buchert et al. 2012) This is in consensus with the UNEP report on recycling rates of metals which have determined the recycling rate for gallium from end-of-life streams to be below 1 % (Graedel 2011).

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According to the primary value chain of gallium the Ga-containing secondary resource and urban mine are identified as follows.

- (1) Secondary resources: industrial residuals
  - i) New scrap from manufacturing of gallium arsenide (GaAs) and gallium phosphide (GaP) wafers.
  - ii) CIGS/thin film solar cells. Pre-consumer waste of CIGS is also recycled
  - iii) Fly ash from coal industry.
- (2) Secondary resources: urban mines
  - iv) Currently, there is no recovery of gallium from end-of-life products

## 2 PRODUCTION FROM PROCESSING WASTE AND HISTORICAL WASTE AREAS

### 2.1 FLY ASH

Even though currently there is no commercial recovery of gallium from coal fly ash (CFA), research and development to treat coal fly ash has taken place during the last decades (Blissett and Rowson 2012) (Fang and Gesser 1996) (GUTIERREZ 1997). At the coal burning power plant, after combustion both gallium and germanium condense from the vapor phase onto the surface of the CFA, thus enriched in CFA relative to the feed coal (Sahoo et al. 2016). Reported gallium concentrations in CFAs range from 37.5-320 ppm (Fang and Gesser 1996) (Font et al. 2007).

Several techniques have been developed for the recovery of gallium from CFA. Sahoo et al. identified several patents and studies for gallium recovery which can be seen in Table 1. (Sahoo et al. 2016)

Table 1 Extraction methods and their recovery efficiencies for gallium from CFA. (Sahoo et al. 2016)

Reference	Method	Chemical reagent/others	Ga recovery efficiency
US Pat No. 4475993 (1984)	Alkali halite melt, electrolysis	Aluminium trichloride	69 %
US Pat No. 4643110 (1987)	Sublimation		Unknown
US Pat No. 4678647 (1986)	Sublimation		Up to 90 %
US Pat No. 4757772 (1988)	Sublimation		Unknown
US Pat No. 4678647 (1986)	Sublimation		Up to 90 %
Arroyo et al (2014)	Acid, alkaline, complexant leaching	Oxalic acid, sulfuric acid	Up to 82 %
Gutiérrez et al. (1997)	Acid leaching	HCl, Amberlite LA-2	83 %
Fang and Gesser (1996)	Acid leaching, flotation	HCl	Up to 80 %

Several patents focuses on sublimation method which main steps are; heating the CFA in an oxidizing atmosphere to vaporize the gallium and germanium, then treating the oxides in a reducing atmosphere to reduce oxides to suboxides, which subsequently precipitate on the surface of sand particles, and recovery of the products from the sand particles using a cold liquid solution. However, this method has problems involving other volatile compounds such as arsenic and sulphur. To manage with this problem a method where CFA is pelletized and treated in the presence of an oxidizing gas at a temperature of about 900°C has been introduced in US patent 4678647 (1986). In this treatment arsenic and sulphur are removed from CFA, so that they will not remain in the gallium concentrates. The oxides are treated in the presence of a reducing gas at the same

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temperature range to reduce the oxides to suboxides. The recovery of gallium suboxides is carried out by condensation at a lower temperature (nearly 700–800 °C) and dissolving the condensed material using an acidic solution. The recovery rate of gallium for this method is up to 90 %. This method can be more economical and more efficient than the alkali halite method.(Sahoo et al. 2016)

Other techniques for the recovery of gallium include using water/acid/alkali leaching of CFA, followed by separation/purification by using precipitation, distillation, ion flotation, adsorption into activated carbon, and solvent extraction (Meawad, Bojinova, and Pelovski 2010). Arroyo et al. optimized germanium and gallium recovery from CFA using different extractants in a wide range of extraction conditions (acid, alkaline, complexant, reducing and oxidizing). The method gained high extraction yields of gallium (up to 82 %) (Arroyo et al. 2014).

Orbite Technologies Inc has been developing a technique to recover valuables from different aluminium containing residues. The technology was identified also for potential red mud treatment in Task 4.1. The overall process concept has been presented in Figure 3.

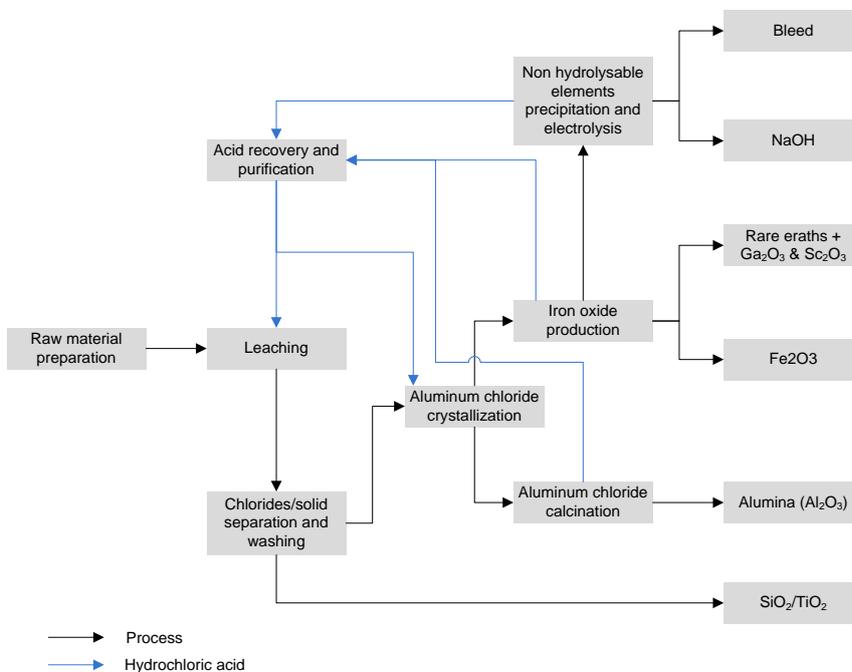


Figure 3 Overall process of Orbite for secondary raw materials such as fly ash to recover i.a. Gallium. (Orbite Technologies INC. 2017)

The method utilizes leaching, precipitation, electrolysis, crystallization, calcination, washing to produce various product fractions for sale.

### 3 PRODUCTION FROM END-OF-LIFE PRODUCTS AND MANUFACTURING RESIDUES

#### 3.1 NEW SCRAP FROM MANUFACTURING OF GALLIUM ARSENIDE AND GALLIUM PHOSPHIDE WAFERS

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High-purity gallium is one of the main components in the preparation of III-IV semiconductors in which gallium arsenide (GaAs) and gallium phosphide (GaP) are of immense importance in electronics. The fabrication of semiconductor devices involves several steps: synthesis and growth of single crystals doped in a controlled manner, sizing of the crystals, slicing, chemomechanical polishing, growth of epitaxial layers by vapor-phase (VPE) or liquid-phase (LPE) epitaxy or MOCVD, and layout formation. The numerous amount of process steps and stringent quality requirements of the final product lead to substantial losses of the materials involved in the process. Typically, the yield to specification does not exceed 20%. The waste includes off-grade single crystals, wafers, epitaxial structures, powders after slicing and lapping, and liquids after etching, which contain expensive components, of which gallium is of greatest value. (Kozlov et al. 2003) It has been estimated that the fabrication of semiconductor wafers generates about 60 % new scrap, with a gallium content ranging from 1 to 99.99 % (Butcher and Brown 2013). Therefore, a large part of the waste from the GaAs industry is recovered for both economic and environmental reasons. (Greber, Greber, and Friedrich 2000) In Table 2, main type of gallium containing wastes from manufacturing industry has been listed.

Table 2 Characteristics of the main types of gallium-containing waste materials from manufacturing industry. (Kozlov et al. 2003)

Process	Type of waste	Weight percent waste	Composition, wt%
LPE and VPE growth of epitaxial structures	Rejected epitaxial structures on GaAs wafers	20-45	GaAs $\geq$ 89; Ga <sub>x</sub> Al <sub>1-x</sub> As or GaAs <sub>x</sub> P <sub>1-x</sub> $\geq$ 11; Te, Si, Sn, Zn = several hundredths; Ga $\geq$ 47
Crystal growth and production of GaAs wafers	Residue in the crucible, crowns and final tapers, rejected crystals	$\leq$ 70	Te, Si, Sn, Zn, Cr = several hundredths; In (for isoelectronic doping) $<$ 5; Ga $\leq$ 48
	Rejected wafers	$\leq$ 6	
	Powder waste after ingot sizing	$\leq$ 10	Te, Si, Sn, Zn, Cr = several hundredths; In (for isoelectronic doping) $<$ 5; O (oxides) $\leq$ 2; Ga $\leq$ 46
	Powder waste after slicing and lapping	$\leq$ 40	
Crystal growth and production of GaP wafers	Residue in the crucible, crowns and final tapers, rejected crystals and wafers	$\leq$ 70	Zn, Fe, Cr, Mn = several hundredths; Ga $\leq$ 68
	Rejected wafers	$\leq$ 6	
	Powder waste after ingot sizing	$\leq$ 10	Zn, Fe, Cr, Mn = several hundredths; O (oxides) $\leq$ 3; Ga $\leq$ 66
	Powder waste after slicing and lapping	$\leq$ 45	
LPE growth of epitaxial structures	Residual Ga flux	$\leq$ 98-99	Ga = 87.5–98.6; GaAs = 1.4–12.5; Sn, Ge, Al, Zn, Si, Te, In, Mg = several tenths; O (oxides) $\leq$ 0.2

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From Table 2 it can be seen that the major amount of material suitable for recycling is constituted by pieces of crystals and powders resulting from the production of single crystals and wafers. Several processes are effective and being used to recover both the gallium either as a metal, a salt, or a hydroxide for recycling, and the arsenic in some form for recycling or disposal (Greber, Greber, and Friedrich 2000). At the crystal growth facilities for clean wafers and bulk GaAs the internal recycling can be carried out by re-melting (Eichler 2012). For less pure manufacturing scrap gallium is typically recovered by dissolving (Kramer 1988) (Chen et al. 2012). In Figure 4 two different approaches to recover gallium from GaAs manufacturing waste is presented.

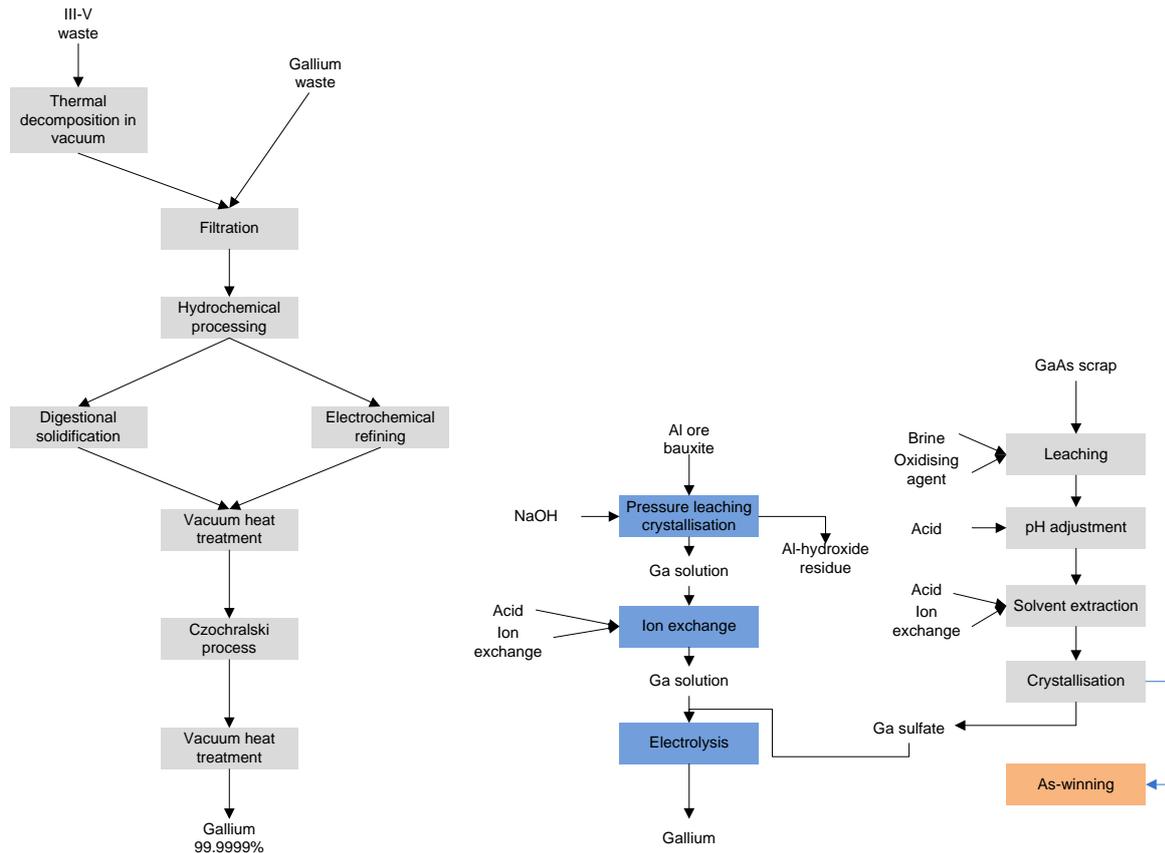


Figure 4 Two different approaches for Ga recovery from manufacturing waste. (Kozlov et al. 2003)(Worrel and Reuter 2014)

Common unit operations in the gallium recovery from new scrap are; dissolution, solvent extraction, electrochemical refining, heat treatment, crystallization. In the global gallium flow analysis, the recovery of gallium in the recycling of new GaAs waste has been estimated to be 71 % (Licht, Peiró, and Villalba 2015).

### 3.2 CIGS/THIN FILM SOLAR CELLS

CIGS solar cells can be divided to chalcogenide solar cells including CdTe (II-VI semiconductor) and to the chalcopyrite family (I-III-VI<sub>2</sub> semiconductors) CuInSe<sub>2</sub> and the alloys Cu(In,Ga)Se<sub>2</sub>, Cu(In,Ga)<sub>2</sub>S<sub>2</sub> and Cu(In,Ga)(Se,S)<sub>2</sub>. (Marwede et al. 2013) In CIGS manufacturing, gallium may be deposited in the absorber cell layer by various technologies: electron-beam (EB), electrochemical deposition, and co-evaporation. During the deposit process only 20% of the total gallium input is deposited in electron-beam (EB) and co-evaporation

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technologies. For electrochemical deposition, the amount deposited is 30% of the total input. (Worrel and Reuter 2014) Based on the fact that 1 MW CIGS panel contains about 3.5-4 kg of gallium, it has been evaluated that 7.5-16 t of gallium are waste during the manufacturing stage (Worrel and Reuter 2014) (Christmann et al. 2011).

Umicore, a Belgian refinery and precious metal recycler, has developed a hydrometallurgical process to recover Cu, In, Ga and Se from CIGS (production) scrap with a refining capacity of 50t/yr (Marwede et al. 2013). Prior the hydrometallurgical treatment CIGS chamber scrapings are fed to their smelter in which In, Ga and Se typically reach a recovery rate of 70 % to 80 %. The Canadian metal refinery 5N Plus has developed processes to recover the elements from CdTe and CIGS residues, targeting a typical recovery rate of 90% or more for metals of interest. (Marwede and Reller 2014)

### 3.3 SUMMARISED DISCUSSION ON PRODUCTION OF GALLIUM FROM EOL PRODUCTS AND MANUFACTURING RESIDUES

Currently gallium is only recovered from manufacturing residues. New scrap from manufacturing of gallium based wafers and CIGS solar cells production scrap are the main waste streams. Depending on the feed the processing method can vary from re-melting (clean wafers and bulk GaAs the internal recycling) to dissolution combined with solvent extraction, electrochemical refining, heat treatment and crystallization for the less pure manufacturing scrap. The recovery of gallium in the recycling of new GaAs waste has been estimated to be 71 % As for the CIGS solar cell production scrap hydrometallurgical treatment processes has been developed to recover gallium. Reported recovery rates for gallium from CIGS has been reported between 70 and 90 %

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## 08 PRODUCTION TECHNOLOGIES OF CRM FROM SECONDARY RESOURCES: GERMANIUM

### 1 GERMANIUM SECONDARY RESOURCES AND PROCESSING TECHNOLOGIES

Germanium secondary raw materials comprise two main material streams:

- New scrap materials, i.e. byproducts, wastes and residues from production of refined germanium market products, such as high quality  $\text{GeCl}_4$ ,  $\text{GeO}_2$  and Ge metal in various forms and shapes, and from manufacturing the products, belonging to germanium applications groups, such as fiber-optics, IR optics, electro-optics, multi-junction photovoltaics and other electronic materials;
- Postconsumer (end – of – life) scrap materials, i.e. spent and damaged germanium-bearing products, such as: optic – fiber cable scrap, broken or decommissioned IR glass devices, multi-junction solar cells scrap, germanium-bearing electronic scrap.

Materials from the “new scrap” streams are usually recycled to the original manufacturing processes. This is the case in germanium refineries, equipped with technical and technological means, necessary for utilization of their own germanium byproducts, as well as, in IR glass and electro-optical material producers plants, where the wastes and scraps, such as materials from machining (cutting, grinding, polishing) can be either directly recycled, being free of alien contaminants, or sent to proper refining step, depending on character and degree of contamination.

During the manufacture of most optical devices, more than 60% of the germanium metal used is routinely recycled as a new scrap. [1]

An exception in those new scrap materials streams are the effluents from optic fiber manufacturing process, which should be treated using special, proprietary method, described further below.

The end-of-life scrap materials, such as window/blanks and lenses from military and civilian surveillance equipment, germanium wafers from damaged multi-junction photovoltaics, broken BGO crystals from scintillators, spent optic fiber cables and other germanium containing electronics are valuable from recycling point of view. The methods for germanium recovery from these material streams seem to be at disposal at the leading germanium processing and refining producers. At least most of them declare the ability to process any germanium-bearing materials of different nature with Ge content over 0.5% (e.g. Unicore).

The effluents from optic fiber manufacturing process should be processed on site due to economic and environmental reasons (Ge recovery, chlorine gas disposal). The commonly used method for optic fiber manufacturing is a modified chemical vapor deposition method (MCVD).

In the MCDV process the main reagents in gaseous forms:  $\text{SiCl}_4$ ,  $\text{GeCl}_4$  and oxygen flowing through rotating slice tube, are heated externally. The other dopants, such as  $\text{POCl}_3$  and  $\text{BCl}_3$ , are also introduced in minor amounts. In hot zone  $\text{SiCl}_4$  and  $\text{GeCl}_4$  reacts with oxygen, forming fine particles of  $\text{SiO}_2$  and  $\text{GeO}_2$ . Created particulate material is melted further into glassy fiber. The oxidation of  $\text{SiCl}_4$  proceeds toward  $\text{SiO}_2$  almost completely, while for  $\text{GeCl}_4$  oxidation efficiency is limited to at most 30%, due to thermodynamic reasons. So, the effluents are composed of unreacted  $\text{GeCl}_4$  (~70% of introduced chlorine gas, being a side product of oxidation reactions, and particulate material, containing mainly fine  $\text{SiO}_2$  particles, which were not melted into glassy fiber).

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The specialists from Bell Technologies invented and then implemented to industrial practice the effective method for germanium recovery from optic fiber production effluents, with Ge recovery rate over 95%. The idea of this invention is presented on the figure below. [2]

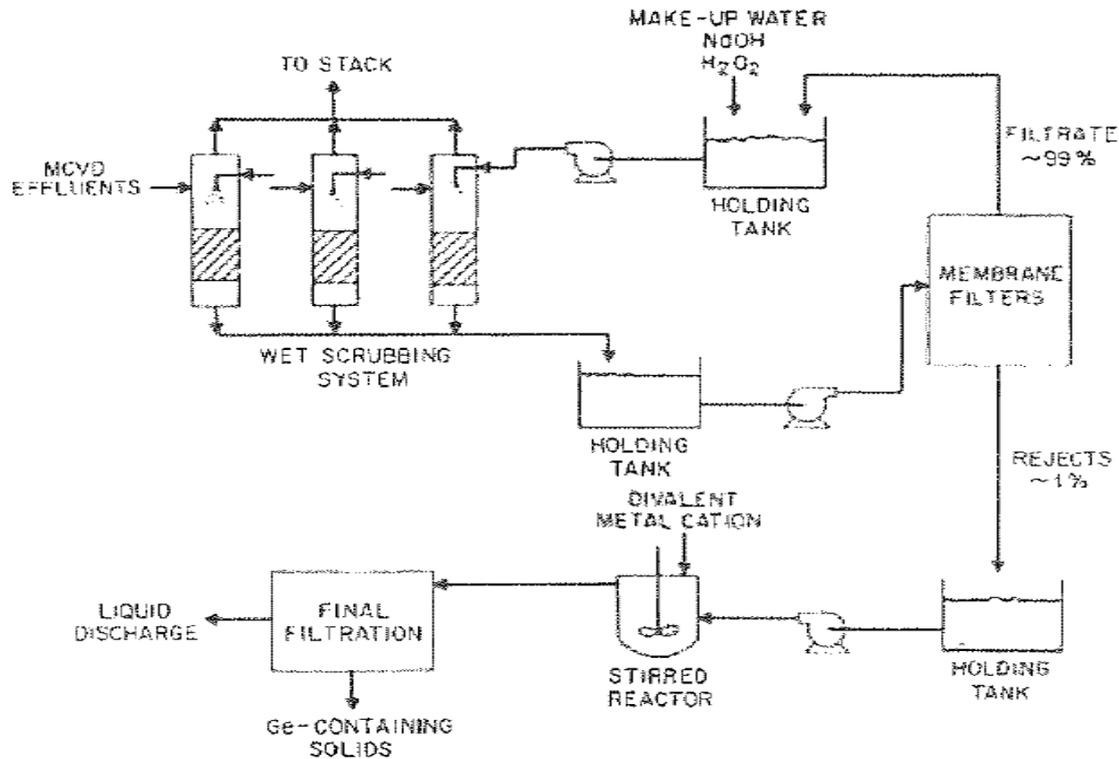
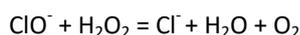


Figure 1 Germanium recovery from MCVD optic fibers manufacturing effluents. [2]

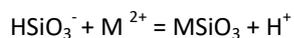
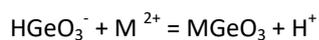
The effluents, containing unreacted  $\text{GeCl}_4$ ,  $\text{Cl}_2$  gas and rejected particles, are introduced to scrubber with circulating aqueous solution of  $\text{NaOH}$  and  $\text{H}_2\text{O}_2$ , working under control of pH and redox potential. The effluent components react with caustic and hydrogen peroxide according to the following reactions:



The circulating scrubbing solution is further filtered on membrane filter to remove solid particles, whence it returns to scrubber, via make-up holding tank, where reagents are supplemented to maintain proper pH and redox parameters.

When Ge concentration reaches determined value small portions of circulating solution are rejected to precipitate the dissolved germanium and silicon according to the following reactions:

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where M is di – or trivalent cation, such as Mg(II), Ca(II), Fe(II), Fe(III), Al(III) and others, preferably  $\text{MgSO}_4$ .

In the end, the precipitated mixture of germanates and silicates is filtered, giving hydrated cake, comprising for example about 20% of solid matter with 12.8% Ge content.

Further processing of filter cake to recover  $\text{GeCl}_4$  can be realized in the same manner as other Ge concentrates, i.e. reacting the cake with concentrated HCl followed by formation of  $\text{GeCl}_4$ . It can be distilled to required purity level, or – according to improved method - with the use of gaseous hydrochloric acid.[3]

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## 09 PRODUCTION TECHNOLOGIES OF CRM FROM SECONDARY RESOURCES: INDIUM

Metallic indium is commonly applied in electronics, as a component of alloys, connectors and low-melting solders. It is mainly used in form of indium-tin oxide (ITO) in the production of liquid-crystal displays (LCD), light-emitting diodes (LED) or plasma screens, which stands for approximately 84% of total global indium consumption. The rest of indium utilization are: 8% - solders and alloys (with Bi, Cd, Pb, Sn), 5% - semiconductors, 2% - Indium compounds, 1% - others [1].

Since LCDs are most common application of indium, it is necessary to provide an efficient method to recover this element from end-of-life LCD panels and wastes. The most widely-used and most environmentally safe are hydrometallurgical methods, which also have the highest possible efficiency of recovery, due to the relatively low content of this metal in such materials [2].

### 1 PRODUCTION FROM END-OF-LIFE PRODUCTS AND MANUFACTURING RESIDUES

#### 1.1 WASTE LCDS

##### 1.1.1 HYDROMETALLURGICAL APPROACH

Hydrometallurgical techniques are more preferable in contrast to pyrometallurgy, due to the easiness of reaction control, lower cost and smaller pollution rate. First of all, appropriate methods of dismantling of end-of-life LCD panels should be conducted. After that, the leaching stage is applied. The leaching process of such wastes is carried out in hydrochloric acid solution, sulfuric acid solution or aqua regia, at high temperatures (80 – 90°C). Obtained solution contains only a dozen of milligrams of indium per liter. That is why the further processing should be provided.

Before obtaining pure indium products (metal or compounds), some intermediate stage is required to separate selective ions from acidic leach solution. The most common methods are: solvent extraction (SX), homogenous liquid-liquid extraction, and ion-exchange (IX).

##### SOLVENT EXTRACTION

Solvent extraction (SX) is a frequently-used method of compound or metal separation. It consists of two immiscible liquids, usually inorganic and organic, that provide the selective transfer of ions from aqueous phase to organic phase. Afterwards, ions should be washed out or stripped with some inorganic solution from resultant, ion-rich organic solution, producing concentrated solution.

Typical extractants for indium separation are: bis(2-ethylhexyl) phosphoric acid (D2EHPA), tributyl phosphate (TBP), Cyanex 272 or Cyanex 923. An adequate extractant is chosen depending on the acidic solution components and their concentration.

## HOMOGENOUS LIQUID-LIQUID EXTRACTION

The difference between this method and SX is that in homogenous liquid-liquid extraction (HoLLE) organic and inorganic phases are in homogenous state at the beginning of the process. Indium present in the acidic leach solution should be formed into metal chelate with addition of some stimulating factor, which could be: changes of pH, temperature, light or addition of organic compounds like perfluorooctanoic acid (PFOA), acetone or tetrahydrofuran (THF). Then, the phases are separated, and one of the resulting liquids contain most of the indium extracted from the aqueous solution. The scheme of HoLLE process is shown on the Figure below:

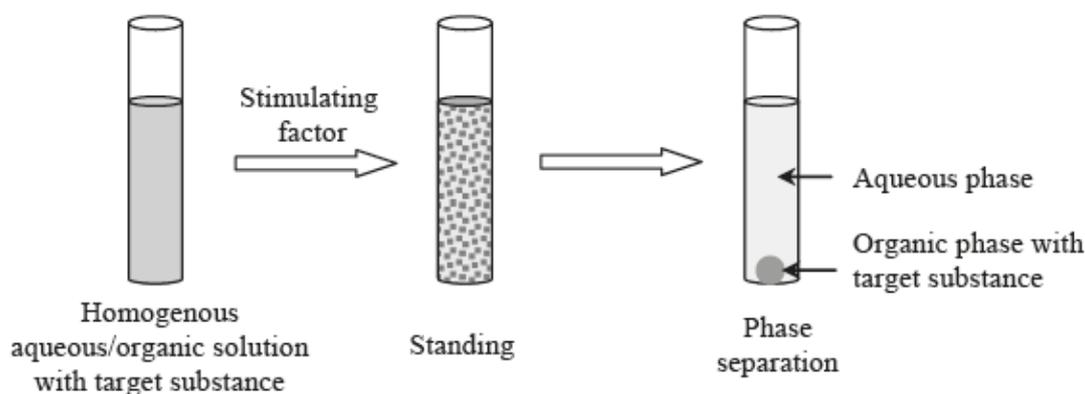


Figure 1 Scheme of HoLLE process.

Decomposition or dissolution methods should be provide to separate indium from obtained liquid solution, but they still need to be investigated by researchers to receive optimal results.

## ION EXCHANGE

solution on the solid phase, which in case of indium separation would be a resin, and then the ionic species is washed out from the ion-rich resin by aqueous phase, producing concentrated solution. There exist some researches made about indium separation by IX techniques, where ion-exchange column could be packed with various resins, such as: XRD-7, Lewatit K-2621, Ionac SR-5, Ionac Sr-12, S950 or Amberlite IR-120P. The selectivity of each resin is the crucial factor while choosing the appropriate resin for the process.

Indium obtained using these techniques, although it may be in a form of indium-rich concentrate, generally exists in form of indium compounds with some impurities. To receive pure product, like metallic indium or pure compounds, some other processes, like chemical precipitation, cementation or electrowinning, should be conducted further.

## CHEMICAL PRECIPITATION

Aluminium and iron show similar precipitation properties to indium. That is why the appropriate agent needs to be chosen in order to precipitate indium from initial solution. Usually In is precipitated from the solution with ammonia or phosphoric acid, forming respectively  $\text{In}_2\text{O}_3$  and  $\text{InPO}_4$ .

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## CEMENTATION

Cementation is a type of precipitation, which is based on the difference in the electrochemical potential of metals. That means the metal ions present in solution are being reduced to solid state, of 0th valence, by addition of other metal of lower standard electrode potential. Since the electrochemical potential of indium is  $E^\circ\text{In}/\text{In(III)} = -0.34\text{ V}$ , mostly magnesium ( $E^\circ\text{Mg}/\text{Mg(II)} = -2.37\text{ V}$ ), but also aluminum ( $E^\circ\text{Al}/\text{Al(III)} = -1.66\text{ V}$ ) and zinc

( $E^\circ\text{Zn}/\text{Zn(II)} = -0.77\text{ V}$ ) are used in this technique. The detailed research about indium cementation was provided by Rocchetti et al., 2016 [4]. They observed that cementation of indium with zinc was an efficient process, however with the increase of time the purity of indium product was decreasing.

## ELECTROWINNING

Indium could be obtained from acid chloride solution in a form of metal of high purity using electrolysis. It is proven by Lee and Oh [5] that initial pH of electrolyte, temperature and current density have negligible effect on current efficiency, which could achieve value of over 90% at current density of  $100\text{ mA}/\text{cm}^2$ , however the initial concentration of indium ions and NaCl needs to be higher than  $50\text{ g}/\text{dm}^3$ . Bisselink and Panjer [6] research concerning indium electrowinning from acid chloride solution, obtained from SX purification established the optimal conditions of this process. To obtain high purity indium ( $\geq 99\%$ ) the electrowinning can be performed at  $-0.8\text{ V}$  vs saturated calomel electrode (SCE) at  $20^\circ\text{ C}$ . The other impurities, such as arsenic, vanadium and zinc remained in the solution.

### 1.1.2 PYROMETALLURGICAL APPROACH

Pyrometallurgical treatment can also be conducted in indium recovery from secondary resources. However, usually it requires multiple stages of high temperatures, which makes this process more complex, with the emission of toxic gases to the environment, which increase the cost of the final product.

## VACUUM CARBON REDUCTION

This technique was implemented in order to produce  $\text{In}_2\text{O}_3$  from blended LCD sample. Research done by He et al. [8], showed that 90% of indium was decomposed, under optimal conditions of  $1223\text{ K}$ , 30wt% carbon addition, and  $1\text{ Pa}$  for 30 minutes. The purity of obtained product, which was  $\text{In}_2\text{O}_3$ , was 99.9%. Proposed by authors reactions of this process are presented below:



## VACUUM CHLORINATION

Method proposed by Ma and Xu [9] consists of two stages: vacuum pyrolysis and vacuum chlorination. For the pyrolysis stage the optimal conditions were:  $300^\circ\text{C}$ ,  $50\text{ Pa}$  and 30 minutes. In vacuum chlorination stage the weight percentage of  $\text{NH}_4\text{Cl}$  to LCD powder was 50wt% and  $450^\circ\text{C}$ . The results of such combination showed that more than 99% of indium was recovered from waste LCD powder. However, the combination of these

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processes was not reported on industrial nor pilot scale. The scheme of this process is shown on the Figure below:

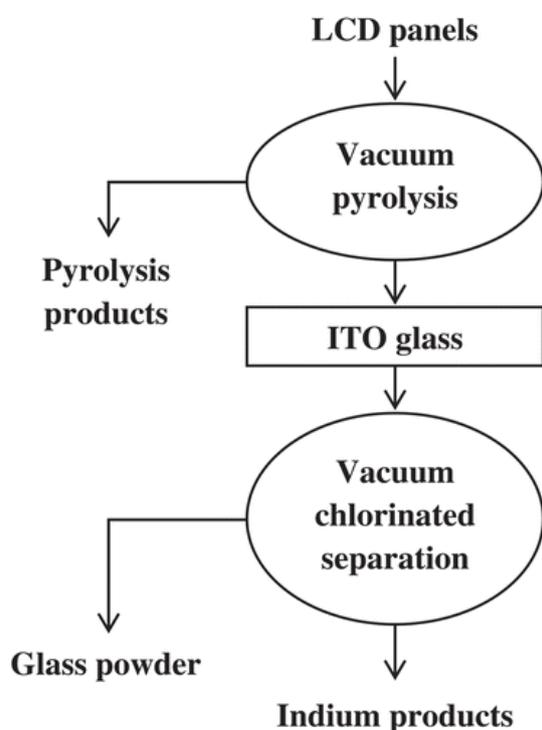


Figure 2 Flow sheet of a process proposed for recycling of waste LCD panels.

The literature overview showed that hydrometallurgy has better advantages over pyrometallurgy in indium recovery from secondary resources processes. The main methods in both of those treatments were described above, but there are also other existing techniques that could be implemented in indium recovery, such as alkali leaching, bioleaching, super- and subcritical fluid extractions or isothermal decomposition [7].

## 1.2 SUMMARISED DISCUSSION ON PRODUCTION OF INDIUM FROM EOL PRODUCTS AND MANUFACTURING RESIDUES

The literature overview showed that hydrometallurgy has better advantages over pyrometallurgy in indium recovery from secondary resources processes. The main methods in both of those treatments were described above, but there are also other existing techniques that could be implemented in indium recovery, such as alkali leaching, bioleaching, super- and subcritical fluid extractions or isothermal decomposition [7].

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# 10 PRODUCTION TECHNOLOGIES OF CRM FROM SECONDARY RESOURCES: MAGNESIUM

## 1 SECONDARY RESOURCES OF MAGNESIUM

Magnesium metal is a highly recyclable material, consuming only 5% of the energy required to manufacture the primary metal. Currently only high quality magnesium scrap can be recycled easily into high purity alloys. In typical magnesium die casting operations, only around 50% of the metal input is converted into components. The residual implies scrap descending from different stages of the die casting process. Casting return material can contain biscuits, sprues, runners, flash, overflows, dross, sludge, scrap parts and uncoated rejects from a later step in the finishing process. If a magnesium part is to perform satisfactorily in a particular application, it has not only to be designed to meet the mechanical requirements but environmental factors, finishing and assembly methods must also be properly considered. <sup>[1]</sup>

Although magnesium is mainly produced from primary resources, there is a significant recycling of secondary resources. The materials flow study of magnesium, as shown in figure 1, is intended to provide a snapshot of the U.S. magnesium recycling industry in 1998.

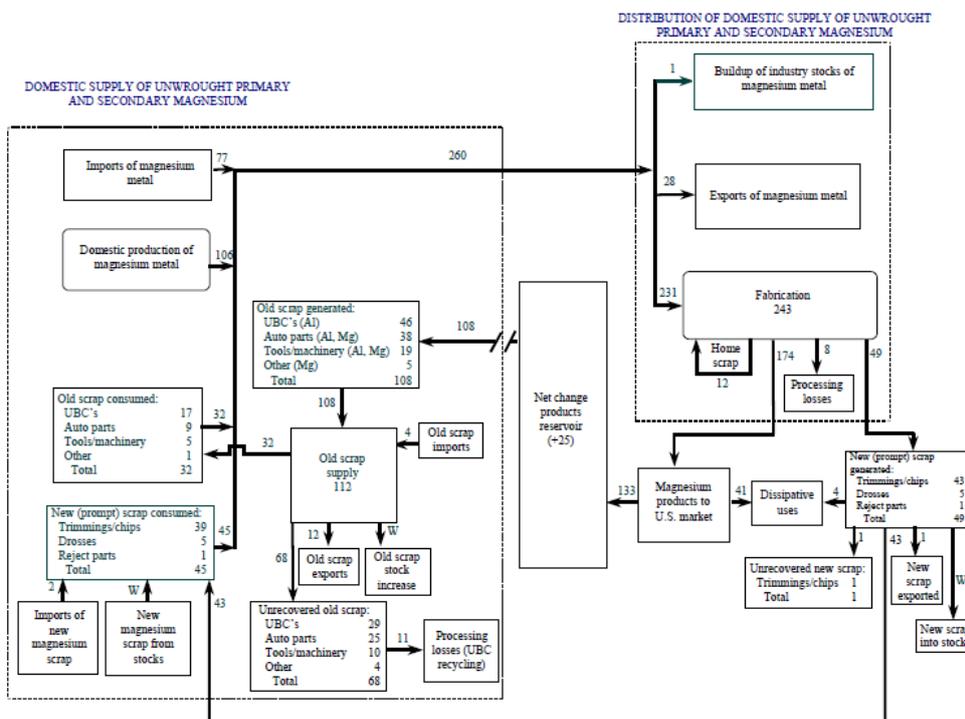


Figure 1 Magnesium recycling flow in United States in 1998. (Figures in thousand metric tons contained magnesium. UBC's, used beverage cans. <sup>[2]</sup>)

## 2 MAGNESIUM PRODUCTION FROM SECONDARY RESOURCES

The majority of scrap is of various magnesium-aluminum alloys which can be reprocessed to a specified composition without much difficulty. A significant volume of magnesium alloys containing zirconium, rare-earth metals, etc. requires physical separation and separate treatment since its admixture with magnesium—

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aluminum alloys degrades both alloy types. <sup>[3]</sup> In 2003 the European Mg-Recycling industry had an installed a capacity of 75,000 ton per year. <sup>[1]</sup>

Magnesium may also be recovered by recycling magnesium chloride produced in the manufacture of titanium. Titanium is recovered from titanium tetrachloride ( $TiCl_4$ ) by the Kroll process, in which magnesium is used as a reducing agent. This reaction produces a pure anhydrous magnesium chloride that can then be fed to an electrolytic cell to convert it back to magnesium metal. <sup>[2]</sup> This recovered magnesium chloride may be used in the feed to the electrolysis of magnesium.

New magnesium-base scrap typically is categorized into different types accordingly to contamination. Type I is high-grade scrap, generally material such as gates, runners, and drippings from diecasting operations that is uncontaminated with oils. Types II, III, and IV are lower graded materials. Type II is oil-contaminated scrap, type III is dross from magnesium-processing operations, and type IV is chips and fines. The most desirable type of scrap is type I. Most of the type I scrap is generated during die-casting magnesium alloys. This scrap is either re-melted at the die-casting facility or sold to a scrap processor. The other types of scrap are either sold to a scrap processor or are used directly in steel desulfurization. <sup>[2]</sup>

Significant quantities of magnesium are contained in aluminum alloys that also can be recycled. Some magnesium is lost in scrap processing, but a significant quantity of the magnesium is recycled with the aluminum alloy. New aluminum-base scrap that is recycled consists is primarily of solids, borings and turnings, dross and skimmings, and other material, e.g. foil and can-stock clippings. Because the main aluminum product that contains magnesium is beverage cans, the principal magnesium-containing, aluminum-base scrap is can scrap skeleton from lids and can sheet clippings. Old aluminum-base scrap consists of a variety of materials, but the most important magnesium-containing component is used aluminum beverage cans (UBC's). Because of the high recycling rate (about 63 percent in 1998 in the United States), UBC's represent about three-quarters of the magnesium-containing, old aluminum-base scrap that is reprocessed. The magnesium in old and new aluminum-base scrap is not separated from the aluminum alloy when it is recycled; rather, it is retained as an alloying component. Therefore, the magnesium recycling industry consists of three main components—old and new magnesium-base scrap, UBC's, and new aluminum-base scrap. In some cases, the new and old aluminum-base scrap is recycled together. <sup>[2]</sup>

At the magnesium recycler the scrap is visually inspected. Because of the resemblance of magnesium and aluminum scrap one of the ways to separate the magnesium from the aluminum scrap is by scratching the metal with a knife. Magnesium tends to flake, whereas the softer aluminum tends to curl. After separating the aluminum-base scrap and any other foreign material, the magnesium scrap is sorted according to alloy.

The sorted magnesium scrap is charged into a steel crucible and heated to approximately 650-700°C so the metal will melt. More scrap will be added and the liquid metal is covered with flux or inhibitive gas ( $SF_6$  or  $SO_2$ ) to prevent reaction between the magnesium and the oxygen in the air. Then the melt is alloyed with e.g. aluminum and manganese, and casted into ingots or die-casted.

### 3 MAGNESIUM RECOVERY RATES

USGS reported that 80 000 ton of magnesium was recovered in 2015. It can be showed in fig.2 that the aluminum recycling, including UBS:s, stands for about three quarters of the total recycling. <sup>[4]</sup>

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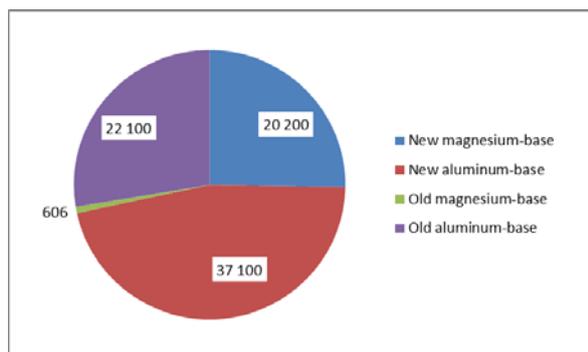


Figure 2 Magnesium recovery from scrap processed in the United States 2015. <sup>[4]</sup>

UNEP reported <sup>[5]</sup> magnesium recovery estimates of functional recycling of 39%, i.e. the ratio of recycled EOL magnesium (old scrap) to produced magnesium containing products. The recycled content, i.e. proportion of recycled magnesium to the total production of magnesium metal was estimated to 33%.

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## 11 PRODUCTION TECHNOLOGIES OF CRM FROM SECONDARY RESOURCES: NATURAL GRAPHITE

### 1 SECONDARY RESOURCES OF NATURAL GRAPHITE

The use of natural graphite in many products is dissipative and this means that a large portion of the natural graphite is lost in the environment. According to the value chain of natural graphite shown in D4.1, potential secondary resources for natural graphite recovery include:

- (i) Middlings and tailings.
- (ii) Manufacturing residuals.
- (iii) End-of-life products, mainly including products for refractories, foundries, brake linings and batteries.

### 2 NATURAL GRAPHITE PRODUCTION FROM SECONDARY RESOURCES

#### 2.1 NATURAL GRAPHITE FROM MIDLINGS AND TAILINGS

The natural graphite ore is concentrated by the multi-stage comminution-flotation process, during which middlings and tailings are generated. A part of these middlings/tailings can be reprocessed by screening-comminution-flotation to recover graphite. However, a part of these is rejected as wastes anyway due to high content of impurities. These rejected part, mainly tailings, are normally used as building materials to produce bricks and cement.[1]

#### 2.2 NATURAL GRAPHITE FROM MANUFACTURING RESIDUALS

There is no information found regarding the recovery of the graphite residuals that generated during the manufacturing process. However, it is believed that most of these residuals are likely to be recovered in-house. As on one hand collecting of these residuals is normally easy by the processors and on the other hand the graphite concentrate in the residuals can be quite high, thus it is economic to recover these materials.

#### 2.3 NATURAL GRAPHITE FROM SPENT REFRACTORIES

The spent refractories are normally used as roadbed materials or sent for landfill, thus these spent refractories are not used as their original purposes or the useful components (e.g. graphite) are not used properly. In one publication it is reported that the MgO-C refractories can be used as foaming agent in the EAF because of their high MgO content.[2] Obviously, the graphite in the refractories in this practice is not recycled either.

According to the literature it is possible to use the spent refractories to produce new refractories, i.e., to recycle the refractories. A conceptual flowsheet for the recycling of refractories is shown in Figure 1. The key processing steps for the recycling include:

- (i) Collecting, sorting, categorizing of the spent refractories;
- (ii) Crushing and pulverization of the spent refractories;
- (iii) Removing of the iron and slag;

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- (iv) Sieving to get the suitable particle size;
- (v) Using the recycled materials to manufacturing new refractories.

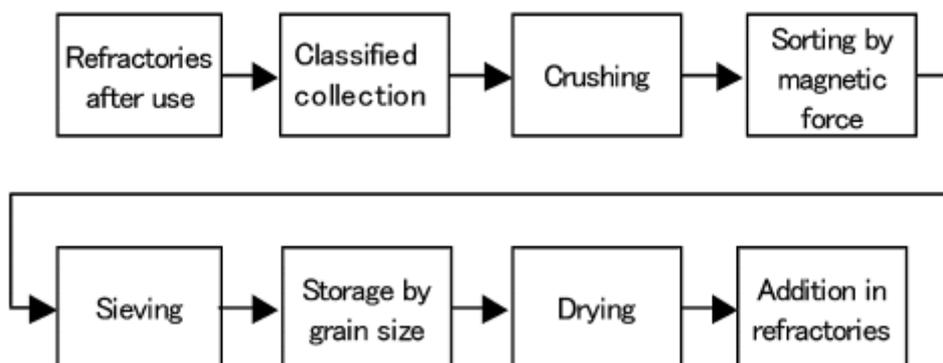


Figure 1 Conceptual flowsheet for the recovery of spent refractories.[3]

## 2.4 NATURAL GRAPHITE FROM SPENT BRAKE LININGS

Friction liners (disc brake liners or drum brake liners) are mainly used in vehicle brakes. The volume of friction liners produced in Europe amounts to 150000 tonnes/annum. The friction liners are only used to approximately 50% before it needs to be replaced. Therefore, every year up to 75000 tonnes of used friction liners are produced. These spent materials are normally disposed as hazardous waste or partially smelted to low quality steel. It is reported that these recycled friction liners can be used to produce new friction liners, thus the graphite in the liners is recycled as well. [4]

## 2.5 NATURAL GRAPHITE FROM SPENT LITHIUM ION BATTERIES

Flake graphite is one of the critical materials for batteries, especially for lithium ion batteries (LIBs). Due to the future market growth of lithium ion batteries for vehicular applications, the consumption of the graphite will be huge. Recycling materials (including graphite) from the spent lithium ion batteries is important to ensure a circular economy. At the moment, there is no reported industrialized process to recycle graphite from the spent lithium batteries; however, it may be technological implemented by the following processing steps.[5]

- (i) Disassembling the LIBs and taking out the graphite electrode plates followed by washing them with an organic solvent to remove collected residue electrolyte from the surface of the electrode.
- (ii) Drying of the plates for evaporation of the solvent.
- (iii) Soaking the dried graphite electrode (from previous step) into HCl acid solution under ultrasonic vibration to separate the graphite film from the copper foil and membrane completely. Moreover, the acidic solution step purifies graphite from the by-products of charge–discharge cycles, solid electrolyte interface layer, and carboxy methyl cellulose (CMC) thickener.
- (iv) Separating the graphite powder from the acidic solution by centrifuging, rinsing, and drying.
- (v) Sieving, polishing, and preparing a negative electrode material from the dried powder to be inserted in a new battery.

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## 12 PRODUCTION TECHNOLOGIES OF CRM FROM SECONDARY RESOURCES: NIOBIUM

### 1 OVERVIEW OF GLOBAL PRODUCTION OF NIOBIUM AND AVAILABLE SECONDARY RESOURCES

Primary niobium reserves are located mostly outside of Europe, with an exception for deposits in Norway and Finland, but their extraction is presently not economically feasible (Makanyire, Sanchez-Segado, & Jha, 2016). Therefore, providing niobium supplies to EU is relying solely on import. The only possible raw material source within Europe is from secondary production. Average global production of primary niobium reached 113000 tonnes in period 2010-2014. The biggest producer of niobium is Brazil, with the 95% of global extraction and 90% of global refining shares and main actors CBMM and Mineração Catalão de Goiás. Second relevant producer is Canada with 4% of total global production of this metal and main actor IAM GOLD. For the remaining 1 % account other seven non-European countries (European Commission, 2017; Yang & Ye, 2016).

Niobium is a metal that is mostly used in production of ferroniobium, which is needed in high strength low-alloy (HSLA) steel production, with final application in automotive, oil and gas pipelines and ship hulls construction. It is also a component of stainless steel and super alloys, which are used in nuclear and aerospace industries, superconducting magnets, capacitors, catalysts and chemical products. All types of steel account for around 86% of European niobium consumption, which is on average 12500 tons per year (European Commission, 2017). Niobium is also used in electronic devices (PCB), optic glass and lenses. Those are the main expected waste streams for secondary raw material. Figure 1 shows main global end use sectors of niobium.

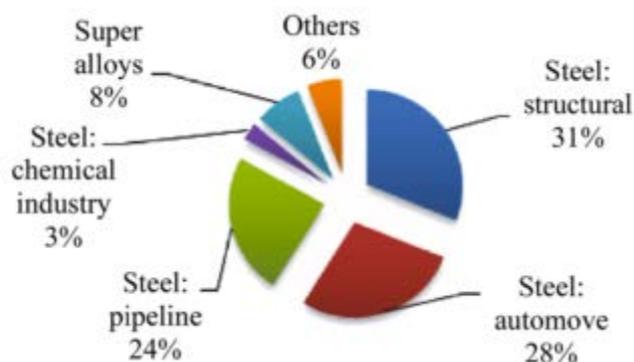


Figure 1 Global end use of niobium in 2010. (Makanyire et al., 2016)

The identified available secondary resources for Nb recycling and recovery are listed below.

- (1) Processing waste and historical waste
  - Slag and sludge from tin plants
  - Mine tailings
  - Slag from metal production
- (2) Urban mines and manufacturing residues
  - Steel containing Nb
  - Super alloys

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- Cemented carbide
- Scrap and waste of fine ceramics
- Spent catalysts
- E-waste

## 2 PRODUCTION OF NIOBIUM FROM SECONDARY RESOURCES

Secondary niobium can be found in two main types of sources: in waste from processing the material containing niobium as well as in end of life products from urban mines and manufacturing residues. Figure 2 below presents a general overview of niobium production and processing from both primary and secondary resources.

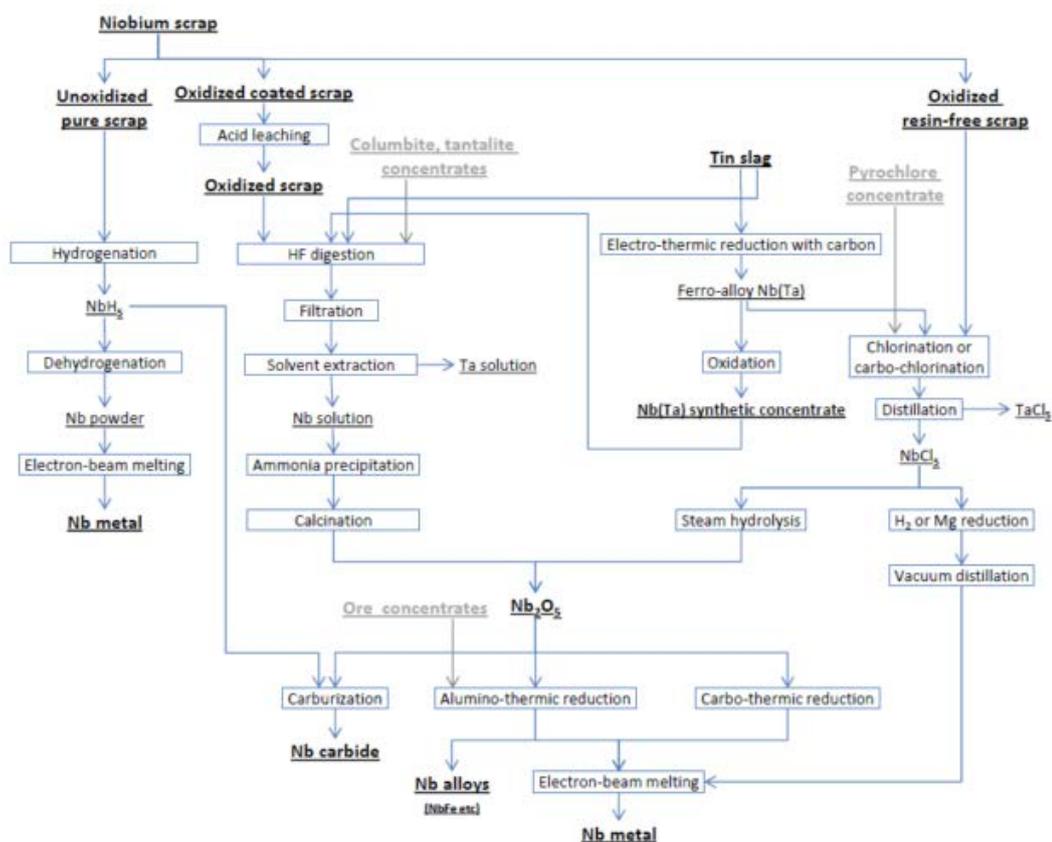


Figure 2 General flowsheet for primary and secondary niobium processing/production. (Sundqvist Oeqvist et al., 2016)

### 2.1 PROCESSING WASTE AND HISTORICAL WASTE

#### 2.1.1 SLAG AND SLUDGE OF TIN PLANTS

Slags of tin plants contain 4-12% or often more  $Nb_2O_5$ . Those resources can be located in Thailand, Nigeria and Malaysia among others (Nikishina, Drobot, & Lebedeva, 2014). However, the production of niobium from tin

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slag is estimated as less than 2% of total global production. Presently, tin slag is not being processed in the industry, since extraction of selective niobium is complicated and is dependent on slag composition (Sundqvist Oeqvist, Ye, Hu, & Yang, 2016).

One of the methods to recover niobium from slags of tin plants is chlorination of the raw material, used also for primary niobium production. Chlorination takes place with carbon and results in obtaining a condensate of oxychlorides and chlorides of niobium (Nikishina et al., 2014). Chlorination at 1000°C of high grade tin slag resulted in extraction of 84% niobium, where carbochlorination at 500°C completely recovered pure niobium compound (Sundqvist Oeqvist, 2016). Chlorination method is known to recover valuable materials in a form suitable for further processing.

Acidic method can be applied as well, by decomposition of concentrates using HF or a mixture of HF and H<sub>2</sub>SO<sub>4</sub>. Niobium can be recovered from created solution by separating it from other materials, usually by extraction (Nikishina et al., 2014). One of the processes has been used to treat slag from Iscor tin plant in South Africa, containing 9% of Nb<sub>2</sub>O<sub>5</sub>. This technique uses magnetic separation of granulates of iron-tin alloy, together with hydrochloric acid and leaching with caustic soda. Another study was undertaken in Thailand, Zaire and Indonesia, which included upgrading the content of niobium and tantalum by alkali and acid leaching treatment and chlorination of leached residue. As a result of this method, upgraded oxides were obtained, containing 60% of niobium-tantalum oxides, which after chlorination resulted in almost pure niobium and tantalum condensates (Sundqvist Oeqvist et al., 2016).

Recovery of niobium from sludge is possible with several processes; one of them is direct dissolution with presence of HF. This method is however difficult and is not preferred due to tungsten interference with the solvent extraction (Sundqvist Oeqvist et al., 2016).

### 2.1.2 MINE TAILINGS

There are reported substantial reserves of niobium that can be found in tailings from ore mines.

In Europe, the biggest recovery potential from mine waste dump is in Macedonia and Greece. Macedonian mine is used for extraction of multiple minerals, for instance Chalcopyrite, Cuprite, Magnetite, Pyrite, Tenorite. Reserves of niobium in the mine waste is estimated at up to 313,3 tons. In Greece, the potential is lower, estimated at 65,5 tons of niobium distributed between 7 locations in the northern part of the country. Those resources come from slag waste in former refinery plants or smelters. In Sweden, waste tailings from iron mines Kiruna and Svappavaara are potential secondary resource of niobium with concentration 11,9 ppm. There are other possible sources of niobium from mine products, waste and ore processing waste located at surface storages of inactive plants in France, Norway and Portugal. However, the data on possible niobium concentrations is not available (Cuesta-Lopez et al., 2016).

Another secondary source is placed in Brazil in the phosphate mining plant Anglo Copebrás in Ouidor. The project aims to recover Nb from phosphate tailings, which can result in niobium production increase of 30% (Sundqvist Oeqvist et al., 2016). Another possible secondary resource is Bayan Obo mine in China, known of the large rare earth metals deposit, with niobium minerals average grade of 0,13%. During the ore production niobium is not recovered, therefore large amounts of tailings with niobium are created. There are many issues connected with niobium recovery from mine tailings. Major complications associated with this process are due to complex composition of minerals, fine-grained dissemination and low grade. Figure 3 presents a new approach for niobium separation and extraction from Bayan Obo mine (Sundqvist Oeqvist et al., 2016).

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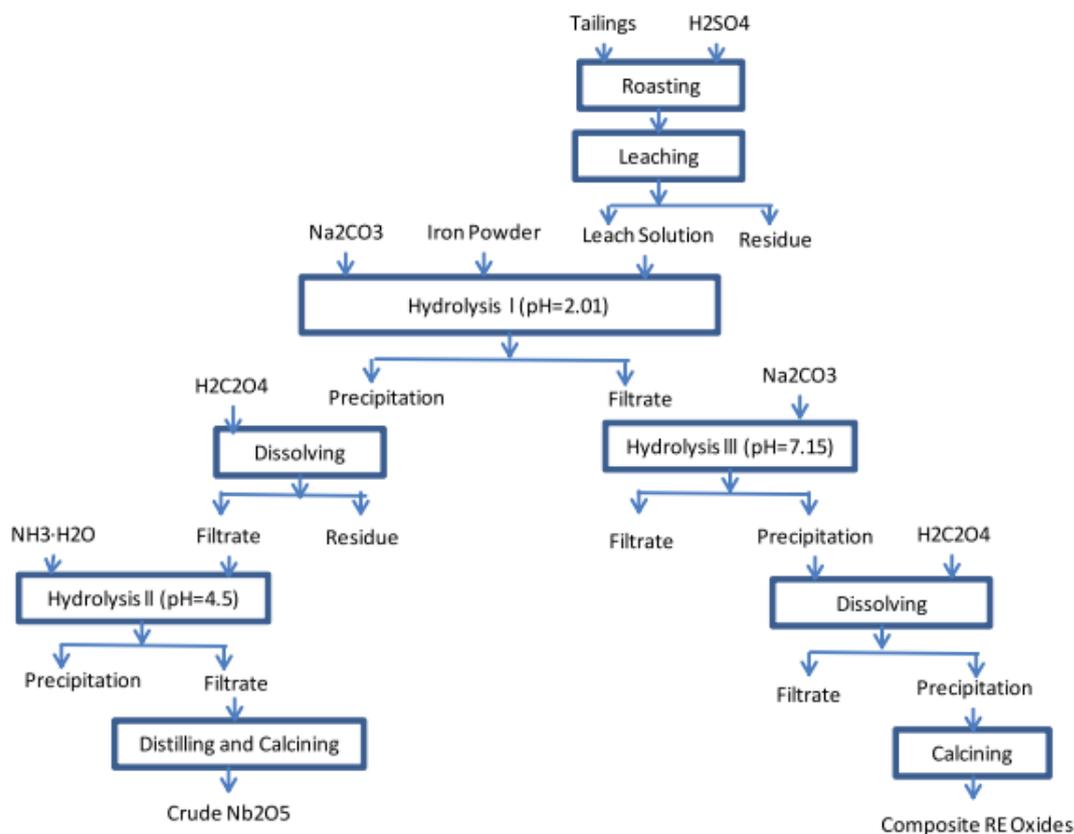


Figure 3 New approach for niobium recovery from Bayan Obo tailings. (Sundqvist Oeqvist et al., 2016)

Several techniques were developed for niobium recovery from tailings. For instance, a sequence of smelting reduction, followed by selective oxidation, dephosphorization and finished with smelting. Pyrometallurgical processes were not possible to apply on a big scale, since recovery by existing metallurgical processes is very difficult. Therefore, a new hydrometallurgical process was introduced. The process of Nb recovery together with rare earth elements starts with extracting them from polymetallic minerals into leach solution by sulphating roasting at temperature 250° C and then leaching at 60° C. Consequently, niobium can be precipitated from the solution after reduction of Ti and Fe ions with iron powders and hydrolysis. The product is ready after removing impurities with acid mixture. The recovery of niobium (60,67 wt% Nb<sub>2</sub>O<sub>5</sub>) from this method can be up to 78% with additional reduction of energy consumption and production cost (Zhang, Liu, Li, & Jiang, 2014)

### 2.1.3 SLAG FROM METAL PRODUCTION

Another secondary resource of niobium can be slag from basic oxygen furnace (BOF). The slag comes from metal production in Baotou Steel China, where Bayan Ore is used. The hot metal includes 0,015-0,034% of niobium, which is mostly oxidised into the slag, where niobium oxide constitutes for 0,2-0,3% Nb. The slag reserves from BOF are estimated as 1,5 million tons per year, which are stored on the site. So far, no promising project was developed to recover those reserves (Sundqvist Oeqvist et al., 2016).

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Residuals from hard metals manufacturing, namely grinding slurries, pressing wastes, drilling pits and cutting inserts can be further processed for niobium recovery. The worldwide estimation of niobium recycling potential is 700 tons, based on tungsten carbide global use. Treatment of hard metal scraps with direct recycling methods makes the material phases recirculate. In indirect methods niobium gets partially dissipated in solid waste, or can be recovered beside other materials (Sundqvist Oeqvist et al., 2016).

## 2.2 URBAN MINES AND MANUFACTURING RESIDUES

### 2.2.1 STEEL CONTAINING NB

Presently, the biggest source of Nb is HSLA and stainless steel. End of life vehicles are presently the most important source of steel containing niobium, since their life span is relatively short, comparing to other applications. A new way to recover more niobium from end of life vehicles is to separate exhaust part and suspension parts from the rest of ferrous metals. The steel for exhaust production contains 0,03-0,3% of niobium, while the vehicle body only 0,02-0,05% (Kurylak, 2016). Therefore, proper separation can be a successful way to increase recovery rate of niobium.

Niobium is not recovered in pure form from stainless steel containing it. The concentration of niobium in stainless steel is 0,04-0,08% (Yang & Ye, 2016). New scrap containing niobium comes mostly from manufacturing of steel and steel products, which is collected and directly re-melted into new stainless steel (Kurylak et al., 2016a) by electric arc furnace and refining in argon oxygen decarburization.

HSLA steel contains about 0,05% niobium (Yang & Ye, 2016). Metallurgical processes used for niobium recovery from steel scraps, also known as microalloys, are the same as for steel production techniques, namely basic oxygen furnace and electric arc furnace. The life span of pipelines for gas and oil, which are the main applications of HSLA, is around 60 years. This means in the near future those products after their end of life may provide a high supply of niobium bearing scrap (Kurylak, 2016).

However, the issue with obtaining high recovery rates of niobium is the fact, that during recycling of high strength steel, as well as stainless steel, around 0,05% of niobium can be oxidised in a slag and eventually lost (Kurylak et al., 2016a).

### 2.2.2 SUPER ALLOYS

Similarly as with steel, niobium is usually not recovered as a mineral from super alloys, therefore the scrap is mostly used to produce more super alloys, by re-melting them together with new material (Kurylak et al., 2016a). Processing of super alloy scrap is usually complex, due to the presence of multiple different alloying elements. What is more, the re-melting technique can lead to 20% loss of valuable alloying material due to oxidation (Kurylak et al., 2016). However, due to high value and use of many critical materials, super alloys scrap is extensively recycled (Kurylak et al., 2016a). Super alloys can contain 3-5,5% niobium, which is the highest concentration comparing with HSLA and stainless steel (Yang & Ye, 2016). Globally about 60-70 tons of niobium per year is used for production of superconducting alloys (Nb<sub>3</sub>Sn, NbTi), however the scale of waste from end of life superconductors is not available. On a laboratory scale one method of niobium recovery from NbTi residues was developed, including chlorination and electrochemical copper winning (Sundqvist Oeqvist et al., 2016).

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Reprocessing of the super alloys can be performed in three ways: pyrometallurgy, hydrometallurgy or a combination of both. The exact recycling route depends on alloy's composition and there is no route specified for niobium (Kurylak et al., 2016). Hydrometallurgical extraction can be done using organic solvents. There are multiple organic solvents that can extract the niobium, yet only few processes are used in the industry, namely processes based on tri-butylphosphate, ketones (MIBK and cyclohexanone) and 2-octanol (Sundqvist Oeqvist et al., 2016).

From pyrometallurgical extraction methods, chlorination deserves more attention. It is a process suitable for breaking down ore concentrates of refractory metals, but also for purification and separation of many other elements that can be found in concentrates as well as for reduction to metallic forms. In case of niobium, during the chlorination other chlorides or oxychlorides can be formed. The product of chlorination reaction can be  $NbOCl_3$  and  $NbCl_5$ . Chlorination can be performed in multiple reactors systems, of which most popular is fluidized bed type (Sundqvist Oeqvist et al., 2016).

Research has been done on materials recovery from super alloy scrap using double membrane electrolytic cell (DEMCC). First, the super alloy scrap is melted, carburized, turned into anodes before being brought to DEMCC. After that, the material is undertaking a series of treatment processes to recover different metals. The process flow chart is described in Figure 4. Although the process described does not separate niobium, it could be expanded by niobium recovery stage (Kurylak, 2016).

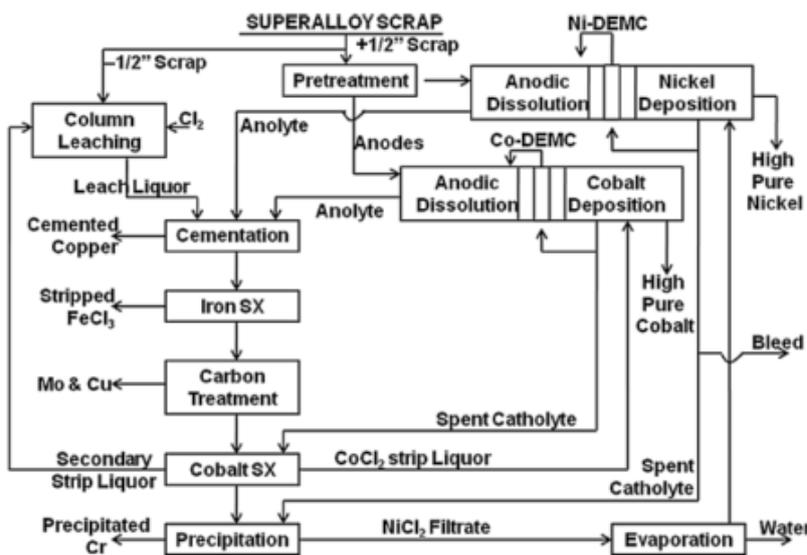


Figure 4 Recycling of super alloy scrap using double membrane electrolytic cell. (Kurylak, 2016).

### 2.2.3 CEMENTED CARBIDE

Scrap from fabrication and cemented carbide tool industries that is well characterized and uncontaminated can be directly reused within the industry for the same purpose with minimal additional processing. The scrap of cemented carbide tools is made of alloy carbide (WC-TaC-NbC) that is cemented with cobalt, can be reused after their separation by treatment with molten zinc. However, if the scrap is contaminated or not well classified, it required chemical processing for constituents' recovery (Sundqvist Oeqvist et al., 2016).

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Typically, the carbide sludge can contain 5,6% niobium (Sundqvist Oeqvist, 2016). Recover of niobium from carbide sludge can be performed similarly to sludge from tin plant. However, for carbide sludge a new scheme has been established (Figure 5), including alkali leaching, acid leaching, soda ash roasting and aqueous processing, which resulted in 48 g/l of niobium in solution. Niobium was then recovered from solution by precipitation with ammonia gas. The overall recovery of niobium was estimated as 85-90%. (Sundqvist Oeqvist et al., 2016).

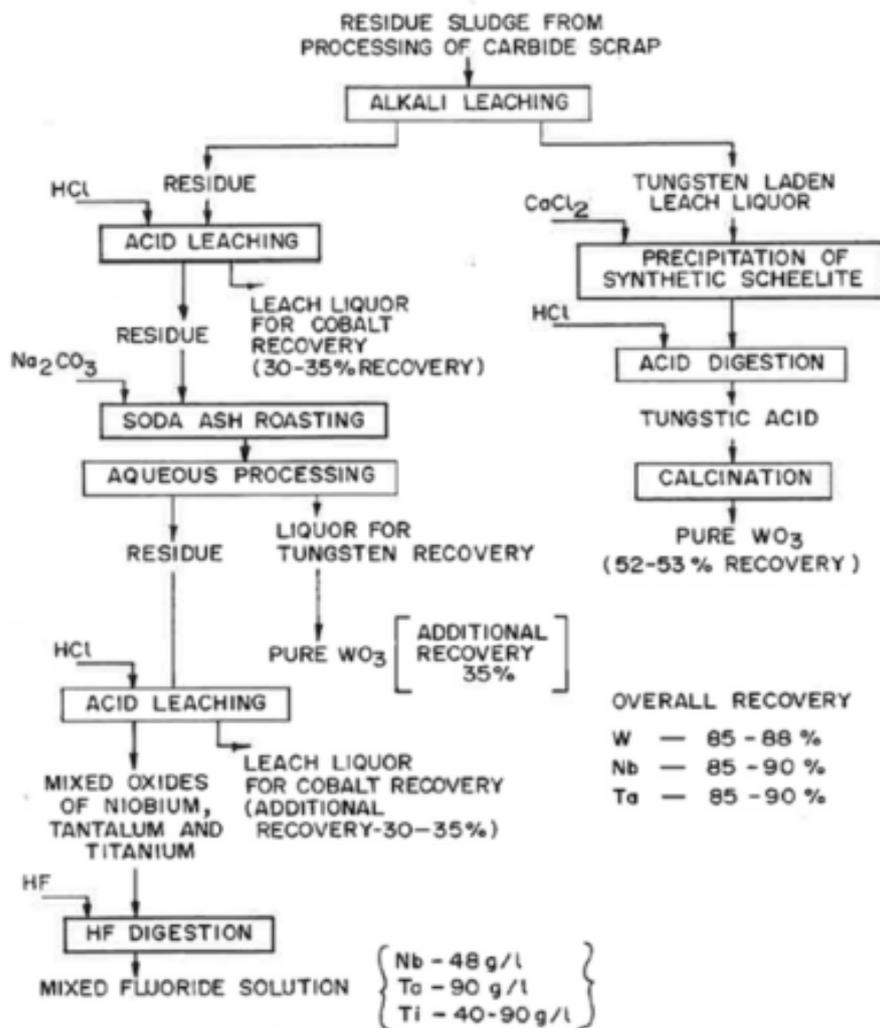


Figure 5 Flowsheet of niobium and other materials recovery from carbide sludge. (Sundqvist Oeqvist et al., 2016)

## 2.2.4 SCRAP AND WASTE OF FINE CERAMICS

Fine ceramics containing niobium are used as:

- structural materials in capacitors for optical lenses, ceramic condensers and electronics,
- functional, heat and abrasion resistant materials used in engines, tools (Witold Kurylak et al., 2016)

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A substantial quantity of waste containing Nb is originated from niobium electrolytic capacitors industry, usually in form of obsolete scrap. The amount of niobium that can be potentially recovered reaches 8-37,5%. Niobium can be recovered by chlorination of ferroniobium, resulting in condensate of niobium pentachlorides, which can be further separated by applying rectification. Other commonly used method is hydrometallurgy (Nikishina et al., 2014).

### 2.2.5 SPENT CATALYSTS

Niobium is widely used in catalysts, however the data on amounts spent on this application is missing. Consequently, the recycling potential cannot be estimated. What is more, currently no industrial recycling technologies are known (Sundqvist Oeqvist et al., 2016).

### 2.2.6 E-WASTE

Niobium can be also found in electronic waste, as a constituent of alloys, coatings that protect from corrosion and abrasion as well as structural ceramics. In form of an oxide it is used in computer screens, TV receivers and cameras. It is estimated that a computer can bear 0.0002 wt% of niobium in the housing and welding alloy, which creates a potential of 1.2 tonnes of niobium from end of life computers in the EU. Small portable storage devices can contain 0.25 wt% niobium (Kurylak, 2016). Niobium can be recovered from printed circuit boards (PCB) of discarded computers, since PCB is the part of electronic waste, where concentration of critical metals is higher than other components. The average content of niobium in scrap PCB is 36 g/ton. (Kurylak et al., 2016). Recovery method that can be applied is called leaching column, which uses sodium cyanide solution. From an experiment using this method, 48.1% Nb was recovered in solution, from where 98.2% of niobium was recovered with activated carbon (Kurylak, 2016).

Presently, niobium is not being recovered from waste electronic equipment due to very low concentrations and high costs (Kurylak et al., 2016), even though in EU there are already collection and separation schemes in place dedicated for such waste. However, increasing amount of electronic equipment entering the market contributes to higher content of niobium as well as other critical materials in waste streams. This, together with increasing collection and separation rates can lead to increased recovery rates of niobium in the future.

## 3 CURRENT RECOVERY RATES

The niobium recovery is rather low, since not more than 20% of this metal is being sourced from recycled materials (Mackay & Simandl, 2014). The end of life recycling input rate for niobium is negligible, estimated at 0.3% (European Commission, 2017). It is probable, that niobium is recycled exclusively from manufacturing scrap (Kurylak et al., 2016a).

Since no data is available for Europe, US statistics can serve as a reference for estimating recycling rates for niobium in EU. As of 1998, the recycled content for niobium in the US was 22%, which is 12% and 10% for old and new scrap respectively. End of life recycling rate for old scrap is 33%, remaining 50% is being lost and 17% is categorised as export. The old scrap ratio is 55% and recycling and reuse is 45-50% for old and new scrap (Yang & Ye, 2016).

## 4 KEY ACTORS IN NIOBIUM RECOVERY

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One of the companies working with critical materials is German H.C. Starck, who processes used materials in order to recover niobium as well as other refractory metals. Residues from production and processing, slags, sludge, super alloys and scrap are recycled into addition for alloys nickel niobium, pure niobium or metal oxide, ready for reuse. The details of internal niobium recycling process are not publicly accessible. The main types of processes implemented in the recycling system of H. C. Starck include mechanical separation, thermal treatment and chemical processing. In mechanical separation, undesired parts are removed from scrap bearing precious metals by milling and other separation techniques. Part of the obtained secondary raw material can be used directly in production. In thermal treatment, scrap and metal powders are melted using electron beam, subsequently material is solidified in a skillet. The product can be further treated with forging, cutting and rolling. Chemical processing includes dissolving material in acid and caustic solution and chemical cleaning to remove impurities (H. C. Starck, 2012).

## 5 CHALLENGES IN MATERIAL RECOVERY

One of the challenges connected with recovery of niobium is not sufficient attention paid to steel scrap composition during recycling processes. The outcome of that is dilution of this element into lower grade material, or lost in slag, if not recovered at later stage. The way to improve the recovery of niobium is to implement more accurate sorting system of steel scrap, depending on the material composition of alloyed elements (Kurylak, 2016).

Since niobium is used mostly in steel manufacturing, its future demand trends will most likely follow those of steel production. Therefore, recycling rates of steel containing niobium will determine the scale of recovery of this metal (Kurylak et al., 2016a).

Separation of niobium from tantalum using solvent extraction usually involves fluorides, since recovery of pure elements is very difficult without them. However, fluorides are responsible for substantial environmental pollution and additionally they increase operational costs of recovery (Sundqvist Oeqvist et al., 2016). Other issues connected with hydrometallurgical processing of niobium and tantalum concentrates are large amounts of residues, loss of reagents, and solid waste amounts over an order of magnitude higher than the useful product (Sundqvist Oeqvist, 2016).

Substitution of niobium is generally possible; however, it may involve lower performance and/or higher price of the end product. Niobium can be substituted in HSLA steel with molybdenum and vanadium, in stainless steel with tantalum and titanium and in high temperature applications with molybdenum, ceramics, tantalum and tungsten (Setis, 2016).

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the EU ( urban mines ).

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## 13 PRODUCTION TECHNOLOGIES OF CRM FROM SECONDARY RESOURCES: PGMs

Platinum group metals (PGMs), constituting of platinum, palladium, rhodium, iridium, ruthenium and osmium, are appreciated for their resistance to corrosion and oxidation, high melting points, electrical conductivity and catalytic activity, which are the properties urging their wide use in industrial applications. (Deplanche et al. 2011) The major application areas of PGMs are listed in Table 1.

Table 1 Some important application areas for platinum group metals. Adapted from (Hagelüken 2012), supplementary information from (JM 2017b; IPA 2017a; Umicore 2017a).

Application area	Platinum	Palladium	Rhodium	Iridium	Ruthenium	Osmium
Catalysts	✓	✓	✓	✓	✓	✓
Electronics	✓	✓		✓	✓	✓
Fuel cells	✓	✓	✓		✓	
Glass, ceramics and pigments	✓		✓	✓		
Medical and dental	✓	✓		✓		✓
Pharmaceuticals	✓	✓			✓	
Photovoltaics					✓	
Superalloys					✓	

### 1 RECYCLING RATES OF PGMs

The PGMs are highly recyclable in technical terms due to their noble characteristics, which means that over 95% recovery for platinum and palladium can be achieved once the scrap containing PGMs reaches a state-of-the-art refining facility. PGMs are refined together with other precious metals, gold and silver. (Hagelüken 2012) The attainable metallurgical yields for rhodium, iridium and ruthenium are somewhat lower but still high. (Gunn 2014) Currently, literature does not acknowledge osmium being recycled in an industrial scale. Technical challenges in the recycling of PGMs do still exist, but the main barriers to recycling of PGMs lie in ensuring the collection of the EoL scrap and in recycling chains around the world. (Hagelüken 2012)

The global averages of EoL recycling rates, and the sector-specific recycling rates for each PGM are presented in Table 2.

Table 2 Estimated global EoL recycling rates of PGMs for the main end-use sectors. Adapted from (UNEP 2011).

PGM	Total EoL recycling rate (%) <sup>1</sup>	Sector-specific EoL recycling rate (%)					Jewellery, coins, medals (%)
		Vehicles <sup>2</sup>	Electronics	Industrial applications <sup>3</sup>	Dental	Others <sup>4</sup>	
Platinum	60-70	50-55	0-5	80-90	15-20	10-20	90-100
Palladium	60-70	50-55	5-10	80-90	15-20	15-20	90-100
Rhodium	50-60	45-50	5-10	80-90		30-50	40-50
Iridium	20-30	0	0	40-50		5-10	
Ruthenium	5-15		0-5	40-50		0-5	

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Osmium	No relevant end-use sectors
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- 1) Total without jewellery, coins (no typical EoL management for these products)
- 2) Autocatalysts, spark plugs, excluding car-electronics
- 3) Including process catalysts/electrochemical, glass
- 4) Including decorative, medical, sensors, crucibles

The key industrial actors refining all forms of PGM containing waste streams in Europe – processing waste, manufacturing residues and end-of-life products – are Umicore and Johnson Matthey. In addition, BASF treats especially automotive catalytic converters in Cinderford, UK, but also other materials in Rome, Italy. Other companies in the PGM refining sector operating in Europe include, but are not limited to, Heraeus, Safina and Vale Europe. (Jha et al. 2013; Umicore 2017d; JM 2017a; BASF 2017; Molotova et al. 2013)

## 2 PRODUCTION OF PGMS FROM PROCESSING WASTE

PGMs are widely used in industrial processes, where they are found in process catalyst residues, various other process waste streams and in mining residues (JM 2017a). All PGMs, except for osmium, are also commonly recycled, either in the process or by an external industrial actor. Recycling of PGMs in industrial processes is strongly market driven due to the high price of PGMs. Therefore recycling forms an integral part of a product's lifecycle within industrial processes and consequently, the highest actual recycling rates of PGMs, even 80-90%, have been reached within industrial cycles. (Hagelüken 2012; Umicore 2017g)

### 2.1 PROCESS CATALYSTS

PGMs are used as their own or as an essential part of many catalysts that are crucial for common chemical syntheses. The PGM catalysts are usually supported on  $Al_2O_3$ , zeolites, carbon black or  $SiO_2$ . (Hagelüken 2006a)

In oil refining and petrochemical processes the main application fields are catalytic reforming, isomerization and hydrocracking, which are catalysed by Pt or Pd, or by combinations of them and other PGMs. Similar PGM loaded catalysts are also used in the production of bulk and speciality chemicals such as nitric acid, hydrogen peroxide, hydrocyanic acid, purified terephthalic acid or vinyl acetate monomer. (Umicore 2017g; Hagelüken 2006a) In the fine chemical and pharmaceutical segment, palladium on activated carbon powder is most frequently used, but also platinum and other PGMs are exploited. (Hagelüken 2006a)

It can be noticed that there is a large variety of support materials and metal compositions within PGM based catalysts. Moreover, the spent catalysts can exist in a solid, wet or in a pure liquid form. These features establish specific requirements for the recycling processes (Umicore 2017g; Hagelüken 2006a). The biggest impact on treatment technology comes from the catalyst support, but also the combinations and absolute loading of precious metals and the presence of other metals involved are important. In addition, the spent catalyst is often contaminated with material from the reaction it was used to catalyse and with other impurities from the process facilities. (Hagelüken 2006a)

In order to recover the PGMs, the first step is to prepare a representative and homogeneous sample of the material for assaying. The results of the assay determine the expected monetary value of the PGM content and define the step in which the material is fed to the recycling process. The assaying technics are widely discussed by (Rao & Reddi 2000).

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In the actual recovery of the PGMs the usual methods are to segregate, crush, ground and then process the spent catalysts by pyro or hydrometallurgical processes. For instance, Johnson Matthey uses smelting, chemical leaching and refining to recover the metals. At Umicore, on the other hand, the spent catalysts are smelted in a furnace to produce a concentrate of metals, which is further processed hydrometallurgically to recover the PGMs. The specific details of the processes are not available in the literature. (Jha et al. 2013)

## 2.2 PRECONCENTRATION

Catalyst feeds need to be preconcentrated, unless the PGM concentration exceeds 30%. The preconcentration can be done by thermal treatment, pyrometallurgical smelting or hydrometallurgical dissolution. The composition of the material to be recycled affects the choice of the method, which have different pros and cons regarding environmental performance and recycling yields. (Hagelüken 2006a) Organometallic catalysts from chemical and petrochemical industries are usually treated thermally. The choice of treatment atmosphere depends on the undesired organic components to be removed. (Jha et al. 2013)

## 2.3 CONCENTRATE REFINING

Catalysts containing PGMs on a soluble support are usually treated in hydrometallurgical processes (Hagelüken 2006a). The principal flow sheet of PGM recovery by hydrometallurgical process route is presented in Figure 5. Hydrometallurgical processing is based on dissolving metals directly or after pretreatment using suitable acidic and alkaline solutions in the presence of reagents such as oxygen, iodine, bromine, chlorine or hydrogen peroxide (Jha et al. 2013). For example, a  $\gamma$ -alumina support can be dissolved by NaOH or  $H_2SO_4$ . The support shifts into a sodium aluminate or aluminium sulphate solution, which can be used in wastewater treatment. The leach residue containing the PGMs is further treated. (Hagelüken 2006a)

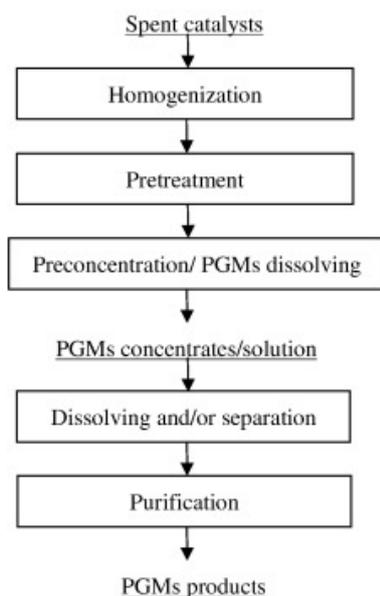


Figure 5 Principal process flow sheet of PGM recovery by hydrometallurgical route. Derived from (Dong et al. 2015).

Metal recovery through hydrometallurgical route is considered low cost and environmentally friendly in comparison to other recycling processes (Jha et al. 2013). However, carbon, coke or hydrocarbons from the catalytic process have to be burnt off before the hydrometallurgical process if their concentration exceeds 3-5%. This part of the process is usually subcontracted, which can cause additional costs, increased process time, and the risk of metal losses. Moreover, certain elements, such as Pb, Ni, As, Hg, can prevent the further use of the aluminate solution and halogens as well can have a negative impact on the process. Therefore, certain levels of insoluble material and contaminations make the pyrometallurgical process a viable alternative for the hydrometallurgical approach. (Hagelüken 2006a)

Insoluble catalysts such as the ones based on  $\alpha$ -alumina, zeolite or silica, or catalysts otherwise unsuitable for hydrometallurgical processes, are treated **pyrometallurgically** by melting in reducing conditions. (Hagelüken 2006a) The principal flow sheet of PGM recovery by pyrometallurgical process route is presented in Figure 6. Pyrometallurgical process is essentially a technique for concentrating PGMs (Dong et al. 2015). The support is slagged, the precious metals are metallurgically collected in a collector metal, usually copper, and the collector metal is then channeled to further wet-chemical processing. Some copper and nickel smelters direct lower melting catalysts into existing systems for the processing of primary and secondary concentrates. These modern integrated facilities, referred to as smelters & refineries, such as the process used by Umicore, combine the advantages of base metal smelters with those of specialised precious metal refiners. Higher flexibility, lower sensitivity to contamination and economic viability are achieved by high capacity, complex process management and after-treatment of primary slag and other sidestreams. In addition, several non-ferrous metals can be recovered simultaneously. (Hagelüken 2006a)

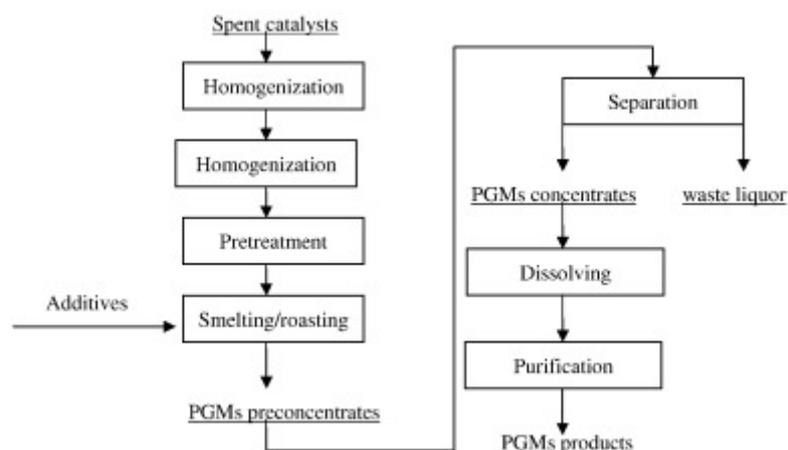


Figure 6 Principal process flow sheet of PGM recovery by pyrometallurgical route. Derived from (Dong et al. 2015).

There is also a separation technique referred to as molecular recognition technology (MRT), where specially designed ligands such as organic chelating agents or macrocycles are used for highly selective PGM separation. Solid materials such as silica gel and polymers are used as supports, to which the ligands are chemically bonded. The MRT products are packed into fixed-bed columns through which the feed solution is passed, and the target metal is removed from the solution. In commercial applications the process is fully automated for continuous operation. (Izatt et al. 2012) MRT products under tradename SuperLig are most often used. (Anastas et al. 2017) The literature doesn't recognise the use of MRT in Europe, but for instance in Houston (Texas, U.S.) SepraMet metal refinery exploits the MRT combined with hydrometallurgical processes in the

selective recovery of PGMs from low grade materials. The absence of organic solvents, ambient temperature, low carbon footprint and high selectivity are regarded as the advantages of the process. (Izatt et al. 2015)

As mentioned earlier, the specific details of the PGM refining processes used in industry remain unknown, but the general descriptions of the processes of some key industrial actors are presented next.

### JOHNSON MATTHEY' PROCESS

1. Evaluation → 2. Smelting → 3. Chemical leaching → 4. Chemical separation.

1. Evaluation: Determining the PGM content of the material in terms of monetary value or quantity of the PGMs and lead time.
  - a. Spent process catalyst feeds are first thermally treated to remove organic residues.
  - b. The particle size of the material is reduced and equilibrated.
  - c. A homogeneous dispersion of components is produced by blending.
  - d. Spectroscopic techniques are used to determine the PGM content.
2. Smelting:
  - a. The spent material is melted at temperatures of over 1200 °C for around 12 hours to separate the non-metallic components.
  - b. The PGM containing portion is collected; two types of metal feeds are produced:
    - i. A silver-based feed containing primarily platinum and palladium.
    - ii. An iron-based feed containing all five of the PGMs.
3. Chemical leaching: multiple leachings to further concentrate the PGMs into solution.
  - a. Silver-based feed is suspended in concentrated acid to slowly leach the silver, platinum and palladium into solution and separate out any gold, which is sent for further refining.
    - i. Silver is removed and further treated into saleable products.
    - ii. A resulting concentrate of platinum and palladium is then dissolved in strong acid.
  - b. The iron-based feed is also acid leached but follows a different chemical treatment route given by the different solubilities of the five PGMs that it contains.
  - c. Result: two distinct liquid solutions, which both pass to the final step, chemical separation.
    - i. One rich in Pt and Pd with trace amounts of Rh, Ir, Ru.
    - ii. Second containing a mixture of all five PGMs.
4. Chemical separation: complex multi-stage process, resulting in five PGMs separated into their final product forms, involving a series of
  - a. solvent extraction,
  - b. evaporation,
  - c. dissolution,
  - d. precipitation,
  - e. filtration to produce highly pure organometallic salts of each PGM, and
  - f. heat treatment to reduce them to the final PGMs.

Material may be introduced into the refining circuit at various stages depending on purity. Feeds and reverts are continually recirculated throughout the circuit. (JM 2017c)

### UMICORE'S PROCESS

1. Weighing and sampling → 2. Smelting → 3. Copper leaching and electrowinning → 4. Refining

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Umicore process combines the features of base metal smelters with those of specialised precious metal refiners, as demonstrated in Figure 7. The main processing steps after evaluation of the material by weighing and sampling are smelting, copper leaching and electrowinning, and final refining. Raw materials can enter the process at the most optimal step, determined by their physical and chemical properties and their value. (Umicore 2017e)

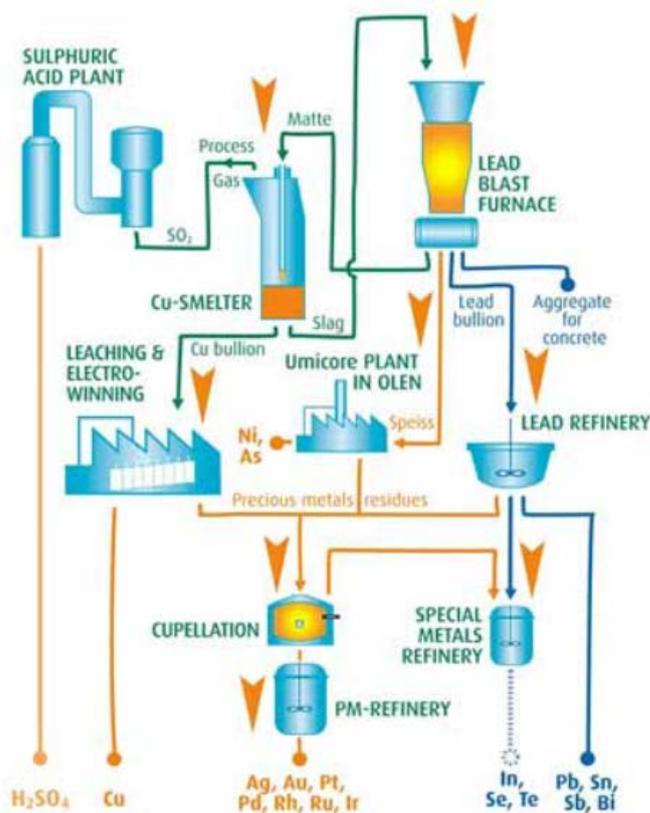


Figure 7 Process flowsheet of Umicore’s integrated metals smelter and refinery. Derived from (Hagelüken 2006b)

The smelter step involves injecting air enriched with oxygen and fuel in a molten bath. The PGMs are separated in a copper bullion, from mostly all other metals, which are concentrated in a lead slag. The latter is treated by the base metal operations of the company. (Umicore 2017e)

After the copper is leached out in the leaching and electrowinning step, the PGMs are collected in a residue that is further refined at the precious metals refinery. The refining combines classical methods such as cupellation with unique internally developed processes not specified in the literature. (Umicore 2017e) The remaining slag from the process can be used as construction material for the built environment (Hagelüken 2006a).

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## 2.4 OTHER PROCESS RESIDUES

There is a large number of other types of process waste containing PGMs. However, the industrial refiners and processes do not differ from those presented under sub-heading 0 2.1 Process catalysts. Therefore, the other process residues are described here only in the form of a table depicting which PGM is present in which waste type:

Table 3 PGM-containing process residues, other than process catalysts. (JM 2017a)

Residue	Platinum	Palladium	Rhodium	Iridium	Ruthenium	Osmium
Down-stream process concentrates from metal refiners	✓	✓	✓	✓	✓	
Reverted process residues from mining	✓	✓	✓	✓	✓	(*)
Distillation residues, wipe and filter cloths from chemical processes	✓	✓	✓	✓	✓	
Mirroring residues from glass industry		✓				

\*) Osmium is commercially produced only as the by-product of refining nickel and other PGMs, with worldwide annual production of approximately 500 kg (Girolami 2012). Therefore osmium may be recycled internally in its refining processes, but the literature does not acknowledge it being recycled externally by industrial refiners, such as the companies mentioned above.

## 2.5 SUMMARISED DISCUSSION ON PRODUCTION OF PGMs FROM PROCESSING WASTE

Production of PGMs from various process wastes is common due to the technical and economic viability of the recycling processes. As the recycling of PGMs from process waste is considered as an integral part of the product's lifecycle, the highest recycling rates of PGMs have been reached within industrial processes.

The key industrial actors in the PGM refining sector in Europe include Johnson Matthey and Umicore. The details of their complex refining processes are not found in the literature, but in general terms, both companies begin with an evaluation step, proceeding then to smelting and various leaching cycles where either silver or copper is used as a carrier metal for PGMs. After the final steps, each PGM is produced in a form of a high-purity powder - a product that is commonly referred to as a PGM sponge. (Umicore 2017c; JM 2017c)

## 3 PRODUCTION OF PGMs FROM END-OF-LIFE PRODUCTS AND MANUFACTURING RESIDUES

This chapter deals with the PGM-containing waste streams constituting of manufacturing residues as well as EoL products. The manufacturing residues cover for example floor sweeps and grindings, whereas EoL products in this context refer both to the materials that have been used in industry sector, such as PGM-containing crucibles for glass industry, as well as those in consumer sector, such as electronics and automotive catalytic converters. As stated in Chapter **Error! Reference source not found.**, PGMs are highly recyclable in technical terms, but their recycling rates drop significantly when the collection of scrap becomes more complicated, as is the case with products that end up in consumer sector. (Hagelüken 2012)

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### 3.1 CATALYTIC CONVERTERS

An autocatalyst is used to convert pollutants from the combustion of fuel into harmless gases in vehicles. It is composed of a ceramic or metallic honeycomb-formed support, which is coated with a solution of chemicals and a combination of platinum, rhodium and/or palladium. The autocatalyst is mounted inside a stainless steel canister and the whole assembly is called a catalytic converter. (IPA 2013)

In typical European emissions systems, a gasoline catalyst system contains 2-3 grams and a diesel system 7-8 grams of PGMs, respectively (IPA 2013). These sum up to 2000 g of PGMs per metric ton of autocatalyst scrap, which is significantly higher than the PGM content in primary resources (on average less than 10 g/t). Despite the apparent attractiveness of this secondary PGM source, the EoL recycling rates for PGMs in automotive applications remain on a global average of only 50–60%, as shown in Table 2. (Hagelüken 2012)

Automotive PGM recycling in Europe is partly impacted by legislation such as the directive concerning the treatment of end-of-life vehicles (EC 2000), which requires removal of catalysts as a part of the EoL treatment. However, as the PGM-containing catalyst is only a part of a larger product, i.e. the car, the market mechanisms related to the vehicles' EoL treatment dictate also the collecting of the catalysts. The problem is realised in cases where old cars are exported outside Europe to countries that lack an appropriate recycling chain. Hagelüken (2012) therefore suggests that transboundary waste shipment rules should be better enforced to limit the export of ELVs in order to increase the PGM recycling within Europe.

The recycling process of catalytic converters begins with a de-canning of the steel canisters where the autocatalysts are confined to. Next, the catalyst is extracted and ground to powder, which is then smelted and refined, and finally prepared for saleable products. (BASF 2015) The process is illustrated in Figure 8. The precise process flow sheets of the industrial refiners remain classified, but follow the general process descriptions given in chapter 0 2.1 Process catalysts, as these processes are not specific for a certain waste type.

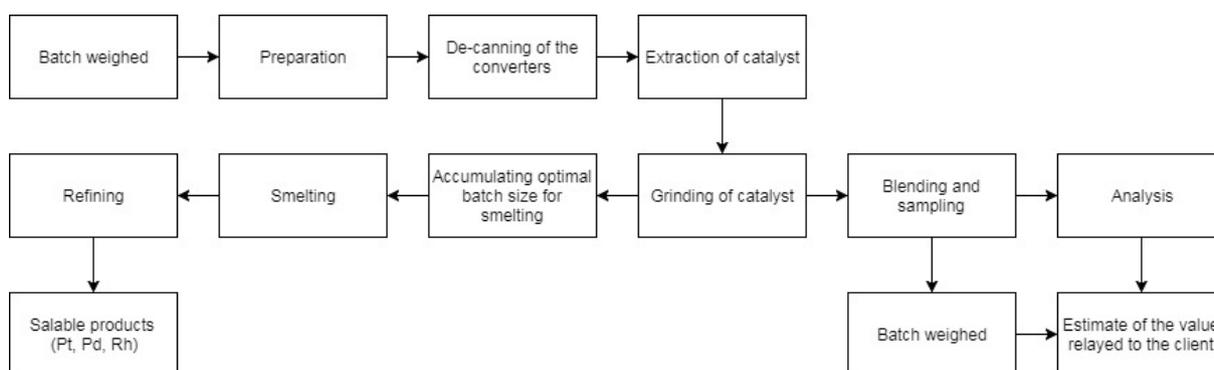


Figure 8 Processing and refining of autocatalysts, as implemented by BASF Metals recycling. Adapted from (BASF 2015).

### 3.2 ELECTRONICS

In electronic applications the recycling rates are currently only 5-10% for PGMs, as was seen in Table 2. The main driving force for the recycling is legislation, such as the EU Waste Electrical and Electronic Equipment (WEEE) Directive (Hagelüken 2012; EC 2012). The largest use of PGMs in electronics is palladium used in printed

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circuit boards (PCBs), therefore the market mechanisms for the handling of EoL consumer products such as PCs, TVs and mobile phones, play an important role in the rates of collection and recycling of the circuit boards they contain. A big challenge occurs when EoL electronics are exported out of Europe. In addition, items being stored by consumers or disposed of through municipal waste collection is also a significant issue. (Hagelüken 2012)

In addition to palladium being used in PCBs, other PGMs are used in capacitors, hard disks and electrode coatings, as depicted in Table 4.

Table 4 PGM use in electronics. (IPA 2017b; JM 2017a)

Type/part of electronics	Platinum	Palladium	Rhodium	Iridium	Ruthenium	Osmium
Multi-layer ceramic capacitors	✓	✓			✓	
Hard disks	✓				✓	
Microprocessors, PCBs		✓				
Electrode coatings	✓	✓	✓	✓		

The quantities of PGMs in electrode scrap, or e-scrap, are again attractive compared to PGM content in primary ores: A ton of used mobile phone handset contains about 130 g of palladium, whereas computer motherboard scrap contains approximately 80 g/t of palladium. (Hagelüken 2012) If a typical consumer notebook computer is examined, palladium is found in many components. The average palladium quantities of each component are shown in Table 5. Knowing the palladium content of each component, the total palladium content of one notebook can be estimated to reach almost 40 mg. (Buchert et al. 2012)

Table 5 Palladium content of a typical notebook and its components. (Buchert et al. 2012)

Notebook component	Weight per unit (g)	Palladium content (mg/kg)	Palladium content (mg)
Motherboard	310	80	25
Memory cards	20	180	4
Small PCBs	28	80	2
Hard disk drive PCB	12	280	3
PCB for optical drive	25	70	2
Display PCB	37	100	4
Total			39

As e-scrap is a continuously changing mix of complex materials, the sampling and assaying of the material feed are crucial steps in the recycling process. For example, regarding the PCB feed at Umicore precious metal refinery, the entire PCBs are shredded down to a size of 4 x 4 cm to obtain a representative sample of the feed. The primary sample from this first step is then further shredded to 7 x 7 mm, after which a secondary sample is taken and prepared to obtain a lab-sample for analysis. No fractions are sorted out but everything is subsequently treated in the smelter operations. (Hagelüken 2006b)

Precious metals, referring to gold and silver in addition to PGMs, are normally recovered as highly valuable by-products from secondary copper production from WEEE, as seen in Figure 9. Suitable components such as

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PCBs, which contain both appreciable amounts of copper as well as smaller amounts of precious metals, are usually subjected to pyrometallurgic processes. The copper functions as a carrier for the precious metals, whereas the less valuable components (e.g. glass, aluminum) end up in the slag. The copper phase is purified by electrolysis, during which the precious metals are concentrated in the anode sludge. Each refining company uses specific processes to recover the precious metals with a high degree of purity at very high recovery rates. (Buchert et al. 2012)

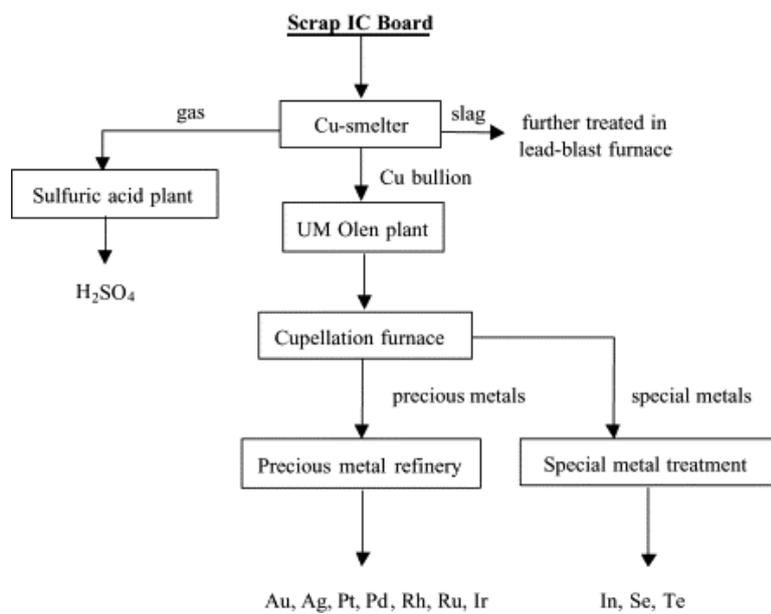


Figure 9 Flowsheet for recycling of e-scrap at Umicore. Derived from (Lee et al. 2004)-

Europe is a leader in the recovery of secondary precious metals in state-of-the-art factories. Due to the fast-growing quantities of electronic waste, considerable expansion of the processing capacities have been made. Buchert et al. (2012) list a couple of these expansions:

- In 2011, the German copper group Aurubis expanded its total recycling capacity in Lünen, North Rhine-Westphalia. The throughput in the existing smelting furnace rose from 275,000 tons to 350,000 tons per year. According to the company, the plant is particularly suited to the treatment of complex recycling materials, including WEEE. Further capacity for recycling electronic waste is located in Hamburg.
- In Scandinavia, the Swedish mining and metals group Boliden owns copper smelters which recover precious metals from WEEE, namely platinum and palladium from PCBs. The company's recycling capacities for WEEE have grown from 45,000 to 120,000 tons per year in 2012, and there is capacity to treat even more. (McCoach et al. 2014)

### 3.3 FUEL CELLS

PGMs are used as catalysts in low-temperature fuel cells, which in turn are used to produce electricity, including powering automotive applications (Wittstock et al. 2016; Umicore 2017b). Platinum is the most commonly used metal, but also Pt-Ru and other Pt alloys, in addition to Pd and Ir based catalysts are already produced commercially (FCS 2017). However, PGM-free catalysts are also being studied (Zelenay 2016).

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The fuel cell vehicles (FCVs) have just entered the retail market in 2015 (Jacoby 2017), which means that the number of FCVs that have currently reached the ELV status, especially in Europe, is very low. There are however some significant efforts, partly organised by EU, that aim to boost the use of FCVs in Europe. These projects plan to deploy over 1400 FCVs across Europe by 2022. (FCH-JU 2016)

Estimates of the platinum content per fuel cell vehicle range from 30 to 42 g, depending on the assumed stack power, albeit no official figures have been published by vehicle manufacturers. Due to the high value of this quantity of platinum, it is likely that platinum recovery will be the major driver for fuel cell recycling, while other materials of the fuel cell constituting minor interest. However, during operation of the fuel cell, small platinum particles may diffuse into the membrane. Excluding the membrane and other parts of the fuel cell from the recycling process may thus limit the recycling efficiency. On the other hand, including the membrane would make the recycling process more complicated. The potential of not only recovering the platinum but the whole membrane for reusing it in new applications has also been identified. However, so far this approach exists only on laboratory scale. (Wittstock et al. 2016)

The presence of fluorine compounds in the membrane electrode assembly (MEA), the core of the fuel cell as depicted in

Figure 10, is customary according to the state-of-the-art, which brings considerable challenges in the recycling of MEA materials. Incineration of the MEAs that contain fluoropolymers leads to the formation of hydrogen fluoride (HF), a toxic compound that is both harmful to health and highly corrosive. The pyrometallurgical approach to recycling would thus require an installation of special protective linings for the furnaces, as well as filter and scrubbing systems to eliminate HF from the off-gas. In addition, any fluorine constituents remaining in the PGM-containing slag could complicate the later separation. From a recycling viewpoint, the absence of fluorine in the membranes would thus be a major advantage of future fuel cell systems. (Wittstock et al. 2016)

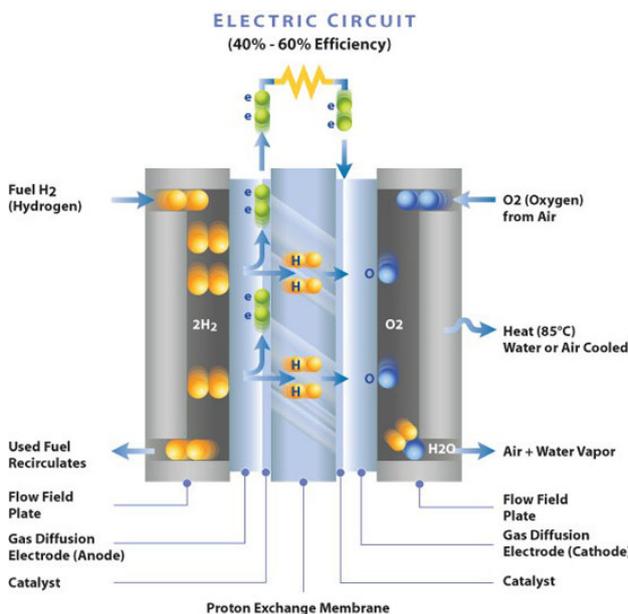


Figure 10 Membrane electrode assembly (MEA) of a low-temperature fuel cell containing the PGM bearing catalystrayer. (Image from Wikimedia Commons, licensed uncer CC BY-SA 3.0)

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Although wider market penetration of fuel cells has not yet taken place, the development of recycling processes is topical, and several patents related to the recovery of PGMs from fuel cells avoiding HF emissions have been claimed (Wittstock et al. 2016). The PGM residues from various stages of the supply chain or prototypes are thus currently recycled by the key industrial actors such as Umicore (Umicore 2017b) and Johnson Matthey, the latter of which lists electrodes, MEAs and production residues, including floor sweeps and spent catalysts, as fuel cell materials they refine (JM 2017a).

### 3.4 JEWELLERY, MINTING AND PLATING

All PGMs except for osmium are used in jewellery: platinum often on its own, or alloyed with iridium or ruthenium. Palladium can be alloyed with other metals or used alone to make jewelry pieces. Rhodium has a use as a non-tarnishing plating for white gold, silver, and other PGMs in jewellery applications. (Clark 2017) In jewellery the PGMs are used in very concentrated levels, which makes them valuable materials for recycling (Hagelüken 2012) – as can be seen by the recycling rates of jewellery presented in Table 2.

In addition to rhodium being used as a plating material for certain jewellery products, PGMs in general are often used in electroplating of surfaces in many applications to provide either a decorative or functional coating on another, more affordable material. Electroplating processes are generally used in areas such as electronic applications, high-frequency engineering, corrosion protection and surface hardening. The coating process is carried out in an electrolyte bath, of which the remaining PGMs can be readily recovered. The more challenging material flow to collect is the PGMs coated on various products. This is because the PGM concentration is very low in these products, and the variety of products is significant, which makes their collection for recycling extremely difficult. Therefore, the PGMs on electroplated products are regarded as PGMs lost from the recycling chain. (Umicore et al. 2005)

Umicore and Johnson Matthey list the following sources of PGM scrap related to jewellery, minting and plating (Umicore 2017f; JM 2017a):

- Jewellery
  - o EoL scrap (rings, chains, rods, ingots)
  - o Watch cases (case and strap alloys)
  - o Other production residues (e.g. floor sweeps, grindings)
- Minting
  - o Blanks (offcuts, rejects)
  - o Other production residues (e.g. floor sweeps, grindings)
- Plating
  - o Flakes, bullions
  - o Ion-exchange resins
  - o PGM scrap

### 3.5 GLASS INDUSTRY

The glass industry most commonly uses platinum, platinum-rhodium alloys and, recently, iridium due to their characteristic high melting points and resistance to corrosion. These metals protect a variety of components and ceramic substrates used in glass manufacture, including thermocouples and furnaces, from erosion by

molten glass and corrosive vapours. (Couderc 2010) PGMs have also significance in glass products such as high-melting special and technical glass, optical glass such as LCD displays, and fibreglass (Umicore et al. 2005).

Within glass industry the recycling chains can be said to be closed, and only 5% of demand is covered by virgin PGMs. This is because refining companies offer the global glass industry complete services from planning to the recycling of PGMs, and these services are commonly used by glass manufacturers. (Umicore et al. 2005)

### 3.6 DENTAL APPLICATIONS

PGMs, namely palladium and platinum, meet the characteristics for oral applications: corrosion resistance, biocompatibility and mechanical strength. Palladium is used in more than 90% of precious metal alloys for dental applications, where it functions as both a base and alloy metal. Platinum, on the other hand, is only used as an alloy element, which is why its used quantities are significantly lower than those of palladium. (Umicore et al. 2005) Dental applications accounted for 2.2 tonnes of palladium demand in Europe in 2015. (JM 2016)

### 3.7 SUMMARISED DISCUSSION ON PRODUCTION OF PGMS FROM EOL PRODUCTS AND MANUFACTURING RESIDUES

The actual recycling technology of PGMs from EoL products and manufacturing residues does not differ much from that used in the refining of process waste from industrial sources. There are however some differences in the whole recycling chain. First of all, as the collection of EoL products is in some cases difficult to organise, the resulting recycling rates of PGMs from certain applications remain very low. A clear example of this category is electronics, which is also a constantly growing feed. However, as commented by Buchert et al. (2012), in Europe the situation is fairly good, as advanced technologies with very good recovery rates are used, and considerable plant capacity is available. Another reason why electronics should gain specific attention by the recycling sector in addition to its collection, is the pre-treatment and sampling of the feed due to its highly unhomogeneous nature.

Fuel cells are currently a small source of secondary platinum due to their low market input, but if their use will expand, and if platinum remains as the state-of-the-art catalyst, they will form a significant feed of secondary platinum.

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## 14 PRODUCTION TECHNOLOGIES OF CRM FROM SECONDARY RESOURCES: PHOSPHATE ROCK AND WHITE PHOSPHORUS

### 1 PRODUCTION TECHNOLOGIES OF PHOSPHATE ROCK AND WHITE PHOSPHORUS FROM SECONDARY RESOURCES

By far the largest share, more than 85%, of the phosphate rock mined worldwide is used to manufacture phosphate fertilizers. The remaining is refined to elemental phosphorus for various chemical compounds, animal feed supplements, or is applied directly to soils. (Jasinski 2013) White phosphorus,  $P_4$ , is an elemental form of phosphorus, produced from phosphate rock. It is used in the production of a range of phosphorus containing chemicals. (European Commission 2017) The global share of phosphate rock and white phosphorus per application area are shown in Figure 11.

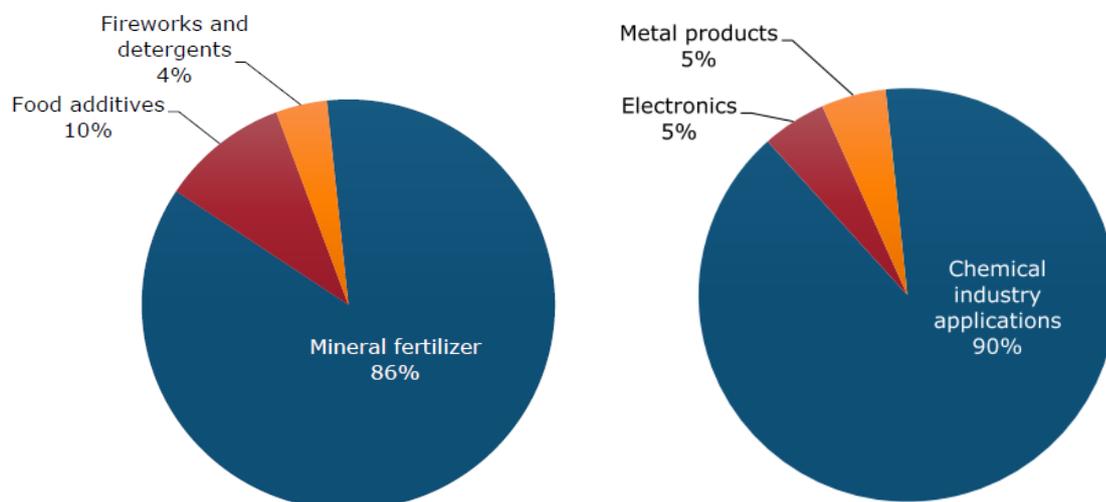


Figure 11 Global use of phosphate rock (EU consumption 7.3 Mt) and white phosphorus (EU consumption 43.6 t), average figures for 2010-2014. (European Commission 2017)

More detailed list of the industry sectors and applications that depend on white phosphorus as a raw material (ESPP 2016):

- Pharmaceuticals
- Medical diet supplements and vitamin production
- Toothpastes (fluorophosphates)
- Electronics grade phosphoric acid
- Agrochemicals: pesticides and herbicides (e.g. glyphosate)
- Fumigation chemicals
- Lithium ion batteries (cathode materials, electrolytes)
- Lubricants/lubricant additives
- Drilling additives (e.g. for shale gas and mining)
- Water cooling and air conditioning circuits (phosphonates), corrosion inhibitors
- Fire safety (Some fire safety chemicals based on phosphorus are produced from phosphoric acid, but part of them are produced from white phosphorus.)

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- Plastic additives
- Catalysts and ligands in the chemicals and petrochemical/refining industries
- Electroless nickel plating (hypophosphites)
- Pyrotechnics (e.g. in transport safety applications)

As the direct use of phosphate rock occurs in rather small-scale, and moreover, because it is chemically decomposed to other substances during this use (IPNI 2011), phosphate rock itself is not recyclable. On the other hand, phosphorus as an element is recyclable to some extent, and therefore refining phosphorus from secondary resources reduces the demand of virgin phosphate rock, the only source of phosphorus. In this report, “phosphorus” refers to all phosphorus compounds that can be produced from secondary sources - it should be noted that phosphorus does not appear in a pure form in nature. No distinction between different phosphorus compounds is made, as the origin of all compounds is the same; phosphate rock. However, white phosphorus is of special concern since it is not produced within the EU (European Commission 2017). Its secondary production is shortly discussed in 0.

Currently, significant amounts of phosphorus are lost, notably in mining, processing, agriculture via soil erosion, food waste, manure, and sewage sludge (Scholz et al. 2014). The share of phosphorus lost in different waste flows due to consumption is illustrated in Figure 12. Several technologies already exist to recycle phosphorus from different sources; however, due to many factors such as lacking economic incentives, insufficient regulations, technical obstacles, only a small percentage of potential secondary resources of phosphorus has been exploited. (Scholz et al. 2014)

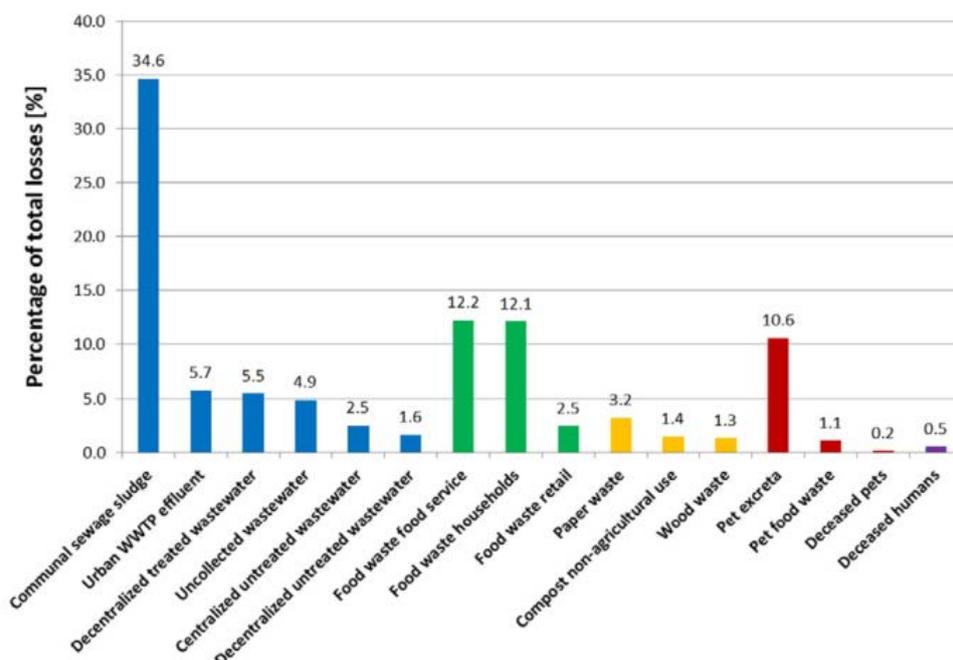


Figure 12 Share of phosphorus quantities in different flows lost from the consumption sector for the EU-27 in 2005; grouped from left to right by waste type: wastewater (blue), food waste (green), non-food organic waste (yellow), pet related waste (red) and deceased humans (purple). Derived from (Dijk et al. 2016).

Phosphorus lost from the recycling chain is not only a question of resource efficiency, but also an environmental issue in the regions where it exists in excess. In aquatic ecosystems, excess phosphorus loads

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can lead to eutrophication that results in oxygen-depleted conditions, where economically important fishes and other aquatic organisms cannot survive. Also drinking water supplies are endangered when algal bloom, deriving nutrition from excess phosphorus, release a toxic substance called algal toxin. (Scholz et al. 2014; Ulrich et al. 2009)

## 1.1 MANURE

One of the main sources of phosphorus for recycling is animal manure, as it is a valuable source of plant nutrients. Phosphorus in manure is similar to commercial fertilizer, meaning that it is readily available for plant uptake. (Scholz et al. 2014) Some studies suggest that phosphorus is even more available for plants in manure than in an NPK fertiliser (Kahiluoto et al. 2015). Substitution of inorganic fertilizers by manure, however, is often not a preferred choice because of several reasons. These are higher transportation cost, difficulty to define the appropriate manure application rate, the risk of transmitting pathogens, and undesirable odour effects. The transport issues result in spreading the manure repeatedly on the fields nearby the livestock farm, resulting in excess amounts of phosphorus in those areas and causing water contamination. (Scholz et al. 2014)

In Europe, manure is almost entirely applied to agricultural land either directly or as a fertiliser derived from it, and therefore the phosphorus it contains can be regarded as recycled, even though in certain areas it is accumulated in the soil instead of being used by the plants. In the future, this stock of phosphorus can potentially be used, but only if the applied fertilisation is balanced in a way that crops are able to utilize residual phosphorus from the soil. (Dijk et al. 2016)

Heavy metals are not an issue in the case of animal manure, in contrast to sewage sludge biosolids, although organic pollutants such as veterinary medicines, antibiotics, biocides and pathogens could be a challenge. However, the main technological issues to be resolved are easing the transportability of phosphorus within the manure matrix, and extracting phosphorus from the manure matrix for further processing. The manure with reduced phosphorus content could then be applied on fields without the danger of resulting phosphorus surplus in the ground. (Scholz et al. 2014)

An approach to increasing the transportability of phosphorus in manure could be to use manure for energy production. Current available technologies include combustion and anaerobic digestion systems designed to capture methane gas and burn it as fuel for electricity generation. Anaerobic digestion does not consume the nutrients in manure but instead leave them in residuals. Anaerobic digestion also reduces pathogen counts and denatures weed seeds in raw manure, and the odors are greatly reduced in the effluent, thereby easing the storage, transport, and application of manure nutrients. On the other hand, also the ash residues from combustion processes contain phosphorus in concentrated form, are free of organic pollutants and could be easily processed into phosphorus fertilizers. (Scholz et al. 2014)

Schoumans et al. (2010) have collected an overview of the possible treatment steps for recovering phosphorus and phosphate from manure. The overview is presented in Figure 13. The details of the processes are discussed in their report.

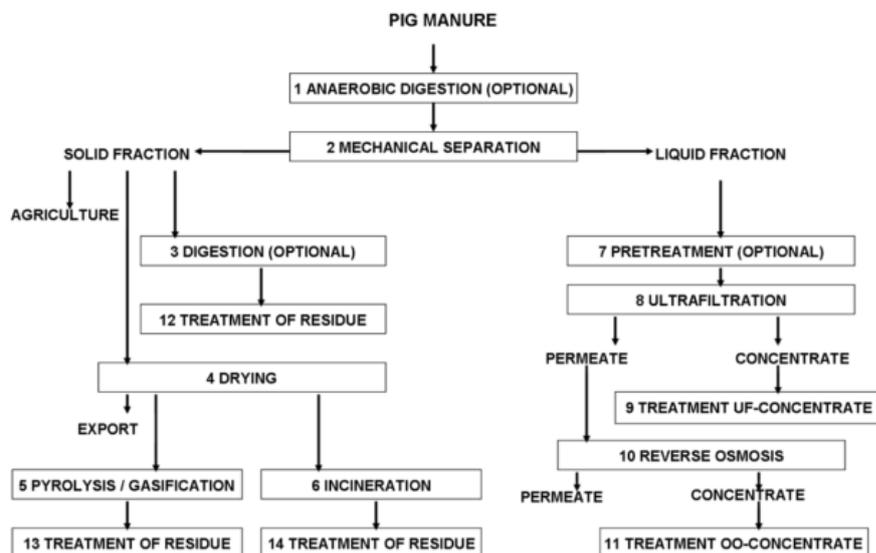


Figure 13 Possible processing steps for recovering phosphorus and phosphates from manure. (Schoumans et al. 2010)

Ash from the incineration of poultry manure is already demonstrated to function as an effective fertiliser (P, K) and, according to ESPP (2015), is currently used in Europe. The commercial processes or the resulting fertiliser products include:

- Fibrophos (UK)
- BMC Moerdijk (The Netherlands)
- BHSL Hydro (Ireland)

The incineration processes are harnessed for electricity production in each of the cases mentioned above.

A Dutch company Friesland Campina, one of the largest dairy cooperatives in the world, has successfully completed pilot projects that extract biogas and create organic fertiliser alternatives from dairy cattle manure. The objective is to scale up these pilots to eventually process 8.5 million tons of manure by 2020. The project is executed in cooperation with waste processing company Omrin, among other companies. (FrieslandCampina 2015)

There are also other cooperatives where organic fertilisers are processed from manure in Europe. Information of these projects are gathered and presented by European Sustainable Phosphorus Platform (ESSP), such as presentations by Dijk (2017) and Thornton (2016).

## 1.2 SLAUGHTERHOUSE WASTE

Slaughterhouse waste is another waste stream rich in phosphorus (Scholz et al. 2014). Bone shred contains even around 100 g P/kg (Lamprecht et al. 2011). More than a third of live animal weight is discarded as inedible waste. These so-called animal by-products are processed to high-quality fats for the oleochemical industry, and to meat and bone meal (MBM) used as protein and phosphorous feed supplements for animals. (Scholz et al. 2014) However, in 2001, restrictions on MBM use for animal feed were made due to the fact that MBM was

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suspected to be the cause of the mad cow disease outbreak. This caused incinerating the MBM and thus creating MBM ash, which is very similar to regular phosphate rock in terms of chemical composition. There are no data available on the amounts of slaughterhouse waste entering different disposal routes. (Scholz et al. 2014)

Several techniques have been developed for phosphorus extraction from animal by-products or its ash (Scholz et al. 2014), and some of them are already in commercial use. These include:

- KalFos (the UK) is made of animal by-products by incineration. The waste material would otherwise be incinerated and landfilled, but is now being returned to agricultural land as a fertiliser. (KalFos 2015; Dijk 2017)
- Honkajoki (Finland) recycles animal by-products that are generated by farms and in slaughterhouses and meat-cutting. Most of the offal generated in Finland undergoes processing at Honkajoki's plants, where it is used to produce raw materials for the energy, feed, fertiliser and oleo chemical industries. (Honkajoki 2017)

Both of the mentioned processes also recover the waste energy generated in the process.

### 1.3 MUNICIPAL SOLID WASTE AND FOOD WASTE

Food waste is a major source of phosphorus in solid waste, about 4 g P/kg TS (total solids). Other sources of phosphorus in solid waste are wood, paper and textile wastes, containing 0.2-0.3 g P/kg TS. (Kalmykova & Karlfeldt Fedje 2013)

In the EU, around 90 million tonnes of food waste annually (Scholz et al. 2014) is formed of the losses in the following steps of the food processing chain (European Parliament 2017):

- Agricultural production (11%)
- Distribution and retail (5%)
- Food processing (19%)
- Food services and catering (12%),
- Final household consumption (42%)

In Europe, the most commonly used treatment option for bio waste (including food waste), calculated by mass, is still landfill. Other options are incineration and biological treatment, which comprises composting and anaerobic digestion. There are only a few countries in Europe where biological treatment, mostly composting, is the main treatment option. (Frohnmaier et al. 2015)

Separate collection of food waste is implemented in several countries worldwide (Scholz et al. 2014). In Europe, countries such as Austria, Switzerland, Germany, the Netherlands, Flanders (Belgium), Sweden and Norway, have been coordinating separate biowaste collection and treatment systems for over 15 years, whereas countries such as the UK, Italy, Finland, Ireland, Slovenia, Estonia and France have made significant development in their collection systems during the same time. In several other countries there is a room for a significant improvement in the collecting of biowaste. (European Compost Network 2016) In any case, effective separate collection of biowaste can be difficult to achieve due to the low collection rate from households and possibly large non-separated waste streams from food distribution and retail, restaurants, and public institutions (Scholz et al. 2014).

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The commercial examples of the recovery of phosphorus from food waste, municipal solid waste or its ashes seem to be small in number. ReGrow (the UK) uses anaerobic digestion to turn food waste into biofertiliser. Food waste is gathered by company called ReFood directly from the waste producers on the private sector. Methane is collected during the digestion process and further processed to be used for energy production either on the site or through the national gas grid. Once all the waste material is fully digested a nutrient-rich liquid is left, and is ready to be used as a fertiliser. (ReGrow 2017; ReFood 2017)

A project called AlgaeBioGas, partly funded by EU in 2013-2016, demonstrated the use of algal-bacterial treatment of biogas digestate from household and industry food waste. The treated digestate could be reused in the process, released to the environment in the form of a fertiliser or used in bioplastics. (AlgaeBioGas 2016; Thornton 2016)

The municipal solid waste incineration (MSWI) ashes could offer a relatively homogeneous and concentrated source for mineral recovery. Even though MSWI ashes generally contain lower amounts of phosphorus compared to wastewater sludge, the advantage is that large quantities of waste ash and slag are available worldwide. The problem with the application of MSWI ashes for agricultural purposes is the presence of trace metals in the recovery product, if the process is not further optimised with the extraction of metals. (Kalmykova & Karlfeldt Fedje 2013)

#### 1.4 WASTEWATER

In addition to animal manure, also wastewater is a significant source of phosphorus. In global scale, wastewater carries approximately 4.6 Mt phosphorus per year, corresponding to more than 2% of the world phosphate rock production. (Scholz et al. 2014) It has also been estimated that the municipal wastewater in European countries contain approximately 1 kg of phosphorus per capita per year. (Egle et al. 2015) 30% of phosphorus in wastewater was recycled globally by the end of the twentieth century. (Scholz et al. 2014)

Direct agricultural application of wastewater, which is still practiced in many parts of the world, and sewage sludge, is the simplest method of phosphorus recycling. However, the availability of phosphorus within sewage sludge for plants is questioned. Due to the potential environmental and health risks primarily from heavy metals, persistent organic pollutants and pathogens in the sewage sludge, acceptance of direct sludge applications is low or decreasing in many European countries. As a consequence, alternative treatments focus on co-incineration (cement kilns, power plants or municipal solid waste incinerators) where phosphorus is lost. (Egle et al. 2015) There is however a lot of variety regarding the destinations of municipal wastewater sludge between different countries even in Europe, as shown in Figure 14.

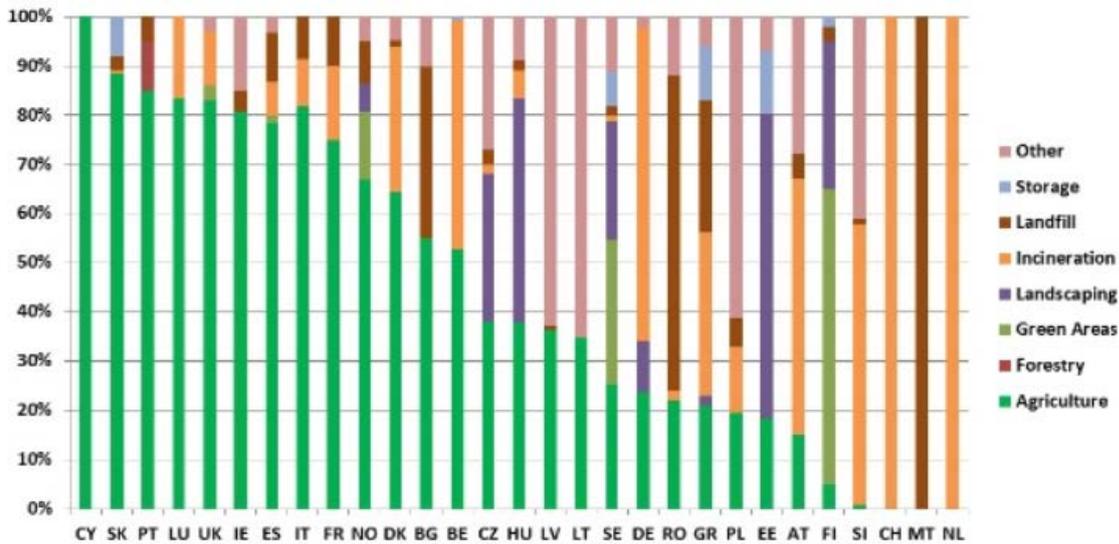
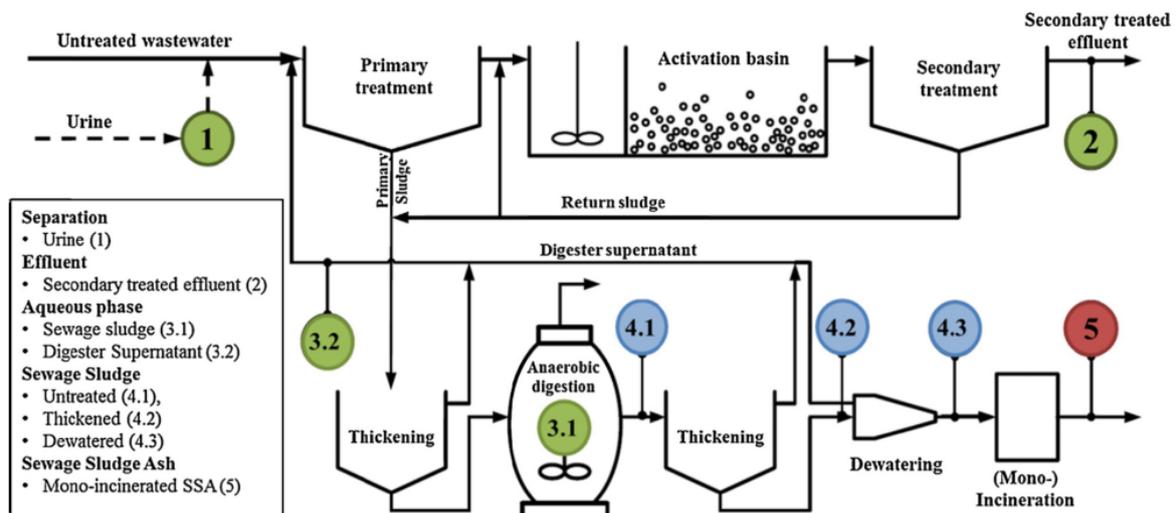


Figure 14 Sewage sludge destinations in EU-27 in 2010. (Dijk 2017) (Original source : EU-project P-REX, FP7)

The removal of phosphorus from municipal wastewater is well established and widely applied; typically, 80-90 % of influent phosphorus is transferred from wastewater to sludge solids by chemical precipitation or biological uptake. (Scholz et al. 2014) Phosphorus recovery by precipitation from sources of dissolved phosphorus, or orthophosphate, has been investigated in detail. Therefore, optimum process parameters, resource demands, effects on wastewater treatment plants (WWTPs) and characteristics of the products are well known. To recover phosphorus from sewage sludge, a first step to make phosphorus dissolved. For this there are various sludge treatment options such as anaerobic treatment, thermal hydrolysis, (wet-)oxidation or wet-chemical leaching. (Egle et al. 2015)

There are several possible access points for phosphorus recovery during the wastewater and sewage sludge treatment. These points, and the characteristics of each flow are presented in Figure 15.



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Source	Mass flow	P concentration/PO <sub>4</sub> -P concentration	P specifics	P recovery potential (%)
Untreated wastewater	200 L cap <sup>-1</sup> d <sup>-1</sup>	~10 mg P L <sup>-1</sup>	Bound/dissolved	100
(1) Urine	~1.5–2 L cap <sup>-1</sup> d <sup>-1</sup>	~150–250 mg PO <sub>4</sub> -P L <sup>-1</sup>	Dissolved	30–50
(2) Secondary treated effluent	200 L cap <sup>-1</sup> d <sup>-1</sup>	~5–10 mg PO <sub>4</sub> -P L <sup>-1</sup>	Dissolved	50–70
(3.1) Digested sewage sludge (SS) (~3.5% TS <sup>a</sup> )	1.6 kg cap <sup>-1</sup> d <sup>-1</sup>	Dissolved part: 20–400 PO <sub>4</sub> -P mg L <sup>-1</sup>	Partly dissolved (10–30%)	10–30
(3.2) Digester supernatant	1–10 L cap <sup>-1</sup> d <sup>-1</sup>	20–400 PO <sub>4</sub> -P mg L <sup>-1</sup>	Dissolved	10–30
(4.1) Digested sewage sludge (~3.5% TS <sup>a</sup> )	1.6 kg cap <sup>-1</sup> d <sup>-1</sup>	1.4 g P kg <sup>-1</sup> sludge	Bound (bio/chem); partly dissolved	90
(4.2) SS thickened (10% TS <sup>a</sup> )	0.6 kg cap <sup>-1</sup> d <sup>-1</sup>	4 g P kg <sup>-1</sup> sludge	Bound (bio/chem)	90
(4.3) SS dewatered (30% TS <sup>a</sup> )	0.2 kg cap <sup>-1</sup> d <sup>-1</sup>	12 g P kg <sup>-1</sup> sludge	Bound (bio/chem)	90
(5) Sewage sludge ash	0.03 kg cap <sup>-1</sup> d <sup>-1</sup>	50–130 g P kg <sup>-1</sup> TS	Bound (chem)	~90

<sup>a</sup> TS (total solids).

Figure 15 Various possible access points for phosphorus recovery during wastewater and sewage sludge treatment and characteristics of each flow. The details of suitable recovery process for each access points are discussed in the review article by Egle et al. (2015), where the contents of this figure are derived from.

Access point 1, urine diversion, although not commonly used, is a relatively established technology and has been tested in several places for example in Germany and Sweden, with consequent nutrient recycling to agriculture. While urine constitutes no more than 1% of the total volume of wastewater, it contains even 50% of the phosphorus. Urine is almost free from heavy metals and pathogens and is easily hygienized by ozone or UV light. Urine can also be evaporated or phosphorus precipitated as struvite, for example, by local solar-driven systems. Through fertilization with separately collected urine, the input of heavy metals in general, to agriculture could be remarkably decreased, compared with spreading of sewage sludge from combined systems. Although human urine contains residual pharmaceuticals and hormones, the level of concentration is much lower than that in animal manure. (Scholz et al. 2014)

For access point 2, secondary treated effluent, no large-scale implementation is known, although patented technology exists, namely REM-NUT. It works using cationic and anionic ion exchange units in housing a natural zeolite or a strong alkaline resin. Even 90% of phosphorus (and nitrogen) is removed from wastewater during the process. The potential recovery of 50-70% is estimated by taking into account the reduced recovery rate of ion-exchangers over time. (Egle et al. 2015)

In cases where direct recycling of either sewage sludge, access points 3 to 4 in Figure 15, or sewage sludge ashes, access point 5, is not possible, technologies are required to remove organic or inorganic pollutants and to transform phosphorus into a bioavailable form or into a raw product that can be used by the phosphorus industry (Scholz et al. 2014). In addition to the review by Egle et al. (2015), EU project P-REX also evaluated nine of these processes, and the results were gathered by Nättorp et al. (2015). The following table lists many of the processes developed for recovering phosphorus from wastewater in addition to the nine studied. It can be seen that the most mature technologies are focused on precipitation methods, whereas processes concentrated on leaching phosphorus from ash are at highest in test production phase.

Table 6 Overview of some technologies developed for recovering phosphorus from wastewater divided by their working principle and their technological maturity. Ones marked with \* were studied in EU project P-REX. (Nättorp et al. 2015).

	Precipitation	Sludge hydrolysis	Thermal (pre)treatment	Ash leaching
In commercial production	Pearl*, AirPrex*, NuReSys, STRUVIA*, PHOSPAQ, Ekobalans, Rephos, PhosphoGreen, NutriTec, Naskeo, Anphos	LYSOGEST, WASSTRIP	PYREG	-

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Demo/test production	P-Roc	Gifhorn*	ASH-DEC*	LEACHPHOS*, ECOPHOS*, RecoPhos
Pilot	-	EXTRAPHOS, Stuttgart*	MEPHREC*, RecoPhos, Cleanphos	TetraPhos

Ostara is a company delivering phosphorus recovery technologies for wastewater treatment plants based on commercial Pearl and WASSTRIP technologies. Their equipment recovers phosphorus from liquid wastewater streams, preventing struvite formation in pipes, pumps and digesters, and reducing sludge volumes and disposal costs. The recovered phosphorus is transformed into a market-ready fertiliser. (Ostara 2017)

The AirPrex technology, also in commercial production, is used at the wastewater treatment plant (WWTP) Amsterdam-West, the Netherlands. The technology is provided by SH+E group, and is also used at other WWTPs in Germany and in the Netherlands. The sludge from the Amsterdam-West WWTP was already used in biogas production before the implementation of AirPrex, but the upgrading of the equipment allowed the recovery of phosphates as well, in the form of a magnesium-ammonium-phosphate fertilizer. (Waternet 2013; Dijk 2017)

The only acknowledged process to potentially produce white phosphorus is RecoPhos, also mentioned in Table 6. The technology was acquired by ICL (Israel Chemicals Ltd) from SGCL Carbon GmbH. The primary input to the process is sludge incineration ashes (or other ashes such as meat and bone ashes) and with further adaptation, potentially WWTP sludge directly. The technology uses electro-magnetically induced heating, which should improve electrical energy efficiency. The process may also allow smaller production units to be potentially viable, although costs of safety, gas cleaning and input material will affect the economy of scale. ICL plans to construct four full scale units in Europe and in the U.S., with the first unit possibly in operation by 2018. (ESPP 2016)

## 1.5 STEELMAKING SLAGS

Phosphorus is present in iron ore and coal at concentrations as low as 0.12 % and, during the processing of these raw materials, is removed into steelmaking slags at concentrations of 2-3 % at the maximum. Since the steelmaking is a very large industry, the amount of phosphorus ending up in slag is considerable. (Scholz et al. 2014) In the steelmaking industry, phosphorus is simply seen as an impurity, which needs to be removed due to its detrimental effects on the mechanical properties of steel. (Matsubae et al. 2016)

The dephosphorisation of steel slag has been intensively investigated; however, the research on the recovery of phosphorus from the slag is limited (Lin et al. 2014). Literature does not acknowledge any commercial processes for the phosphorus recovery from steelmaking slags, but studies have been conducted, including those by Matsubae-Yokoyama et al. (2009), Diao et al. (2012), and Lin et al. (2014).

Currently, the steelmaking industry generally employs a technology referred to as an LD converter, characterized by the production of two different slags, with the phosphorus concentrated in one of them. The technology allows using pig iron with relatively high phosphorus content. (Matsubae et al. 2016)

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Matsubae et al. (2016) have estimated that the amount of phosphorus lost through steelmaking slags totalled approximately 70 kton in Europe in 2013, whereas the amount lost worldwide was over 850 kton. As the global phosphate rock production was 228,000 kton in 2013, they further estimated that the hidden phosphorus flow from the steelmaking was equivalent to 4% of the global phosphorus supply in that year. As the reserves of high-grade iron ore will become depleted, the industry will turn to low-grade deposits with higher phosphorus content. As the amount of phosphorus in the iron ore will gradually rise, even larger amounts of phosphorus will be separated into slags in future. (Matsubae et al. 2016)

## 1.6 OTHER INDUSTRIAL WASTES

Many industrial manufacturing sectors require high-quality phosphoric acid, which is often produced from elemental phosphorus. It is used, for example, as a catalyst and for removing impurities. Although the consumption of elemental phosphorus is minor from the quantitative point of view, it is strategically important especially for high-tech industries. (Scholz et al. 2014)

In Europe, a Swiss company Febex offers a regeneration of phosphoric acid contaminated with copper, after being used in the polishing or electrolytic stripping of copper pieces. The regenerated phosphoric acid is 99.99% pure. (Febex 2015)

Industrial chemical processes, such as producing ethanol, also use large amounts of phosphoric acid, which acts as a catalyst. According to Scholz et al. (2014), the recovery of phosphorus from these sources has been put into operation, and the recovered phosphorus is reused in fertilizers.

Another potential source for secondary phosphorus is phosphoric acid from edible oil refining process, where it is used to remove impurities from crude vegetable oil. Since no harmful substances are used in the edible oil refining process, the phosphorus recovered from process waste and wastewater would be well suitable for agricultural products. (Scholz et al. 2014)

Solid phosphoric acid (SPA) catalysts are widely used also in the petroleum industry. van der Merwe (2010) studied the suitability of spent SPA catalyst to be converted to fertiliser, and concluded that there are no toxicological obstacles for its use in a fertiliser, and that it was approximately as effective as a superphosphate fertiliser when used in alkaline soil.

Pulp and paper production is another industry disposing large volumes of P-containing waste. The waste is usually incinerated in order to reduce the volume, and most of it is landfilled. The phosphorus content of the ash is only 0.1%, but because of the large waste volumes, 11 Mton in the EU annually, considerable amounts of phosphorus are disposed. (Scholz et al. 2014)

## 2 SUMMARISED DISCUSSION ON PRODUCTION OF PHOSPHORUS FROM SECONDARY RESOURCES

The recycling rates of phosphorus, as fractions of the total input into related sectors are 73% in animal production, 29% in food processing, 21% in consumption and nearly 0% in non-food production in Europe, as estimated by Dijk et al. (2016). These results show relatively modest recycling of phosphorus, with the exception of manure in animal production, which is almost entirely recycled in Europe. For example, ash from the incineration of poultry manure is demonstrated to function as an effective fertiliser and, according to ESPP

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(2015), is currently used in Europe in several commercial stage applications such as Fibrophos in the UK, BMC Moerdijk in The Netherlands and BHSL Hydro in Ireland.

The relative easy access to phosphorus-containing waste has resulted in a situation where the recycling of phosphorus is in the hands of many operators from varying fields, such as those from fertiliser and renewable energy production in addition to waste(water) treatment. There are also examples of significant cooperation between the producers of phosphorus-containing waste and renewable energy production plants, such as animal production farms providing manure for biogas production, while phosphorus cycles in the process from manure to a fertiliser product.

The removal of phosphorus from municipal wastewater is well established and widely applied; typically, 80-90 % of phosphorus is transferred from wastewater to sludge solids by chemical precipitation or biological uptake. (Scholz et al. 2014) However, there is a great diversion in the sewage sludge destinations between the EU countries. (Dijk et al. 2016) A number of commercial processes are in use to recover phosphorus from wastewater, including Pearl, AirPrex, NuReSys, Struvia, Phosphaq, Ekobalans, Rephos, PhosphoGreen, NutriTec, Naskeo, Anphos, Lysogest, Wasstrip and Pyreg.

Collection and treatment of food waste separate from other municipal waste enables recycling of nutrients through composting, while both energy and nutrients can be recycled via biogas production since the residue can be tapped in agricultural applications. Preventing biowaste from ending up as landfill also restrains the subsequent liberation of methane in the atmosphere. Even though separate food waste collection is organised in many European countries, its effective execution may be challenging due to the low collection rate from households and possibly large non-separated waste streams from private sector. (Scholz et al. 2014) The commercial instances of the recovery of phosphorus from food waste, municipal solid waste or its ashes seem to be small in number. One example is ReGrow in the UK, which uses anaerobic digestion to turn food waste, separately collected from the private sector, into biofertiliser.

The phosphorus reserves stored as ashes or put to landfills are considered as theoretically available, but according to present knowledge, they cannot yet serve as profitable secondary resources. (Montag et al. 2015)

Only one process in Europe is acknowledged to produce white phosphorus  $P_4$  from secondary resources, namely RecoPhos by ICL. The technology, which uses sewage sludge incineration ashes (or other ashes) as an input material, is currently in demo phase. (ESPP 2016) If implemented in a commercial scale in the future, the process is of great importance since white phosphorus is currently not produced within the EU from primary resources either (European Commission 2017).

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## 15 PRODUCTION TECHNOLOGIES OF CRM FROM SECONDARY RESOURCES: REES

### 1 STATE OF THE ART PRODUCTION OF REES

According to the categorization by Binnemans et al. (2013), recyclable current and future rare earth (REE) containing applications can be divided into three groups as follows:

- Pre-consumer production scrap and residues:
  - Magnet swarf and rejected magnets (Nd, Dy, Tb, Pr)
  - Rare earth containing residues from metal production or recycling: post-smelter and electric arc furnace residues (Ce, La, critical REEs), and industrial residues such as phosphogypsum and red mud (all REEs)
- End-of-life products
  - Phosphors used in fluorescent lamps, LEDs, LCD backlights, plasma screens, and cathode-ray tubes (CRT) (Eu, Tb, Y (Ce, Gd, La))
  - Permanent magnets used e.g. in cars, mobile phones, hard disc drives, computers, consumer electronics, industrial applications, electric bicycles and vehicles, hybrid electric vehicle motors, and wind turbine generators (Nd, Dy, Tb, Pr)
  - Nickel metal hydride batteries (NiMH): rechargeable and electric vehicle batteries (La, Ce, Nd, Pr)
  - Others, e.g. glass polishing powders (Ce), fluid cracking catalysts (La, Ce, Pr, Nd), optical glass (La)
- Landfilled industrial residues containing REE
  - Phosphogypsum, red mud etc. (All REEs). (Binnemans et al. 2013)

In principle, the recycling and recovery of REEs from many secondary sources is technically feasible (Kooroshy et al. 2015), and there are and has been numerous research and development actions ongoing in this field (Binnemans et al. 2013, Jones 2017). However, according to the estimate by UNEP (2011) the end-of-life (EoL) recycling rate for all REEs is below 1%, which shows that the recycling activities have not reached the commercial scale, but stayed mostly at the laboratory scale (Sebastiaan et al. 2015, Tsamis & Coyne 2015). Although the estimate is made few years ago, the situation may be even worse nowadays. Since Solvay closed its REE separation plant in 2016, there has not been industrial scale recycling of REEs in Europe (Jones 2017, Pellegrini et al. 2017).

There is a need for new innovative and cost efficient recycling processes that could minimize the environmental effects compared to primary production (Binnemans et al. 2013). Up to now, in relation to end-of-life products only the recycling of fluorescent lamps and rechargeable batteries have been at industrial scale (ERECON 2014, Gambogi 2017), whereas the commercial scale recycling and recovery from pre-consumer waste is mostly focused on permanent magnet scrap (European Commission 2014). However, several challenges need to be overcome for commercially viable, large-scale recycling of rare earths. Some of these bottlenecks are listed below: (Schüler et al. 2011, UNEP 2011, Buchert & Manhart 2012, ERECON 2014, Wall 2014)

- Quantity of REE materials available for recycling is unknown: There is knowledge gap related to the current and future availability of REE materials in end-of-life products.
- Lack of incentives: The low price of rare earths has been a significant factor to a low recycling rate as the economy of recycling processes is very reliant on the market value for the metals.

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- Inefficient collection of rare earth containing end-of-life applications: An efficient collection of many REE containing end-of-life applications does not exist leading to insufficient and often non-selective collection rates. In addition, waste exports in developing countries reduce the REE potential available.
- The content of REE per application is low: The current recycling systems are planned and optimized for recycling base metals significant concentrations. Therefore, they are not optimal for the recovery of REEs, which are typically present in low concentrations in complex structures.
- Complex recycling processes: The REE applications and their components are currently complex, making the disassembly and separation of components and metals complex. Currently there are no incentives for manufacturers and designers to develop recyclable products/REEs. Also the losses in different collection and processing stages are quite high. If common pre-treatment processes for electronic waste are used, REEs end up as fine particles and are therefore lost. Pyrometallurgical processing is not suitable for REEs, as they tend to end up diluted in the form of their oxides in slags, but require both physical and chemical treatments that can be both energy and reagent intensive.

In addition, some applications are just entering the market or have long lifetime, and therefore have not reached their end-of-life yet in large numbers. It may take 10-20 years before these applications are recyclable in a larger scale. (Buchert et al. 2012, Schüller et al. 2011)

## 2 PRODUCTION FROM PROCESSING WASTE AND HISTORICAL WASTE AREAS

Many industrial process wastes, such as bauxite residue (red mud), phosphogypsum, mine tailings, metallurgical slags, coal ash, incinerator ash, and wastewater streams contain REEs. Although the rare earth concentration in these secondary resources is low compared to end-of-life products, their vast volumes lead to substantial total amounts of REEs stocked in these wastes, therefore making them interesting source for rare earth recovery. (Koen Binnemans et al. 2015)

While most attention goes to the recycling of rare earths from pre-consumer metal (magnet) scrap and swarf and end-of-life products, much less has been devoted to industrial process residues and their previously landfilled stocks (Binnemans et al. 2015). In the next sections, an overview of the production of the most important industrial processing wastes; residues from thermal treatment (coal ash, incinerator ash), metallurgical slags, as well as wastewater streams, are given. The overview is mostly based on the recent review article by Binnemans et al. (2015), and concerns all REEs together. In this report, magnet swarf and rejected magnets are categorized as manufacturing residues and discussed in Section 1.2.4 on permanent magnets, whereas phosphogypsum, bauxite residue (red mud) and mine tailings are discussed in WP4.1 deliverable.

### 2.1 RESIDUES FROM THERMAL TREATMENT: COAL ASH AND INCINERATOR ASH

Rare earths are present in coal as trace elements. In the coal burning process rare earths end up in the bottom and fly ashes (Querol, Fernández-Turiel, and López-Soler 1995) in oxide form and their concentration in the ash varies from 0.1 wt-% to more than 1.0 wt-% (Blissett, Smalley, and Rowson 2014). As coal burning is still a common energy production method, coal ashes could provide an important source of REEs (Całus-Moszek and Białecka 2013). Industrial scale processes were not found from the literature reviewed, but some research actions aiming to recover rare earths from coal ash were listed in the report by Binnemans et al. (2015).

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Also oil shale ashes contain rare earths, however their extraction is challenging due to high Fe and Al contents relative to REEs. Furthermore, incinerator ashes may contain rare earths, but in such low concentrations that their recovery is not feasible (Binnemans et al. 2015).

## 2.2 METALLURGICAL SLAGS: POST-SMELTER AND ELECTRIC ARC FURNACE RESIDUES

Pyrometallurgical recycling of metals from WEEE, and catalysts in electric arc furnaces or non-ferrous smelters create slags with a low concentration of rare earths. Therefore, economic feasibility of recycling these REEs is challenging. (Binnemans & Jones 2011, Binnemans et al. 2015) According to Binnemans et al. (2015), the major European metal recyclers Umicore, Aurubis, and Boliden, do not recover REEs from their WEEE recycling slags.

For example in the Umicore's WEEE recycling process, the high affinity of REEs for oxygen causes their ending up in copper smelter slag in diluted form, and further to the lead blast furnace slag. The slag contains mostly cerium, which demand is low. Generally, the dilution problem should be solved in order to enhance the recovery of REEs from slags. Acid leaching is applicable method for removal of rare earths concentrated into solid REE rich phases. (Binnemans et al. 2015)

However, a combined pyro/hydrometallurgical process for NiMH battery recycling has been developed by Umicore and Solvay. The pyrometallurgical process is based on Umicore's Ultra High Temperature (UHT) smelting technology, and generates a slag with relatively high concentration of rare earths. The REEs processed to concentrate were formerly further treated with Solvay's REE recovery process (Umicore n.d., Binnemans et al. 2015). However, due to the strong decline in REE prices (especially yttrium) Solvay stopped its REE recycling operations in 2016 (Sgarioto 2017), and the current status of the REE recovery from NiMH recycling slag is therefore unclear.

Research on the recovery of REEs from slags has been limited so far (Binnemans et al. 2015). Binnemans et al. (2013) point out the problematics concerning the REEs in metallurgical slags. Although in optimal case REEs should be removed prior to smelter, in reality lot of it end up in slags in low concentrations, cerium being the most abundant. From the technology point of view, it would be possible to recover REEs. However, it should be kept in mind that the recovery process could generate in quantity of new waste. In addition, the use of leaching chemicals in slag treatment could affect negatively on the current use of slags as construction or building materials. As commercialization of new recovery processes could generate also undesirable effects, life cycle assessment (LCA) studies are needed to prove the overall environmental benefits of the concepts. (Binnemans et al. 2013)

In addition, pyrometallurgical processes used to recover metals from ores generate slags containing REEs. Their recovery is discussed in Task 4.1 deliverable.

## 2.3 WASTEWATERS

Wastewaters, such as acid mine drainage (AMD) from sulphide rock bearing mining areas, may also be a potential, yet largely unexplored, source of rare earths. It is known that amongst the other metals, AMD often contains notable amounts of rare earths. The research on the recovery of REEs from AMD is not vast, but ion-exchange and chelating resins could perhaps be used for recovery. (Binnemans et al. 2015)

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## 2.4 OTHERS: HISTORICAL WASTE AREAS

Binnemans et al. (2015) states that municipal waste landfills are not potential sources of rare earths, as wide-ranging use of REEs in consumer applications is quite new subject. However, in specialized industrial landfills the situation may be opposite (Binnemans et al. 2015). As an example, the Solvay's process that was in operation until 2016 also utilised La Rochelle's plant historical loss of yield as a feedstock material. In fact, the historical loss of yield represented a key part of the feedstock used in the process at least between 2010 and 2015. (Solvay 2015) See Section 1.2.1 for more information on Solvay's process.

## 2.5 SUMMARISED DISCUSSION ON PRODUCTION OF REES FROM PROCESSING WASTE AND HISTORICAL WASTE

There are only limited amount of knowledge on the mineralogy of the different REE rich phases in slags. More research concerning these phases could help in developing more effective leaching procedures. Also new methods enabling the REE recovery, especially from the dilute leachates but also from other dilute aqueous solutions, are needed. Due to the low REE concentrations in industrial waste streams and historical wastes, the zero-waste recovery processes dedicated especially to dilute waste streams are of importance and need to be developed. (Koen Binnemans et al. 2015)

The large volume of industrial wastes containing REE makes them interesting from the recovery point of view, although the concentration of REEs in these streams is typically low. REEs could be also recovered from historical industrial waste areas as a part of their remediation. So far, the recycling of rare earths from these streams has not attracted much attention, but in case the prices for heavy earths will rise, the situation may well change. In these cases, it would be beneficial to find recovery solutions also to the other residues arising from the processing wastes as well. (Koen Binnemans et al. 2015) However, in the situation where the prices of REEs remain low, the low concentration feedstocks probably remain unutilized.

## 3 PRODUCTION FROM END-OF-LIFE PRODUCTS AND MANUFACTURING RESIDUES

For secondary resources (such as magnets) pre-processing is necessary. (Kooroshy et al. 2015) Therefore, secondary REE recycling process typically includes collection, dismantling and separation steps followed by a final recovery or refining of the REE material (Nicoletopoulos n.d., Tsamis & Coyne 2015). Most recovery processes are based on hydrometallurgy. (Figure 1)

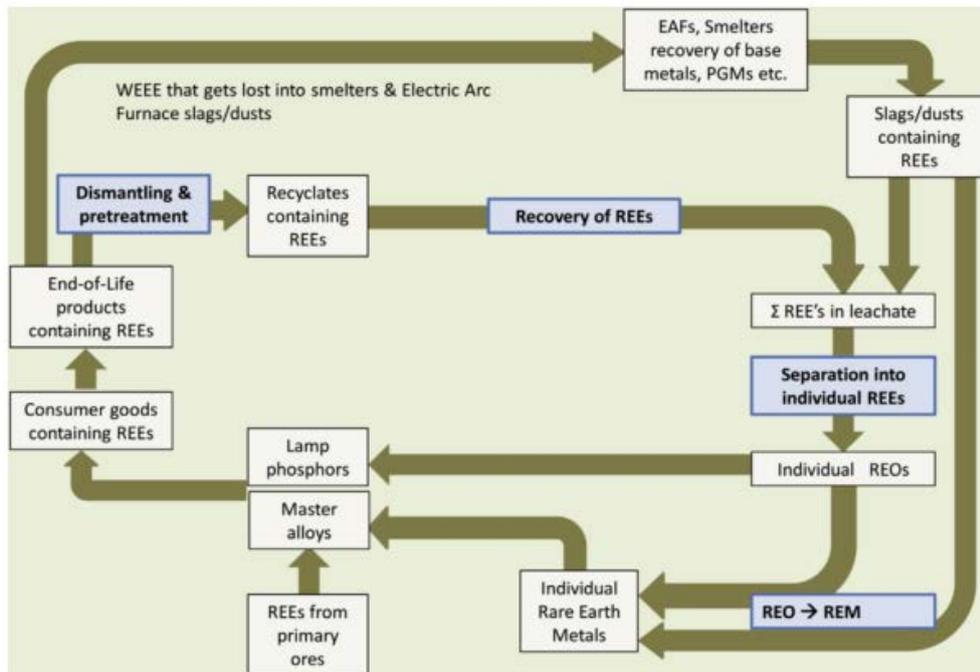


Figure 1 A simplified flowsheet for REE recycling (Koen Binnemans et al. 2013).

Hydrometallurgical processing includes a selective dissolution and precipitation of metals of interest using strong acids or bases. The main processes used in the treatment of REEs include leaching and solvent extraction. The basic processes are similar to those used for raw ores. In addition, ion exchange and precipitation studies have been carried out for REE extraction, but compared to solvent extraction they are not very relevant nowadays. (Kumar et al. 2016)

Great deals of leaching technologies have been developed for secondary sources. Mostly acid or alkaline procedures are used for leaching of REEs in these processes. Especially the leaching behaviour of NdFeB magnets, lamp phosphors and NiMH batteries have been widely studied. Liquors obtained through leaching are separated using solvent extraction to extract REEs from the liquor selectively. Solvent extraction is a basic technique for separation and extraction of single metals or getting their mixed solutions and compounds. REE extraction from leached solutions such as chloride, nitrate, and thiocyanate has been studied with various organic anionic, cationic and solvating extractants. The difficulties in REE separation result in their similar chemical and physical properties and low separation factors. The purity and quality of the compound dictates the value of metal. In solvent extraction, separation and purification of REE is made from acidic or alkaline leached solution that contains different types of metallic impurities, e.g.  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ , and  $\text{Pb}^{2+}$ , influencing the product quality. (Kumar et al. 2016)

Companies that are or have been active in the field of REE recycling and recovery are listed below. Note, that the list is not comprehensive. A French company Solvay has been the only industrial scale recycler of secondary REEs in Europe, and according to Rollat (2012), Solvay's facility in La Rochelle, was in fact the only plant outside of China basically capable of separating all REEs, including the heavy ones. However, Solvay closed down its REE separation plant in La Rochelle in 2016 (Pellegrini et al. 2017, Sgarioto 2017) due to decreased prices of primary REE metals, which has caused a significant loss in competitiveness of recycled materials (Sud Ouest 2016). In addition, Solvay ceased its lamp phosphor recycling actions as well due to decreasing demand for phosphors and economic unprofitableness (Jones 2017). Despite the challenging situation, in June 2017 an American

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recycling company Rare Earth Salts announced its plans to start commercial scale recycling of REEs from EoL lamps (Rare Earth Salts 2017).

– Magnets

- Solvay, La Rochelle (France): A hydrometallurgical process for the recovery of Nd, Pr, Dy and Tb from permanent magnet concentrate produced by Solvay's magnet recycling partners. Magnets originate e.g. from hard disc drives, electric vehicles and windmills. (Smith et al. 2012) According to Tsamis & Coyne (2015), the process is "Mature generally but still in lab scale in relation to REE".
- Hitachi Ltd. (Japan): Automated separation process and dry extraction method (processing without acids) for recycling of REE magnets from hard disk drives, motors, air conditioners and other electrical compressors. In 2011 the process was in the pilot phase, and commercialization was planned by 2013. (Oakdene Hollins 2011, Walters & Lusty 2011). In 2014, Hitachi announced a pyrometallurgical process, which uses molten Mg as an extraction medium, for the recovery of Nd and Dy. (Bailey 2015)
- Santoku Corporation (Japan): A recycling route composing of hydrometallurgical processing started in 2012 to recover Nd and Dy from air conditioner's motor magnets and magnet production scrap. (Binnemans 2014, Vander Hoogerstraete et al. 2014, Santoku 2015)
- Shin-Etsu Chemical Co Ltd (Japan): Ion-exchange and dehydration and calcination for recovery of REEs e.g. air conditioners. In addition, electrolytic REE extraction used. (Oakdene Hollins 2011, Reisman et al. 2012)
- REEcycle (U.S.): A patented process to recover REE from EoL applications. The company focuses on recovery of Nd and Dy from magnets, potential to recover 15 different REEs. (REEcycle 2015)
- Other R&D activities: E.g. General Electric (U.S.), Showa Denko KK (Japan), Mitsubishi with Panasonic and Sharp (Japan) (Walters & Lusty 2011, Reisman et al. 2012)

– Phosphors

- Solvay, La Rochelle and Saint-Fons (France): Separation and purification of REEs (La, Ce, Eu, Tb, Y) from luminescent powders removed from the lamps, which were then formulated to new phosphor powders and used in the lamp production (Solvay 2015) (Figure 2). The process used to be at the commercial scale until 2016.
- Rare Earth Salts (U.S.): The company announced in June 2017 that it has successfully commissioned a commercial separation unit for recycling of REE oxides from fluorescent lamps (Rare Earth Salts 2017).
- Other R&D activities: E.g. General Electric (U.S.), REEnewal Corporation (U.S.), OSRAM (Germany), Philips (the Netherlands), CMI (U.S.), Técnicas Reunidas Technology Centre (Spain) and REconserve (the Netherlands) (Walters & Lusty 2011, Langer 2012, Otto & Wojtalewicz-Kasprzak 2012, REEnewal Corporation 2013, Alvarez et al. 2015, Bailey 2015, Machacek et al. 2015).

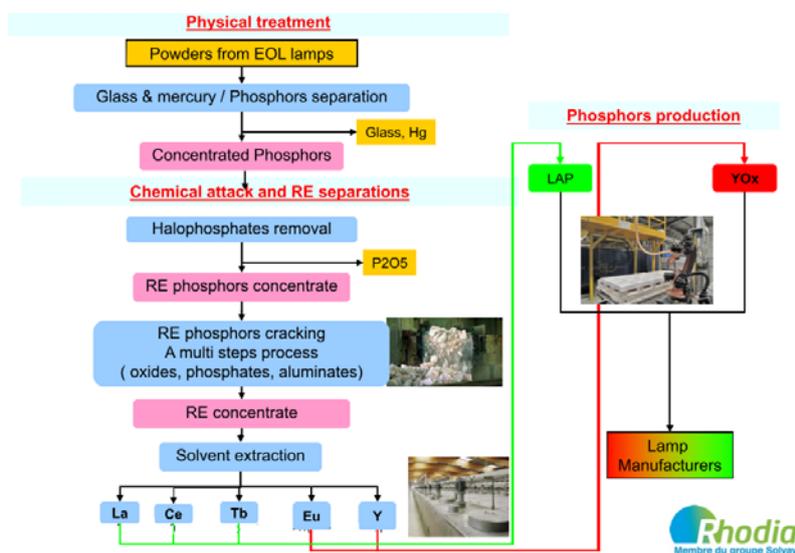


Figure 2 Solvay's process (Rollat 2012).

- NiMH Batteries
  - Umicore (Belgium) and Solvay, La Rochelle (France): Solvay co-operated with Umicore to refine REE concentrate (containing La, Ce, Pr, Nd) recovered in the Umicore's UHT battery recycling process (combined pyro/hydrometallurgical process) (Smith et al. 2012).
  - Honda and Japan Metals & Chemicals (Japan): Molten salt electrolysis process (de Lima 2015) for the extraction of REEs from NiMH Batteries collected from Honda's hybrid vehicles (Honda 2012)
  - Other R&D activities: E.g. Mitsui Metal Mining Co (Japan), Toyota (Japan) (Walters & Lusty 2011, Reisman et al. 2012)
- Other electronic waste
  - E.g. Kosaka Smelting and Refining (Japan) (a subsidiary of Dowa Holdings) (Reisman et al. 2012).
- Sludges (glass-polishing and magnet)
  - Hydrometal SA (Belgium): The company has recycled (by means of hydrometallurgy) ~1200 T REO from glass polishing sludge and magnet sludge since 2011. (Ferron and Henry 2015)

Although some mature technologies for REE recycling have been developed, the number of potentially recyclable applications is still very limited as research activities are mostly focused on lamp phosphors, permanent magnets and rechargeable batteries. Europe has no current production of primary REEs, but there is an increasing amount of REEs present in different applications. Recycling from secondary sources would be beneficial, as it would e.g. reduce the dependency on foreign (Chinese) resources, and create environmental benefits compared to primary REE mining and processing. (Schüler et al. 2011, Binnemans et al. 2013) On the other hand, the current low prices of the primary rare earths act as a barrier for recycling as obtaining economic profitability is very challenging.

It is also necessary to develop new innovative processes to recycle different REEs independently, as developed technologies often result in complex mixtures requiring further purification (Bailey 2015). The challenge in REE recovery from secondary sources lies in providing suitable concentrates for economically viable processing, not

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in the extraction chemistry itself. Therefore, the focus of the research should be on physical separation and concentration. Although the chemistry of extraction is known, knowledge on handling unusual impurities that may be present in recyclates must be attained. (UNEP 2013)

In the next sections, more detailed descriptions of the state of the art production technologies for different end-of-life products and manufacturing residues to recover REEs are presented.

### 3.1 PHOSPHORS IN LIGHTING APPLICATIONS (FLUORESCENT LAMPS, LEDS)

Rare earths are essential in phosphor substances used when aiming to accomplish the impression of natural light (Buchert et al. 2012, Deubzer et al. 2012). There are two main groups of phosphors that are used in significant quantities: a) garnet phosphors; cerium doped YAG (yttrium aluminium garnet) and TAG (terbium aluminium garnet), or LuAG (lutetium aluminium garnet) based on yttrium, terbium and lutetium, and b) europium doped ortho-silicates (Deubzer et al. 2012). Typical applications where phosphors are used are e.g. fluorescent lamps, LEDs, LCD backlights, plasma screens, CRTs, and different medical applications.

Phosphors contain several REEs in oxide form (Kooroshy et al. 2015), and the REE content in phosphors varies typically between 5–25 wt-% (Bailey 2015). Generally, yttrium is the most dominant REE in phosphors, but the content of REEs varies between different applications and manufacturers. For example, according to study by Punkkinen et al. (2017) fluorescent lamps seem to have higher levels of lanthanum, cerium, yttrium, europium, and terbium compared to LED bulbs. In contrast, the content of gadolinium is higher in LED bulbs than with compact fluorescent lamps (CFLs). Although yttrium is the most abundant REE in both lamp types, its content is many times higher in fluorescent lamps than in LEDs. In addition, lanthanum and terbium are used in fluorescent lamps but they may not be present in LEDs.

Manufacturing of phosphor containing applications generates some production losses, although in relatively small quantities. Therefore, pre-consumer recycling of these manufacturing residues is not a matter of high importance, for instance when compared to the production of permanent magnets. (Binnemans et al. 2013) No information on recycling activities concerning manufacturing residues was found from the literature reviewed.

Both CRTs and plasma screens represent a vanishing technique, but their stocks are still existing (Kooroshy et al. 2015). The recent market penetration of LEDs has decreased the market share of the fluorescent lamps containing more REEs, and according to ERECON (2014) also in the backlighting markets LCDs have been displaced by LEDs. In addition, it is assumed that the markets will move towards OLED TVs (Kooroshy et al. 2015). From the recycling point of view, ERECON (2014) has arranged the different applications in the decreasing order of interest as follows: fluorescent lamps, LCD backlights, plasma screens, CRTs and LEDs.

Due to the reuse, recycling and recovery requirements set for the lighting products by the European legislation, the collection and recycling of fluorescent and LED lamps is already a common practice, except for the phosphor powder part, that has been landfilled after its separation (Kooroshy et al. 2015) or alternatively temporarily stored for later processing (Binnemans & Jones 2014, Binnemans & Jones n.d.). Due to the wide ranging use of phosphor containing lighting products, the amount of waste phosphor generated is enormous (Liu et al. 2014) and thus potential for recycling. The fact that collection and recycling infrastructures are already in place is another advantage (Bauer et al. 2011). However, the recycling of the REE phosphors from waste phosphor is not easy (Liu et al. 2014), although compared to permanent magnets their recycling process is more straightforward (ERECON 2014).

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Direct reuse would be the simplest method, but due to many reasons presented in the literature, such as variations in phosphor mixture compositions, it can be only recommended to be used in special cases, e.g. if the lamp producer is able to recycle its own lamps. Belgian company Indaver, in collaboration with Philips Lighting, has developed a method based on identification of the characteristic fluorescent spectrum of the lamp phosphor coating to be able to recycle the phosphor containing part from Philips' linear fluorescent lamps. There are also several physical and chemical methods that can be used to separate phosphor mixtures in individual components, and to overcome the issue of differing phosphor mixtures used by the lamp manufacturers. However, as also the physicochemical methods have many drawbacks, and although the third method, hydrometallurgical recovery of the REE content, is the most drastic one, it is also the only way to obtain the high-purity REE oxide end products (Binnemans et al. 2013, Binnemans & Jones 2014, ERECON 2014). The advantages and disadvantages of the different methods are presented in Table 2.

Table 1 The pros and cons of different lamp phosphor recycling methods (Binnemans et al. 2013).

Direct re-use	<ul style="list-style-type: none"> <li>• Very simple method</li> <li>• No chemical processing required</li> </ul>	<ul style="list-style-type: none"> <li>• Only applicable to one type of fluorescent lamps, because different lamps make use of different phosphor mixtures</li> <li>• Phosphors deteriorate over the lifetime of the lamp</li> </ul>
Separation of phosphors in individual components	<ul style="list-style-type: none"> <li>• Relatively simple process</li> <li>• No or limited amounts of chemicals are consumed</li> </ul>	<ul style="list-style-type: none"> <li>• Very difficult to obtain very pure phosphor fractions</li> <li>• Separation process may change the phosphor particle size</li> <li>• Phosphors deteriorate over the lifetime of the lamp</li> </ul>
Recovery of REE content	<ul style="list-style-type: none"> <li>• Generally applicable to all types of phosphor mixtures</li> <li>• Same processing steps as those for extraction of REEs from primary ores</li> <li>• Gives very pure RE-oxides that can also be used for other applications</li> </ul>	<ul style="list-style-type: none"> <li>• Many process steps required before obtaining new lamp phosphors</li> <li>• Consumption of large amounts of chemicals</li> <li>• Generation of large amounts of waste water</li> </ul>

In principle, the hydrometallurgical recycling process for the recovery of REEs from phosphors requires the following steps: (K. Binnemans and Jones 2014)

1. Collection of EoL lamps
2. Physical treatments
  - a. Separation of phosphor from other material fractions
  - b. Purification of the phosphor to remove impurities (glass particles and mercury)
3. Chemical treatments
  - a. Transformation of the phosphor fraction into a REE concentrate
  - b. Separation of the REE concentrate in the individual metals
4. Production of new lamp phosphors. (K. Binnemans and Jones 2014)

The physical and chemical treatments are presented in the next sections.

### 3.1.1 PHYSICAL TREATMENT

Before hydrometallurgical treatment, lamps must be pre-treated and their REE fraction assessed to determine the type and quality of the phosphor. The separation of phosphor from linear fluorescent lamp is rather easy as phosphor can be blown out from the cutted ends of the tube and then collected (so called 'end cut' method). Other lamp types need to be crushed and shredded first, after which the broken glass particles and metals are separated from the phosphor by sieving. As the sieving process cannot remove the finest glass particles, the glass content in phosphor fraction can be even 50 wt-% after the sieving. The fine glass in phosphor powder dilutes its REE content, thus diminishing the value of it. In addition, glass complicates the further recycling process. (Smith et al. 2012, Binnemans et al. 2013, Kuchta 2013, ERECON 2014)

Crushing processes can be categorized into dry or wet processes, both being used in an industrial scale. Wet process is operated in liquid to capture the mercury and avoid its vapour contamination. In dry process, the metals, glass, and mercury containing phosphor powder are separated using separation equipment in closed or vacuum environment. After the first separation, mercury is separated from the phosphor powder. Commercial techniques for dry separation have been developed especially in Japan, but also e.g. in Canada, UK, and USA. (Wu et al. 2014)

An example of a commercial separation process is presented next. The Swedish company Nordic Recycling recycles lamps collected from Sweden, Norway and Denmark (J.L Richter 2014) using a wet oxidation process. LED lamps, although not containing mercury, are currently collected and treated together with fluorescent lamps (Jessika Luth Richter and Koppejan 2016). The company uses both dry and wet processes: (Nordic Recycling 2017)

#### 1. Dry process by crushing for compact fluorescent lamps, short fluorescent lamps and crushed lamps

- Manual separation from unwanted waste, drying
- Crushing by screws, magnetic or whirl stream separation to remove metals
- Drumming of glass, phosphor powder and other crushed lamp material to spread the material with the aim to get the phosphor powder into the air. The phosphor powder is then sucked up and filtered out.
- Separation of glass, and other crushed materials

#### 2. Dry process by end cutting for linear fluorescent lamps

- Drying and sorting according to lamp size
- Manual feeding into a machine for end cutting
- Removal of mercury contaminated phosphor powder from the lamps using an air-stream. Sucking up of the phosphor powder and transportation to a filtration process
- Crushing and sorting of glass according to level of cleanliness
- Treatment of the ends containing glass, metals and phosphor powder contains separation and crushing in a crush machine

#### 3. Wet process by automatic oxidation, for all lamp types

- Crushing of lamps in a closed facility
- Washing by tumbling in a fluid with chemicals for oxidization and binding of mercury
- Separation of phosphor powder and mercury into closed tanks in order to be recovered

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- Separation of cleaned glass, metals, and other materials free from mercury using metal-, whirl stream and sieve separators. (Nordic Recycling 2017)

Compared to dry processes, oxidation process generates lower mercury emissions, and requires less manual handling. The process generates a “fluorescent powder mix” containing phosphors and <1000 mg/kg mercury (Nordic Recycling 2017) that is of higher quality and formed in larger quantities. Previously, the powder mix was sold to Solvay (Jessika Luth Richter and Koppejan 2016) for separation and purification of REEs, which were then formulated to new phosphor powders and used in the lamp production. However, as mentioned, Solvay stopped the recycling of REEs in 2016 (Sgarioto et al. 2016, Pellegrini et al. 2017).

### 3.1.2 CHEMICAL TREATMENT

Similarly to primary processing of REE ores, the recovery of REEs from waste phosphor powder requires chemical attacks, such as alkali fusion to improve the dissolving efficiency and leaching to dissolve REEs into solution, from which they can be recovered by precipitation or solvent extraction (Binnemans et al. 2013, Wu et al. 2014). Leaching of phosphors is carried out with acids. Differences in solubility of different REEs allow for their selective recovery using different types of acids and temperatures (C. Tunsu and Retegan 2016). Alkali fusion is a thermal decomposition method for insoluble substances that destructs the structure of substances and enables their transition to soluble form. The purpose of chemical precipitation is, by adding chemical reagents such as oxalic acid or oxalate as precipitants, to precipitate the REE ions in a solution into insolubles, whereas extraction is used to obtain high purity individual REEs. Solvent extraction (liquid–liquid extraction) and supercritical fluid extraction are the two common methods used for REE extraction in literature studies. (Wu et al. 2014) Solvent extraction leads to higher purity and enables separation of individual rare earths, compared to precipitation. Many times, however, precipitation and solvent extraction treatments are combined. (C. Tunsu and Retegan 2016)

Many different types of combined recycling processes are developed and presented in the literature, such as combinations of a) dismantling, acid leaching and solvent extraction b) crushing, acid leaching and chemical precipitation c) two-step acid leaching and ionic liquid extraction, and d) alkali fusion, acid leaching and chemical precipitation. (Wu et al. 2014) Two examples representing a “typical” recycling process for phosphor powders are presented in Figure 6.

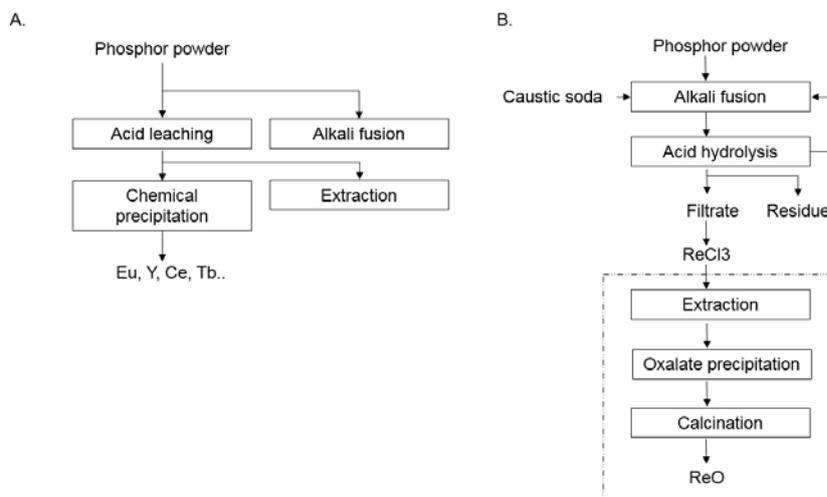


Figure 3 Recycling processes examples for phosphor powder recycling by (Wu et al. 2014) (A) and (Liu et al. 2014) (B) (modified).

According to Tunsu et al. (2015) the leaching of gadolinium, cerium, and lanthanum is more challenging procedure compared to e.g. the leaching of the yttrium and europium, due to chemical differences between different phosphor types, and therefore requires e.g. the use of different types of acids or increased temperatures, or longer time periods. The difference in solubility between phosphor types is typically utilised in selective leaching of different REEs. (Tunsu et al. 2015)

## SOLVAY

Due to the strong decline in REE prices (especially yttrium) Solvay ceased its REE recycling operations in 2016. The price decline is caused by the fast market penetration of LEDs (Sgarioto 2017), in which smaller quantities of REEs are used compared to the fluorescent lamps. However, the process is still the only European process operated in a commercial scale for the recovery of REEs from lighting products, and can be therefore described as state of the art technology. The process is further described in the next sections.

The Solvay's separation plant in La Rochelle, France, was the world's longest-running and perhaps the most advanced solvent extraction plant to separating and purifying REEs. As an only facility outside China (Rollat 2012, Solvay 2014), the plant was capable to separate both LREEs and HREEs, and separate and purify all of the 17 REEs (Kooroshy et al. 2015). According to Buchert et al. (2012) Solvay's two plants in La Rochelle and Saint-Fons were the first ones anywhere in the world carrying out the recycling of REEs from post-consumer waste. The decision for investment was made in 2011 (Solvay 2014) and the activities were planned to be focused on:

- Historical loss of yield from La Rochelle's plant (all rare earths) (most important raw material)
- Production losses from magnet manufacturing (Pr, Nd, Dy)
- End-of-life products:
  - Phosphor powder from lamps (La, Ce, Tb, Eu, Gd, Y)
  - NiMH batteries (La, Ce, Pr, Nd) in cooperation with Umicore. (Solvay 2015)

The process for lamps was the only industrial process worldwide operated on a commercial scale, and the REE recycling unit was opened in 2012 (Koen Binnemans 2013). The process was based on solvent extraction, which

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is, according to (Solvay 2014) the only industrial scale process used for REE separation. No process details are known, but roughly speaking the process contained the following steps: (e.g. Solvay - LOOP 2014, Machacek et al. 2015, Solvay 2015, Royen & Fortkamp 2016) (Figure 3 and Figure 7)

- Separated phosphor powders from different recyclers were first transported to St. Fons chemical separation plant for halophosphate removal. There phosphors were suspended in a water solution and underwent a chemical attack concentrating the REEs. The concentrate was then separated from the liquid, dried, and sent to La Rochelle plant for purification and separation.
- In La Rochelle, the REE concentrate was first led to pyrometallurgical thermal treatment, followed by de-slurrying which contained the resuspension, filtration and washing phases. After de-slurrying, treatment with nitric acid dissolved the material, and REEs (lanthanum, cerium, europium and gadolinium, terbium, and yttrium) were separated by solvent extraction. Finally, separated REEs were precipitated, filtered, and calcined and reformulated into new phosphors precursors, mainly  $Y_2O_3:Eu^{3+}$  (YOX) and  $LaPO_4:Ce^{3+}, Tb^{3+}$  (LAP), which could be used in the production of new lamps.

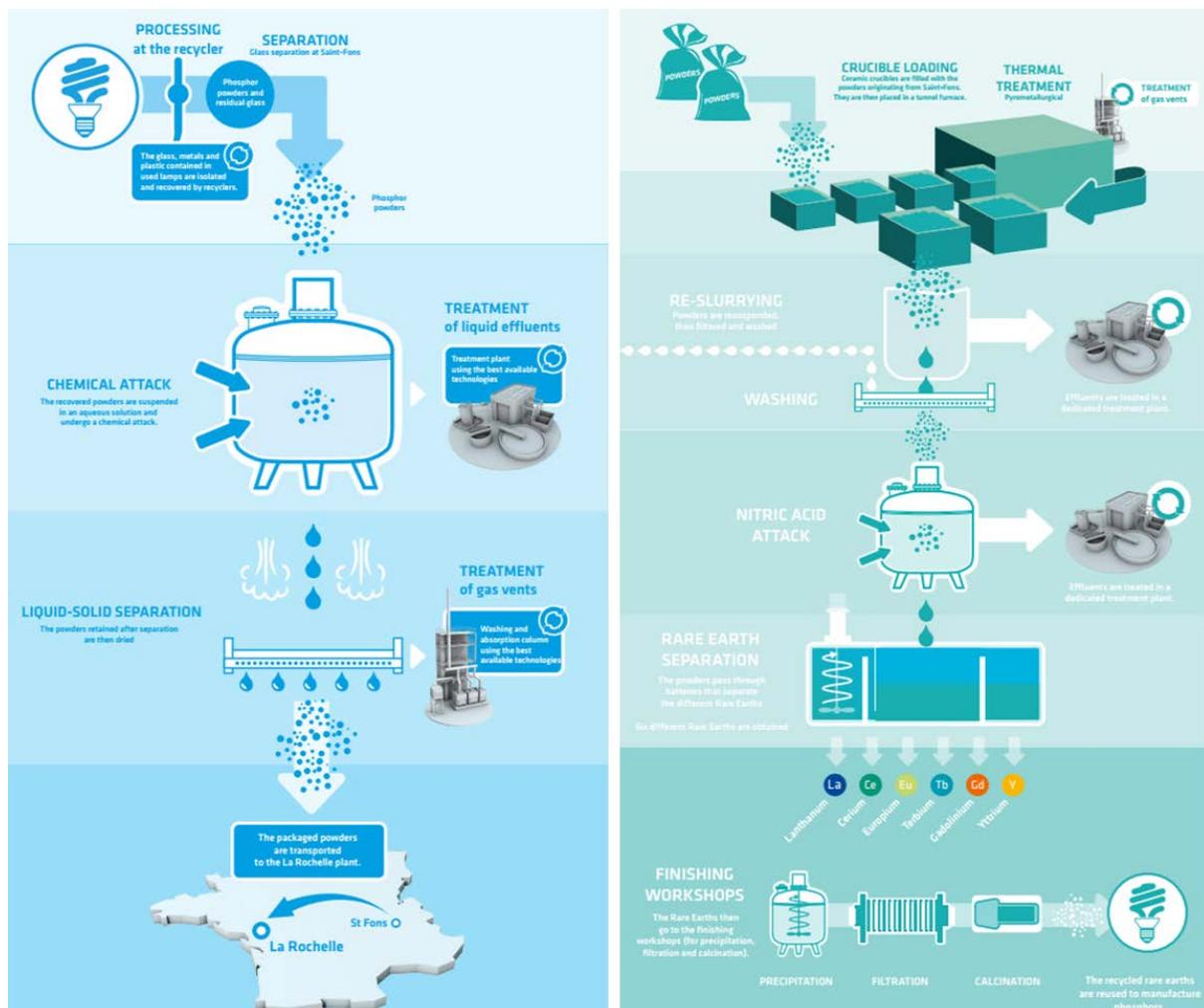


Figure 4 Solvay's lamp recycling process (Solvay - LOOP 2014).

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According to the process patent, the yield of REEs was around 75 to 80% (Braconnier and Rollat 2010) and the recovered REEs preserved fully their original properties (Worrel and Reuter 2014). The objective of the industrial scale process was to treat 3,000 t/a of lamp waste, and result in 90% waste stream valorisation by recovering 10-20% of rare earth oxides, and recycling 10-50% by-product glass and 70-80% by-product phosphate (Solvay 2014).

## RARE EARTH SALTS

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An American company Rare Earth Salts (RES) announced in June 2017 that it has successfully commissioned a commercial separation unit for recycling of REE oxides from fluorescent lamps. The company is aiming at the monthly production of 18 tonnes of yttrium, europium, terbium, cerium, and lanthanum oxides with a standard purity of 99.9%. In the company website, the separation technology is defined as cost efficient and environmentally friendly. The manufacturing feeds can be recycled to avoid waste generation. (Rare Earth Salts 2017)

The recovery process used is not described on the company website, but the company has a patent according to which the process is suitable for primary and secondary production of REEs. The patented process contains the following phases (Figure 8): (Brewer 2016)

- Leaching of crushed material with mineral acid(s) (e.g.  $\text{HNO}_3$ ) with a  $\text{pH} < 1$ , to form a solution containing REE ions, solids, and at least one metal ion. Heating may be used to improve REE extraction.
- Separation of solids from liquids to form liquid REE ion leachate
- Precipitation of metal ion(s) (e.g. Fe) by titration with MgO, followed by its separation
- Treatment of liquid REE concentrate to obtain precipitated concentrate
- Heating of REE precipitate in air (calcination) to form REE oxide concentrate
- Mixing of REE oxide concentrate with an ammonium salt and heating in a dry air or nitrogen, resulting in a mixture of anhydrous REE salts in an aqueous solution
- Separation of REEs from the liquid with electrowinning process, in which REEs are plated using a sacrificial anode
- After REE concentrate precipitation, magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2$ ) is recovered to MgO and nitric oxide ( $\text{NO}_x$ ) from the remaining solution.  $\text{NO}_x$  is bubbled through  $\text{H}_2\text{O}$  to regenerate the acid. (Brewer 2016)

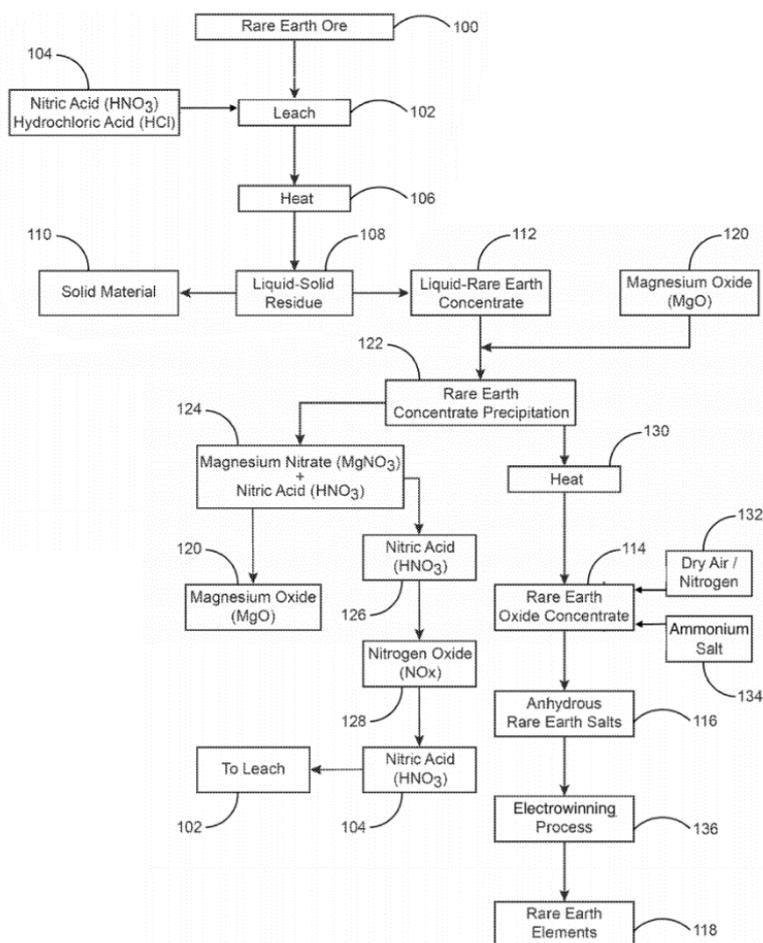


Figure 5 Patent by Rare Earth Salts (Brewer 2016, modified).

## HYDROWEEE CONCEPT

One of the aims of the HydroWEEE Demo project, financed by European Commission under the 7<sup>th</sup> Framework Programme, was to build an industrial scale stationary demonstration plant for the recovery of REEs from WEEE. The plant was installed in the premises of an Italian WEEE treatment and recycling company Relight, and the construction of the plant was finalized in 2014. (Sgarioto 2017) Another aim was to build a mobile treatment plant for the hydrometallurgical recovery of metals and high value elements from WEEE (European Commission 2016). The mobile plant was constructed and demonstrated in the premises of GreenTronics, Romania (de Michelis 2017).

The stationary plant uses hydrometallurgical recovery process developed in the first phase of the project (Sgarioto 2017). Originally, the process was directed especially for the recovery of yttrium from phosphor powders from lamps and CRTs, but also europium, gadolinium, terbium, cerium, and lanthanum could be recovered using the process. A flowsheet of the process is presented in Figure 13. In the process, phosphor powder is first leached with sulphuric acid, then filtrated, and precipitated using oxalic acid. After the second filtration, formed REE oxalates are calcined to form REE oxides. Residual solution is treated with lime, and could be either reused or disposed. A batch type process is able to treat around 400 tonnes of phosphor powders annually, generating around 165 tonnes of semi-finished REE oxalate product with around 97% REE content (Y,

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Eu, Gd, Tb, Ce, La). (Sgarioto, Ferrari, and Kopacek 2016) The aim was to sell the oxalate formed in the process to Solvay for further processing and separation into individual REEs (Sgarioto 2017).

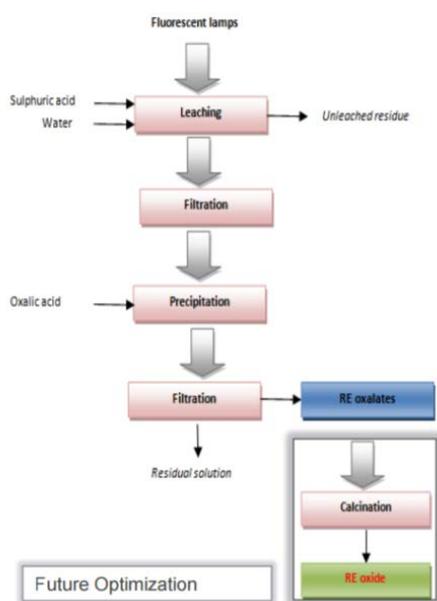


Figure 6 A process flowsheet for HydroWEEE Demo process (Sgarioto et al. 2016).

However, unforeseen and strong decline in REE prices in general and especially for yttrium (caused by the fast market penetration of LEDs), caused the deterioration in demand for secondary (yttrium) products. Therefore, the project group decided to focus on the recovery of terbium instead due to its higher economic value to be able to generate a profitable process. (Sgarioto 2017)

An efficient leaching of terbium requires more aggressive conditions compared to leaching of europium and yttrium, for example. Alternatively, calcination of the feed material with an alkaline material converts rare earth phosphates in oxides and thus more easily dissolvable form. (Innocenzi et al. 2016) To be able to reach a higher recovery yield of terbium, a calcination step was added before the leaching step in the beginning of the original process (Sgarioto 2017).

Interestingly, researchers from the HydroWEEE Demo project have recently published an article concerning the recovery of terbium from fluorescent powders, although this process has so far apparently been tested only at laboratory scale. In their article, Innocenzi et al. (2016) conduct a process analysis for the acid leaching process based on statistically optimized experimental conditions. Based on the experiments, a process flowsheet was created (Figure 14) containing the following phases:

- Fluorescent powder calcination: Calcination with KOH at 900 °C
- Washing to remove soluble residual compounds and filtration: Washing with H<sub>2</sub>O at RT, followed by filtration
- Terbium leaching and filtration: Leaching with 5 M HCl at 90 °C, followed by filtration
- Ca sulphate precipitation and filtration: Precipitation with H<sub>2</sub>SO<sub>4</sub> at RT, followed by filtration
- Rare earth oxalate precipitation and filtration: Precipitation with oxalic acid (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>), followed by filtration
- Oxalate calcination to oxides: Calcination at 600 °C. (Innocenzi et al. 2016)

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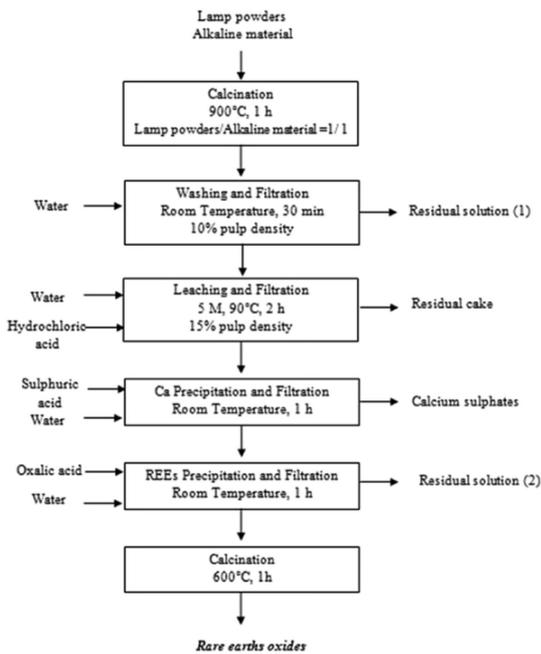


Figure 7 A process for recovery of terbium and other REEs from spent phosphor powders (Innocenzi et al. 2016).

Super Pro Design software was used to test and simulate the process developed. Based on the simulation, it would be possible to recover around 160 kg of REE oxides with a purity of 99% from 1 tonne of waste. (Figure 15) Around 70% of Eu and Y, and 80% of Tb, Ce and La could be recovered using the process described. (Innocenzi et al. 2016).

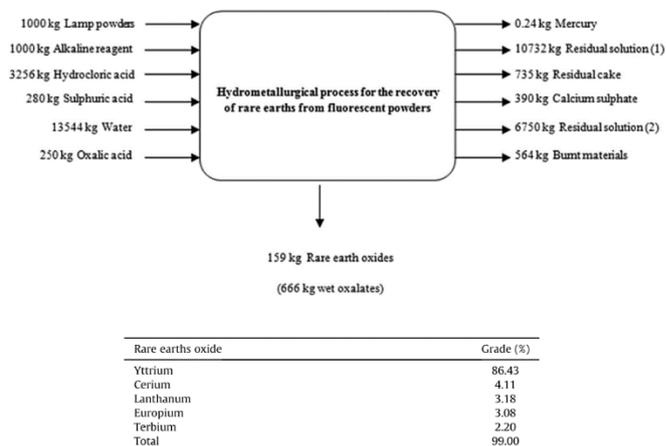


Figure 8 Simulated mass balance and REE oxide composition of the final product (Innocenzi et al. 2016).

## OTHER PROCESSES

Also several other processes for the recovery of REEs from phosphors have been developed. E.g. OSRAM (Germany) has a patented process for the recovery of REEs. The OSRAM's process consists of the following steps: (Figure 9)

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- Mechanical separation of coarse fraction
- Separation of halophosphates using cold diluted hydrochloric acid
- Leaching of easily soluble components (mainly Y and Eu oxides) using hot diluted hydrochloric acid
- Leaching of poorly soluble components (REE phosphates) using hot concentrated sulphuric acid
- Grinding of aluminate phosphors and its treatment with acid or alkali
- Final treatment (precipitation of REE as oxalates, transformation of the oxalates in oxides). (Otto & Wojtalewicz-Kasprzak 2012, Langer 2012)

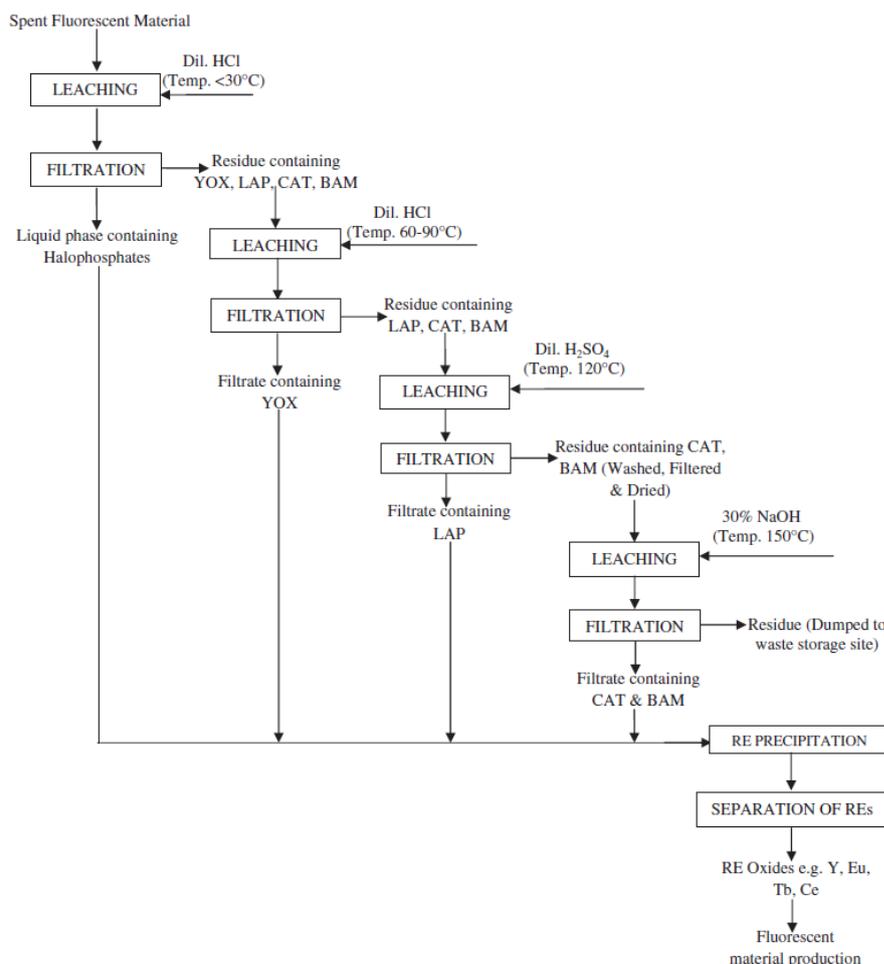


Figure 9 OSRAM's multistep leaching process for REE recovery by Otto & Wojtalewicz-Kasprzak (2012) (Jha et al. 2016).

Apparently the process has been tested at pilot scale (Machacek et al. 2015), but the current status of the OSRAM's process is unknown. Among the other lamp manufacturers, at least Philips has also had pilot scale projects regarding to recovery of phosphors (Machacek et al. 2015). Other processes have been developed e.g. by REEnewal Corporation (U.S.) (patented) (REEnewal Corporation 2013), CMI (U.S.) (demonstrated) (Bailey 2015) Técnicas Reunidas Technology Centre (Spain) (for Eu and Y, piloted) (Alvarez et al. 2015), and REconserve (the Netherlands) (for Eu and Y, piloted) (Kesber 2011).

In addition, it is possible that China has recycling and recovery activities regarding to phosphors, but information on these processes was not found. However, Liu et al. (2014) mention an alkali fusion and the

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traditional extraction separation being the only commercial REE recycling method from waste phosphor powders in China. According to Chinese patent CN 101307391A by (Ni 2008), by using this method it is possible to recover Eu, Tb, Ce and Y.

### 3.2 DISPLAYS

Apart from their use in general lighting applications, REEs are also used in the luminescent material in displays, mobile phones, notebooks and vehicle dashboards. In CRT and LCD technologies rare earths are used in the phosphor substances in the background illumination, whereas in plasma displays and OLEDs rare earths are used in the displays themselves. (Buchert et al. 2012) Each different technology uses different types and compositions of phosphors; the phosphor composition used depends on the colour requirements of the end product (Peiró, Méndez, and Ayres 2011). LCD displays with LED background illumination contain also other critical materials than REEs, as indium is used in their semiconductor dies.

Both CRTs and plasma displays represent a vanishing technique, but there are still some waste stocks existing (Kooroshy et al. 2015). The recent market penetration of LEDs has decreased the market share of fluorescent lamps containing more REEs, and also in the backlighting markets CCFL-backlit (cold-compact fluorescent lamp) LCDs have been displaced by LED-backlit LCD displays containing less REEs. In addition, it is assumed that the markets will soon move towards OLED TVs (Kooroshy et al. 2015). Commercial scale recycling of EoL displays exists in different countries, but these are focused on the recycling of the metal and glass, not the rare earths. It seems that the rare earths are not currently recycled from these applications, and compared to the recycling of phosphors from EoL lamps, relatively little research have been devoted to this subject.

The situation with displays is somewhat similar to the general lighting applications, as their market moves towards less rare earth containing applications, and it can be expected that this trend probably leads to even decreasing interest on their recovery. Therefore, it is not very likely that recovery processes focusing on just the rare earths used in displays will be commercialized in the near future.

### 3.3 NICKEL METAL HYBRID BATTERIES

Rechargeable batteries are used as a power source in many electronic products. Nickel metal-hydride (NiMH) batteries are amongst the most effective rechargeable battery types currently used. The main uses of NiMH batteries include rechargeable AA and AAA batteries, power tools, and most importantly hybrid electric vehicles (HEVs) (Cristian Tunsu et al. 2015) (57% of the usage of NiMHs (Koen Binnemans et al. 2013)). More than 95% of HEVs contain a NiMH battery. Their safeties in manufacturing and use, flexibility in design, low maintenance and cost, high power and energy densities, as well as environmental acceptability generate advantages compared to other battery types, e.g. Li-ion batteries (Pollet, Staffell, and Shang 2012). It is estimated that the amount of HEVs will increase in the coming years, leading to increased waste amounts (Innocenzi et al. 2017) and therefore causing a need for more efficient recycling methods (Petranikova et al. 2017).

REEs in NiMHs are incorporated into the negative electrode, which function is to reversibly produce a metal hydride compounds mixture (MH). The “metal” of anode is actually an intermetallic compound; most commonly AB<sub>5</sub> (containing LaCePrNdNiCoMnAl), but also AB<sub>2</sub> (VTiZr-NiCrCoMnAlSn) is sometimes used. (Brunot et al. 2013, Innocenzi et al. 2017) Typically, EoL NiMH batteries contain around of 36–42% Ni, 3–4% of Co, and 8–10% of mischmetal consisting of REEs (La, Ce, Pr and Nd) (Müller and Friedrich 2006), whereas the

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REE content in hybrid electric car batteries is around 7% (i.e. around 2.5 kg of REEs in every Toyota Prius battery) (Buchert 2010).

Commercial scale recycling processes for EoL batteries are available, e.g. Accurec in Germany, SAFT in Sweden, and SNAM in France recycle NiMH batteries as well as other battery types (Punkkinen et al. 2017). However, commercial processes are not focused on the recovery of REEs, but for example in case of NiMH batteries, of the other metals such as nickel, chromium, and iron (Panayotova and Panayotov 2012). The recycling of REEs is still on the research and development stage. Hydrometallurgical processes are often preferred to pyrometallurgical ones when considering the recovery of REEs in general, and this is also the case with rechargeable batteries, as most of the research work done has focused on hydrometallurgical treatment. Nevertheless, also some pyrometallurgical processes have been reported. The advantages and disadvantages of these two methods are presented in Table 2.

Table 2 The pros and cons of different methods for REEs recycling from NiMH rechargeable batteries (Koen Binnemans et al. 2013).

Method	Pros	Cons
Hydrometallurgical routes	<ul style="list-style-type: none"> <li>• Low investment costs</li> <li>• Recycling of different waste fractions possible (cathode and anode materials, metals from casing) that can be marketed separately</li> </ul>	<ul style="list-style-type: none"> <li>• Battery dismantling and separating the different components requires several manual operations</li> <li>• Large chemical consumption</li> </ul>
Pyrometallurgical routes	<ul style="list-style-type: none"> <li>• Well-developed technology</li> <li>• Energy recovery from plastic casings and other organic components</li> <li>• Same processing steps used for extracting REEs from slags as from primary ores</li> </ul>	<ul style="list-style-type: none"> <li>• High investment cost for furnace</li> <li>• REEs need to be extracted from slags</li> <li>• REEs are obtained as mixtures requiring further separation</li> </ul>

In addition, some general bottlenecks related to recycling of rechargeable batteries are presented below:

- It is difficult to attain high collection rates for small items like rechargeable batteries used in consumer applications.
- There are several types of rechargeable batteries and no standardized marking of battery chemistry, which may make sorting difficult. Different battery types need also different recycling methods.
- A part of the batteries is sold integrated in the products (e.g. in some smartphones) and not designed for easy disassembly. This may decrease the recycling rate of batteries. Easy disassembly of batteries would also ease the de-pollution of the main device and decrease risks to workers.
- Lack of coordination between the actors in the battery value chain.
- Depending on the situation, it can be either a benefit or a problem if the electronics recycler separates the batteries.
- Car batteries are not designed for other applications although they can be rebuilt. However, this requires a lot of resources.
- Economic feasibility of recycling
  - dismantling/reuse of batteries costs more than producing a new one
  - high logistics costs, organization of efficient logistics needed
  - complex and energy-intensive processing to battery grade
  - high costs of recycling vs. low value of the recycled products
- Uncertainty in battery chemistry developments complicates estimation of the feasibility of battery recycling business.
- Regarding to REE recovery
  - research is at the early stage. (Punkkinen et al. 2017)
  - high complexity of the hydrometallurgical processes (Scott 2009).

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In their recent review article Innocenzi et al. (Innocenzi et al. 2017) divide recycling processes for EoL NiMH batteries into physical/mechanical, pyrometallurgical and chemical processes. By combining different chemical processes such as acid leaching and selective precipitations or solvent extractions both REEs and base metals can be recovered. Mechanical and thermal treatments mostly recover either base metals or generate a REE rich slag for further refining, and therefore these treatments are usually utilized as pre-treatment methods prior to chemical processing. (Innocenzi et al. 2017) E.g. mechanical pre-treatment step is required prior to hydrometallurgical processing to obtain better recovery rates. Manual dismantling and separation of the anode and cathode is recommended for HEV NiMH batteries (REEs are present only in the anode), whereas for small portable batteries crushing and grinding is the typical method used. (Cristian Tunsu et al. 2015)

Innocenzi et al. (Innocenzi et al. 2017) divide chemical processes into:

- Solid-liquid extraction processes: After the pre-treatment, the fine NiMH battery powder is selectively leached, most commonly with sulphuric or hydrochloric acids at different concentrations. The research has focused into two different routes: either recovery of metals, such as Ni, Mn and Co, or recovery of metals and REEs both.
- Recovery of REEs and metals from leaching solutions: selective precipitation, solvent extractions, electrochemical processes, and adsorption are used, often by combining different operations to complex series. Liquid extraction is the method most commonly used in the literature for the selective separation and recovery of base metals after REE precipitation. (Innocenzi et al. 2017)

Examples of the typical processes combinations used are:

- Combination of physical, mechanical and thermal processes
- Combination of acid leaching and chemical precipitation
- Combination of acid leaching, solvent extraction and chemical precipitation
- Combination of acid leaching, chemical precipitation and electrochemical process
- Combination of acid leaching, precipitation and adsorption (Innocenzi et al. 2017)

Industrial processes for NiMH battery recycling exist, however, only very few of them focusing on REE recovery. These processes are overviewed in the next sections.

### 3.3.1 UMICORE AND SOLVAY

Umicore's (Hoboken, Belgium) and Solvay's (La Rochelle, France) combined pyro/hydrometallurgical treatment process was the first industrial technology used for recycling REEs from NiMH batteries (Reisman et al. 2012). In addition to REEs, also base metals can be recovered with the process (Koen Binnemans et al. 2013) (Umicore 2017) (Smith et al. 2012) (Innocenzi et al. 2017).

The REE recovery started up in 2011. The process details are not available, but the pyrometallurgical process is based on Umicore's Ultra High Temperature (UHT) smelting technology, which is suitable for processing both NiMH and Li-ion batteries (Koen Binnemans et al. 2013) (Figure 11). The capacity of Umicore's UHT furnace is 7,000 t/a (Umicore 2017). At least in the beginning, the process was optimised for EoL portable NiMH batteries only (Koen Binnemans et al. 2013) (K. Binnemans 2012).

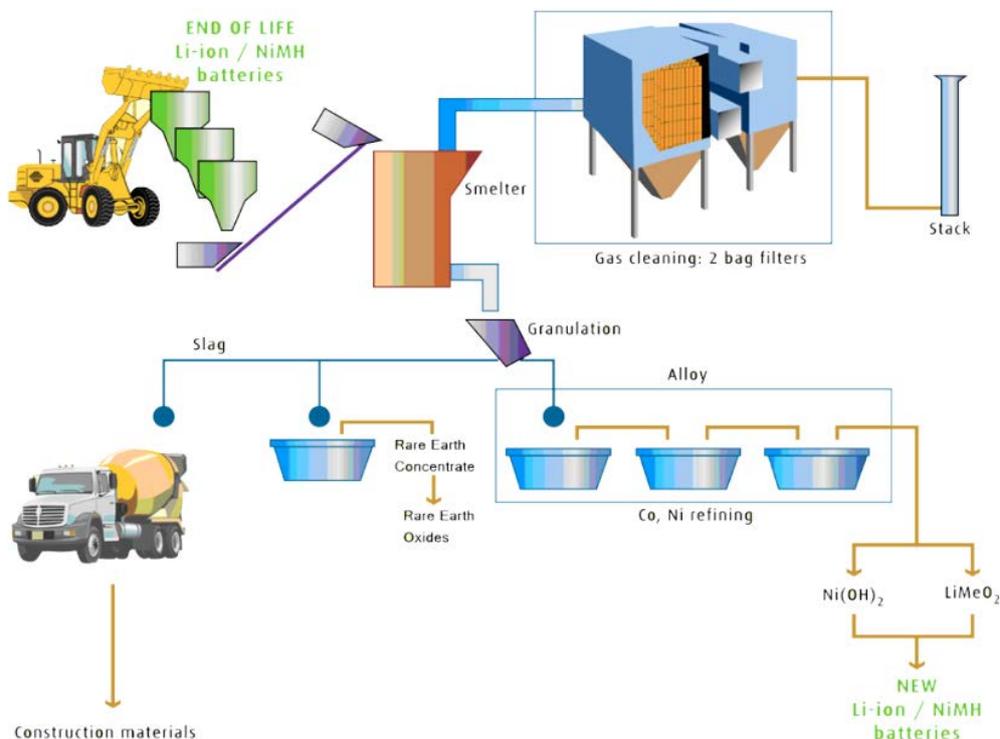


Figure 10 Umicore's recycling process for EoL NiMH / Li-ion batteries (K. Binnemans 2012).

In the UHT process, batteries are fed in a furnace with coke and a slag former. Oxygen-rich air is injected into the furnace. Smelting produces a metal alloy containing Co, Ni, Fe and Cu, and a slag of a mixture of oxides (Ca, Al, Si, Fe, Li) with relatively high concentration of rare earths (La, Ce, Pr, Nd). (Koen Binnemans et al. 2013) (Smith et al. 2012) (Innocenzi et al. 2017) The REEs processed to concentrate were formerly refined by Solvay's REE recovery process (Koen Binnemans et al. 2013) (Umicore 2017) (Smith et al. 2012) (Innocenzi et al. 2017), which is described in Chapter 1.2.1. However, due to the strong decline in REE prices (especially yttrium) Solvay stopped its REE recycling operations in 2016 (Sgarioto 2017), and the current status of the REE recovery from NiMH recycling slag is therefore unclear.

### 3.3.2 HONDA MOTOR AND JAPAN METALS & CHEMICALS

Honda Motor in cooperation with the Japan Metals & Chemicals developed a hydrometallurgical process based on molten electrolysis for the recovery of REEs from NiMH batteries of Honda's hybrid vehicles. In the process, after the pre-treatment phases, acid leaching is used to recover REEs in oxide form. Molten salt electrolysis is then applied to these oxides resulting in REEs in metallized form. The metallized REEs can be reused as negative electrode materials in new batteries (Figure 11). With the process, a REE purity of more than 99 % has been achieved, and more than 80 % of REEs in NiMH battery can be extracted. The process was successfully tested at least in 2013 (Honda Motor Co 2013), however, no later references on the process was found, and it remains unclear whether the process is still in use today.

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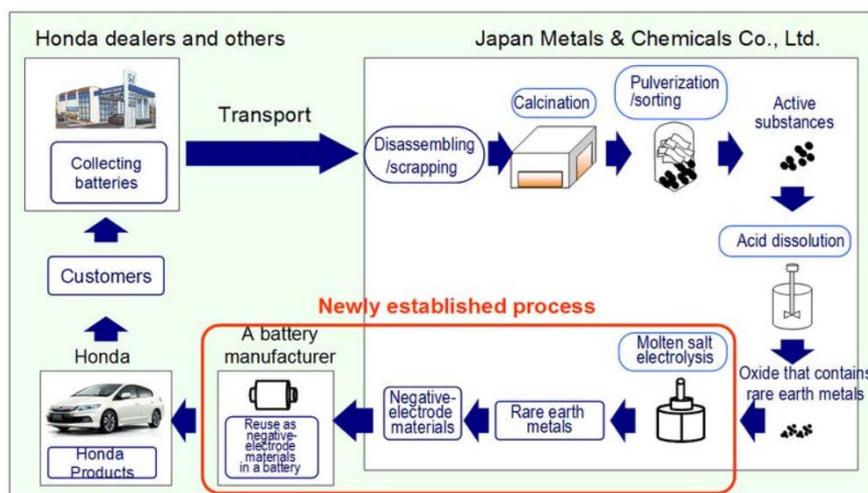


Figure 11 Honda’s and Japan Metals & Chemicals’ process for NiMH battery recycling. (Honda Motor Co 2013)

### 3.3.3 OTHER PROCESSES

In addition, Innocenzi et al. reported the main relevant patents in their article (Innocenzi et al. 2017). These patents, as well as the industrial processes for REE recovery from EoL NiMH batteries are listed in Table 4.

Table 3 Industrial processes and patents relative to the recycling of REEs from EoL NiMH batteries (Innocenzi et al. 2017, modified).

Umicore (Belgium) and Solvay (France)	Industrial (Solvay stopped its REE recycling operations in 2016)	NiMH, Li-ion	Pyro/hydro	Alloy containing base metals (Ni, Co, Cu, Fe). Slag of a mixture of oxides (Ca, REEs)
Japan Metals & Chemicals and Honda Motor (Japan)	Industrial (?)	NiMH	Hydro	REE oxides
Patent 2011/113860A1, Akkuser (Finland) (Pudas, Erkkilä, and Viljamaa 2011)	Patent / Industrial (Technology used at industrial scale, apparently REEs not recovered (Recser Oy 2012))	NiMH, Ni-Cd, alkaline	Mechanical	Powders containing Co, Ni, Fe, Al, Cd and REEs
Patent US 8246717 B1, Toxco (USA) (Novis Smith and Swoffer 2010)	Patent	NiMH	Mechanical	Ni(OH) <sub>2</sub> and the AB <sub>2</sub> and/or AB <sub>5</sub>
Patent US8696788, Retrieval Technologies (USA) (Novis Smith and Swoffer 2014)	Patent	NiMH	Hydro	AB <sub>5</sub> , Ni as metal
Patent EP2444507 A1, Montanuniversität Leoben (Austria) (Luidold and Antrekowitsch 2010)	Patent	NiMH	Hydro	REEs as sulphates
EP2788517 A2, Xylon Technical Ceramics (USA) (Burlingame &	Patent	NiMH	Hydro	REEs and Zr as oxide

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Burlingame 2012)				
WO2014144463 A1, The University Of Houston System (USA) (Jacobson & Samarasekere 2014)	Patent	NiMH	Hydro	REEs as oxides

### 3.4 PERMANENT MAGNETS

The most common type of permanent magnet is so-called NdFeB magnet; neodymium, iron and boron containing magnet, with the formula  $Nd_2Fe_{14}B$ . Depending on the end application, NdFeB magnet may also contain a small amount of dysprosium, praseodymium, terbium, and gadolinium (Yang et al. 2017). The average percent by weight REE consumption distribution of magnets is 69.4% neodymium, 23.4% praseodymium, 5% dysprosium, 2% gadolinium, and 0.2% terbium (Morgan 2010). Typically REE permanent magnet contains about 31–32 wt% REEs (mainly 21–31 wt% (Nd + Pr), 0–10 wt% Dy, plus small amounts of Gd and Tb) (Kozawa 2011).

Around 23,000 tonnes ( $\pm 15\%$ ) of rare earth oxides were used for producing permanent magnets in 2012, consisting of 17,640 tonnes of Nd; 3,600 tonnes of Pr; 835 tonnes of Dy; 500 tonnes of Sm; 360 tonnes of Gd, and 70 tonnes of Tb (European Commission 2014).

NdFeB magnets are utilized in several end applications in different industry areas. The largest application group is the motors and generators which represent around 34 % of the market share followed by HDD, CD, DVD and transportation applications with 14 and 11 % shares respectively Figure 12.

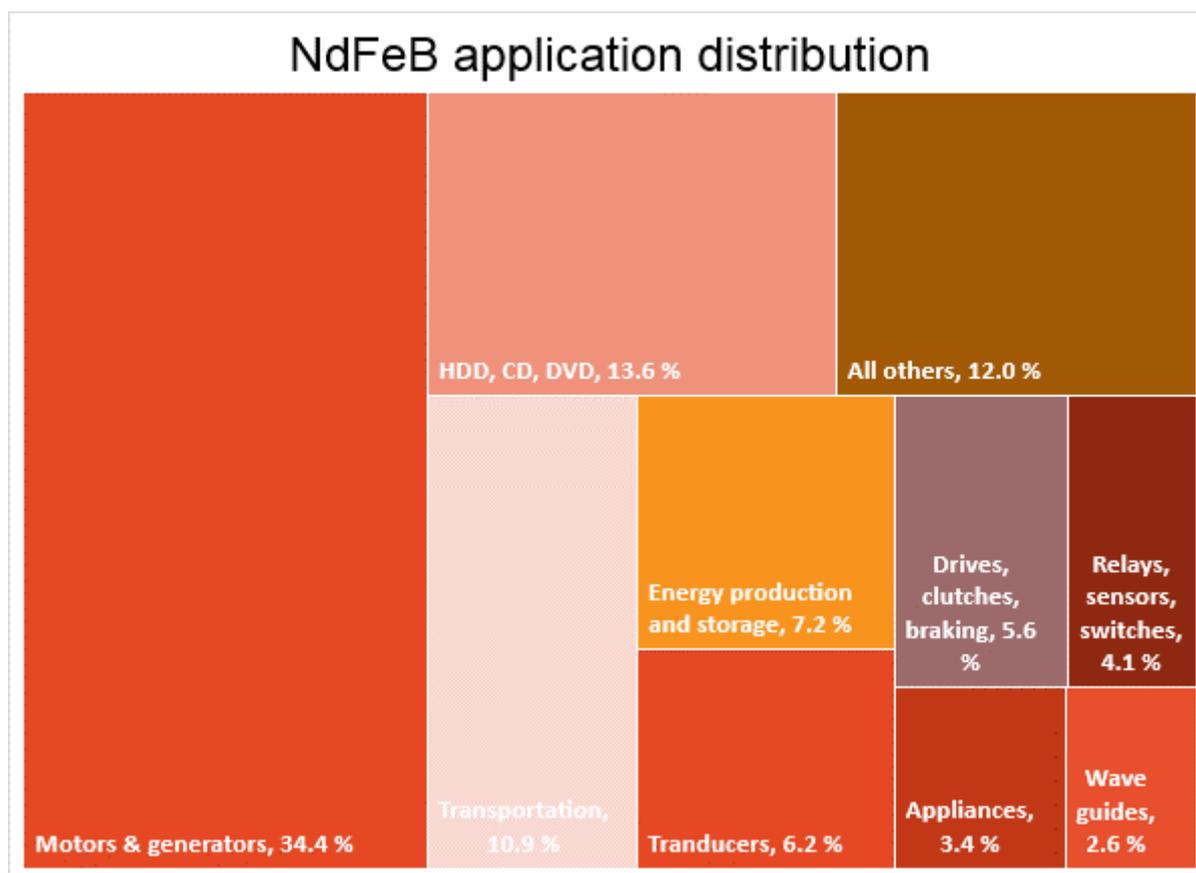


Figure 12 NdFeB end application distribution in 2012 (Yang et al. 2017).

Beside NdFeB magnets, samarium cobalt magnets (SmCo) are utilized in aerospace, automotive, sensor, loudspeaker, motor and military applications. It is not as strong magnet as NdFeB magnet, but offers high coercivity (resistance against demagnetization), good corrosion resistance and excellent thermal stability. Due to their lower energy product and higher price, their market share is very small (less than 2%). (Koen Binnemans et al. 2013) Typical SmCo magnet is composed of: Sm 10-30 %, Co 50 %, Fe <20 %, Cu 8 %, Zr 4 % and Gd <8 % (Ferron and Henry 2015).

The recovery actions concerning permanent magnets are mostly focused on the recovery of major REE components Nd and Dy, (also Pr and Tb). However, the commercial efforts have focused solely on the recovery of REE from manufacturing residues (swarf etc.) not from EoL (Yang et al. 2017). Within EoL most of the processing methods are still at various research and development stages. It is estimated that in the coming 10–15 years, the recycled REEs from EoL permanent magnets will play a significant role in the total REE supply in the magnet sector, provided that efficient technologies will be developed and implemented in practice (Yang et al. 2017).

An overall description of different proposed treatment and recovery methods for magnet recycling is presented in Table 4.

Table 4 An overview of the advantages and disadvantages of the different recycling methods for REE magnets (Koen Binnemans et al. 2013).

Direct re-use in current form/shape	<ul style="list-style-type: none"> <li>• Most economical way of recycling (low energy input, no chemical consumption)</li> <li>• No waste generated</li> </ul>	<ul style="list-style-type: none"> <li>• Only for large easily accessible magnets (wind turbines, large electric motors and generators in hybrid and electric vehicles)</li> <li>• Not available in large quantities in scrap currently</li> </ul>
Reprocessing of alloys to magnets after hydrogen decrepitation	<ul style="list-style-type: none"> <li>• Less energy input required than for hydrometallurgical routes</li> <li>• No waste produced</li> <li>• Especially suited for hard disc drive magnets (little compositional change over the years)</li> </ul>	<ul style="list-style-type: none"> <li>• Not applicable to mixed scrap feed, which contains magnets with large compositional variations</li> <li>• Not applicable to oxidized magnets</li> </ul>
Hydrometallurgical methods	<ul style="list-style-type: none"> <li>• Generally applicable to all types of magnet composition</li> <li>• Applicable to non-oxidized and oxidized alloys</li> <li>• Same processing steps as those for extraction of rare earths from primary ores</li> </ul>	<ul style="list-style-type: none"> <li>• Many process steps required before obtaining new magnets</li> <li>• Consumption of large amounts of chemicals</li> <li>• Generation of large amounts of waste water</li> </ul>
Pyrometallurgical methods	<ul style="list-style-type: none"> <li>• Generally applicable to all type of magnet compositions</li> <li>• No generation of waste water</li> <li>• Fewer processing steps than hydrometallurgical methods</li> <li>• Direct melting allows obtaining master alloys</li> <li>• Liquid metal extraction allows obtaining REEs in metallic state</li> </ul>	<ul style="list-style-type: none"> <li>• Large energy input required</li> <li>• Direct smelting and liquid metal extraction cannot be applied to oxidized magnets</li> <li>• Electroslag refining and the glass slag method generate large amounts</li> </ul>
Gas-phase extraction	<ul style="list-style-type: none"> <li>• Generally applicable to all types of magnet compositions</li> <li>• Applicable to non-oxidized and oxidized alloys</li> <li>• No generation of waste water</li> </ul>	<ul style="list-style-type: none"> <li>• Consumption of large quantities of chlorine gas</li> <li>• Aluminum chloride is very corrosive</li> </ul>

Beside hydro- and pyrometallurgical methods, direct re-use, reprocessing after hydrogen decrepitation and gas-phase extraction has been listed as proposed treatment method (Table 4). As stated in the Table 4, direct recycling and re-use is only relevant for the large magnets. In all other cases the REE magnet alloys need to be further processed. For applications where the composition distribution of the REE magnets is very narrow among the different manufacturer (e.g. computer hard disc drives, HDDs), one can consider direct use of the alloy by powder processing or by remelting of the recycled magnets to REE master alloys for the production of new REE magnets. In other cases, it has been recommended to separate the rare earths from the transition metals and other elements (e.g. boron) present in the magnet alloys. After which the recycled REE mixture is separated to individual REEs. (Koen Binnemans et al. 2013)

Another classification between different treatment methods for rare earth permanent magnets has been presented by Ferron & Henry which is illustrated in Figure 15. (Ferron and Henry 2015)

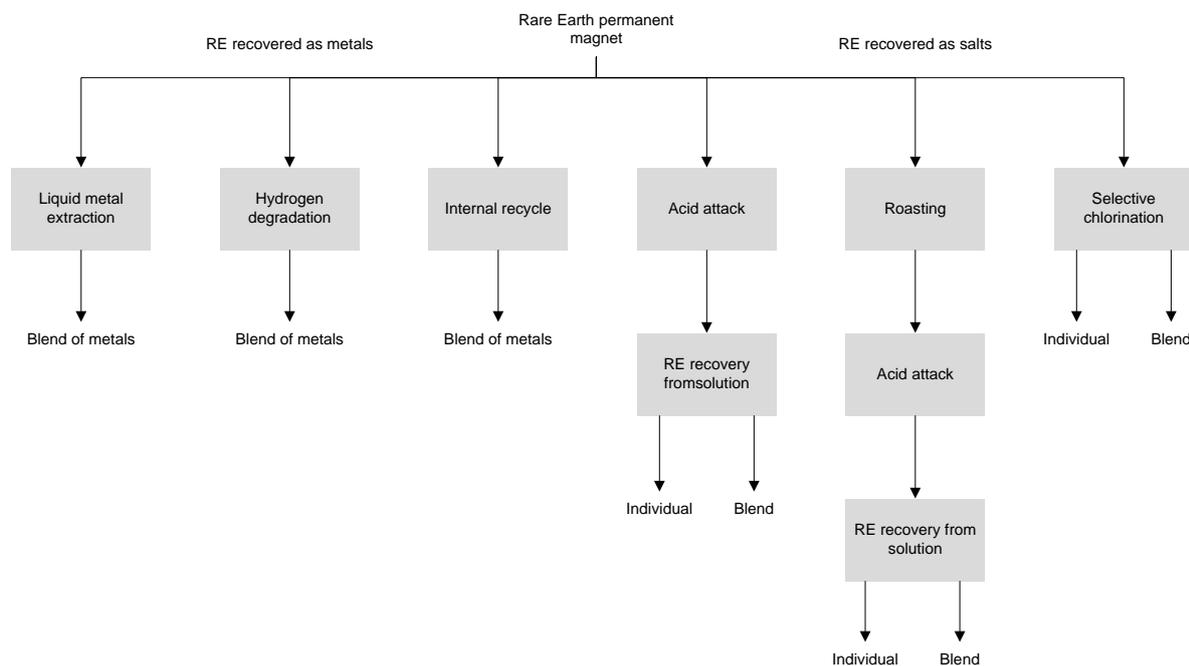


Figure 13 Simplified flow chart of various treatment options to recycle REE magnets. (Ferron and Henry 2015)

From Figure 15 it can be seen that depending on the objectives of the recycling as well as the feed material, different type of treatment methods can be utilized. For example, it is relevant to know whether the target is to recover the REEs as a blend or separate as metals or as oxides.

In the following sections, treatment methods for manufacturing residues, permanent NdFeB-magnets (EoL) and SmCo -magnets (EoL) are presented separately.

### 3.4.1 MANUFACTURING RESIDUES (NDFEB - MAGNET SWarf AND REJECTED MAGNETS)

The manufacturing process of REE magnets produces large amounts of scrap and other residues, because of the cutting, grinding and polishing operations. Up to 30% of the starting REE alloy can be lost during the manufacturing process. Recycling of this scrap is being performed by the magnet manufacturing companies, but only few details about the actual recycling processes have been presented (Koen Binnemans et al. 2013). In addition, it has been reported that there is little information regarding the volume of the pre-consumer NdFeB scraps/residue available for recycling (Önal 2017).

Almost all permanent magnets (80 % market share) are produced in China (Yang et al. 2017). Currently, there are only a few facilities for the refining of intermediate products (alloys) and final permanent magnet producers located in Europe. European companies are mainly focused on manufacturing semi-finished or finished products that contain permanent magnets. (Schüler et al. 2011)

These wastes are produced before the magnetization of the bulk magnet at which time they do not require any de-magnetization step before their recycling. In addition, since they are not covered with any surrounding material (casings, etc.) as in the case of the EoL wastes, they do not need any physical separation treatment (e.g. dismantling). As a result, recycling of pre-consumer scrap/residue is relatively easier than those entrapped

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in EoL products. As long as the material is not severely oxidized due to abrasion (cutting, grinding, etc.) or corroded due to exposure to salty/acidic/humid environments and contaminated by organics (e.g. cutting fluids), pre-consumer scraps/residues can be directly fed back to the production stream. Otherwise (e.g. swarf/sludges) they have to be treated by a separate recycling route. After removing the organic contaminants, the collected wastes are forwarded to hydrometallurgical treatments to recover the REE but the details are not disclosed by the manufacturers. (Önal 2017) Some indicative descriptions of manufacturing scrap treatment in conjunction with other magnet waste treatment has been described by Santoku Corporation and Hitachi. These are described more detailed in the next section.

Different metallurgical processes at different technology- readiness levels (TRLs) to recover the REEs from pre-consumer (manufacturing) NdFeB magnet scrap that are relatively clean and homogenous, as well as have a high REE content has been developed: (Yang et al. 2017)

- hydrogen decrepitation,
- chemical vapor transport,
- liquid metal extraction,
- hydrometallurgical processing,
- pyrometallurgical slag extraction.

### 3.4.2 PERMANENT NDFEB-MAGNETS (EOL)

Permanent NdFeB magnets have various life cycles depending on the end-applications: from 2-3 years in consumer electronics to 20-30 years in wind turbines. In addition, the size of the magnets ranges from less than 1 g in small consumer electronics to about 1 kg in electric vehicles (EVs) and hybrid and electric vehicles (HEVs), and can be as large as 1 000–2 000 kg in the generators of modern wind turbines. (Yang et al. 2017) This leads to very diverse and dynamic secondary source of NdFeB magnets.

Currently, no commercial operation has been identified in Europe for recycling the EoL NdFeB permanent magnets and the recovery of the associated REE content. Most of the processing methods are still at various research and development stages. It has been emphasized that one of the main challenges for recycling NdFeB magnets from EoL consumer products, is the physical dismantling and enrichment of small NdFeB magnets in diversified scrap. Except for generators and motors in wind turbines and EV/ HEVs, the REE permanent magnets are not pre-dismantled, due to their relative small size. The EoL electronic equipment (WEEE) are generally shredded as a whole after the removal of the hazardous components/materials. Due to the strong permanent magnetism, the small magnets will stick to ferrous scrap (steel) after shredding and physical separation using such as magnetic separators. In addition, a small extent of magnets are trapped to the non-ferrous particles if the magnets are not liberated during the crushing. Currently, almost all small permanent magnets used in consumer electronics (at relatively low collection rate), after collection and shredding operation, are lost into ferrous or nonferrous scrap. As a result, dismantling and separate processing of NdFeB-magnets from EoL product can be more preferred option over shredding. (Yang et al. 2017)

Beside the current challenges in the pre-treatment of NdFeB magnets from small EoL products, challenges exist also in the recovery step. As stated in the previous chapter, in order to make the metallurgical recovery from EoL products economically feasible, pre-dismantling and up-concentration through physical processing is critical. Currently, during the pyrometallurgical or hydrometallurgical recovery processes of the major metals, REE's (in Fe or non-Fe fractions) end up into slag or residue fractions from where they are not recovered.

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Several different metallurgical approaches (both hydro- and pyrometallurgical) for the future research and development of REE magnet recovery from EoL products have been identified. (Yang et al. 2017)

Some feed (magnet) specific treatment concepts have been introduced mainly in Japan. For example, Hitachi Metals has developed a mechanical dismantling and separation technique for NdFeB-magnets in computer hard disc drives (HDD) using rotational drum Figure 17. In the first step, through vibration and impact by tumbling, the screws holding the HDD casing become loose and the magnets can be separated out of the casing. This will take roughly 30 minutes resulting to a rough capacity of 200 HDD per hour. After the tumbling, manual sorting of separate components can be performed. The separated voice coil motors (VCM) are then fed to demagnetization and further on to a magnet recovery machine, which separates the rare earth magnet from yoke. (Binnemans et al. 2013, Baba et al. 2013, Yang et al. 2017)

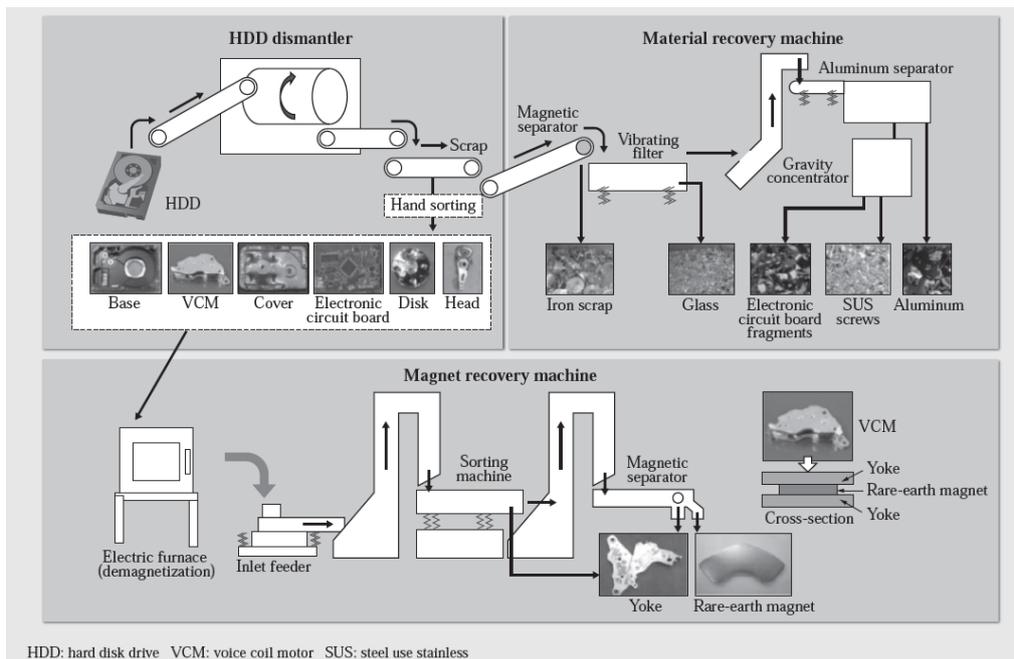


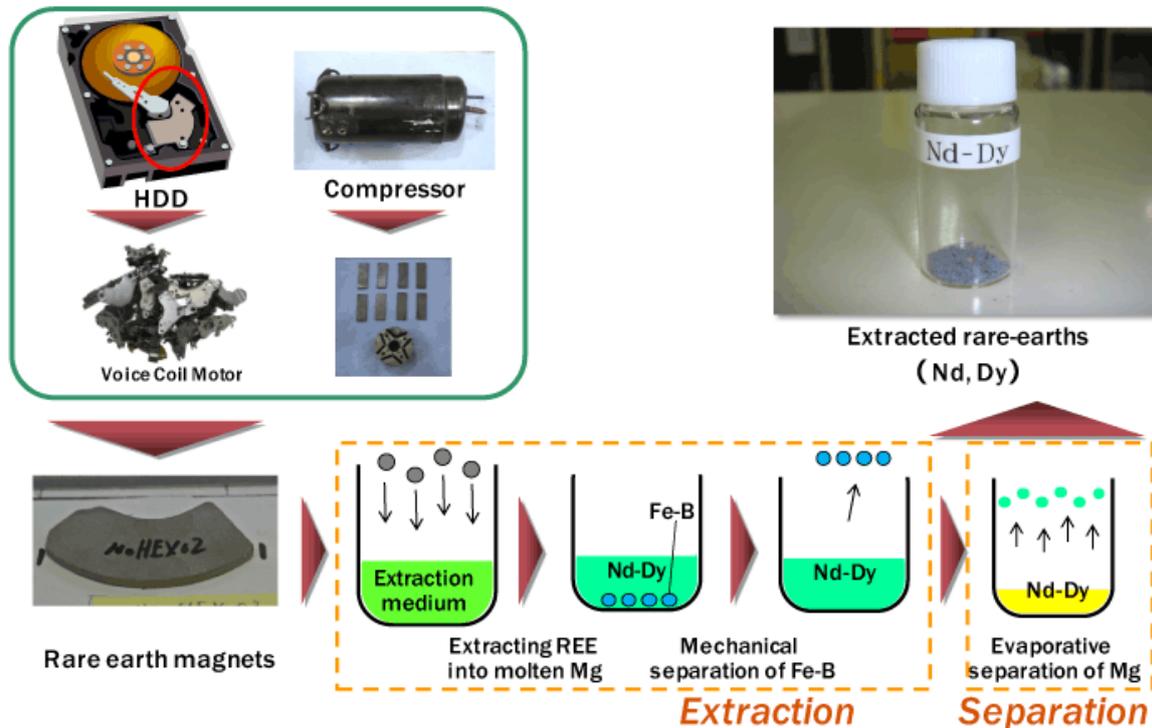
Figure 14 A schematic description of the HDD magnet process developed by Hitachi (Baba, Hiroshige, and Nemoto 2013).

Hitachi has applied similar type of approach also to recover NdFeB magnets from the compressors in the air conditioners. In this case after cutting the casing, the rotors in the compressor are disassembled with a rotor ejecting machinery. In order to safely collect the NdFeB magnets, the magnets are demagnetized by non-thermal demagnetization using resonance damping demagnetization at room temperature. Finally, through vibration to the rotor in the NdFeB magnet remover, the NdFeB magnets inside the rotor are separated and collected. Hitachi aimed to implement the new technique in 2013, and expected it will provide some 60 tons of REEs per year, or about 10% of the entire Hitachi Group's REE needs. (Binnemans et al. 2013, Baba et al. 2013)

Beside pre-treatment and dismantling, Hitachi Metals has developed pyrometallurgical method to recover rare earth metals from the magnets separated at the pre-treatment step. This method uses molten Mg as an extraction medium, for the recovery of Nd and Dy. (Bailey 2015, Hitachi n.d.)

## Pyrometallurgical recovery process

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Figure 15 Pyrometallurgical recovery process for Nd and Dy from magnets developed by Hitachi. (Hitachi 2017)

Hitachi Metals have stated in their Growth and action plan for 2017-2018 that “aggressive investment in the magnet alloy manufacturing process and recycling process” in order to optimize material flows (Akada 2017).

Beside Hitachi Metals, Santoku Corporation started in 2012 a recycling route for neodymium and dysprosium from air conditioner’s motor magnets and magnet production scrap (Koen Binnemans 2014). In Figure 19 a rough description of the Santoku process has been presented. First after demagnetization for 6 hours in 573 K, the magnets are grinded to particle size less than 75  $\mu\text{m}$  with a jaw crusher. Next, the powder is oxidized in a NaOH solution at elevated temperatures for 12 hours, after which the rare earths are leached selectively by a pH controlled HCl solution and further on separated from other elements by solvent extraction with 2-ethylhexyl phosphonic mono-2-ethylhexyl ester (PC-88A) extractant. Finally, magnet alloys are prepared by molten salt electrolysis. During the filtration after dissolution, a ferrous extraction residue is produced. It has been stated that Santoku has developed a process to recover iron and boron from this residue by using thermite reaction, in which FeB and a slag are formed and separated. (Binnemans 2014, Vander Hoogerstraete et al. 2014, Santoku 2015)

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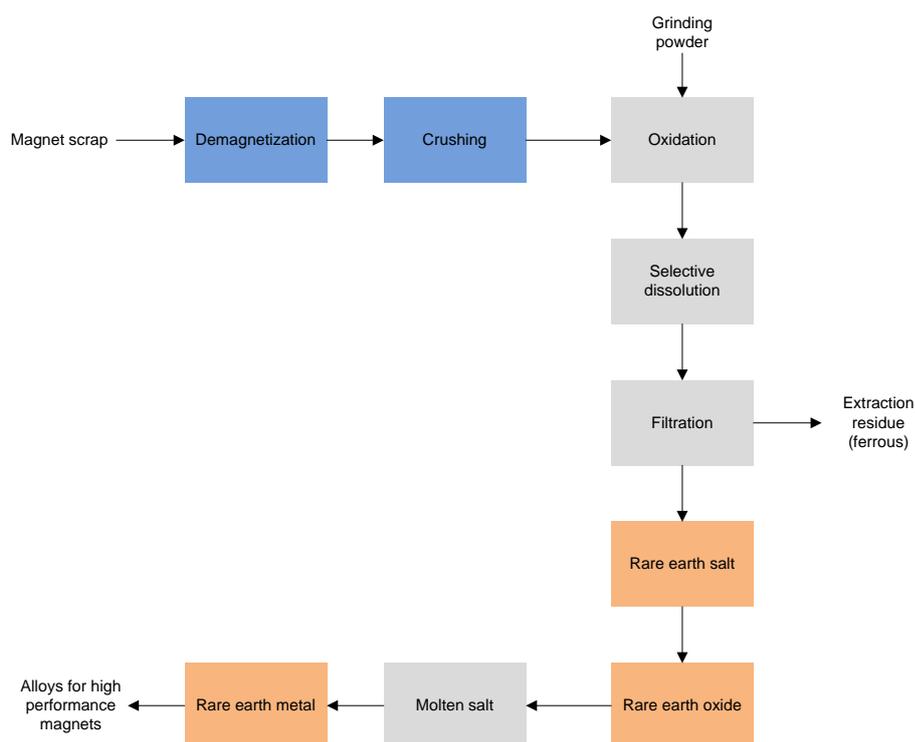


Figure 16 Schematic flow chart of the Santoku NdFeB magnet scrap recycling. (Binnemans 2014, Santoku 2015)

It has been estimated that approximately 5-10 years period is required to set up a recycling practice (Yang et al. 2017).

Magnetic refrigeration is a new technology that has not been widely commercialized yet. Therefore, the research interest towards the recovery of gadolinium from the magnetic refrigeration units has not been extensive either. However, it is probable that leaching and solvent extraction or precipitation is applicable processes to be used for recovery. It is likely that those extractants and ion exchangers currently commercially available will be also suitable for this kind of recovery purposes. (C. Tunsu and Retegan 2016)

Other companies that are or have been active in the field of REE recycling and recovery from magnets are listed below:

- Shin-Etsu Chemical Co Ltd (Japan): Ion-exchange and dehydration and calcination for recovery of REEs e.g. air conditioners. In addition, electrolytic REE extraction used. (Oakdene Hollins 2011, Reisman et al. 2012)
- REEcycle (U.S.): A patented process to recover REE from EoL applications. The company focuses on recovery of Nd and Dy from magnets, potential to recover 15 different REEs. (REEcycle 2015)
- Ganzhou Recycle Hi-Tech Co. Ltd (China): the company operates a plant that recycles 8000 t/a of magnet scrap resulting in 2000 t/a of REO production. (Ferron and Henry 2015)
- Showa Donko KK (Vietnam): The company has built a recycling plant to recycle permanent magnet scrap and capable of covering 10 % of their needs or 800 t/a of REE. (Ferron and Henry 2015)

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Other R&D activities: E.g. General Electric (U.S.), Showa Denko KK (Japan), Mitsubishi with Panasonic and Sharp (Japan) (Walters & Lusty 2011, Reisman et al. 2012)

### 3.4.3 PERMANENT SMCO-MAGNETS (EOL)

Previous efforts on recycling of REEs from permanent magnets focused on the SmCo magnet scrap recycling due to the higher intrinsic value of SmCo scrap and because of the NdFeB magnets' lower popularity. Both the recycling of samarium and cobalt from SmCo magnets was economically justified in the early 1990s, whereas this was not the case for NdFeB magnets. The recycling of SmCo scrap is also made easier due to the fact that there is only one rare earth element (samarium) to recover. In addition, the SmCo magnets do not possess a protective coating, which would be needed to take into account in the recovery process. (Koen Binnemans et al. 2013)

Rhodia Solvay Group (previous Rhône-Poulenc) developed an aqueous process for the recycling of valuable elements from SmCo<sub>5</sub> and Sm<sub>2</sub>(Co, Fe, Cu, Zr)<sub>17</sub> swarf (Bounds 1994). The SmCo swarf is dissolved in mineral acid such as sulfuric, nitric, hydrochloric or perchloric acid. Samarium and the transition metals such as Co, Fe, Cu are dissolved if present in the metallic or oxidic form in the swarf. Zr remains undissolved and can be separated from the solution by filtration. The selection of the specific acid primarily depends on the further processing of the solution. For example, nitric or hydrochloric acid are preferred for a solvent extraction process, whereas sulfuric acid can be used with selective precipitation. Samarium can be almost completely precipitated as an oxalate or as a sulfate double salt with an alkaline metal or ammonium. The oxalate can be precipitated by the addition of oxalic acid. From a samarium sulfate solution, the double salt Sm<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 2Na<sub>2</sub>SO<sub>4</sub> · 2H<sub>2</sub>O can be precipitated by the addition of sodium sulfate. Also other hydrates can be formed. Samarium oxide (Sm<sub>2</sub>O<sub>3</sub>) can be obtained by calcination of the oxalate or the sulfate double salt. The transition metals won't precipitate by oxalic acid or by sodium sulfate under these conditions. Finally, precipitated samarium salts can be separated from the solution by filtration. (Koen Binnemans et al. 2013) This type of approach has been presented in Figure 20. Instead of selective precipitation, samarium can also be removed from the acidic solution by solvent extraction with tri-nbutylphosphate (TBP) or with di-(2-ethylhexyl) phosphoric acid as extractants (Bounds 1994). Within this, samarium is extracted selectively leaving behind the transition metals.

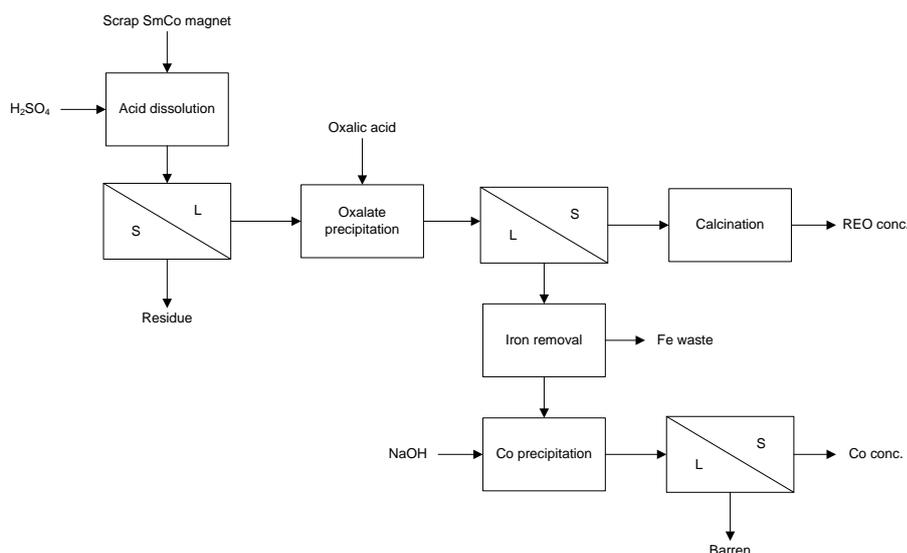


Figure 17 Simplified process flow sheet to recycle SmCo magnets. (Ferron and Henry 2015)

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## 3.5 OTHER APPLICATIONS

In this section, other minor applications that have been reported to contain REEs are presented shortly.

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### 3.5.1 SPENT CATALYSTS

Rare earth elements are used in different type of catalysts in different industries such as petrochemical and automotive industry for different purpose. Therefore, these have been presented separately in the next two sections.

#### FLUID CRACKING CATALYSTS

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Fluid catalytic cracking (FCC) catalysts are extensively used in the petrochemical industry to break the long-chain molecules into shorter ones. The rare-earth content is approximately 3.5 w% composed mainly of lanthanum, followed by cerium, praseodymium and neodymium with smaller amounts (Wang et al. 2017, Ye et al. 2017; Zhao et al. 2017). The rare-earth ions help to stabilize the zeolite structure of the catalyst. This application consumes approximately 50% of the world production of lanthanum. (Binnemans et al. 2013, Krishnamurthy & Gupta 2016) So far, there has been hardly any industrial scale recycling of rare earths from FCC catalysts (Binnemans et al. 2013, Ferella et al. 2016). The studies on recycling have mainly focused in leaching with acidic solutions (Wang et al. 2017, Ye et al. 2017, Zhao et al. 2017).

In fact, the annual mass flow of around 600,000 t FCC catalysts that typically contain at least 2 % of REE indicate to a considerable potential for REE recycling from this particular application (Krishnamurthy and Gupta 2016). When considering that at the moment nearly all of spent FCC is recycled as a raw material for concrete and mortar production as partial replacement of sand and cement powder (Ferella, Innocenzi, and Maggiore 2016). In addition, apart from technical process issues in recovering REE from catalysts, the advantages of a robust and live business-to-business relationship between the catalyst suppliers and oil refineries augurs well for a high collection rate of the spent catalysts for recycling. Similar type a scenario already exists for the platinum-group metals. (Krishnamurthy and Gupta 2016)

#### AUTO CONVERTERS

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In automotive exhaust catalysts, beside precious metals (platinum, palladium, rhodium), rare earths (mainly cerium) are present to e.g. increase the efficiency by which nitrogen oxide is reduced to nitrogen. The content of cerium oxide in catalytic converters varies between the vehicle type and model and therefore not quantified actual cerium content is available. However, Bleiwas have reported some general cerium oxide content estimates from 50 to 100 grams per converter. (Bleiwas 2013)

While precious metals are efficiently recycled via pyrometallurgical process, REEs are lost to slags. Since the concentration of cerium in the slags is low and because cerium has a rather low intrinsic value compared to other rare earths, no efforts have been made yet to recover cerium from the slags. (Binnemans et al. 2013, Krishnamurthy & Gupta 2016)

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### 3.5.2 METAL ALLOYS

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REEs are also used in metal alloys. For example, terbium containing specialty alloys can be used e.g. for magneto-optic recording purposes (Behrendt et al. 2007, Puchy 2011) due to magneto-optic properties of terbium. Minidiscs that were manufactured by Sony until 2013 (Knight 2013) used Tb-Fe-Co alloys (Behrendt et al. 2007).

In addition, praseodymium is used as an alloying element with magnesium for producing high-strength metals for the aircraft industry. Further on in metallurgical applications, gadolinium is used for the improvement of the workability and of the resistance of iron, chromium, and related alloys to high temperatures and oxidation. (Voncken 2016)

No reported production or recycling of terbium, praseodymium or gadolinium from metal alloys were found from the literature reviewed.

### 3.5.3 OPTICAL GLASSES

Special optical glasses are needed for example in lenses of cameras, binoculars, and microscopes. They usually contain lanthanum (more than 40 w% of  $\text{La}_2\text{O}_3$ ), but sometimes gadolinium or yttrium are used instead. The recycling of spent optical glasses could generate around 1.6 kt of REE oxides annually. (Koen Binnemans et al. 2013) However, there are not many references available on R&D actions regarding to their recycling, and no commercial processes were found.

### 3.5.4 GLASS POLISHING POWDER

An important bulk application of rare earths is the use of cerium oxide ( $\text{CeO}_2$ ) as a glass polishing powder. Depending on the literature source, the annual cerium oxide glass polishing powder consumption varies between 5,600 and 16,000 tons (European Commission 2017, Tercero Espinoza et al. 2013). For decades, a slurry of cerium oxide in water has been known as the best polishing agent for glasses. Cerium oxide is especially used in high-tech applications such as the polishing of glasses for LCD screens, car windows, mirrors, optical lenses, but also for several types of cut gemstones. High-quality polishing powders need to fulfill very strict requirements with respect to its particle size distribution. These particle size requirements make the recycling of polishing powders for re-use in high quality applications difficult. In addition, spent polishing powder is heavily contaminated by small silica particles originating from the polished glass surface, as well as alumina particles from hydrolysis of poly(aluminum chloride), which is added as a flocculant. (Koen Binnemans et al. 2013) In Table 5 a typical polishing powder content before and after its use has been presented.

Table 5 Typical composition of the polishing powder and its waste (Krishnamurthy and Gupta 2016).

Component	Polishing powder (w%)	Spent polishing powder (w%)
$\text{La}_2\text{O}_3$	34.2	17.8
$\text{CeO}_3$	43.8	22.1
$\text{Pr}_6\text{O}_{11}$	3.4	2.3
$\text{Nd}_2\text{O}_3$	10.9	5.1
BaO	2.62	0.67
$\text{SiO}_2$		12.6

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Al <sub>2</sub> O <sub>3</sub>		24.8
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Currently no commercial activities beside Hydrometal S.A. in Belgium which recycles 1200 t of REO from glass polishing sludge and magnet sludge (Ferron and Henry 2015) could be found for cerium recycling from glass polishing powder. The studies on cerium recycling from polishing powder have focused either on extending its use by removing silica with physical beneficiation (e.g. flotation) and/or alkali leaching or recovering cerium by means of acidic leaching followed by extraction from leach solutions (Rao Borra et al. 2017). The schematic flow diagram of Hydrometal S.A. process can be seen in Figure 18.

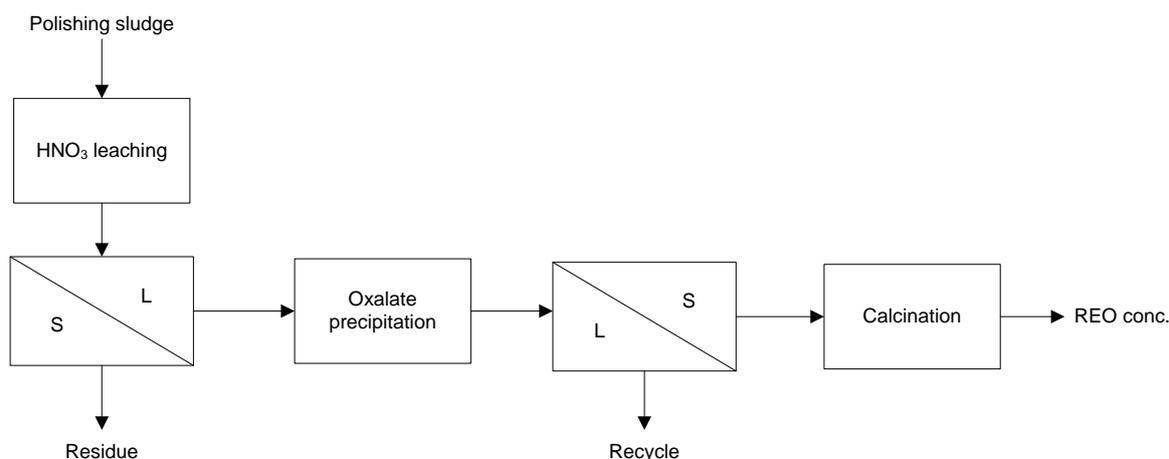


Figure 18 The Hydrometal S.A. process to treat polishing sludges. (Ferron and Henry 2015)

### 3.6 SUMMARISED DISCUSSION ON PRODUCTION OF REES FROM EOL PRODUCTS AND MANUFACTURING RESIDUES

The REE recycling potential has been estimated to range from about 5,600 tons to 10,700 in 2020. The rough estimation highlights that the REE urban mining can make a significant contribution for the overall REE supply, especially for regions without primary REE production. However, as discussed by Grosse, it must be noted that in a market where the global consumption of a resource grows more than 1 % per annum, REE recycling cannot replace primary mining of REE ores but rather complements it (Grosse 2010) by helping to solve the balance problem and avoiding producing a large oversupply of lanthanum and cerium due to the mining of REE ores primarily for neodymium production (Koen Binnemans et al. 2013).

Based on several studies it can be concluded that some steps towards industrial recycling of lighting applications, permanent magnets and EoL NiMH batteries have been taken in the previous years although most recycling processes are still in R&D stage (Binnemans et al. 2013, Innocenzi et al. 2017, Yang et al. 2017). As for other applications or residues containing rare earths, one has to be realistic about the recycling options (Koen Binnemans et al. 2013).

For the phosphors in lighting applications the collection and recycling of fluorescent and LED lamps is already a common practice, except for the phosphor powder part, that has been landfilled after its separation (Kooroshy et al. 2015) or alternatively temporarily stored for later processing (Binnemans & Jones 2014, Binnemans & Jones n.d.). Solvay, the only European company operating in commercial scale for the recovery of REEs from

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lighting products, ceased its REE recycling in 2016 due to the strong decline in REE prices (especially yttrium). The price decline is caused by the fast market penetration of LEDs (Sgarioto 2017), in which smaller quantities of REEs are used compared to the fluorescent lamps. Therefore, the other phosphor streams that are used in different types of products (e.g. plasma screens, LCD backlights, LEDs) especially require further research at the collection and dismantling stages.

The recovery actions concerning permanent magnets are mostly focused on the recovery of major REE components Nd and Dy, (also Pr and Tb). However, the commercial efforts have focused solely on the recovery of REE from manufacturing residues (swarf etc.) not from EoL (Yang et al. 2017). Within EoL most of the processing methods are still at various research and development stages. It is estimated that in the coming 10–15 years, the recycled REEs from EoL permanent magnets will play a significant role in the total REE supply in the magnet sector, provided that efficient technologies will be developed and implemented in practice (Yang et al. 2017).

The current industrial battery recycling processes are mostly based on pyrometallurgy, although from the REE recovery point of view hydrometallurgical processes would be more beneficial, due to the capability of hydrometallurgical treatment to selectively recover different metals with high grade and yields, whereas in pyrometallurgical processes REEs need to be further extracted from slags. However, hydrometallurgical processes typically generate a large amount of waste waters, consume chemicals and require mechanical pre-treatments. (Innocenzi et al. 2017)

It is estimated that the amount of NiMH batteries will increase in the future, and it is an environmental necessity to assure their safe disposal. There is a need to develop more straightforward, cost efficient and energy intensive processes that consume less chemicals and require less waste water treatment. In addition to economic aspects, not only the environmental and eco-efficiency aspects but also social and ethical measures have an important role in the development of successful industrial treatment processes. (Innocenzi et al. 2017)

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## 16 PRODUCTION TECHNOLOGIES OF CRM FROM SECONDARY RESOURCES: SILICON METAL

### 1 SECONDARY RESOURCES OF SILICON METAL

There are a lot of secondary resources that contain silicon; however, only a number of them can be used to recovery silicon metal or silicon. This is probably due to the reason that silicon recovery from most of the secondary resources is not profitable. According to the value chain of silicon metal shown in D4.1, potential secondary resources for silicon metal recovery include:

- (i) Cut-off silicon scrap from ingots and sludge from the cutting of the ingots. According to the literature, more than 100 000 tons of silicon metal waste is generated every year and the waste are largely from the ingot crystallization and wafer manufacturing.[1]
- (ii) End-of-life products, mainly scrap of Si-containing aluminium scrap and scrap of solar panels.
- (iii) Other End-of-life products, such as solar panels.

### 2 SILICON METAL PRODUCTION FROM SECONDARY RESOURCES

#### 2.1 SILICON METAL FROM CUT-OFF SILICON SCRAP OF INGOTS

Poly-crystalline silicon ingot for the wafer production is produced by directional solidification (such as Bridgman process). During the solidification, the impurities (such as iron, aluminium, SiC, and  $\text{Si}_3\text{N}_4$ ) are rejected to the top of the ingots. Thus this top part needs to be cut off. In case that an ingot with a mass of 250–300 kg is produced, the top of the ingot, ranging from 110 to 120 mm thick and around 10% in mass of the whole ingot needs to cut off. To give a square shape for wafer production, further 5–20 mm must be removed from the side of the ingot to give the ingot a square shape. Mono-crystalline silicon ingot for wafer production is produced by, e.g., the Czochralski process. The preparation of the ingots for wafer production also involves the cut-off of the sides. The generation of cut-off silicon scrap from the silicon ingots is illustrated in Figure 1. The cut-off sides from the Poly- and mono-crystalline ingots are usually recycled back to the ingot casting processes, while the top cut-off from the poly-crystalline silicon ingot is normally sold as scrap to the steel industry. [2], [3] It is also reported that the impurities in the top cut-off can be removed by refining processes, such as filtration[2][3] and particle sedimentation under electromagnetic field[4]. However, the processes are not reported to be commercialized at the moment.

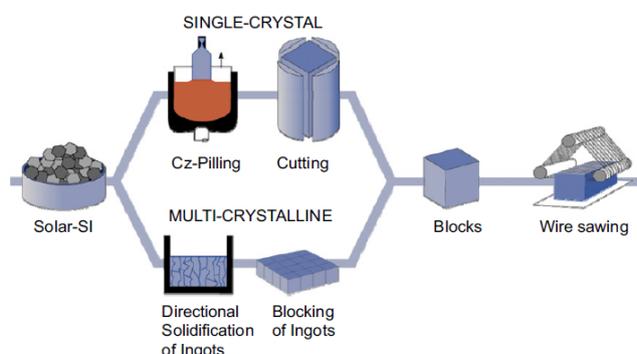


Figure 1 Generation of cut-off silicon scrap from the silicon ingots.[3]

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## 2.2 SILICON METAL FROM CUTTING SLUDGE

More than 80% of the current solar cell production requires the cutting and grinding of large silicon ingots, during which around 50% of silicon is lost in the sludge. The sludge from the cutting and grinding process contains large quantities of silicon metal in the form of fines.

Important parameters for recycling and upgrading of silicon metal powder from the sludge include chemical purity of the sludge, chemical compositions of the impurities as well as particle size distribution of the materials. ReSiTec has developed a process to recover silicon metal powder (purity >99%) from the cutting sludge (purity from 50%) and at the moment ReSiTec is producing more than 500 tons high-purity silicon metal powder per year from the recycled sludge. [1] In ReSiTec process the treatment methods used for the recycling include:

- (i) Chemical treatment.
- (ii) Mechanical wet separation (water classification, hydrocyclones, filtration and powder cleaning);
- (iii) Mechanical drying (drying, electrostatic separation, jet-milling and classification).

The final process flow sheet for specific waste depends on the particle size distribution, density, types and level of the impurities. It is reported that the recycling process is quite energy-saving (< 1kWh/kg) compared to the conventional silicon metal production (11-15 kWh/kg for metallurgical grade silicon metal production).

## 2.3 SILICON METAL FROM SI-CONTAINING ALUMINIUM SCRAP

Although aluminium alloy has a very high recycling rate from the end-of-life products (e.g. 85-95% for aluminium alloys used in the transport and building sectors), the same recycling rate does apply to the alloying elements (such as Si) in the aluminium alloys. This is due to the fact that the Si-containing aluminium scrap is seldom sorted out from the aluminium scrap containing no silicon. Further, in some cases during the re-melting of the recycled aluminium scrap, silicon is taken as one of the undesirable elements and be removed.

The recovery of the silicon from the Si-containing aluminium scrap relies on the proper sorting of the scrap and use the scarp for producing Si-containing aluminium alloys. At moment, the silicon recovery in this regard is believed to be zero.

## 2.4 SILICON METAL FROM END-OF-LIFE SOLAR PANELS

The end-of-life solar panels contain silicon wafers, which is made from silicon metal of high grade. Further, some scrap also contains toxic elements, such as lead and cadmium. Therefore, from the economic and environmental points of view, the end-of-life solar panels need to be recycled. Within European Union the scrap of solar products belongs to the waste of Electrical and Electronic Equipment (WEEE).

At moment SolarWorld process is a known industrialized process for the recovery of silicon from the solar panels.[5], [6] In this process end-of-life solar panels are thermally treated during which plastic components are burnt in a complex semiconductor-protecting process at 600 °C. Remaining materials such as solar cells, glass and metals are separated manually. Glass and metal are sent for recycling. Un-broken wafers are re-etched to wafers while the broken ones were recycled as silicon material. The process can recover more than 84% of the input solar module weight. Over 90% of the glass can be recovered for use in new products and 95% of the

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semiconductor materials for use in new solar modules. The flowsheet of the Solarworld process is shown in **Figure 2**.

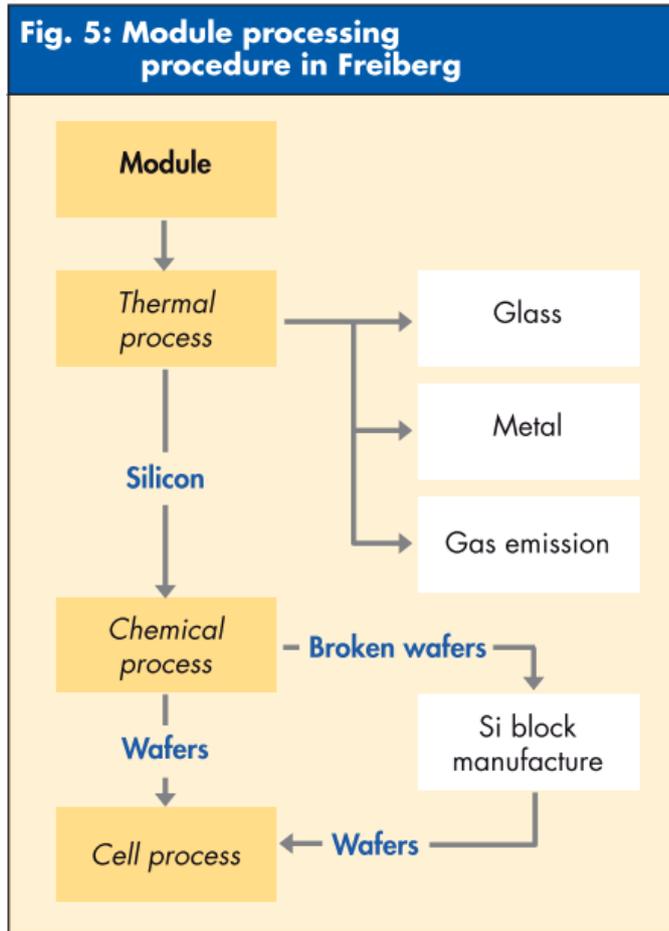


Figure 2 Flowsheet of the solarworld process.[5]

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## 17 PRODUCTION TECHNOLOGIES OF CRM FROM SECONDARY RESOURCES: TUNGSTEN

### 1 OVERVIEW OF GLOBAL PRODUCTION OF TUNGSTEN AND AVAILABLE SECONDARY W RESOURCES

Tungsten (W) ores are mined as a main product. Its average global yearly primary production reaches 82,000 tons, while in EU it is 2,175 tonnes. EU is importing 2,810 tonnes of primary material in form of ores and concentrates and exporting 1,320 tonnes on average. EU import reliance is estimated at 44%. The major world producers are China with 84% of total share and Russia with 4% share. (European Commission, 2017). In Europe, several tungsten mines locations were identified, namely in England, Spain and Portugal.

In EU tungsten is mostly used for mill and cutting tools, mining and construction tools and other wear tools due to its properties (hardness, the highest melting point of all elements). Other applications include lightning and electronic uses, high speed steels, aeronautics and energy uses. Figure 1 shows the shares of each end use for this material (European Commission, 2017).

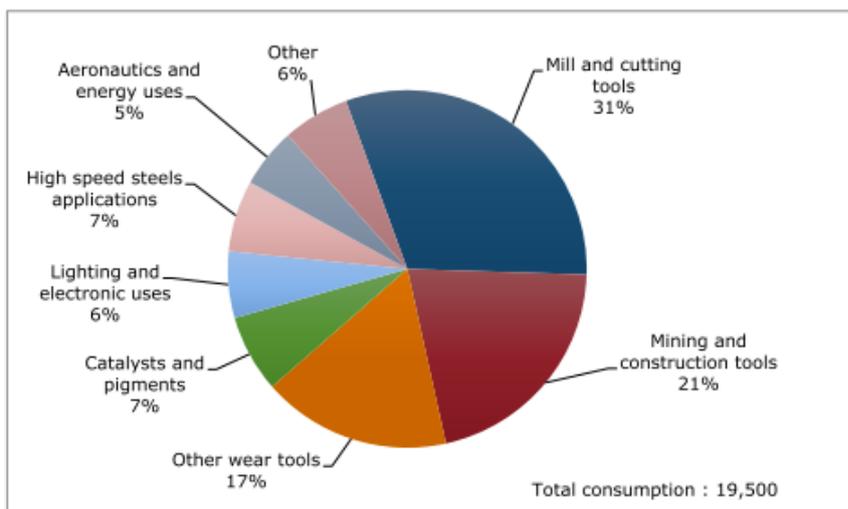


Figure 1 End uses of tungsten in EU. (European Commission, 2017)

Recycling of tungsten containing cemented carbide scrap uses up to 79% less energy and causes 40% less CO<sub>2</sub> emissions in comparison to extracting tungsten from ore. Recycling of tungsten has big potential in efficient secondary raw material production. Mined earth before processing contains about 0.3-0.5% W. It was calculated that 15 tons of earth needs to be mined in order to obtain the same tungsten yield that can be recycled from 70 kg of carbide (Sandvik Hyperion, n.d.).

Identification of secondary resources containing tungsten is presented below.

- (1) Processing waste and historical waste
  - Waste rock
  - Mill tailings

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(2) Urban mines and manufacturing residues

- Cemented carbide
- Heavy metal alloy scrap
- Mill scale
- Grinding sludge
- Drill bits
- E-waste
- Spent Ni-W catalysts

## 2 PRODUCTION OF TUNGSTEN FROM SECONDARY W RESOURCES

Secondary tungsten can be found in two main types of sources: in waste from processing the material containing niobium as well as in end of life products from urban mines and manufacturing residues.

### 2.1 PROCESSING WASTE AND HISTORICAL WASTE

#### 2.1.1 WASTE ROCK

Large amounts of waste rock that contain tungsten come from surface mining, mostly from open-pit mines of copper, uranium, phosphate, iron and taconite. Waste rock consists of coarse, blocky or crushed material in wide range of sizes, which is usually removed with mining overburden and stored due to low, if any practical mineral value. The scale of waste rock generation in US is about 0.9 billion tons per year. In Europe, large amounts of historical waste in form of mine tailings are in Panasqueira, Portugal. The mine is generating nearly 100 tons of waste rock daily and tungsten is present in slimes. However, the recovery from ultrafine grain size is problematic. The high intensity magnetic separation wasn't able to separate wolframite from magnetic minerals present in the tailings. Gravity separation with three stage process with sulphide flotation in between has potential to recover wolframite in concentration of 50-55%  $WO_3$ .

Tungsten-bearing tailings from Spanish mine Barruecopardo contain on average 0.093%  $WO_3$  in size smaller than 1 mm and 0.088%  $WO_3$  in size above 1mm. Dumps from the same mine contain 0.044 and 0.022%  $WO_3$  respectively. It was found, that a direct processing using spiral could reduce operation cost of recovery operations, by eliminating crushing step.

In Bom-Gorhon high grade ore deposit in Russia, the tailings generated during mining operations are estimated at 100 thousand tons, which contain 0.1-0.35%  $WO_3$  (Sundqvist Oeqvist, Ye, Hu, & Yang, 2016).

Tin tailings from mine in Bolivia contain 0.64%  $WO_3$ , together with Cu and Sn. First, copper is separated by chlorination segregation technique and flotation. Next, high intensity magnetic separation is applied, followed by gravity separation. Under optimal conditions, the processes can result in recovery of 60.32%  $WO_3$  grade.

Research has shown several patents for tungsten recovery. One of those methods used tungsten containing material and tailings in production of tungsten compound. In the process aluminium oxide or aluminium salt and phosphate or oxide of phosphorus was used. Next processing steps included 4-5 times leaching of ammonium para-tungstate (APT) crystal, precipitation of artificial white calcium tungstate (Sundqvist Oeqvist et al., 2016).

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### 2.1.2 MILL TAILINGS

Mill tailings are composed of very fine particles, which are rejects from screening, grinding or raw material processing. The scale of mill tailings is about 450 million tons per year generated from iron, copper, taconite, lead, zinc ores processing. It was estimated, that in 2010 25.6 kt of  $WO_3$  was lost in mine tailings and 4.7 kt in processing residues. (Sundqvist Oeqvist et al., 2016).

There were several activities in the past to establish potential of tungsten recovery from historical waste sites. In Canada in 2011 North American Tungsten Corporation Ltd. organised a drilling program to estimate tonnage and grade of unrecovered tungsten in mine tailings. Samples of tailing dump site were also taken in Spanish La Parrilla mine with high concentrations reported (Sundqvist Oeqvist et al., 2016).

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## 2.2 URBAN MINES AND MANUFACTURING RESIDUES

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### 2.2.1 CEMENTED CARBIDE

Cemented carbide, which comprises 70% of all tungsten used in Europe (Witold Kurylak, 2016), is mostly used for production of tools, that after their end of life can be recycled using several, mostly direct recycling methods.

One of the main recovery techniques is zinc process. It is the direct recycling method, where the scrap is transformed into tungsten carbide-cobalt alloy powder directly in a furnace. The process starts with sorting the scrap according to its grade, then it's cleaned, crushed and immersed in molten zinc with argon gas at high temperature ( $900^{\circ}C$  or higher). Molten zinc is reacting with cobalt and creates a porous cake, because of the volume expansion of the scrap. Subsequently the zinc is distilled under vacuum, leaving a material which is crushed to obtain a powder. The powder can be further purified by electrochemical treatment, if needed. In the end, the powder can be directly reused for production of new cemented carbide elements. The steps of this process are shown in Figure 2. The zinc process for tungsten recycling has many advantages. It is attractive economically in comparison to chemical treatment. Moreover, it has environmental benefits due to zinc recovery and reusing and lack of emissions in the furnace process (W Kurylak et al., 2016).

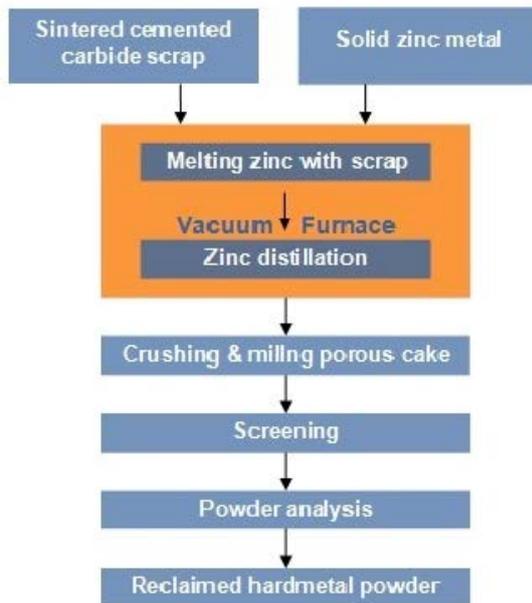


Figure 2 Zinc processing of cemented carbide scrap. (ITIA, 2011)

Another method is the chemical treatment of tungsten carbide (WC) scrap. An example of chemical method, which is used usually for unsorted scrap is the oxidation-leaching process, where scrap is first oxidized in high temperature and put under alkali treatment, which enables tungsten carbide conversion into tungstic oxide or sodium tungstate. Next step is the leaching and purification, after which tungstic oxide can be reused as secondary raw material in production of new elements (W Kurylak et al., 2016).

Sandvik Hyperion uses chemical solution treatment, where tungsten is converted into ammonium paratungstate and together with APT from primary tungsten ore is processed to obtain tungsten carbide (Figure 3) (Sandvik Hyperion, 2016).



Figure 3 Steps in tungsten carbide recovery in Sandvik Hyperion. (Sandvik Hyperion, 2016)

Direct recycling can be performed also by cold stream process (Figure 4). Scrap is first sorted by grade, then treated with air blast, in order to accelerate particles against the object with energy sufficient to result in fracture of the scrap. The obtained material is classified by air to recover fine particles, which can be reused directly (W Kurylak et al., 2016).

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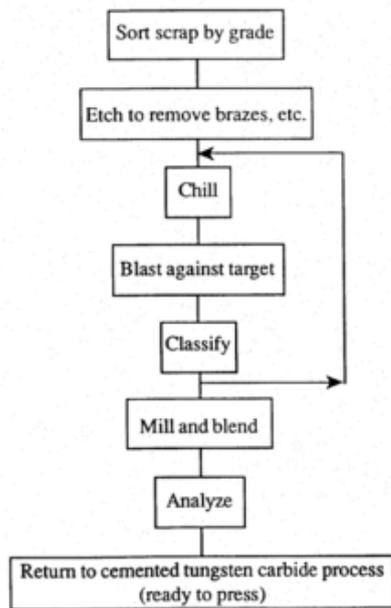


Figure 4 Flow chart of cold stream process for tungsten recovery.

Selective dissolution process is a semi-direct recycling method, where the specific component of the scrap is chemically dissolved, leaving the other components unchanged. It can be used for binary or ternary-phase alloys (W Kurylak et al., 2016).

There is ongoing research on new cemented carbide recovery techniques. One of those methods is recycling tungsten using molten salt solution (Figure 5). Molten salt is used to produce  $\text{Na}_2\text{WO}_4$  aqueous solution from cemented carbide. Then, an ion exchange treatment in a resin tower converts it into  $(\text{NH}_4)_2\text{WO}_4$  solution. It is believed, that this method allows to adsorb about 3 times more tungsten as the conventional amount (W Kurylak et al., 2016).

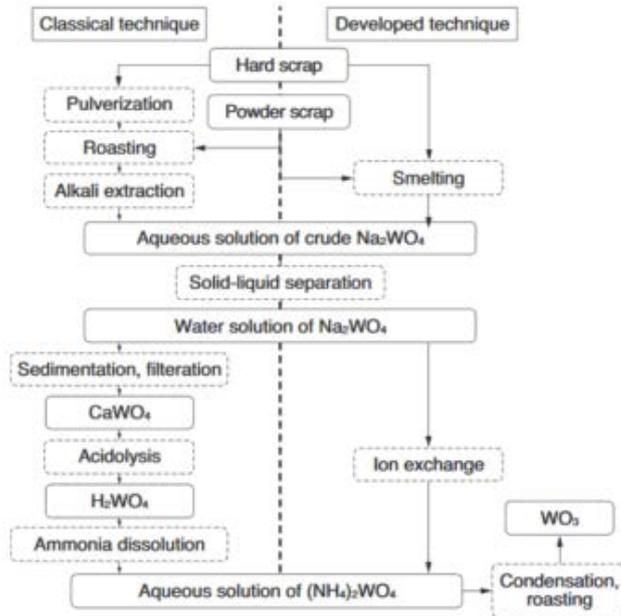


Figure 5 Flow chart of tungsten recovery with molten salt

Another new method has been developed for recycling of tungsten carbide rollers, used in steel industry in metal forming process. The content of WC in this source can be up to 85% in weight. The recycling method includes three steps. First, scrap rollers are crushed into crystallites, which are then melted in furnace together with other W scrap and metal to obtain a specific chemical composition. The mixture is re-melted and electroslag refined, resulting in roll collar ingots that are brought to heat treatment, including quenching and annealing. The product (tungsten alloy roll) contains 20% tungsten and has the same performance as primary material (Witold Kurylak, 2016).

## 2.2.2 HEAVY METAL ALLOY SCRAP

Heavy metal scrap is most preferably recovered as metal powder, by oxidation of the scrap, milling, screening and hydrogen reduction. The powder can be subsequently mixed with another metal alloy powder and used in manufacturing of new elements. Alternatively, tungsten can be recycled as tungsten carbide in melt bath process (Figure 6), where heavy metal is melted in Fe-C. As a result, tungsten is converted into WC, which can be treated accordingly, for example with zinc process (W Kurylak et al., 2016).

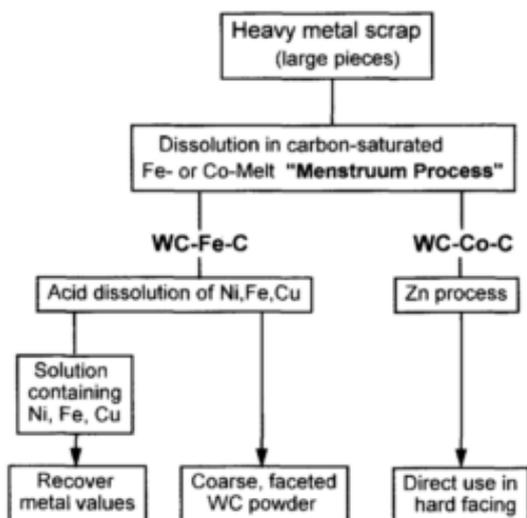


Figure 6 Flow chart of melt bath process (W Kurylak et al., 2016)

Other methods include coldstream process, menstruum process, melting and chemical processing, electrolysis and leach-milling (W Kurylak et al., 2016).

### 2.2.3 MILL SCALE

During casting and rolling mill processes of tungsten-bearing steel in oxidant atmosphere, the mill scale is generated. It has chemical composition similar to steel, except the oxygen content, and can be recycled directly in integrated plants as raw material. The mill scale constitutes for 2% of the produced steel. It was reported, that Brazilian mill scale from small mill plant contained 0.83% W. In Erasteel, high speed production plant in Sweden, the amount of tungsten in mill scale was estimated at 1-5%, depending on the type of steel. Tungsten can be recovered from mill scale by reduction and used directly in steel production for instance by feeding it in electric arc furnace. Alternatively, tungsten can be recovered as pure material into APT, as described in Figure 6 (Sundqvist Oeqvist et al., 2016).

### 2.2.4 GRINDING SLUDGE

Tungsten-bearing grinding sludge is a residue from forming of metal elements with presence of cooling water or oil, for example high speed steel, or cemented carbide containing tungsten. The sludge contains extremely fine metal elements, grinding media, solid contaminants and cutting oil. Although grinding sludge contains many undesired materials, the amount of tungsten is considerable and can be recovered. The oil contained in the grinding sludge need to be removed due to the risk of explosive burnt and pollutant generation. It can be done by high pressure filter. If the sludge will be recycled in a smelter, the non-metallic compounds and phosphorus also need to be removed by gravity concentration and magnetic separation. In order to produce secondary ferrotungsten or tungsten alloy in smelting furnace, the clean residue need to be briquetted first. Another possibility is to recover W from grinding sludge by hydrometallurgical technique of NaOH pressure leaching (Figure 7). In this process, sludge and swarf are dissolved in the NaOH solution, resulting in production of APT, which is an intermediate product for W metal powder and W carbide production (Sundqvist Oeqvist et al., 2016).

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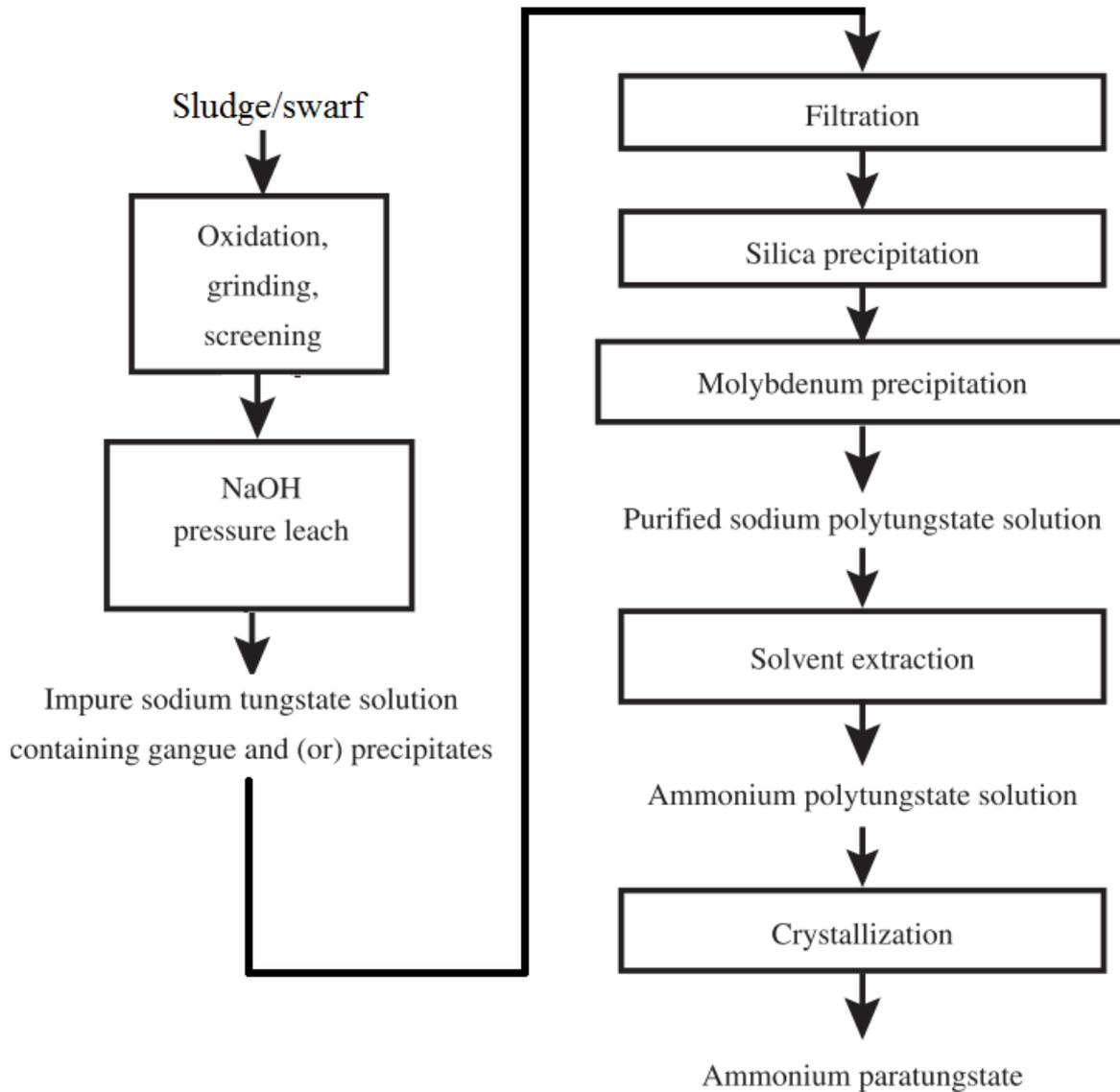


Figure 7 Flow diagram of tungsten recovery from sludge with hydrometallurgical process. (Sundqvist Oeqvist et al., 2016)

### 2.2.5 DRILL BITS

Drill bits, used in oil and gas industry can be an important source of secondary tungsten. Those materials are complex alloys of manganese, copper, nickel, zinc and tungsten. Research has shown, that around 1,000 tons of W is lost in drill bits, which are not presently recycled due to lack of suitable technology (Witold Kurylak, 2016).

### 2.2.6 E-WASTE

Minor quantities of tungsten can be traced in printed circuit boards (PCB), used in wiring, contacts, electrode emitters and heat sinks. A new research has shown possible method to recover W from wastewater of PCB

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recycling. Test of the method has shown, that wastewater contained 600 ppm of tungsten, among other metals in smaller concentrations. The process is called emulsion liquid membrane (ELM) and is commonly used to separate metal ions and also hydrocarbons or biological compounds. Emulsion is prepared by mixing extractant, surfactant and organic diluent with aqueous stripping agent containing NaOH, at speed of 6000 rpm. The emulsion and wastewater was mixed at 300 rpm, then separated and broken by heating. The process is shown in Figure 8. The technology is still at early stage of development, but the tests results has shown, that the separation of W from wastewater is possible (Witold Kurylak, 2016).

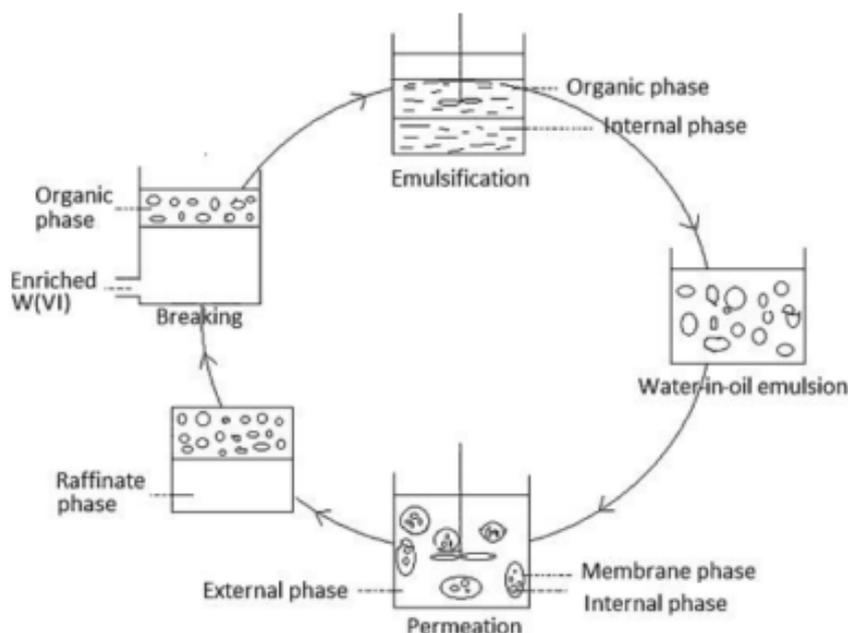


Figure 8 Flow scheme of ELM process.

### 2.2.7 SPENT NI-W CATALYSTS

A research was conducted to recover tungsten from spent selective catalytic reduction (SCR) catalysts used in chemical industry. The amount of tungsten used is rather small, however it comprises 40% of the price. A method used to recover tungsten includes pressure leaching reaction with soda digestion process, using NaOH as leaching agent. The obtained solution contained tungsten and vanadium. The latter can be separated by precipitation with  $\text{Ca}(\text{OH})_2$ . Tungsten is converted into APT by reaction using  $\text{NH}_4\text{OH}$ . The method is proved to successfully recover both metals (Witold Kurylak, 2016).

Catalysts containing tungsten can be recycled the same way as NiMo catalysts, using pyro- and hydrometallurgical methods (W Kurylak et al., 2016).

## 3 CURRENT RECOVERY RATES

The end of life recycling input rate for tungsten is 42% in (European Commission, 2017). The recovery rate from mine tailing and processing residues was not reported (Sundqvist Oeqvist et al., 2016).

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## 4 KEY ACTORS IN TUNGSTEN RECOVERY

Sandvik Hyperion is a company with head office in the USA, which provides cemented carbide, cubic boron nitride and diamond solutions globally. The company also implemented recycling program for cemented tungsten carbide recovery. They collect and process used tools, production wastes, grinding sludge, filters in order to obtain new source of raw materials (Sandvik Hyperion, n.d.). Wolfram Bergbau und Hütten AG (WBH) is accompany within Sandvik placed in Austria, which is claimed to be world leader in recycling of cemented carbide (Sandvik Hyperion, 2016).

Another company working on critical materials recovery in EU is German H.C. Starck. The company gathers waste from refractory metals and ceramic materials production and processing stages, super alloy scrap, slag, sludge and transform them into secondary raw materials. In particular, tungsten is recovered also from catalysts used in chemical industry. The internal recovery technology of H. C. Starck is not available; however the company uses three main types of processing. By mechanical separation undesired materials are removed from valuable metals by milling. Thermal treatment involves electro beam and solidification in a skillet. Chemical processing takes place in presence of acid and caustic dissolving solutions and includes removing impurities (H. C. Starck, 2012).

## 5 CHALLENGES IN MATERIAL RECOVERY

The recovery of tungsten is well established, especially using direct recycling methods. However, the barrier in tungsten recycling is secured supply of W-bearing scrap. What is more, usually hydrometallurgical reprocessing methods require substantial amounts of energy and reagents, which makes the processes not profitable. Additionally, recycling plants of this type produce a lot of waste and effluents, which can have negative impact for the environment (Witold Kurylak, 2016).

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## 18 PRODUCTION TECHNOLOGIES OF CRM FROM SECONDARY RESOURCES: BARYTE

### 1 STATE OF THE ART OF BARYTE VALUE CHAIN

The next figure shows the value chain of baryte:

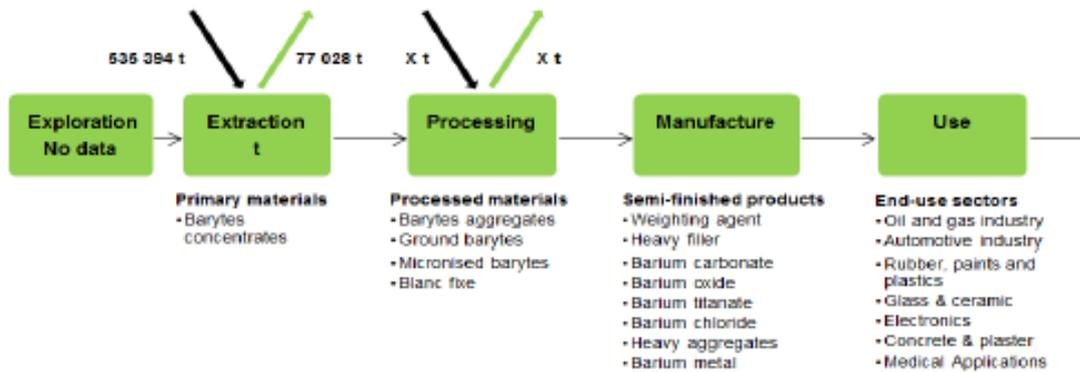


Figure 1 Simplified value Chain for Baryte.[1]

The most important use of barytes, is as a weighting agent to increase the density of drilling fluids, principally for oil and gas exploration.

Non-drilling applications of barytes are comparatively small, although still important because of their high value. Baryte is used as heavy filler in rubber, paint and plastics applications. Some specific applications include use in automobile brake and clutch pads, automobile paint primer for metal protection and gloss, use as a weighting agent in rubber, and in the cement jacket around underwater petroleum pipelines. In the metal-casting industry, barite is part of the mold-release compounds.

Because barite significantly blocks x-ray and gamma-ray emissions, it is used as aggregate in high-density concrete for radiation shielding around x-ray units in hospitals, nuclear powerplants, and university nuclear research facilities. Ultrapure barite is used as a contrast medium in x-ray and computed tomography examinations of the gastrointestinal tract.[2]

In the chemical industry, baryte is used for the preparation of barium compounds, notably barium carbonate ( $BaCO_3$ ) that is used in the production of special glass, as an ingredient in high-fire glazes, and in the brick and tile industry (BRGM, 2014).  $BaCO_3$  is increasingly used in electronic components, such as electronics ceramics and capacitors. Barium meal (barium sulphate) is used in radiodiagnosis.

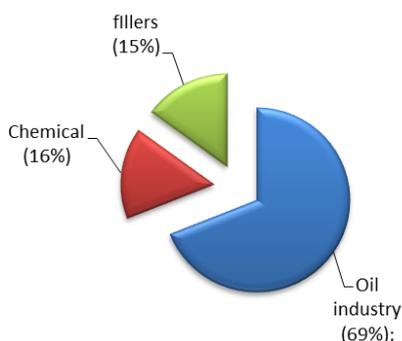


Figure 2 Own source (Data from the Barytes association).[3]

## 2 RECYCLING

The recycling of baryte is thus null.[4] Baryte is barely re-used.

Although barite is critical for drilling, it is a small percentage of any drilling project’s total cost, which includes all stages from the initiation of a well’s drilling to its completion. For this reason, little barite is recycled for re-use beyond that “cleaned” in a centrifuge or another device at a drill site. However, because of increased barite prices and disposal costs, there is increased interest in the development and implementation of low-cost technologies to treat used muds that will meet specifications.[5] Recovering drilling muds is often practical and cost-effective and is an environmentally sustainable process. Recycling and reusing the muds can help companies save money on disposal costs, reduce truck traffic besides saves barite consumption.[6]

In most other applications, baryte is not recovered (fillers etc.) and cannot be recycled. [7]

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## 19 PRODUCTION TECHNOLOGIES OF CRM FROM SECONDARY RESOURCES: BISMUTH

### 1 OVERVIEW OF GLOBAL PRODUCTION OF BISMUTH AND AVAILABLE SECONDARY BI RESOURCES

Bismuth (Bi) is a new material on the EU's critical raw materials list, added in assessment performed in 2017. Bismuth is mined as by-product of lead, tungsten and copper ores and concentrates. The reliable quantitative data on bismuth mining was not available. The metal is processed mainly in China, which holds 82% share of global supply. The remaining share of Bi refining belongs to Mexico and Japan, with 11% and 7% share respectively. On average 8,180 tonnes of Bi is refined globally, whereas about 0,8 tones is estimated to be processed in European Union (EU). The EU is completely reliant on Bi import in form of refined material (refined bismuth) of purity at least 99,8%, which is transformed into Bi-bearing finished products (European Commission, 2017).

Since bismuth is non-toxic material, it is mainly used in production of chemicals, that find applications in pharmaceutical products, cosmetics and animal feed. In medicine, Bi-bearing compounds (De-Nol, Pepto-Bismol) are applied clinically as anti-ulcer agents for gastrointestinal disorders. Bi can be also found in nuclear medicine, antitumor and antimicrobial studies. Second biggest group of Bi applications are fusible alloys, where it replaces more harmful metals, like lead in solders. The remaining 10% share of applications are additives for metallurgical products and smaller industrial applications, such as pigments, coatings and electronics (European Commission, 2017). Figure 1 presents main applications of Bi.

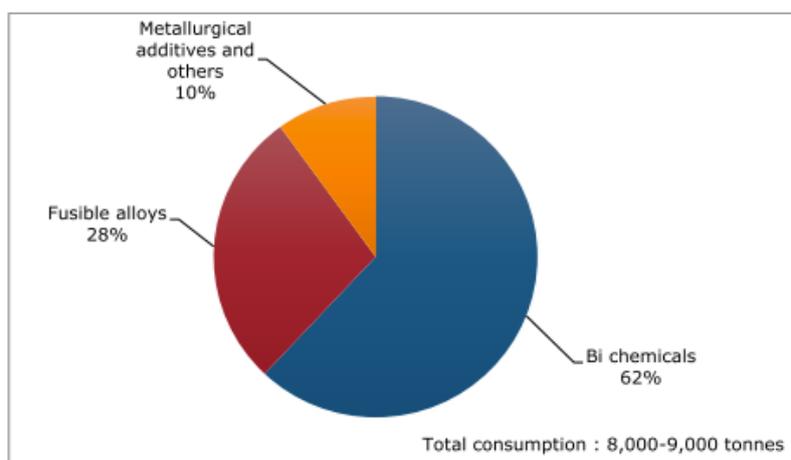


Figure 1 Main applications of bismuth. (European Commission, 2017)

Identification of secondary resources containing tungsten is presented below.

- (1) Processing waste and historical waste
  - Tailings
- (2) Urban mines and manufacturing residues
  - E-waste
  - Copper smelter converter dust

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- Aqueous solution

## 2 PRODUCTION OF BISMUTH FROM SECONDARY BI RESOURCES

Secondary bismuth can be found in two main types of sources: in waste from processing the material containing niobium as well as in end of life products from urban mines and manufacturing residues.

### 2.1 PROCESSING WASTE AND HISTORICAL WASTE

#### 2.1.1 TAILINGS

Bismuth is reported as present in wolframite-scheelite tailings, which are usually processed to recover tungsten. Research has been done on tailings recovery method, including an experiment using suspended vibration cone concentrator in gravity concentration-flotation process. It resulted in two concentrations, one cleaner and one rougher, where the second one was processed further by flotation, in which Mo, Bi and W were floated. The obtained concentrates included bismuth concentrate 15.9% at recovery of 57.8% (Sundqvist Oeqvist, 2016).

Bismuth can be found in milling tailings historical deposits containing mainly tungsten in forms of hubnerite and scheelite, located in Chita region in Russia, however the concentration of Bi is not known (Sundqvist Oeqvist, Ye, Hu, & Yang, 2016). Other sources of bismuth minerals in form of Bismuthinite are reported to be present in flotation tailings in Macedonia, and in unprocessed mine products and waste in Portugal (Cuesta-Lopez, Barros, Ulla-maija, & Willersinn, 2016).

### 2.2 URBAN MINES AND MANUFACTURING RESIDUES

#### 2.2.1 E-WASTE

Bismuth can be found in materials coming from dismantled printed circuit boards (PCB) used in multiple electronic devices, for example computers, mobile phones and televisions. It is used in low concentrations in solder to alter its properties and low melting point casting alloy with tin. One method to recover valuable materials from scrap PCBs is pyrolysis in a fixed bed reactor (Figure 2). In order to separate metallic and organic materials, scrap PCBs are pyrolysed at 800°C for 135 minutes. After exiting the reactor, pyrolysis gases and oils are collected in water and ice condensers and glass wool trap. Subsequently, the obtained products are analysed. After performing pyrolysis, the material turned out to be very friable which allows easy separation. Bismuth, as well as other metals, is present in the residue ash, which was ashed at 600 °C, acid digested and analysed. The product yield composed of mixed metals included 77 mg/kg, 68 mg/kg and 5.6 mg/kg of bismuth (fraction <600 µm) in scrapped PCB from computers, television and mobile phones, respectively. In order to recover different constituents, further processing is required (Hall & Williams, 2007). Another source indicates high temperature pyrometallurgical process can be used to extract metallic components from spent PCBs, by shredding, oxidizing to remove plastic parts and melting in high frequency induction furnace. Subsequently, metallic component can be separated in molten state from remaining oxides. It was stated that metals recover over 95% is possible, however no information of bismuth recovery rate was mentioned in this study (Lee, Jeong, Kwon, Jang, & Han, 2005).

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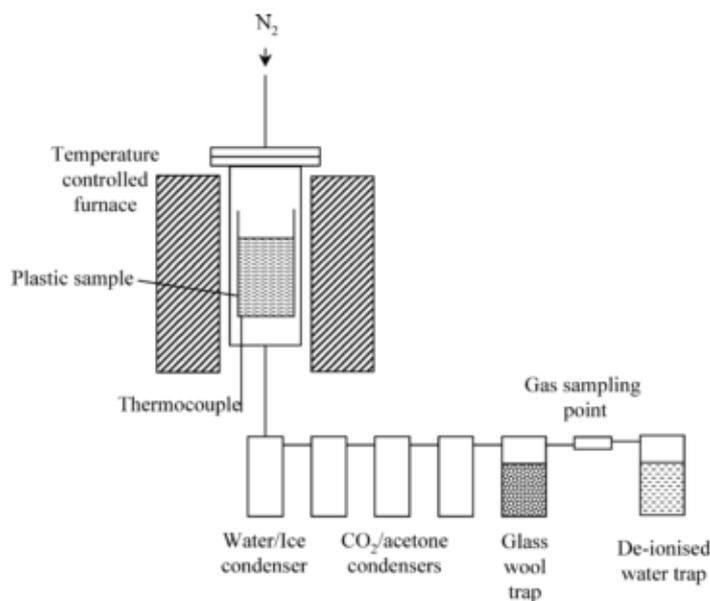


Figure 2 Scheme of fixed bed reactor used for pyrolysis. (Hall & Williams, 2007)

## 2.2.2 COPPER SMELTER CONVERTER DUST

Converter dust from copper smelter is a source of secondary bismuth as well as other materials. The volume of dust generated during smelting of copper is about 5-10% of the input, which contains many impurities and at the same time valuable materials, namely As, Sb, Bi, Cd and Pb. There is an incentive to separate bismuth from the dust, because Pb smelters do not allow secondary materials with content of bismuth higher than 0.02% due to its interference with silver recovery and its properties altering the ductility of lead. Most of commercial recovery techniques from dust are based on pyrometallurgy. For example, acidic-chloride leaching of converter dust is a promising technique, which has not been used in industry yet (Ha, Kwon, Park, & Mohapatra, 2015).

An economically viable method to recover Bi from converter dust using hydrometallurgical method will be presented. First stage comprises of pre-treatment of converter dust in order to recover copper, which is the main constituent of the material. This was done by leaching out Cu, Zn, As, Cd from the dust with diluted  $H_2SO_4$  solution and further processing the solution. Remaining residue was the material for bismuth recovery, which consisted of 5.3 wt% of Bi. Next step is the bismuth leaching process, where the most optimal conditions were the presence of 100 g/L  $H_2SO_4$  and 60 g/L NaCl, temperature  $70^\circ C$ , time 120 minutes and pulp density of 20%. This resulted in 92% leaching efficiency and Bi concentration in aqueous phase 9.6 g/L, 420 ppm. The subsequent purification processes include removal of Pb, Ag, Cu, Te, Sb from leach solution by  $SO_2$  reducing agent; separation of  $BiOCl$  by hydrolysis using water as precipitating reagent; conversion of  $BiOCl$  cake into  $Bi_2O_3$  with alkali solution. The final product ( $Bi_2O_3$ ) is separated by filtering, washed and dried, which resulted in chemical composition of 88 wt% Bi. The purity of  $Bi_2O_3$  was calculated as 97.8% (Ha et al., 2015). Figure 3 presents flow chart of the recovery process.

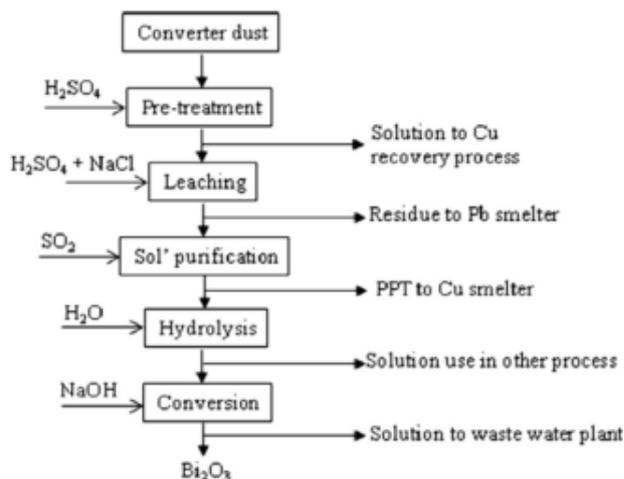


Figure 3 Flow chart of Bi recovery from converter dust. (Ha et al., 2015)

### 2.2.3 AQUEOUS SOLUTIONS

Research has shown, that bismuth can be recovered from synthetic solutions ( $\text{H}_2\text{SO}_4$  and  $\text{HCl}$ ) used in leaching of mineral metallurgical processing of lead, copper and tin. The recovery was performed by supported liquid membranes (SLM) with tri-n-octylphosphine oxide (Cyanex 921) as extractant. This method enables separation of chemical compounds by a thin layer of organic solution absorbed in pores of polymeric support. The membrane is an intermediary separating the feed phase, containing elements that need to be removed, and the stripping phase, where the element is recovered. The metal transfer from feed to stripping solution through the SLM includes few stages, namely complexation reaction between extractant and solute at the feed solution-SLM interface, diffusion of the complex that was formed through SLM, release of solute in stripping solution by decomplexation reaction at SLM-stripping solution interface and diffusion of extractant from the last interface to the feed-SLM in order to restart transfer process. The Bi transport through SLM continues until the Bi-Cyanex complex is not present in the membrane. Scheme of the process is shown in Figure 4. The experiment has proven method to be feasible in Bi recovery. The highest Bi recovery was obtained using feed solution with 0.5 M  $\text{HCl}$ . Bismuth concentration of  $100\text{mgL}^{-1}$  in the feed solution required 480 minutes in order to transfer 90% of this metal (Gonzalez, Navarro, & Saucedo, 2008).

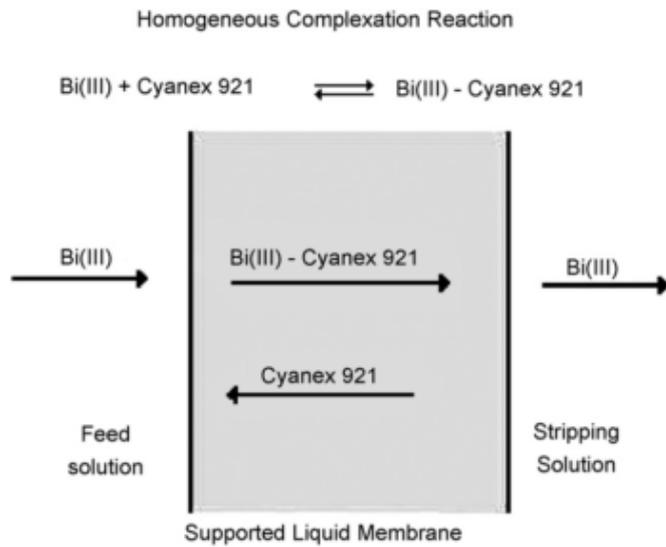


Figure 4 Scheme of bismuth transfer through SLM. (Gonzalez et al., 2008)

## 2.2.4 FUSIBLE ALLOYS

The second biggest share of bismuth uses are fusible alloys, where Bi replaces harmful metals in solders (European Commission, 2017). However, no information was found either on recovery technologies for those applications, or for undertaken recovery activities.

## 3 CURRENT RECOVERY RATES

The research has shown very little information on recovery of bismuth from end of life products. Experiments were found on Bi recovery from other metals processing, however there is no information whether these methods are implemented in the industry. The end of life recycling input rate is very low, estimated at below 1% (European Commission, 2017). Bismuth is difficult to recycle from end of life products, it is mostly recovered from production processes of copper and lead refining (Umicore, n.d.).

In United States it was estimated that less than 5% or 80 tones bismuth consumption was recovered from new and old alloy scrap (Anderson, 2017).

## 4 KEY ACTORS IN BISMUTH RECOVERY

In the EU a big player on Bi market is Canadian 5N Plus, with a subsidiary in Belgium. It specializes in refined bismuth, Bi-bearing chemicals and low melting point alloys production. The company could have refining capacity in EU, however there is no data available to support this statement (European Commission, 2017). The company has four recycling sites placed in Germany, Malaysia, Laos and Canada, processing waste and residues from primary metal production yet there is no information whether the recovery includes bismuth (5N Plus, 2017).

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Europe's largest producer of Bi vanadate ( $\text{BiVO}_4$ ), a pigment used in paints and coatings, is BASF (European Commission, 2017). Although the company has ongoing recycling activities of precious metals, there is no mention of bismuth among them (BASF, n.d.).

American company The Eagle Metal Group claims to recycle bismuth from multiple Bi-bearing scrap, namely ingots, chips, sludge, powders and other. No additional information is available on processes involved and obtained recovery rates (Eagle Metal Group, 2015).

## 5 CHALLENGES IN MATERIAL RECOVERY

The difficulties of bismuth recovery come from the way it is used in final applications. The metal is usually dissipated in products like pharmaceuticals or pigments, which makes the recovery problematic (European Commission, 2017; Umicore, n.d.). The recovery of bismuth scattered in applications like medicines, paints, cosmetics and bismuth-bearing bullets is not possible with present technology. In case of solders, which become smaller in size and contain less Bi, the economically feasible recovery decrease respectively. However, solders with higher content of silver are more valuable and therefore worth the effort of retrieving.

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## 20 PRODUCTION TECHNOLOGIES OF CRM FROM SECONDARY RESOURCES: HAFNIUM, HELIUM AND SCANDIUM

### 1 HAFNIUM

Hafnium is a very special metal when it comes to recycling, both because of the very special fields of applications but also because it is a metal which often is used or produced in connection with Zirconium. Hafnium and Zirconium are mutually mixing and the quantities of zirconium in hafnium, or the opposite, can vary significantly from case to case. Hafnium is often present in applications like: nuclear industry (reactor technology), super alloys and microprocessors. Due to this, there are very few recyclers dealing with the recycling of Hafnium.

One of the recyclers is Quest Metals (QUE 2017), a company located in Humble, Texas, USA, specialized in high temperature alloy and counted as one of the largest in the world. The company is purchasing pure hafnium and hafnium containing alloys like: PWA 1422, C103, MarM247. There is no information about the methodology used for recycling of Hafnium.

Another company specialized in high temperature recycling is Monico Alloys (MON 2017) situated in Rancho Domingues, California, USA. The company has been founded in 1979 and its main activity is Titanium scrap, however it is now also recycling other high temperature metals as well. Besides a very brief description of the mechanical processing of the hafnium containing scrap, no other details are given on how the metal is recycled. No quantities of the incoming materials are given.

The Eagle Metal Group (EAG 2017), in Schereville, USA is also offering services on recycling hafnium, including the nuclear sources. It is not clear if the company is only buying, pre-processing and selling hafnium or also recycling by melting the metals.

In Europe, Walch Recycling & Edelmetalle in Baudenbach (WAL 2017), Germany is offering services on noble metals, where hafnium is mentioned. However, the company is recycling or is only buying and pre-processing the metals.

There are no reports on the quantity of hafnium present in metallic scrap or how much is collected or recycled per year of any other time unit.

There is very little information about how the hafnium is actually recycled, however there are a few numbers of recycles, as mentioned above, which are dealing with the metallic scrap. One can easily conclude that hafnium recycling is scarce in the world and the methods used for actual recycling is insufficiently addressed or reported.

### 2 HELIUM

There is no obvious secondary source of helium which can count as a waste stream, or the possibility to recycle helium from a spent source. The only recycling of helium is only discussed for the helium producers, like Linde (LIN 2017). However, the recycling system is mainly made for the purpose of mitigating the losses of helium while loading/unloading vials or instrumentation.

Another company looking at similar approach is VIC Leak detection, from US (VAC 2017).

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ALD Vacuum System INC (ALD 2017), from US is claiming that there is a patented system in operation for Helium, Argon and Nitrogen Recycling. In this case as well, the recycling/reclaiming is only in conjunction with mitigating the potential losses from systems already using helium.

### 3 SCANDIUM

Scandium is known to be used in different alloys for improving different parameters/properties: refines the grain structure (strength) while preserving the desired material properties; superior heat stabilizer in solid oxide fuel cells (SOFCs); used in lighting, lasers and medical applications).

There is no data readily available to account of the amount of Scandium available in secondary or industrial waste streams.

RUSAL (RUS 2017, REC 2014), in Russia, is currently building a pilot for recycling of scandium as a measure of mitigation of their own production cost, meaning that the recycled scandium is from their own production spills of aluminium.

There are no other reported recycling activities for Scandium in the world (ERN 2014).

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## 21 PRODUCTION TECHNOLOGIES OF CRM FROM SECONDARY RESOURCES: NATURAL RUBBER

Natural rubber is harvested from rubber tree, mainly grown in Southeast Asia. The EU is fully relying on imports of natural rubber. The tire industry is the largest consumer of natural rubber, accounting for about 75% of the demand in the EU. Other product destinations within the EU can be divided into three categories: industrial products, consumer products, and latex products. Only approximately 0.9% of the natural rubber from primary resources is currently being replaced by secondary natural rubber. (European Commission 2017)

### 1 PRODUCTION FROM LATEX WASTE

About 10-15% of the consumed rubber ends up as waste in latex-based industries. The formation of waste latex rubber is due to the unstable nature of the latex compound and the strict specifications in the quality of latex products. These latex rejects contain only lightly cross-linked rubber, which are available in large quantities. Therefore, these scrap latex rejects are considered as potentially valuable sources for recycling. The use of powdered latex rejects as filler in epoxidised natural rubber were studied by Mathew et al. (2001). In another study waste natural rubber latex was blended with polystyrene (Boondamnoen et al. 2012). However, no information was found of commercial or even pilot scale utilisation of latex waste rubber.

### 2 PRODUCTION FROM END-OF-LIFE PRODUCTS AND MANUFACTURING RESIDUES

#### 2.1 DEVULCANIZATION

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

#### 2.2 MANUFACTURING SCRAP

In addition to lightly cross-linked latex waste, also large amounts of rubber scrap are produced in typical rubber manufacturing processes. These include (Forrest 2014):

- Stamping out of gaskets from cured sheet rubber: 20-40% waste
- Injection moulding processes due to moulding flash: 30-50% waste
- Extrusion processes to produce final product: 2-5% waste

The utilization of these waste streams requires effective devulcanisation treatments, as discussed above. One devulcanisation process that has received a lot of publicity over the past few years is the Watson Brown high shear mixer (HSM). The HSM technology involves subjecting the waste rubber to a high shear environment within a specially designed mixer to break the sulfur crosslinks, adding an optimised amount of sulfur to the

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resulting compound on a two-roll mill and then revulcanising it. The technology has been scaled up from laboratory to commercial scale machines. (Forrest 2014; Kraemer & Maddever 2012)

## 2.3 TYRES

The main rubber types in tyres are natural rubber and styrene-butadiene rubber (SBR). Their respective shares depend on the size of the tyre (or the vehicle), so that, in general, the smaller the tyre, the smaller the proportion of natural rubber. The ordinary passenger car tyre is therefore manufactured using a blend of SBR/NR at a ratio of around 60:40, a truck tyre of 30:70 respectively, and a large tyre for an earth-moving construction vehicle from natural rubber only. (Forrest 2014)

In Europe, 46% of the end-of-life tyres (ELTs) are recycled as material and 49% as energy. 5% is considered as residual waste. The energy recovery is almost entirely (91%) accounted for by use in cement kilns. Of this amount, 25% is still recycled in the clinker. Other 9% of tyres recycled as energy are used in direct energy production. Recycled tyres become secondary raw materials for new products. Closing the loop, or using ELTs as raw material for new tyres is not yet within reach, due to the strict safety regulations, environmental performance and technological constraints. (Scott 2015)

As the composition of a tyre is very complex, any rubber recovered from an ELT may contain a mix of different compounds. Separating and devulcanising these compounds in order to recycle them is a very challenging task. Therefore, the rubber in ELTs is often recycled in its entirety as shred, crumb, granulate or powder. The material has many profitable properties, such as shock absorption, noise reduction, resistance against changes of temperature and against chemical degradation. (Scott 2015)

Aliapur (France) is a notable industrial actor in the ELT business: the company collects about 300 000 t of ELTs annually, of which more than 40% is directed to material recycling for the following applications (Aliapur 2017a):

- Acoustic screens and sound barriers
- Asphalt rubber
- Athletic tracks, sports areas and playgrounds
- Car parts (in thermoplastic composites)
- Concrete (to improve properties)
- Equestrian floors
- Moulded objects (particularly as urban furniture, such as speed bumps, bases for signs)
- Rail filler block systems (for vibration control and electric insulation)
- Retaining walls
- Synthetic turf

Companies called Recipneu (Portugal) and TIRES S.p.A. (Italy) have also similar product applications derived from ELTs (Recipneu 2017; TIRES S.p.A. 2013). However, the literature doesn't acknowledge that virgin natural rubber would have been used in these applications. Therefore, even the natural rubber is recycled through these applications as a material, ELTs replace mainly nonrenewable natural resources and thus the demand for primary natural rubber cannot be seen offset at all by reusing ELTs.

A company called Rubber Products (Latvia) has released Next Generation Rubber (NGR), an alternative to natural and synthetic rubber devulcanised from ELTs. It is claimed that NGR can replace up to 70% of

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natural/synthetic rubber of a product without very slight, or zero, decrease in quality. It can be used in the production of high-quality rubber goods, including tyres. (Rubber Products 2016)

There are also research initiatives pursuing to develop methods for closing the loop for ELTs. For example, currently on-going project TREC, driven by Michelin, is aiming to create a micropowder that can be used as a raw material in the production of new high-performance tyres. The studied methods are micronization and selective devulcanization using biotechnologies. (Protéus 2014) Some possible routes to recycle ELT material are summarised in Figure 16.

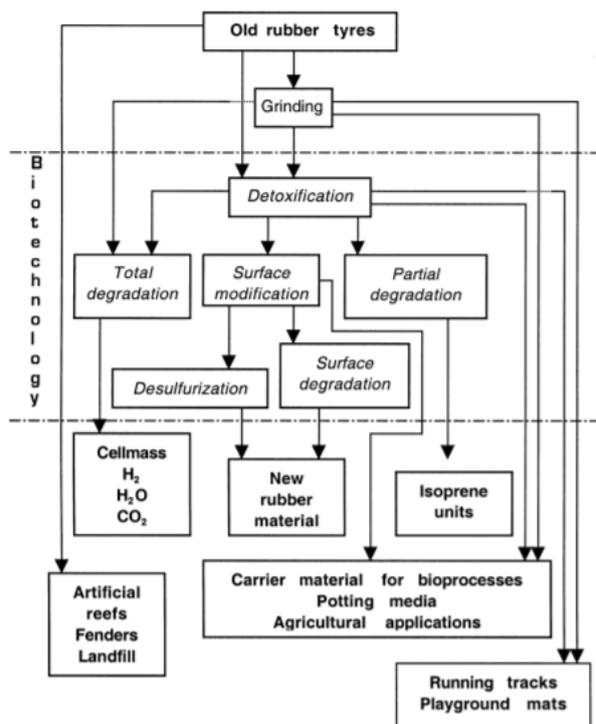


Figure 16 A diagram of possible methods for ELT material recovery. (Bredberg et al. 2004)

Some of the used tyres are still in a condition that enables their direct reuse after a quality control, or use after retreading, which means that the worn tread is replaced with a new one (Aliapur 2017b). In 2015, out of 3.87 Mt of used tyres managed in Europe, 678 000 t, or 17.5%, were reused, either directly, after retreading or through exports (ERTMA 2015). Reusing of tyres can be considered to replace a share of the virgin natural rubber resources.

### 3 SUMMARISED DISCUSSION ON PRODUCTION OF NATURAL RUBBER FROM SECONDARY RESOURCES

Recycling natural rubber is technically challenging due to the facts that rubber products are vulcanised and contain a variety of additives. In terms of quantity, used automotive tyres compose the most attractive source of secondary natural rubber. However, due to the complex structure of tyres, and due to the strict safety regulations that control their performance, the material from end-of-life tyres (ELTs) is mostly used in other applications in the form of powder or granulates, than re-used in tyres. In these other applications, the ELT material rarely replaces virgin natural rubber. There are however commercial examples of devulcanising

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technologies that will possibly enable large-scale utilisation of ELTs as a raw material for tyre manufacturers in the future.

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## 22 PRODUCTION TECHNOLOGIES OF CRM FROM SECONDARY RESOURCES: TANTALUM

### 1 OVERVIEW OF GLOBAL PRODUCTION OF TANTALUM AND AVAILABLE SECONDARY TA RESOURCES

Roskill estimates consumption in 2015 at about 1800t contained Tantalum, which is a little below the 2008 peak. They also stated that the consumption of Tantalum in EU is almost impossible to estimate.

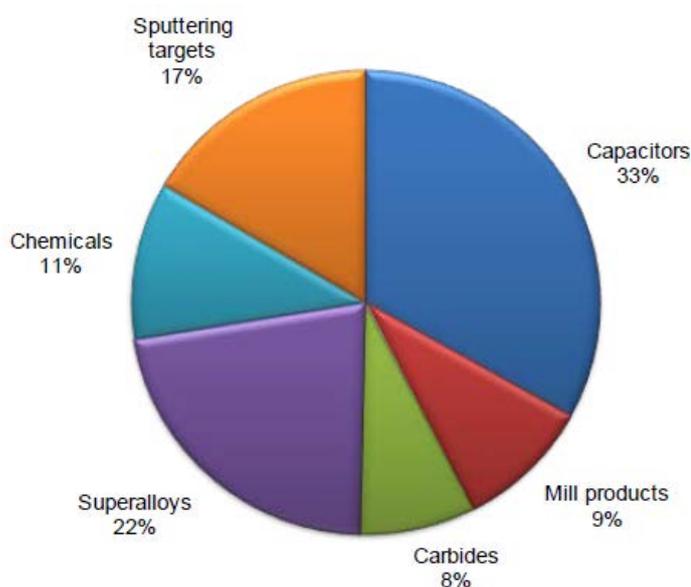


Figure 1 Estimated world consumption of Ta by application, 2015. Source : Roskill

The main application for Ta is in electronics, being the largest single use in capacitors. Also sputtering targets are another major application for tantalum. Sputtering is a method of applying thin films of metal to a substrate and is used in the manufacture of storage media, inkjet printer heads, electronic circuitry and flat-panel displays, among others. The target is the source of the metal that is deposited. Targets are generally recycled after use. Tantalum chemicals have a very wide range of applications and are intermediates in the manufacture of other products that are often destined for the electronics industry. Superalloys are a variety of high-performance alloys that are used in, for example, aerospace (jet engines) and land-based gas turbines. As aircraft design and performance expectations improve, the alloys involved become more sophisticated and the loading of tantalum in alloys is increasing. A lot depends on the outlook for the commercial aerospace industry, particularly Airbus in the EU context. Tantalum carbides are used in cutting tools. This is probably a declining market for tantalum. Tantalum mill products have a very wide range of uses, including chemical processing equipment, ballistics and surgical implants [1].

The tantalum recovery from secondary sources ensures up to 10% of the total Ta supply (up to 25% in USA). The main secondary sources are scrap and wastes of metal tantalum and its alloys.

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These wastes are represented by rejects of ingots of vacuum-arc remelting, shaving, clipping of half-finished products, green ends and rejects of fillets, and screening of powder. Low-grade wastes consist on distillates from screens of electron-beam and vacuum-arc furnaces [2].

Tantalum can be extracted as a by-product of tin smelter waste, where normally ranges between 8-10% in oxide form, and sometimes reaching 30%. Tantalum can also be found in waste from uranium mining operations.

Moreover, Ta can be found in municipal waste landfills, industrial landfills (WEEE recycling companies) and incineration slags [3]. The knowledge about recovery potential of Ta from landfills is limited, being estimated that the recovery of Ta alone is not feasible due to the low concentrations [4].

## 2 TANTALUM PRODUCTION FROM SECONDARY SOURCES

The common method (Fig.1), unchanged for decades, to extract Tantalum from concentrates, tin slags and scraps, is to digest the ore at high temperature in a sulfuric acid – hydrofluoric acid mix and, after filtering out the insoluble minerals, apply a solvent extraction with methyl isobutyl ketone (MIBK) or liquid ion exchange using an amine extractant in kerosene. The result is highly purified solutions of Ta and Nb, from which Ta is crystallised, as potassium flourtantalate (“KTaF”) by reaction with potassium fluoride [5].

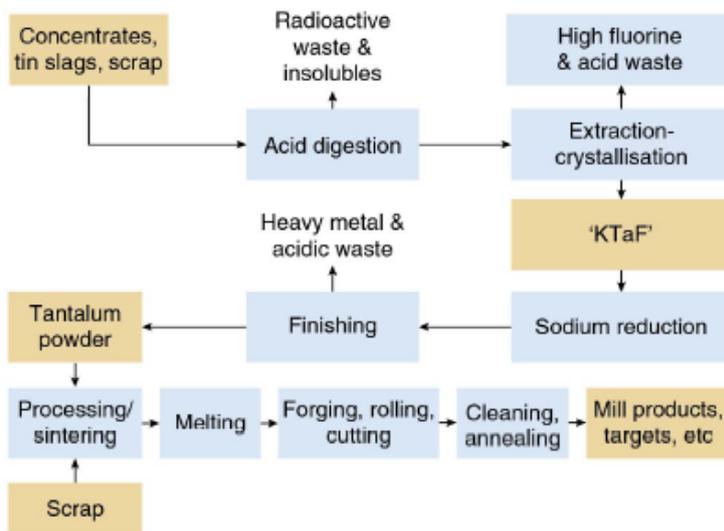


Figure 2 Schematic flowsheet for the production of Ta from concentrates, tin slags, and scrap. [5]

### 2.1 TANTALUM RECOVERY FROM SCRAP

The tantalum scrap can be processed into powders using hydrogenation or fluorination. The method of chemical dissolution and repeated precipitation or the electrochemical method can be used during its processing with the purpose of fabricating Ta<sub>2</sub>O<sub>5</sub> [2].

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Also, Ta oxide can be fabricated by the chlorination of scrap. Formed  $TaCl_5$  of technical purity grade is purified by distillation and reduced with hydrogen to  $Ta_3Cl_8$ , then niobium is removed from the latter, which is chlorinated to  $TaCl_5$  again. The latter is dissolved in alcohol with the formation of tantalum alcohochloride, which is subjected to hydrolysis in the presence of carbon. Due to this, high-purity  $Ta_2O_5$  is formed [2].

## 2.2 TANTALUM FROM INCINERATION BOTTOM ASH

The common method is first to store the slag at least one day for integration of carbon dioxide and to make it less wet and sticky. After, the slag is treated at the incineration plant. Metal pieces and particles are separated by sieving, crushing, and mechanical separation (magnetic, eddy current). Sensor separators can also be used for identification of specific metals. If the target is also separate recovery of specific valuable metals, hand picking of e.g. capacitors from the metal flow may be a viable alternative, although in many cases not cost-effective [4].

## 2.3 TANTALUM RECOVERY FROM SUPERALLOYS

To recycle Ta from superalloys, the alloy is subjected to anodic oxidation in the aqueous solution of organic compounds and salts. Methanol, ethanol, isopropanol, and acetyl acetone are used as the former. Halogenides, sulfates, and nitrates of alkali and alkali-earth metals are recommended as salt additives. [2]

## 2.4 TANTALUM FROM PYROMETALLURGICAL SLAG

Tantalum is easily oxidized and is found in the slags produced after pyro-metallurgical processes. By using electrothermic reduction process, the slag is upgraded to a Tantalum-oxide content as high as 50%. Carbothermic, metallothermic, and hydrogen reduction can be applied to extract Tantalum. Also, electrolysis in molten salt can be applied, vacuum sintering or electron beam or plasma processes [3].

## 2.5 TANTALUM EXTRACTION FROM TIN SLAG

A flow-sheet for Nb/Ta recovery is shown in Figure 2 [6]:

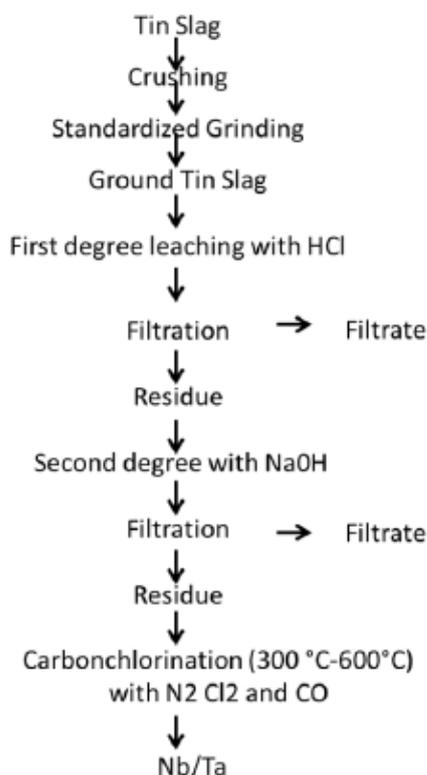


Figure 3 Flow-sheet of Nb/Ta recovery from tin slag.

During the pyrometallurgical extraction of tin from cassiterite, Ta oxides and other metal oxides are concentrated in the slag [7]. Tantalum can be extracted as a by-product of tin smelter waste, at around 14%.

Conventional methods used for the extraction of Ta compounds from tin slags consist of full dissolution with HF, HF + sulfuric acid, or smelting in electric furnaces. These processes are limited either by economic or environmental considerations [7]. Tantalum is also extracted from cassiterite placer middlings using shaking tables, and magnetic and electrostatic separation methods. Low-grade smelter wastes can be upgraded by electrothermic reduction yielding a synthetic concentrate with up to 50% Ta and Nb oxides [8].

Bullatovic and De Silvio developed a process for removal of zircon, tantalum and columbite impurities from tin gravity concentrate, applying direct flotation of tin with sulphosuccinate collector modified with fatty alcohol ester sulphate, mixed with the depression of the metals with organic acids and sodium silicate, reaching the upgrading of SnO<sub>2</sub> to 90% [9].

An US parent reports a method for beneficiating Ta and Nb from tin slags, by heating the slag in the presence of enough carbon to convert the Ta and Nb oxides to a hearth product containing the Ta and Nb as carbides in a mixture with a carbon-containing iron alloy; separating oxidic gangue constituents from the hearth product; reacting the hearth products with an amount of sodium nitrate such as to insure oxidation of all metallic constituents of the hearthproduct to their respective highest-valence heat-stable oxidic form of sodium salt, together with a source of additional sodium oxide in amount of at least 25% by weight of sodium nitrate; leaching the resulting reaction product with hot water; subjecting the hot-water insoluble constituents of the

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reaction product to reaction with an aqueous mineral acid to convert the tantalum and niobium constituents to their hydrated oxides and to dissolve the sodium and iron constituents, and separating the resulting aqueous phase from hydrated oxides to leave as a residue a beneficiated mass of the tantalum and niobium oxide constituents of the starting tin slag [4] [10].

### 3 CURRENT RECOVERY RATES

The production of Ta from secondary sources (tin slags, manufacturing and EoL scraps) has grown between 2008 and 2012 [11]. Ta recycling accounts for around 20% of world total supply. The figures are not known for Europe, as no information is found about the production of Ta from secondary sources in the EU private companies [12].

### 4 KEY ACTORS IN TANTALUM RECOVERY

Table 1 lists the main companies that recover Tantalum from secondary sources in EU. Few countries recover Tantalum in EU and Germany concentrates the activity.

Table 1 EU stakeholders in Tantalum extraction from secondary sources.

Company	Country	Activity
Avon Specialty	UK	Recycling
Buss&Buss	Germany	Recycling
ELG Utica Alloys	UK	Recycling
GMH Stachow-Metall	Germany	Recycling
H.C.Starck	Germany	Recycling
Innova Recycling	Germany	Recycling
Metherma	Germany	Recycling
Nordmet	Estonia	Recycling
Imerys Ceramics	France	Ta from kaolin mining
Strategic Minerals	Spain	Ta from tin mining

### 5 CHALLENGES IN TANTALUM RECOVERY

There are several innovative processes but most them are not tested on pilot scale. In some cases, the information on maturity of processes is missing. The techno-economic analysis often lacking, and it is difficult to compare the potential benefits of new processes with the current industrial processes. There is need of more research.

Barriers in current processing are:

- Non-selective leaching resulting in large amounts of impurities also being dissolved
- Current extractants used in SX processes are not optimized for specific application
- Environmental issues are associated to the use of HF and fluorides, therefore alternatives should be desirable
- The extraction leads to generation of substantial solid wastes
- Ta can be easily get oxidized and is therefore often lost in slags

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The need for innovation includes:

- Improved selectivity for processing and leaching techniques -> increasing the Nb/Ta concentrations
- Development of leaching and solvent extraction processes without need for HF and fluorides
- Development of more robust extractants with higher efficiency in non-fluoride media
- Increased recycling of effluents to reduce liquid and solid waste, this may need development of purification steps for the chemicals
- Development of combined, well adapted hydro-pyro metallurgical processes [13].

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## 23 PRODUCTION TECHNOLOGIES OF CRM FROM SECONDARY RESOURCES: VANADIUM

### 1 SECONDARY RESOURCES OF VANADIUM

According to the value chain of vanadium shown in D4.1, V-containing secondary resources include: (i) tailings, mainly from the mineral processing of titaniferous magnetite ore; (ii) residual materials from the roast-leach processing; (iii) low-grade slag generated during the various smelting processes; (iv) end-of-life products, mainly including steel scrap/alloys and spent catalysts and (v) other industrial residual materials, such as fly ash.

At the moment there is no production processes for the extraction of vanadium from titaniferous magnetite ore tailings, from the roast-leach residuals, from the low-grade slag generated from the smelting processes, although extraction of iron and titanium has been reported.[1], [2]

### 2 VANADIUM PRODUCTION FROM SECONDARY RESOURCES

#### 2.1 VANADIUM FROM STEEL/ALLOY SCRAP

Based on fact that vanadium is largely used for steel production (especially HSLA steels), it is believed that V-containing steel scrap is the prevailing secondary resources of vanadium, which can be recycled. Further, from the technical and economic points of view, it is much easier and more profitable to recycle the steel scrap. The steel scrap could be further classified as new steel scrap and old steel scrap. The new steel scrap is generated in the manufacturing processes and this kind of scrap has known composition and usually segregated by material specification and returned to controlled-atmosphere induction furnace operations, where the scrap is melted into a product having the desired chemistry. The old steel scrap refers to the scrap from EOL products. This type of scrap has different shapes and varying chemical compositions.

According to the applications of vanadium, the V-containing steel scrap can be classified as low-vanadium-alloyed steels (especially HSLA steels), special steels and vanadium alloys. Vanadium use in low-vanadium-alloyed steels is almost entirely dissipative and this means that the recycling rate of vanadium from old steel scrap is almost zero. This is on one hand due to the low vanadium content in the steel scrap (e.g. 0.01-0.15% vanadium in the HSLA steels[3], [4]); on the other hand this is due to the fact that recovery of vanadium from steel scrap is chemically impeded under the oxidizing conditions in steelmaking furnaces. The vanadium in the end is lost in the dust and slag while only the iron content in the steel scrap is recycled. [5] Vanadium in the special steel scrap and vanadium alloy scrap are possible to be recycled, if these scrap is processed under reducing condition (such as in the Electric arc furnace with addition of strong reducing agent) or recycled by melting under vacuum condition.[5] The loss of vanadium from the special steel scrap and vanadium alloy scrap could be probably due to the discard of these materials and dilution of the vanadium into other steels products, in which vanadium is not considered as an effective alloying element.

#### 2.2 VANADIUM FROM SPENT CATALYSTS

V-bearing catalysts are associated with hydrocarbon recovery and refining in the oil industry. Spent catalysts are normally recycled due to the hazardous and toxic nature of the chemicals in the spent catalysts as well as

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due to the fact that, beside vanadium, the spent catalysts also contain other valuable elements. A typical spent catalyst contains 5-16% S, 1-8% Mo, 1-13% V, 1-3% Ni, 10-30% C and 20-30% Al in the form of alumina ( $Al_2O_3$ ).[6]

In general the processing of spent catalysts includes several of the following steps:

- 1) Roasting under oxidizing atmosphere to eliminate the C and S contents in the spent catalysts;
- 2) Crushing/grinding to get fine materials;
- 3) Roasting with soda or treated with acid convert the metal oxide into other forms;
- 4) Precipitation/ion exchange to separate one metal to another;
- 5) Smelting in the arc furnace to convert the metals in the spent catalysts into alloys.

A list of industrialized processes for recycling spent catalysts is shown in Table 1. One example of the process is shown in Figure 1, which is developed by Gulf Chemical & Metallurgical Corporation, the world's largest recycler of spent petroleum catalysts.[7] In this process, the spent catalyst is roasted with sodium salt in the hearth furnace under oxygen atmosphere; the resulting materials after cooling are subjected to grinding and water leaching. By filtration the obtained solid is charged into the DC arc furnace to produce metal alloy and fused calcium aluminate; the obtained liquor is further treated and used to extract molybdenum and vanadium oxides. The company only recovers molybdenum and vanadium, whereas the Ni-Co alloy is sent to plants specialized in separation of Ni from Co. Swerea MEFOS has developed a process using a DC furnace to recover Mo, Co and Ni into a metal alloy, which can be used for special steel production, while the generated vanadium enriched slag can be used for FeV production.

Table 1 Commercial processes for the recycling of spent catalysts by different companies. (The information is collected from [8])

Company	Key processing steps
Gulf Chemical and Metallurgical Corporation	Soda roasting + water leaching + precipitation + smelting
CRI-MET	Two-stage caustic pressure leaching
Eurecat	Decoking + leaching with caustic soda + ion exchange
Taiyo Koko Company	Soda ash roasting + water leaching+ precipitation
Full Yield Industry	Soda ash roasting + leaching + precipitation
Moxba-Metrex	Decoking + sulfuric acid leaching + solvent extraction
Quanzhou Jing-Tai Industry	Low-temperature calcination + leaching with $H_2O_2$ + precipitation/ion exchange
Metallurg Vanadium	Pyrometallurgical process to convert metals in the catalysts to alloys
German (GfE Metalle and materialien GMBH, AURA Metallurgie GMBH and Spent Catalyst Recycling GMBH )	Hydo- and pyro-metallurgical methods (specific methods are not clear)
Nippon Catalyst Cycle Co.	Roasting + leaching + solvent extraction

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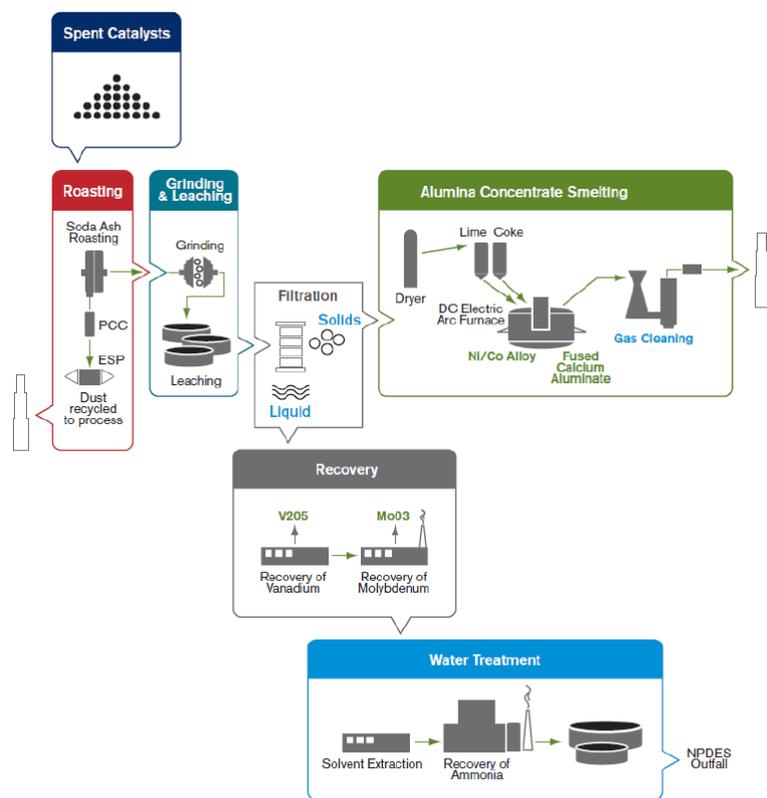


Figure 1 Process diagram of the Gulf Chemical Corporation treatment.[7]

### 2.3 FLY ASH FROM HEAVY FUEL POWER PLANTS

Vanadium is a trace element present in some crude oils and the vanadium content can be up to 500 ppm (for example, the heavy oil from Venezuelan). The combustion of these crude oils produces fly ashes that contain a high content of vanadium, nickel, iron, aluminium, silicon, sulfur and non-burnt carbon. The chemical compositions of the fly ashes vary a lot with their origins. In general, it contains 2.5–40% vanadium ( $V_2O_5$ ), 0.8–6% nickel (NiO), 0.7–8.6% iron ( $Fe_2O_3$ ), 0.5–14.6% aluminium ( $Al_2O_3$ ), 2.5–24.8% silicon ( $SiO_2$ ), 2–30% sulfur and 1–54% for carbon.[9] Due to the high vanadium content in the fly ash, it is considered as one of the important secondary resources of vanadium.

According to the literature the vanadium extraction from the fly ash can be implemented either by hydro-metallurgical processing or pyro-metallurgical processing. [7], [9]–[12] The most commonly applied processes are direct acid leaching, direct alkali leaching, acid leaching after roasting, alkali leaching after roasting and water leaching after roasting. [7] One example of the direct alkali leaching process is shown in Figure 2. In this process the oil fly ash from power plants for the selective recovery of vanadium was performed in a two-step procedure, consisting of an alkaline leaching using sodium hydroxide and a selective precipitation or solvent extraction procedure. The best results show that vanadium can be extracted from fly ash via a two-step procedure, consisting of an alkaline leaching using sodium hydroxide and a precipitation procedure. At Mintek, a complete pyro-metallurgical process was developed. The process include a drying stage at moderate temperatures of about 150 °C, a de-carburization and de-sulphurization (pre-treatment) stage, and finally a smelting step in a DC arc furnace. The test results show that ferrovanadium alloy containing more than 15% vanadium and 6% nickel can be obtained and the vanadium recovery is more than 89%.

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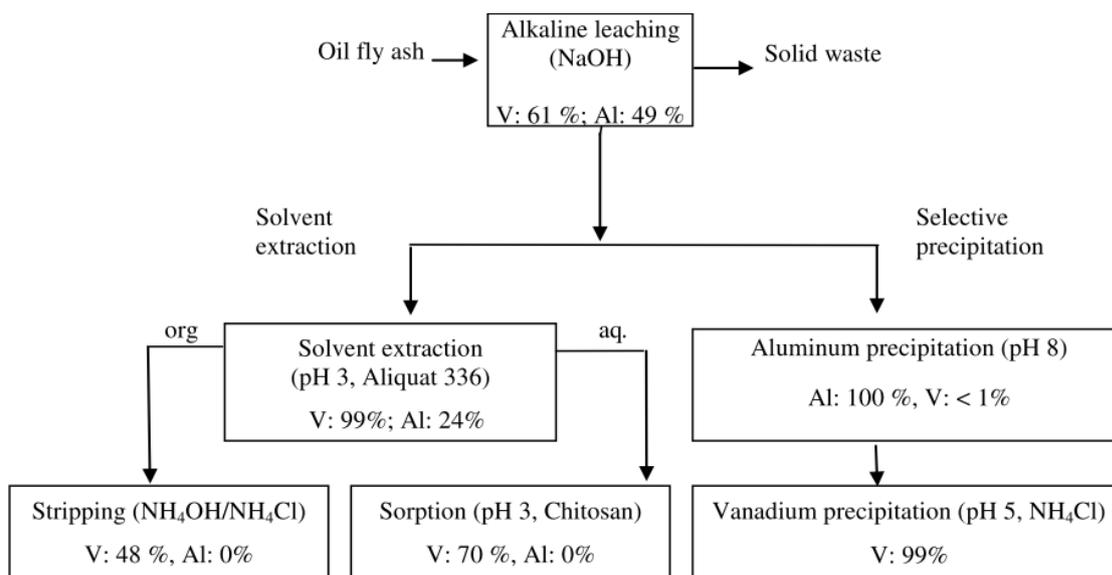


Figure 2 Integrated process for oil fly ash treatment (the total recovery of selected metals at each step is reported as percentage of total metal content in the waste material). [9]

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