



SCREEN

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Technological gaps inhibiting the exploitation of CRMs secondary resources

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Summary

Technological gaps inhibiting the exploitation of CRMs secondary resources

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DELIVERABLE 6.2:

TECHNOLOGICAL GAPS INHIBITING THE EXPLOITATION OF CRM SECONDARY RESOURCES

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ABOUT THE SCRREEN PROJECT

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

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

SCRREEN will contribute to improve CRM strategy in Europe by:

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

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

SUMMARY

This document presents a gap and innovation capacity analysis in order to pinpoint technologies that have to be developed to unlock available unexploited secondary resources. Based on WP3 outputs on secondary resources, methods for secondary mining and collection of industrial waste resources are explored. Newly produced wastes possible to collect in the waste streams as well as material in intermediate storage and landfill are considered.

Existing and innovative methods for pre-treatment of waste streams in general are investigated for their potential use for waste containing CRMs. Existing and innovative methods for hydro- and pyro- metallurgical methods for recovery of CRMs from waste are listed and described. The constitution of each waste with potential for recovery is reviewed and when applicable the possible hinders for using a specific method are identified and alternative methods explored.

When available, life cycle assessment (LCA) results are presented on the new scenarios considering several impact categories in order to compare obtained results with global CRMs conventional processes. Key elements (hot spots) are identified and several improvements strategies are proposed in order to reduce detected environmental impacts.

INTRODUCTION

Numerous CRM secondary resources have been identified (WP3). Some of them are today exploited by using technologies derived from the primary production, or specifically developed (WP3).

In order to unlock the whole potential from these secondary resources, innovative developments are required.

However, all the potential secondary resources do not have the same valorization perspectives. D62 come back to these resources and points out relevant ones for which more R&D would be required.

TECHNOLOGICAL GAPS/BARRIERS ON SECONDARY RESOURCES

ANTIMONY

1. THE SECONDARY RESOURCES

Mine & metallurgical wastes: there is lack of data to quantify the waste arising from mining and processing activities in the EU. Primary production of antimony takes place outside the EU. Although some activity may take place in the EU mainly in Portugal according to [1], more information could not be found.

Scraps: Antimony containing scraps are [2] [3] [4]:

- Flame retardant products containing antimony such as plastics, construction materials, electronics, textiles and coatings;
- In metals such as ammunition, in lead-acid batteries and in other alloys;
- Other applications such as a heat stabilizer in plastics and in CRT glass;

Apart from lead-acid batteries that have their own dedicated recycling route [2], other antimony containing wastes are mostly following the municipal solid waste (MSW) route. In the case of lead-acid batteries, an almost fully closed-loop recycling exists whereby secondary antimonial lead is introduced in the primary route for new lead-acid battery manufacturing. Depending on the country, antimony containing wastes will be landfilled or incinerated. It is estimated that MSW contains between 10 – 60 mg of Sb per kg [4]. An overview could not be found on the flows of antimony in the end-of-life phase for the EU in the form of a material flow analysis to identify the main flows of antimony, but similar studies have been performed for other countries like Switzerland [2].

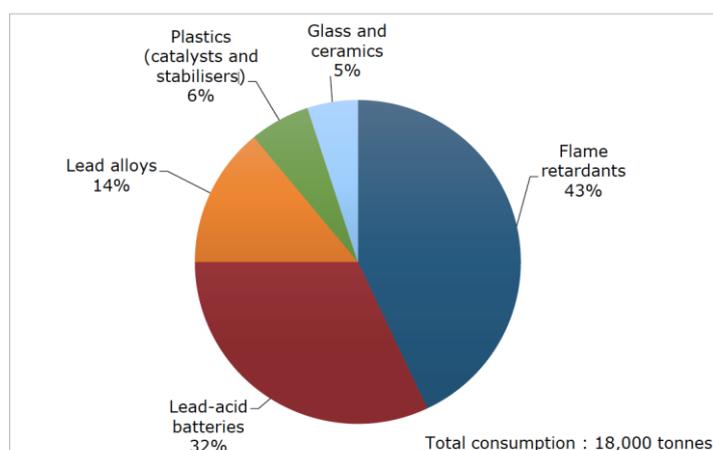


Figure 1 - EU end-uses of antimony in 2014 [3]

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Figure 1 illustrates the end-uses of antimony within the EU. It is very clear that flame retardants and the lead acid batteries are the two largest Sb applications.

2. EXISTING PROCESSING ROUTES – GAPS & BARRIERS

Two different recovery routes of secondary antimony can be identified according to the life-cycle stage [3]: recovery from mine and metallurgical wastes and recovery from the incineration of EoL products such as the ones described in the previous section.

2.1 MINING AND METALLURGICAL WASTES

Mine and metallurgical wastes containing antimony arise from the production of lead, copper, gold and antimony. These wastes have different concentrations of antimony and present a potential for recovery. Most of this potential lies outside the EU.

2.2 SCRAPS

Secondary sources of antimony from scrap include those products that have dedicated closed-loop recycling schemes and EoL products that end up in the normal MSW collection system. It can be seen from Figure 1, that the biggest concentration of antimony in the EU can be found in flame retardant (FR) plastics followed by lead-acid batteries as seen in Table 1. Goods pertaining to households have the highest concentration of antimony which can be available in large quantities from fly-ash following MSW incineration and in other household goods.

Table 1 - Sources of antimony scrap at the incineration phase [2]

Stream	Sb content (mg/kg)
MSW (in fly-ash)	10-60 (100-1300)
Construction waste	64
Sewage sludge	3.5
Imported waste	10-60
Automotive shredder residue and household goods	330
Tyres and rubber	136

These FR plastics which have become a ubiquitous source of concern in waste management have on average between 5-30 wt% of antimony trioxide. On the other hand, ABS and HIPS plastics frequently contained in WEEE consist an important source for the recovery of antimony .. Currently, there are no dedicated routes to recover antimony in FR plastics [3] whether specifically aimed at WEEE or other types of plastics. Furthermore, a large part of

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WEEE generated in the EU is not declared for recycling [5] which poses an additional problem for effective collection and processing of antimony-rich plastic waste.

On the other hand, lead-acid batteries enjoy a very well established closed-loop recycling scheme which allows for a very high recycled content of antimony in lead-acid batteries [2] [6] [3] [4] resulting in almost all of the secondary available antimony in the market coming from the recycling of lead-acid batteries.

Given this, and as reported in [2] [3] [4], most of the antimony has been either exported in the form of plastic waste or is sitting in landfills across Europe.

3. INNOVATIVE PROCESSING ROUTES – GAPS & BARRIERS

3.1 MINING AND METALLURGICAL WASTES

Exploitation of antimony rich mining and metallurgical wastes in the EU is limited to smelters of lead, copper and antimony. Many lab-scale experiments have been conducted throughout recent years on the attempt to further recover antimony from the residues arising from mining and smelting industry. Below a summary of these techniques is provided for different metallurgical extraction processes.

Lead: Both in the primary or the secondary production of lead, pyrometallurgical processes are followed while simultaneously residues such as flue dust, slag, dross and skim are produced. In Table 2 and Table 4, an overview in antimony content of these residues is shown. The recovery of antimony from these residues can be done with for example alkaline sulphide leaching of smelting residues (95% antimony recovery). Other more residue-specific recoveries are shown in Table 2.

Copper: Antimony is a known impurity in copper containing ores and its occurrence can be seen at different stages of copper production [3]. In Table 3, an overview of the antimony content in copper production residues is shown. Different processes can be used to recover the antimony content of copper. Initially, antimony can be removed from copper ores by using alkaline sulphide leaching which may reduce the antimony content of the primary ore to 0.1%. Although there are many experimental lab-scale success stories, no industrial application could be found in the literature.

Gold: Sulphide ores containing gold and antimony may be a source for secondary antimony from industrial wastes. In the process of producing gold from these ores, a large quantity of antimony may be disposed to the environment in resulting waste streams [3]. The application of different hydrometallurgical pre-treatments to these ores may result in recovery rates of

antimony of up to 98 % that instead would be discarded as waste. Most common pre-treatment processes are chemical leaching, roasting, bacterial oxidation, pressure oxidation and ultrafine grinding. Each pre-treatment is adapted depending on the type of ore and its impurities [3]. The followed techniques to recover antimony are alkaline sulphide leaching of the gold bearing ore followed by recovery of antimony by electrodeposition (recovery of 90 % up from 18 %). Other techniques include the use of different hydrometallurgical processes such as antimonite floatation, sodium dimethyldithiocarbamate treatments and bio-treatment of ores (recovery of 95-98 % of antimony).

Table 2 - Antimony content in residues of lead processing and its recovery techniques [4]

Residue	Sb content (wt%)	Recovery technique	Antimony recovery (%)
Harris dross	8.2	HCl leaching	95
Smelter speiss, skims and flue dust	3.3, 31.7, 42.4	Alkaline sulphide leaching using Na ₂ S and NaOH	99.8
Sb dust	42.4	Reduction smelting, alkaline refining and oxidation	99.8
Slime	63.6	<ul style="list-style-type: none"> Chlorinated (Cl₂) leaching + continuous distillation Volatile oxide formation Vacuum dynamic flash reduction 	<ul style="list-style-type: none"> 95 - 93.6
Slag	30	Carbothermic reduction of slag	92.4 @ 800 °C

Table 3 - Antimony content in residues of copper processing [4]

Residue	Sb content (wt%)	Recovery technique	Antimony recovery (%)
Flue dust	3.1	<ul style="list-style-type: none"> Kerosene desulfurization+chlorine leaching+hydrolysis Leaching using Na₂S 	<ul style="list-style-type: none"> 90.8 6.6
Anode slime	3.0-24.6	<ul style="list-style-type: none"> Leaching using Na₂S [6] Hydrolysis recovery of Sb₂O₅ Alkaline sulphide leaching Alkaline fusion leaching 	<ul style="list-style-type: none"> 95 97 99.3 -
Electrolyte	1.0	<ul style="list-style-type: none"> Use of adsorbents with aminophosphonic acid functional Other techniques with lower success described in [4] 	<ul style="list-style-type: none"> 95 <90

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Antimony: In the primary production of antimony, industrial residues produced at several stages of the manufacturing process. These can be in the form of tailings, flue dust, slag, liquation residue or refining residue [3]. In most cases, these end-up being buried in landfills either around the processing smelter or stockpiled [7]. In Table 4, antimony contents in processing residues are depicted according to [3]. In an effort to reduce sulphur emissions from antimony production, ZnO is used to fix the sulphur as ZnS thus resulting in greater antimony recovery rates. Most of the process residues resulting from the manufacturing of antimony are sent back to smelt in the blast furnace.

Table 4 - Antimony content in residues of antimony processing [3]

Residue	Sb content (wt%)
Smelter slag	1.11
Smelter flue dust	23.4
Gas treatment slag	0.69
Refining residue	34.9-37.8
High-Sb slag	32.0-39.5
Sb oxidation residue	63.0

3.2 SCRAPS

The most promising sources of recovery for secondary antimony are:

1. MSW incineration ashes
2. Metal oxide varistors (MOV)
3. FR plastics in WEEE and other wastes
4. Halophosphate (HALO) lamp phosphors

1) Recovery from MSW incineration ashes

As reported in [3] many different techniques to successfully remove antimony from boiler, flue dust and fly ash have been carried out. These sources are of particular interest because of the availability of antimony in these carriers, as shown in Table 5:

Table 5 - Antimony content in MSW ash

Antimony content in MSW ash	Sb content (mg/kg)
Bottom ash	10-400
Boiler ash	200-1000
Fly ash	260-1100

Another source of antimony is in the air pollution control (APC) devices in incineration plants. The undertaken experiments to remove antimony from ash include:

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- The use of hydrochloric acid (HCl) solution to leach antimony (20 % recovery) [4]
- Citrate solutions and citric acid to remove heavy metals from bottom ashes [3]

It has been proved that the most promising process is the use of HCl to remove heavy metals from MSW incineration ashes and in particular antimony. Finding a way to selectively separate elements may be the challenge ahead for the successful recovery of antimony from bottom ash. It has been reported that in Sweden, Stena Metall AB uses the HALOSEP process to purify MSW fly ash to lower the acidity level of fly ash to comply with landfill regulations. More investigation is needed to successfully recover antimony. This can be done with a two-step process where an initial low-pH leaching is proceeded by the use of an organic acid such as tartaric acid [4].

2) MOV

Recovery of the antimony content inside MOVs has been experimentally carried out in [4]. MOVs are composed of around 3-5 (wt%) of antimony which is used in the MOV to reduce the size of the ZnO grains in the MOV. To successfully recover the antimony content from MOVs, a carbothermic reduction process is conducted resulting in the volatilization of the antimony phase. This process results in a recovery of around 70 % of the antimony content after condensation of the gases [4].

In this process, after processing 1 ton of MOVs, approximately 30 kg of antimony trioxide could be recovered. The challenges of this process are to investigate how to reduce the required temperature to volatilize the antimony phase.

3) FR plastic

Antimony trioxide is a commonly used component for the making of FR plastic especially in non-halogenated plastics. To efficiently recover antimony from plastics, sophisticated sorting lines are needed to identify plastics that may contain antimony. This can be implemented with existing technology such as XRF sorting. Research has been conducted in the direction of the decomposition of antimony-rich plastics with pyrolysis methods by many experimental methods described in [3]. None of them operates at a large industrial scale and with a range of recovery efficiencies of secondary antimony.

The CreaSolv process has been developed to separate FR plastics from WEEE and has further been deployed by Unilever for the recycling of plastic sachets¹. The process, consists of mechanically reducing the size of WEEE followed by solvent-based process [8] to remove the brominated flame retardant (BFR) from the FR plastic stream. Antimony trioxide could

¹ <https://www.unilever.com/news/press-releases/2017/Unilever-develops-new-technology-to-tackle-the-global-issue-of-plastic-sachet-waste.html>

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potentially be recovered from this process after a regeneration of the used CreaSolv solvents. This can be done in a regeneration unit as depicted in Figure 2. In reference [8], it is reported that pursuing a full recovery of antimony was not the scope of the project, being this the production of secondary pellets from FR plastics originating from WEEE. Nevertheless, antimony industry showed their interest in taking this secondary source of antimony depending on the level of purification of the secondary material.

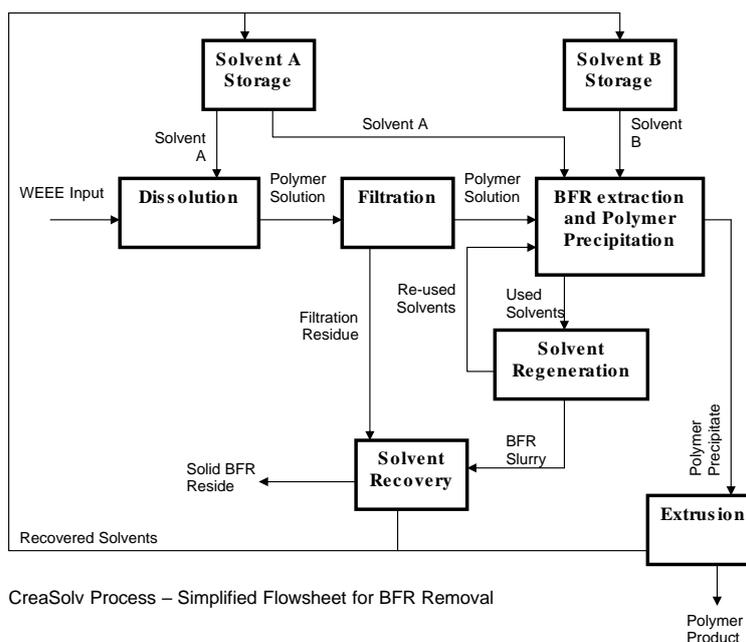


Figure 2 - The CreaSolv simple process flowsheet

With the current push of the EU to increase selective recovery of WEEE, there is an increasing possibility of direct recovery of antimony from FR plastics part of WEEE which are mainly ABS and HIPS. It appears that the high content of toxic brominated compounds may pose a threat to the pyrolysis of the plastic fraction of WEEE thus further research is needed in that sense to improve the toxic profile of the resulting pyrolysis products. Given the increased importance of antimony, recyclers focus on the recovery the metal fraction of WEEE may find it suitable in the future to exploit the non-metal fraction to extract other compounds [3].

In reference [9], the use of super critical fluids (SCF) to degrade BFR plastics was reviewed. The use of isopropanol was pointed to be the most successful organic SCF to remove a high percentage of oil from the BFR sample. After a mixing process in a vessel with the mixture of SC-isopropanol and bromine (Br), KOH was added and it resulted in a solid KBr salt. Such process resulted in the fixation of 94 % of the bromine content of ABS and HIPS FR plastics used in WEEE. The KBr salt that was obtained could be potentially used as a secondary resource, but no mention is made in that study.

4) Halophosphate (HALO) lamp phosphors

The recovery of antimony from these lamps can occur in combination with the traditional recovery of REEs. In France, Solvay operates a recycling facility fully dedicated to the recycling of fluorescent lamps for the recovery of REEs where more than 1 kiloton per year of lamps are processed [3] although it is not clear if due to falling market prices of REEs the activity is still ongoing². Due to the absence of REEs in the HALO, Solvay ignores this stream to focus on other fluorescent lamps containing REEs [10]. Despite the large concentration of material in a single facility, the extraction of antimony has not been yet carried out where around 0.5-1 wt% can be found in such lamps. Reference [10] reports a recent lab-proven process to fully recover antimony from lamp phosphor waste by using HCl followed by a selective extraction using the ionic liquid Aliquat 336 leading to >99.99 % of antimony recovery under the form antimony trioxide. This process leads to full valorisation of all fractions of lamp phosphor waste.

4. LIFE CYCLE ASSESSMENT DATA

A life cycle assessment comparison between the existing and the innovative techniques for the antimony recovery by secondary resources is not feasible as there is a lack of raw available data in second case. Innovative techniques have been tested only in laboratory scale for specific scrap materials. As pointed out in [9], the lack of LCA data creates barriers for future direction in the support of one of the methods to obtain secondary antimony. Scholars have performed an LCA on FR in plastics [11], but no data could be found on the specific recovery process of antimony from FR plastics. In the case of MSW incineration, focus has been put on the pyrolysis-gasification of MSW but antimony and other metals in that study were assumed to be landfilled and not recovered despite the known potential linked to other technologies [12]. In the processes of landfill of MSW residues such as from pyrolysis or incineration, the impact category with the largest impact is aquatic depletion because of the presence of toxic metals for the environment in the residue [12]. Thus, with the recovery of antimony and other metals, such impacts could be prevented.

There is a clear research gap in the provision of concrete LCA data for novel methodologies of antimony recovery from secondary resources as most of the methodologies presented in the previous section are lab-scale. Many studies have been done on the processing of WEEE or MSW but the LCAs never consider the recovery of antimony or other toxic compounds and its resulting impact. Without such data it is hard to reach a conclusion in terms of primary versus secondary antimony. The benefits of secondary plastic from WEEE have been reported [13] but so far research has not been done one step further into obtaining other individual

² <https://www.solvay.com/en/innovation/open-innovation/european-life-projects/loop-life-project>
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components of FR plastics. The production of primary antimony in 2008 accounted for 12.9 kgCO₂/eq per each kg of primary antimony.

In reference [8], an LCA has been conducted on the CreaSolve recovery process with the aim of pointing out to benefits arising from the removal of BFRs from FR plastics found in WEEE. Unfortunately, the scope of the study was the analysis of the substitution of virgin oil to produce FR plastics compared to producing secondary pellets from WEEE dibrominated FR plastics thus leaving out of the system boundary the recovery of antimony.

5. SUMMARY

The recovery of antimony by mining and metallurgical wastes in EU cannot be accurately identified as there is a lack of enough available data, although some activity does take place within the EU in terms of production of primary antimony. There exist several potential sources of secondary antimony whether at the processing phase or from EoL products. Flame retardant plastics take-up a large share of primary antimony and they mostly are used in electronic equipment. Given that electronic equipment has their own collection route, recovery of secondary antimony from WEEE seems to be a viable route for secondary antimony. Moreover, through the exploitation of MSW incineration ashes, antimony can also be recovered, although more research is needed into the necessary leaching processes. In Sweden, a dedicated niche market has been set-up which includes the closed-loop recycling of metal oxide varistors for the recovery of zinc, antimony and other metals such as bismuth. A similar large-scale close-loop recycling already exists in the case of lead-acid battery where secondary antimonial lead is fully recovered. There is lack of LCA data to objectively assess which technology should be pursued in terms of recovery of secondary antimony. Key recovery routes have been identified in this report and should be further investigated.

BARYTE

1. THE SECONDARY RESOURCES

The mineral baryte, barium sulphate, is used as a filler additive in rubber, paint, ceramics, paper, plastics, glass and high-density concrete and plaster weighting agent in oil and gas well drilling fluids.

Baryte is extensively used in the oil and gas drillings industry, about the 69–77% of globally produced baryte is used as a weighting agent for drilling fluids in oil and gas exploration to suppress high formation pressures and prevent blowouts. Baryte is mostly dissipated and cannot be recycled, only recovery at the drill site is possible [14], [15], [16].

The mineral is also used in added-value applications which include filler in paint and plastics, sound reduction in engine compartments, coat of automobile finishes for smoothness and corrosion resistance, friction products for automobiles and trucks, radiation-shielding cement, glass ceramics and medical applications. Furthermore, it is also used for the synthesis of barium carbonate which is a component of LED glass for television and computer screens (in cathode ray tubes). Currently, there is no functional recycling of baryte from most of these applications, however, they have potential to be recycled.

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

2. EXISTING PROCESSING ROUTES – GAPS & BARRIERS

Baryte is barely re-used or recycled [17]. 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 reuse beyond that "cleaned" in a centrifuge or another device at a drill site. 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 [18].

In most other applications, baryte is not recovered (fillers etc.) and cannot be recycled [6].

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3. INNOVATIVE PROCESSING ROUTES – GAPS & BARRIERS

3.1 MINING AND METALLURGICAL WASTES

Bhaskar Raju, G. (2016) reports about the barite deposit at Mangampet, one of the world's largest deposits containing around 61 million tonnes of recoverable barite. Beneficiation of low grade barite dumps interlocked with schist and slate gangue was studied using amine as collector (reverse flotation) to avoid the collector coating on barite. Instead of conventional flotation cells, flotation column was opted due to inherent advantages. Laboratory tests indicated that the barite concentrate assaying 95 % BaSO₄ could be obtained with a recovery of around 70 % in a single stage column flotation. The recovery was improved to 85 % by incorporating scavenging flotation by conventional cells. Based on the laboratory results, commercial flotation column to treat 700 tpd was designed and commissioned. The quartz removal in commercial column was estimated using Dobby and Finch model. Good agreement was observed between predicted and experimental results of quartz elimination [19]

Heinrich, G (1989) reports about the origin and composition of secondary barite raw materials as well as their behaviour during froth flotation studies. Five possible barite sources were investigated: mining wastes, mill tailings, black ash process residues, neutralization slurries from barite bleaches and drilling sludge. With the exception of the neutralization muds, all materials proved to be floatable, partly following preparatory measures such as grinding, intensified dispersion, inactivation of barium sulphide with iron (II) sulphate and inactivation of coal-like substances with lignine sulphonate. The optimal pH value for barite flotation varies between pH 8 and 9.5. In spite of the degree of liberation and the presence of watersoluble substances, the solids surface area and the presence of fine grained calcium minerals and coal like substances govern the efficiency of concentration. The extension of the retention times during cleaning flotation or carrier flotation of the cleaning wastes enable a reduction in the loss of barite in the finest particle size range [20].

3.2 POST-CONSUMER RECYCLING

Barite can be recycled for reuse beyond that “cleaned” in a centrifuge or another device at a drill site. 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. Dual Gradient Systems propose the barite recycling [18], with the following objectives:

- Reduce environmental impact offshore and onshore.
- Reduce mud cost.

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- Keep mud on location / avoid transportation of mud and barite.
- On remote locations around the world no need for an onshore mud plant near by
- Cost of barite is on the rise

Recycling is achieved through two steps [18]:

- 1) Separate the drilling mud into an un-weighted part and a high density part,
- 2) The unit splits the mud into heavy and light mud, the heavy mud or spike mud will be added later to weight up the system as required while drilling ahead or a new well. The light mud will be used to start a new well after riser and BOPs (blowout preventers) are run. Or store in a hull tank.

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

4. LIFE CYCLE ASSESSMENT DATA

A number of researches are focused on the environmental impact of baryte mud in marine environment [16]. The results show that baryte cannot be considered as a totally chemical inert material as, in several cases, it contains traces of several heavy metals (such as mercury and lead) that can be released in the marine environment at the drilling process. The disposing practice of baryte wastes is not well defined. The most common practice is the burial in pits covered with a synthetic landfill liner. The method presents effectiveness and low operating cost, however, on the other hand harmful components can migrate from the pit and contaminate usable water resources. Therefore, further attention should be given to the barite disposing focusing on novel practices and valorization processes [21].

Burial is the most common practice that used for the disposing of baryte-bases drilling mud wastes. Commonly, the solids are buried in a pit used for collection and temporary storage of waste mud and cuttings after the liquid is allowed to evaporate. Pit burial is a low-tech method that does not require wastes to be transported away from the well site, and, therefore, is widely used by many operators. On the other hand, burial doesn't consist an appropriate method in case mud wastes that contain high concentrations of oil, salt, biologically available metals, industrial chemicals, and other materials with harmful components that could migrate from the pit and contaminate usable water resources. Secure landfills are specially designed land structures which employ protective measures against off-site migration of contained chemical waste via leaching or vaporization using a synthetic landfill liner [22].

Incineration is an alternative waste management choice in case of barite mud which is frequently contaminated with oil amounts. Incineration is one of the best thermal treatment disposal options because thermally treated wastes are decomposed to less hazardous by-products. Controlled incinerators operate at sufficient temperatures for complete thermal decomposition of hazardous wastes [22].

In this context, 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. Recovered muds and residues contain oil, metals, and other materials introduced during well preparation and drilling. “Used” mud, or mud no longer required or satisfactory for drilling, and residues recovered from drilling muds and cuttings, are commonly disposed of in lined pits, landfills, and placed underground by injection wells [23].

Barite recycling at the drilling site through centrifugation reduces the environmental impact both onshore and offshore and avoids mud transportation.

5. SUMMARY

Baryte is extensively used in the oil and gas drillings industry, about the 69–77% of globally produced baryte is used as a weighting agent for drilling fluids in oil and gas exploration to suppress high formation pressures and prevent blowouts. Baryte is mostly dissipated, only recovery at the drill site is possible.

A number of researches are focused on the environmental impact of baryte mud in marine environment. Barite recycling at the drilling site through centrifugation reduces the environmental impact both onshore and offshore and avoids mud transportation.

In most other applications, baryte is not recovered (fillers etc.) and cannot be recycled [24]. Alternative flotation processes for the recovery of barite from mining wastes, mill tailings, black ash process residues, neutralization slurries from barite bleaches and drilling sludge have been researched by different authors.

Further attention should be given to the barite disposing, focusing on novel practices and valorization processes.

BERYLLIUM

1. THE SECONDARY RESOURCES

Based on CRM Factsheets published by the EC DG Growth in June 2017 and D3.2, significant recycling rates have been identified for beryllium among other CRMs [6].

During the production of beryllium, so-called “new” scrap is generated, which usually is returned to the production line and recovered.

“Old” scrap, or end-of-life products containing beryllium are also recycled and beryllium recovered, however only high amounts of materials are reprocessed, such are military aircraft parts or products used in aerospace industry.

There are significant losses due to this fact, and the beryllium contained in smaller components usually disappears or is diluted in other waste streams.

Beryllium is mainly used for alloys and in ceramics, but is also utilised in its pure form, as beryllium metal for specialised high-tech applications. While products can be expected to have a long life, some of them, including those employed for military technology, are not returned to the industry. On the other hand, the aerospace industry can be a major source for recycling. The secondary resources of beryllium in EU member states are presented in Table 6.

Table 6. Be applications and related products with potential for recycling.

Compound	Applications	Potential secondary resources
Be metal	Steel alloys Aircrafts Shipbuilding & trains Mechanical equipment & industrial motors	Old scrap New scrap
Be ceramics	Moulds for rubber, plastics and glass	
CuBe alloys	Automotive electronics Audio systems Electric and electronic connectors Battery Undersea fiber optic cables Others	ELV WEEE

2. EXISTING PROCESSING ROUTES – GAPS & BARRIERS

This chapter describes the generation and recovery of beryllium scrap is generated at various stages of production based on findings of SCRREEN deliverables D4.2 Production technologies

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of CRM from secondary resources and D4.3 Circular Economy and zero waste aspects and business models of production.

a) 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

b) Post-consumer recycling (old scrap)

Beryllium is not recycled from end finished products (BeST [25]), 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).

2.1 MINING AND METALLURGICAL WASTES

Metallurgical processing of mining and metallurgical wastes aiming to the recovery of beryllium have not been identified within the EU so there is an absence of available data concerning such processes.

2.2 NEW SCRAP

The “new” Beryllium scrap is generated and recovered at various stages of production. Scrap generated during the manufacture of beryllium metals and alloys, and during the fabrication of beryllium products. The European industry generates a lot of “new scrap” (around the half of the beryllium input), during this manufacture step, which is totally sent back to producers outside Europe for reprocessing (European Commission 2017 [6]).

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 [26]).

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.

NGK Berylco France is the only Be recycler in the EU, other world leader recycling plants, Monico Alloys and Materion, are located in the USA.

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. [27]

2.3 POST-CONSUMER RECYCLING (OLD SCRAP)

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 [28]). The stock accumulated in landfill in the EU over the last 20 years is estimated around 610 t of beryllium content.

a) Pure beryllium components

Disassembling and processing old scrap are economically viable processes only for large volumes of materials with high beryllium content, such as military aircraft parts and products used in the aerospace industry.

However, pure beryllium metal components used in technological applications have extremely long lifetimes, and therefore return to the recycle stream very slowly. Some, because of applications in space, or because of their sensitive military nature, do not return at all. When pure beryllium components do finally return, they can be easily recycled.

Much of the beryllium metal is contained in nuclear reactors and nuclear weapons, which are difficult to recycle and may have been contaminated. These applications are rarely dismantled, and the beryllium may have been lost during testing (Cunningham 2004 [29]).

c) Beryllium alloy 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).

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The alloy makes up approximately 0.15% of the copper used in electrical equipment which, during preprocessing 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).

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

- REACH. The threat of being included in the Candidate List of substances of very high concern for Authorisation could be a gap. In 2014, was included in the PACT (Public Activities Coordination Tool)

Beryllium has already been subjected to an RMO-Analysis and the outcome of the assessment has been that it is “Appropriate to initiate regulatory risk management action”.

- Occupational Exposure Limit (OEL). During the Risk Management Option analysis (RMOA) one of the actions defined was the “Setting of an OEL” The Setting of an OEL by the Scientific Committee on Occupational Exposure Limits (SCOEL) has set as a necessary step forwards for the regulation of beryllium. Such an OEL may serve as a basis for further regulatory measures. This regulatory option indicates the high potential for risk reduction capacity and equivalent high health benefits for the workers. On the other hand, additional costs for the measures for exposure reduction may incur e.g. plants with encapsulated equipment. However, considering the investment for the continuous improvement, the additional costs would be proportional to the benefits arising from exposure reduction. (Source: RMOA CONCLUSION DOCUMENT)

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

3. INNOVATIVE PROCESSING ROUTES – GAPS & BARRIERS

3.1 MINING AND METALLURGICAL WASTES

Not identified

3.2 NEW SCRAP

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

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scrap, to the technological industry to be used again in the building process of technical equipment.

Copper-beryllium alloy scrap can be recycled by re-melting in conventional melting equipment to segregate the metals and make them usable to different purchasers again. If it is not possible to recycle the alloys, the copper-beryllium containing components or solid copper beryllium are landfilled, shredded or incinerated. The copper-beryllium scrap that does not contain other metals like for instance, iron, aluminium, cadmium, lead and similar, has fairly good recycling potential. Copper-beryllium is harmless to handle and use in service, although before it can be recycled at end of life it has to be separated from other potential alloys (European Copper Institute 2016).

NGK BerylCo (2015) even states that copper-beryllium can be 100% recycled “without altering its unique characteristics”. At Monico Alloys (n.d.) beryllium is mostly recycled from beryllium scrap and beryllium alloy scarp, mostly from automotive electronics, computers, optical-media products applications and other consumer driven products....

3.2 POST-CONSUMER RECYCLING (OLD SCRAP)

Copper-beryllium alloys are often used in connectors, springs, switchers and other small components, recovery of beryllium metal from such 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) (BeST) [25].

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. 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.

Despite this low EOL RR, the market for Beryllium is expected to grow over the coming decades. In the STOA Report (2017) [30] “Towards a circular economy waste management in the EU” examines the role of the waste management in the context of a circular economy transition. A preliminary analysis on the assessment of the opportunities for material recirculation is reported in the study and beryllium appears as a high potential material. The report estimates that all beryllium inputs to the EU are imported (175.3 tonnes) and it is

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estimated that 45 tonnes are present in landfill and tailing within the EU; no data about functional recycling are available.

The potential innovative routes for the recycling of electronic equipment is disassembly of old products, also called de-manufacturing. Demanufacturing can be profitable, but barriers, such as the lack of an adequate collection infrastructure, limited and cyclical markets for recovered materials, and products that are not designed to be disassembled and recycled, exist. A major source of material for demanufacturing is institutions that frequently update equipment owing to software updates and technology requirements. Shredding is another option that can be used to recycle computer equipment. Components, which range from laptops to mainframes, can be shredded, and the materials separated. This is an efficient way to recycle large volumes of computers, such as units formerly leased to businesses (Cunningham L.D 2004c) [29].

4. LIFE CYCLE ASSESSMENT DATA

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.

According to (BeST) [25], Beryllium-copper is a sustainable material that can be 100% recycled without altering its unique characteristics. Recycling beryllium-copper involves savings of 75% of the energy required to produce the primary metal, reduced emissions and reduced waste storage and disposal costs.

5. SUMMARY

The recovery of Be by mining and metallurgical wastes has not been identified in the EU.

Recycling of new scrap (beryllium copper) is taking place with high recovery rates, NGK BerylCo is the main EU plant recycling beryllium, the process involves savings of 75% of the energy required to produce the primary metal, reduced emissions and reduced waste storage and disposal costs.

Recycling of old scrap (post-consumer) is reported to be negligible, main barriers are 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).

BISMUTH

1. THE SECONDARY RESOURCES

Mining and metallurgical wastes

Like many other minor metals that are co-produced from the purification/refining of major metals, secondary bismuth availability from mining and metallurgical wastes depends heavily on the availability of residues. Bismuth is mostly dependant on lead, copper or tungsten refining routes [31]. According to reference [32], bismuth can be found in several places in Europe associated with waste rock and mill tailings from the production of tungsten. The known sources are listed in Table 1:

Table 7 - Availability of bismuth from tungsten rich secondary deposits

Material type	Ore type	Location
Milling tailings	Hubnerite and Scheelite	Bom-Gorhon, Russia
Flotation tailings	Bismuthinite	Sasa, North Macedonia
Mine products and unprocessed waste	Bismuthinite	Borralha, Portugal
Mine products and unprocessed waste	Bismuthinite	Vale das Gatas, Portugal

In the case of copper mining and metallurgical waste, Poland possesses one of the largest sources of disposed wastes [33]. In what is called the Polish Copper Basin, an estimated 705 million m³ of mining waste have been landfilled over the past 60 years. The primary copper ores used are known to contain bismuth at an unknown concentration. It was not possible to verify whether the company in charge of the Polish Copper Basin extracts or not bismuth from the primary copper ores. But assuming that is not the case, bismuth must still be present at tailing dumpsites.

A recent project carried out by the French Geological Survey (BRGM) aimed at characterizing the contents of several tailings dumps across France [34]. The rationale behind mapping old tailings dump sites is that by knowing which metals were being extracted in the past and what were used processes, it is possible to estimate the presence of certain valuable elements in the tailings dump sites. It was found for example, that in a 19th century lead-silver mine, the

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old methods of concentration of ores were very poor and this led to massive discards. The size of the dumpsite is 87,000 m³ in which bismuth concentrations are unknown. But given the nature of the primary ores exploited at the time like bismuth-bearing galena, spharelite, pyrite and others, the researchers believe that valuable elements must be inside these old tailings' dumpsites.

Scraps

In Europe, the main end-uses of bismuth are bismuth related chemicals (62 %), fusible alloys (28 %) and metallurgical and other additives (10 %). Bismuth used in the chemical industry is mostly present in pigments and pharmaceuticals which make the bismuth in these end-uses to be dissipative [6]. The dissipative fate of bismuth in the chemical end-use incentivizes manufacturers to develop solutions for wastewater treatment plants (WWTP) to remove bismuth and other problematic elements [35].

Research has been conducted to analyse the bismuth concentration in sewage sludge in Stockholm by means of a substance flow analysis (SFA). The scope of the SFA study was to analyse the sewage sludge composition of the Hendriksdal WWTP discharging 750,000 people that took as scope the Hendriksdal WWTP that discharges 750,000 people [36]. The main sources of end-products that have been identified as carriers of bismuth are plastics, paints, electronics, chemicals and other minor applications. These sources of bismuth led to an inflow into Stockholm of 55 tonnes in 2012. Although most of these products containing bismuth ended up in the waste collection system, some of it, like cosmetics and other dissipative products, ended up in the WWTP. The most significant source of bismuth in the analysed WWTP was cosmetics which represented 28 kg out of a total of 116 kg. Households contributed with 48 kg while businesses and other facilities with the remaining. The authors underline the fact that due to lack of legislation in terms of safe disposal of bismuth in the manufacturing environment, the amount of bismuth that has been found in the study might not depict reality when it comes to bismuth release to the environment.

Bismuth is widely used in fusible alloys like solders and other applications due to its low melting point and as a replacement for lead. Other uses of fusible alloys are safety devices that are heat dependent like boilers, sprinkler systems, etc. Given the dispersity of the end-use, some promising new routes to recover secondary bismuth include PCBs and other electronic equipment where solder has been deposited. The latter points to the fact that in the process of recovering WEEE, bismuth could also be recovered. Umicore in Belgium recovers bismuth in the recycling process of smartphones and other WEEE [37], while in Sweden Boliden also processes WEEE and is able to recover bismuth from the copper refining operation [38]. In metal oxide varistors (MOV), mass fraction of bismuth trioxide is 5.1 wt%. The exact content of bismuth or other minor composing elements of EEE could not be found.

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This is mainly because bismuth is not part of the list of important elements in EEE. Nevertheless, in reference [39], a bismuth mass fraction of some EEE has been examined based on the Boliden operation in Sweden. The reported bismuth concentrations in the treated e-scrap are: 0.17 wt% in PCBs, 0.01 wt% in car electronics and <0.004 wt% in PCs. This highlights the very low concentration of bismuth in WEEE which makes it hard to recover. According to reference [40], 900 tonnes/year globally of bismuth are used in the manufacturing of EEE. In another recent study, the concentration of bismuth in WEEE is reported to be 0.01 wt% in internet routers, 0.004 wt% in mobile phones and 0.006 wt% in smartphones [41]

The use of bismuth as an alloying element for its properties mostly occurs in steel or aluminium [31]. These additions can be around 0.1 – 0.5 wt% in steel and 0.2-0.7 wt% in aluminium. Adding bismuth improves machinability and reduces the need of lead. Given the size of the steel market in Europe, knowing the share of steel alloy containing bismuth would be a good indication of the recovery potential of bismuth from this resource and of the needed strategies to address future recovery of bismuth from EoL steel alloys. Currently the fate of bismuth in the recycling route of alloys is dispersion into ferrous or non-ferrous scrap.

2. EXISTING PROCESSING ROUTES – GAPS & BARRIERS

2.1 MINING AND METALLURGICAL WASTES

According to what has been defined above as mining and metallurgical wastes containing bismuth, no information could be found on existing processing routes for secondary bismuth.

2.2 SCRAPS

Existing processing routes for secondary bismuth from scraps include WEEE operations where bismuth and many other elements are recovered. Such examples have been mentioned above as for example Umicore or Boliden. These traditional copper smelters incorporate WEEE with the traditional copper smelting route and are able to extract many of the elements inside WEEE. In the case of bismuth, this is mainly in solder material used while manufacturing PCBs. Privately held companies do not report recovered/processed amounts, and thus it is hard to estimate the amount of secondary bismuth recovered from these sources. A source indicates that Umicore's facility in Hoboken may process around 350,000 tonnes of precious metal-bearing scrap, while Bolinden's Rönnskär plant has the capacity to process 100,000 tonnes [38]. In Umicore [37], the recovery of elements such as bismuth occurs in the base metals operation (BMO). Here, the BMO processes by-products from the precious metals operation (PMO) and aims at extracting a certain number of base and special metals (bismuth included). The BMO

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uses as input the lead slag coming from the PMO and other raw materials are reduced into lead bullion. The lead bullion is then further refined in the lead refinery using a Harris process. The flowsheet can be found online in the Umicore's website³ or in reference [37].

The processing route to recover bismuth in Boliden is somewhat similar to Umicore. In Umicore, recent efforts have been made towards focusing more on the recycling of e-scrap while in Boliden's Rönnskär plant, the complex process flow installed today is the result of the need to process very complex concentrates from the region [37]. In both cases, bismuth is reported to be recovered.

In terms of the other applications mentioned in the previous section, most of them are dissipative and thus lost to the environment. The lack of environmental regulation to impede releases of bismuth to wastewater or to air could in the future open up new ways of recovering secondary bismuth from dissipative uses like chemicals, pigments, alloys, etc [36].

3. INNOVATIVE PROCESSING ROUTES – GAPS & BARRIERS

3.1 MINING AND METALLURGICAL WASTES

No information was found regarding innovative processing routes for mining and metallurgical waste such as the ones reported in section 1. Nevertheless, increased attention has been given to improving the recovery efficiency of bismuth from refining residues or novel techniques to reduce the use of reagents in hydrometallurgical processes. Below a summarized view of the novel lab-scale processes is shown.

Copper smelter residues

Dusts from the refining process of copper smelters may contain up to 5-10 % of all the mass of primary material entering the refinery [42]. This phenomena lures researchers into developing research aimed at recovery materials that may be lost and end-up polluting the surrounding environment [43].

Copper smelter flue dust leaching

Research has been conducted on the efficient recovery of bismuth together with arsenic from copper smelter flue dusts [44]. The studied residue may contain up to 3.0 wt% of bismuth. In the past these residues were leached to recover copper and zinc, but little effort was done to recover other elements in these dusts. The main focus of the research underpins the need for efficient recovery of all residues from smelting operations. Although the research may be

³ www.umicore.com

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innovative in China where environmental regulations lag behind tighter ones in Europe, Umicore as an example processes dusts and other by-products from the PMO in the BMO to particularly recover these otherwise “lost” elements from the copper smelter flue dust. The applied principle in reference [44] consist in leaching the copper smelter flue dusts using H_2SO_4 – $NaCl$ following precipitation at pH 0.8-3.0 where a recovery of 95 % was obtained for bismuth at the final process. The process is depicted in Figure 3.

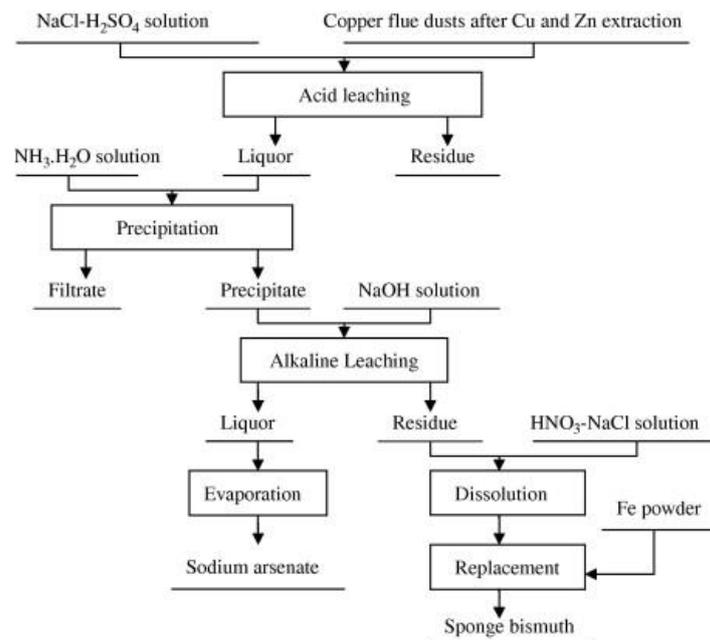


Figure 3 - Separation and recovery of materials from scrap printed circuit boards [44].

Copper smelter converter dust

Similar to what has been performed with copper smelter flue dust, in reference [42] researchers have used H_2SO_4 – $NaCl$ to leach Bi followed by SO_2 reduction to remove impurities (see Figure 2). The purified solution was then precipitated by hydrolysis where a final product Bi_2O_3 was synthesized from the $BiOCl$ combined with $NaOH$ solution at high temperature. This led to an overall process recover efficiency of around 90 %.

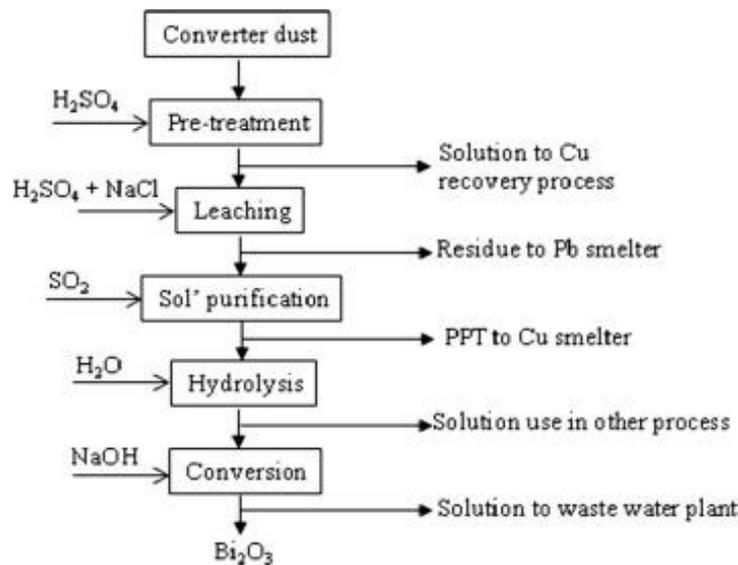


Figure 4 - Process flow diagram for Bi recovery from copper converter dust [42].

Supported liquid membrane (SLM)

As an alternative to the recovery of bismuth from the leaching with H_2SO_4 – $NaCl$, research has been conducted in the direction of providing more environmentally friendly ways of obtaining bismuth. The reduced use of organic phase allows for the use of highly selective extractants thus reducing the risk of environmental damage. The main principle behind this process is the facilitated transport mechanism which operates as a “closed-loop” recycling system where the solute $Bi(III)$ ($BiONO_3$ dissolved in HCl and/or H_2SO_4) is mixed with the extractant (Cyanex 921) and following process where $Bi(III)$ moves through the SLM to the stripping solution following a difference in the concentration gradient inside the SLM. The working principle is show in Figure 5.

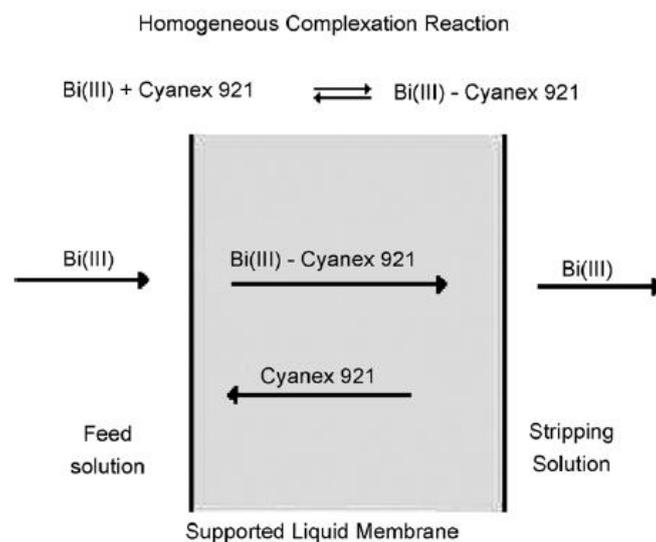


Figure 5 - Schematic diagram of the $Bi(III)$ transfer process through SLM using Cyanex 921 as extractant. From [45].

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Following a transfer time of 160 minutes, a Bi(III) transfer of around 80 % could be obtained in the stripping solution when 17.92 mg/L of Bi(III) in 2 M H₂SO₄/0.5 M HCl where used as feed solution and the membrane made of polyvinylidene difluoride (PVDF) impregnated with 0.3 M Cyanex 921.

Emulsion liquid membrane (ELM)

Another technique to extract bismuth ions from a solution is the ELM [16]. This method has several advantages such as high mass transfer ratios due to the large surface area, and lower operational costs. The working principle described in this method involves the use of an extractant (D2EHPA) and a non-ionic surfactant (TritonX-100) for the recovery of Bi(III) from a nitrate medium. In the beginning, an emulsion is prepared by mixing TritonX-100 with D2EHPA with 0.5 M of sulfuric acid. This emulsion was added to the feed solution containing 500 ppm of Bi(III) nitrate. Bi(III) ions and D2EHPA form a complex that diffuses through the liquid membrane and interface with the inner droplets. Representations of the process are depicted in Figure 6 and Figure 7.

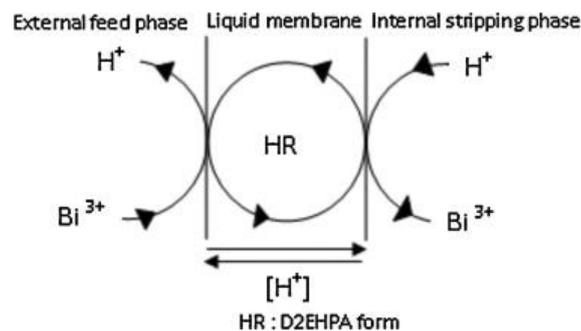


Figure 6 - Schematic mechanism of Bi(III) ions transport by the D2EHPA extractant by EoGLM technique.

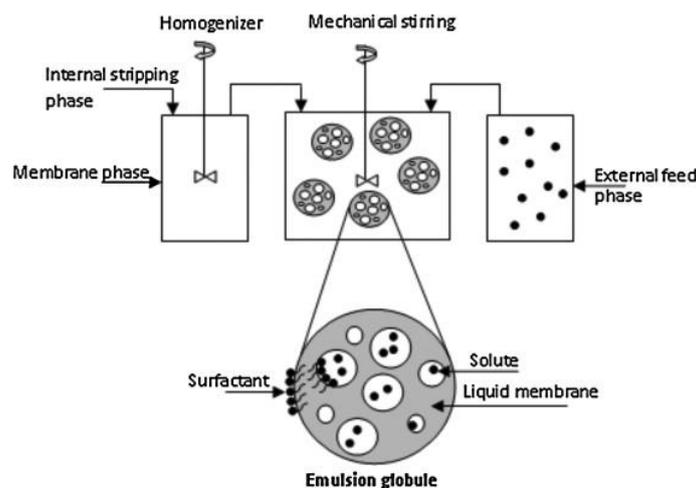


Figure 7 - Graphical implementation of the EoGLM technique [46].

3.2 SCRAPS

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Novel routes for the recovery of bismuth from scraps pertain mostly to the processing of WEEE either by pyrometallurgy or hydrometallurgy. PCBs are the main focus of the current research aimed at extracting bismuth from these sources of WEEE given the replacement of lead by bismuth in PCB solder. Flame retardant (FR) plastics used in WEEE are a source of toxic emissions. If burned, these FR plastics convert into dioxins, furanes and other harmful substances [37]. Dedicated specialized installations are required to cope with these harmful emissions. While in Umicore such installations exist, and FR plastics can be safely subject to high temperatures inside a smelter without harmful emissions to the environment, the same does not occur in other parts of the world. Hence, novel methods to treat WEEE are currently being researched where vacuum metallurgy separation (VMS) appears to be the most promising route to recover bismuth and other elements with high vapor pressure [47] [48]. VMS has the additional advantage of requiring less energy (low temperature) and operates at low pressure. Furthermore, volatile organic fractions can be recovered in the oil or gas.

Pyrolysis under nitrogen atmosphere

Pyrolysis of PCBs allows for both recovery of organic and non-organic fractions of PCBs [49]. The high-temperature in a pyrolysis process will melt the solder material and can be recovered in the pyrolysis residue char. The experiment carried out in reference [49] consists of a small reactor where 20 mg of PCB from 3 different sources (PCs, TVs and mobile phones) are placed and heated up to 800 °C for 135 minutes. Oils and off-gases are analyzed to check for their composition but the most important part for bismuth recovery is the analysis of the residue char. The pyrolysis chars were ashed at 600 °C according to EN ISO 3451-1:1997 in order to determine the metal and organic content of the chars. Bismuth was found in concentrations ranging from 301 mg/kg in PCs, 75 mg/kg in TVs to <5.6 mg/kg in mobile phones. The study did not investigate means to extract bismuth or other element from the pyrolysis chars.

Vacuum metallurgy separation (VMS)

Vacuum centrifugal separation and vacuum pyrolysis

In a two-step process, researchers have separated from the pyrolysis residue the solder material using a vacuum centrifugal process [50]. A reactor was kept at 600 °C at 0.4 KPa for 30 minutes. The residue from the first pyrolysis was sent to a vacuum centrifugal machine kept at 20 Pa where the reactor first heats the residue up to 400 °C to melt the solder. Afterwards the centrifugal machine starts to operate for 10 minutes under 1200 rpm to remove the solder from the sample (c.f. Figure 8).

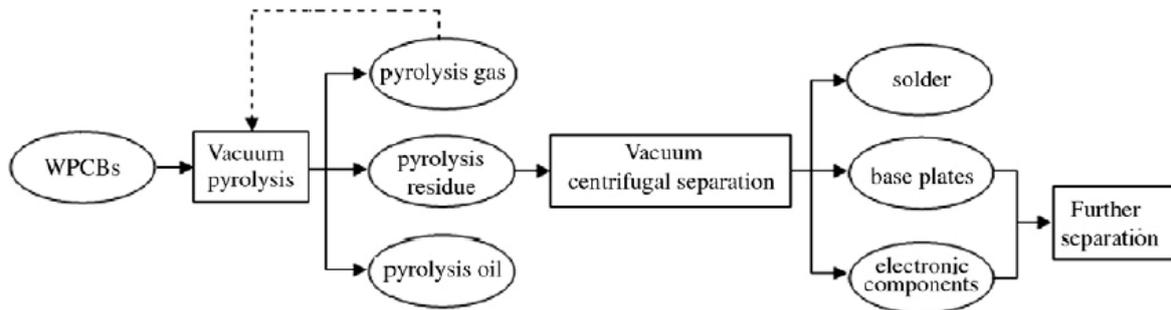


Figure 8 - Process flowchart of the recovery process using EoL PCBs. From [50].

The aim of the study was not to recover the solder material but to use this two-step method to liberate electronic components which are put together by using solder for further recovery. In the study, it is mentioned that solder can be directly re-used but no attempt has been done to prove the claim.

Separation through evaporation

In [51] [52] the focus has been put on the evaporation under vacuum of elements with high vapor pressure such as cadmium, lead, zinc and bismuth. This route has been researched because of the very different vapor pressures between copper (2.54×10^{-6} Pa) and bismuth (8.76 Pa) at near vacuum conditions and 730-754 °C. The experiment consisted in using two types of metal mixtures such as a binary and a multi-metal mixture. In the binary mixture, 95 wt% of copper is used with any of the other elements.

In the first experiment, the different binary mixture was put into a reactor at vacuum levels between 1 and 10 Pa for 30-150 minutes at temperatures between 69-754 °C. Bismuth was successfully separated by over 95 % at 730 °C for a sample mass of 8 g and height of 11 mm and particle sizes of 0.08-1.2 mm.

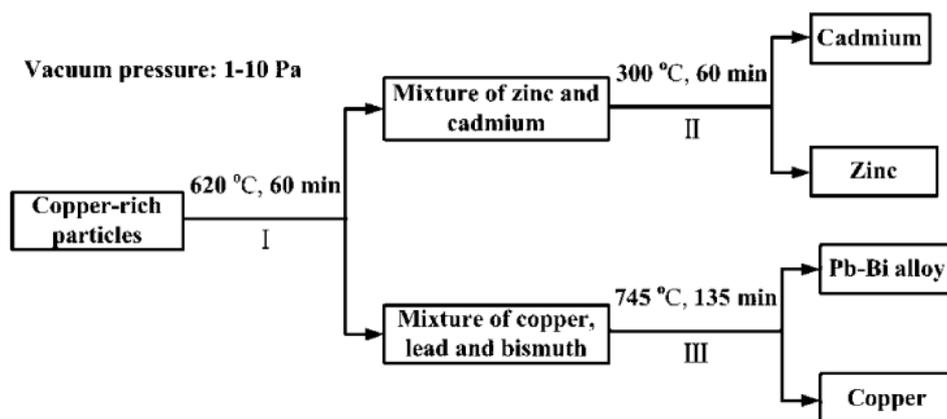


Figure 9 - Flowchart of the VMS system [50].

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In the case of the second mixture, the multi-metal mixture, firstly as shown in Figure 9, cadmium and zinc are separated from the sample in the vacuum reactor at 620 °C for 60 minutes. The mixture of copper, lead and bismuth are then further heated up at 745 °C for 135 minutes. This yields a pure lead-bismuth alloy and residual copper.

The electrical power consumption of the furnace was 700 kWh/tonne and with a processing capacity of 0.4 tonne/h. The authors carried out an economic analysis of the process whereby only looking at the processing costs and material yields, the process would be feasible.

4. LIFE CYCLE ASSESSMENT DATA

There seems to be a lack of LCA data regarding the above described processes of recovering secondary bismuth. The primary production route has been described in [53] where the combined GHG emissions are 51 kgCO₂eq/kg_{Bi}.

In [54] [55] the problematic of allocation of impacts according to the LCA standard ISO 14041 is dissected whereby the implications of co-production of metals are linked with the allocation methods required to perform an LCA. This challenge in the allocation of impacts along the process chains arises from the fact that like bismuth and other elements, they are co-produced partially from ores and partially from residues of carrier metal refining. This complex process chain adds a layer of complexity in the LCA study [55].

With the advancement of European legislation in the sense of preventing heavy metals ending-up in waste, the substitution of lead in solder for EEE has been the subject of an LCA to assess the different impacts between lead alloys and other non-lead alloys to be used in solder [54]. It appears that replacing lead by tin and other elements like bismuth will lead to greater negative environmental impact especially in human toxicity related to landfill of lead material as can be seen in Figure 10.

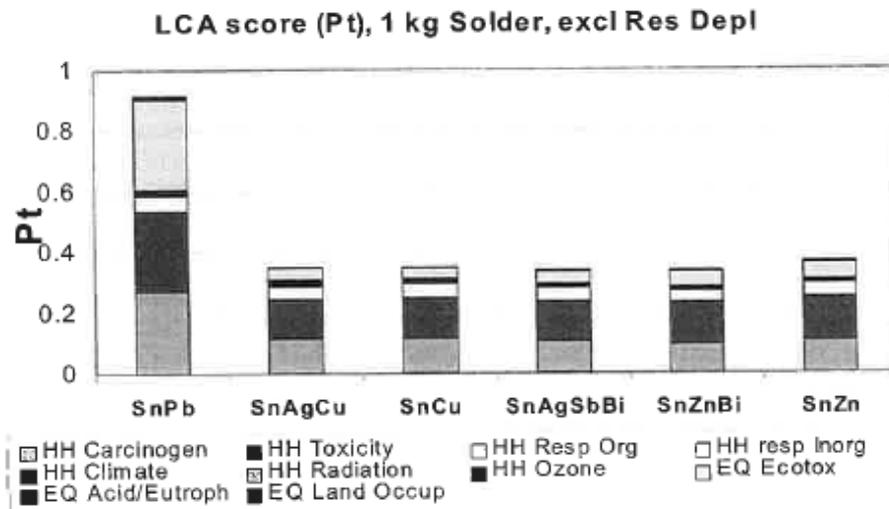


Figure 10 - LCIA scores (Eco-indicator 99) for 3 types of soldering without resource depletion.

Nevertheless, and as discussed in reference [54], making targeted policies to combat the EoL, i.e., waste generation unveils another reality when the resource depletion is considered. Resource depletion deals with the complexity of the supply chain of the downstream metals that are obtained from the carrier metal. This nuance can be seen in Figure 11 where SnPb alloy solder has the overall smaller score because of the inclusion of resource depletion in the picture.

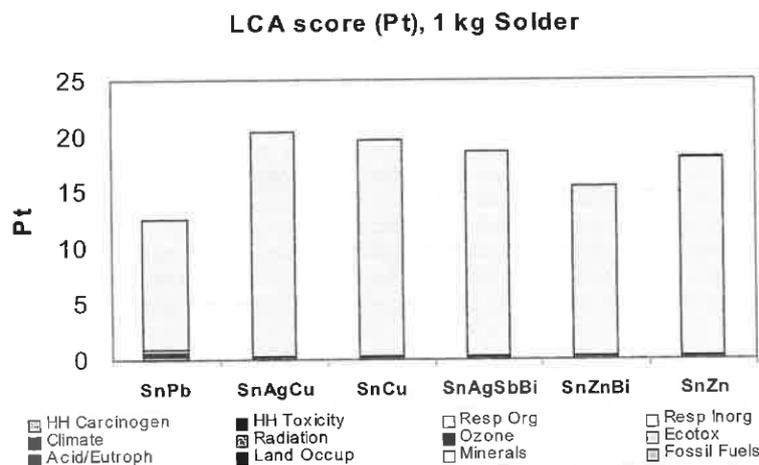


Figure 11 - LCA impact from different alloys used in solder. From [54].

This pinpoints the need to have clear waste management policies and that the whole supply chain of metals has to be considered when changing elements. If lead alloy solder would be properly recycled, then keeping lead alloys would be preferable in what regards substitution with bismuth-tin alloys according to the study.

5. SUMMARY

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Abandoned mine tailings across Europe may contain large amounts of bismuth but it is hard to estimate the concentration. Whether or not bismuth is economically feasible to extract from these deposits in combination with other main elements will dictate the fate of these hibernating stocks. Scrap sources in Europe are related to WEEE since the quantification of bismuth in steel alloy accumulated as stock in Europe needs further research and the chemical applications are mostly dissipative. An European-wide detailed substance flow analysis study on the flows of EEE would be able to predict how much bismuth Europe imports in the form of EEE given that such knowledge does not exist to date. Secondary bismuth is currently produced from WEEE by European large copper smelters through dedicated centralized routes. Few data exist on this process thereby leaving quantification to pure assumptions. There are new promising routes to recover secondary bismuth from WEEE but at a very small scale and mostly in China where environmental regulations are more lenient therefore attracting more attention by research. This research is still quite new and has not been echoed in Europe since bismuth attracts less attention than other more pervasive elements like indium. LCA data on secondary processing of bismuth is incomplete and it might be associated with the complexity of the supply chain of downstream metals. Studies have shown that substituting lead by bismuth-tin alloys is not the best solution to deal with this toxic element. Increased resource depletion arises from using other elements for the same function.

BORATES

1. THE SECONDARY RESOURCES

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

Borates, boron-oxygen compounds, comprise a broad suite of minerals which may also include borosilicates (despite being included in the grouping “borates”), that are used for the production of different boron compounds, chiefly boric acid. The boron compounds are used in a great number of applications including glass and fibre glass, household products, ceramics, and nutrients for agriculture. Because of the nature of these applications, boron/borate recycling is mainly prevented.

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.

The secondary resources of borates in EU member states are presented in Table 8.

Table 8. Borate applications and related products with potential for recycling.

Applications	Potential secondary resources
metals	old scrap new scrap
animal feed&fertilizer, feed and food additives chemical products industrial fluids detergents	(dissipative applications)
ceramics borosilicate glass textiles	secondary material (not functional recycling)
electrical equipment	WEEE

2. EXISTING PROCESSING ROUTES – GAPS & BARRIERS

This chapter is based on findings of SCRREEN deliverables D4.2 Production technologies of CRM from secondary resources and D4.3 Circular Economy and zero waste aspects and business models of production.

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 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.

There are two types of recycling:

- 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. 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 [56].

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.

2.1 MINING AND METALLURGICAL WASTES

Metallurgical processing of mining and metallurgical wastes aiming to the recovery of borates have not been identified within the EU so there is an absence of available data concerning such processes.

2.2 POST-CONSUMER RECYCLING

The functional recycling of boron is null [57]. The principal gap is that the products containing the borates are not likely to be recycled considering these products are consumed with use:

- Fertilisers: an essential micronutrient for plant growth, crop yield and seed development.
- Wood preservatives: Borates are used to treat wood to ward off insects and other pests.
- Detergents: Used in laundry detergents, household and industrial cleaning products. Borates enhance stain removal and bleaching, provide alkaline buffering, soften water and improve surfactant performance.
- Chemicals (excl. Fertilisers, wood preservatives and detergents): Used for chemicals such as fire retardants.
- Industrial Fluids: Used for metalworking fluids, and other fluids used in cars, antifreeze, braking fluid etc.
- Metals: Used as an additive for steel and other ferrous metals as its presence ensures higher strength at a lower weight

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

Secondary materials result mostly from non-functional recycling. Borosilicate glass is currently not separated from boron-free container and flat glass. It means that boron in waste borosilicate glass is likely to end up in the manufacture of new glass containers or glass wool and it does not replace primary boron in the new production of borosilicate glass. Moreover, waste from ceramics is mostly used as a construction material. [56]

3. INNOVATIVE PROCESSING ROUTES – GAPS & BARRIERS

3.1 MINING AND METALLURGICAL WASTES

N.a.

3.2 POST-CONSUMER RECYCLING (OLD SCRAP)

Although nowadays the borates are not recycled from end finished products, (the end of life functional recycling input rate is almost 0%), the STOA Report (2017) “Towards a circular economy waste management in the EU” [58] identifies as a high potential material. This report

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assesses the role of the waste management in the context of a circular economy transition. A preliminary analysis on the assessment of the opportunities for material recirculation is reported in the study. The materials studied are grouped into four categories, Batteries (1), electronic and electrical products (2), other manufactured products including alloys, catalytic convertors and glass, (3) and industrial processes and construction (4). Borates are identified in this third group as high potential.

Several commercial forms of borates as sodium perborate, Perboric acid, Sodium peroxometaborate, Lead bis(tetrafluoroborate), Diboron trioxide, Boric acid, Disodium tetraborate, Tetraboron disodium heptaoxide (hydrate) have been identified as Substances of Very High Concern (SVHC) under REACH legislation and were added to the candidate list [59] These compounds have also been classified as toxic for reproduction.

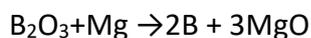
The non-functional recycling is quite high in some of the end of life products. The “mixtures of concrete, bricks, tiles and ceramics» are identified in the list of C&D Waste classification (code 17 01 07) in the EU Construction & Demolition Waste Management Protocol [60].

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

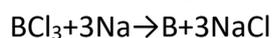
The study [61] tests the suitability of glass residues for geotechnical engineering applications, depending on the size of the recycled glass sources. As results, only fine and medium sized glasses show a behaviour similar to natural aggregates, while coarse recycled glass has been found to be unsuitable for such application. From an environmental perspective, using the recycled glass as filling material, meets the requirements of environmental protection authorities in the country where the study was conducted, Victoria (Australia).

Paper [62] reports a patented recovery process of boron from scrap materials that can be used on several recycled scrap sources. The boron contained scrap found usable is elemental boron, boron carbide, any boron compound or a mixture of compounds. If the boron is associated with combustible organic material, for example polyethylene tape, it is preferably burned to get rid of the combustible material. It is preferable to crush the scrap material to form fine powder to facilitate the process. The process begins by heating the scrap material to temperatures ranging between 750 °C and 1100 °C. The heated material is contacted with steam to hydrolyse the contained boron to boric acid. Adding steam allows obtaining an aqueous solution of such acid which is recovered. Potassium hydroxide is added to convert boric acid to potassium borate. Adding hydrofluoric acid converts the potassium borate to KBF₄. The final step consists in adding 80% to 120% by volume of ethyl alcohol to precipitate KBF₄. The precipitated crystals can be removed by any conventional means such as filtration,

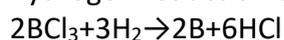
centrifugation and decantation etc. Beside the described technic, a variety of well-known process allows the conversion of several boron-based compounds to elemental boron by electrothermic, electrochemical and direct pyrolysis procedures:



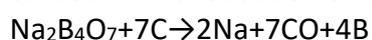
alkali metal reduction of boron halides



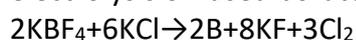
hydrogen reduction of the halides



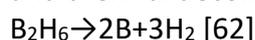
carbothermic reduction of borates



electrolysis of fused borates or other boron containing compounds



and thermal decomposition of boron hydrides



4. LIFE CYCLE ASSESSMENT DATA

In [63] EPA identifies the process waste streams in extraction/beneficiation and mineral processing steps in Trona plant (California). Such study can provide useful information of wastes produced during the first phases of borates life cycle. During borate ore processing two main wastes are produced: gangue and wastewater. Gangue solids are generated from the initial production of sodium borate decahydrate. According to EPA such waste are generally inert insolubles, even though they can contain some other element as natural more impurities. In Trona plant, it contained 0.08 % natural arsenic mineral realgar. The solid wastes from ore residues and the evaporation wastes were sent to evaporation ponds usually located on site.

Wastewater from washing, contains borax and other salts, is stored in evaporation ponds. During boric acid production three main residues are identified: spent sodium sulphate, waste liquor, underflow mud. According to EPA spent sodium sulphate do not exhibit any characteristic of hazardous waste. Some waste liquor is produced after the boric acid is filtered. In the specific case of the considered plant, such residue contained arsenic. Such component was present as a natural impurity in the ore. Underflow mud, as spent sodium sulphate, is not considered as hazardous waste.

In [64] an LCA of borax and boric acid production in China was reported. It is possible to individuate the main wastes of such process which can be compared with similar procedure within the EU. During both borax and boric acid production, the mother liquor is obtained and recycled by returning it to the batch feeder. Likewise, cooling water can be recycled. Depending on the ore's grade more or less solid waste is produced. From borax production

boron mud is the solid residue, it is alkaline and hard to dissolve. The residue is mostly stockpiled, but it could be used as a secondary resource. When stockpiled it can pollute water, soil and atmosphere. The solid waste resulting from boric acid production is called slag and contains serpentine, forsterite, gypsum, and some H_3BO_3 . The residue generated by the boric acid production plant can be used to produce boric magnesium fertilizer or brick. The reported study points out the importance of the background energy used during the process, it is important to evaluate the quality of the energy source in terms of pollutants content and try to use the cleanest possible energy source. This is a general principle applicable to all processes which need energy coming from fossil sources or electricity.

5. SUMMARY

There is a significant stock of boron in landfill accumulated over years. The recycling process can be divided into two possible pathways: functional and non-functional. The former is null because products containing borates are consumed with use, for example fertilizers, wood preservatives, detergents, etc. Non-functional recycling depends on the collecting practices: good separation would allow to increase the amount of recycled borates. Some alternative recycling techniques have been individuated. LCA conducted on some specific plants ore country (China) allowed to individuate some potential environmental issues due to borates production and some good practices to limit such contamination have been pointed out.

COBALT

1. THE SECONDARY RESOURCES

The secondary resources of cobalt in EU member states are presented in Table 9 [65] [66] [67]. As it can be seen, the resources (solid wastes) originated by the metallurgical processing of primary ores are very limited, while there is an absence of available data concerning their exact deposited amounts and the efforts that have been possibly performed for their processing at commercial scale. On the other hand, there is a variety of Co-containing scrap materials which, more or less, are currently processed by EU Companies. The main unexploited or low-exploited Co containing scrap components in EU are: (a) the superalloys which mainly are recycled by a limited number of Companies in UK and (b) the varistors. Innovative methods for the recycling of these two Co containing scrap sources will be bellow described.

Table 9. The main cobalt secondary resources in EU [65] [66] [67].

Secondary resources	Process scale
Metallurgical wastes	
Copper smelter slags (UK)	Laboratory
Nickel slag (Finland)	No available data
Urban mining	
Cermets (tungsten carbide – cobalt)	Commercial (Ceratizit SA and Tikomet Oy)
lithium-ion batteries	Commercial (Umicore)
Superalloys (jet engines)	Commercial (Companies closely associated with the aerospace industry in UK)
Catalysts	Commercial (Umicore)
Magnetic alloys	Commercial (Swift Levick Magnets)
Varistors	Laboratory scale focused only on Zn recovery

2. EXISTING PROCESSING ROUTES – GAPS & BARRIERS

2.1 MINING AND METALLURGICAL WASTES

There is an absence of available data concerning the metallurgical processing of mining and metallurgical wastes aiming to the recovery of cobalt.

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2.2 SCRAPS

Umicore Company in Belgium processes around 350,000 tonnes/year of more than 200 different types of scrap recovering a wide number of precious metals such as Ag, Au, Pt, Pd, Rh, Ir, Ru, In, Se, Te, Cu, Bi, Sb and Co. Cobalt is recovered by cermets (tungsten carbide – cobalt tools), lithium-ion batteries and catalysts. There is only a rough description of the recycling processes that are followed by the company. Figure 12 presents the recycling process of Li-Ion batteries as it is followed by Umicore [68]. Cobalt oxide (Co_3O_4) is recovered and re-used for the construction of batteries cathode via a route which includes the smelting, refining and selective oxidation of the initial scrap. **There is a lack of available data concerning specific gaps and barriers on this recycling process.**

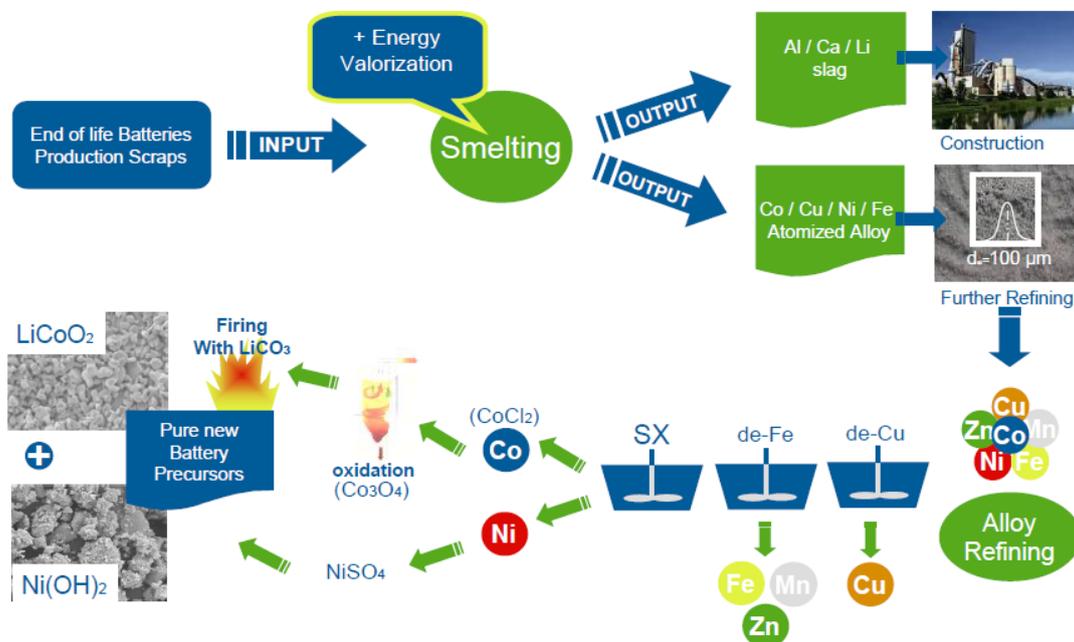


Figure 12. Li-ion batteries recycling process followed by Umicore Company [68].

It has been also reported that scrap of Co-containing catalysts, which are used for the removal of sulphur in petrochemical refining, the conversion of natural gas to diesel fuel and the manufacture of plastics, are collected and processed in Germany. Co-containing cermet scrap (mainly tools) are commercially recycled by Ceratizit SA and Tikomet Oy Companies. Superalloys scrap are recycled by companies associated with the aerospace industry in UK.

3. INNOVATIVE PROCESSING ROUTES – GAPS & BARRIERS

3.1 MINING AND METALLURGICAL WASTES

The exploitable, Co-containing, mining and metallurgical wastes are limited in EU countries. The generation of significant amounts (20 t/h) of slags with a 0.5% w/w Co content has been

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reported in Harjavalta (Finland) metallurgy plant (Boliden Company), where nickel sulfides are processed through flash smelting [66]. Unfortunately, there are no available data concerning the processing of this slag and a further investigation should be necessary.

Unexploited Co-containing copper slags have been deposited in IMI James Bridge secondary metal plant at Walsall, England. A study concerning the recovery of valuable metals from this type of slags has been performed. The developed method include their oxidative (pre)-roasting at 550 °C followed by the roasting by the addition of pyrite at the same temperature for 2 h. Subsequently, the roast is submitted to leaching with boiling water. The results were encouraging in case of cobalt extraction which exceeds 90%. However, on the other hand, the technological barrier of the developed method is focused on its low Cu extraction (<20%) [67]. The simultaneous effective extraction of copper and cobalt is necessary of the commercialization of the slag treatment processes. Therefore, as a future investigation, the leaching of Co-containing copper slags with alternative gentle reagents is proposed, while in any case, a detailed identification of similar deposited slag material in EU territory should be performed.

3.2 SCRAPs

A description of innovative techniques for the recycling of superalloys and varistors aiming to the recovery of Co are below described. Both these two scrap components are low-exploited in EU.

Superalloys

Superalloys are high melting temperature, excellent creep resistance, anti-corrosive, and oxidation resistant alloys which they are used in applications in which continuous extreme temperature environments ($T > 1000$ °C) are taking place such as gas turbines of aircraft engines and power plants. In most of cases superalloys are Ni and Fe–Ni-based with a general formula Ni/Co/Ni–Fe. The content of Co in Ni based superalloys reach 20%, while also exist Co based alloys with cobalt content up to 55%. Several pyrometallurgical, hydrometallurgical and pyro/hydro metallurgical processes, mostly at laboratory scale, have been developed for the recycling of superalloys. **Pyrometallurgical processes, and more specifically, re-smelting and selective oxidation, have been proved problematic** as they present a number of disadvantages such as: high burnt-out or oxidation losses up to 20 %, high electrical energy consumption and generation of vast amounts of solid wastes [69]. The hydrometallurgical processing of superalloys includes the leaching with hydrochloric acid and the recovery of cobalt and other valuable metals through solvent extraction. **Hydrometallurgical processes present a number of disadvantages such as: difficulties in solid-liquid separation, high corrosive environments, elevated consumption of acids** [69].

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The above disadvantages can be eliminated using a pyrometallurgical pre-stage processing which includes the sulfidization of the scrap to produce a matte which can subsequently more effectively leached in the presence of chlorine [70].

An alternative process for the processing of superalloy scrap that has been proposed and tested at laboratory scale is based on the electrochemical decomposition (Figure 13). Superalloy material is used at both the cathode and anode, while the polarity of the electrolysis current was reversed. Using electrolytes of 15–25 wt% HCl at 70 °C and 50 Amps and a resulting voltage of 3–4 V, a 20 % dissolution of the total superalloy mass was achieved [69] [71]. The filtrate that contains mainly Ni, Co and Cr which are precipitated to their corresponding metal hydroxides and can be further processed via electrorefining. The undissolved superalloy containing oxides of Ta, Re, W, and Mo can be subjected to oxidative-caustic leaching. After the solid–liquid separation, an ion-exchange process is suggested for Re recovery. **The method present a number of advantages such as: simultaneous extraction of various metals and lower amount of wastes in comparison to conventional pyro and hydro metallurgy routes [69]. However, the yield of the electrochemical decomposition and the metals separation efficiency should be further studied.**

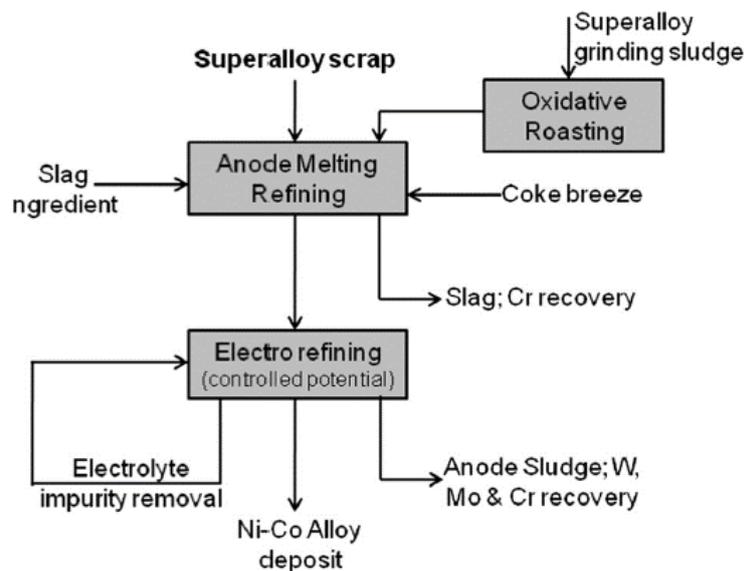


Figure 13. Laboratory tested method based on the electrochemical decomposition for the recycling of superalloys aiming to recovery of various metallic values [71].

A second alternative recycling processing of superalloys comprises the controlled melt carburization (partial carbon-reduction) and oxidation of the initial scrap. The pyrometallurgically treated scrap rich in cobalt is used as an anode in the second electrolytic deposition step, while a slag rich in Cr is generated. The method introduces a double-membrane electrolytic cell (DMEC) in which high purity cobalt-nickel mixture is deposited.

Although the process has been successfully tested and high purity Co-Ni is collected, it presents large metal losses (50% w/w Mo, 99% w/w W and 35% w/w Co) in the slag [72].

Varistors

Metal oxide varistors (MOVs) are housed in surge arresters, devices that used to protect electrical equipment from over-voltage transients caused by external (lightning) or internal (switching) events, and composed by zinc oxide (90 wt%), antimony (3–5 wt%), bismuth (3–5 wt%), cobalt (1 wt%) and nickel (1 wt%). Few thousand tons of MOVs scrap are annually produced in EU. Only in Sweden it was found that 132 tons of MOVs scrap were produced in 2013. Due to its high concentration in Zinc and other critical elements such as cobalt, antimony and bismuth, the MOVs recycling is favorable instead of landfilling [73] [74].

Laboratory efforts for the recycling of MOVs, mainly focused on the recovery of zinc, have been recently performed [73] [74]. The MOVs scrap is leached with sulfuric acid and the leaching solution is submitted to electrowinning for the recovery of zinc. The liquor contains Co and Ni impurities which are removed through cementation process using copper sulfate and $K_2C_8H_4O_{12}Sb_2 \cdot 3 \cdot H_2O$ as activators. **The recovery of Co, Ni and other critical metals by the remaining solid mixture it deserves to be investigated.**

4. LIFE CYCLE ASSESSMENT DATA

A life cycle assessment comparison between the existing and the innovative techniques for the Co recovery by secondary resources is not feasible as there is a lack of raw available data in second case. Innovative techniques have been tested only in laboratory scale for specific scrap materials. However, important LCA data can be found concerning the comparison of metallic Co (or Co compounds) produced by primary and secondary resources.

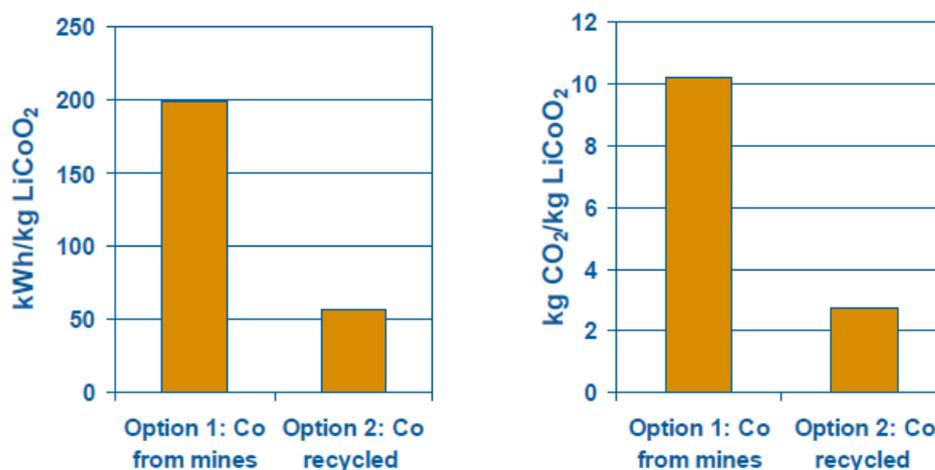


Figure 14. Energy consumption (left) and CO₂ emission (right) for production of 1 kg of LiCoO₂ by primary and secondary (via batteries recycling) resources [68].

An interesting LCA study concerning the synthesis of LiCoO_2 by primary resources in comparison to its formation by a recycling process has been reported. Lithium-cobalt oxide is used a cathode in Li-ion batteries. The study was based on the recycling process of Umicore Company (as it has been previously described) using as a functional unit the NiMH battery of Toyota Prius car model [68]. The results showed that about a 70% decreasing in the energy consumption and the CO_2 emission is achieved in case of LiCoO_2 production through the recycling process (Figure 14).

The environmental benefits of LiCoO_2 -containing batteries recycling can be further proved by eutrophication and photochemical ozone creation indicators. The relative values of these indicators is dramatically reduced in case of Li-ions batteries collection and processing (Figure 15).

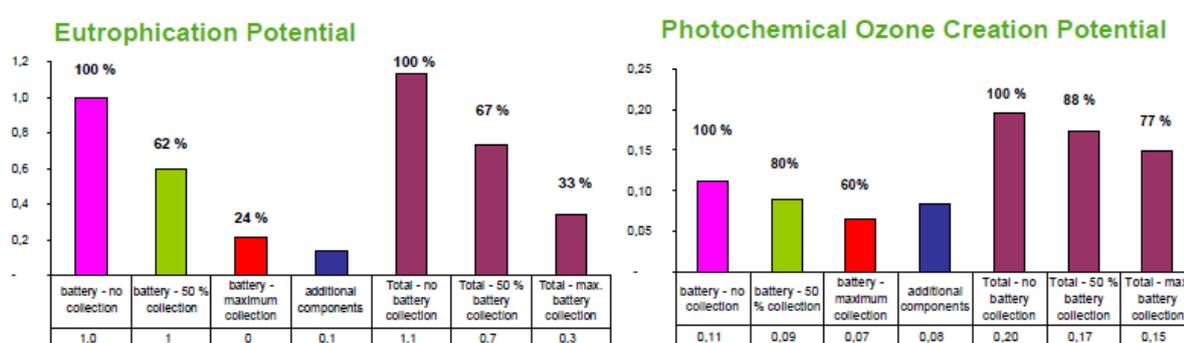


Figure 15. Decreasing of eutrophication (PO4 equivalent percentages) and photochemical ozone creation (ethylene equivalent percentages) phenomena by the processing of end-of-life Li-ion batteries [68].

5. SUMMARY

The recovery of Co by mining and metallurgical wastes in EU cannot be accurately identified as there is a lack of enough available data. It has been reported that Co-containing slags have been deposited in Nickel metallurgy plants in Finland, while Co-containing copper smelting slags exist in UK. On the other hand, the cobalt urban mining is highly developed in EU countries as several companies are involved in the recovery of metallic cobalt or cobalt compounds by catalysts, cermets, Li-ion batteries and various magnetic alloys. Innovative processing methods should be focused on the processing of superalloys and varistors which are relatively low-exploited. In case of varistors recycling, various critical raw materials can be simultaneously extracted with zinc. The technological barriers that should be overcome are related with the Co extraction yield by complex polymetallic scraps such as superalloys and varistors. Currently available LCA studies indicate, according to several indicators, the environmental benefit and the energy saving in case of LiCoO_2 production by the recycling of Li-ion batteries.

COKING COAL

THE SECONDARY RESOURCES

As described in D4.2, different streams of secondary resources of coking coal were mapped. 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, by-products from the coking plant as tar, oils, etc. as well as waste plastics and petroleum coke. However, as the coke quality is significantly influenced by less suitable coking materials already at a few percent such replacement is in general possible. 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. [75], [76].

The requirements on coke quality are high and quite well defined at the same time as the coking process characteristics and coke quality achieved are strongly linked to the quality of coking coal. The most common coking process uses density charging are not feasible for high ratios of secondary or low-quality materials.

GAPS & BARRIES – PROPOSED PROCESSING ROUTES

MIDLINGS/TAILINGS AND MANUFACTURING RESIDUALS

Potential coking coal resources in terms of mining tailings or low quality coals can be treated by flotation. Such treatment is e.g. developed in India in order to make low quality and secondary resources suitable for cokemaking. [77] Part of the low-quality coal or coal sludge could be recovered for use in coke making. However, the probably high ash content of enables only a small amount that can be used in the coking coal blend. Further, high S residues can be processed also. [78] Improved and innovative processing techniques may increase the recovery from existing streams of coking coal.

USE OF RESIDUES FROM THE COKE PLANT

Secondary materials from the off-gas treatment plant, collected dust collection as well as screened off fines from the produced coke can be added to the coking coal blend. Coke fines are inert material and do not contribute to the plastic phase formation during coking and the total amount of inert material will have an upper limit depending on the overall coking blend

and procedure. Tars and oils may increase the bulk density of coking coal blend and are quite usable in stamp charging but may cause too high wall pressure in density charged coke ovens.

USE OF WASTE PLASTICS

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 if using a specifically developed process as described in Delivery 4.2. 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. [79]

USE OF PETROLEUM

Petroleum coke is a residue from the petroleum industry and some types with suitable properties are quite commonly used in the coking coal blend. The types used are in general those with suitable grindability and lower S content. Its low ash content is favourable as it increases the C content in coke but as petroleum coke is an inert material the possible added amount is restricted.

INNOVATION POTENTIAL

There are need for further developments of methodologies that can enable higher amounts of secondary materials including inert materials. The methodologies may include e.g. stamp charging technologies [80] with different additions of oil, tar, binder (e.g. hypercoal) [81] [82] [83] etc, modified coking procedure for enhancement of plastic phase formation [84] including coal blend adaptation for both density and stamp charging, also innovative coking processes for use of alternative materials [79]. Further development of alternative coking processes as the one in Scope 21 that enables higher pressure during coking should give a new opportunity using secondary materials [85].

SUMMARY

Secondary materials possible to use in the coking coal blend are mainly tailings, by-products generated in the coking plant, screened of coke fines, residues from petroleum industry and waste plastics. However, to increase the possible use of secondary materials there is need for development of methodologies for coke making.

GERMANIUM

1. THE SECONDARY RESOURCES

Ge minerals are mined worldwide as a by-product of other metals, mostly Zn, Cu, and Pb. The technology exists for Ge extraction from coal fly ashes and Zn residues, but other Ge secondary sources are listed, as they offer opportunities for Ge extraction and some innovative methods (point 3) have been found for its use as Ge sources.

Coal fly ashes

Ge species as GeS_2 , GeS and GeO_2 , that are soluble in water, are produced during coal gasification and retained in fly ashes, in minerals as sphalerite, wurtzite, and galena, respectively. These fly ashes are usually reused in construction materials, as cement, without previous Ge recovery. The economic value of coal production would be increased if the potential by-products were recovered [86], although not all coals contain traces of Ge. As an estimation, about 2000 tons of Ge are annually discharged in stack gases to the atmosphere from coal combustion in the UK. Ge and Ga content of coal ashes was stated to exceed primary refinery production by a factor of 200 [87]. In 2013, 56% of the primary Ge was extracted from coal ash in China, Russia and Ukraine [88], so it is a practice and technology that exist, **although it is not being applied in all worldwide coal production industries.**

Zn refinery plant residues

In 2013, 33% of primary Ge was extracted as a by-product of Zn production [88]: from Zn smelter flue systems and dust [89].

Cu-Pb production slag

During Cu and Zn smelting, Ge and Zn are accumulated in slag. As a result, Ge content increases to 0.05 % [90].

Concentrated brines from desalination systems

Critical metals that are present in seawater, remain in the brines that come from desalination systems, so they can be extracted before returning the brine to the sea, decreasing thus environmental problems and increasing the economic benefits. Dirach *et al.* (2005) estimated that 0.01 t/y of Ge could be extracted from a brine rejected by a reverse osmosis plant at la Skhira (Tunisia), which would mean a value of 0.02 M\$/y. The extraction of Ge would be accompanied by the extraction of other valuable metals as Mg, Rb, P, In or Cs [91], improving the economics of desalination.

Solar panels waste

Photovoltaic installations are growing, and its recycling will play a significant role, relieving pressure on the prices of critical materials [92], as Ge.

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Fiber optic cable waste

35-40% of Ge production worldwide is used in fiber optic cables, in the form of GeO_2 . The optical fibers, 5-10% of the cables, contain approximately 0.086% of Ge.

The rapid development of optical technology produces high amounts of wastes, as gases exhausted from the fiber manufacturer, which have no proper disposal and are hazardous [93] [94].

Computers

Computers dismantled or shredded contain only minute amounts of Ge in their electronic parts [89].

2. EXISTING PROCESSING ROUTES – GAPS & BARRIERS

Currently, Ge is extracted as a by-product of Zn production and from coal fly ash (EC, 2014), and recycled in fiber optics manufacturing.

Coal fly ashes

In coal combustion, metals of their mineral part go into the slag, which remains in the combustion space and volatile ashes, and is carried away along with gaseous combustion products. In the two cases, hydrochloric acid or chlorine are used to treat the concentrates, and then GeCl_4 is hydrolysed to obtain GeO_2 , and hydrogen reduction is applied if Ge metal is wanted [95]. Typical Ge concentration in coal fly ashes is <0.03% [88].

Ge is also extracted with a pyrometallurgical route, being followed by a separation process as distillation, solvent extraction or ion exchange [96].

Conventional processes to recover Ge from coal fly ashes present the following problems: they are **difficult to be satisfactory for its economic and environmental effect**, and the **recovery ratio of Ge is not enough** [97]. Also, the **stabilization of the residual sludge should be done for decreasing the release of toxic trace elements to the environment** [98].

No production of Ge in EU is reported from coal fly ashes, although EU has much potential for it, due to the presence of several coal production industries (Poland, Germany, Czech Republic, United Kingdom, Greece, Spain, Bulgaria, Romania, Hungary). There is a need for investment in technology and research to reach the cost-efficient Ge recovery from coal fly ashes in EU.

Zn plant residues

In electrolytic Zn plants, Ge is separated chemically during the purification of the electrolyte prior to electrolysis. If its concentration is high enough in the separated solids, its recovery is economic and possible. Ge can be recovered from Zn refinery cementation residues, or copper

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cake [99]. Normally, the zinc refinery residue is leached by sulphuric acid and solvent extraction processes are developed for its recovery, purification and concentration [100]. Also, from flue dusts Ge is extracted by: 1) Zn refining, 2) distillation under non-oxidising condition, 3) recovery of the distillation residue, 4) formation of GeCl_4 by leaching the distillation residue with HCl, 5) hydrolysis for GeO_2 production and 6) reduction (optional) to metallic Ge with hydrogen at 760°C [89].

As in the case of coal ashes, no Ge production is stated in EU from Zn plant residues, but Zn production is carried out in Sweden, Poland, Ireland, Finland, Greece, Bulgaria, Spain, and Portugal [101]. Conventional leaching agents are used in the Ge recovery, as sulfuric acid, and commercial extractants. No use of cheap and green solvents is stated.

Scraps from the photovoltaic industry

Umicore treats scraps by two different techniques [88]:

- Pyrometallurgical route: scraps are fed to a smelter to produce a Ge concentrate which is converted to GeCl_4 by chlorination. This product is then hydrolysed and converted to GeO_2 , which is reduced by crystal pulling to obtain single Ge crystals.
- New hydrometallurgical route: no data are found.

Fiber optics production

Bell Labs, USA, developed a method to extract hazardous wastes from the gases exhausted from fiber manufacture, being recovered Ge from fiber-optic since the mid-1980s. Ge in fiber optic cable is around 4%. The extraction rate was more than 70% of the wasted Ge, resulting in a multimillion-dollar saving in Ge purchase costs. The process is confidential [94]. **No Ge recycling from fiber optics is found but fiber optics production already takes place in EU. For example, Fibrain (Poland), Prysmian Group (Italy) or Nestor cables (Finland) manufactures fiber optic cables, although the lack of data and information in the Ge recycling and its procedures.**

Supply from recycling

Around 30% of global Ge is estimated to be supplied by recycling, mostly from scrap generated during the manufacture of fibre-optic cables and infrared optics. This “new” scrap is fed back into the production process. But, concerning EoL products, very little recycling exists (2%). Ge is dispersed in most products. Very few used end-products are collected separately to be recycled: optical fibres go into non-functional recycling in C&D waste, solar cells for satellites are not recovered and only some Ge is recycled from an old scrap of IR optics such as used mobile phones. **Ge is contained in EoL products at low-grade, so it is technically and economically difficult to be recovered [102]. Fibre-optic cables have a long residence time in their applications, so recycling volumes for old scrap are rather low, but it can have high recycling potential in the future [89].**

Gaps & Barriers

Given the **low refining capacities and inefficiencies**, only 42.7 and 39.9 tons of Ge are produced worldwide from Zn leach residue and coal fly ash, respectively, which are less than 2% of the Ge available. **EU mining capacities must be expanded to meet the global supply of Ga and Ge in the future. This needs financing. For Ge recycling from end-of-life products, technological advances are needed** [103].

3. INNOVATIVE PROCESSING ROUTES – GAPS & BARRIERS

Coal fly ashes

Font *et al.* (2005) took advantage of the solubility of Ge species in water and tested several water-based extraction tests: water from the cooling chamber of the plant, water from the gas cooling system and from the desulphurisation process from flue gas cleaning. They reached high Ge extraction (up to 84%) at 25°C [86].

Flotation of Ge from fly ash aqueous leachates containing also other metals and metalloids was performed by Hernández-Expósito *et al.* (2006), by using a complexing agent (catechol) and a surfactant (dodecylamine) as a collector. Ge recovery was of 100% and the extraction of impurities was reduced [96]. Floated Ge was recovered by roasting, obtaining GeO₂ of high purity.

Kalderis *et al.* (2008) studied the characterization and treatment of wastewater produced during the hydro-metallurgical extraction of Ge from fly ash. This wastewater can contain several metals that can cause a damage to the environment as As, Ni, or Sb. They used calcium hydroxide precipitation combined with reverse osmosis, reaching a metal removal of 97.5%, obtaining a stream concentrated in catechol which could be reused in the Ge extraction, thus reaching a circular economy approach [104].

Arroyo and Fernández-Pereira (2008), applied a simple hydrometallurgical method for Ge recover from fly ash, by using water as lixiviant and subsequent concentration and separation of Ge by complexation with catechol and solvent extraction with organic reagent diluted in kerosene [105]. They reached extraction of 90% Ge. In 2009, the same group upscaled the process to a pilot plant, but the recover was around 50% Ge [106]. After this, Torralvo and Fernández-Pereira in 2011, used ion-exchange procedures based on Ge complexation with catechol in an aqueous solution followed by its retention onto a conventional strongly basic anionic resin (IRA-900). They obtained Ge retention of 96.1% [107].

To overcome the environmental problems of conventional methods, Zhang and Xu presented in 2016 a metallurgical process for recovering Ge from coal fly ash consisting of vacuum reduction, achieving 93-96% Ge extraction. They did experiments at pilot scale, achieving

94.64% of recovery. The process was considered a step beyond conventional processes, reducing the use of water and residue production [97].

Haghighi *et al.* (2018) studied the recovery of Ge from leach solutions of fly ash using solvent extraction with Alamine 336 and Cyanex 923 extractants. Tartaric acid was required as complexant to convert Ge to anionic species in amine extraction, while oxalic acid was used as complexant in the case of Cyanex 923. After extraction, Ge was stripped from leachates with 1-2 M HCl solutions. They considered Aliquat 336 as an economical and industry-friendly extractant for Ge solvent extraction [108].

Zn refinery plant residues

Kul *et al.* (2008) [99] studied the recovery of Ge and other valuable metals with sulfuric acid leaching from the copper cake of a zinc plant, containing 700 ppm of Ge, together with other valuable metals as Cu, Zn, Cd, Ni, or SiO₂. The optimum collective extraction of Ge and other valuable metals was at 60 and 85 °C, during 1 h and sulfuric acid concentration of 150 gpl using a S/L ratio of 1/8 g/cc. The leach recovery of Ge was 78%, and other metals like Co, Ni, Fe, Cu, Cd and As were poorly leached, so the second step for Ge recovery was needed. Nusen *et al.* (2015) reviewed the extractants used for Ge recovery, and most of them were not commercially available [100].

Nusen *et al.* (2015) [100] proposed a recovery of Ge from a synthetic leach solution (1g/L Ge and 1M sulfuric acid) of Zn refinery cementation residues by using commercial extractants LIX 63 and Ionquest 801. They selectively extracted Ge.

Lui *et al.* (2016) studied the extraction of Ga and Ge from Zn refinery residues by pressure acid leaching [109]. They decreased losses of Ge and Ga by adding silica and leached Ge from leach slurry by adding calcium nitrate at optimum conditions, recovering 94% Ge, and 98% Ga.

Fupeng *et al.* (2017) focused on the Ga and Ge leaching, but also the removal of Fe from Zn refinery residues. They first leached Zn and Cu, reaching a Ge enrichment of 300%, and after they recovered 96% Ga and 99% Ge at optimum conditions, removing iron by ultrasound-assisted precipitation. After iron removal, Ga and Ge were extracted by the organic system with N235 and TBP in kerosene [110] [111].

Liu *et al.* (2017) developed a new method for extracting Ga and Ge from Zn refinery residues in H₂C₂O₄ solutions containing H₂O₂. The achieved 98.86% Ge extraction and 99.32% Ga extraction, with a minor concentration of the rest of metals, except for Fe, whose extraction was of 30.25%, so the next step was the leachate purification by ultrasound-assisted iron powder replacement method, reaching 98.31% Fe removal. Ga and Ge were separated by solvent extraction with N235+TBP and stripping with sulfuric acid and NaOH [112].

Concentration brines from desalination systems

Le Dirach *et al.* (2005), extracted Ge in a final phase of a process to extract strategic metals from brine rejected by a desalination unit [91]. Ge was recovered being crystallized in the form of GeO_2 and the solid was exposed to gaseous hydrochloric acid, obtaining GeCl_4 , which was then hydrolysed to obtain GeO_2 , which was reduced to pure Ge by roasting under a reducing atmosphere of hydrogen. They stated a **need of complete protocol validation, determination of the mechanism of phosphates precipitation, the optimal formula of used Al, validation of the use of HCl and not nitric acid during Ce extraction, scrubbing and stripping, determination of optimum conditions, etc.**

Solar panels waste

The recovery of Ge from waste solar panels was performed by Kuroiwa *et al.* in 2014. They used complexation by catechol, membrane adsorption and elution with HCl and solvent extraction with trioctylphosphine oxide (TOPO). They extracted 81% of Ge [113]. The same year, Yi and coworkers published an article about the metals recovering from recycled photovoltaic modules, and **Ge was not considered in the metals that can be recovered in a near future from these wastes** [114], but no reasons were found.

Optical fibers

Chen *et al.* (2017) developed a recycling process for Ge recover from waste fiber optic cables, doing the pre-treatment, leaching of the fiber and Ge extraction from silicon. Ge and Si were first dissolved by sulfuric acid and hydrofluoric acid, and then Ge was recovered with Trioctylamine (TOA), and stripped by NaOH. They estimated that with optimal conditions, Ge recovery could be up to 99% [93], leaving 1% silicon residual.

Cu-Pb production slags

In 2008, Chirkst *et al.* proposed a method for extraction Ge and Zn from Cu-Pb production slags, consisting of a Ge leaching and autoclave extraction of Zn into alkali solutions [90].

González *et al.* (2017) developed a method to extract Ge from Cu smelting flue dust, based on extraction with water, but apart from Ge, they also extract Li, and Rb, between 97.2 and 100%.

Computers

Ge recyclability from PCs was estimated 0% [115]. The major challenge is the effective collection of old devices and cost-effective separation of metals [89].

Gaps & Barriers

In general, studies for Ge recovery from secondary sources are limited and only performed (except for one case) at lab scale. High recovery rates have been obtained, but no process upscaling nor testing in an industry environment has been performed. Also, there is a lack of products valorisation, economic and market analyses. Talking about Technological Readiness

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Levels (TRL), the technology for Ge extraction from some secondary sources would be at TRL 3, validated at lab scale, but there is a need to go on further steps to increase the TRL. To that aim, financing is needed. To reach all these objectives, a lack of data about Ge production on EU exists. No Ge is produced in EU from primary sources, but some recyclers claim to produce Ge from secondary sources as UMICORE (from electro-optic materials). However, no data about quantities of Ge production from recycling is found.

4. LIFE CYCLE ASSESSMENT COMPARISON BETWEEN EXISTING AND INNOVATIVE TECHNOLOGIES

The only study found about LCA of Ge production from primary and secondary sources is from Robertz *et al.* (2015) [88], who studied and compared the LCA between the Ge production (pyrometallurgical and hydrometallurgical route, point 3.7) from photovoltaic industry scraps and primary production of ultrapure GeCl_4 and single Ge crystals Ge [88]. All the info in this point 4 comes from that study.

Data from secondary sources came from Umicore data, an EU company who supplies Ge-based materials. The study functional unit was 1 kg of Ge as ultrapure GeCl_4 or Ge single crystal. Figures 1-6 show the results obtained by the authors.

For the production of ultrapure GeCl_4 , the main contribution to the impact linked to primary production from coal is linked to the coal raw material, either with emissions during its burning or with its extraction and treatment. Main contributions of secondary GeCl_4 production are linked to the production of energy sources and production of main reagents for the leaching and chlorination.

For the production of Ge single crystals, the main contributors to impact scores are electricity, nitrogen and hydrogen. The most contributor to the impact is the GeCl_4 production step (at least 80%). Comparing pyro and hydro routes for the production of 1kg GeCl_4 from scraps, the hydro route had a lower impact in all categories, due to use of fossil fuels in the smelting process and refractory bricks. Benefits of metal recycling are highlighted.

Comparing the production of GeCl_4 by primary and secondary routes, primary production had 100 times more impact than a secondary route.

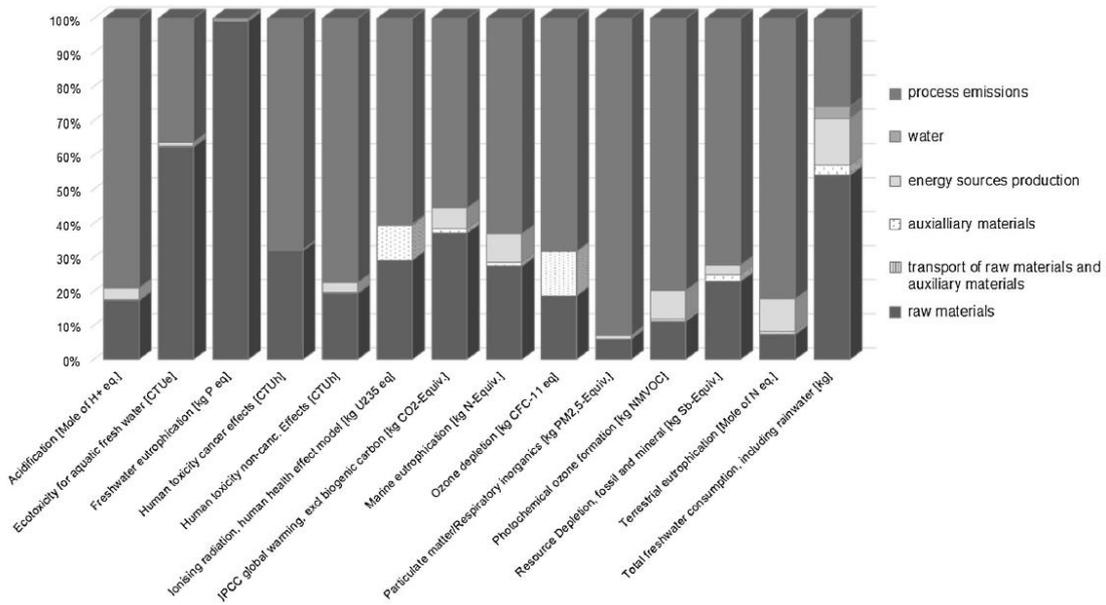


Figure 16. Contribution to the impact of the primary production of 1 kg GeCl₄ from coal (from Robertz *et al.* 2015 [88])

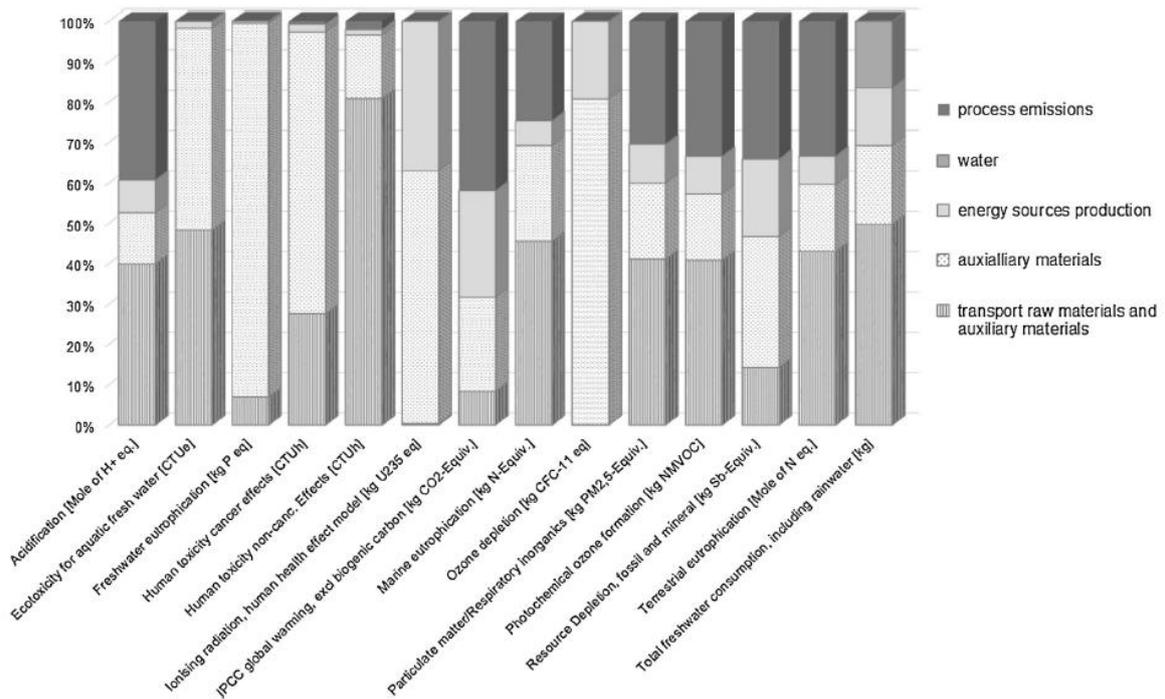


Figure 17. Contribution to the impact of the secondary production of 1 kg GeCl₄ from PV production scrap via the pyrometallurgical route (from Robertz *et al.* 2015 [88])

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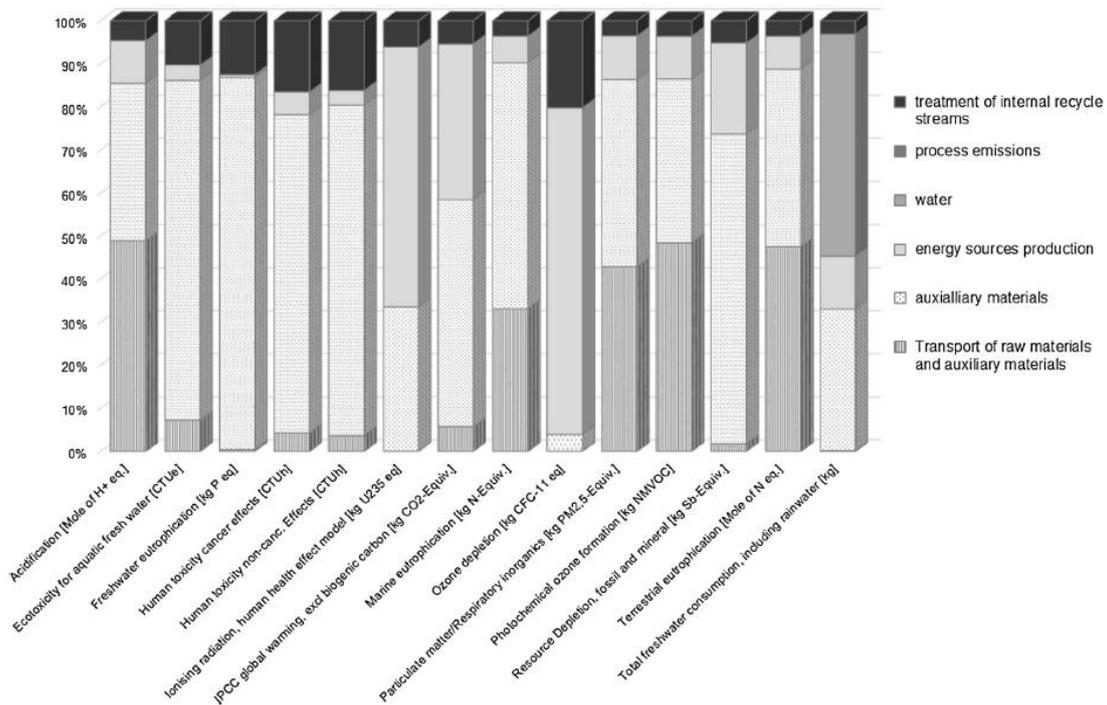


Figure 18. Contribution to the impact of the secondary production of 1 kg $GeCl_4$ from PV production scrap via the hydrometallurgical route (from Robertz *et al.* 2015 [88])

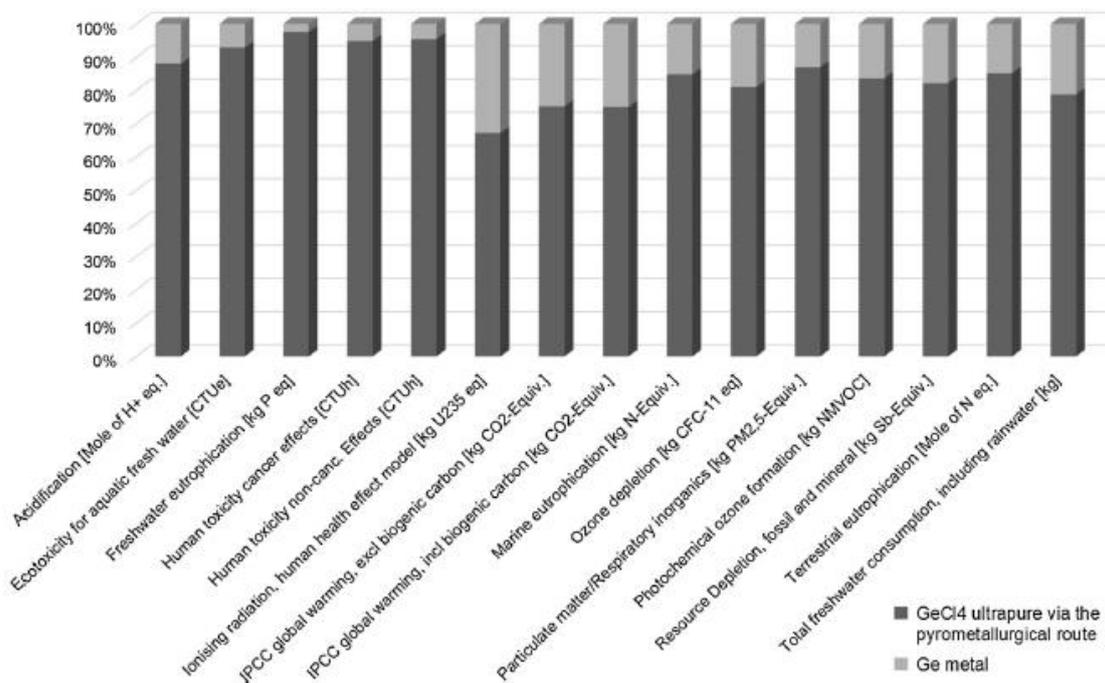


Figure 19. Relative contribution of the production of ultrapure $GeCl_4$ to the production of 1 kg Ge crystal from PV production scraps via the pyrometallurgical route (from Robertz *et al.* 2015 [88])

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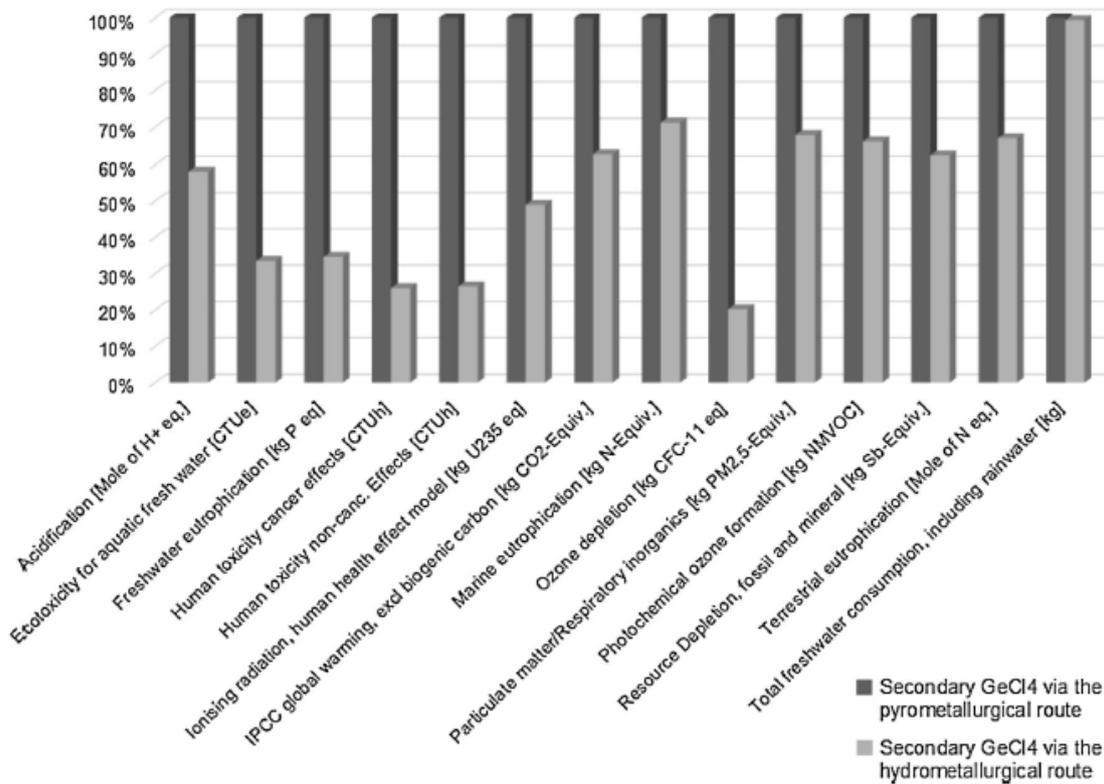


Figure 20. Comparison of the impacts for the production of 1 kg ultrapure GeCl₄ from PV production scraps via the pyrometallurgical and hydrometallurgical routes (from Robertz *et al.* 2015 [88]).

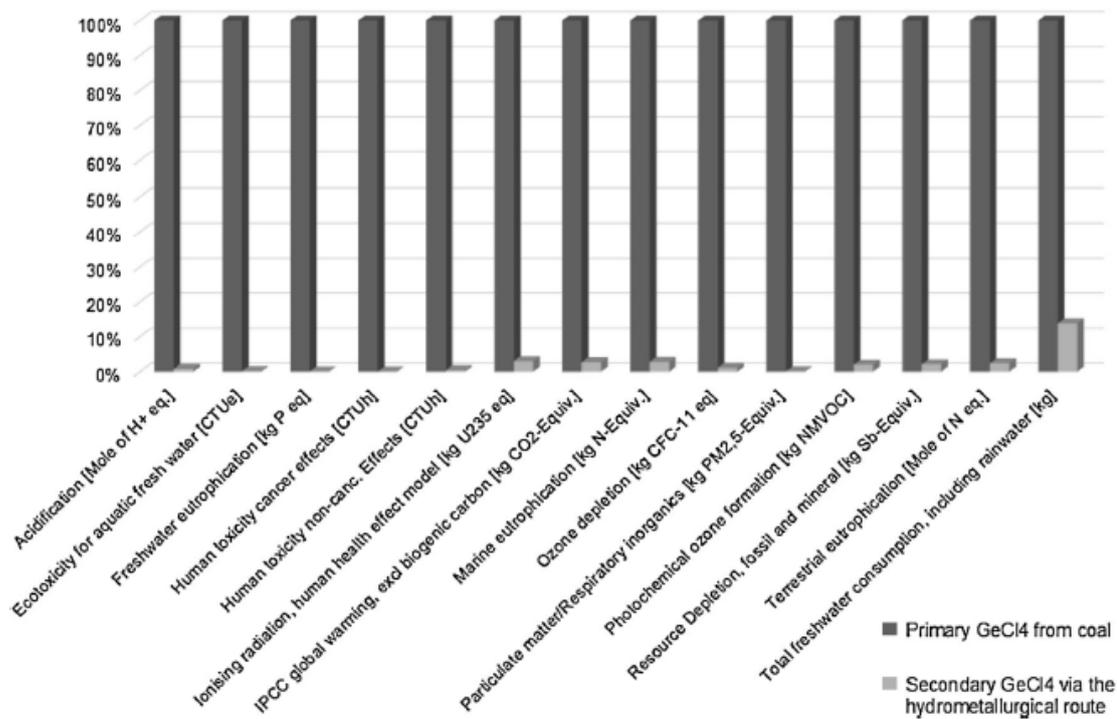


Figure 21. Comparison of the impacts for the production of 1 kg ultrapure GeCl₄ from PV production scraps via the hydrometallurgical route and from coal (from Robertz *et al.* 2015 [88]).

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5. SUMMARY

Ge is produced as by product of other mineral production or from secondary sources, mainly from fly ashes from coal production or from Zn-refinery residues. In EU, there is no production of Ge, only some companies in EU are recycling Ge from EoL products as for example Umicore (Belgium), Recylex (France), and Chemical and Technical developments Ltd (UK), but the technical processes are confidential, and no data about the Ge production from recycling is available.

The technical processes developed at lab scale to recover Ge are based on leaching with conventional reagents and extractants. To make the processes “greener and cheaper”, thus encouraging the implementation of technologies for example in coal and zinc EU industries, and to be able to extract Ge at low concentration in EoL products, new simple, selective and flexible methods must be developed. For example, no studies have been found about the use of non-aqueous solvents, as for example Ionic Liquids or Deep Eutectic Solvents, which could offer an alternative to the conventional solvents.

In general, a lack of data is found about Ge production from secondary sources, only some studies about innovations in Ge extraction, mainly centred in coal ashes and Zn refinery residues. Catechol is usually utilised as a complexing agent for Ge. As commented, all studies except one of them are experimental at lab scale, and although high Ge recoveries are reached, there is a need of processes upscaling and demonstration in an industrial environment, and valorisation of the obtained products and economic analyses. This needs financing and interest. There are many projects funded by H2020 aiming at CRM recovery, but none of them targets Ge directly. There is a need for cluster creation considering all Ge EU stakeholders, and initiatives to reach Ge production and recycling in EU.

Relative Life Cycle Analyses, only one study has been found comparing the primary production of Ge and secondary production from PV panels production scraps. The results show the advantages of recycling over primary production in this case, but this study is specific for that case and more studies comparing another end of life products and secondary sources would be needed to generalize the advantages of recycling over primary production.

HAFNIUM

1. THE SECONDARY RESOURCES AND EXISTING PROCESSING ROUTES

Recycling of hafnium is very low in Europe, the end-of-life recycling input rate⁴ being estimated by EU to 1% in 2017 [6]. This is most probably due to its contamination when used in the nuclear industry and to its low percentage content when used in superalloys [116]. Secondary resources includes scrap from the manufacture of electronic devices in the form of used sputter targets and evaporation sources for example, principally in the manufacture of microprocessors, from plasma cutting electrodes and from Hf-containing alloys (e. g. HfZr, HfTa, HfNb etc.). Only few information is available on the process implemented for the recycling. The only identified technology is the cold crucible continuous casting which seems to be implemented by the industrial platform Tita-Creuset located in France for remelting of materials. Some companies purchasing hafnium scraps for recycling have also been identified (like PA-Metals in Germany), however no information on the process is available.

It could also be mentioned that even if it is likely that waste hafnium from production processes are reintroduced in the process [116]. However, similarly as for the scrap recycling, no information on the processes has been found in the literature.

2. INNOVATIVE PROCESSING ROUTES

Due to the low recycling rate of hafnium scrap or waste, it is very difficult to find information regarding innovative processing route.

The only technology which was found is the Electron Beam Melting and Refining (EBMR) which is industrially employed for melting and metal purification (Figure 22). It was shown to be a proper refining method for recycling hafnium in scraps [117]. Indeed, hafnium in scrap is oxidized which means that its reuse is possible after treatment aiming to remove the oxygen and to decrease the oxygen concentration in the composition. The EBMR is a proper refining method for this purpose since the oxygen is in the solid metal scrap as oxides that pass to the liquid pool at heating. Part of them dissolves or dissociates in the liquid pool volume and another part moves and reaches the top surface (the interface molten pool / vacuum) and also dissociates due to the low relative weight. Due to the higher temperatures at the surface and the contact with the vacuum environmental, the level of dissociation of the oxides and the efficiency of the refining processes are higher [117]. This method was studied in various

⁴ The end-of-life recycling input rate measures the ratio of recycling from old scrap to EU demand of a given raw material, the latter equal to primary and secondary material supply inputs to the EU.

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projects performed by the Institute of electronics in Bulgaria [117] [118]. However, there is a lack of available data concerning specific gaps and barriers on this recycling process.

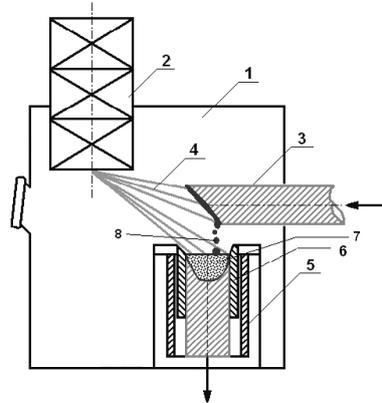


Figure 22 : Principal scheme of the electron beam melting and refining drip process: 1 – vacuum chamber; 2 - electron optical system; 3 - horizontal feeder of the started metal rod; 4 – electron beam; 5 - pulling mechanism; 6 - water-cooled crucible; 7 - molten pool (in the water-cooled crucible); 8 - generated droplets (from [117]).

3. SUMMARY

The recovery of Hf contained in scraps and waste in EU cannot be accurately identified as it is hardly implemented. There is then a lack of enough available data, both on current and innovative recycling processes.

INDIUM

1. THE SECONDARY RESOURCES

1.1 MINING AND METALLURGICAL WASTES

Secondary indium from mine & metallurgical waste can be mainly recovered through hydrometallurgical processes with leaching of dusts, fumes and slags resulting from zinc and lead smelting processes [6] [119] [103]. Since the production of primary indium is highly dependent of other major metals like zinc, lead and copper, the availability of secondary indium from this processing route depends largely on the demand of these major metals [120]. In the known Portuguese zinc and zinc-lead deposits, it is estimated that indium exists at a concentration of between 20-1100 ppm but no data exists on actual indium extraction [6]. In France and Belgium, two companies that are dedicated to zinc refining also produce indium from imported ores/residues. Nystart in France has the capacity to produce 70 tonne/year while in Belgium, Umicore produces indium from residues of the lead-copper smelting operation and has a capacity of 30 tonne/year. In Germany PPM pure metals upgrades indium from 4N to 7N. Other producers of indium have been identified in Italy (Pertusola), Germany (Preussag GmbH, V.E.B., Berzelius Metalhuetten GmbH) and England (Capper Pass Ltd., Johnson Matthey Ltd.) [121].

The estimation of the recovery potential of indium from zinc smelting residues has been reportedly hard to estimate [119]. Despite this hurdle in the quantification of the potential in the EU for indium recovery, the known processes from which indium can be obtained are explicated in the following paragraphs.

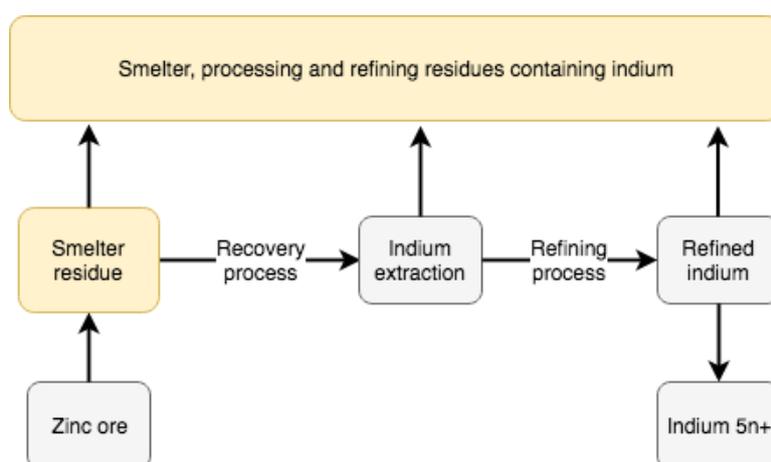


Figure 23 - Simple depiction of the indium refining process and the accumulation of residues across the processing chain.

In this section, a difference has to be made between the way indium is traditionally extracted via extractive metallurgy from zinc residues and what can be considered a secondary indium resource which may come from landfilled residues of the zinc/indium refining process. This very important nuance was considered when defining what a secondary resource is in terms of mining and metallurgical wastes as a source of secondary indium. A representation is shown in Figure 23.

In a 2013 study, a global substance flow analysis (SFA) targeting indium was performed where the combined residues from mining and smelting and refining amounted to 90% of primarily available indium in indium-bearing zinc ores [119]. In 2015, another study performing a detailed SFA for indium at the global level, found that over 60% of the available indium in zinc/lead ores was discarded in the form of smelting/refining residues [103]. While in a third study in 2014, the ratio of discards is estimated to be between 73-78% [122]. By 2050, the efficiency of indium processing may increase to 50% due to technological advancements [122]. These high inefficiencies in indium processing result in the accumulation of indium from the refining process in the form of residues. These are either landfilled or can be re-used. It appears that recovery of secondary indium from known hibernating stocks (landfilled residues) will be only feasible once the market price of the metal reaches a certain feasibility threshold [121].

1.2 SCRAPs

One of the main sources of scraps are new scraps from the production of indium-tin oxide (ITO) coating for flat-panel displays (FPD) [6]. Since production of these electronic displays takes place in Asia, most of secondary recovery of indium from ITO takes place there. During the production, sputtering of indium in the manufacture of FPD, a substantial part of sputtered indium cannot be fully imbedded into the semiconductor layer and it is directly recycled in-house. This source of secondary indium through manufacturing losses is a known stream of new scrap for FPD manufacturers [119]. The same happens in the manufacture of thin-film solar PV cells where manufacturing efficiency prevents full usage of the material. It is estimated that up to 27% of the sputtered material is not efficiently used and is thus recycled [119].

The EU end-use market composition of indium is reported in Figure 24. From the composition of the use of indium in the economy, it can be seen that a substantial share of indium will end-up in WEEE where FPDs, solar cells and other electric/electronic applications make up most of the potential availability of secondary indium if dedicated recycling routes are established.

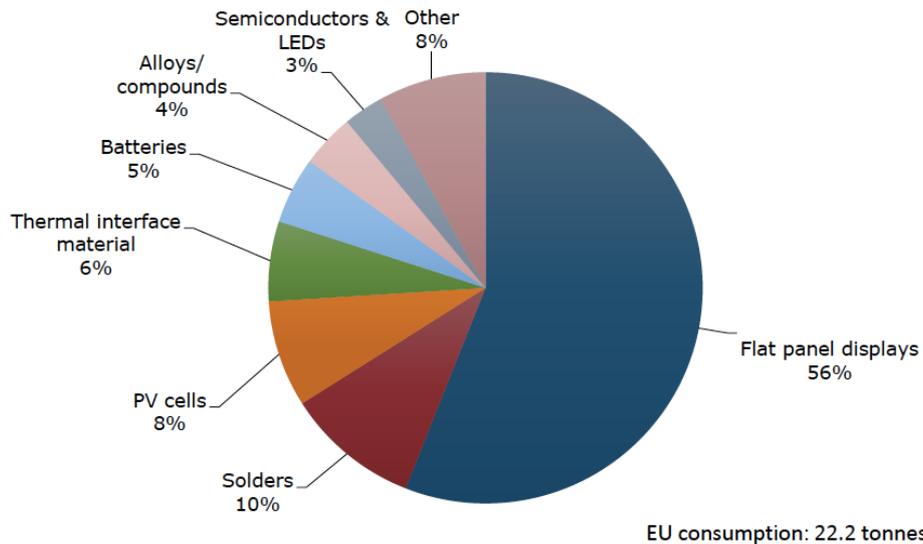


Figure 24 - End-uses of indium in products across the EU. From [6].

From a literature review, it can be understood that the potential sources of secondary indium from scraps include manufacturing scraps and EoL products containing indium. They are further discussed below.

Manufacturing scrap: In the first case, sputtering deposition of ITO in the fabrication of FPDs produces considerable amounts of industrial discards. These occur mostly outside of the EU therefore will not be considered (given the scope of the analysis being the EU geography). Nevertheless, these seem to be the largest potential source of secondary indium from scraps followed by manufacturing losses of LEDs [103]. These fabrication processes mostly benefit from in-house secondary indium resulting from the established closed-loop recycling schemes [123].

EoL products containing indium: In 2018, a material flow analysis (MFA) has been conducted which highlights the potential for indium recovery from secondary scrap sources [123] for Europe in 2014. In this study, the largest end-use applications containing indium are: glass coatings⁵ (66%), electrical and semi-conductor⁶ (19%), metallurgy⁷ (13%) and other uses (3%). In Figure 25, the concentration of indium in Europe in 2014 in a range of EoL products/applications is depicted to support the aforementioned ratios.

⁵ Glass coatings include FPDs in electronic devices, structural glass, etc.

⁶ LEDs and solar cells

⁷ Zinc and lead alloys, soldering, other alloys

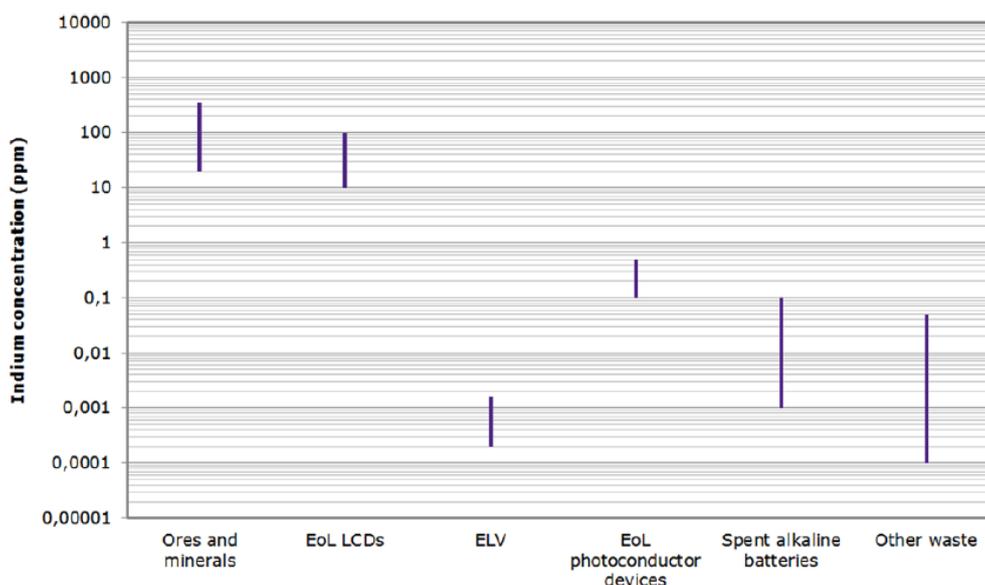


Figure 25 - Different concentrations of indium across a range of products and applications including primary ores. From [123].

2. EXISTING PROCESSING ROUTES – GAPS & BARRIERS

While indium recovery from mine and metallurgical waste is itself already a secondary process of recovery, i.e., indium is mainly extracted from zinc ore smelting residues, in the case of EoL products, indium is widely interspersed between glass coatings and other applications.

2.1 MINING AND METALLURGICAL WASTES

No data could be found on the processing of secondary indium from the waste sources highlighted in Figure 23. This may result from the fact that only with favorable market conditions, refiners of indium-bearing zinc ores will decide to use those hibernating stocks of indium under the form of landfilled slags and other discards [122].

2.2 SCRAPS

Based on the aforementioned sources of secondary indium from scraps, FPDs (glass coatings), electric applications and metal alloys present the biggest potential for secondary indium from scraps. More details are given below.

FPDs

In terms of FPDs, the presence of indium amounts to 0.01 wt% which comes from an estimation of 102 mg_{indium}/kg_{FPD} [8]. A common problem with EoL FPDs in Europe, is the case where these are incinerated leading to a complete loss of the indium-rich ITO layer [124]. The quantity of FPDs entering this route is not known. To date, in Europe, there is no known facility

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dedicated to the recovery of indium from EoL FPDs. In Asia for example, Sharp, which is one of the largest manufacturers in the world of FPDs, has implemented a dedicated FPD recycling process which can recover up to 90% of indium [125]. This simple and environmentally friendly process is depicted below in Figure 26.

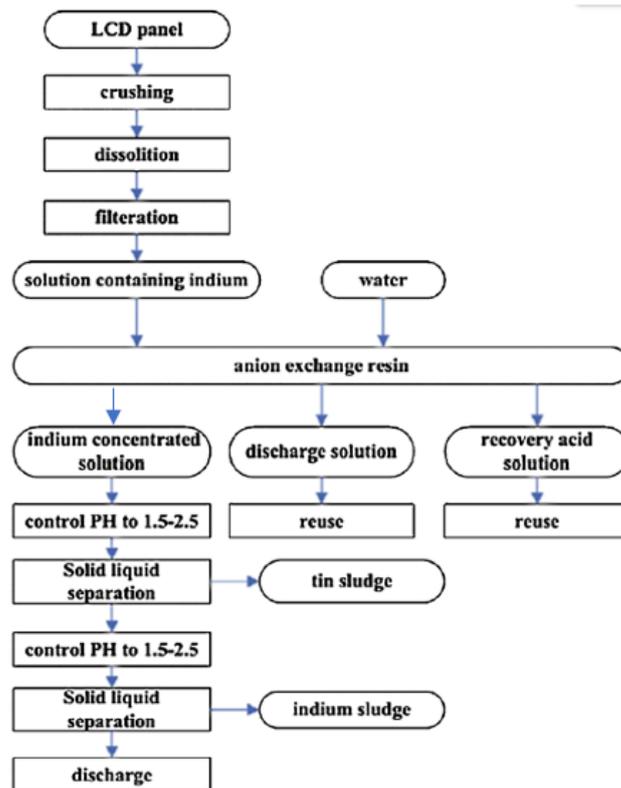


Figure 26 - Sharp's FPD recycling process. From [126].

Electric applications

Electric applications which include LEDs and thin-film PV cells also do not seem to be an exploited source of secondary indium in the EU. LEDs may contain 4 wt% of indium [7] while thin-film PV cells such as CIGS and CdTe may contain on average 16.5 kg_{indium}/MW [127] [128]. Currently, PV cells containing indium are a very small share of the PV market where only FirstSolar which manufactures CdTe cells appears to have a solid take-back recycling system for EoL modules.

The potential for indium recovery from PV cells is very dependent on the price of the raw minerals [128]. Hence, the future supply of indium from this application will depend on (a) the growth of this market which will result in EoL availability in 25 years and (b) the evolution of

the recycling costs inherent to the recovery of indium from CIGS cells [128]. The reported recycling efficiency is around 90% for indium from EoL CIGS PV cells.

No information could be found on the recovery of secondary indium from EoL LEDs. In literature [103], a substantial in-house closed-loop recycling is reported which amounts to a recycling content of $\pm 50\%$.

On an industrial scale, co-production of secondary indium in the EU takes place at two distinct places aimed at the recycling of WEEE: (1) Umicore in Belgium and (2) Rönnskär in Sweden [129].

1. Umicore processes in its base metals operation the by-products of the precious metals operation that are triggered by the need to recover precious metals from WEEE. The recovery of indium occurs in the base metals operation where residues from the lead blast furnace are refined into a series of special metals including indium.
2. Rönnskär smelters process the vapor phase from the lead furnace for the recovery of indium and other metals.

Metal alloys

No information was found of concrete recovery routes. Nevertheless, indium flows in secondary metal scrap are known to be tramp elements in different alloys.

3. INNOVATIVE PROCESSING ROUTES – GAPS & BARRIERS

3.1 MINING AND METALLURGICAL WASTES

One of the pointed sources for future availability of secondary indium from mining and metallurgical wastes are the current hibernating stocks resulting from the landfilling of mining/smelting/refining residues [3]. The most important point for the future attractiveness of such a source of secondary indium is the market price of the metal. To recover indium, a normal hydrometallurgy process would be applied to this landfilled residue. Given the expected improvements in processing efficiencies, a substantial amount of indium could come from these sources. A known source of indium is in Namibia in the Tsumeb lead mine. There, landfilled residues are estimated to contain 490 tonne of indium [103].

3.2 SCRAPS

As discussed in section 2.2, the main sources of secondary indium from scraps are FPDs, electric/electronic applications and metal alloys/soldering material. FPDs represent the largest potential for secondary indium recovery and therefore they require a closer look at the

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most promising recovery processes being researched at the moment. Indium recovery from FPDs also attracts attention from the scientific community because of its high concentration per tonne of material when compared to primary ores [125] (c.f. Figure 25). A typical FPD contains 86.52 wt% glasses, 12.81 wt% organic materials and 0.02 wt% indium [130].

FPDs

In reference [125], a very extensive review has been done on the current state-of-the-art processes that may enable in the future the roll-out of large-scale processes to recover indium from FPDs. In that research, 2 main examples of the potential recovery routes of indium from EoL FPDs are presented:

1. Vacuum-pyrolysis followed by vacuum-chlorination [130] (see Figure 27): The process has a recovery rate of indium of approximately 99.50%. Furthermore, all organic elements and glass of the FPD can be recovered in what is claimed as an eco-friendly way due to the almost complete recovery of the chlorinated agent. Vacuum-pyrolysis occurs at 573K at 50 Pa where 82.03% of the organic elements are converted either into oil (79.10 wt%) or gas (2.93 wt%). The separation of indium from the pyrolysis residues occurs through crushing (0.16mm) of the ITO glass followed by the mixing with solid ammonia chloride (NH_4Cl). This mixture is subject to a vacuum-chlorinated separation at 673K for 10 min at an atmosphere of 0.09 MPa and 50 wt% of ammonia chloride to ITO glass powder. The total duration of the process is ± 40 min. The resulting glass from the vacuum-chlorinated separation process can be further used for brick making or other fabricated products requiring such type of materials. In the lab-scale conducted experiment, 50 panels weighing 14,418 g yielded 1,460 g of oil, 54 g of gas, 331 g of organic residue and 12,477 g of ITO glass. The ITO glass chlorination yielded 5.55 g of indium. For this reaction, only 10 g of NH_4Cl were used due to the recycling of the NH_4Cl .
2. Leaching of non-crushed ITO glass with sulfuric acid: In another less destructive process, researchers have tried to keep intact most of the components of the FPD including the glass, the indium and the liquid crystals [131] (c.f. Figure 28 and Figure 27). Indium is leached from the ITO glass using sulfuric acid with the addition of manganese dioxide. This led to an indium recovery rate of 89 %, while after using organic solvents to pre-treat the FPD to remove glues. This process is rather lengthy and not much data exists on the performance of the process.

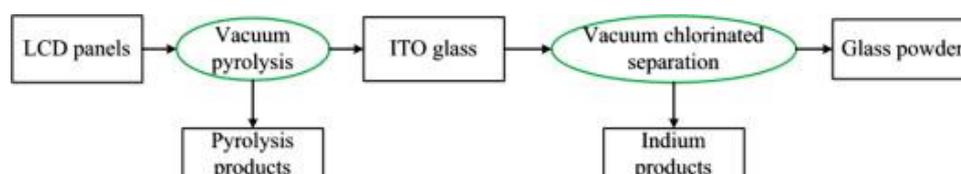


Figure 27 - Vacuum-pyrolysis & vacuum-chlorination flowsheet as proposed in [130].

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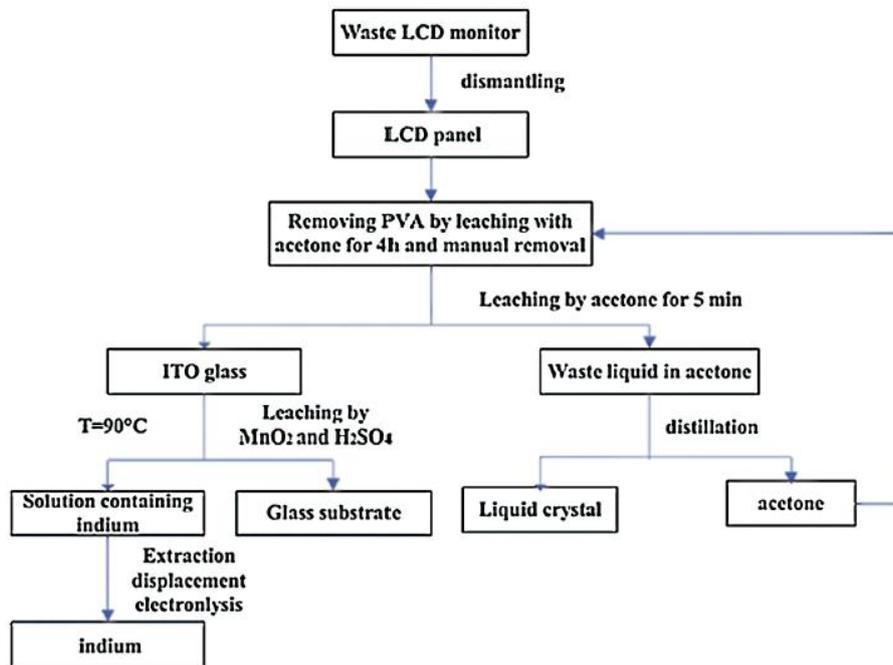


Figure 28 - Indium recovery from FPD flowsheet proposed in [131].

Despite the 2 methods mentioned before, it would be too extensive to make a detailed state-of-the-art of all lab-scale initiatives that have been performed to extract indium from FPDs. Reference [125] provides more detailed analysis on all types of recovery steps possible such as using different leaching agents and pre-treatments.

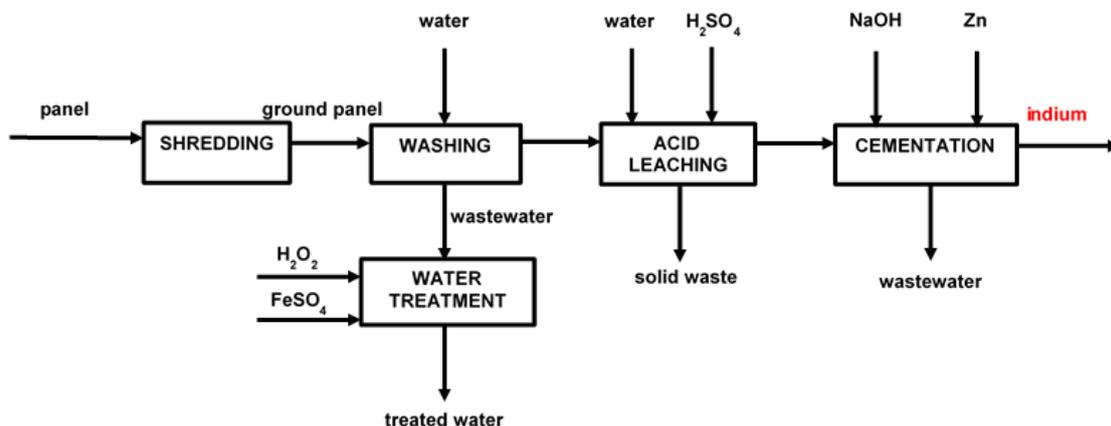


Figure 29 - Process flowsheet for the obtention of secondary indium from EoL FPDs. From [132].

In Europe, research has been conducted in the direction of using hydrometallurgy process to recover indium from EoL FPDs [133]. It is the first attempt to use a cementation process to the leached solution. In reference [133], a hydrometallurgy process is used where leaching with hydrochloric acid followed by zinc cementation is performed on EoL FPDs (c.f. Figure 29). During the cementation process, zinc concentration, pH and concentration times were

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modelled at a temperature of 55-60°C. It was found that at pH around 3 and zinc concentration of >5 g/l, indium recovery efficiencies were above 98 %. The researchers proposing this recovery route have also performed an LCA where the results will be discussed in the next section.

In 2009 in Austria, a trial was conducted to assess the economic feasibility of recycling FPDs [124]. This study took into consideration all the inherent costs of a non-automated recycling operation where disassembly of the FPDs was done manually. The goal was to assess the material yield from the waste heap and the time necessary for the disassembly of each FPD (TV screen, PC screen, etc). It was concluded that at the 2009 material prices, the operation would have a revenue of -4.3€/PC screens and 5.43€/TV screen. Thus, it pinpoints the importance of having automated processes in place where labor costs are very high [129] [134].

In a recent simulation to assess the recyclability of a smartphone [134], it was found that regardless of the recovery route applied to the EoL phase of the smartphone, indium could always be recovered from pyrometallurgy followed by hydrometallurgy. In this study it is also highlighted the importance of the pre-treatment phase to avoid contamination in the subsequent metallurgical processes.

Metal alloys and solder

In metal alloys, reference [123] points to the fact that due to dispersion of metal alloys in metal scrap, indium-containing alloys are lost either to the ferrous fraction or to the non-ferrous fraction in metal recycling. If selective separation would be performed, full recovery of indium could be done more efficiently. On the other hand, recovering indium from metal scrap requires facilities that are equipped to do so and that is not the case most of the times. In the case of metal scrap recycling, indium is mostly lost to slags or becoming a tramp element in different steel alloys [103].

4. LIFE CYCLE ASSESSMENT COMPARISON BETWEEN EXISTING AND INNOVATIVE TECHNOLOGIES

FPD

In reference [135], an LCA comparison is done on four different processing routes for EoL FPDs: (1) landfill, (2) incineration, (3) dismantling followed by partial recovery of FPD elements but not the ITO coated glass and (4) total recovery of the elements of the FPD including the indium content through leaching following by cementation. The recovery process of indium has been depicted in Figure 29.

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In terms of GHG emissions as an impact category, the results are shown in Figure 30 in terms of kgCO₂eq. It can be seen that processing route (3) results in lower GHG emissions when compared to full indium recovery. Nevertheless, in processing route (3) no indium is recovered and thus not relevant in terms of comparing indium recovering routes.

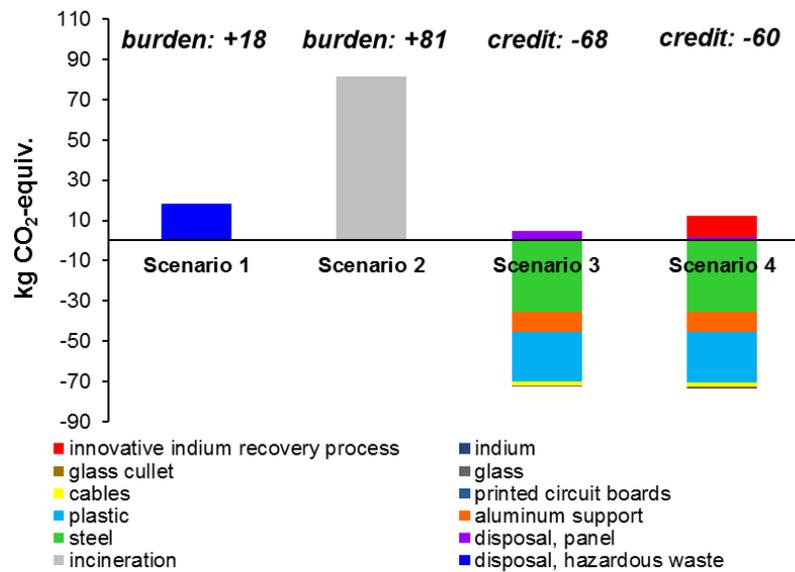


Figure 30 - GHG emissions from the 4 different processing routes. The functional unit is 100 kg of EoL FPD. From [132].

On the other hand, when looking at acidification as another impact category, the results were also similar with processing route (3) leading to smaller impacts. The researchers have identified the main bottleneck of the innovative processing route (4) as being the water/energy consumption during the wastewater treatment process of the residues of the leaching phase. Improvement of this phase with more recirculation would lead to better performance of (4) in terms of GHG emissions. Increasing recirculation would lead to a decrease in the leaching efficiency which would decrease the amount of indium recovered. Perhaps the use of ammonia chloride as done in [130] could lead to a significant decrease of the environmental impacts arising from the disposal of hydrochloric acid. In reference [130], an LCA study was not performed but the recycling of the reagent after the leaching process would certainly improve this negative impact.

Given the importance of the pre-treatment of FPDs for the downstream recovery of valuable elements, in reference [136] an LCA study was performed on two possible pre-treatment routes to be applied to FPDs: (1) crushing the FPDs followed by incineration plus acid leaching of the bottom residue and (2) electric disassembly followed by acid leaching. The scope of the LCA did not go beyond the leaching phase into the recovery of indium. It did include the product of hydrochloric acid which has been pointed before in this report as a major source of GHG emissions being one of the main concerns from the environmental impact of indium

recycling. On the other hand, the wastewater treatment phase required to safely dispose the reagents was not included in the study thus leaving a small research gap in that sense. The results from the LCA are shown in Figure 31 where it can be seen that electric disintegration has a clear advantage over conventional grinding followed by pyrolysis. The former has the potential to reduce environmental impacts by 70% in the case of GHG emissions.

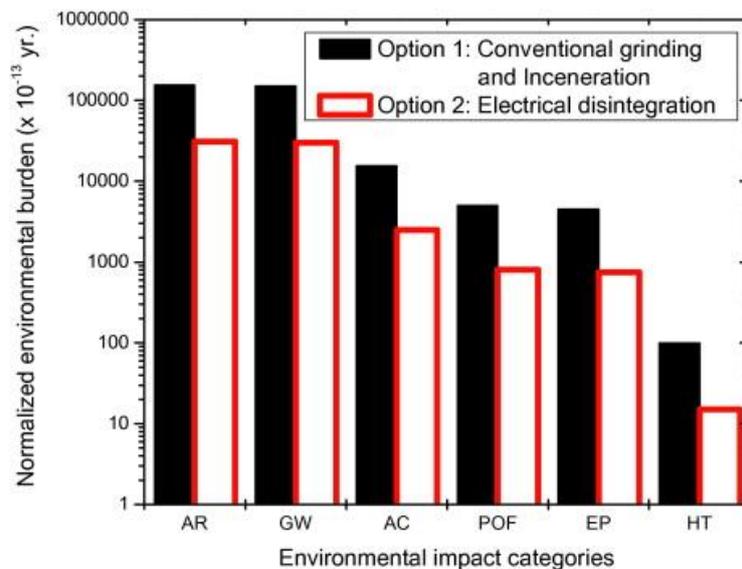


Figure 31 - Normalized environmental impact for all impact categories. AR is abiotic resources, GW is global warming potential, AC is acidification, POF is photo-oxidant formation, EP is eutrophication and HT is human toxicity. From [136].

The nature of the different functional units chosen by the researchers hampers a straightforward conclusion in terms of the “best” processing route based on available LCA data. In the first study, the scope of the analysis includes the environmental benefits of recycling plastics, steel, aluminium, etc., while in the second one, the best processing route is depicted without considering the environmental impact of recycling the other components of the FPD and of indium itself. From a LCA perspective it would have been interesting that the new indium recovery route proposed in reference [132] through cementation would have considered electric disassembly instead of crushing. As reported in reference [136], electric disassembly leads to lower environmental benefits when compared with crushing.

Despite the aforementioned nuances in the environmental pros and cons and scope constraints of the studies, a conclusion can be drawn on the environmental impacts of secondary indium production from FPDs.

To produce 1 kg of primary indium, an estimated 150 kgCO₂eq are needed according to 2008 data [137]. This includes cradle-to-gate data for the mining/concentration, purification and refining processes. By simple extrapolation from the data presented above in the indium cementation process, 100 kg of FPDs yielded 10 g of indium and accounting for ±10 kgCO₂eq.

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Following the same logic, to produce 1 kg of indium around 10,000 kg of EoL FPDs would be needed and the environmental impact related to climate change would amount to ± 1000 kgCO₂eq would be emitted. This is more than 6x when compared to the primary route. If the whole process is included, then the environmental benefit of recycling 10,000 kg of EoL FPDs would be -6,800 kgCO₂eq. While the cementation process leads to a positive environmental burden, considering all the components of the FPD and the subsequent benefits of recycling, it can be concluded that the supply of indium from this source would lead to environmental gains that can surmount the negative impact of the cementation process.

CIGS solar PV cells

An LCA has also been performed for the recovery of indium from CIGS solar PV cells using hydrochloric leaching from crushed CIGS cells. Two different processing routes are considered: (1) crushing followed by ethylene-vinyl acetate (EVA) incineration and subsequent landfilling and (2) crushing followed by ethylene-vinyl acetate (EVA) incineration and subsequent hydrometallurgical processes to recover indium and also gallium and selenium.

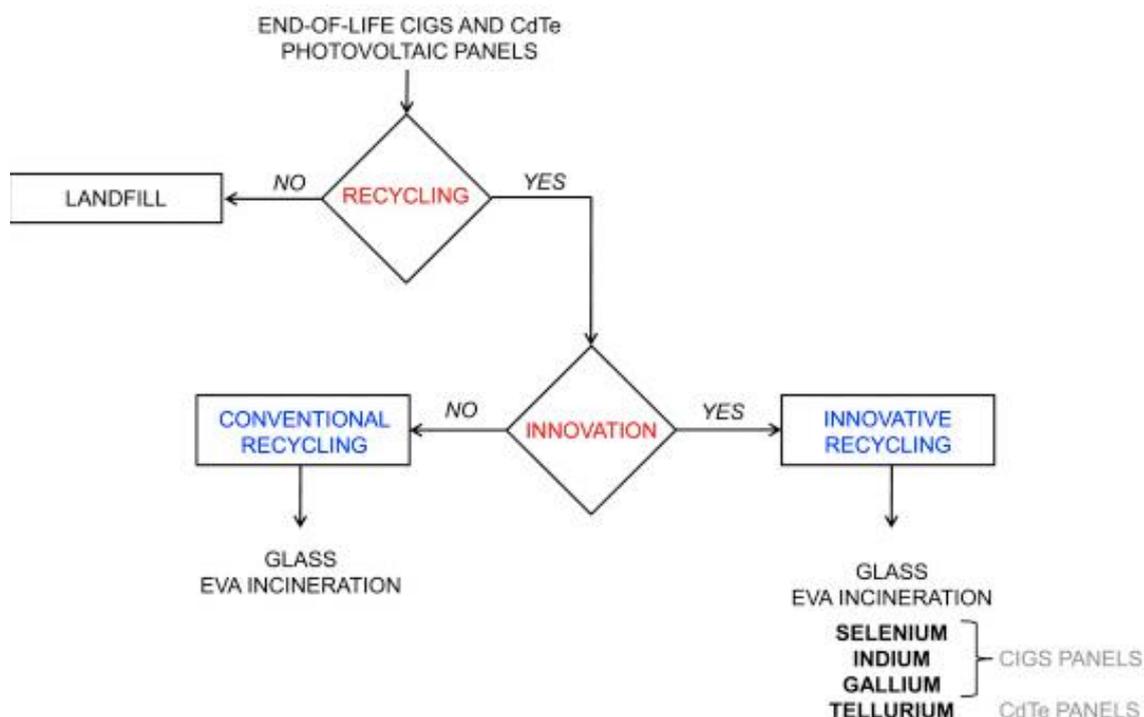


Figure 32 - CIGS solar PV cell incineration scenarios [135].

It was again observed that the reagents used for the innovative processing routes such as hydrochloric acid were responsible for offsetting the positive environmental impacts coming from recycling indium and other scarce metals. Detailed results of each impact category can be found in reference [135].

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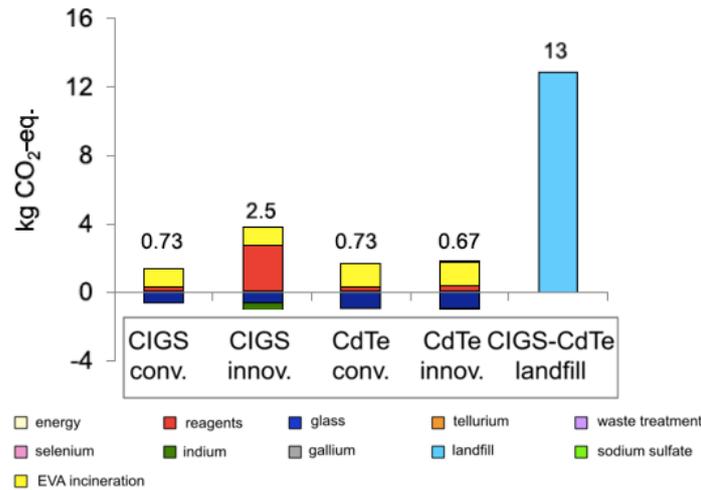


Figure 33 - GHG emissions from the EoL recovery routes for CIGS solar PV cells. Adapted from [135].

In Figure 33 it can be seen the reagent use and disposal followed by the incineration of EVA represent the highest source for GHG emissions. The large negative impacts associated with the use of reagents is in line with the LCA on the recovery of indium through cementation. This problem must be addressed in future research.

In Figure 34, a summary can be found of the weighed environmental impacts of the different processing routes. It can be seen that the innovative processing route (2) – *CIGS innovative* has more environmental impacts than processing route (1) – *CIGS conventional*. This is due to reagents used in the hydrometallurgical processes and subsequent energy needs. Increasing the concentration of indium in the EoL scrap could be a way to solve this discrepancy.

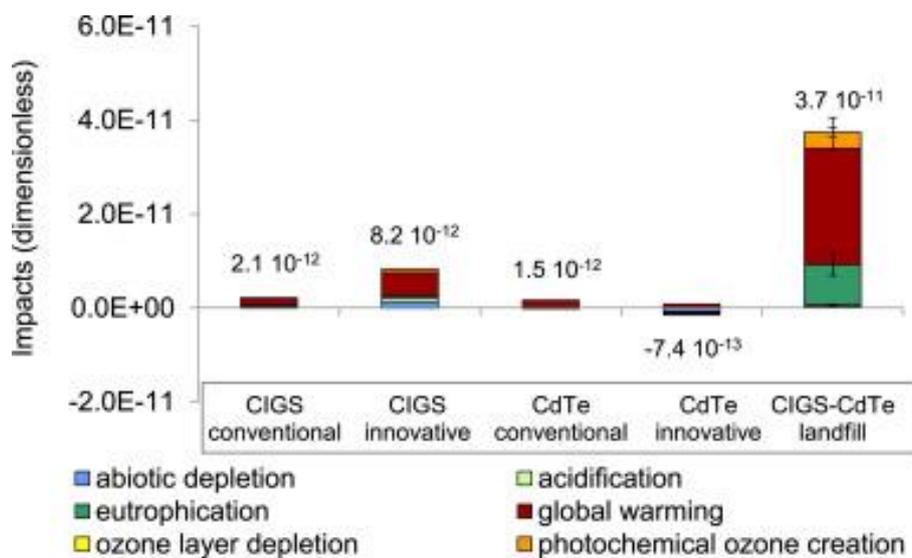


Figure 34 - Summary of the weighed environmental impacts of CIGS solar PV cell recycling.

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5. SUMMARY

Indium is largely available from EoL scraps and there is enough material in stock in society and in EoL material to close the gap of primary demand. Nevertheless, dispersion of the metal in a multitude of products combined with lack of policies aimed at the recovery of this metal causes it to be lost to landfills or as tramp element in metals recycling. New processing routes exist where indium could be recovered from its biggest application which are FPDs. This promising processing routes could supply secondary indium from this source of WEEE but require further analysis into the full life-cycle impacts of the use of different chemicals in the process of recovering indium. Combining the recovery efforts to gain more metals in the recycling operations and to have higher concentration of metal per tonne of WEEE may be a way to improve the environmental and economic performance of the recovery process. The market price of indium seems to be an important factor in the availability of secondary indium from hibernating stocks rich in refining/mining residues. In Europe, focus should be put on the recovery of secondary indium to use in domestic industries requiring refined indium. Such industries include PV and metallurgy as an example. Europe plays an important role as an exporter of refined indium in the current industrial landscape. Despite this position, further added value may come from prioritizing FPD recycling in an effort to reduce the reliance on foreign imported material.

MAGNESIUM

Main Authors: Daniele Mirabile Gattia, Tiziana Beltrani (ENEA)

Contributor: Giovanni Di Girolamo (ENEA)

1. THE SECONDARY RESOURCES

The use of Magnesium for technological and consumer applications has faced cyclic oscillations during decades. Magnesium has been largely used during Second World War for components of aircrafts and different producers were present in Europe.

The importance of Magnesium is strictly related to its properties, in particular mechanical and low density, 1.78 g/cm^3 . It is largely used for production of components in the following sectors: transport, steel industry and electronics, medical; moreover it is used as reducing agent for obtaining pure elements as Be, Hf, Ur, Zr and Ti from their metal halides. In the case of transport sector it is largely used in aircrafts, trains and automobiles, while it is used for the realization of chassis for notebook, tables and phones. In the steel production, which adsorbs the about the 15% of Magnesium consumption in the world, it is used as desulphurizing agent.

Magnesium can be produced by electrochemical processes and extracted by dolomite, magnesite and carnallite ore, sea water, brine. Magnesium concentration in seawater, dolomite and magnesite is 0.13%, 13% and 28% respectively. The Pidgeon process, a pyrometallurgical one based on silicothermic reduction of magnesium oxide, requires high quantity of energy (366 MJ/kg of Mg) and presents low efficiency, but its capital cost is competitive with respect to electrolytic processes [138].

According to EC reports, Magnesium is mainly produced and supplied by China which accounts for 87% global supply and 94% of supply to EU [6]. Up to now, important facilities for Magnesium production are located in China, Russia, Israele, Kazakhstan, Brazil and other countries (Figure 35). Norsk Hydro, from Norway, ended production in 2001, but the country is largely funding projects to reopen its plants. About 7388 tons of Mg were produced in 1992 in China, while by 2015 the production increased till about 852 ktons. Dead Sea Magnesium Ltd, which is a joint venture between Volkswagen and Israel Chemicals Ltd., produces Magnesium from sea water. Substantially in EU the upstream steps of the value chain are absent for Magnesium, not because of the absence of raw materials, rather because of hegemony of China in its production and recent drastic reduction of production plants in EU.

MAGNESIUM: ESTIMATED PRIMARY WORLD PRODUCTION, BY COUNTRY ^{1,2}						WORLD ANNUAL PRIMARY MAGNESIUM PRODUCTION CAPACITY, DECEMBER 31, 2015 ¹	
(Metric tons)-						(Metric tons)	
Country	2011	2012	2013	2014	2015	Country	Capacity
Brazil	16,000	16,000	16,000	16,000	15,000	Brazil	22,000
China	675,000	698,000	770,000	874,000	852,000 ³	China	1,600,000
Israel ²	26,300	27,300	27,400	26,000	19,300	India	900
Kazakhstan ⁴	21,400 ^r	21,200 ^r	13,000 ^r	9,500 ^r	8,100	Israel	34,000
Korea, Republic of	--	2,500	7,500	10,000	10,000	Kazakhstan	30,000
Malaysia	200 ³	-- ³	150	--	--	Korea, Republic of	10,000
Russia ⁴	58,000 ^r	65,000 ^r	66,000 ^r	62,000 ^r	60,000	Malaysia	15,000
Serbia	-- ^r	-- ^r	-- ^r	-- ^r	--	Russia	80,000
Turkey	--	--	--	--	200	Serbia	6,000
Ukraine ⁴	9,000 ^r	10,300 ^r	9,400 ^r	7,200 ^r	7,700	Turkey	15,000
United States	W	W	W	W	W	Ukraine	22,000
Total	806,000 ^r	840,000 ^r	909,000 ^r	1,000,000 ^r	972,000	United States	63,500
						Total	1,900,000

¹Revised. W Withheld to avoid disclosing company proprietary data; not included in -Total.- -- Zero.
²Totals and estimated data are rounded to no more than three significant digits; may not add to totals shown.
³Includes data available through October 4, 2016.
⁴Reported figure.
⁵Includes magnesium consumed for titanium sponge production.

Figure 35. Primary world production of Magnesium till 2015 [139]

Four new projects are going to be realized before 2020: Qinghai Salt Lake in China (100 ktpy), Alliance Magnesium in Canada (50ktpy by 2018), Latrobe in Australia (40 ktpy by mid2019) and SilMag in Norway (65ktpy in 2018) [140]. In Canada two projects considers to recover magnesium from Asbestos mine tailings and serpentine-bearing asbestos tailings. In Australia a feasibility study considers to recover 5k tpy of Magnesium from coal fly ash.

Considering that magnesium is largely imported from other countries in EU it should be taken into consideration the possibility of recycling it.

In Figure 36 magnesium recovered from scraps processed in USA in 2014 and 2015 are reported. The table considers mainly magnesium/aluminium alloys in the form of ingots, magnesium alloys castings and aluminium alloys

MAGNESIUM RECOVERED FROM SCRAP PROCESSED IN THE UNITED STATES, BY KIND OF SCRAP AND FORM OF RECOVERY ¹		
(Metric tons)		
	2014	2015
KIND OF SCRAP		
New:		
Magnesium-base	17.200	20.200
Aluminum-base	38.000 ^r	37.100
Total	55.200 ^r	57.400
Old:		
Magnesium-base	653	606
Aluminum-base	24.300 ^r	22.100
Total	25.000 ^r	22.700
Grand total	80.200 ^r	80.000
FORM OF RECOVERY		
Magnesium alloy ingot ²	W	W
Magnesium alloy castings	10.500	11.100
Aluminum alloys	68.900 ^r	67.300
Other ³	722 ^r	1.710
Total	80.200 ^r	80.000

¹Revised. W Withheld to avoid disclosing company proprietary data; included in "Other."
²Data are rounded to no more than three significant digits; may not add to totals shown.
³Includes secondary magnesium content of both secondary and primary alloy ingot.
⁴Includes chemical and other dissipative uses, cathodic protection, and data indicated by symbol W.

Figure 36. Data about Magnesium recovered from scrap processed in the USA in 2014 and 2015 [139].

In Table 1 potential secondary resources fluxes for Magnesium are reported.

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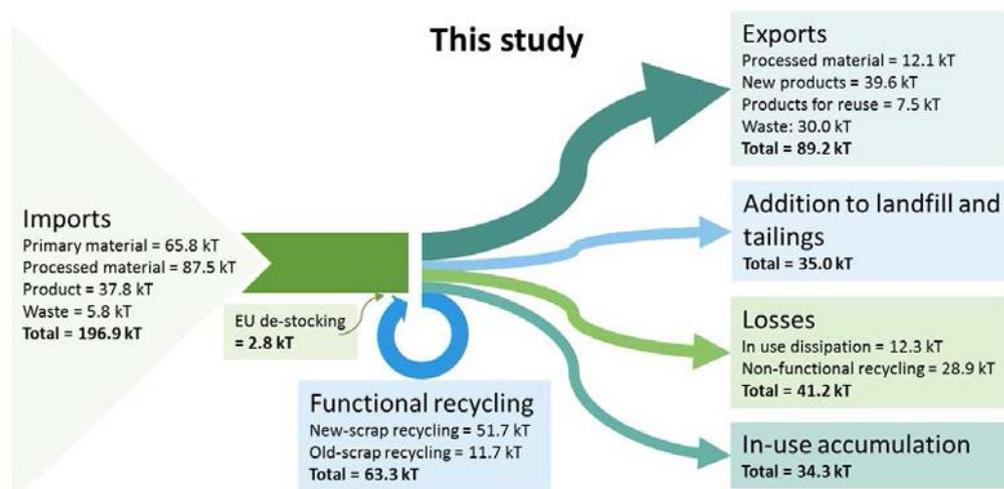
Table 10. The main potential magnesium secondary resources.

Secondary resources	Companies
Metallurgical wastes	
Slags from desulphurization processes	-
Mining	
Asbestos mine tailings and serpentine-bearing asbestos	MagOne Products Inc (Canada)
Process waste	
coal fly ash	Latrobe (Australia)
Processing	
Die casting processes	Generally in-situ scrap recovery
End of life products	
Dismantled components from ELV	-
Dismantled components from consumer goods (notebook, camera etc.)	-

One of the main use of magnesium is as alloying element in aluminium alloys to enhance mechanical properties, workability and corrosion resistance. The main products are for packaging, transport and construction sectors. Aluminium recycling plants can recover Al and its alloys. In this case Magnesium remains mainly as alloying element.

In Die casting processes of Magnesium a large number of scraps are produced, with properties comparable to as-produced primary material, which can be reintroduced in the production chain or addressed to other processes.

After the publication of European Commission’s material System Analysis (MSA) on CRMs the International Magnesium Association published a new report with some new indications on magnesium’s usage and end of life within the EU [141]. In Figure 37 a key output of the report, Sankey diagram of the inputs and end-fates of magnesium in EU, is reported.



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Figure 37. Sankey Diagram showing main results of the study performed in 2017 from the International Magnesium Association [142]

In this figure:

- ‘Old’ scrap refers to EoL, post-consumer scrap and ‘new’ scrap to the scrap generated in manufacturing processes which generally has a known composition and origin [143]
- In-use accumulation/de-accumulation refers to the change, either positive or negative respectively, in Mg stockpiled in products being used in the EU in a given year.

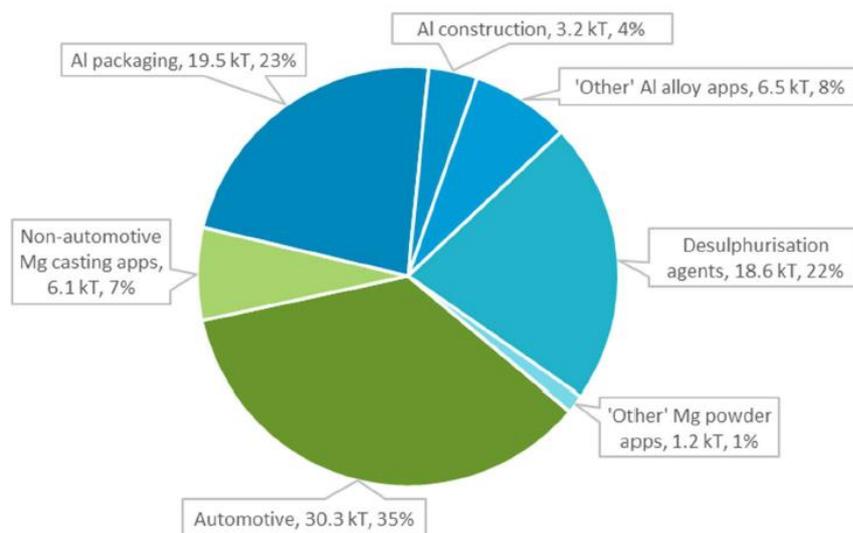
As reported in [142] an increase of the recycling rates of Magnesium could be obtained by improving collection from EoL Al-Mg alloys beverage cans and vehicles, correct sorting and diverting of alloys having Magnesium as base material, better slag utilization by the Al and steel industries.

The report of the International Magnesium Association suggests that the separation of ELV should be implemented in order to increase recovery of components and magnesium scrap diverting them to remelters, which retain magnesium in their input materials.

Secondary magnesium can be recovered from scraps in plants for ingots and castings production and in smelters by scraps of aluminium alloy.

In die casting process, which accounts for more than 30% of primary magnesium metal consumption, Hydro Magnesium [144] and Magnesium Elektron [145] defined a similar classification of scraps which considers mainly clean, sorted or dirty scraps, chips, and sludge.

Desulphurization of iron and steel represent another important fraction of magnesium consumption and mainly sludges are produced.



Note: No Mg available from EoL aerospace applications (nearly all exported for reuse) or nodular cast iron (where all Mg is dissipated in use).

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Figure 38. Magnesium available in EoL products in EU in 2012 [141].

In Figure 38 the amount of Magnesium available in EoL products in EU in 2012 is reported (from [141]) It is possible to observe how larger fractions come from the automotive, packaging and steel production sectors.

2. EXISTING PROCESSING ROUTES – GAPS & BARRIERS

2.1 MINING AND METALLURGICAL WASTES

During metallurgical smelting processes, as the production of steels, it is necessary to remove sulphur being it detrimental for the mechanical properties of steels and for compliance with specifications. The magnesium, which is added to molten iron, captures Sulphur forming magnesium sulphide which is collected from the surface. The magnesium used is mainly deriving from primary resources. Slags, containing magnesium, are generally not recovered probably due to transport costs. About 41% of slags from desulphurization processes are landfilled [141]. These slags, after suitable treatments, can be used for other applications, as building materials reducing the amount of natural resources and lowering environmental impacts of magnesium production processes [146].

2.2 SCRAPS

Actually Magnesium recycled derive from melting of pure scraps and eventually cleaned and sorted components. The process is affected by the presence of impurities as Fe, Co, Ni and Cu which in some cases cause an increase in the costs of the recycling process. For this reason large fractions of recovered magnesium are not recycled at all, differently in the case of aluminium secondary alloys, as for example A380, which is present on the market. If magnesium is obtained by remelting clean scrap the energy requirement is of 1 kWh/kg instead of 30-35 kWh/kg [147] [148].

Recycling methods of magnesium depend on the class of scraps to be processed. In the case of class 1, pure and clean scraps, two types of processes are present: flux-based and flux free refining. In the first case a largely used process is the batchwise recycling by use of salt. In the second furnace, Figure 39, molten magnesium is protected by covering gas [149]. This process presents some advantages as low cost of the equipment and even dirty scraps can be processed, but it is affected by impurities in the molten magnesium. Systems for continuous melting under flux have been realized by Hydro Magnesium. In the second case, flux-less refining, a salt flux is not used and a protective atmosphere is required.

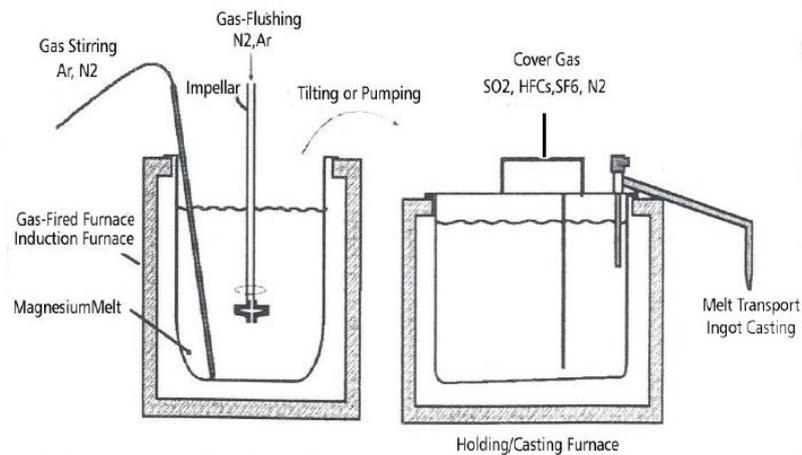


Figure 39. Flux refining process [150].

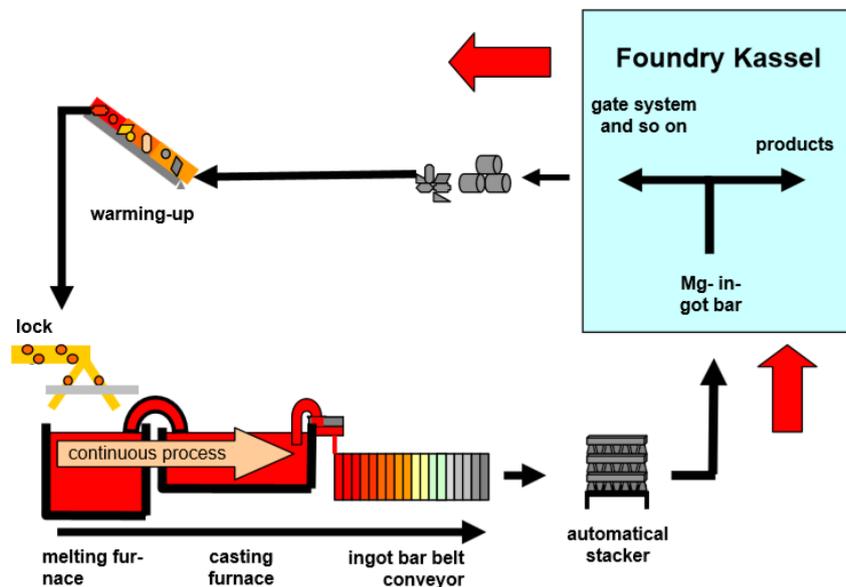


Figure 40. Volkswagen plant Kassel own recycling center is reported [149]

In Figure 40 the Volkswagen plant Kassel own recycling center is reported [151]. Scraps are recovered after pressure die-casting and the production plant realized its own magnesium secondary cycle.

3. INNOVATIVE PROCESSING ROUTES – GAPS & BARRIERS

3.1 MINING AND PROCESSING WASTES

As just reported before in Canada two projects considers to recover magnesium from Asbestos mine tailings and serpentine-bearing asbestos tailings. MagOne Products Inc declares that their process has a Carbon footprint (T CO₂eq/T Mg metal) (Excluding credits for by-product

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sale and improvement to raw goods sourcing) of 5-8, with respect to 26 and 18 of Pidgeon and Electrolysis processes [152].

In Australia a feasibility study considers to recover 5k tpy of Magnesium from coal fly ash using a combined hydromet/thermal reduction [153]. The fly ashes are a waste stream from brown coal power generation. The process considers to use chemicals to reduce S, Fe and Si to tolerable levels and to successively perform a thermal reduction process. The plant is expected to start operation within 2018.

3.2 SCRAPs AND DISMANTLED COMPONENTS

One of the problems related to Magnesium recovery is the presence of contamination, for example due to coatings or alloying elements. For example, in order to increase the mechanical properties and creep resistance of Magnesium, rare earths are largely used for alloying (Y, Ce, Ga, Er, Dy, La, Sc, Sm). The opportunity of recovering also these fractions from secondary resources should be taken into consideration when estimative costs of recovery and recycling plants have to be determined.

In other cases protective coatings on magnesium alloys are present. A patent from Fujitsu Ltd considers a method to remove coatings from coated magnesium alloys products, for example from casings of notebook (epoxy and acrylic resin). Moreover the inventors claimed the preparation of Mg alloy obtained from casings of notebooks [154].

Hyundai Motor Co owns a patent on an apparatus for recycling magnesium from scraps. The authors claim that the system remove impurities (as Fe, Ni, Cu, Si etc.) included in magnesium alloy scraps. The patent considers, in particular, scraps from die casting process [155].

Actually components made of magnesium alloys from ELV (generally class 8) are minimally recovered because of low quantity in vehicles as well as of time consuming and high costs for dismantling.

The increased application of Magnesium and its alloys in the automotive sector is driven, by the need to produce lightweight and more efficient vehicles with reduced emissions. The use of magnesium parts in vehicles is actually within few tens of kilograms on average (in many cases not higher than 10 kg), depending on the type of vehicle. In [156] the use of magnesium in vehicles produced by Hyundai and Kia Motors Corporation is reviewed. In these vehicles magnesium is used for different parts as seat frame, steering column housing, lock body, driver air bag housing and steering wheel core, which for 80% is made of magnesium alloy AM50A (Figure 41).

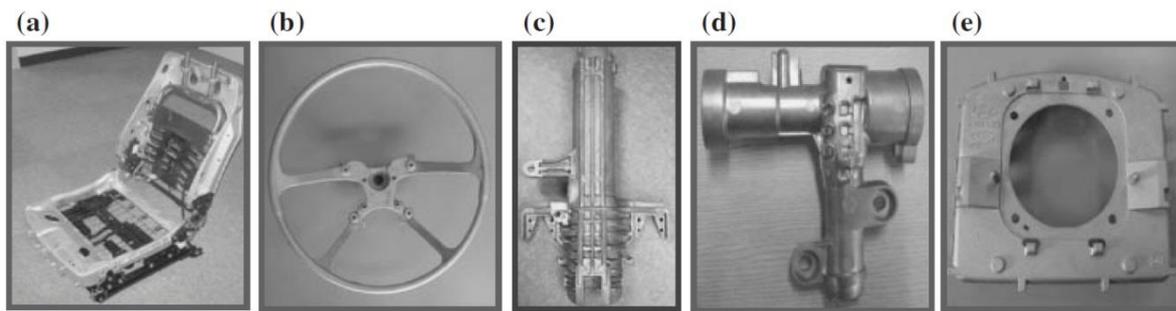


Figure 41. Magnesium interior parts in Hyundai and Kia motors corporation: (a) seat frame, (b) steering wheel core, (c) steering column housing, (d) lock body and (e) driver air-bag housing. Reprinted from [144]

Manual transmission case and engine head cover can be realized using AZ91D alloy. Rear seat back frame has been realized in AZ31 extruded alloy.

Even in aircraft the use of lightweight magnesium alloys is expected to be largely used in the next future [157].

As an increase of the use of Magnesium in transport sector is expected in the next future processes which consider the recovery not only of scraps but also of dismantled components have to be implemented.

An interesting and innovative approach is to consider alloy design in order to develop secondary magnesium alloys which is impurity tolerant with a composition between standard AZ and ZC systems. In fact for some alloys it's difficult to reach same specifications as primary magnesium, in particular for end-of-life components. These secondary alloys, contaminated with Ni or Cu, should present ductility and corrosion properties comparable to the high purity standard alloys [143].

4. LIFE CYCLE ASSESSMENT DATA

Cherubini et al. investigated the LCA of four production processes: Bolzano, Magnetherm, AM and Pidgeon, being the last one the worst in terms of emitted gases at the local scale and for the GWP and AP indicators. The authors consider obviously that recycling would be an opportunity in order to account for the increased demand for magnesium but also that it's not still implemented [158].

A Life cycle assessment comparison between the existing and the innovative techniques for the magnesium recovery by secondary resources is not feasible as there is a lack of raw available data in the second case. Innovative techniques have been tested only in laboratory scale for specific scrap materials. In [159], a LCA comparison is done on two different scenarios for the end-of-life of magnesium vehicle parts: 1) recycling of magnesium within the

aluminium cycle, 2) recovery of the magnesium itself for secondary magnesium alloys or for the steel industry. Figure 42 presents the results for the categories of global warming potential (GWP), eutrophication, acidification, and resource depletion. The energy consumption for the vehicle treatment is much lower than that for aluminium alloy processing. Thus, the potential environmental impacts of this process are significantly lower as well. Regarding GWP, the vehicle treatment contributes 4% of the overall emission of 3.8 Kg CO_{2eq}/Kg material. For the other categories, the contribution of the end-of-life vehicle treatment ranges from 2% to 7%. The dominant factor for all end-of-life processes is the energy consumption. Material consumption during aluminium alloy processing plays a minor part.

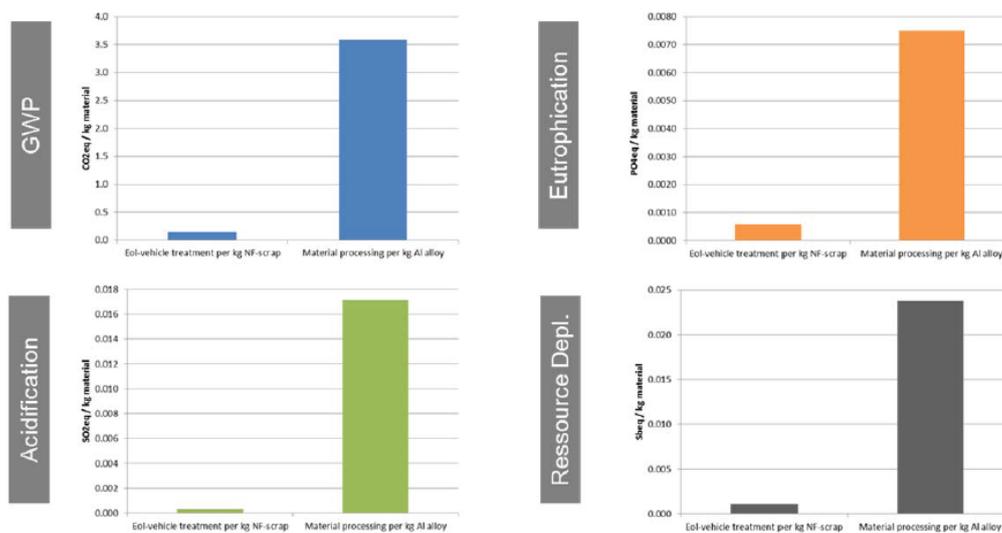


Figure 42. Results of the impact assessment for standard scenario [Ehrenberger and Friedrich 2013]

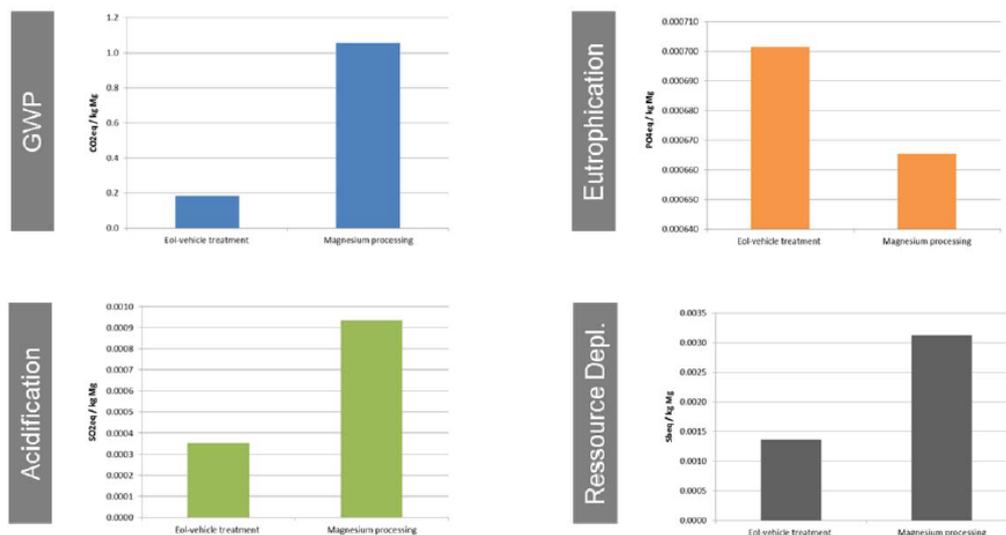


Figure 43: Results for impact assessment of alternative end-of-life scenario [Ehrenberger and Friedrich 2013]

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Figure 43 depicts the results for the impact categories of this scenario. Due to the lower energy consumption of the magnesium recovery process, the overall emissions and resource depletion are lower compared to the first scenario. The amount of greenhouse gas emissions in this case is 1.1 Kg CO_{2eq}/Kg material. This model is not generally applicable, as the data source for this scenario is only one plant. The treatment of the end-of-life vehicle is again of minor importance except for the eutrophication category.

Currently, the recycling of magnesium as an alloy additive within the aluminium life cycle can be seen as standard recycling path. The aluminium market potential is expected to be sufficiently high in the midterm to adsorb all of the end-of-life magnesium from the postconsumer scrap of transportation applications. As long as the economic restrictions and a lack of applications for secondary magnesium alloys exist, the recycling of magnesium as pure metal will not occur. Nevertheless, there are feasible technologies for material separation and secondary alloy production that would enable the establishment of a second market for magnesium.

5. SUMMARY

The 97% of magnesium EU demand is supplied from Chinese production. In the past different magnesium production facilities were present in Europe. On the other hand a large increase in the use of magnesium is expected in the next future, principally driven by the transport sector. For these reasons, recycling magnesium is strategic for EU and Mg is considered a critical raw material.

The Mg EoL-RIR (end-of-life recycling-input-rate, measuring the percentage of Mg coming from scrap in the total amount of Mg entering the EU) is only 7%, because of the dispersive nature of any magnesium applications, according to IMA, as well as of low efficient collection and recycling routes.

Suitable secondary sources of magnesium are first of all clean scrap from die-casting processes, while other classes of scraps could be sent to desulphurisation process in the steel industry. In many cases after sorting the scrap requires a cleaning process. Some plants for magnesium die-casting processing own a recycling center (Volkswagen). Shredded scrap from ELV belongs to class 8, which can be recycled with difficulty, but the expected increase of magnesium in transport sector and the directives on car recovery and recycling (target 85%) will probably facilitate the reduction of landfilled wastes containing magnesium. In 2012 the average content of magnesium in cars was about 4.1 kg. As reported by the International Magnesium Association, better dismantling procedures should be implemented for magnesium and aluminium alloys components and also implementation of collection of beverage cans (with average magnesium content of 1.6%).

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In Australia a feasibility study considers to recover 5k tpy of Magnesium from coal fly ash using a combined hydromet/thermal reduction. The fly ash are a waste stream from brown coal power generation. The process considers to use chemicals to reduce S, Fe and Si to tolerable levels and successively perform a thermal reduction process. The plant is expected to start operation within 2018. In Canada two projects considers to recover magnesium from Asbestos mine tailings and serpentine-bearing asbestos tailings, drastically reducing the carbon footprint respect to Pidgeon and Electrolysis processes.

An innovative approach, which could reduce gaps and barriers, considers to perform alloy design in order to evaluate secondary magnesium alloys, with composition comprised between AZ and ZC alloys, which are still tolerant to corrosion. Other approaches consider treatments to recover magnesium from EoL consumer products as chassis of notebooks, cameras, etc.

Relative Life Cycle Analyses, only one study has been found comparing the recycling of magnesium within the aluminium cycle from recovery of the magnesium itself for secondary magnesium alloys or for the steel industry. The results show the advantages of the second scenario compared to the first one, but further development and research are needed in waste management cycle.

NIOBIUM AND TANTALUM

1. THE SECONDARY RESOURCES

The secondary resources identified for Nb and Ta are:

- **Tin slags:** containing 4-12% of Nb₂O₅, the Nb production from Sn slags is estimated at less than 2% of total Nb production [160].
- **Mine tailings:** in EU, the biggest potential of mine waste dump is in North Macedonia and Greece. In mine wastes of North Macedonia, Nb is estimated at up to 313.3 tons, while 65.5 tons of Nb are estimated in mine wastes of Greece. In Sweden, waste tailings from Fe mines are potential secondary sources of Nb, being at 11.9 ppm. In Spain, Strategic Minerals are producing Ta and Nb in Penouta Mine since 2017.
- **Urban mines and manufacturing residues:** the biggest application of Nb is HSLA steel. EoL vehicles are the most important source of steel containing Nb, as their lifespan is relatively short. In stainless steel, Nb is at 0.04-0.08% [160].
- **Super alloys:** can contain 3-5,5% Nb (Nb₃Sn, NbTi superalloys) [160].
- **Capacitors with a Ta anode:** capacitor scrap is a mixture of metal Ta, its oxides, and manganese, in which the Ta content is higher than 90% [161].
- **Spent catalysts:** data of amounts spent on this application is missing. Recycling potential cannot be estimated [160].
- **Cemented carbide:** scrap from cemented carbide tool industries is made of alloy carbide WC-TaC-NbC. Carbide sludge can contain 5.6% Nb [160].
- **E-waste:** it is estimated that a computer can have 0.0002% Nb in the housing and welding alloy, which creates a potential of 1.2 tons of Nb from EoL computers in the EU [160].

2. EXISTING PROCESSING ROUTES – GAPS & BARRIERS

- **Tin slags and sludges**

To extract Nb from tin slags and sludges, one method is the chlorination of the raw material with carbon, which results in a condensate of oxychlorides and chlorides of Nb. At 1000 oC, the Nb extraction is 84%. Carbochlorination at 500°C results in complete recovery of the pure Nb compound [160]. Conventional methods for extracting Nb from tin slags consist of full dissolution with HF or H₂SO₄, or smelting in arc furnaces, **but these methods are limited by economic or environmental considerations.**

Also, the recovery of Nb from sludges is possible with direct dissolution in HF **but is difficult and not selected due to tungsten interference with the solvent extraction** [160]. **More selective methods are needed for Nb extraction from tin production sludges.**

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The common method to extract Ta from concentrates, Sn slags and scraps, is to digest the ore at high T in a sulfuric acid-HF mix and after filtering out the insoluble minerals, apply a solvent extraction with 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 KTaF by reaction with potassium fluoride [162]. **MIBK is the most commonly used extractant due to its high selectivity for Ta and Nb, low density and low viscosity, but is fire- and explosion-hazardous and readily soluble in aqueous solutions.**

- **Mine tailings**

Penouta Mine in Spain is developing a separation process to recover Sn, Ta and Nb from concentrate mineralisation (64.4% cassiterite, 21.5% columbo-tantalite and 8.7% of Nb and Ta oxides). The concentrate is reduced by a mix of coke and CaCO_3 in a gas oven at 1200°C . This process results in Sn concentrate (98.4% Sn) and in a slag where Nb and Ta are concentrated (25.5% Ta_2O_5 and 21.4% Nb_2O_5). This concentrate is leached in HF/ H_2SO_4 and after extracted by liquid-liquid extraction with commercial extractant Cyanex 923 [163]. **Commercial extractants are expensive, and maybe some studies with the use of solvometallurgy (ionic liquids and deep eutectic solvents) could maximise the selectivity and extraction. Deep eutectic solvents are also green and cheap solvents, and continuously more being developed for selective metal extraction.**

- **Urban mines and manufacturing residues**

Nb in residues from steel production is collected and directly re-melted into the production route. **One challenge is to pay attention to steel scrap composition during the recycling processes. A way to improve the Nb recovery is to implement a more accurate sorting system of steel scrap, depending on the material composition of alloying elements [160].**

- **Cemented carbide**

Nb from carbide sludge can be performed similarly to sludge from Sn plant.

- **E-wastes**

The EoL devices are collected for recycling issues. SoA recycling processes for printed circuit boards are based on pyrometallurgical approaches that focus on the Cu and precious metal recovery, and additional elements as Pb, As, In or Te can be recovered by integrated approaches. However, Ta is not recovered and ends up in the slag, being oxidised. **Due to the low Ta content, the extraction is uneconomically and energy intensive.** Recycling is established for new Ta capacitor scrap and concentrated slags, with recycling rates of 20-30%, but the **processes are unknown [164].**

- **Lump Ta wastes:**

The simple method to recycle them is by electron-beam melting to produce ingots, with the previous removal of surface contaminants with liquid Ca or Mg, and after dissolving in HCl [161].

- **Ta scraps:**

Can be processed into powders by hydrogenation or fluorination. Chemical dissolution and precipitation or electrochemistry can be used in the processing for creating Ta₂O₅. Also, the scraps can be subjected to chlorination, followed by distillation of TaCl₅ and reducing with hydrogen to Ta₂Cl₈. Nb is removed from the latter, which is chlorinated to TaCl₅ again, dissolved in alcohol with the formation of Ta alcohochloride, and hydrolyzed with carbon to produce high purity Ta₂O₅ [161].

- **Superalloys**

The alloy is subjected to anodic oxidation in the aqueous solution of organic compounds and salts for Ta recovery. Methanol, ethanol, isopropanol, and acetylacetone are used as the former. Halogenides, sulfates, and nitrates of alkali and alkali-earth metals are recommended as salt additives [161]. **This process requires the use of non-green and expensive solvents, that could be replaced with innovative green solvents. At present, it is only possible to recycle Ta alloy scrap into low-value Ta mill products [165].** In the case of Nb, **no waste collection by separate brands exists**, so a common technology was proposed by GIREDMET, consisting in the hydrogenation of the wastes and subsequent grinding, averaging, and sampling of the specimen for analysis. After, depending on the Nb content, the processing method is selected. For example, for samples >90 % Nb, electrolytic refining can be applied, as well as chlorination and hydrometallurgical processing. Also, wastes of Nb alloys can be processed into Nb alloys again, which is more effective [161].

- **Ta and Nb from capacitors**

Several technologies can be used to recover Ta from capacitor scraps: 1) cutting the capacitors with the isolation of Ta articles, 2) processing by: a) grinding the articles and their processing with obtaining Ta₂O₅, b) melting the pressed articles in a vacuum-arc or an electron-beam furnace with carbon. Regeneration of Ta from capacitor wastes can be performed by fluoride method at 450°C, obtaining TaF₅ which can be reduced (1000-2000°C) with oxygen. The final product is capacitor Ta powder [2]. High process temperatures require a **high cost of energy**. Also, for recycling Ta from capacitors, acid leaching to separate Ta from all other parts can be applied. MnO₂ content is transferred into water-soluble manganese chloride using HCl treatment [5].

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Separation of Nb from Ta using solvent extraction usually involves fluorides, since recovery of pure elements is very difficult without them. **Fluorides are toxic to the environment and expensive. Other issues connected with hydrometallurgical processing of Nb and Ta concentrates are large amounts of residues, loss of reagents, solid waste amounts over an order of magnitude higher than the useful product [1].**

3. INNOVATIVE PROCESSING ROUTES – GAPS & BARRIERS

- **Tin slags, sludges, mine tailings**

Turgis and coworkers have recently developed a method for L-L extraction of Ta (V) from a sulfuric acid solution containing also Nb, replacing MIBK extractant by task-specific hydrophobic ionic liquids based on piperidinium, imidazolium or pyridinium cations bearing ketone moieties. They obtained promising results, comparable to those with MIBK for the IL based on piperidium. Also, the [EPipMIBK][NTf₂] IL is stable over a wide electrochemical potential window, and no reduction of the ketone is observed, which opens the possibility to electrodeposition of Ta using such system [166]. **These are promising results, overcoming the environmental hazards of MIBK extractant. Upscaling of the process and testing in a real environment would be needed.**

- **Urban mines and manufacturing residues**

From EoL vehicles, a way to separate Nb is to separate exhaust part and suspension parts from the rest of ferrous metals. The steel for exhaust production contains 0.03-0.3% Nb. **There are no recovering methods now for Nb from EoL vehicles [160].**

- **Super alloys**

At the lab scale, one method of Nb recovery from NbTi residues was developed, including chlorination and electrochemical copper winning. Reprocessing of the superalloys can be performed in 3 ways: pyrometallurgy, hydrometallurgy or a combination of both. **There is no route specified for Nb. For extracting Nb, some organic solvents are used in industry as MIBK and cyclohexanone, or 2-octanol [160]. More research is needed as superalloys are an important source and they are usually recycled by re-melting. Recycling is difficult because many metals are present in the alloy, making the process expensive. The waste generated, use of fluorides and organic solvents are common problems.** Lessard *et al.* (2015) developed a new technology platform based on the iodization of Ta alloy scrap to produce volatile Ta iodides that can be condensed to form fine powders. These powders are after reduced with H in a plasma furnace to produce Ta metal powder with uniform particle size which can be used to fabricate capacitors [165].

- **Cemented carbide**

The new scheme was established including alkali leaching, acid leaching, soda ash roasting and aqueous processing, which resulted in 48 g/l Nb in solution. Nb was then recovered by precipitation with ammonia gas. Overall Nb recovery was estimated as 85-90% [160]

- **Spent catalysts**

No industrial recycling technologies are known [160].

- **E-waste**

Nb can be recovered from printed circuit boards scraps of discarded computers, where the content of Nb is 36 g/ton, by leaching column, which uses NaCN solution. 48.1% of Nb was recovered in solution, from where 98.2% of Nb was recovered with activated carbon. **Nb is not being recovered from e-waste due to very low concentrations and high costs, even though in Eu there are already collection and separation schemes in place dedicated to such waste [160]. Several raw materials extraction methods could be developed and thus the recovery would be cost-efficient, with also, for example, green cheap solvents to maximise the process economics.** The main application of Ta is in capacitors, as said before. Some innovations on Ta extraction from capacitor scraps is the heat and size screening developed by Fujita and co-workers in 2014. The different heat stabilities of the applied materials lead to a sequential separation, reaching Ta powder with 16%Ta, and recovering 70% of the existing Ta in the capacitor. **Full recovery is not possible yet, so research is needed in this field [167] [164].**

- **Capacitors**

Mineta and Okabe (2005) developed a method based on oxidation treatment at elevated temperature followed by mechanical separation and chemical treatment to recycle Ta from capacitor scraps, and they reached a Ta powder with 99% purity, by magnesiothermic reduction of the obtained Ta oxide powder [168]. **Environmental pollution is caused if the organics of capacitors wastes are not properly disposed of. The recycling of the organics is important for recovering valuable parts.** This way, Niu *et al.* (2017) developed a method to recycle the organics based on Ar pyrolysis. The organics were decomposed and converted into oils and gases, which were reused as energy sources [169].

In **MSP-REFRAM H2020 project, the technological gaps of Ta and Nb recovery from secondary sources were studied.** The results were that although being available several innovative processes, most of them are not tested on a pilot scale. In some cases, the information on the 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 for 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 the specific application.
- Environmental issues are associated with the use of HF and fluorides; therefore, alternatives should be desirable.
- The extraction leads to the generation of substantial solid wastes.
- Ta can be easily get oxidized and is therefore often lost in slags

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 the 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 [162] [170].
- Upscaling of potential results of at lab scale.

In the case of solvent extraction, there are some opportunities as the use of Ionic Liquids, which have no evidence in the literature about its use for separation of Nb and Ta, although some research regarding their individual electro-deposition from ILs has been developed [171].

4. LIFE CYCLE ASSESSMENT COMPARISON BETWEEN EXISTING AND INNOVATIVE TECHNOLOGIES

Tantalum

A Life Cycle Assessment (LCA) of Ta primary and secondary production was performed in MSP-REFRAM H2020 EU project (Deliverable 3.4) [172]. Results for primary production are based in the previous paper called “Life Cycle Assessment of Metals: A Scientific Synthesis [173]”, which reported the results shown in Figure 1 for Ta considering a cradle to gate approach of Ta primary production. The Ta secondary production study in which LCA was based was a tin slag-processing flow diagram consisting in the following steps: 1) Comminution process, 2) Pyro and hydrometallurgy upgrading of ground concentrate to synthetic concentrate, 3) Solvent extraction and separation of Ta₂O₅ and 4) reduction of melting for producing metallic Ta and its purification.

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Impact category	Value	Units	Consideration
Global warming potential	260	Kg CO ₂ eq / kg	Medium impact
Cumulative energy demand	4,360	MJ eq / kg	Medium impact
Terrestrial acidification	1.7	Kg SO ₂ eq / kg	Medium impact
Freshwater eutrophication	1.5 E-01	Kg P eq / kg	Medium impact
Human toxicity	1.2 E-04	CTUh/kg	Medium impact

Figure 44 Ta environmental data from [173]

A comparison between primary and secondary sources LCA, from MSP-REFRAM project Deliverable 3.4 [172], is shown in figures 2-4.

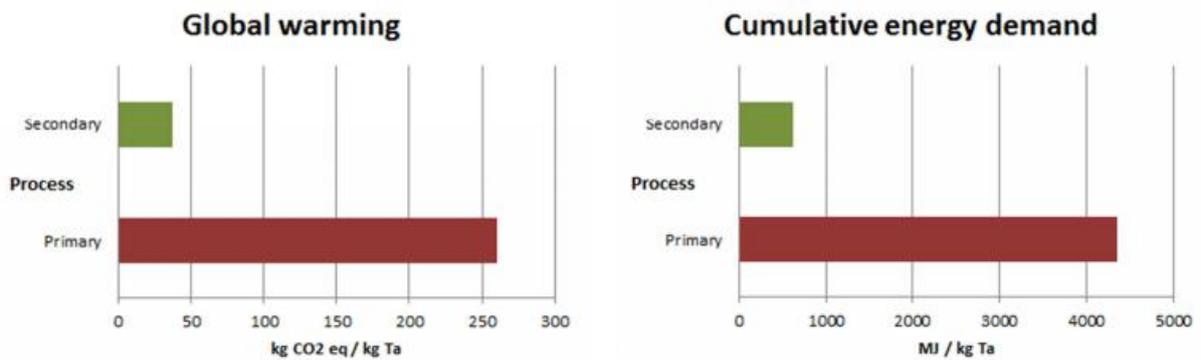


Figure 45 Global warming (left) and cumulative energy demand (right) of Ta primary and secondary production processes

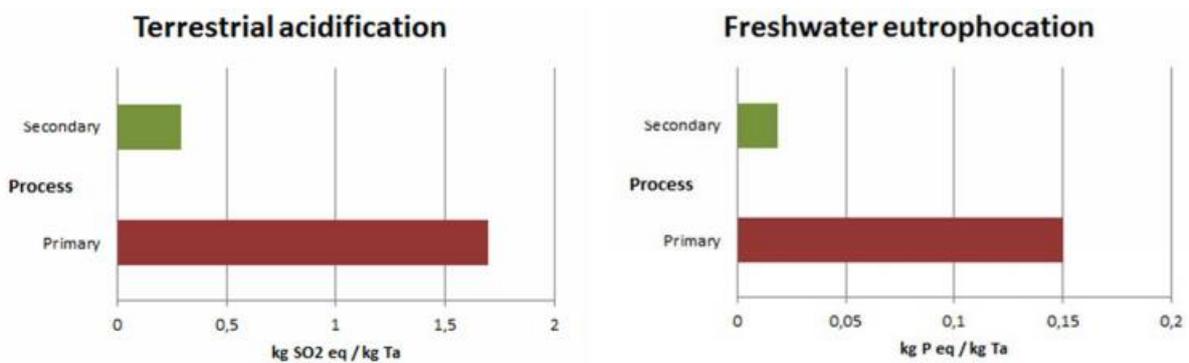


Figure 46 Terrestrial acidification (right) and freshwater eutrophication (right) of Ta primary and secondary production processes

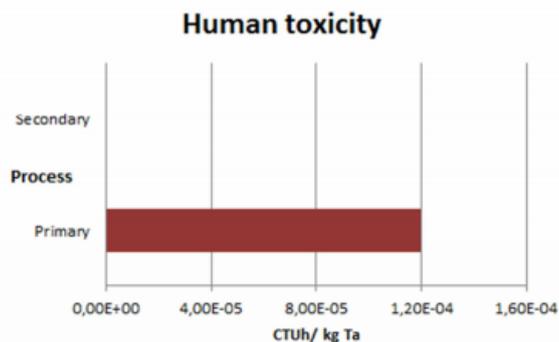


Figure 47 Human toxicity of primary and secondary production of Ta

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For all the environmental impact categories, there is an important difference between primary and secondary Ta production processes impact. In the first four indicators, the recovery process implies 15 % of the environmental impacts of the primary process, while human toxicity is even lower. As waste management was not considered in the study, the objective is that waste management does not exceed the difference between processes impacts. **Further development and research are needed in the waste management. The recovery process studied offers a good opportunity for recycling in terms of the environmental impact. However, this is not a general tendency, and each process for extracting Ta from secondary sources should be studied with the LCA to obtain specific data and make conclusions for taking decisions.**

Niobium

No studies about LCA applied to Nb secondary production have been found. D3.4 of MSP-REFRAM show a comparison (Fig. 5) of environmental results for refractory metals primary production based on the article from Nuss *et al.* (2014). Nb is the metal with lower impact to global warming, low impact in cumulative energy demand in comparison with Ta and Re, the lowest impact to terrestrial acidification and human toxicity, and low impact to freshwater eutrophication.

Impact category	Ta	Re	W	Nb	Mo
Global warming potential (kg CO ₂ eq / kg)	260	450	12.6	12.5	5.7
Cumulative energy demand (MJ eq / kg)	4,360	9,040	133	172	117
Terrestrial acidification (kg SO ₂ eq / kg)	1.7	11	0.29	0.053	0.16
Freshwater eutrophication (kg P eq / kg)	1.5E-01	3.5E+01	9.3E-6	3.7E-03	0.54
Human toxicity (CTUh/kg)	1.2E-04	5.9E-02	3.4E-05	6.4E-06	9 E-04

Figure 48 Refractory metals environmental comparison

5. SUMMARY

There is a high potential for producing Ta and Nb in EU from secondary sources. Main Ta application is in capacitors, which is present in the electronic end of life devices, and main Nb application is in steels, which are produced and used in EU different companies and sectors. These are only some examples of the available Nb and Ta secondary sources.

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Technology exists for recover Nb and Ta from tin slags and sludges, mine tailings, urban mines and manufacturing residues, cemented carbides, lump Ta wastes, Ta scraps, super alloys and capacitors, but research is needed to make the processes more environmentally friendly and cost-efficient. In this line, there are many innovations which propose new methods, but all of them at laboratory scale. There is a need of novel processes upscaling and demonstration in an industry environment, and still the development of new specific and selective solvents replacing HF and fluorides, and novel extractants to make the processes greener and inexpensive.

With regards to life cycle analysis, here a favourable analysis for secondary extraction is presented, but prior to considering a new method for Ta and Nb recovery from secondary sources, an LCA should be performed considering the specific application and method.

NATURAL GRAPHITE

THE SECONDARY RESOURCES

As described in D4.1, different streams of secondary resources of natural graphite were mapped as middlings/tailings, manufacturing residuals and end-of-life products (mainly including products for refractories, foundries, brake linings and batteries).

GAPS & BARRIES – PROPOSED PROCESSING ROUTES

MIDDLEINGS/TAILINGS AND MANUFACTURING RESIDUALS

Middlings and tailings which contain natural graphite, they can be hardly used to extract the natural graphite. This is due to the fact that further beneficiation by, for example, comminution, could downsize the graphite flake and thus decrease the economic value of the extracted graphite. It was reported that the graphite tailing can be potentially used to produce concrete; [174] The manufacturing residuals are normally recycled in-house during the manufacturing processes of different graphite-bearing products.

END-OF-LIFE PRODUCTS

According to D4.1, refractory and battery are two sectors that use a large quantity of natural graphite. Therefore, the spent refractories and batteries are two resources with high potential of graphite recycling. However, at present the recycling of graphite from these spent materials are very limited.

Graphite recycling from spent refractory

Graphite is often found in basic refractories, combined with magnesia, alumina or spinel. Among these refractories, MgO-C refractories used in the EAF is of high interest for recycling; this is due to the relatively cleanness of this type of spent refractory in combination with the relatively short lifespan of EAF linings (in the order of weeks). The recycling of spent refractory can be classified into three aspects.

- (i) Recycling of graphite-containing spent refractory as slag former. Due to the presence of C and MgO, the spent refractory after crushing can be used as slag former or conditioner in the EAF steelmaking process. The lab-scale trials in the induction furnace and the full scale trials in the EAF have shown the benefits of using spent MgO-C refractory. However, the particle size, feeding rate, addition amount should be

- controlled. [175] [176] The recycling of graphite in this way is the simplest and avoids the costly landfilling of this waste material; however, the graphite is not recycled.
- (ii) Recycling of graphite-containing spent refractory as new refractory products. By careful sorting, cleaning, crushing/grinding, the spent MgO-C refractory can be used to produce new MgO-C refractory bricks. In the literature, it was demonstrated that the remanufactured bricks containing up to 30% recycled spent refractory has almost identical properties as low-grade MgO-C bricks [177] [178] [179] or Al₂O₃-C-SiC bricks [180]. Recycling of the spent refractory in this aspect is deemed as higher value recycling; however, this recycling method is quite limited, being estimated at only 7% of refractory raw material demand. The challenge for recycling refractory in this method lies in the difficulty of separating spent refractory by type and grade, and the contamination of refractories during the service makes it difficult to meet the high-quality demands for refractory raw materials. Further, the state-of-art in the recycling industry is manual sorting, which is highly error-prone and requires a priori knowledge. This limits the amounts of the well-sorted spent refractory available in the market. Automated sorting according to the type and grade of the spent refractory may enlarge the recycling rate and quality of the refractory; however, this requires future development. [177]
- (iii) Recycling graphite-containing spent refractory as graphite and base refractory materials. [181] In one study it is demonstrated that magnesia and graphite in the spent MgO-C refractory can be separated by mineral processing method. The separated graphite concentrate contains 85.42% carbon and 5.60% magnesia; while, the separated magnesia concentrate contains 95.70% magnesia and 1.60% carbon. Recycling of the spent refractory in this aspect is of highest value, as the graphite and magnesia were separated and could thus be used for producing high-grade refractory or for other applications. However, the recycling process at moment is not cost-effective and the recycled materials cannot compete with the virgin materials in the aspects of quality and price.

Graphite recycling from spent batteries

Due to the rapid growth demands of lithium-ion batteries, a lot of spent Li-ion batteries is expected to be generated in the future. Nowadays, several Li-ion battery recycling processes are being developed and the graphite recycling is included in the recycling process. The recycling methods in general can be classified as pyro-metallurgical process, hydro-metallurgical process and direct recycling physical process. The characteristics of the recycling process are summarized in Table 11.

Table 11. Classification, characteristics and status of graphite recycling process [9].

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Recycling process	Pyrometallurgical	Hydrometallurgical	Direct physical
Temperature	High	Low	Low
Materials recovered	Ni, Co, Li, Mn, Fe, Zn in alloy	Metal salts, Li ₂ CO ₃ or LiOH	Cathode, anode, electrolyte, metals
Graphite recycling status	Used as reducing agent or burned as energy source	Graphite can be separated if pre-mechanical separation is applied	Recovers potentially high-quality graphite

In the pyro-metallurgical process, the battery materials are normally processed in a smelting furnace, during which the graphite were either burnt or used as reducing agent. Therefore, no graphite from the batteries is recycled in this process. In the hydro-metallurgical process the Li-ion batteries are normally processed firstly by mechanical crushing and separation; then the active materials fraction is subjected to leaching to extract the Co, Ni, Mn, Li, etc. There is no commercial activity showing that graphite or carbon can be recovered by hydro-metallurgical process. However, it is demonstrated that a magnetic separation in the hydro-processing process (shown in Figure 49) can be used to separate the graphite from active materials in the Li-ion batteries. This process may produce highly pure electrode active metallic components and graphite with unaffected particle sizes and crystallography during the separation process. Due to lower economic value of graphite compared to Co, Ni, Mn, Li, etc. materials in the Li-ion batteries as well as the high recycling/refining cost, graphite in the hydro-metallurgical processing process is often taken as residue, which may be reused in lower quality applications. The direct physical process is designed for the recovery of battery grade materials for reusing in new LIBs production with little or no additional modification. The process involves multiple physical and chemical processes with a low temperature and energy requirement to separate battery components. This process can recover all active materials and metals, including graphite. The direct recycling process is limited by processing the batteries with known chemistry. Further, in order to reuse the recovered materials in new batteries, extra purification or reactivating steps maybe necessary. Nowadays, this process is not commercialized yet. [182]

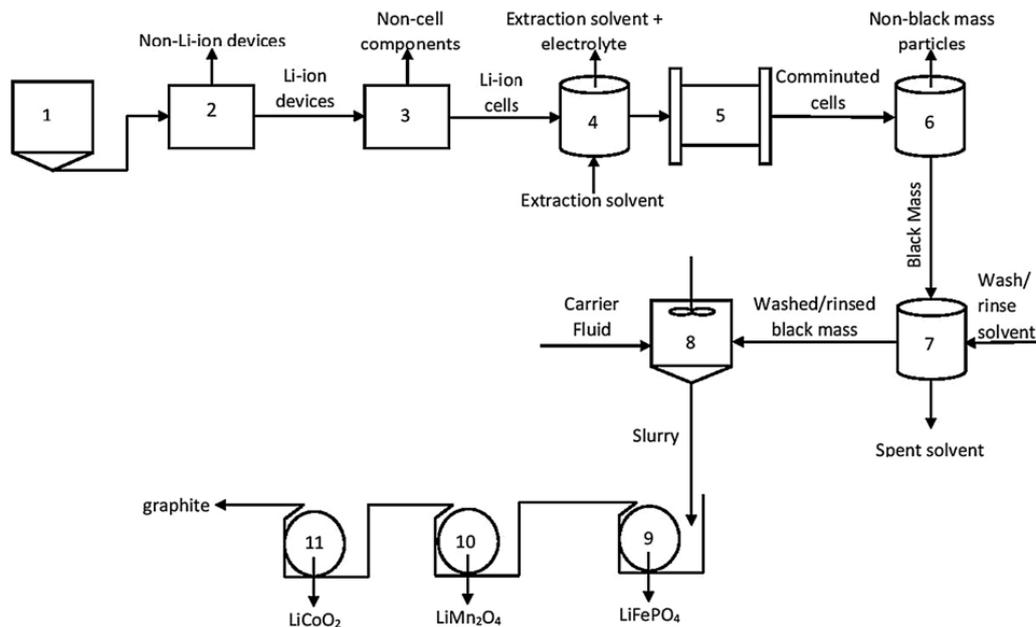


Figure 49. Cell recycle process using a staged magnetic separation of electrode active materials by increasing magnetic field intensities. [181] [183] [181] [183]

SUMMARY

Graphite-containing refractory (especially the MgO-C refractory) and Li-ion battery are identified as two sources of secondary graphite, which possess high recycling potential. With respect to graphite-containing refractory, there exist technologies to recycle the graphite-containing refractory as slag former, as product and even as separated graphite. However, due to the difficulties of sorting and cleaning the spent refractory, the recycling rate of graphite at moment is still very low. With respect to Li-ion batteries, different recycling technologies are being developed with focus mainly on the valuable materials (Co, Ni, Mn, Li, etc.); graphite can be recycled as well, however, there is no economic recycling/refining process or the economic incentive for recycling is low.

PLATINUM GROUP METALS (PGMS)

1. THE SECONDARY RESOURCES

Platinum group metals (PGMs) have an important catalytic properties. In addition, platinum metals have natural beauty, making it a valuable jewelry in many parts of the world. The automotive industry is expected to strongly influence the future demand of PGM, while the demand for platinum jewelry is expected to grow significantly in major Asian economies, particularly in China. The platinum-metals in applications should also increase in parallel with the growth of the global economy. PGM recovery from urban mines is very attractive activity for both academic and industrial sectors, because of their concentration in different devices from urban mines. Typically, concentration is more than 1000 ppm, which is 100 times higher than natural ores and high prices. Europe already has a very strong position in recycling and refining of PGMs with major industrial players: Umicore, BASF chemical company, Johnson Matthey and Boliden.

Precious metals in e-waste:

Most PGMs can be found in PCB scrap, mobile phone scrap, spent. Theirs concentrations in WEEE are around 10 g/t – 10 kg/t, accounting for 40%–70% of the total economic value of this waste [184]

PGMs in scrap automobile catalytic converters:

According to [185], the automobile industry sector consumes more PGMs (Pt, Pd, and Rh), and the demands from this industry account for 35%–60% Pt and Pd, and about 95% Rh. These three precious metals are mostly used in automobile catalytic converters.

Figure 50 shows the flow of PGMs in the recycling circuit. It shows that the PGMs can be extracted from different by-products from mining waste until secondary products from industrial applications, automotive and other applications such as electronics.

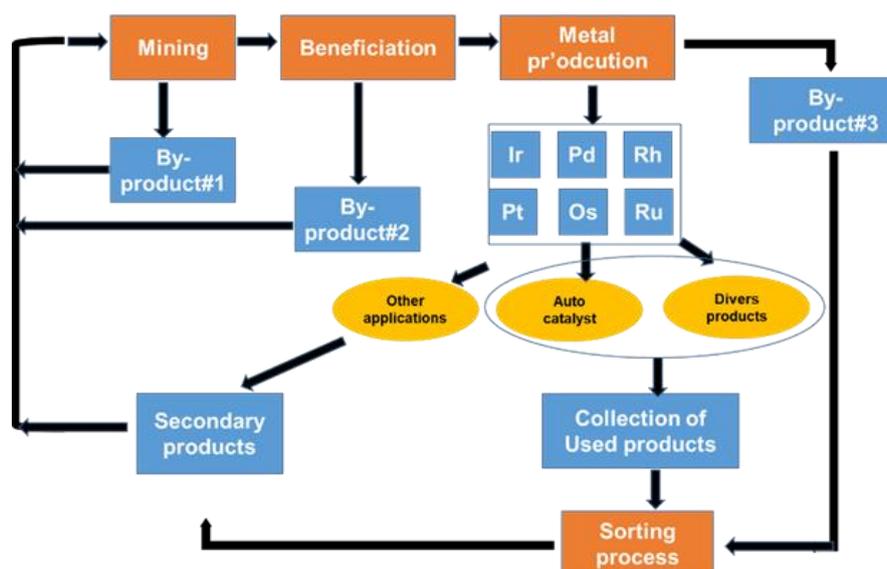


Figure 50. PGM Flow stream in recycling circuit

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MINING AND METALLURGICAL WASTES

The Rare Precious Metals (RPMS) may present in certain tailings, smelting slag, dusts from metal smelting furnaces and spent furnace refractory lining [186]. For example, some precious metals can be extracted from flotation tailing of polymetallic sulfides. The steel slag contains oxide phases bearing PMs, and mostly are landfilled because the recycling of these metals is not economically feasible. The accumulation of their huge volume make a serious problem for the environment and it is considered as a neglected source of RPMS. Several National and European projects focusing on PGM recovery from mining and metallurgical wastes are going on.

2. EXISTING PROCESSING ROUTES – GAPS & BARRIERS

The automotive industry will use more PGMs in the future and will have an impact on the PGMs demand, while jewelry demand for platinum is expected to see significant growth among the key economies of Asia, such as China. The price of PGMs attracts economic actors to fully, recover them from the equipment containing these metals. The PGMs are effectively recycled from the end-of-life products because of their high prices. Except in some cases where their quantity is very small. In recent years, their recycling has contributed to the supply of the platinum market. The overall recycling rate is in the order of 60% - 70% for Pt and less for Rh. The United Nations Environment Program (UNEP) published in 2011 an estimate of the recycling rates of PGM from the end-of-life products (Table 12) [187].

Table 12. Estimated recycling rates of PGM in EOL products ([187])

Recycling rates from	Pt	Pd	Rh	Ru	Ir
Automobile catalyts	50-55%	50-55%	45-50%		
Jewellery	90-100%	90-100%	45-50%		
WEEE	0-5%	5-10%	5-10%	0-5%	
dental applications	15-20%	15-20%			
Industrial applications	80-90%	80-90%	80-90%	40-50%	40-50%
Other applications (medical, laboratories,...)	10-20%	15-20%	30-50%	0-5%	5-10%
Global recycling rate from EOL products	60-70%	60-70%	65-60%	5-15%	20-30%

As new technologies based on the catalytic properties of PGMs, such as fuel cells, will be increasingly used around the world. The demand for PGMs recycled is expected to continue to increase in the coming years, According to the European Commission (2010), the recycling rate of PGMs of automotive catalyts in Europe is less than 50%. This is due to certain catalyts that are not collected in Europe (older cars exported to Africa). In order to improve the recycling rate of the PGMs resulting from the catalyts, it is necessary to increase the collection rate to bring the catalytic converters back into the recycling circuits, with a growth rate of 5% per year, this maximum rate of supply, recycling will fall to 56% [188]. According to Graedel et

al, [187], the recycling of PGMs from jewellery (90-100%) has no impact on the market compared to that of automotive catalysts

Table 13. Conventional technologies of PGM recovery from urban mines

Technologies	Operation units
Mechanical/physical	Manual disassembly, crushing, sorting, pre-processing phase in the process of PGMs recovery from wastes.
Pyro-metallurgical	Includes mainly high-temperature incineration, vacuum carbo-thermal reduction and chlorination volatilization
High-temperature incineration	The Precious metals are recovered from residues and obtained with electrolytic or fire refining Using this technique, Umicore recover PMs Ag, Au, Pt, Pd, Rh, Ru, Ir, and the In, Se, and Te from WEEE.
Vacuum carbon-thermal reduction	Reduction of the RPM oxides to metals with reducing agents under high-temperature conditions (1000°C for 30 min).
Chlorination volatilization	Uses chlorinating agents to form metal chlorides at moderate temperatures. This technology is very expensive and it is not suitable for small and medium-sized enterprises.
Hydrometallurgical technology	Includes upgrading of metal content by mechanical-physical pre-treatment, extracting, and refining to recover the RPMs by pyro-/hydro/bio-metallurgical methods. Innovative hydrometallurgical technologies have been developed, in the past decades, to solve the problem of equipment corrosion and environmental pollution. These technologies were gradually applied in industry for the recovery of RPMs from urban mines.
Dissolution and leaching	Aqua regia and cyanide leaching are efficient methods but produce toxic fumes and cause an environmental problem. The substituted agents are: halide, thiourea, and thiosulfate. Organic oxalate, succinic acid oxalic acid were tested and compared with strong inorganic H ₂ SO ₄ acid, HCl and HNO ₃ weak organic acids in order to reduce the environmental loads under the same conditions of high leaching rates and efficiency
Separation/purification	Solvent extraction (mature technology), adsorption on activated carbon, ion exchange, precipitation, cementation, and electrolysis were developed to purify ionic form of RPMs in the solution. For example, Pd was extracted from leaching solution by diisoamyl sulfide (S201). Recovery of 99.5% Pd (II).
Bio-metallurgical	It is an alternative process to recover RPMs from urban mines and includes two main approaches: bioleaching and bio-sorption.
Bioleaching	Chromobacterium violaceum (C. violaceum) has been widely applied for RPM recovery from e-waste. The potential of microbial mobilization of metals as cyanide compound from solid materials is a novel type of bio-cyanidation that might find industrial application.

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Bio-sorption	Several bio-sorbents (microorganisms, algae, bacteria, yeasts, fungi, and even bio-waste materials) have been developed to accumulate RPMs efficiently. This technology is the most environmentally friendly.
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Figure 51 show the flowsheet of rare and precious metals recovery from electrical waste and spent catalysts using traditional process

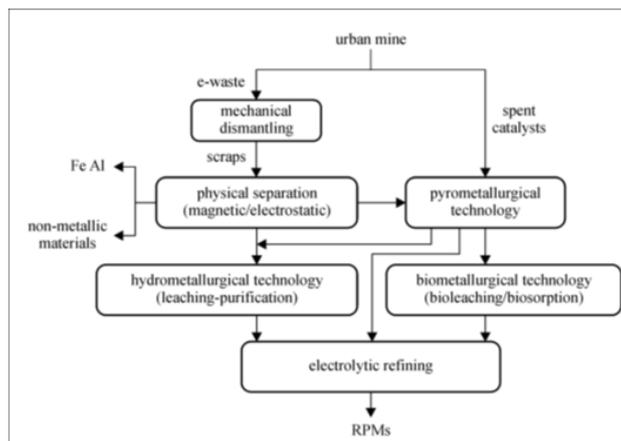


Figure 51. Flowsheet of conventional process of recovering rare and precious metals from e-waste and spent catalysts [189]

3. INNOVATIVE PROCESSING ROUTES – GAPS & BARRIERS

Several innovative processes were mentioned in the literature, and most of them are tested on laboratory scale. It is needed to improve their maturity which is missing. It needs more research on these innovative processing routes, where the techno-economic analysis often lacking, and it is difficult to compare the potential benefits of new processes with the current industrial processes. The innovative processes are shown in Table 14

Barriers in current processing are:

- Dispersion of PGMs in heterogeneity industrial wastes
- Non-selective leaching resulting in large amounts of impurities also being dissolved
- Environmental issues are associated to the use of toxic acids, therefore alternatives should be desirable
- Generation of substantial solid wastes during extraction of PGMs technologies that must be taken in consideration.

Table 14. Innovative technologies of PGM recovery from urban mines

Technologies	Operation units
Electrochemical	It is an alternative technology to recover RPMs from urban mines. This process may use less chemical input to leach RPMs and recover them on a cathode for further processing. This technology offers a fast and ecological way to recover RPMs from waste.

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Supercritical fluid (SC)	This technology has been introduced in the last decade in order to destroy organic parts in e-waste and to recover RPMs. SC based on increasing temperature and pressure to the supercritical point. The combination of supercritical water oxidation (SCWO) and Sc-CO ₂ may extract 93.7% of the Pd and 96.4% of the Ag from E-waste.
Mechano-chemical	This technology deals with physico-chemical transformation of materials by mechanical forces (shear, impact and squeezing) in ball mill. Several reagents has been used with wastes in ball mill to transform metals in soluble form for further step. Using this technique, the recovery rate of RPMs from wastes could be significant higher than with conventional hydrometallurgical methods.
Ionic liquid	It is an alternative technique to conventional organic solvents. This technique is mainly applied in separation methods. It is recently applied for extraction of RPMs. In literature, it is found that by using Ionic liquid containing nitrile functional group; Ag and Pd were efficient selectively extracted from water. However, the ionic liquids are more expensive than conventional solvents

4. LIFE CYCLE ASSESSMENT DATA

Generally, it is a difficult issue to obtain a precise information on the recovery of the PGMs out of the Catalytic Converters' scrap, because the manufacturers generally keep the information on the complete composition of their products as confidential, and the contents of the PGMs, vary from product to product and from model to model [190]. Some LCA studies have been conducted to compare the recovery methods of PGMs (pyro metallurgy and hydrometallurgy) from the point of view of environmental impact. The study was not completely achieved because of LCA data which are confidential.

5. SUMMARY

PGMs are efficiently recovered from our end-of-life products and this reassures us for the future. The systems developed for this efficient recycling make it possible to minimize the use of the natural resource of metals and to guarantee the secure sufficient supply of strategic metals for future generations. It also allows stabilizing metal prices and limiting environmental impacts.

Several electronic devices in urban mines contain a variety of valuable RPM resources. As urban mines contain very high concentration of RPMs, these wastes may considered as renewable resources. In past decades, the extensive research was performed and applications were developed on RPMs recovery from urban mines. Pyrometallurgical method was the most applied technology to recovery PGMs from e-wastes (Boliden, Umicore, Aurubis). Hydrometallurgical method has more advantages; however, it presents several challenges from environment point view. The bio-metallurgical process is the most promising

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technologies for bioleaching of RPMs in e-wastes. Because of the complexity of urban mines, all processes developed to, completely, recover PGM are not achieved.

The combination of the described processes is the best way to develop a process that will allow the full recovery of PGM from urban mines in the future. The most attractive process is the flexible process capable of recovering PGM from different waste matrices.

PHOSPHOROUS – PHOSPHATE ROCK

1. THE SECONDARY RESOURCES

Phosphate rocks supply one of the most vital components to the production of fertilizers, phosphorous. The importance of fertilizers for modern agriculture cannot be overstated, and despite the broad range of countries with suitable geology for phosphate production, supply is threatened in a growing world. Due to the nature of its main uses, phosphates and phosphate rocks cannot be recycled yet, however, alternative uses of waste streams from biological/vegetable sources may become increasingly functional. Potential secondary sources for phosphorous are individuated in animal feed, fertilizer and feed and food additives, particularly from sewage sludge, incineration ash, meat and bone meal ash.

The following sections are based on deliverable D4.2 and D4.3 by SCRREEN [191] [192]

2. EXISTING PROCESSING ROUTES – GAPS & BARRIERS

2.1 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. [193] Some studies suggest that phosphorus is even more available for plants in manure than in an NPK fertilizer. [194] 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 odor 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. [193]

In Europe, manure is almost entirely applied to agricultural land either directly or as a fertilizer 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 fertilization is balanced in a way that crops are able to utilize residual phosphorus from the soil. [195]

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. [193]

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 generate electricity.

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Anaerobic digestion does not consume the nutrients in manure leaving 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. [193]

Ash from the incineration of poultry manure is already demonstrated to function as an effective fertilizer (P, K) and, according to ESPP (2015) [196], is currently used in Europe. The commercial processes or the resulting fertilizer 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.

2.2 SLAUGHTERHOUSE WASTE

Slaughterhouse waste is another waste stream rich in phosphorus [193]. Bone shred contains even around 100 g P/kg [197]. 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. [193] However, in 2001, restrictions on MBM use for animal feed were made due to the fact that MBM was 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. [193]

Several techniques have been developed for phosphorus extraction from animal by-products or its ash [193], 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 fertilizer. [198]; [199]
- 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, fertilizer and oleo chemical industries. [200]

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

2.3 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. [201]

In the EU, around 90 million tons of food waste annually [193] is formed of the losses in the following steps of the food processing chain [202]:

- 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. [203]

In several other countries there is a room for a significant improvement in the collecting of biowaste. [204] 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 [193].

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 optimized with the extraction of metals. [201]

2.4 WASTEWATER

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. [193] It has also been estimated that the municipal wastewater in European countries contain approximately 1 kg of phosphorus per capita per year. [205] 30% of phosphorus in wastewater was recycled globally by the end of the twentieth century. [193]

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. [205]

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. [193] 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. [205]

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 52.

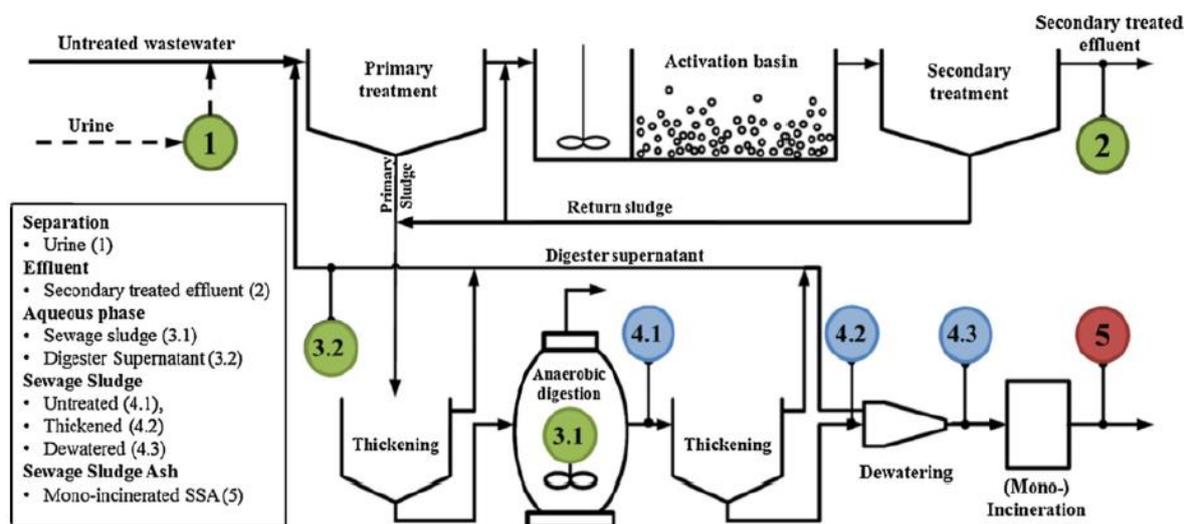


Figure 52. Access points for phosphorus recovery during the wastewater and sewage sludge treatment [205]

Access point 1, urine diversion 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 to agriculture could be, in general, 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. [193]

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. [205]

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In cases where direct recycling of either sewage sludge, access points 3 to 4, 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 [193] Some experimental and commercial technologies, developed for this purpose, are reported in section “*innovative processing routes*” of this report.

2.5 METALLURGICAL AND INDUSTRIAL WASTES

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. [193] 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. [206]

The dephosphorization of steel slag has been intensively investigated; however, the research on the recovery of phosphorus from the slag is limited [207]. Literature does not acknowledge any commercial processes for the phosphorus recovery from steelmaking slags, but studies have been conducted, including [207].

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. [206]

Matsubae et al. (2016) have estimated that the amount of phosphorus lost through steelmaking slags totaled 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. [206]

OTHER INDUSTRIAL WASTES

Industrial chemical processes, such as producing ethanol, also use large amounts of phosphoric acid, which acts as a catalyst. According to [193], the recovery of phosphorus from

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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. [193]

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. [193]

3. INNOVATIVE PROCESSING ROUTES – GAPS & BARRIERS

Withers et al. (2015) [208] proposed the 5R strategy intended to close the phosphorus cycle in Europe. The five Rs are: Realign P inputs, Reduce P losses to waters, Recycle P in bioresources, Recover P from waste, and finally if necessary Redefine our food system.

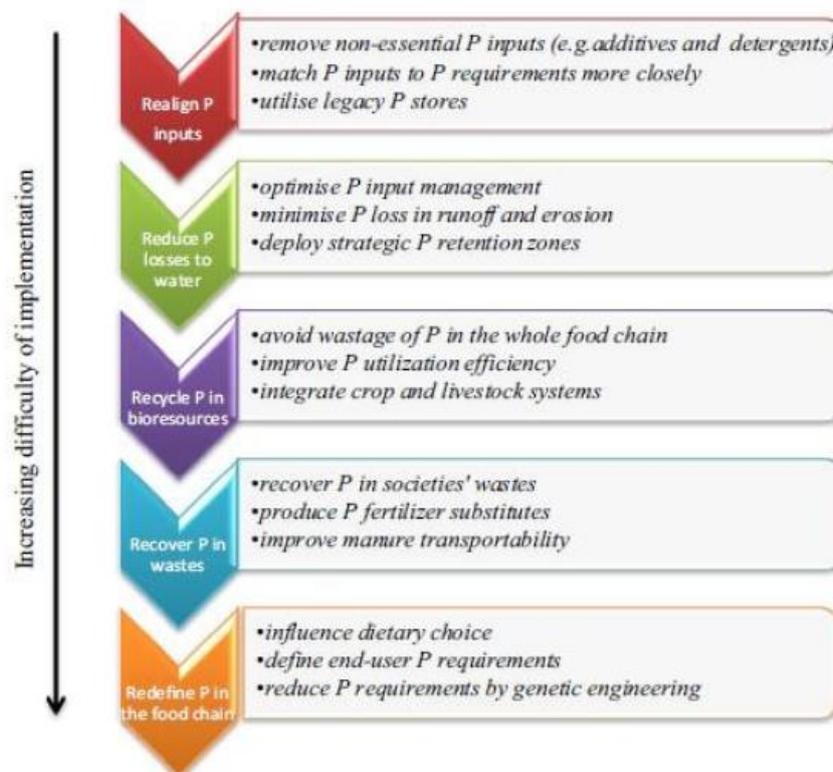


Figure 53. The 5R strategies to reduce Europe's dependency on phosphate rock-derived P [208]

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A guide for decision-making relatively to phosphorous recovery and reuse is presented in [209]. In this paper it is pointed out the importance of taking a broad approach which involves all systems, instead of focusing on specific technologies which could turn out to be an ineffective money and energy inversion.

3.1 MANURE

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. [210]

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 [199] and [211]

3.2 MUNICIPAL SOLID WASTE AND FOOD WASTE

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 biofertilizer. 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. [212]; [213]

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. [214]; [211]

3.3 WASTEWATER

In table 15, an overview of some technologies developed for recovering phosphorus from wastewater, divided by their working principle and their technological maturity, are presented. The ones marked with * were studied in EU project P-REX. [215].

Table 15. Overview of some technologies developed for recovering phosphorus from wastewater [215].

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

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	Anphos			
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 [216].

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. [217]; [199]

3.4 METALLURGICAL AND INDUSTRIAL WASTES

STEELMAKING SLAGS

In [207] a study is presented about the recycling of phosphorous from P-bearing slag. The presented technic involves SiO₂, Al₂O₃ and TiO₂ melting modification of converter slag and phosphorus-rich phase extraction by magnetic separation. The addition of such compounds produced an increase in P₂O₅ content in non-magnetic substances and phosphorous recovery rate. Such recovery rate using SiO₂, Al₂O₃ and TiO₂ modifications resulted, respectively, 84.75%, 82.16% and 74.46%.

OTHER INDUSTRIAL WASTES

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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. [218]

Solid phosphoric acid (SPA) catalysts are widely used also in the petroleum industry. Van der Merwe (2010) [219] 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.

4. LIFE CYCLE ASSESSMENT DATA

Phosphorus is lost (1 550kt/ year of P content) to the environment due to dissipative use or to landfill. Secondary materials flow results mostly from post-consumer recycling (around 180 kt/year of P content). Losses of phosphorus occur along the whole phosphorus chain in all stages including mining losses, losses due to soil erosion, crop losses as well as food losses. In the waste sector losses occur e.g. when phosphorus-rich materials end up in landfill or in sewage sludge. Further losses can occur if manure is not used appropriately for crop production. Accumulation of phosphorus in agricultural soils is also one factor causing the losses. [220] [221]

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

There are both direct and indirect environmental impacts of phosphorus use resulting from the consumption of resources (such as water, energy, phosphate rock), mismanagement and the generation of waste either in large volumes or with high toxicity, which can in turn pollute receiving environments and damage ecosystems.

Environmental impact of phosphate tends to concentrate two aspects. Firstly, there are localized impacts during the mining and processing of phosphate rock (such as water pollution). Secondly, ecological impact of phosphorus leakage from agricultural soils to aquatic ecosystems. Phosphorus lost from the recycling chain is not only a question of resource efficiency, but also an environmental issue in the regions where it exists in excess. In aquatic ecosystems, excess phosphorus loads can lead to eutrophication that results in oxygen-depleted conditions, where economically important fishes and other aquatic organisms cannot survive. Also drinking water supplies are endangered when algal bloom, deriving nutrition from excess phosphorus, release a toxic substance called algal toxin. [221]

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5. SUMMARY

The main secondary sources of phosphorous can be found in manure, slaughterhouse waste, municipal solid waste and food waste, wastewater, steelmaking slag and other industrial waste. The main issue involved in the manure reutilization as a fertilizer is the excess of phosphorous that can derive from its application with consequent water contamination, as well as the risk of spreading pathogens present in the manure. Relatively to the slaughterhouse waste, there is few data available relative to the waste stream, but it has been proved that significant phosphorous recovery can be obtained from animal's bones. Municipal solid waste and food waste could represent a significant source of phosphorous from secondary production, due to the big amount of such waste produced yearly. Currently, most of the biowaste in Europe ends up in land fill, although a bio treatment, involving composting or anaerobic digestion could provide significant nutrients recovery and energy generation. Wastewater represent, probably, the most important secondary source of phosphorous, since it contains 2% of the world phosphorous production. Nowadays the removal of phosphorous from wastewater is good developed, reaching 70-80% of phosphorous removal. Another secondary source has been individuated in steelmaking slag, particularly from iron and coal. Since a significant production corresponds to such industry, the same can be assumed about the residues produced, thus the significance of such source for phosphorous recovery. Unfortunately, according to the literature, there is no commercial active process to recover phosphorous from steelmaking slag. Several methods and technologies have been studied and the technological advances will allow to have the technological means to recover more and more phosphorous, nevertheless, it is important to adopt a broad policies approach, taking into account all systems, so to coordinate the efforts made toward a global phosphorous security.

REE - EUROPIUM, GADOLINIUM, TERBIUM

1. THE SECONDARY RESOURCES

The secondary resources of europium, gadolinium and terbium in EU member states are presented in Table 16. There are no available data concerning the content (and the potential recovery) of Eu, Gd and Tb in mining and metallurgical residues. The concentration of these elements in specific solid industrial residues such as phosphogypsum and red mud should be further investigated. The recovery of Eu, Gd and Tb from end-of-life fluorescent lamps is technologically feasible and has been achieved commercially for a short time in Europe.

Table 16. The main cobalt secondary resources in EU [222] [223].

Secondary resources	Process scale
Metallurgical wastes (Eu-Gd-Tb)	
No referred data	No referred data
Urban mining - Eu	
Fluorescent lamps	Commercial scale by Solvay plant in La Rochelle (activating until 2016)
PVs, lighting and electronic wastes	RECLAIM project
Urban mining - Gd	
Fluorescent lamps	Commercial scale by Solvay plant in La Rochelle (activating until 2016)
Permanent magnets	
Urban mining - Tb	
Fluorescent lamps	Commercial scale by Solvay plant in La Rochelle (activating until 2016)

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

2. EXISTING PROCESSING ROUTES – GAPS & BARRIERS

2.1 MINING AND METALLURGICAL WASTES

There are no sufficient data concerning the existence and the potential recycling of mining and metallurgical residues containing notable concentrations of Eu, Gd and Tb in the EU.

2.2 SCRAPS

Solvay Company (former Rhodia) was operating in the sector of end of life fluorescent lamps recycling until 2016. The chemical separation plant was installed in La Rochelle, France. The recycling activities were interrupted due to the REEs price decreasing. Solvay had developed a flow sheet for the recovery of REES (Eu, Gd and Tb among them) from a mixture of halophosphate and REE phosphors. According to the patent for the process, the final yield of REEs was about 80%. The processing capacity was of 3,000 tonnes of lamp waste/year, which corresponded to the forecasted European waste production for 2020. The final commercial products of Solvay Company, through a sequence of physical and chemical processes (Figure 54), consist of REO oxides mixture, glass (by-product) and phosphates (by-product) [222].

The main barrier concerning the sustainable recycling of fluorescent end-of-life lamps is not technological and it is related with the small supply amounts of scrap. Despite the socio-economic benefits of lamps recycling, some recyclers continue to see the small amount of the collected end-of-life material as a significant barrier and prefer the small cost of landfilling. In the following section, the most significant technological gaps barriers that have been found out through the research experience are mentioned.

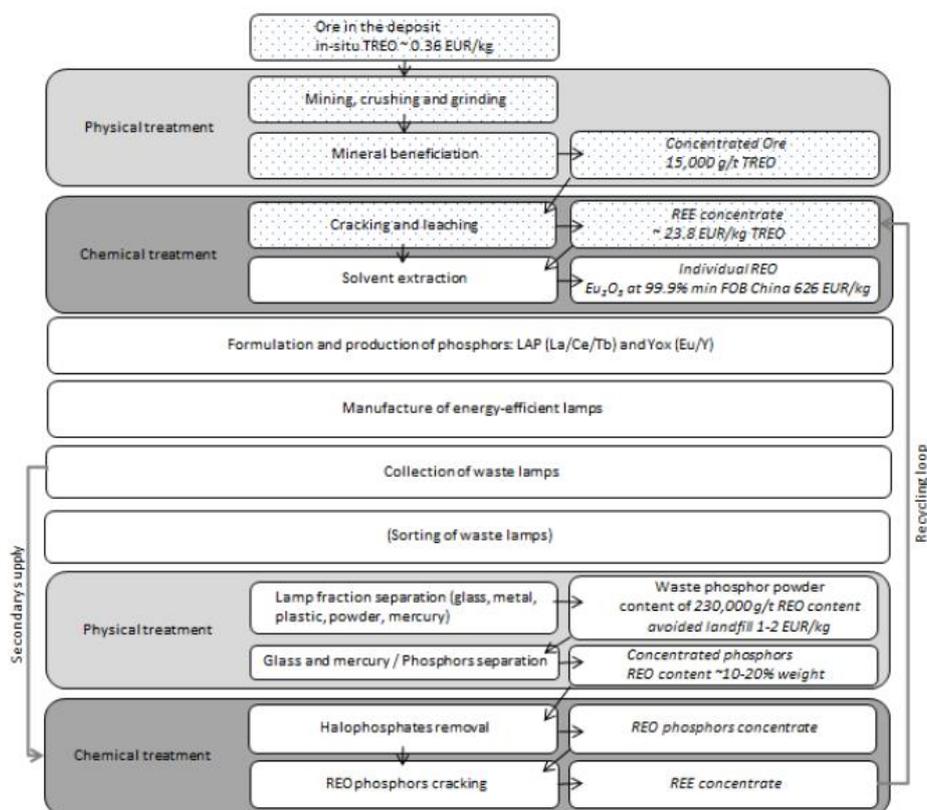


Figure 54. The flowsheet of Solvay Company for the recovery of REEs (among them Eu, Gd and Tb) from fluorescent lamps [222].

3. INNOVATIVE PROCESSING ROUTES – GAPS & BARRIERS

3.1 MINING AND METALLURGICAL WASTES

The concentration of Eu, Gd and Tb in metallurgical-chemical industry residues has been reported only in few cases in the literature. Europium as EuPO_4 has been detected in phosphogypsum at low concentrations (few dozen ppm) [224] [225]. Europium (and scandium) content has also been found in blast furnace iron slags in China in which it is contained in phyllosilicate (phlogopite) phases. The use of dodecyl-ammonium acetate is proposed as a potential process for the separation of the Eu-rich phyllosilicate phase [5]. **The Eu content in phosphogypsum disposals in EU countries it deserves to be further investigated.**

3.2 SCRAPs

Large EU research projects

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Europium was successfully recovered by fluorescent powder from fluorescent lamps within the framework of RECLAIM project. The scrap was initially treated with a mechanical process to crush the glass and thereby, be able to remove the tube ends (metallic or plastic parts) by means of a magnetic and eddy current separation. By sieving, the glass and fluorescent powder were separated. The process took place in an automated and isolated line, including an industrial vacuum cleaner with active carbon filters, to assure the capture of mercury (Figure 55). The chemical processing of the mechanical treated material comprises [223]:

1. The selective pre-leaching of the calcium content minimizing any losses of europium. Calcium is considered a contaminant of the final product produced downstream in the process and therefore its elimination upstream is crucial to produce a marketable Y/Eu concentrate.
2. The selective leaching of the targeted elements from the Y/Eu enriched solid produced in the pre-leaching stage.
3. The precipitation of Y and Eu from the pregnant liquor solution from the leaching stage aiming to the production of marketable Y-Eu concentrate.

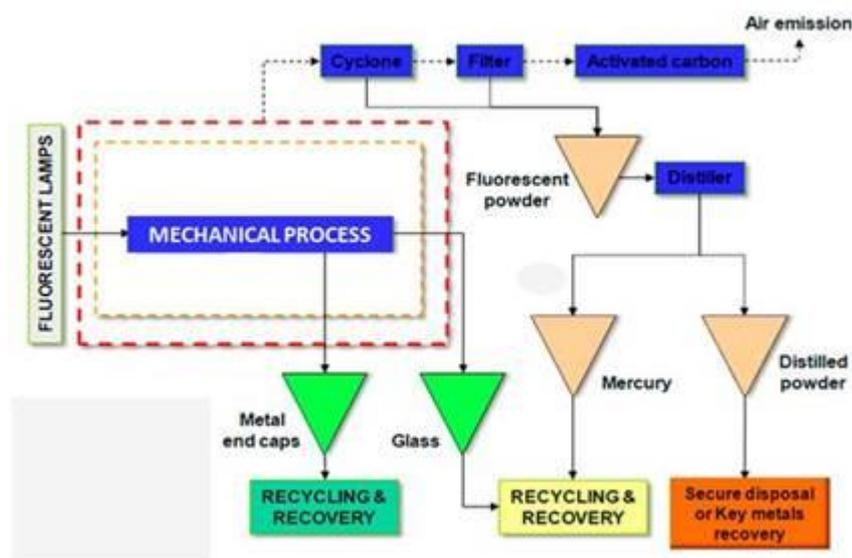


Figure 55. RECLAIM EU project for the recovery of Eu from end of life fluorescent lamps [223].

The processing route was tested at a pilot scale operating at continuous mode (maximum time=few days). A total of 415 kg of spent fluorescent lamps dust were processed in the pretreatment unit yielding a total of 235 kg of REE concentrate. A europium quantity of 127g was daily being produced. **The project proved that the recycling of Eu using at a continuous mode automated at a significant extend, using spent fluorescent lamps as a feed, is technologically realizable.**

Physical separation-enrichment of spent fluorescent lamps

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The efficient separation-enrichment of compact fluorescent lamps (CFLs) which contain significant amount of the RE trichromatic phosphor consists the major processing barrier. The manual separation is not possible and therefore during mechanical dismantling the broken glass pieces are separated from the phosphor powder by a wet or dry sieving operation. However, it is impossible to remove the very fine glass particles. The lamp phosphor fraction can contain up to 50 wt.% of glass and constitutes about 3 wt.% of the mass of a fluorescent lamp. The remaining glass amount contaminates the leaching solutions with silicon during chemical processing and separation. The lamp phosphor fractions can also be contaminated by zinc sulfide phosphors from cathode ray tubes (CRTs) of old color television sets and computer monitors. Electrostatic and pneumatic separation techniques have been tested for the beneficiation of lamp phosphor material obtaining, however the results were poor primarily due to dusting of powders during the test [226] [227] [228]. **The two-liquid flotation technique has been proposed to overcome of the technological gap of the separation step.** The flotation medium is complex composed by a polar (water) and a non-polar solvent (hexane, eptane etc.). The phosphors are collected in the interface of the two solvents. A 90% separation efficiency in case of red phosphors has been reported [229].

Leaching of phosphors and REEs separation

The leaching behaviour of various phosphor materials consist the main chemical processing barrier. Halophosphate phosphors and $Y_2O_3:Eu^{3+}$ readily dissolves in diluted acids but the rare earth phosphate phosphor $LaPO_4:Ce^{3+}, Tb^{3+}$ presents a resistance in acids. Leaching tests with sulphuric acid showed that europium can be recovered with a 98% yield using 1.5 kmol/m³, temperature concentration at 70°C for 1 h, however there was poor dissolution of cerium, lanthanum and terbium [230]. **Porob et al. (2012) have proposed a novel dissolution process using molten sodium carbonate at 1000 °C.** The fused material can be subsequently leached under more gentle conditions presenting a high terbium recovery [231].

Efficient separation (>98% purity for Eu and 92% for terbium) of REEs originated by the processing of spent fluorescent lamps has been reported using chelating resins such as iminodiacetic and nitrilotriacetic acids [232].

Gadolinium recovery from spent optical glasses

A hydrometallurgical process for the leaching of REE containing spent optical glassed has been reported in the literature [233]. The method was tested in glasses containing 43.12 wt.% lanthanum oxide, 9.37 wt.% yttrium oxide and 4.60 wt.% gadolinium oxide. The approach involves the initial conversion of RE from a borosilicate phase to the hydroxide form using sodium hydroxide followed by hydrochloric acid leaching of the residual solids from the conversion (Figure 56). Under the optimum conditions (leaching with HCl acid at 368 K for 30

min), recoveries of 99.4%, 100% and 100 for La, Y and Gd respectively were achieved. The REE chlorides concentrations in the final solution were found: 36.54 g/L La, 7.38 g/L Y and 3.93 g/L Gd. **The use of strong alkaline and acid solutions consists the main disadvantage of the process.**

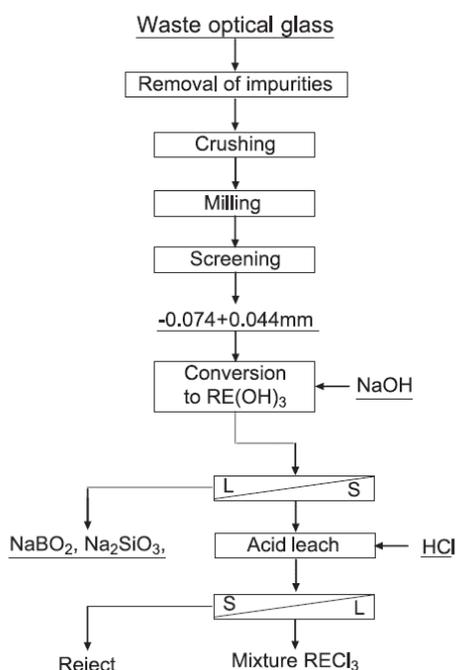


Figure 56. Developed process for the recovery of gadolinium from spent optical glasses [233].

4. LIFE CYCLE ASSESSMENT DATA

There is a lack of detailed LCA data concerning the recycling of fluorescent lamps which consist the main secondary resource for the recovery of Eu, Gd and Tb. However, a number of studies [234] [235] support that the recycling of phosphors contained in fluorescent lamps presents a societal value in the form of forgone costs of protecting human and environmental health and safety as the mining of primary REES resources involves the exposure and handling of radioactive elements (such as uranium and thorium) that have been related to higher health risks, for example to cancer. Additionally, the chemical processing of the primary resources involves the use of various harmful chemicals and greenhouse gasses.

5. SUMMARY

End of life fluorescent lamps consist and main secondary resource for the recovery of europium, gadolinium, and terbium in which contained in the phosphor materials. The main technological barriers that have been reported for the concern: (a) the physical separation of phosphors in case of compact fluorescent lamps (CFLs) in which the manual is separation and

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the concentrate is contaminated with glass content and (b) in the efficient leaching of phosphors mixture due to their different acid resistivity behaviour. However specific technologies that have been recently developed and tested at laboratory scale, such as two-liquid flotation and fusion with molten salts can potentially improve the recycling sustainability.

REE - HOLMIUM, ERBIUM, THULIUM, YTTERBIUM AND LUTETIUM

Rare earth minerals (RE) are a group of 17 elements, which include the lanthanide group, plus scandium and yttrium. These are present in 0.08% in the earth's crust, in minerals, generally in oxidized form. It is characterized by particular physical-chemical properties that give it great economic value and use in a wide variety of applications.

The large group of the REE is sub-divided according to their atomic weight into: heavy rare earth elements (HREE) and the light rare earth elements (LREE). LREEs are subdivided into (from the lightest to the heaviest): La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, **Ho, Er, Tm, Yb, Lu**; in this case holmium, erbium, thulium and ytterbium are considered heavy rare earth elements. LREE are up to 200 times more abundant than HREE and odd atomic number REE are more abundant than the even number elements.

Between them, cerium is the most abundant, more than copper; lanthanum (La) and neodymium (Nd) are more abundant than lead, nickel and cobalt; even though the thulium (Tm) and the lutetium (Lu) are more abundant than platinum ore elements, being the thulium (Tm) four times more abundant than the silver.

The applications of these minority elements are limited and are focused on the field of laser fibers as doping elements to improve optical properties and achieve higher performances or efficiencies as catalysts in industrial processes [236]. **Holmium**, for example is used in medical technology laser and is actually being used in urology surgeries and could be used as well on foreign bodies' removal from the tissues or organs (bladder, uterus, prostate, ...); by instance, Holmium is also used in other fields, such as electrochemistry and filaments for vacuum tubes, as neutron absorber in nuclear reactors, or as a coloring agent in glass. **Erbium** is used as an alloy metal for vanadium for a better manipulation, as well as to form spring steel. Also erbium oxide, which is pink, is used to color glass and to make lasers that will operate at room temperatures and use as control rods in nuclear fission reactors. **Thulium** is used as small, portable X-ray generators. It also has limited use as an alloy metal with other metals and has experimentally been used in some laser systems that contain thulium-doped fibers. **Ytterbium** is used in similar applications for a small portable X-ray source and as an alloy to make special types of strong steel and their oxides of ytterbium are used to make lasers and some synthetic gemstones. **Lutetium** is used as catalysts in the cracking refining process of crude oil and to speed up the reaction in some hydrogenation processes [236] [237], as well as to form the compound Lutetium yttrium silicate scintillation crystal (LYSO) for detectors in positron emission tomography (PET) [238].

In all, it has been considered that these 5 rare earths belong to the same HREE subgroup and have a similar field of application, grouping them within this deliverable, which is described below.

1. THE SECONDARY RESOURCES

First of all, there are European projects such as EURARE and ASTER that aim to evaluate and manage the potential of renewable energy resources in Europe and develop new, efficient and sustainable methods for processing the mineral potentials of RE Europe. We must highlight the European projects EURARE [239], ASTER [240] and ProMine [241].

REEs are not scarce; in fact, they are more common in the earth's crust than many other metals, such as gold, tin or uranium. However, the exploitable part is inferior to the rest. These available reserves greatly exceed world production. It also naturally occurs together in mineral deposits, although the specific distribution through rare earths varies among reservoirs. In general, HREEs are a much smaller part of the total rare earth content than LREEs in minerals containing rare earths.

1.1 MINING AND METALLURGICAL WASTES

Europe has a wide range of geological substrate and, therefore, has great potential for the presence of deposits [242]. The discoveries of the oldest deposits enriched in HREE and in LREE have been made in Greenland and the Nordic countries (Denmark, Norway, Sweden, Finland), but also geological studies reveal that countries such as France, Greece and the United Kingdom can be found resources. Less significant deposits enriched with LREE have also been found in the coastal areas of northwestern France, Greece and the western Balkans, including Turkey. A number of small rare earths cases have been identified in a wide range of other countries, including the United Kingdom, Spain, Portugal, Italy and Germany. However, an adequate evaluation is still required to help lay the foundations for REE knowledge in the medium-long term [243].

The major sources of REE in Europe are in Norra Kärr being a large and heavy deposit located in the center-south of Sweden; in Kvanefjeld south of Greenland we have another important deposit. Due to their size and degree of evolution, they have to ensure the European supply of RE in the coming decades. Other sources include alkaline rocks, such as those found in the Gardar province in southwestern Greenland (Kvanefjeld and Kringlerne) and the carbonatites of Fen in Norway and Sokli in Finland and the little mermaid of Norra Kärr in Sweden [244].

The most of the known resources are contained in this ores: Bastnaesite is a rare earth fluorocarbonate mineral [245], which predominantly contains LREE (La, Ce, Pr, Nd, Sm, Eu, Gd

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and Sc). After chemical-physical treatment, bastnaesite ore concentrates contain between 40-60 % of RE [245] [246]. Monazite is another rare earth phosphate mineral, containing mostly LREE and some HREE (Tb, Dy, Ho, Er, Tm, Yb, Lu and Y), more than bastnaesite [246]. Monazite concentrates can contain up to 70% REE after physical treatment. Xenotime is maybe the most common HREE mineral, which occurs as an accessory mineral in granite, gneiss, and other igneous and metamorphic rocks. Zircon and fluorite are also important hosts for REE. Zircon favors the HREE but only contains trace or minor quantities. Also, laterite is locally enriched in HREEs and yttrium.

On the other hand, Ion-adsorbed clays are relatively rich in HREE and are becoming increasingly important REE resources in the primary industry. In the matrix of these clays the RE ions have been adsorbed, although these clays have a very low concentration in weight, but their ease of processing makes them a valuable resource of REE [244].

There are many potential REE ore deposits in a wide variety of rocks and minerals, in total more than 200 rare earth minerals [247] approved by the International Mineralogical Association, some others are: cerianite, fluorecite, gadolinite, keiviite, loparite, among others.

There is a lack of available data on metallurgical waste of REE as elements are scarce in mining process and thus in the metallurgic industry.

1.2 SCRAPS

The waste is generated in different steps of the rare earth value chain. This includes the extraction and refining stage, in the case of tailings and slags, during the processing of "new scrap", such as chips from the manufacture of magnets, and when the products reach their end of useful life which is called "old scrap metal", which is finally discarded, usually to landfills.

Very efficient pyrometallurgical processes have been developed for the recovery of metallic values of electronic scrap, used vehicle exhaust catalysts and industrial waste catalysts. For example, the French company Solvay uses the slags can be used to separate and produce some concentrates of rare earths, for example commercially recycling Lutetium oxide from scraps [248]. Also, group Umicore operates in an integrated smelting and refining plant for scrap metal recovery from electrical and electronic waste. In both cases, several metals are recovered but it is still not very developed for the recovery of rare earths. The RE ends in oxidized diluted form in the slag of the so-called "copper smelting" where the RE content of these slags consists largely of cerium, also some neodymium and for the rest is not entirely clear [249].

2. EXISTING PROCESSING ROUTES – GAPS & BARRIERS

Due to a smaller scale use, there are currently no techniques applied industrially or as patents for the recovery of secondary resources of these five elements of heavy rare earths. They are still in the testing phase and on a laboratory scale; however, the most common process is based on leaching of the dust product with an acid, to then subject the solution to extraction (in one or several stages) with a solvent such as 2-ethylhexylphosphoric or DEHPA. Diluents are also commonly used. Finally it is precipitated and it is intended to recover the element with the greatest purity possible. Some research shows that it is possible to recover rare earth in the form of oxides or phosphates [249] [250].

3. INNOVATIVE PROCESSING ROUTES – GAPS & BARRIERS

Currently, several devices or waste containing RE are recovered or recycled, but the truth is that, in the short and medium term, it is likely that recycling efforts are focused on the recovery of commercially viable rare earths. Normally, these are present in the products in high concentrations that are valuable from the economic and industrial point of view. Therefore, a detailed analysis leads to the conclusion that recycling efforts should probably be oriented towards priority products, but at the same time, the process should be economically viable.

Therefore, a series of key barriers have been examined and identified that will say if it is worth to carry out the recycling process:

- Identification of these priority products that contain more rare earths. It must be done in waste streams based on a detailed market analysis.
- Collection of these identified products in sufficient quantities to make recycling viable on a commercial scale.
- Detection of the component or material containing rare earths in the scrap, for example, a magnet, a tube or a battery.
- Separation of the components of the rest of the waste by dismantling, manual or mechanical classification, or any other process designed to isolate the smallest fraction that contains most of the rare earths.
- Extraction of rare earth containing material from the components, this could be in the form of an alloy, oxide or salt.
- Refining the fraction separated for an alloy, compound or element.

- Reprocessing of purified elements or alloys in a new form of material, for example, a magnet or a phosphor.

Recycling could have a significant impact on the most critical elements, but in this case the elements in question are placed with a low priority.

The list of priorities is as follows:

1. Permanent magnets (Nd, Pr, Dy, Tb, Sm)
2. Phosphors (Eu, Tb, Y, Ce, Gd, La)
3. Batteries (La, Ce, Nd, Pr)
4. Polishing compounds (Ce)
5. Catalysts (La, Ce, Pr, Nd, Y)
- 6. Others uses (Ho, Er, Tm, Yb, Lu)**

Efforts to recycle rare earths should be concentrated in the first two sectors on this list of priorities: magnets and phosphors. This is because there are commercial recycling technologies on an industrial scale for the recycling of rare earth batteries [250].

In the case of rare earths that we discuss in this report one has to be realistic about the recycling options since these elements are mainly used in lasers nanofibers, polishing compounds and catalysts are less critical; and the refractory character of the materials in question makes their recovery particularly difficult and not economically profitable [251]. For example, it does not make sense to develop recycling schemes for the recovery of RE from laser crystals or catalysts, because they are part of complex components or devices and also the volumes used are very small. The cost of recovery would be very high and would not be economically profitable. However, many of the technologies used in the recycling of the first three sectors could be common to other elements of RE.

The issue is that REs had limited commercial interest at the beginning of the 20th century, therefore, they have received little funding or attention for the exploration and design of new processing routes; but the reality is that commercial recycling of RE is still extremely low and although there are lab-level research efforts on recycling [252] [253] [254], and although RE recovery rates are effective, usually only 1% of rare earths were recycled in 2011 which is a very low recycling rate.

This is mainly due to inefficient collection, technological difficulties and, especially, lack of incentives [255] [187] [256]. Being a growing market there is still considerable uncertainty about the size of the potential market for recycled RE materials, the faster the demand grows, the longer the life of the products. In addition, the final products that are intended to be recycled contain a complex mixture of metals that changes over time as a result of

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technological advances, sometimes the collection procedures of the final product are scarce or do not exist. Another problem may be the high cost of collecting and transporting final products to recycling facilities. It is necessary to be clear about the recycling process as an integrated part of a value chain, the design of the final product and the incorporation of these elements. Public awareness of the imminent loss of these crucial resources is low and one must be aware of their critical nature [257].

Another limitation that blocks future developments in the REE recycling is the lack of profitable methods to purify the mixtures generated during the recycling of some devices.

Some recent advances in research in this area provide information on approaches that can address this problem. For example, Bogart *et al* [257] [258] developed an organic compound that could bind to the ER cations, allowing the formation of different compounds for the LREE and the HREE, with the LREE forming aggregates while the HREE compounds were not added. This generated solubility differences that were large enough to allow effective separation of LREE and HREE by filtration [257] [258]. These techniques are used in permanent magnets and fluorescent bulbs. This new approach to RE recycling can be scalable and can provide a significant step towards increasing the recycling capacity of a wide variety of RE-containing end products. Years ago, Japanese researchers were able to recover Neodymium and Ytterbium through gel particles of alginic acid biopolymer [259]. Recently, Peng Chen *et al.* [260] reported the first efforts to recover Lutetium from LYSO scraps. They developed a novel green Ionic Liquid (IL)-mediated resin system that contains CHON-type extractant and green hydrophobic ILs and applied it for the management of high-priced rare earth wastes containing Lutetium (Figure 57) This process has the advantages of high recovery of Lutetium, simple flowsheet and environmentally friendly. However, there is an energy consumption problem in the process of the microwave-assisted hot acid leaching. It is planned to apply this processing route to the practical recovery of rare earth secondary resources, especially for the recovery of Lutetium, in the waste and resources recovery industry.

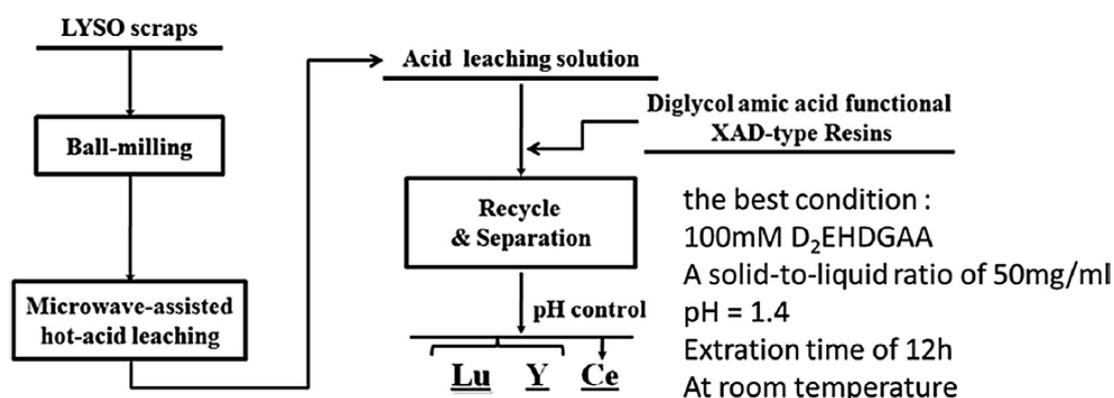


Figure 57. Diagram showing the recovery of Lu rare earth secondary resource from waste LYSO using a wet process and diglycol amic acid functional XAD-type resin. Figure taken from Ref [260].

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4. LIFE CYCLE ASSESSMENT COMPARISON BETWEEN EXISTING AND INNOVATIVE TECHNOLOGIES

As we have said before, the volumes of recycling of rare earths is still small, however a drastic improvement in recycling rates at the end of the life of REE can be seen as a strategic need, even more in countries that do not have or have few rare earth mineral deposits.

Some authors [250] differentiate between (1.) direct recycling of pre-consumer scrap manufacturing or REE waste; (2.) urban post-consumer mining (variety of complex materials) end-of-life products; (3.) mining of historic landfills (future), urban and industrial waste containing REE. The first two approaches are more oriented to products with high RE content such as permanent magnets, batteries and lamp phosphors. Binnemans and collaborators [250] say that much less attention has been paid to industrial waste, which usually goes to landfills (Figure 58). These waste streams can include metallurgical slag, "red mud" bauxite waste, phosphogypsum, tailings from mines, and waste water flows.

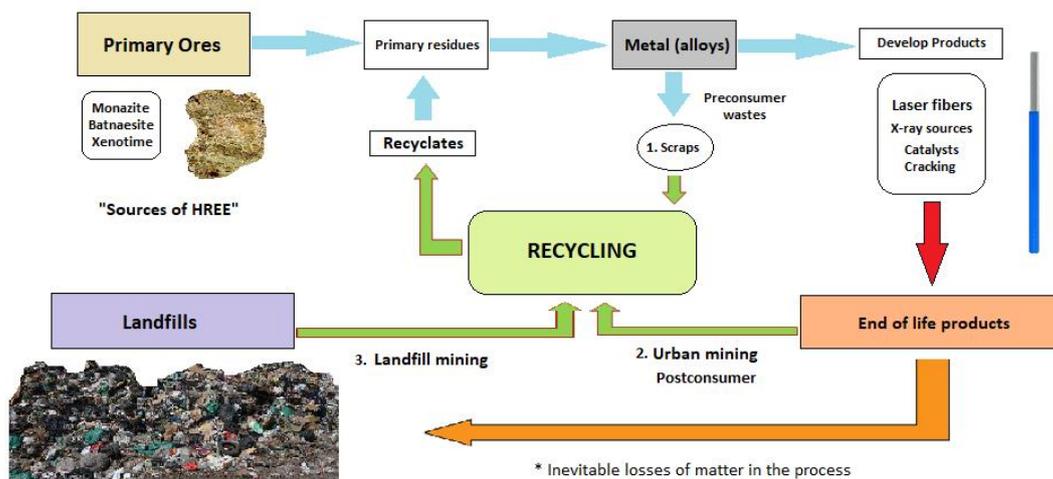


Figure 58. Ways to close the rare earth loops in a circular economy. Modified from Jones *et al.* (2011) [261].

Considering that rare earths play an important role in permanent magnets, phosphor lamps, rechargeable nickel-metal hydride batteries, catalysts, it is necessary to develop products that are as environmentally friendly as possible in accordance with European objectives that aim for a transition to a circular economy. One advantage of recycling is that these valuable resources must be returned to the industry through the cited "urban mining" and thus reduce primary extraction. The extraction and subsequent processing of rare earths as a primary source is involved in most cases with radioactivity from radioactive elements of natural deposits, as is the case of thorium or uranium; therefore, with recycling as a secondary source elements free of radioactive impurities will be obtained.

Although the recycling of rare earths also requires complex processes with physical-chemical treatment and energy transport, it is possible to safeguard the important amounts of energy, chemical products and emissions in the chain that is carried out in primary processing. It is expected that most recycling processes would limit atmospheric emissions, protect groundwater, acidification, eutrophication and climate change [262].

5. SUMMARY

These five elements (Ho, Er, Tm, Yb, Lu) of heavy rare earths (HREE) are extracted from mineral sources such as bastnaesite, monazite and xenotime present in several Nordic European countries mainly.

In the absence of significant primary economic and operational deposits in the territory, recycling and reuse of REE become a significant alternative to balance market needs and primary resources [263]. Thus, these routes are presented as a necessity for a sustainable use of resources. Although efficient routes have already been developed for basic metals (Al, Cu, Fe, Zn,...) and for precious metals (Ag, Au, Pt,...), but for ERs the work is in progress. Traditionally, most of the research on the recycling of RE has been directed towards the chemical processing of collected recyclates, similar to the case of primary resources. However, recently research activities have been intensified for the development of efficient recycling technologies, and are expected to increase in the next years. However, current developments can not recover the small quantities that are present in these modern products efficiently, but there are laboratory experiments that can be applied in the industry to eliminate this barrier. There are several pilot studies at the laboratory level, but they are still very underdeveloped and are not implemented at the patent level. It should take some years from successful research to industrial implementation.

On the other hand, it is also difficult to estimate the recycling potential of RE in the near future due to the dynamic development of the system respect to the growth rates of different applications and their useful lives, changes in material compositions and uncertainties on the recycling schemes in development. But it is expected that will be focused on the key applications: magnets, batteries and accessories for lamps.

Besides, there are several advantages of recycling and there are no radioactive elements as occurs in the primary extraction, the composition of the concentrate obtained is less complex, are in higher concentrations and there are small pure volumes of the element in question.

Finally, an efficient recycling requires the development of new routes that are environmentally friendly, fully integrated and logistically viable

REE - LANTHANUM AND CERIUM

Lanthanum and cerium are two light Rare Earth Elements (REE). Lanthanum is the third-most abundant of all the lanthanides, making up 39 mg/kg of the Earth's crust, behind neodymium at 41.5 mg/kg and cerium at 66.5 mg/kg. It is almost three times as abundant as lead in the Earth's crust. They are mainly used in

- Alloys
- polishing/pickling & etching powders
- catalysts for automotive and oil industry
- ceramics
- glass
- NiMH batteries
- Permanent magnets in hybrid and electrical vehicles (Ce only)
- Phosphors (Ce only)

A few years ago, Ce was identified as a potential substitute of dysprosium in permanent magnet [264]. The use of Ce in permanent magnet could reduce by 80% the need in Nd and Dy following a study of the German Fraunhofer of 2018 [265].

The end of life recycling input rate for these two elements is close to 0 (around 1% of the cerium from polishing powders and 1% of the La from Fluid cracking catalysts, glass, ceramics, and batteries).

La and Ce are often used under the mischmetal form. A typical composition includes approximately 50% cerium, 25% lanthanum, and 15-18% neodymium with other rare earth metals (cerium mischmetal) but a lanthanum mischmetal is used currently used in NiMH batteries. So far, a typical hybrid automobile battery for a Toyota Prius requires 10 to 15 kilograms of lanthanum.

The current production of CeO₂ is about 54,400 t (32% of RE oxides). About 40,000 t of RE oxides are consumed by glass industry, out of which about 16,000 tons are being used for polishing applications. Cerium dioxide is the main component (40 – 99%) in glass polishing powders. It is also used for polishing silicon wafers and ceramics [266].

The global application of REE including La and CE are listed below (Figure 59), with their respective content (Table 17) [267]

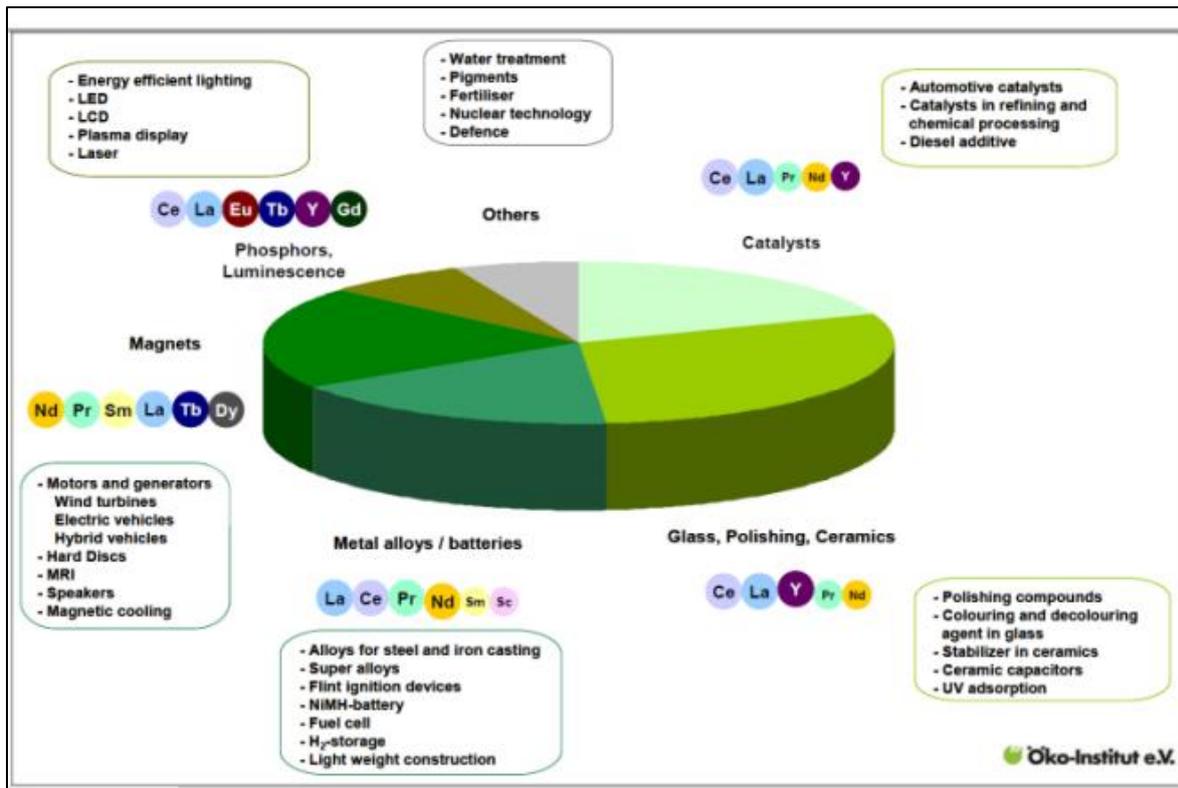


Figure 59. Global application of REE (from IVL report C211, 2016 [267])

Table 17. REE usage by application, in % (from IVI report C211, 2016, [267])

Table 4. REE usage by application, in %. From (Binnemans et al., 2013)

Application	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Other
Magnets			23.4	69.4			2	0.2	5		
Battery alloys	50	33.4	3.3	10	3.3						
Metallurgy	26	52	5.5	16.5							
Auto catalysts	5	90	2	3							
FCC	90	10									
Polishing powders	31.5	65	3.5								
Glass additives	24	66	1	3						2	4
Phosphors	8.5	11				4.9	1.8	4.6		69.2	
Ceramics	17	12	6	12						53	
Others	19	39	4	15	2		1			19	

^a The percentages are estimated average consumption distribution by application; the actual distribution varies from manufacturer to manufacturer.

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1. THE SECONDARY RESOURCES

1.1 MINING AND METALLURGICAL WASTES

There is almost no available data concerning the metallurgical processing of mining and metallurgical wastes aiming to the recovery of cerium and lanthanum. Presently, only limited information is available with respect to the mineralogy of the different rare-earth rich phases in bauxite residue, phosphogypsum and metallurgical slag.

Knowledge of these phases could aid the development of new more efficient leaching processes. There is also a need for methods that allow efficient recovery of rare-earth ions from dilute aqueous solutions, not only from waste water streams, but especially from the dilute leachates. Since the concentrations of rare earths in industrial waste residues are low compared to primary rare-earth ores, tailored, zero-waste processes dedicated to the recovery of rare earths from these dilute waste streams must be developed.

1.2 SCRAPS

Recycling is often difficult because of the way that REE are incorporated as small components in complex items, or are part of complex materials. The processes required are energy intensive and complex. Nevertheless, new scraps generated during the manufacture of alloys are an important secondary source, mainly in a closed loop. Although the concentrations of rare earths in such streams are low - typically less than 1% rare-earth oxides - since the available waste volumes are huge, the total amount of rare earths in these waste fractions is very substantial, so that they can represent a potentially relevant alternative source of rare earths. The main issue is that the concentration of each element is very different from one alloy to the other, depending on its main application. Traceability can be an issue to identify the right alloys to recycle to recover Ce and La.

One of the main resources of Ce and La is the polishing powder waste. The waste slurry generated after glass polishing contains cerium together with other REEs (mainly lanthanum, neodymium and praseodymium), silicon, iron, aluminium, zinc, sodium etc. The concentration of the elements other than REEs in glass polishing waste depends on the chemical composition of the glass, additives and flocculants. The abrasive properties of polishing powder diminish due to the enrichment of the slurry with other elements with time and affect the quality of product adversely. Currently, the waste generated after polishing (CeO₂: 8-80%) ends up in landfills. Recycling of this waste not only contributes to the proper utilisation of natural resources but also makes recycling of valuable REEs possible. In addition, the recovered cerium can be converted to cerium metal and used in high value aluminium and magnesium alloys and steels [266].

Table 18. Global recycling potential for REE from magnets, NiMH batteries and lamp phosphors ([267] [250])

Application	Estimated REE stocks in 2020 (tons)	Estimated average lifetime (years)	Estimated REE old scrap in 2020 (tons)
Magnets	300,000	15	20,000
Phosphors	25,000	6	4167
NiMH batteries	50,000	10	5000
Total	375,000	-	29,167

According to the data compiled by IVL in 2016 [267] (Table 18 above, from Binnemans 2013 [250]) on the global potential for REE recycling, combined with the La and Ce content for each application, in 2020, about 2000 tons of La and 2500 tons of Ce could be recovered from phosphors, 25000 tons of La and 17000 tons of Ce from batteries.

2. EXISTING PROCESSING ROUTES – GAPS & BARRIERS

Most of the REE recycling research (including Ce and La) has been directed towards the chemical processing of the collected REE recyclates, in a way that is reminiscent of the processing of rare-earth primary resources (REE ores). However, an efficient recycling of these rare earths requires the development of environmentally-friendly, fully integrated and logistically sound recycling flow sheets, including dismantling, sorting, pre-processing, and pyro-, hydro- and/or electrometallurgical processing steps to recover the REEs from magnets, batteries, lamp phosphors and other products/components. A status of the current production routes from secondary resources is available in SCRREEN D4.2, but it addresses REE in general, with no specific focus on La and Ce, for which specific uses exist.

The main resources are addressed below and each time, the barriers or gaps are highlighted

2.1 MINING AND METALLURGICAL WASTES

Phosphogypsum, from Lutskiy et al., 2018 [268]

The most promising industrial waste for REE recovery in general is the phosphogypsum (PG). Phosphate rocks (mainly in the form of mineral apatite) are mined and either solubilized (acid leach) to produce wet-process phosphoric acid, or smelted to produce elemental phosphorus. PG is a by-product of the phosphoric acid wet-process. The manufacturing of phosphoric acid is a highly waste generating activity; around 5 tons of PG are produced for every ton of

phosphoric acid manufactured. The huge production of these unwanted by-products, i.e. over 100-280 Mt/yr of PG worldwide, has promoted the searching of new recycling alternatives. PG usually contain significant amount of rare earth elements (REE), approximately an average of 460 ppm (from 100 to 800 ppm depending on the resource). However, this amount is very low compared to the REE content of primary resource such as the Mountain Pass mine, with more than 5% of REE (Table 19). And this mine was closed a few years ago because not financially viable...

Table 19. Main fraction of the sum of lanthanide oxides in industrially processed ores and phosphogypsum (from Lustkyi et al. [268])

Raw materials	Mass fraction Ln ₂ O ₃ , %
Phosphogypsum	from 0.1 to 0.8
Mountain Pass (USA), bastnesite ores	from 7.0 to 10.0
Bayan Obo (China)	from 3.0 to 5.4
Loparite ores of the Kola Peninsula	from 0.3 to 0.8
Afrika, the Kola Peninsula	from 0.4 to 2.0
Canada, bastnesite ores	less than 1.7
Scrub-Oaks (USA), magnetite	less than 1.4

Direct leaching with mineral acids or some organic agents for extraction of REE from PG has been studied and indicated that it is technically feasible, but also that further research is needed prior to any industrial implementation. A further step for the only recovery of La and Ce will anyway be necessary if the mischmetal is not relevant. This separation step is complex and will also impact the viability of the process

Previously, a few studies have been conducted to investigate the recovery of REEs from PG. A nice review is provided by Walawalkar in his master degree thesis, Graduate Department of Chemical Engineering and Applied Chemistry, University of Toronto, 2016 [224]. In his thesis, he compared the efficiency of 3 acids for the leaching of Ce and La from PG (Figure 60). HNO₃ remains the best, whatever the conditions. A two steps extraction, either with HCl or HNO₃ could allow a more efficient recovery (Figure 61). Here again, the main barrier would be the cost of the HNO₃ versus HCl or H₂SO₄. So far, most of the concepts have been based on H₂SO₄, which is the less efficient leaching acid. A combined LCA/LCC would be needed for orienting an industrial process.

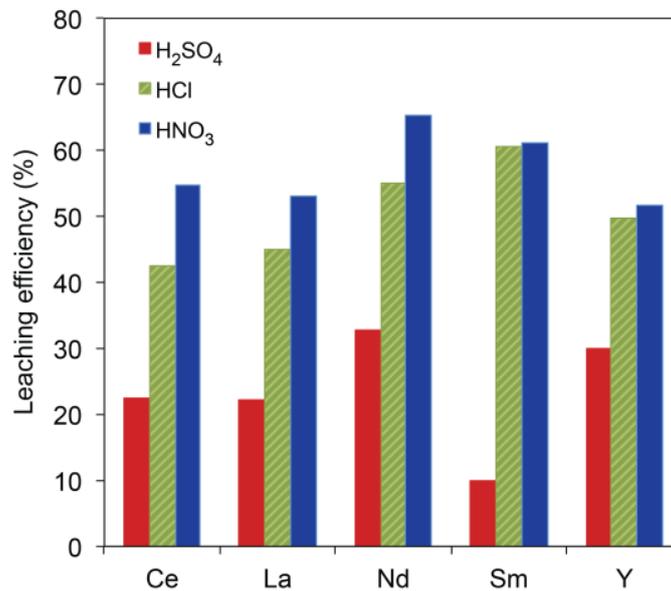


Figure 60. Leaching efficiency of Ce, La, Nd, Sm and Y after 20 minutes residence time using H₂SO₄, HCl and HNO₃ as the leaching agent at 1.5M concentration, 80°C and S/L ratio of 1/8. (from Walawalkar, 2016, [224])

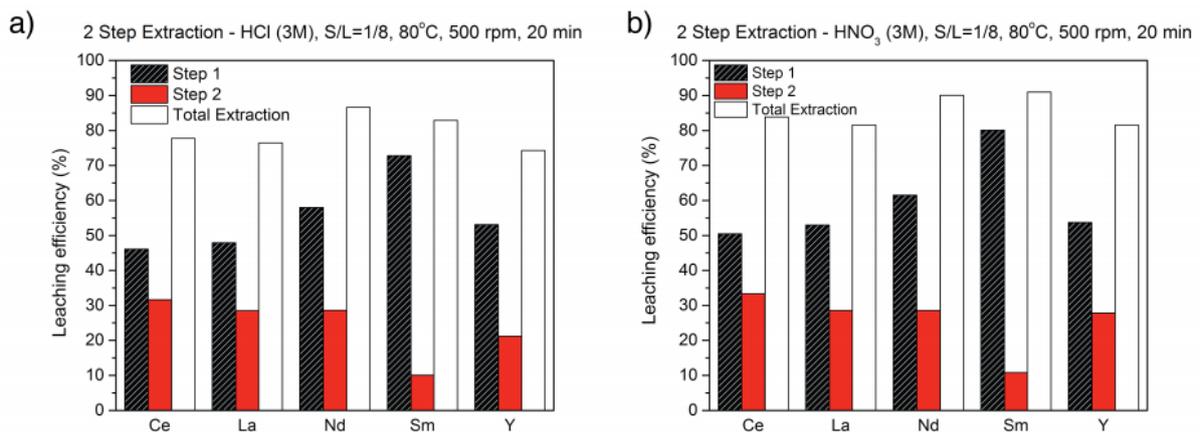


Figure 61. Two-step leaching process for a) HCl at 3M and b) HNO₃ at 3M (from Walawalkar, 2016, [224])

In 2016, Sinha et al. [269] wrote a review on the recovery and recycling of lanthanum from various. This paper covers more than 200 references, with among others the recovery of La from phosphogypsum and phosphoric acid, but also end of life products that will be addressed in the next section. If the proposed process flowsheet seems efficient, it has however to be reminded that the average content of La in PG is very low (100-200 ppm max) (Figure 62). Again, the process involves an acid leaching, HNO₃ being the most efficient, followed by solvent extraction

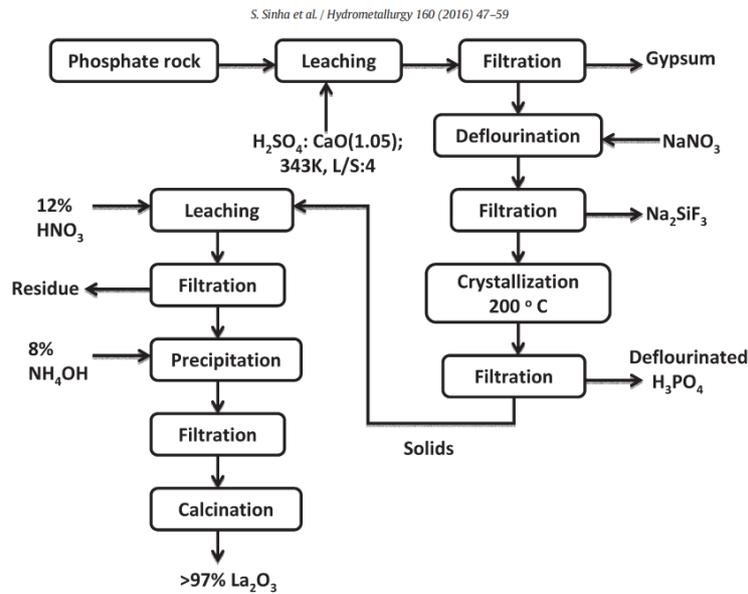


Figure 62. Process flowsheet for the recovery of lanthanum oxide from wet phosphoric acid (from Shina et al., 2016, [269])

Also in 2018, Rychkov et al. published a paper on the same topic [270]. The method is mainly based on a leaching by sulfuric acid (Figure 63 and Figure 64).

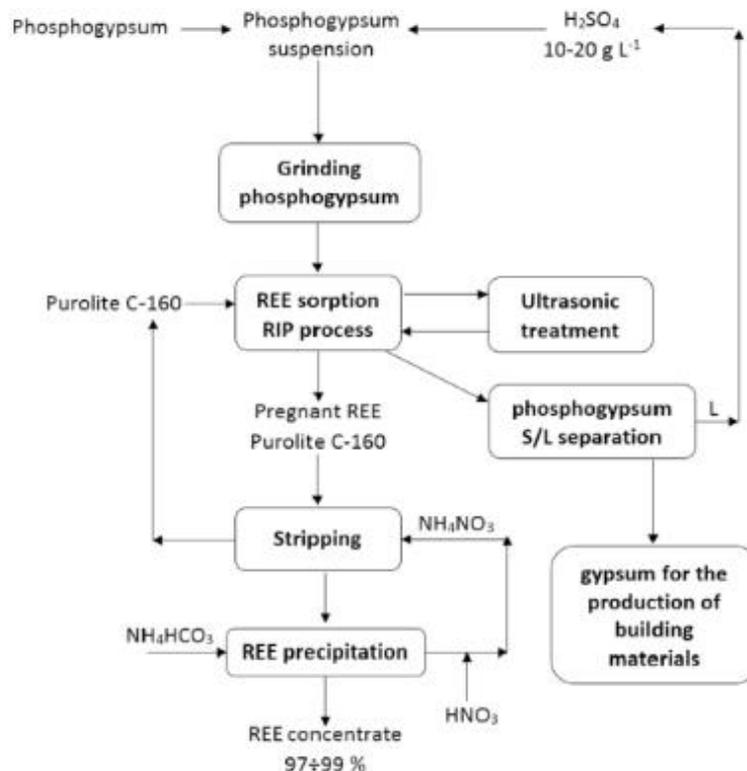


Figure 63. Conceptual flowsheet for REE recovery from phosphogypsum through leaching by sulfuric acid (from Rychkov et al. 2018, [270])

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Table 1
Chemical composition of phosphogypsum.

Element	Ca	P ₂ O ₅	F	Cu	Zn	As	H ₂ O	REE ₂ O ₃
Content, %	25	1.5	0.5	0.01	0.09	0.006	40	0.44

Table 2
Influence of phosphogypsum activation on REE leaching.

Grinding treatment	US	sorption	The degree of REE recovery at various sulfuric acid concentrations, %			
			5	10	20	30
no	no	no	13.77	17.61	18.12	17.17
yes	no	no	21.45	32.12	60.28	67.30
no	yes	no	10.40	26.28	29.27	23.88
yes	yes	no	27.44	45.26	63.43	66.91
no	no	yes	39.90	47.10	49.25	50.26
yes	no	yes	57.86	61.34	69.02	68.12
yes	yes	yes	56.36	71.92	72.55	72.07

Table 3
Chemical composition of the eluate.

Element	Ca	Fe	Sc	Y	Σ REE
Concentration, mg L ⁻¹	8770.00	16.60	0.8	45.0	1454.96

Table 4
Chemical composition of the REE concentrate.

Element	Ca	Fe	Al	Sr	Na	K	Σ REE	H ₂ O+carbonates
Content, %	1.0	0.66	0.13	0.07	0.1	0.1	48.6	49.34

Figure 64. Additional data from REE recovery from phosphogypsum through leaching by sulfuric acid (from Rychkov et al. 2018, [270])

The main conclusion of their work is reported here:

Recovery of REE from phosphogypsum using sulfuric acid leaching is a complex technical task. Joint co-crystallization of REE together with gypsum provides a low degree of REE leaching. In this work, we suggested to use three methods of activation (mechanical grinding treatment, ultrasonic impact and resin-in-pulp process) in order to intensify REE recovery from the phosphogypsum. Simultaneous use of all three methods resulted in the increase of degree of REE recovery from the phosphogypsum from 15 to 17% to more than 70%. Concentration of sulfuric acid used in the process was only 10-20 g/l. A concentrate containing approximately 50% of REE (corresponding to 97-99% Ln₂O₃) was obtained using 400 g/l ammonium nitrate solution as an eluent followed by REE carbonates precipitation from the eluent by ammonium hydrocarbonate solution.

Bauxite residue (Red mud)

Red mud are a huge stockpile of REE, mainly due to the huge amount of this waste, and unfortunately, not because of their REE content, often reported around a few hundreds ppm

In 2016, Sinha et al. wrote a review on the recovery and recycling of lanthanum from various resources [269]. This paper covers more than 200 references, with among others the recovery of La from secondary resources such as red muds.

An interesting statement, that could be a barrier, is that the efficiency of the recovery depends of the type of red mud. For example, in a studied Indian red mud, La is in a complex Al-Si matrix. Here again HNO₃ is the best leaching agent and an addition solvent extraction step using DEHPA and Cyanex compounds is required.

However, when lanthanum is found to be associated with Allanite (La) mineral, at the lab scale, a 99.9% recovery using 3 M H₂SO₄ at ambient temperature (~35 °C), S/L: 1/100 in 1 h was possible. For the solvent extraction step, it has been found that Cyanex 301 had higher specificity for lanthanum compared to DEHPA and Cyanex 272 with 0.15 M organic concentration at pH 2.

On the same topic, Borra et al (2). published a review on the recovery of REE from red mud in 2016 [271]. The main route relies on a HCl leaching.

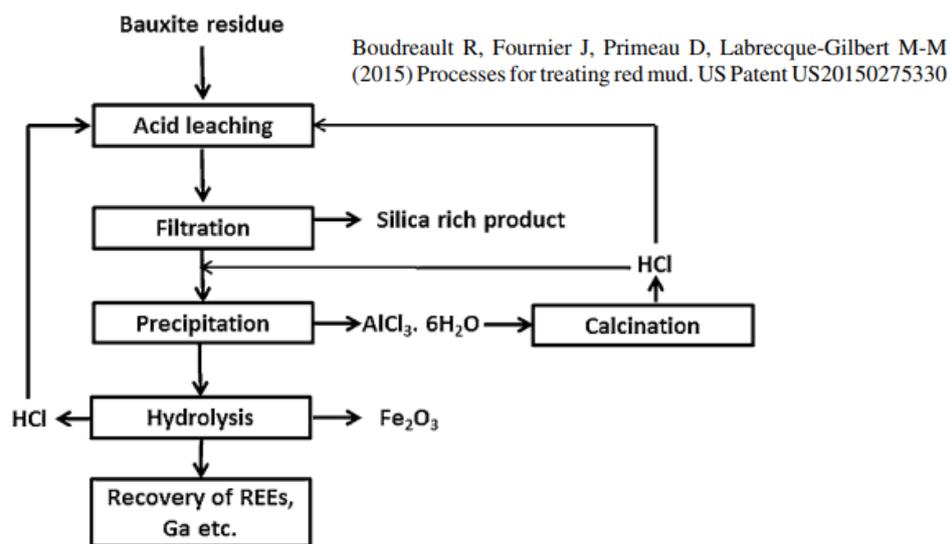


Figure 65. Conceptual flowsheet of Orbite process, adapted from Boudreault et al. (from Borra et al., 2016)

Mine tailings

The ENVIREE project studied the opportunity of recovering REE from mine tailings. The first issue was the identification of tailings with no or very low uranium/thorium content. A few EU deposits of interest have been selected (COVAS in Portugal, New Kankberg in Sweden). The production of concentrate was possible on both samples. However, no efficient leaching using mild conditions, as were the objectives of the ERAMIN ENVIREE project [272], has been found, despite the numerous conditions tested. The concentrate could be treated on the same way than the primary ore, but this energy intensive step would limit the attractiveness of such a recycling.

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2.2 SCRAPS

Few studies address the La and Ce recovery from scraps.

Polishing powders

A review was written in 2018 by Borra et al. (3) on the topic [273]. The paragraphs below in this section are from his review.

The main drawback identified was that the physical or physicochemical separation processes like sieving, flotation etc, were not self-sufficient (40% of recovery with 40% of purity), with a high difficulty to remove silica particles. Therefore subsequent chemical separation processes are required for further purification, i.e. for the removal of silica and/or other elements. An alkali leaching process was proposed but it is complex and poorly efficient.

Therefore an acid leaching was proposed instead the combination of physical separation and alkali leaching. This acid leaching alone was not efficient due to the poor solubility of CeO₂. A slight recovery increase (10%) can be obtained if the powders are roasted before leaching. However, the roasting step for a small increase in cerium recovery is difficult to be justified and this has a strong impact on the viability of the process.

Further works main on synthetic compounds showed that the recovery of cerium or lanthanum mainly depends on the nature of different compounds in the polishing powder (mineralogy). For example, if the lanthanum is present in a phosphate or fluoride phase then it is difficult to dissolve.

As the direct acid leaching of CeO₂ is difficult, the use of a reductant such as Potassium iodide or H₂O₂ can help in decreasing the required acid concentration and leaching temperature. This is the methods used by HYDROMETAL in Belgium for the by reductive leaching of CeO₂ in the glass polishing powder with nitric acid together with H₂O₂. They chose nitric acid lixiviant as it is selective towards silica and alumina. They used higher temperature for diffusion of acid into the silica matrix and also to enhance filtration. This is one of the only semi-industrial example of Ce recovery from secondary resources

Once the REE are in the leaching solution, different methods can be used for the recovery of cerium such as double salt precipitation, oxalate precipitation, carbonate precipitation, hydroxide precipitation and solvent extraction.

FCC recycling

Fluid catalytic cracking (FCC) process requires REE based catalysts, mainly based on La and Ce catalytic activity. A paper from YE Sishi et al. presents one recycling route in 2017 [274].

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The process is based on a HCl leaching followed by solvent extraction using a phosphoric acid.

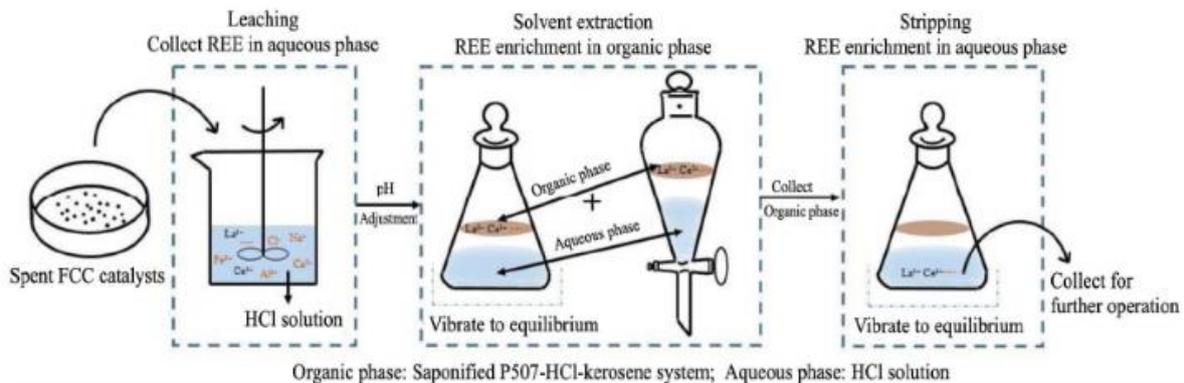


Figure 66. Schematic diagram for recovery of rare earth from spent FCC catalysts (from YE Sishi et al., 2017, [274])

Table 1 Chemical composition (wt.%) of the spent FCC catalyst

Element	Fe	Na	Ca	La	Ce	Re	Al
Content	0.55	0.11	0.28	1.69	1.57	3.27	23.55

Table 2 Leaching efficiency of different ions in several operation conditions

	10 g catalysts with 110 mL 1 mol/L HCl		10 g catalysts with 110 mL 2 mol/L HCl		5 g catalysts with 110 mL 1 mol/L HCl	
	C/(mg/L)	**L/%	C/(mg/L)	L/%	C/(mg/L)	L/%
Fe	0.8±0.016	16.1±0.32	0.76±0.038	15.22±0.76	0.41±0.07	16.29±2.78
Na	1.32±0.045	100±3.41	1.31±0.073	100±5.57	1.47±0.03	100±2.04
Ca	3.8±0.2	100±5.26	4.09±0.17	100±4.16	4.72±0.23	100±4.87
La	11.79±0.63	76.62±3.70	11.67±1.02	75.84±6.63	5.49±0.14	71.38±1.82
Ce	13.67±0.83	95.49±4.47	13.53±1.24	94.51±8.66	6.47±0.43	90.34±6.00
RE	25.46±0.73	85.71±2.05	25.2±1.13	84.84±3.80	11.96±0.28	80.52±1.88
Al	50.64±1.43	23.65±0.67	47.53±1.88	22.2±0.88	21.3±1.51	19.89±1.41

*The volume of hydrochloric acid solution was fixed as 110 mL. C stands for concentration. **L stands for leaching efficiency

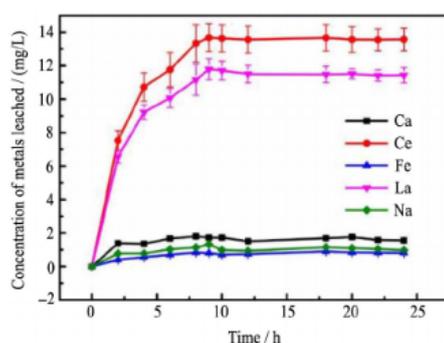


Fig. 2 Variation of metal concentrations with leaching time

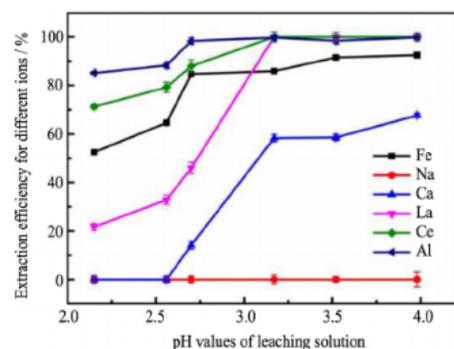


Fig. 3 Effect of leaching solution pH values on extraction efficiency for different ions

Figure 67. Additional information on the recovery of rare earth from spent FCC catalysts (from YE Sishi et al., 2017, [274])

After leaching, at the extraction step, Fe and Al are quantitatively co-extracted with La and Ce. Ca is partially extracted and Na is not extracted. At the stripping step, Fe and Al are less back-extracted than Ce and La, (only 20%) leading to a purification of the final product. The authors report that the kinetics is complex; and that more investigations are needed. The

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main barrier could be the complexity of the flowsheet for the quantitative recovery of the pure products.

NiMH batteries (From Sinha et al. [269])

Nickel-metal hydride batteries (NiMH) contain rare earths (RE) and a variety of valuable metals such as nickel and cobalt. The batteries in use are mainly AB or AB₂ type or in mixture, where A stands for La or rare earth alloys and B for Ni, Co and Al respectively. Often now, La has been substituted by Mischmetal, with a La content up to 18–28% of the total mixture. Hydrometallurgical routes are the basis of processing spent Ni-MH batteries for recovering lanthanum and other precious metals with an acid leaching (HCl or H₂SO₄) followed by a combination of different separation techniques, making the whole flowsheet complex.

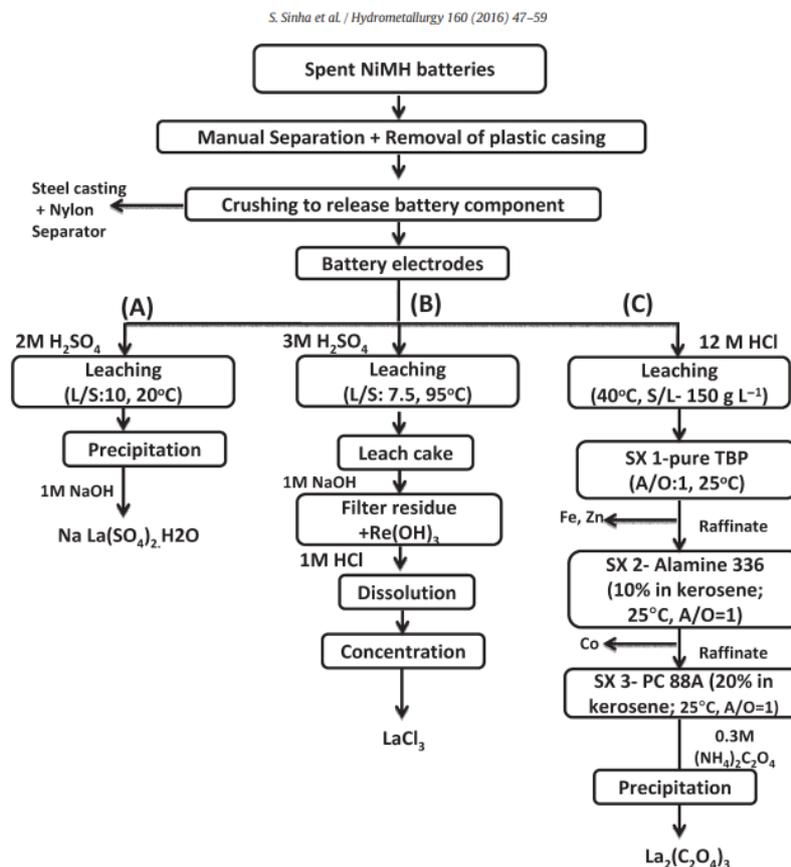


Figure 68. Process flowsheet for the recovery of LaCl₃ (A,B) and lanthanum oxalate (C) from spent NiMH batteries (from Shina et al., 2016, [269])

Lanthanum glass (From Sinha et al., [269])

Lanthanum-containing glass with higher high refractive index and a low dispersion, find many applications in optical lenses, for use in cameras, microscopes, binoculars or

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microscopes can contain ~40 wt.% of La_2O_3 . It is estimated that upon recycling spent optical glass could yield about 900 t of lanthanum oxides per year, which plays a spectacular role in estimated worldwide end use of lanthanum. However, lanthanum and other rare earth borosilicates are not directly dissolved by hydrochloric acid. A treatment using hot concentrated sodium hydroxide solution (55 wt %) at 413 K, followed by leaching using 6 M HCl as lixiviant at L/S of 8 and 363 K for 30 min allowed a quantitative recovery of the La.

2.3 SUMMARY

La and Ce are the most common REE in primary ore and therefore in secondary industrial waste such as phosphogypsum and red mud. As a consequence, they are also the most used in the industry, but always alloyed or combined with complex materials. Rich scraps or end of live products such as polishing powders or FCC catalysts could be treated for their recovery.

However, all the studies described above, and performed along the last 30 years, have been developed mainly at the laboratory scale. A few of them went to the pilot test and so far, none of them at the industrial scale except the UMICORE/SOLVAY experience that ended in 2016 and Hydrometal SA in Belgium. The company has recycled (by means of hydrometallurgy) ~1200 t of REO from glass polishing sludge and magnet sludge since 2011.

The main barriers identified are the complexity of the materials to be treated leading to a complexity of the processes to be implemented, even if they always combined quite simple process bricks such as acid or alkali leaching, carbonate or oxalate precipitation and solvent extraction. A general is the poor leachability of the Ce and La elements. When the material is too refractory, a roasting is proposed, limiting again the viability of the process.

If the production of cerium mischmetal (and at a lower extent lanthanum mischmetal) could be quite easily implemented, the recovery of pure cerium or pure lanthanum is more problematic, relying on complex solvent extraction processes such as the one used by Solvay at the La Rochelle Plant.

Polishing powders seem to be the most promising resource, very rich in Ce and La, and manageable in a short loop, these powders being used by the industry and therefore, easier to collect.

3. INNOVATIVE PROCESSING ROUTES – GAPS & BARRIERS

REE recovery in general, and therefore La and Ce recovery from secondary resources in particular, have been extensively studied since the REE crisis in 2008. However, the main barriers remain the necessary steps very often involved in quite similar in all the processes:

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acid or alkali leaching, high temperatures, more or less selective precipitations, complex solvent extraction...

Numerous projects have been implemented both on the REE value chains with ERECON and on the processing. When addressing La and Ce, permanent magnets are not to be considered, but polishing powders, batteries and FCC catalysts remain important applications of La and Ce. In the near future, Ce could be also used in permanent magnets.

All these projects have allowed a lot of innovative studies, the most recent being the use of room temperature ionic liquids at the leaching or at the solvent extraction step [275]. More work is undergoing in this research team with RTIL based processes.

If their usage looks promising, the main barrier is the return on investment with their high cost. A lot is still needed to better understand the chemical mechanisms involved, in particular when using RTIL/water mixtures. A high recycling yield of these RTILs is also required if applications for low grade ore treatment are foreseen. Their use in EOL or scrap recycling could be easier. All these statements are still to be assessed.

In 2015, Sinha et al. wrote a review on the recovery and recycling of lanthanum from various resources (Metallurgical processes for the recovery and recycling of lanthanum from various resources—A review, *Hydrometallurgy* 160 (2016) 47–59) [269]. This paper covers more than 200 references, with among others the recovery of La using innovative methods such as *bio-sorption processes. with estimated advantages over traditional way like cost efficient, high efficacy or selectivity for metal extraction, regeneration with no chemical sludge and other metabolite generation with an exclusive characteristics of faster kinetics of adsorption and desorption, and its major applicability in situ process technologies. Adsorption of lanthanum have been attempted using different bioadsorbents like bacteria, activated carbon from rice husk, bamboo charcoal and algae, among which algae was proven to be efficient one for lanthanum uptake. However, if this technics can be very specifically targeted to separate a relatively pure solution of lanthanum and other rare earth elements, many parameters can affect the process performances, often difficult to master with working on genuine waste materials.*

Concerning secondary industrial waste, the main barrier is the low REE content, even if La and Ce are the most concentrated REE. Treating these secondary waste just for the recovery of REE, and in particular La and Ce with a low value (around 5-6\$ per Kg for a pure metal and 2\$ for the pure oxide), seems difficult and therefore, the driver should be either on an environmental remediation (as for red mud) or for the usage of the waste for other applications (building, aggregates, cement...). The recovery of La and Ce would just be an added value.

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Prices

	Units	Light Rare	Last Price	YtD%
Nov 16	\$ USD/tn	Cerium >99%	6,365.83	10.24%
Nov 16	\$ USD/tn	Cerium Oxide >99.5%	2,025.49	-25.83%
Nov 16	\$ USD/tn	Lanthanum >99%	5,570.10	-3.53%
Nov 16	\$ USD/tn	Lanthanum Oxide >99.5%	2,061.66	-17.43%

For all these promising processes, more modelling, more simulation and finally more pilot tests are required (even if one have just been performed in REE4EU, with no La or Ce as REE), and in particular with a long operation time, to really confirm their added value.

If the need of pure La of pure Ce increases in the future, innovation, or even breakthrough would be needed to develop efficient and simple processes in order to recover each element separately. However, if their market price remain so low, there is low chance for a viable recycling process.

4. LIFE CYCLE ASSESSMENT COMPARISON BETWEEN EXISTING AND INNOVATIVE TECHNOLOGIES

No LCA are available on the recycling of the aforementioned secondary resources whatever existing or innovative technologies. LCAs are available on REO production from primary ore, on permanent magnet production from primary ore or from recycling, but these magnet do not contain Ce and La. For the study on the recycling, so far, only the core processes were studied, without the collect and potential sorting or pre-treatment step.

Knowing that most of the potential processes proposed for the treatment of the secondary resources are not far from the processes used to treat the primary, some tentative comparison could be carried out but would be dangerous. Indeed, concerning PG or red-mud, the REE concentration is often about 10 to 100 times lower than in primary ores. If the process impacts are driven by the total amount of waste material treated and not by the amount of REE produced, the results could be worse than for the primary production.

Already, for the primary production, one can see that the REE concentration of the deposit strongly impact the LCA results. The two figures 69, 70 are from Marx et al. [276].

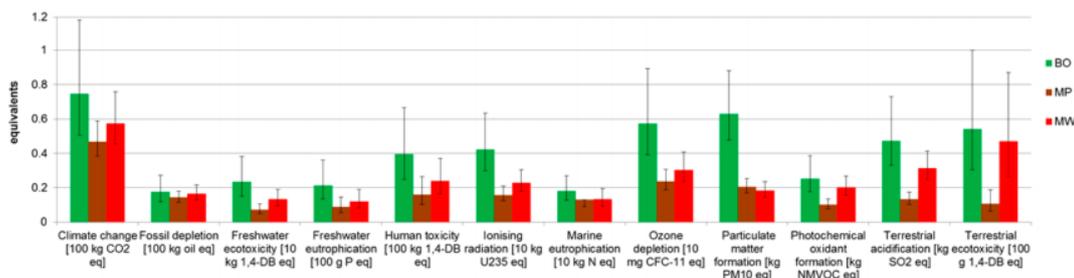


Figure 69. Environmental impacts of a 1kg NdFeB magnet with three production pathways (from Marx et al., 2018, [276])

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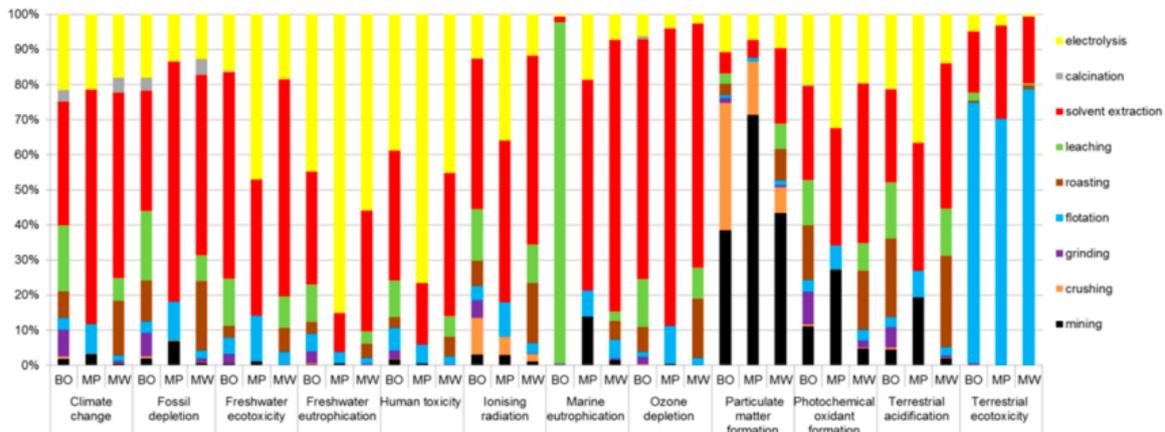


Figure 70. Share of single processes on total impacts of 1 kg Nd production (from Marx et al., 2018, [276])

The primary production of magnets, one can see that the mining and pre-treatment represent only 5 to 20% of the impacts except for particulate matter formation and terrestrial ecotoxicity. Most of the indicators are driven by the leaching, the solvent extraction and the electrolysis to produce the REE under metallic form. These steps are the same in most of the proposed recycling schemes on secondary materials but with a leaching that will require to treat much more materials. The other steps should not be very different. At the end, no big difference are expected between primary production and secondary production if leaching, solvent extraction and electrolysis are used.

Innovative process should rely on much less impacting steps if one wants to develop more sustainable recycling strategies.

5. SUMMARY

Secondary resources containing REE in general have been identified in D3.2 and potential production routes described in D4.2. Secondary industrial waste often contained a REE mix in which La & Ce are often the most abundant REE. However, the total content is 10 to 100 times lower than in primary ores. When looking more precisely at La & Ce, some scraps or EOL products are of higher interest thanks to a high La and/or Ce content, such as optical glasses, polishing powders, NiMH batteries or FCC catalysts. However, the amount to be treated annually is low.

Also today, the market price of La and Ce is very low (6\$/kg for the pure metal, 2\$/kg for the pure oxide), limiting the potential development a recycling market.

In terms of environmental impact, if the recycling strategies rely on the same process used for the primary production, no significant difference is expected.

Only a breakthrough in the selected processes could bring an added value for the development of a sustainable secondary production of La and Ce.

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REE - NEODYMIUM, PRASEODYMIUM, DYSPROSIUM, SAMARIUM

1. THE SECONDARY RESOURCES

The main secondary resources of neodymium, praseodymium, dysprosium and samarium are presented in Table 20. There are no available data concerning the existence of secondary metallurgical wastes containing Nd, Pr, Dy and Sm in Europe. The end-of-life permanent magnets and NiMH batteries consist the main secondary resources of these metals. Neodymium (NdFeB) and samarium-cobalt magnets are contained in electric vehicles motors, wind turbines and in several electric and electronic equipment (WEEEs), such as hard disk drives (HDD) and air conditioners. Currently, there is not a commercially scaled up process for the recovery of elemental REEs from permanent magnets [250]. Hitachi Company has developed a commercial technique for the automatic dismantling of magnets contained in hard drive discs and air conditioning systems [277]. Umicore N.V. and Rhodia (now owned by the Solvay group) have developed a method based on Umicore's patented UHT smelting technology to recover material from NiMH and lithium-ion batteries [278]. Significant amounts of neodymium and praseodymium are contained in nickel metal hydride vehicle batteries. Minor amounts of neodymium are added for the construction of specific ceramics, such as neodymium zirconate ($Nd_2Zr_2O_7$), which are used as room-temperature semiconductor laser diodes [279]. There are no available data concerning the development of a recycling methodology for the recovery of Nd from EoL cermaics due to the limited amounts of these specific materials.

Table 20. The main cobalt secondary resources in EU [250] [277] [278].

Secondary resources	Process scale
Metallurgical wastes (Nd-Pr-Dy-Sm)	
No available data	No referred process
Urban mining - Nd	
EoL magnets	Commercial for the dismantling processing Pilot-large scientific project for metallurgical processing
Batteries	Commercial
Ceramics	No developed method
Urban mining - Pr	
EoL magnets	Pilot-large scientific project
Batteries	Commercial
Urban mining - Dy	
EoL magnets	Pilot-large scientific project
Urban mining - Sm	
Magnets	Laboratory scale

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2. EXISTING PROCESSING ROUTES – GAPS & BARRIERS

2.1 MINING AND METALLURGICAL WASTES

There are no available data concerning the existence and the potential recycling of mining and metallurgical residues containing notable concentrations of neodymium, praseodymium, dysprosium and samarium. The presence of Nd in Greek red mud has been reported in the literature [280], however at low amounts rendering the recovery of the metal economically non feasible.

2.2 SCRAPS

Dismantling

The automated dismantling of magnets contained in hard drive discs and air conditioners has been applied commercially by few companies at limited scale [250]. The Hitachi Group (Japan) has developed an automatic mechanical dismantling and separation technique for NdFeB magnets in HDDs and air conditioners, using a rotational drum. The screws fixing the HDD become loose via vibration and tumbling and the magnets can be separated out of the casing in about 30 min. The designed apparatus can process 100 HDDs per batch and 200 HDDs per hour, much faster than manual dismantling at a rate of 12 units per hour. Hitachi and Mitsubishi Materials consortium have developed a similar technology to recover the NdFeB magnets from the compressors in air conditioners. After cutting off the casing, the rotors in the compressor can be removed and treated by either non thermal demagnetization using resonance damping demagnetization at room temperature or alternatively by thermal demagnetization at 400–500 °C. Furthermore, Mitsubishi Materials examines the separation of NdFeB magnets from direct drive (DD) motors in washing machines through thermal demagnetization for the removing the resin bounding.

Metallurgical processing

NiMH-batters contain 8 – 10 % REE, among them Pr and Nd, which are generally lost in the smelter slag when the batteries are melted down to recover nickel. **Umicore N.V. and Solvay group have developed a method based on Umicore's patented UHT smelting technology to recover material from NiMH and lithium-ion batteries** [278]. An industrial pilot plant started in Hoboken, Belgium, in 2011 is supposed to be able to handle 7,000 tonnes of batteries per year. The batteries are fed into an oven with coke and slag formers (the main part of the energy need is supplied by plastic materials and organic electrolytes from the batteries themselves) and REE end up in the slag, which can then be treated to produce a REE concentrate which is sent to Solvay's REE separation facility in La Rochelle, France, to produce

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REO. **Honda Motor Co started recovering REE from NiMH batteries in a facility belonging to Japan Metals & Chemicals Co [278].** The batteries are collected, dismantled, calcined and pulverized. The powder is separated into different fractions and fractions containing REE are dissolved in acid to produce REO. Rare earth oxides are further treated by molten salt electrolysis to produce REE in metallic form. **There are no available data concerning the commercial metallurgical processing of permanent magnets aiming to the extraction of metallic REEs.**

3. INNOVATIVE PROCESSING ROUTES – GAPS & BARRIERS

3.1 MINING AND METALLURGICAL WASTES

The extraction of selected rare earth elements from bauxite residue by dry digestion method followed by water leaching has been investigated [281]. Red mud from the industry Aluminum of Greece with an average Nd content of 100 ppm was chosen for the experiments. Kinetic studies performed with HCl and H₂SO₄ demonstrated that about 40% of neodymium can be extracted in case of HCl-based dry digestion method, but the concentration in the leachate was limited to approximately 6–8 mg L⁻¹. The results show that the method is not economically feasible in case of neodymium recovery due to the high cost of acids that are required for the digestion.

3.2 SCRAPS

Recovery of Nd, Pr, Dy and Sm from end-of-life magnets

Direct recycling

Researchers at the University of Birmingham developed a methodology for the direct recycling of NdFeB magnets using the hydrogen decrepitation (HD) process. The magnet scrap is jet milled and the produced powder is aligned, pressed and re-sintered at 1080 °C [282]. This procedure is repeated four times with a progressive fall in the density and in the magnetic properties. The procedure is then repeated but with the addition (blending) of a fine powder of neodymium hydride after the first cycle. It was found that the addition of 1 wt.% of neodymium at each stage was sufficient to achieve the density and the magnetic properties of the recycled magnets at the 4th cycle (Figure 71).

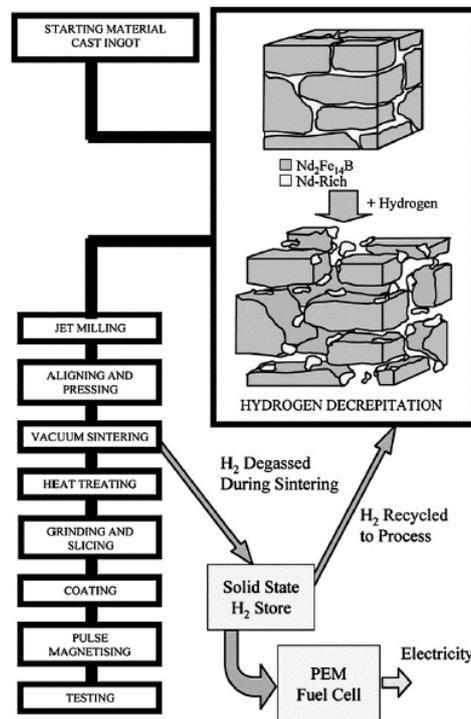


Figure 71. Birmingham University process for the direct recycling of NdFeB magnets [282].

Elemental recovery

The elemental recovery of Nd, Pr, Dy and Sm from permanent magnets scrap has been performed through various techniques, however a number of technological disadvantages and barriers has been reported. **The hydrometallurgical processes are complex and multistep, while large amount of chemicals are consumed and large amounts of waste water and effluents are generated. On the other hand, the pyrometallurgical processes require a high energy impute. Additionally, direct smelting and liquid metal extraction cannot be applied to oxidized magnets. Electroslag refining and the glass slag method generate large amounts of solid waste [250].**

The recent approach for the elemental recovery of REEs from end-of-life magnets is based on the combination of hydro and pyro metallurgy. NdFeB magnet scrap can be successfully roasted in order to change the form or state of REEs, so that the roast product could be more selectively dissolved hydrometallurgically for REEs, leaving Fe and other constituents in the magnet and the scrap stream in the solid residue. Selective chlorination roasting of magnet scrap is performed using metal halides such as $MgCl_2$ to convert the REEs into molten $NdCl_3$ and $DyCl_3$ at 1000 °C [283]. The produced $RECl_3$ ($NdCl_3$ and $DyCl_3$) were distilled at elevated temperatures to separate from the Fe-based residue. Sulfation roasting, followed by water leaching permits the separation of more than 95 wt.% of REE in the leaching solution with no iron present. Iron leaching residue forms a marketable hematite-dominated byproduct that

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can be used as a red pigment. Dupont and Binnemans [284] developed a new recycling process combining microwave roasting of NdFeB magnets and solvent extraction with carboxyl-functionalized ionic liquid betainium bis(trifluoromethylsulfonyl) imide, [Hbet][Tf₂N]. Iron remains in the ionic liquid phase, while Nd, Dy, and Co are present in the aqueous phase. By selective stripping and precipitation steps, the REEs could be recovered as a mixture of Nd₂O₃/Dy₂O₃ (to be separated in a separate process), cobalt is recovered as CoO, and the ionic liquid [Hbet][Tf₂N] could be regenerated.

Recovery of Nd, Pr, Dy and Sm from NiMH batteries

The recovery of neodymium and praseodymium from spent from hybrid electric vehicle batteries has been recently optimized. The recycling method is based on the sulfation, selective roasting, and water leaching successively [285]. Both the cathode and anode materials of a Panasonic Prismatic Module nickel metal hydride (NiMH) battery have been tested. The optimal conditions for each step of the process were determined and it was found out that 8 mol/L of sulfuric acid is sufficient for the sulfation with a solid-to-liquid ratio of 1/5. The optimal roasting conditions was determined to be 850 C for 2 h. Under optimal conditions, 96 wt.% of Nd and Pr can be obtained in the aqueous phase with negligible contamination of Ni and Co. The Ni and Co remained in solid phase as oxides together with traces of aluminum, zinc, and iron oxides. This method provides a way for the separation of the REEs from nickel, cobalt, and other elements present in the NiMH battery, into a leachate suitable for further processing.

Various novel recycling methods have been developed for the recovery of Nd, Dy, Pr and Sm from EoL permanent magnets and metal hydride batteries. However, almost in all cases, the experimental tests have been performed using pure single stream scraps that have been previously submitted to dismantling and shredding. Adaptation of these technologies to the dilute and complex EOL magnet scrap is a necessary step aiming to the upscaling. Additionally, the recovery of the major metals and materials in the dilute magnet waste stream (e.g., shredder products) is an important factor for the total success of the permanent magnet and batteries recycling [250]. It has been proved that no single metallurgical process can be successful for the efficient recovery of the REEs from their EOL secondary resource, and a combination of hydrometallurgical, pyrometallurgical, and/or electrochemical technologies will be the future solution.

4. LIFE CYCLE ASSESSMENT DATA

A life cycle assessment study has been performed in case of direct recycling of NdFeB magnet [286]. It was found that direct recycling lowers environmental impacts by 64-96%. The most significant processing steps of direct recycling that contribute 77-95% of the total

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impacts were identified to be the: 1) hydrogen mixing & milling (13-52%), 2) sintering & annealing (6-24%), and 3) electroplating (6-75%) (Figure 72). The inputs from an industrial point of view, which play key roles increasing these impacts, are the electricity (24-93% of the total impact) and the nickel (5-75%) for coating.

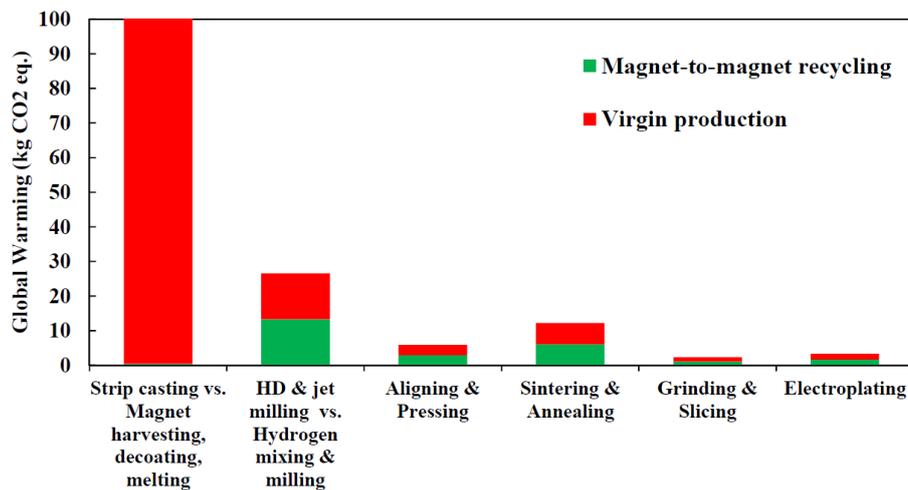


Figure 72. Global warming potential of various processing steps in virgin production and direct recycling for 1kg of NdFeB magnet [286].

5. SUMMARY

Permanent magnets and metal hydride batteries consist and main secondary resources for the recovery of neodymium, praseodymium, dysprosium and samarium. The dismantling of permanent magnets from HDDs and air conditioners have been commercially developed by few non-European companies. **The various forms of EoL devices containing permanent magnets consist the main barrier for the development of an automatic dismantler for general appliance.** The recovery of metallic neodymium and praseodymium by metal hydride and Li-ion batteries has been commercially attempted by limited number of European companies. The recovery of Nd, Pr, Dy and Sm by EoL permanent magnets via numerous novel processes is described in the literature. These processes have been successfully tested at laboratory or pilot scale using shredded scrap that is pure and composed by single devices. **The investigation of Nd, Pr, Dy and Sm recovery at actual conditions using multi-composed scrap is necessary in order the recycling sustainability be proved.**

REE - YTTRIUM

The rare earth elements (REE) represent a group of 17 chemical elements that include 15 lanthanides, plus yttrium (Y) and scandium (Sc). All these elements have similar physical and chemical properties, which provide excellent characteristics for a variety of modern applications, from batteries in hybrid cars and matches for illuminated displays in electronic devices to permanent magnets used in computer hard drives and wind turbines. In addition to these applications, they are used independently or as a mixture, or as an addition to other chemical compounds and / or metal alloys, because of this they are called "vitamins" due to their exclusive properties and the fact that only minor amounts are needed. to improve the performance of the final products [287].

Yttrium is always found with the rare-earth elements, and in some ways it resembles them. Although it is sometimes classified as a rare-earth element, it is listed in the periodic table as the first element in the second row, in the period 5 of the transition metals. It is thus also classified as the lightest in atomic weight of all the rare-earths [236].

Although yttrium metal alone is not very useful, it has many unusual applications. When combined as an alloy or as a compound with other elements. For example, when combined with iron, it is known as garnet ($Y_3Fe_5O_{12}$), which is used as a "filter" in microwave communication systems. When garnets are made of aluminum instead of iron, they form semiprecious gems of garnet ($Y_3Al_5O_{12}$) that resemble diamonds. Aluminum garnets are known as "YAG" solid-state lasers because they are capable of intensifying and the strengthening of a single frequency of light energy that is focused through a crystal of garnet. YAG type lasers have found uses in the medical industry and as cutting tools for metals.

When combined with oxygen and europium, yttrium produces the red phosphorus used as a coating on color television screens to produce the bright red color. Yttrium is also used as a metal alloy and as a high temperature coating on iron and steel alloys. It is used as a substance to deoxidize (remove oxygen) during the production of non-ferrous metals, such as vanadium. Yttrium has the ability to "capture" neutrons, making it useful in nuclear energy industry. It is also used in the production of various types of semiconductors. Therefore, it has a wide variety of applications [236].

1. THE SECONDARY RESOURCES

The main secondary resources of yttrium in the EU can be a great way of recovery and recycling so as not to depend on primary resources. We can identify them according to two main categories: (a) mining and metallurgical waste and (b) waste.: (a) mining and metallurgical wastes and (b) scraps.

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1.1 MINING AND METALLURGICAL WASTES

Yttrium cannot be found as a free element in nature. It occurs in most bastnäsite ores, monazite ores, xenotime ores, ion-absorption clays and gadolinite [288] [289]. In Europe, xenotime ore can be found in some places of Norway as Flekkefjord, Arendal and Tvedestrand, Ytterby, also in Sweden on Resarö Island, near Vaxholm, and in Switzerland on the Binntal, Valais. Monazite, which is a dark, sandy mixture of elements and contains about 50% rare-earths, including about 3% yttrium [236]. The bastnäsite ore is in karst bauxite deposits in Hungary, Greece and the Balkans region, as well as in carbonatites, a rare carbonate igneous intrusive rock, at the Fen Complex, Norway. Some bastnäsite has been found in the unusual granites of the Langesundsfjord area, Norway. Gadolinite is found in Ytterby, Resarö, Vaxholm, Uppland, Sweden.

1.2 SCRAPS

Yttrium application and respected industrial sources for recycling are the following:

- Phosphors originated from LCDs, computers, X-ray tubes, light bulbs and TV-sets.
- Glasses UV resistant glass, optical and thermal control glasses.

Solvay Group, a chemical group headquartered in Brussels, has officially opened two rare earth metals recycling plants in France focused initially on low-energy light bulbs because the recovery channels already existed. The light bulbs have an ample amount of six different rare earths—lanthanum, cerium, terbium, yttrium, europium and gadolinium—which Solvay it is in position to recycle while preserving 100 percent of their functional properties. The company Eco Recycling in Northern Italy was responsible of the design, construction and start-up of two demonstrative plants (2013-2014) to recovery of rare earths (Yttrium, Terbium, Gadolinium, Lanthanum) from fluorescent powders of lamps [290].

The Rhodia, a subsidiary of the Solvay group, began recycling the rare earths like Yttrium from phosphor dust in 2012. This process treats more than 2000 tons a year of recycled phosphor dust. There were two facilities associated with the recycling, the Saint Fons and La Rochelle facility in France. The overall recovery is approximately 80% [288]. In addition, a German lighting company in Freiberg, Narva Light Sources GmbH, in conjunction with a phosphor dust recycler, FNE Freiberg, and TU Freiberg are currently commercially recycling rare earths from phosphor dust via the SepSelsa process [291]. The recoveries are generally higher for end of life phosphor dust for europium and yttrium ranging from 81-100% versus 71-92% for production scrap, respectively [288].

2. EXISTING PROCESSING ROUTES – GAPS & BARRIERS

Some current strategies for rare earth recycling are acid/basic leaching or solvent extraction. Some of these industrial-applied methods have been developed and improved by Solvay, OSRAM and TU Freiberg [292] [293] [294] [295] [296]. A detailed overview of the most recent scientific literature that describe yttrium recovery from different sources (ores and scraps) can be found in Ref. [289] [297]. Here, we highlight the following studies for recovering Y from scrap. Resende and Morais [298] studied sulphuric acid leaching of Y scrapped from computer monitors, showing that leaching efficiency depends mainly on the acid/sample ratio and the percentage of solids. The result was 96% of Y leached in 1.5 hours of leaching at room temperature. Rabah [299] studied the recovery of yttrium from fluorescent light tubes using a mixture of sulphuric/nitric acids as the leaching agent. At critical conditions, i.e. autoclave digestion, at 125 °C, 4 h and 5 MPa using a mixture of sulphuric/nitric acids, the Y dissolution reached 96.4%. Morais et al. [300] studied the recovery of Y from the material scraped from colour TV screens using sulphuric acid as the leaching agent, where Yttrium dissolution was 95% when conducted at 90 °C, 2 h of leaching, acid/sample ratio of 1000 kg/t and 40 w/w% solids. Resende and Morais [301] showed the technical viability of the recovery of Y presents in the coating powder of the inner surfaces of panel computer monitors. The recovery of Y can be done by employing sulphuric acid digestion followed by water leaching. The main factors influencing Y dissolution are the acid/sample in the digestion step and the solid percentage in the leaching step. The water used in the second scrubbing can be reused in the leaching step, minimizing water consumption and increasing the metals content in the liquor. Yang et al. [302] used di-(2-ethylhexyl) phosphoric acid (DEHPA) and kerosene as extractant and diluent, respectively, achieving 99% of yttrium recovery in 2 M HCl solution. On the other hand, De Michelis et al. [303] employed several acids to dissolve rare earths with a subsequent precipitation with oxalic acid. This technique allowed obtaining yttrium oxalate (99% of recovery). Innocenzi et al. [304] instead attempted yttrium recovery using NaOH solutions for yttrium precipitation from acidic solutions. In this research, 95% of yttrium recovery was achieved. Ernesto de la Torre et al. [305] recovered Yttrium from cathode ray tubes (CRTs) that were manually dismantled. The resulted powder was leached with HNO₃, and then the solution was submitted to solvent extraction with di-(2-ethylhexyl) phosphoric acid (DEHPA) using n-heptane as a diluent. For re-extraction, HNO₃ was used again, and yttrium was precipitated by adding four times the stoichiometric amount of oxalic acid, reaching 68% yttrium purity (Figure 73).

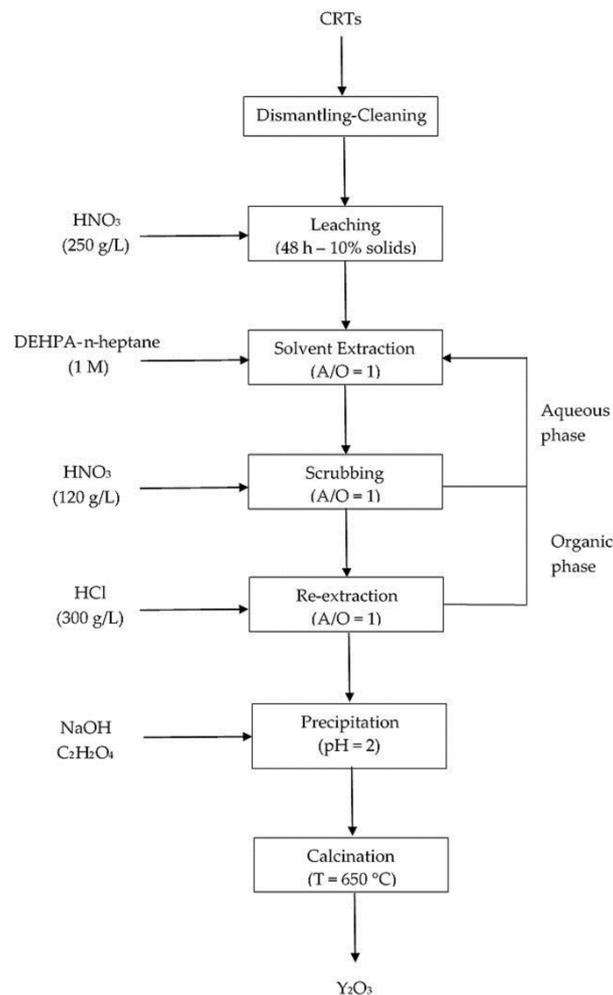


Figure 73. Process flow diagram for yttrium oxide recovery from cathode ray tubes (CRTs) powder [305].

3. INNOVATIVE PROCESSING ROUTES – GAPS & BARRIERS

In the SepSELSA project, the solid-state chlorination was studied for mobilizing Rare-Earth elements from waste streams [291]. Instead of hydrochloric acid this kind of chlorination decomposes NH_4Cl thermally to release up to 400 °C hot HCl gas. After cooling the resulting solid metal chlorides may be easily dissolved in pH-adjusted water. Without producing strongly acidic wastes and with NH_4Cl as cheap source for hydrogen chloride, solid-state chlorination provides various advantages in terms of costs and disposal. So far, this is one of the few methods that have been able to make their way from the laboratory to industrial production [306]. Figure 74 shows a comparison of solid-state chlorination with industrial-applied recycling processes for fluorescent lamp scraps.

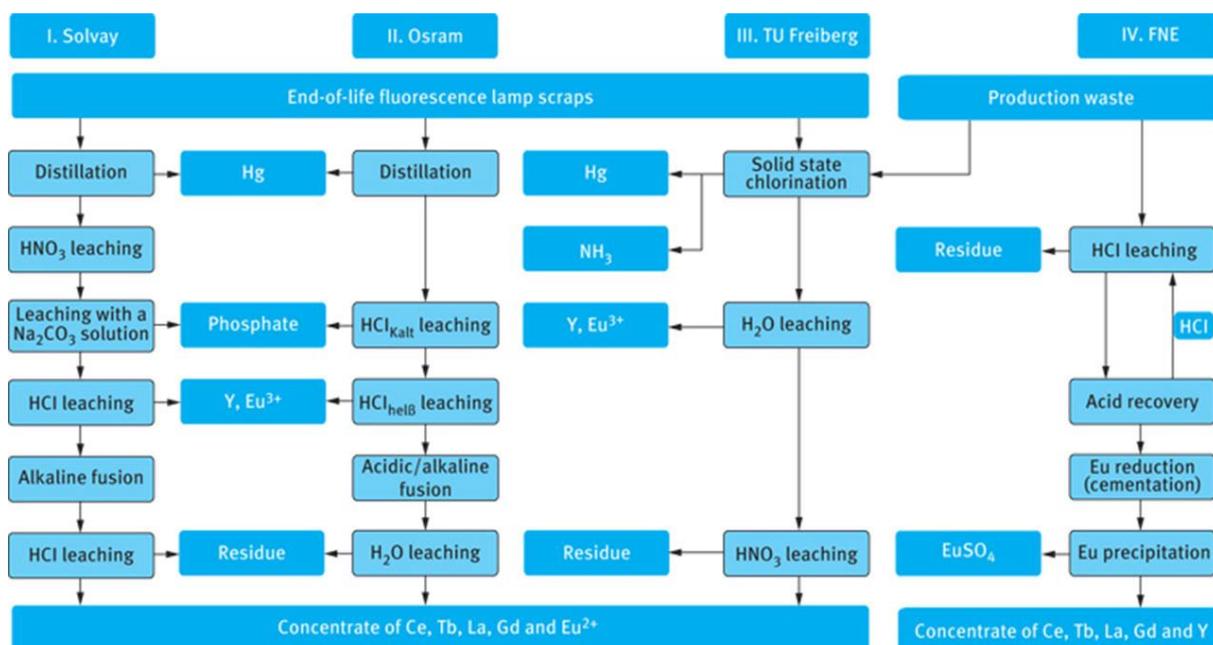


Figure 74. Comparison of solid-state chlorination with industrial-applied recycling processes for fluorescent lamp scraps. Figure taken from Ref. [291].

In the European Project Reclaim [223], a first pilot plant was developed for the recovery of Yttrium and Europium from spent fluorescent lamps powders. This plant has been built and operated at Técnicas Reunidas (TR) Technology Centre (Madrid, Spain), with Pretreatment (to remove Calcium), Leaching (to selectively solubilize Y enriched solid produced in the pretreatment stage), Neutralization and Precipitation Units (to selectively precipitate Y from the pregnant liquor solution from the leaching stage), by TR and the punctual collaboration of RELIGHT's staff. The production rate is shown to be 2256 g/day of Yttrium from the collected powder.

Another European project RECYVAL-NANO [307], focused on the recovery of indium, yttrium and neodymium metals from Flat Panels Displays (FPD), one of the most growing waste sources. The treatment facilities of Coolrec Belgium located in Tiselt (Belgium) were made available for the project development. Yttrium metal was recovered from their stream using HCl as leaching acid and Cyanex 923 and DEHPA as extractants. In addition, combined processes including precipitation were assessed. Due to the high L/S values required to extract the entire metal content during leaching processes, an alternative route based on selective precipitation steps was proposed. This methodology developed has the advantage that is suitable to treat a complex mixture of metals following the whole steps or only a part, therefore being a versatile route to be tailored for Waste Electrical and Electronic Equipment (WEEE) complex wastes where significant amounts of valuable metals such as indium, yttrium but also gold or silver are present.

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In the European project EURARE, it was studied the application of ionic liquids (ILs) for recovery of Yttrium and other REE from WEEE wastes and concentrates [308]. ILs consist of an organic cation and an inorganic or organic anion, and what makes them so attractive is that the almost infinite cation-anion combinations allow us to tailor IL properties, rendering them as designer solvents. In this project, ILs were used as: (i) lixiviants for low grade REE resources, (ii) solvents for REE liquid-liquid extraction and separation, and (iii) electrolytes for REE electrodeposition. The application of ionic liquids as an alternative to conventional metallurgy is driven by the need to find more efficient and environmentally-friendly metallurgical processes for REE dissolution-separation and production.

The European projects HydroWEEE (2009–2012) [309] and HydroWEEE demo (2012–2016) [310] aimed to study the innovative hydrometallurgical process to recover metals from WEEE, with particular interest for fluorescent powders of CRTs and lamps. In the first project a mobile plant was used to test hydro-metallurgical processes to extract Yttrium, and others metals from WEEE in a high purity, while the second project tried to build two industrial, real-life demonstration plants (1 stationary and 1 mobile) in order to test the performance and to prove the viability of the processes from an integrated point of view (technical, economical, operational, social) including the assessment of its risks and benefits to the society and the environmental.

4. LIFE CYCLE ASSESSMENT COMPARISON BETWEEN EXISTING AND INNOVATIVE TECHNOLOGIES

The novel processing route called solid-state chlorination provides various advantages in terms of costs and disposal, because it doesn't produce strongly acidic wastes and makes use of NH_4Cl as cheap source for hydrogen chloride. On the other hand, the development of processing routes based on ionic liquids as an alternative to conventional metallurgy could give more efficient and environmentally-friendly metallurgical processes for REE dissolution-separation and production.

5. SUMMARY

Yttrium can be extracted from different secondary resources as some ores like bastnäsite ores, monazite ores, xenotime ores and gadolinite, which can be found in some places in Europe, as well as from scraps (phosphors originated from LCDs, computers, X-ray tubes, light bulbs and TV-sets, etc). The use of Yttrium, especially for high-tech products are increased in recent years and combined with the scarcity of the resources and the environmental impact of the technologies to extract them from ores make the recycling waste, that contain Y, a priority. Some current strategies for Yttrium recycling are acid/basic leaching or solvent extraction.

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Some companies in Europe are currently commercially recycling Yttrium from scrap like Solvay Group, Eco Recycling, Rhodia and FNE Frieberg. In the last years, several European projects were carried out to improve and develop novel strategies for recycling Yttrium. For example, in the SepSELSA project it was developed a successful new approach called solid-state chlorination which could provide various advantages in terms of costs and disposal.

SCANDIUM

1. THE SECONDARY RESOURCES

EU imports the total of the required scandium amount from Russia (67%) and Kazakhstan (33%). The production of Sc in EU by secondary resources is feasible in the near future as the appropriate technologies are quite well established. Red mud, the aluminum industry residue, consists the most significant secondary resource for Sc extraction. It is estimated that about 5-6 million tonnes of red mud are annually generated in EU [311], with a Sc concentration which is ranged between about 70 and 100 ppm [312] [313] [314]. Greece and Hungary are the main red mud producers in EU. The recovery of Sc from red mud presents an increasing interest as; (a) the valorization of the residue consists a crucial environmental subject and (b) several metallic values (such as Fe, Ti, Zr, REEs) can be simultaneously extracted. On the other hand, there are no data concerning the existence of notable urban resources containing scandium. As it has been already described, Sc is mainly used for the production of specific aluminum alloys while Sc_2O_3 , is used for the construction of electronic devices. Future applications concern its use for the synthesis of Sc-containing fullerenes for medicine purposes [315]. Unfortunately, the urban Sc-rich wastes have not be quantified in European level. Table 21, quotes the main potential secondary scandium resources.

Table 21. The main scandium secondary resources in EU.

Secondary resources	Process scale
Metallurgical wastes	
Red mud	Laboratory, pilot
Urban mining	
Sc-Al alloys	No recycling investigation
Scandium oxide in solid oxide fuel cells	No recycling investigation
Scandium oxide in electronic devices (laser, LEDs etc.)	No recycling investigation

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Scandium in fullerenes	Studies at laboratory scale
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2. EXISTING PROCESSING ROUTES – GAPS & BARRIERS

2.1 MINING AND METALLURGICAL WASTES

It has not been reported the commercial extraction of Sc by mining and metallurgical wastes.

2.2 SCRAPS

Scandium contained in a number of materials such as: in Sc-Al alloys in specific airspace applications and constructions (including baseball bats and bicycle frames) and as Sc₂O₃ in solid oxide fuel cells, electronic devices (laser, LEDs etc.). However, there are no data concerning a commercial recycling process for scandium extraction possibly due to the low total amount Sc-containing scrap.

3. INNOVATIVE PROCESSING ROUTES – GAPS & BARRIERS

3.1 MINING AND METALLURGICAL WASTES

The extraction of scandium by the aluminum industry residue (red mud) has been attempted at laboratory and pilot scale, however it has not been applied commercially. The Orbite Company has developed a processing route which comprises the intensive leaching of red mud with hydrochloric acid at high temperature after the granulation of the residue in extra fine particles (Figure 75). All the metals (except titanium, but including rare earth elements) dissolve as chlorides. Specifically, alumina and iron dissolve to form aluminum chloride (AlCl₃) and ferric chloride (FeCl₃). Further processing via hydrolysis allows the selective recovery of the remaining metals in the leachate, such as scandium, magnesium, gallium, scandium, and REEs [316].

The extraction of scandium form red mud at pilot scale has also been performed by Uralsky Alumina Refinery Company (Russia). The productivity of the pilot plant is about 200 kg/month [317]. The respective flowsheet is presented in Figure 76. The red mud is leached with sodium bicarbonate in a vertical reactor (Figure 77). The scandium hydroxide phase is carbonized according to the equation:



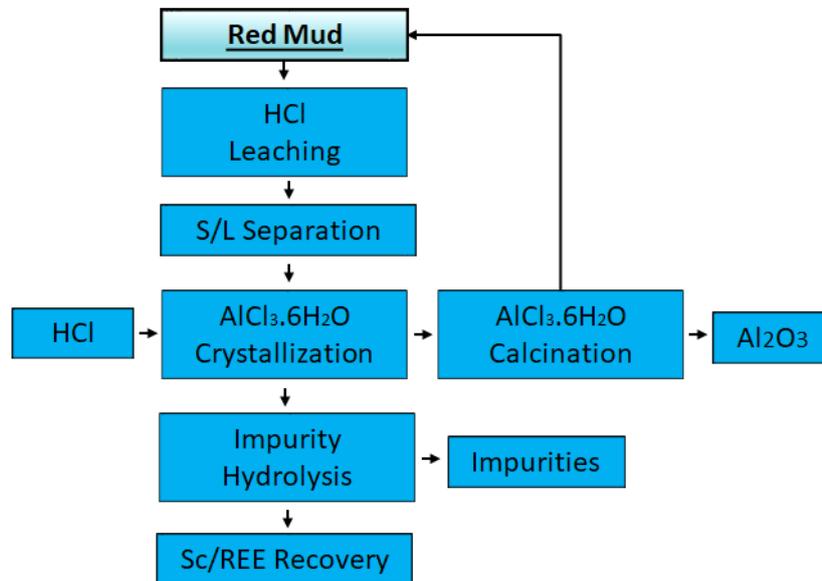


Figure 75. Orbite company flowsheet for the extraction of metallic values from red mud – among them scandium [316].

The iron and aluminum phases remain in the solid phase, while Ti and Zr are received from the liquor with hydrolysis. Scandium is precipitated using NaOH. The main advantage of the method is its low environmental impact as NaHCO₃ consists a gentle leaching agent. However, the method should be further optimized due to the low recovery degree (approaching 30%). Experimental tests indicate that the recovery degree is strongly affected by the leaching temperature and the P_{CO2} in the reactor.

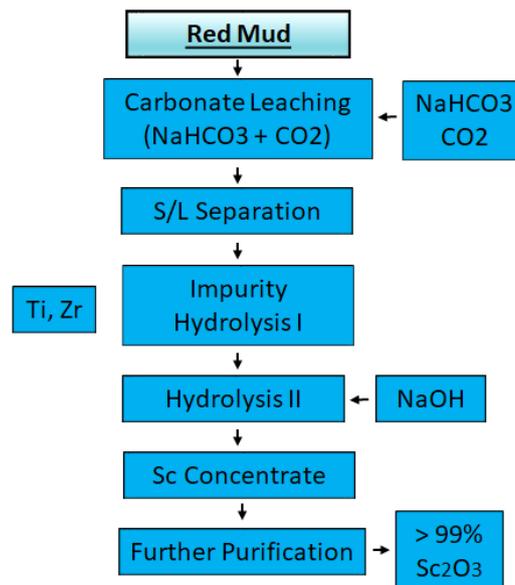


Figure 76. Flowsheet of the Kamensk Uralsky Alumina Refinery (Russia) for the extraction of metallic values from the red mud [317].

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Figure 77. Pilot-scale project (vertical reactor) designed by Kamensk Uralsky Alumina Refinery (Russia) for the extraction of metallic values from the red mud [317].

3.2 SCRAPs

A process for the recycling of Sc-fullerene nanoparticles has been developed at laboratory scale. Fullerenes constitute a distinct allotrope of carbon nanomaterials presenting a unique cage-like structure and electron-deficient nature lead to extraordinary properties. The potential applications of complex Sc-fullerene particles include the design of high-performance MRI contrast agents, X-ray imaging contrast agents, photodynamic therapy and drug and gene delivery [318]. The recycling of a medical waste rich in Sc-fullerene particles has been attempted. The method, which is described in Figure 78, comprises the high temperature processing of the waste using arc plasma and heating in air atmosphere at 750 °C aiming to the recovery of the Sc_2O_3 amount [319].

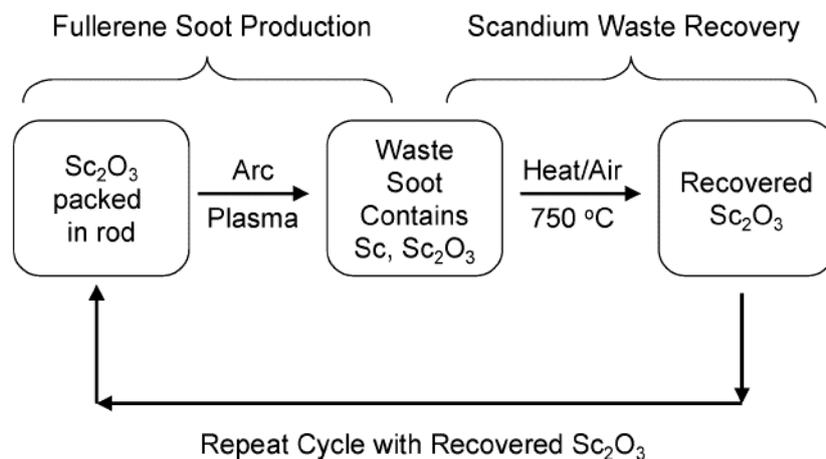


Figure 78. Recovery of scandium by potential Sc-containing fullerene wastes [319].

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

5. SUMMARY

Scandium is not currently extracted by secondary resources in European Union despite the production of Sc-containing red mud at significant quantities (5-6 million tonnes annually). The concentrations of Sc in red mud are ranged between 70 and 100 ppm rendering its recovery feasible according to the established technologies that have been tested at pilot scale. On the other hand, the recovery of Sc by urban wastes consists a complex issue due to a number of reasons such as: (a) there is a lack of information concerning the amount of Sc-containing electronic wastes and whether this material collected and processed by the recycling companies, (b) there is a small number of specific cutting-edge devices containing Sc – therefore the potential recovery amounts are limited. **In conclusion, red mud residue consists the most remarkable secondary resource of scandium. The EU recycling policies should encourage the aluminum/alumina companies regarding the extraction of Sc from red mud. Initially, semi-industrial plants, according to the already existence technologies, could be designed and operate.**

SILICON

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1. THE SECONDARY RESOURCES

The element silicon is not a mineral, since it does not occur in nature: its most common form is SiO₂, or silica dioxide, which is a mineral; this is quartz or common sand's basic constituent. The majority of silicon refined each year - about 80 percent - is produced as ferrosilicon for use in iron and steelmaking. Ferrosilicon can contain anywhere between 15 and 90 percent silicon, depending on the requirements of the smelter. Silicon metal, which can be classified into metallurgical and chemical grades, is used primarily as a deoxidizing and alloying agent in the production of iron and steel; it is also used by the aluminium industry in the production of wrought and cast products. Production of silicon metal and silicon-containing alloys is extremely power intensive.

Demand for silicon metal comes also from the chemical industries as the basic raw material in the manufacture of many chemical products and intermediates, such as silicones and silanes.

An estimated 15% of the world production of metallurgical grade silicon is further processed into high-purity silicon for use in the semiconductor industry [320]: this typically is the "nine-9" purity, nearly defect-free single crystalline material.

Solar cells can tolerate higher levels of impurity than integrated circuit fabrication and there are proposals for alternative processes to create a "solar-grade" silicon.

Potential secondary resources for silicon recovery can include:

- (i) Aluminium-silicon alloys;
- (ii) Scraps from ingot top cut and related wastes from the sawing slurry;
- (iii) Defective, broken and semi-finished products and related end-of-life products.

2. EXISTING PROCESSING ROUTES – GAPS & BARRIERS

Silicon is not currently recovered from post-consumer waste, moreover most chemical applications are dispersive, thus not allowing for any recovery.

The recovery of contained silicon in metallic scrap such as aluminium alloys, cast iron and steel is incidental to that of the primary metal; some silicon is recycled internally in smelters when fines or off-grade material are remelted.

About silicon wafers, there is research on their recycling, however it has not yet materialised in marketable solutions; during the production process only 45–50% of the silicon feedstock reaches the end, all other is lost as waste in the processes like sawing and block cutting.

A large part of the current production of silicon wafers is used in the production of photovoltaic solar panels; the economic viability of solar photovoltaic (PV) modules recycling is still unfavourable, and an efficient collection network is a relevant prerequisite [321]. Si-based panels are poor of valuable materials, and their recycling cost is always higher than the landfilling one, making recycling an unfavourable economic option [322].

In recycling plants, the mechanical separation of the major components and materials of PV panels is the focus: the major components of c-Si panels, including glass, aluminum, and copper, can be recovered at cumulative yields greater than 85% by panel mass through a purely mechanical separation. The attention of companies is more focused on thin-film modules recycling, guaranteeing a higher profit thanks to the presence of precious materials [323], even if, this still achieves high material recovery by panel mass, some valuable materials (that are small in mass) such as silicon and silver may not fully be recovered [324]. A few techniques to purify the solar grade silicon waste are discussed by Dong [325].

3. INNOVATIVE PROCESSING ROUTES – GAPS & BARRIERS

3.1 RECYCLING OF TOP-CUT SILICON SCRAP FROM INGOTS

After directional solidification in the Bridgman and block-casting processes, the regions showing presence of solid particles are cut off from the ingot. Usually 10-20 mm is cut off from the sides of the ingot. The cut regions have a maximum concentration of impurities since the impurities with low partition ratios are present in high levels in the top of the cast ingot, and the concentration of impurities with high ratios is high in the bottom of the ingot. As a result, the top of the ingot is highly contaminated with impurities such as SiC, Si₃N₄, boron, phosphor, iron, aluminum, etc. While the bottom and sides are recycled and used again in the solidification process, the top-cut is sold as scrap to the steel industry. A considerable amount of silicon is lost this way from. Making it possible to recycle silicon scrap would reduce the cost of solar cells [326] [327].

Work on recycling top-cut silicon scrap by filtration has been performed recently. The technology of filtration is established in the aluminum and steel industries to remove harmful inclusions. Top-cut silicon scrap is melted in a high vacuum furnace at around 1500°C. Filtration with ceramic foam filters has proved to be very efficient (around 97 %) for removal of SiC and Si₃N₄: almost all inclusions larger than 10 µm can be removed through this technique [327].

3.2 SILICON FROM SLUDGE

More than 80% of the current solar cell production requires the cutting of large silicon crystals. While in the last few years the cost of solar cell processing and module fabrication could be

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reduced considerably, the sawing costs remain high.

The ingots are mainly cut by the multi-wire slicing technology [328]. Cutting is achieved by abrasive slurry, which is supplied through nozzles over the wire web and carried by the wire into the sawing channel. The slurry consists of a suspension of hard grinding particles. Today, SiC and diamond are the most commonly used abrasives. Both materials are very expensive and account for 25 to 35% of the total slicing cost. The volume fraction of solid SiC particles can vary between 20 and 60% and the mean grain size between 5 and 30 μm . Kerf loss is of about 180 μm when wafers between 200 and 300 μm are cut. So, during wafer cutting, almost 50% of silicon is lost in the sludge [9]. Since large quantities of slurry and SiC are used during sawing much research is done on recycling sludge. Kuniaki [329] developed a method to recycle the sludge by forming ceramics. In this method sludge is put into an iron pot and heated at 1140°C. In this step, Al, Na and Ca are removed while silicon remains as residual or an oxide. Then, the sludge is mixed with kaolin, containing quartzite, clay, feldspar, pottery stone etc., to a ratio of up to 60% kaolin. In the next step the mixture is calcined in a specific temperature and is ready to be used in pottery, building material (brick, roofing tile), paving stones etc. Almost the same method for using the silicon sludge in the porcelain materials was developed by Yuji [330]. The recovered silicon slurry is added to the body containing ground and formulated porcelain or the starting material of ceramic wares containing a variety of components and additives, then, the mixture is formed, and fired to give ceramic wares. Thus, the silicon powder can usefully be utilized without soil pollution. Generally, since the water content of the silicon sludge is high, dehydration is employed to adjust the water content, if it is used as a starting substance for ceramic wares.

3.3 SILICON FROM OPTICAL FIBERS WASTES WITH THERMAL PLASMAS

Optical fibers, which are made of ultra-high pure silica glass containing a little germanium dioxide at the center called core, are key components of Information and Communication Technologies (ICTs). Production has increased with continued, rapid and sustained growth. The total optical fiber prepared by ultra-high-pure silica reached 29.8 million km corresponding to 810 ton of silica containing 370 ton of silicon in Japan in 2001. In addition, roughly similar amounts of pure silica were defective and wasted during the production process in the factory. According to the estimate, the trend for next 7-year aggregate growth is about 23%. Optical fibers used are a type of hazardous waste at present leading to waste of resources with ultra-high purity silica and high energetic potential without satisfactory treatment methods. Therefore, treatment and recycling of used and defective optical fibers is becoming more and more important. Here the research done on recycling of optical fibers by thermal plasmas is mentioned. Material recycling processes using thermal plasmas are promising for hazardous wastes treatment, because thermal plasmas have unique

advantages, such as high enthalpy to enhance the reaction kinetics, high chemical reactivity, oxidation and reduction atmosphere in accordance with required chemical reactions and rapid quenching to produce chemical non-equilibrium materials.

A new way of silica optical fiber wastes recycling for feedstock supply of SoG-Si on the basis of harmless treatment with hydrogen-argon thermal plasmas is reported by Ma, Ogura, Kobayashi and Takahashi [331]. A plasma generator and a reactor with a continuous supply system of silica fiber pretreated reactant are employed in the process. The copper nozzle and the quartz reactor with water-cooled were hand made. The raw material for plasma reactions in optical fiber is pretreated at 900°C under air atmosphere to remove the coating resin around the silica optical fiber.

3.4 SILICON FROM END-OF-LIFE PHOTOVOLTAIC PANELS AND THE RESIELP PROJECT

In July 2012 the Directive 2012/19/EU of the European Parliament and of the Council on Waste Electrical and Electronic Equipment (WEEE) has included the photovoltaic panels and established percentages and deadlines for their recovery and recycling. This Directive established that recovery and recycling should be 85% and 80% since 2018, respectively.

According to recent studies, the recycling of crystalline photovoltaic modules could have significant economic and environmental benefits, given that this technology occupies over 90% of the present PV module market [324] [325].

For the recovery and recycling processes from the waste PV crystalline modules it is necessary to disassembly the panel in its components. Generally, the first step is the removal of the aluminum frame, followed by removal of the EVA layer, in order to separate the glass from the cell [332] [333].

Thermal treatment is generally used for the separation of all component of the PV module after removing alumina frame. Similar heat treatment separation also used by First solar is making easier the cells recovery and their subsequent treatment.

The processes to obtain polycrystalline solar-grade silicon can be divided into two main categories: chemical and metallurgical routes.

1) The chemical routes can provide very pure silicon even for electronic purposes, but it needs large and expensive plants (Siemens process).

2) The metallurgical routes are performed by a combination of subsequent pyro- and hydro-metallurgical refining steps to obtain solar-grade silicon from metallurgical-grade. As the metallic impurities can be removed by directional solidification this is the final step in all of metallurgical processes. Before that, the non-metallic contaminants (like B and P) must be eliminated from the silicon. For this reason, several processes are combined, for example slag

refining, vacuum refining, formation of volatile species, acid leaching, plasma refining, gas blowing, simultaneous reactions, solvent refining.

The metallurgical processes need significantly lower energy consumption than the chemical route. On the other hand, they have to face particular challenges. In recent years, there has been a great deal of progress in metallurgical processes for solar-grade silicon feedstock production [334] [335]. In the purification process it uses four phases arranged in four-layers with appropriately set density in which the melting and purification of the silicon is assisted with molten steel.

The ReSiELP Project (*Recovery of Silicon and other materials from End-of-Life Photovoltaic Panels*) is mainly based on the valorization of Silicon, besides other materials as Silver, Copper, glass and Aluminum from photovoltaic panel at end of their life. RESIELP is funded by EIT Raw Materials in 2017 and it will last three years.

Three pillars have been identified in ReSiELP:

- The Recovery of the EOL panels;
- The Silicon refinement;
- The re-use of glass for building materials development.

RESIELP brings together technologies from different fields to recover and purify critical and precious raw materials in an environmentally friendly and circular economic process with a product-centric zero-waste approach.

Below the ReSiELP process flow focused on silicon recovery:

First, the EOL PV panels are collected and submitted to heat and hydrometallurgical treatments that will be performed in new plant. From this process, different raw material will be recovered: copper, aluminum and silver and will be directly placed on the market. In addition, as wastewater treatment methods will be tested for recovering water from hydrometallurgical wastewater and reduce the environmental impact of the processes.

The recovered silicon will be purified in the new plant in order to produce Solar Grade silicon (Si-SoG). The purification line in ReSiELP project means the consecutive steps of the process to reduce the concentration of boron and phosphorus at once.

The novelty of the ReSiELP technology for treatment of EOL PV panels is that:

- Silicon and silver will be recovered, besides the glass and the aluminum frame already recovered in some EOL PV recycling plants. The silicon recycling will decrease the high energy consumption required for the production of silicon from quartz.
- New purification methodology is used by one of the partner of ReSiELP to achieve high purity silicon which can be re injected in the PV value chain. During the three years of the project, the technology of the process will be raised from the actual TRL 5 to TRL 7. An added value of the process is that all the recovered metals will be easy placed

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on the market. ReSiELP technology implement treatment processes allowing to recover critical and precious raw materials, as Silicon, from EOL PV modules as well as glass, aluminum (Al) and copper (Cu) via a thermo-hydrometallurgical process.

- Silicon refinement The second main challenge is to produce, from silicon recovered through above process, silicon at a level sufficient for re-injection into the PV value-chain. This is done via a liquid-metal with additional phase refining process develop. In production of solar-grade silicon by metallurgical techniques metallurgical-grade silicon is used typically as a starting material. The silicon recovered from disassembling end-of-life solar panels could be a suitable secondary raw material for recycling and can be turned into a new solar grade material. Though this silicon is doped by boron or phosphorus and contains some other contaminants coming from the frame, electric contacts and the disassembling processes, the concentration of lots of impurities is less than in metallurgical-grade silicon. Considering this the silicon from end-of-life panels could be a competitive secondary raw material in production of solar-grade silicon.

4. LIFE CYCLE ASSESSMENT COMPARISON BETWEEN EXISTING AND INNOVATIVE TECHNOLOGIES

No studies about LCA applied to silicon secondary production from ingot, sludge and optical fibers wastes with thermal plasmas have been found.

Instead, there are some papers about LCA data regarding the above described processes of recovering secondary silicon from end-of-life photovoltaic panels. In reference [336], a LCA comparison is done on four different processing routes: (1) landfill, (2) incineration, (3) reuse, (4) recycling (mechanical, thermal and chemical routes) for end of life approaches for crystalline silicon (c-Si) solar modules, based on a combination of real process data and assumptions.

In Figure 79 and Figure 80 are reported the results for global warming (GWP), human toxicity-cancer effects (HTP-CE and HTP-nCE), freshwater eutrophication (FEuP), freshwater ecotoxicity (FEcP) and abiotic depletion of elements potential (ADP) impacts for multi and monocrystalline silicon modules.

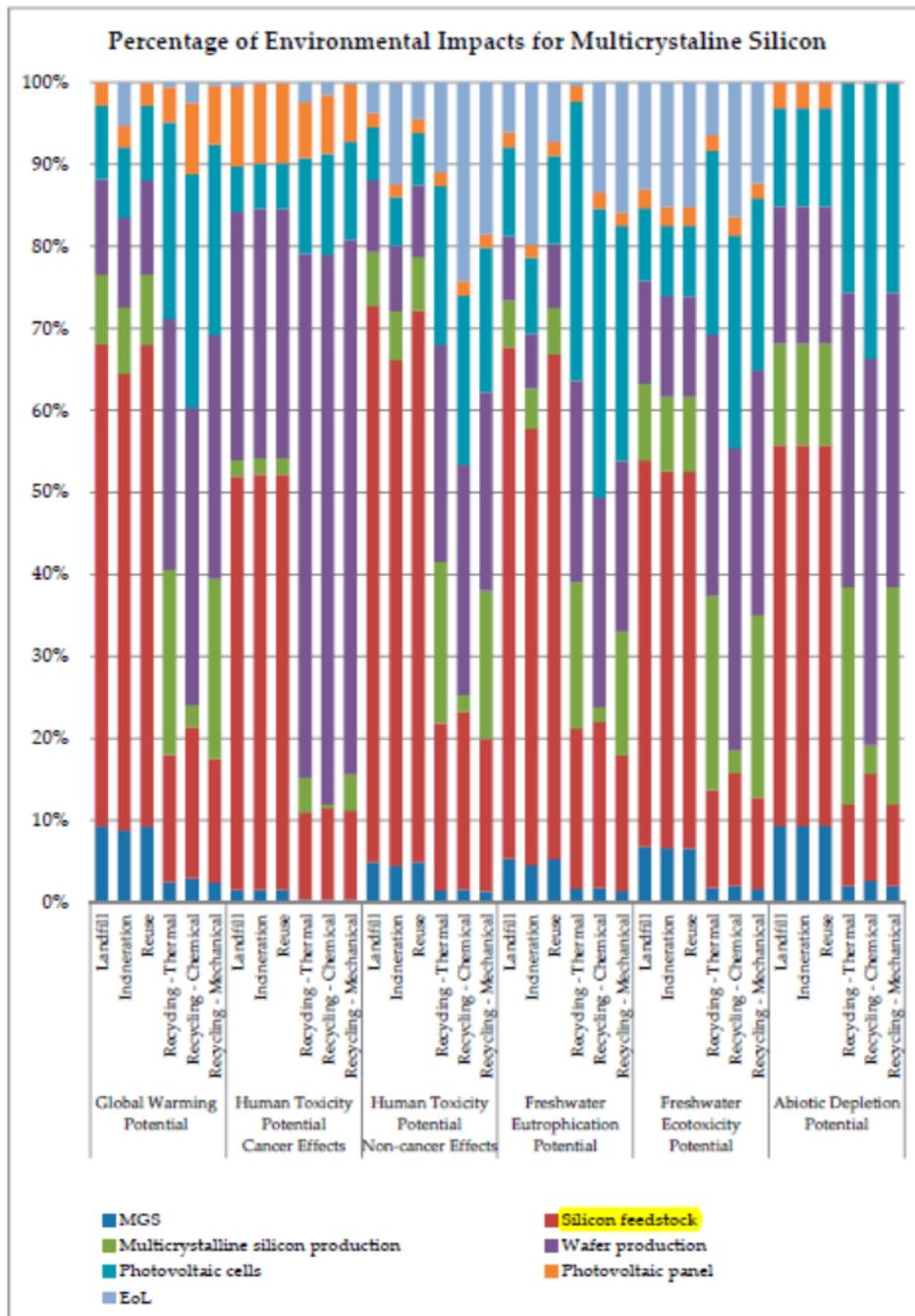


Figure 79: relative environmental impacts for different end-of-life scenarios considering multi-crystalline silicon solar modules: landfill, incineration, reuse and recycling (thermal, chemical and mechanical) [336].

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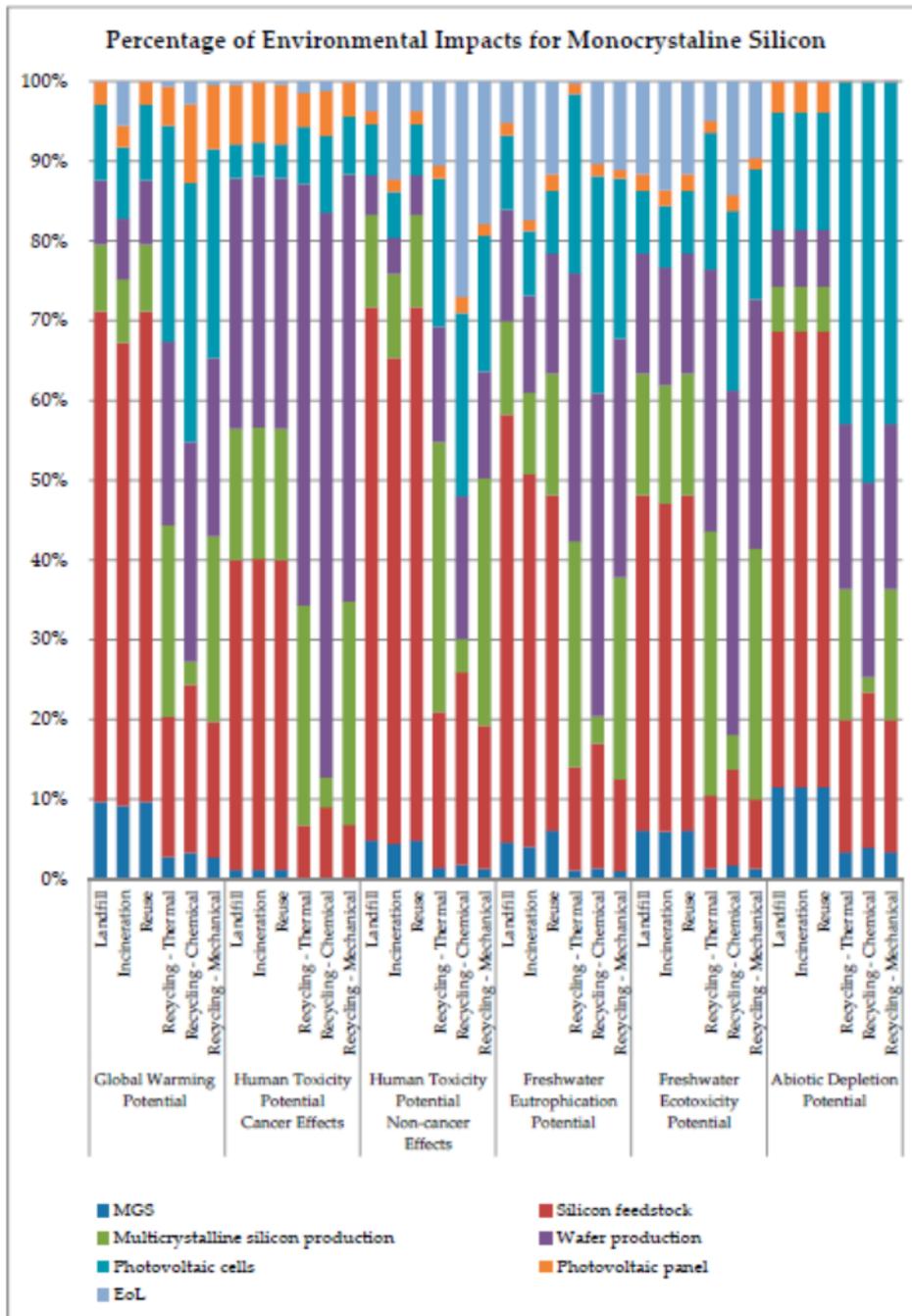


Figure 80: relative environmental impacts for different end-of-life scenarios considering monocrystalline silicon solar modules: landfill, incineration, reuse and recycling (thermal, chemical and mechanical) [336].

The impact assessment was performed using one of the most recent and up-to-date LCA methods, the ReCiPe method [337].

The comparison of all scenarios studied, presented by indicators, shows that lower environmental impacts can be achieved through recycling methods. That result is mainly due to the recycling and reuse of part of the raw materials (e.g., silicon and silver) and the glass

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and aluminum from the frame, which confirms the importance of high-value recycling processes compared to other disposal solutions that cannot reuse or recycle the individual components. It can also be observed that the incineration process produces the worst impacts compared with other EoL scenarios, mainly because this process uses more primary energy than the other methods presented in this LCA. The chemical approach shows low impacts. However, the use of toxic chemicals should always be observed in any environmental analyses.

Latunussa *et al.* [338] discussed the application of the Life Cycle Assessment methodology to an innovative process for recycling of PV waste panels. The processes have been developed at a pilot scale under the FRELP project co-funded by the European Life programme. The functional unit of the study was the treatment of 1000 kg of crystalline silicon waste PV panel.

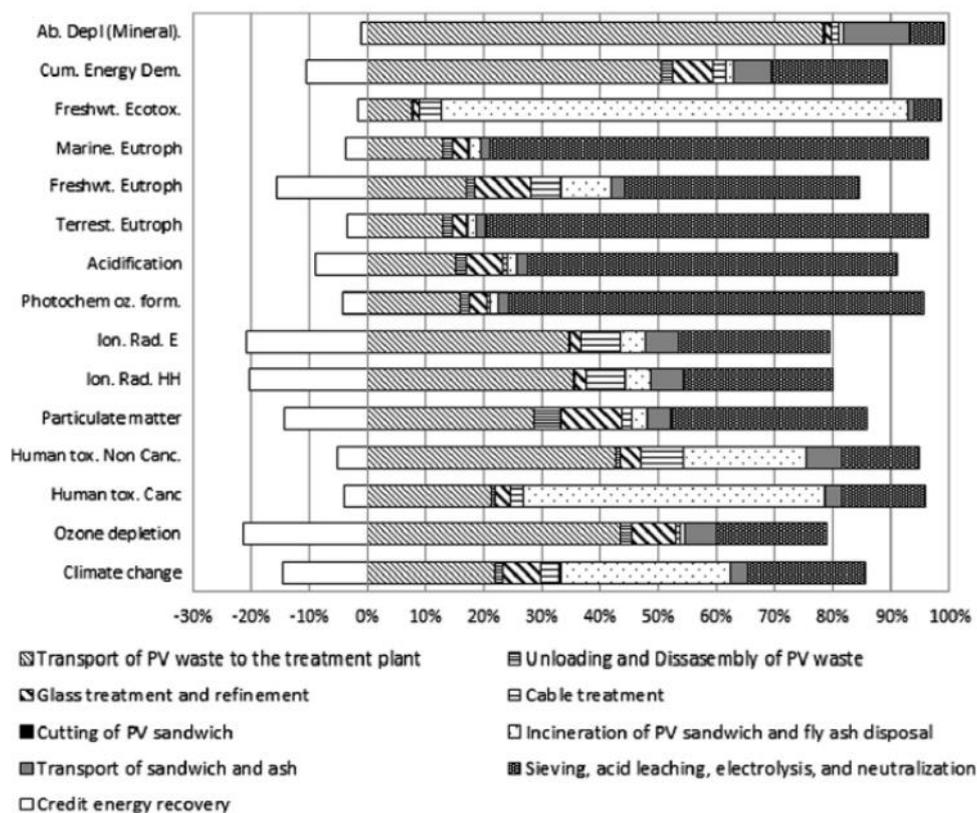


Figure 81: contribution of each phase to the overall environmental impacts of the recycling of 1000 kg of silicon PV waste. [338]

The result of the LCIA phase shows that the recycling of PV waste is beneficial for all impact categories, i.e. the impacts due to recycling are lower than the potential benefits achievable by the production of secondary raw materials (Figure 81). This innovative method of PV waste treatment clearly shows a higher environmental benefits when compared to other methods currently adopted in WEEE recycling plants. These plants are, in fact, affected by higher loss of materials, including precious metals and materials critical for the EU. The results of the LCIA

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also indicate the impact contribution made by each unit of process in the innovative recycling process, thereby identifying potential opportunities for improvement. The analysis of the material fractions separated from the PV waste also enabled the potential benefits due to recycling the different materials to be estimated.

In reference [339], a LCA comparison is done on two different EoL scenarios, having in common the thermal treatment of the EoL panel and differing by the recovery rate (and likely by the related costs and resources investment). The different impacts of two treatment phases for the two metals are graphically shown as percentages in Figure 82, in so suggesting that efficiency improvements are much needed in the recycling phase (refining, purity upgrade, etc.). Figure 83 compares the normalized values, referred to the usual functional unit, of the aluminum and silicon recycling processes. The highest impacts generated by the aluminum recycling process affect freshwater eutrophication and human toxicity; in both cases the largest contribution (at least 90%) is associated to the use of alligants whilst a much smaller contribute is attributed to electricity (1-3%). The silicon recycling process mainly affects freshwater eutrophication, the largest impact of which is associated to electricity, hydrochloric acid and sodium hydroxide for a share of 79%, 14% and 5%, respectively, and human toxicity, where the main impact comes from electricity (70%), hydrochloric acid (23%) and sodium hydroxide (5%).

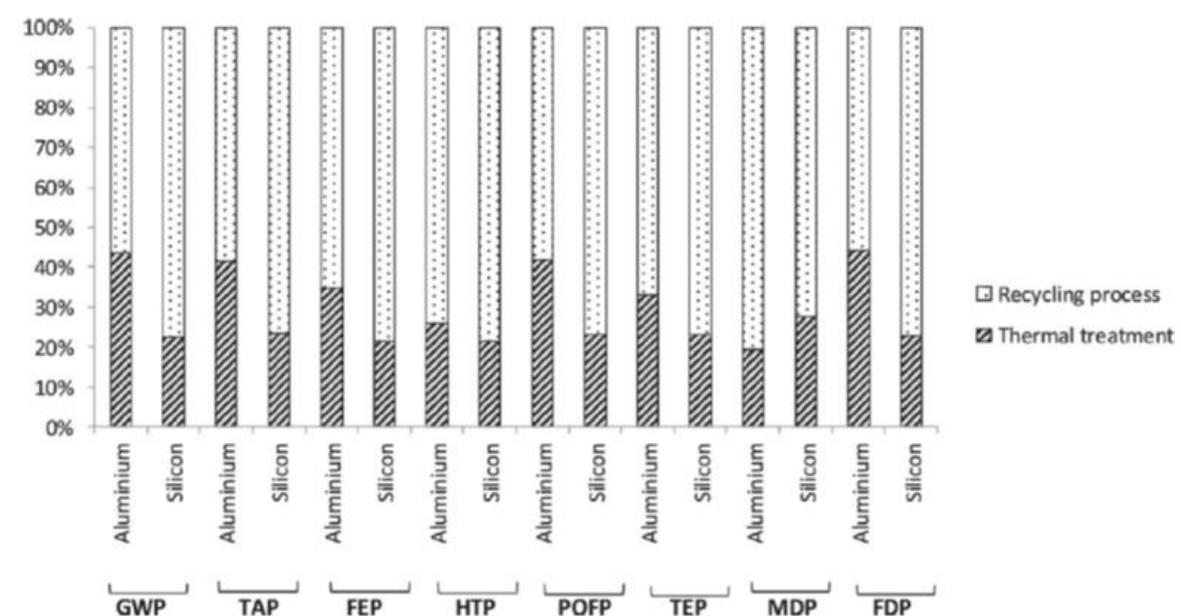


Figure 82: Percent impact contribution of thermal treatment and recycling processes for aluminum and silicon recovery [339].

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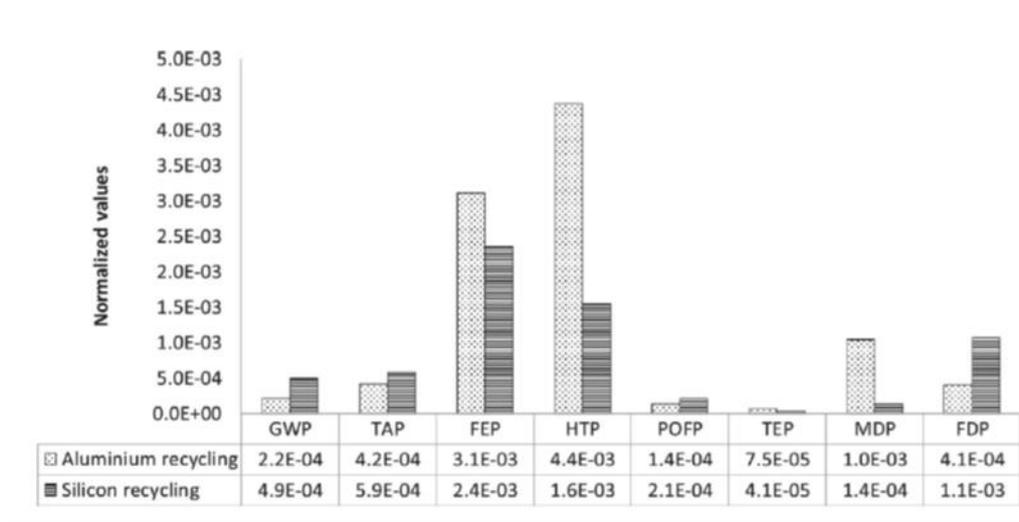


Figure 83: Normalized impacts of the aluminum and silicon recycling processes [339].

The analysis of the results shows that the recovery process of the PV panels has clear advantages from energy and environmental points of view in all impact categories analyzed, in particular freshwater eutrophication, human toxicity, terrestrial acidification and fossil depletion. The main environmental benefits arise from the recovery of aluminum and silicon. Further analysis can be developed from this study to assess the potential benefits related to the recycling of the recovered materials and to compare the impacts of the PV waste treatments with the impacts of the other life cycle stages.

5. SUMMARY

In the present document, silicon recovery, recycling and refining from secondary sources are analyzed. Emphasis is on the refining and recycling of silicon for PV industry and from end-of-life panel. The reason is the immense growth of photovoltaics every year, where silicon is the dominant PV material with more than 98% of PV cells and modules based on it. This growth requires more and more silicon feedstock.

During the process of multi-crystalline production, more than two-thirds (68%) of the silicon feedstock that enters the PV production chain is lost during the different production steps in the form of different types of silicon containing waste. This quantity represents a potential silicon feedstock, especially since the quality of this silicon at the beginning was exactly matching the requirements of the PV production. In order to efficiently recycle silicon, the production and refining processes need to be clearly understood.

Regarding the silicon from end-of-life panel, it is important to highlight that over the past ten years, photovoltaic installations have grown at a rate exceeding all predictions. Considering a lifetime of PV panels of about 25-30 years it is expected in the world, millions tones of EoL PV

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panels will be available from 2025-30 and exponential growth is expected. Their treatment is becoming a crucial issue especially since July 2012, date on which PV panels were considered as WEEE waste and consequently concerned by the Directive 2012/19/EU of the European Parliament on waste electrical and electronic equipment (WEEE). This Directive fixes the annual collection and recovery targets (mass %). The advantage is the recovery of all the materials contained in the panels, so increasing economical revenues from the process. The disadvantage at moment can be the poor availability of end-of-life panels so the treatment can be not still economic convenient, depending also on the fresh metals prices.

With regards to life cycle analysis, here a favourable analysis for recycling of silicon PV panel is presented. The report shows that, when waste crystalline-silicon (c-Si) photovoltaic panels are recycled to produce secondary raw materials, relevant environmental benefits can be obtained. The results show the advantages of recycling over primary production in these case, but these studies are specific for those case and more studies comparing another end-of-life products and secondary sources would be needed to generalize the advantages of recycling over primary production.

TUNGSTEN

1. THE SECONDARY RESOURCES

Tungsten is a relatively rare metal, with highly specialised applications, particularly within old-style incandescent lamp manufacture, special alloys and hard materials, as well as catalysts and military applications. Due to its characteristics, specific applications and relatively high value, tungsten is very amenable to recycling.

Cemented carbides, also called hard metals, are the most important usage of tungsten today. Tungsten monocarbide (WC) is the main constituent which has hardness close to diamond. Hard metal tools are applied for the shaping of metals, alloys, ceramics and other materials. About 54% to 72% of tungsten in the world are used for hard metals. Steel and alloys, mill products such as lighting filaments, electrodes, electrical and electronic contacts, wires, sheets, rods etc., and a widespread variety of chemicals are other important uses of tungsten.

In hard metal applications, tungsten included in monocarbides can be relatively easily recycled with established technologies. In turn, in steels and in other applications where tungsten is diluted in the material, its recycling is problematic, and tungsten cannot really be recovered.

For the moment, secondary production is only being done in Germany (by H.C. Starck, Buss & Buss Spezialmetalle) using existing tungsten products, but it is difficult to establish the exact amount being produced. According to 2013 data from the International Tungsten Industry Association (ITIA), the recycling rate (RR) was 50% in Europe and the United States, compared to only 30% in Japan [340].

For the analysis of existing routes, gaps and barriers and potential innovative processing routes of tungsten secondary resources, they have been classified follows:

(1) Processing waste and historical waste (mining and metallurgical wastes)

- Waste rock
- Mill tailings

(2) Urban mines and manufacturing residues (new scrap and old scrap)

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

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New scrap: waste from processing the material containing niobium

Old scrap: end of life products from urban mines and manufacturing residues

2. EXISTING PROCESSING ROUTES – GAPS & BARRIERS

This chapter describes the recycling of tungsten from secondary resources based on findings of SCRREEN deliverables D4.2 Production technologies of CRM from secondary resources and D4.3 Circular Economy and zero waste aspects and business models of production.

MSP REFRAM project⁸ deliverables have also been considered: D3.2 State of the art on the recovery of refractory metals from secondary resources [341]; D3.3 Innovation potential on the recovery of refractory metals from secondary resources [342], D4.2 State of the art on the recovery of refractory metals from urban mines [343] and D4.3 Innovation potential on the recovery of refractory metals from urban mines [344].

The recycling of tungsten has been done for some decades and it is already technically possible to recycle most types of scrap and turn them directly into new products or convert them to APT. The methods for extracting W from the wastes include direct recycling, semi-direct recycling, pyro-metallurgy and hydro-metallurgy, they are most often used for the recycling of cemented tungsten carbides, which comprises 70% of the tungsten usage in Europe [345], [346]:

- a) Direct recycling. The wastes are transformed into powder with the same chemical composition of the wastes by chemical and/or physical treatment; thereafter the powder is used to produce new products.
- b) Semi-direct recycling. Heavy metal pieces (such as cemented carbide scrap pieces) are selectively dissolved by chemical method, leaving undissolved tungsten carbide to be recycled.
- c) Pyro-metallurgy. Scrap is smelted in the furnace and the tungsten in the scrap is used as alloying element and thereby recycled.
- d) Hydro-metallurgy. Chemical methods are applied to recycle tungsten in the form of compounds, which can be used as a substitute of tungsten ore.

The techniques that are needed for pre-treating of W-bearing scrap depend on the types of wastes and the way in which they are to be recycled. These techniques include the following:

- Physical dismantling/sorting and/or sorting by chemical analysis into different grades. The sorting will lead to a purpose-oriented recycling of various W-bearing waste;

⁸ <http://prometia.eu/msp-refram/>

- Crushing, screening, milling and grinding. This will produce a waste being adapted to a specific recycling process;
- Acid cleaning to remove the impurities;
- Roasting, chlorination, alkali fusion, oxidation and electrolytic dissolution, etc. The tungsten is transformed into other compounds (such as APT, ammonium paratungstate) that can be recycled in an easy way.

The biggest barriers regarding tungsten recycling are securing a steady supply of scrap. Additionally, tungsten carbide made from scrap may not always have the same properties as freshly produced tungsten carbide and might only be used for some applications as low-grade products. The purity cannot be controlled, and further treatment is necessary if the quality of the product is important. One of the biggest challenges is making the process profitable as these methods are very energy intensive and require a lot of reagents. Solutions might be to develop processing plants that can recover multiple metals and can turn them into high quality end-products. Another issue is that these plants produce a lot of effluents and waste.

Sometimes direct physical re-using (for example for high-grade scrap like cemented carbide) seems to be more efficient than feeding into the recycling process.

2.2 MINING AND METALLURGICAL WASTES

WASTE ROCK AND TAILINGS

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.

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% WO₃.

A pilot plant testing is currently being undertaken by ERAL (a Spanish gravity concentration consulting firm) to assess the concentration on the fraction -2 mm tailings existing in the dumps of La Parrilla Mine. The preliminary test undertaken on some 100 metric tons of tailings sieved to -2 mm showed excellent recovery of the scheelite with a good concentration rate. A

second spiral concentration was performed on concentrate from a first spiral passage giving a very good concentrate [341].

Tungsten-bearing tailings from Spanish mine Barruecopardo contain on average 0.093% WO₃ in size smaller than 1 mm and 0.088% WO₃ in size above 1mm. Dumps from the same mine contain 0.044 and 0.022% WO₃ respectively. It was found, that a direct processing using spiral could reduce operation cost of recovery operations, by eliminating crushing step. [347]

Furthermore, research has shown several patents for tungsten containing tailings recovery [341]:

- A method using tungsten containing material including scheelite concentrate, highcalcium wolframite and its tailings, tungsten slime and refractory low-grade tungsten ore as material in producing tungsten compound. The addition of certain amount of aluminium oxide or aluminium salt and phosphate or oxides of phosphorus, 4-5 times leaching of ammonium paratungstate crystal obtained after the evaporation and crystallization of ammonium tungstate solution with 2-4% ammonium nitrate or ammonium chloride solution, and the precipitation of artificial white calcium tungstate from the ammonium paratungstate mother liquor and leaching liquor by adding ammonia water and sodium sulfide to regulate its basicity and then adding calcium chloride.
- A method relates to a process for recovering tungsten from low grade tungsten containing tailing (0.04 to 0.08% WO₃). This wet process includes a buffer pool classification, flannel chute roughing, roughing shaker, yurts selection and shaker sweep the election process.
- A method for the processing of tungsten-bearing ores containing sulphides and precious metals. The gold-containing sulphide and tungsten are separated by magnetic separation. Rough tungsten concentrate is subject to flotation so that high-grade tungsten concentrate is obtained.

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 WO₃ was lost in mine tailings and 4.7 kt in processing residues [342].

2.3 NEW SCRAP

Tungsten scrap is a very valuable raw material due to its high tungsten content in comparison to ore. Contaminated cemented carbide scrap, turnings, grindings and powder scrap are oxidized and chemically processed in a way similar to that used for the hydrometallurgical

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processing of tungsten ores. The recovery of W from minerals, mine tailings or scrap follows common process steps [1].

- Digestion: In concentrated NaOH (40-50%) at 100-150°C or by high-pressure digestion with dilute NaOH.
- Purification: Sodium tungstate solutions are filtrated and precipitated to remove impurities. Sodium ion concentration must be reduced from 70 g/L to < 10 mg/L. After purification, it is subjected to a Tungsten concentration procedure.
- Solvent extraction: The same procedure of that for primary resources.
- Ion exchange resin: Sodium tungstate solution is contacted with a strongly alkaline ion exchange resin in the chloride form, causing the tungstate to be adsorbed. Desorption is carried out with ammonium chloride solution. Elements such as Si, P, As and Mo can also be removed.

Other tungsten containing scraps and residues might require a modified process [342] [348].

CEMENTED CARBIDE

Cemented carbide is mostly used for production of tools, which can be recycled after their end of life using several, mostly direct recycling methods. There are two main types of recycling processes applied: **chemical process** in which scrap goes through the same hydrometallurgical process as concentrates from tungsten mining and **zinc process** in which scrap is processed directly into tungsten carbide-cobalt alloy powder in a furnace process.

The most common method is the chemical process, which involves the separation of the carbides from the binder phase or oxidation followed by alkali leaching. However, coarse powders are formed, the cost is high and large amounts of chemicals are required.

Chemical process

The method consists of 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 [344].

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 84) [349].

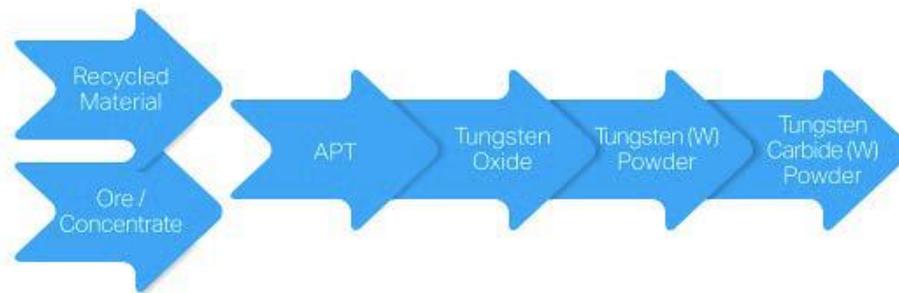


Figure 84 Steps in tungsten carbide recovery in Sandvik Hyperion.

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°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 85. 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 [344].

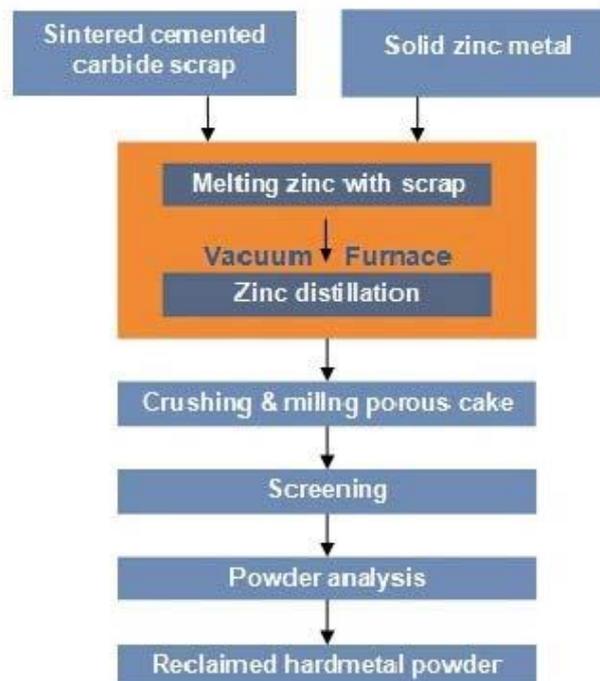


Figure 85 Zinc processing of cemented carbide scrap [347].

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Direct recycling can be performed also by cold stream process (Figure 86). 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 [344].

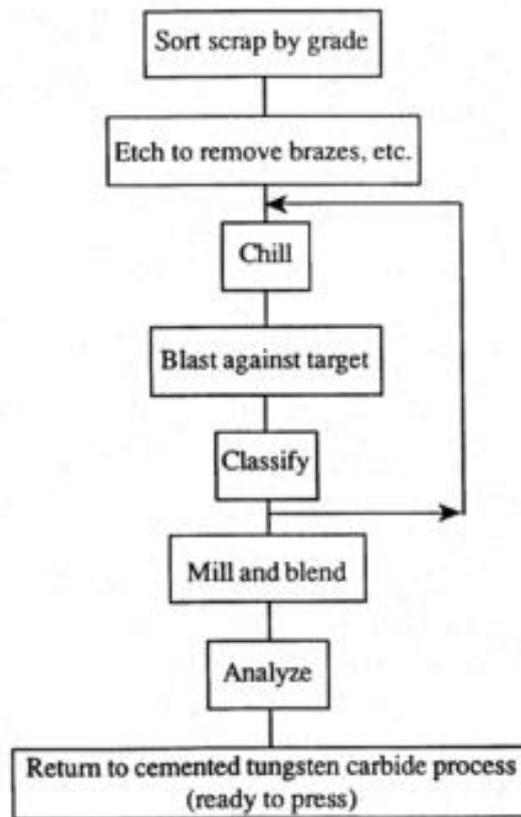


Figure 86 Flow chart of cold stream process for tungsten recovery.

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 87), 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 [343]

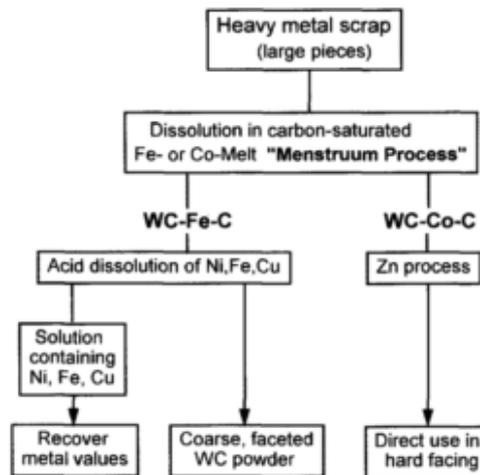


Figure 87. Flow chart of melt bath process [343].

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. 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. The same leaching technique as that used for swarf can be applied.

For some oily mill scale, the oil in the mill scale, in some cases, needs to be removed, for example, by the vacuum distillation method before it can be used, as the direct use of oily mill scale can result in the emission of volatile organic compounds, including dioxins [350].

Alternatively, tungsten can be recovered as pure material into APT by the hydrometallurgical process, as described in Figure 87 [341].

GRINDING SLUDGE/SWARF

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.

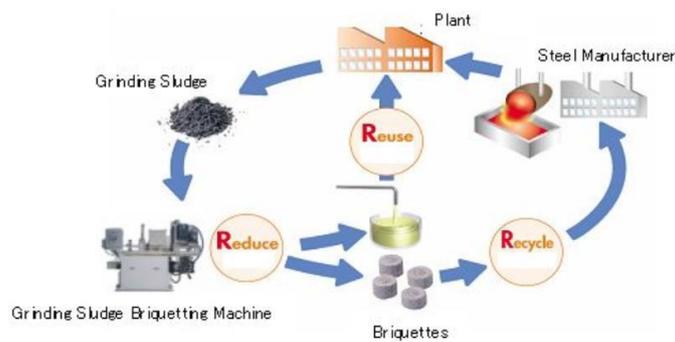


Figure 88 Grinding sludge recycling System [351]

After proper processing, grinding sludge/swarf briquettes can be charged into the smelting furnace to produce FerroTungsten or Tungsten alloy. In this way, the Tungsten in the scrap is recovered from the steel in the end.

Another possibility is to recover W from grinding sludge by hydrometallurgical technique of NaOH pressure leaching (Figure 89). 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 [341].

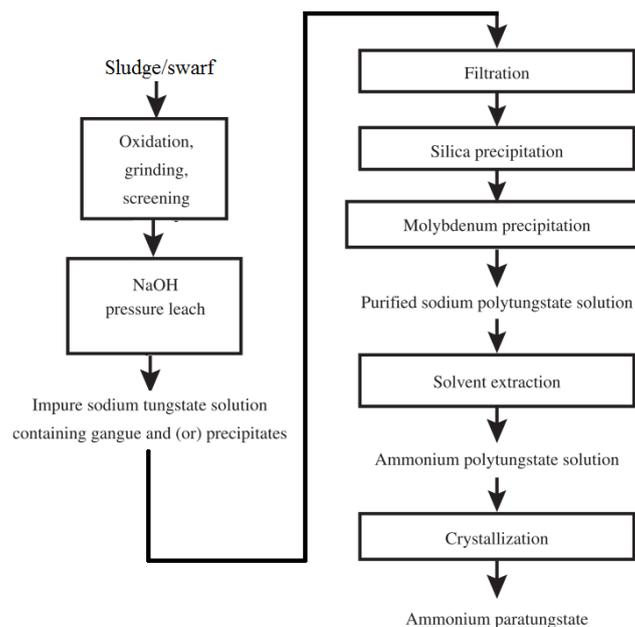


Figure 89. Flow sheet for the recovery of tungsten from sludge/swarf by the hydrometallurgical process ([341] revised from [346]).

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Some shortcomings of this method are the formation of coarse powders, high treatment cost and it requires large amounts of chemicals.

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 [344].

2.4 POST-CONSUMER RECYCLING (OLD SCRAP)

Most of the existing processing routes for new scrap would be also applicable to old scrap, so post-consumer tungsten recycling is not necessarily restricted by technological availability. The main barriers for achieving higher recycling rates are dispersion, dilution and the lack of collection infrastructure [352]. The market price is an additional constraint. Even if the price for tungsten concentrates has been increasing since the last decades, recycling is in most of the cases still too expensive. Besides recycling, substitution by other materials might be a more convenient alternative for some applications. Additionally, the material efficiency is often increased by re-designing the same products with less tungsten. In some cases, about 90 % of the tungsten content was reduced by re-designing specific carbide tools [352].

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 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. The technology is still at early stage of development, but the tests results has shown, that the separation of W from wastewater is possible [344].

3. INNOVATIVE PROCESSING ROUTES – GAPS & BARRIERS

3.1 MINING AND METALLURGICAL WASTES

Mining and quarrying activities in Europe generate approximately 55% of total industrial wastes, according to a recent Eurostat report. Most of these wastes are directly dumped on land or deposited in landfill sites [353]. The potential for reuse of waste-rock piles of

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Panasqueira tungsten mine was discussed. Such materials must have suitable properties for technical-artistic value-added applications, such as conservation, restoration and/or rehabilitation of historic monuments, sculptures, decorative and architectural intervention, or simply as materials for building revetments.

Using tungsten mine tailings as the main raw material in ceramic substrates was successfully prepared by conventional ceramic sintering process. Material properties including density, porosity, corrosion resistance performance, mechanical strength were measured and showed that the ceramic substrate from tungsten mine tailings could be potential in applications [353].

On the other hand, the complex and difficult tailings material, historically untreatable at Panasqueira mine is now thought more amenable to processing because of recent advances in process technology (e.g., high efficiency slimes gravity separators, new flotation reagents etc.). The problem is that many of the other minerals in the tailings are also of high specific gravity or are strongly paramagnetic with little relative differential between them and the wolframite. The main focus of the development reported here was to find an efficient route to achieve the differential separations needed for the fine sizes that are present [341], [354].

A new process route for ultrafine wolframite recovery was developed [354] to enable the efficient reprocessing of historical mine tailings as well as current plant slimes tailings from Panasqueira mine in Portugal. Much of the wolframite in these tailings is below 25 microns in size and is associated with a complex mixture of other minerals including zinc, copper and other sulphides, tourmaline, siderite, ferromagnetic and other strongly magnetic material.

Flotation, magnetic separation and gravity concentration testwork, at both laboratory and pilot scale on the historical mine tailings and on the current slimes tailings of the plant were conducted. Gravity separation testwork with a multi-gravity separator and some work also using the Kelsey jig and Duplex separators were carried out. A three stages process with intermediate sulphide flotation could potentially produce a wolframite concentrate of 50-55% WO₃, a reasonable recovery. Because W minerals are very fine particles such as wolframite in the tailings from Panasqueira mine is below 25 µm, complex mineralogy and low-grade combined enrichment techniques (flotation, magnetic and gravity separations), complicated approaches and strict control of conditions (reagents, intensities, dispersions) are needed for effective recovery of these W minerals. The economic feasibility is still not clear [354].

Recovery of W from slimes was experimentally investigated through a process of centrifugal separation and sulphide flotation. The centrifugal separation process contained one time of roughing and four times of cleaning and the sulphide flotation process contained one time of roughing, one time of scavenging and one time of cleaning [342].

A low-cost operation processing tungsten-bearing dumps and tailings produced from the Barruecopardo tungsten mine has been evaluated [355]. The characterizations of the materials (dumps and tailings) are shown that the percentages of -1 mm and +1 mm fractions are 73% and 23% in the tailings and 38% and 62% in the dumps. For the finer grained tailings with a higher overall grade and importantly a higher proportion of -1mm direct processing through a gravity separation spiral would reduce operating costs (no crushing required) and thereby improve the operating margin.

At La Parrila mine in Spain [356], the -3mm tailings was processed in 1986 from the current operation consisting in cyclones, spirals, and shaking tables. Tungsten recovery was reported to be of some 70% and Sn some 60%.

3.2 NEW SCRAP

CEMENTED CARBIDE

There is ongoing research on new cemented carbide recovery techniques.

Semi-direct recycling of cemented carbides

The Christian Doppler Laboratory for Extractive Metallurgy of Technological Metals in Austria has an ongoing research on the recycling of cemented carbides [357]. Current methods are based on a modulation of the primary route or the zinc-process. The zinc method depends much on the quality of the scrap and remaining coating material reduces the usability of the product. The complete processing is also not ideal.

The laboratory's research deals with an alternative where the coating is detached from the carbides during a leaching step. Also, the binder material is removed during this phase. The remaining hard phase is analysed and based on its quality a suitable treatment for reuse is sought. Cobalt that is dissolved during the leaching step is recovered by adequate hydrometallurgical techniques. A kinetic research is done to get a good understanding of the leaching characteristics. Also, a detailed analysis of the respective elements and their interactive interference is performed. Supported by metallographic observation a kinetic model is then made from which an efficient and effective process route can be derived for the material.

Recycling of scrap tungsten carbide roll collars

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

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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 [344].

Y.T. Liao, T.Wu and T.Chou have reported a research on recycling scrap tungsten where crushed crystallites of scrap tungsten carbide roll collars are mixed with swarf, dropped into a centrifuge and then processed by electroslag remelting. After heat treatment refinement, recycled tungsten alloy roll collars containing only 20% tungsten are made. This experiment demonstrates that tungsten carbide roll collars made by powder metallurgy can be reused after being scrapped to make recycled tungsten alloy roll collars by melting. The trial production data for the recycled tungsten alloy roll collars provide strong evidence that their wear performance and cost savings are better than ordinary alloy collars and that they effectively reduce consumption of tungsten [358].

A method for the recycling of tungsten from roller collars from a steel mill proved to be an efficient way to reduce tungsten consumption. However, it should be tested first if this method is also useable in European steel mills and also acquiring the right equipment might be difficult [5].

A method for the recycling of tungsten from roller collars from a steel mill proved to be an efficient way to reduce tungsten consumption. However, it should be tested first if this method is also useable in European steel mills and also acquiring the right equipment might be difficult. For the recycling of catalysts, the main difficulty would be getting a steady supply of secondary material. The methods for recycling the drill bits and waste-water streams are still in the early stages of development [344].

Recycling using molten salt

This technique of recycling tungsten is reported by T. Ishida and T. Itakura [359] [344]. This method uses molten salt solution to obtain an aqueous solution of Na_2WO_4 from cemented carbide. After this treatment, the aqueous solution of Na_2WO_4 is converted into an aqueous solution of $(NH_4)_2WO_4$ by an ion exchange treatment. The molten salt solution- and ion exchange treatments is explained below.

- a) Molten salt is used to produce Na_2WO_4 aqueous solution from cemented carbide. Then, an ion exchange treatment in a resin tower converts it into $(NH_4)_2WO_4$ solution. It is believed, that this method allows to adsorb about 3 times more tungsten as the conventional amount [344].

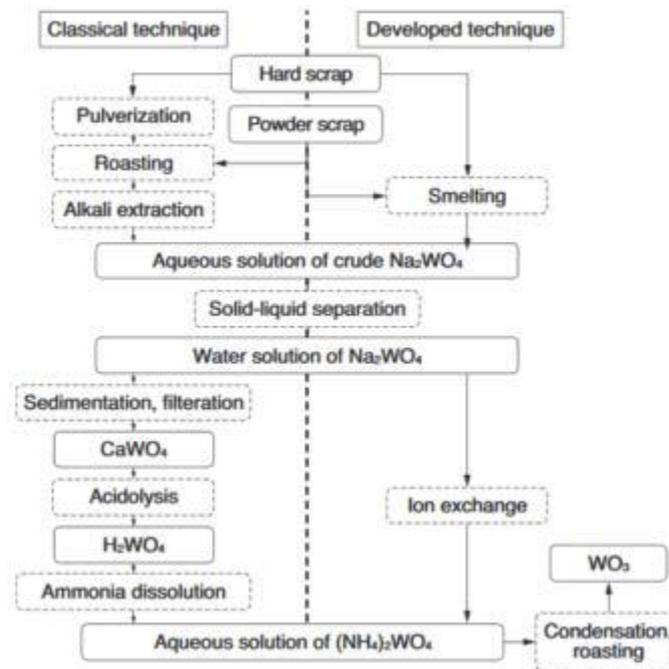


Figure 90. Flow chart of tungsten recovery with molten salt.

- b) After the molten salt treatment, the aqueous solution is conducted through a resin tower filled with ion exchange resin. The purpose of the ion exchange treatment in the tungsten recycling process is to obtain an aqueous solution of $(NH_4)_2WO_4$ by so arranging that WO_4^{2-} ions contained in aqueous solution of Na_2WO_4 are adsorbed on the anion exchange resin and are eluted by ammonium salt such as NH_4Cl . With this method, it is shown that it is possible to adsorb approximately three times as much tungsten as the conventional amount. There seems to be a problem with some side reactions, which resulted in the resin tower becoming clogged, but these could be solved by keeping the aqueous solution basic [359].

Acidic Leaching with Nitric and Phosphoric Acid

The process for industrial scheelite leaching is the treatment with sodium hydroxide or sodium carbonate in an autoclaving process [342], [360], [361]. Additionally, the scheelite can be treated in an acidic leaching step with hydrochloric acid to produce tungstic acid. This process has several disadvantages, as a solid-colloidal layer of tungstic acid covers the unreacted particles and hinders the reaction [362].

In a study of Zhang et al. [363], [364], scheelite was leached with a mixture of phosphoric in nitric acid (less corrosive to equipment than HCl) to produce a phosphotungstic acid solution, which is further treated by solvent extraction and the raffinate is recycled to the ore leaching

stage. Here, the phosphoric acid acts as chelating agent and avoids tungstic acid precipitation. This decreases the acid consumption and wastewater amount showing the results high recovery rates. There is no further acid needed prior the solvent extraction step. The proposed flowsheet is depicted in Figure 92.

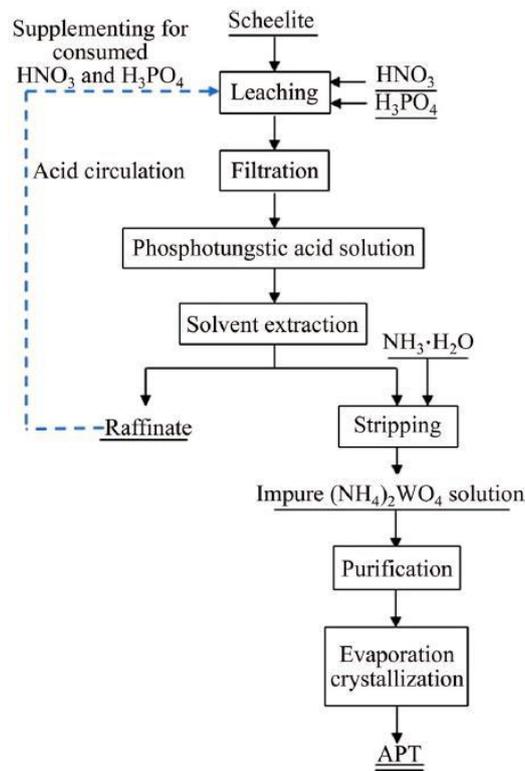


Figure 91. Flowsheet for APT production with acidic leaching with nitric and phosphoric acid [364].

Biosorption

In a study of Ogi et al. (2016) [342], [365], W is recovered selectively from W bearing scrap by biosorption. For W biosorption, E. coli and beer yeast have high uptake capacities of 0.16 g W/g biosorbent and 0.29 g W/g biosorbent respectively, which is comparable to ion-exchange resins. A study reveals that this biosorption process is still more expensive than that of the ion-exchange resin D301, but the required amount of chemicals is relatively small. Large amounts of acid and base substances are not necessary to remove W from the adsorbent, which is an advantage. A flowsheet of recycling of used WC tip is shown in Figure 92.

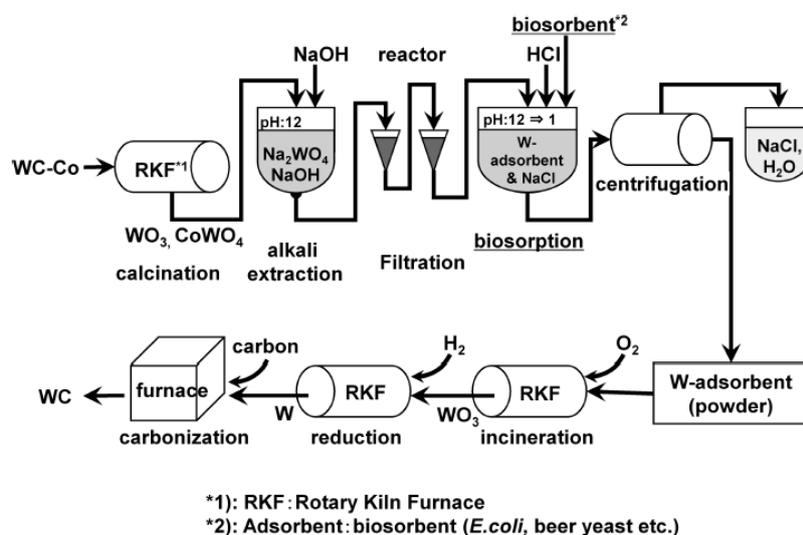


Figure 92. Flowsheet of tungsten recovery by biosorption. [365]

A feasibility study reveals that this biosorption process is still more expensive than that of the ion-exchange resin D301, but the required amount of chemicals are relatively small; large amounts of acid and base substances are not necessary to remove tungsten from the adsorbent, which is a significant advantage.

Direct Solvent Extraction from Alkaline Medium

The traditional hydrometallurgical recovery of W includes an alkali leaching, which is followed by a solvent extraction step [342], [366], [367]. This solvent extraction has to be conducted in acidic media (pH 2 - 3). Thus, lots of acid is needed to neutralize and acidify the leach liquor and the valuable alkali (Na_2CO_3 or NaOH) and acid (H_2SO_4 or HCl) become useless inorganic salts. Additionally, anionic impurities of P, As, Si, Sn cannot be removed, because of the formation of heteropoly acid. The precipitation of those impurities leads to a loss of W [368]. Therefore, the direct solvent extraction of W from alkaline medium was studied. The breakthrough was the application of quaternary ammonium carbonate salts as extractants. [369]

Two major problems have restricted the industrial application for this process: poor phase separation and a relatively low tungsten concentration in the strip liquor (approx. 100 g/l) resulting in high energy consumption in the following crystallization of APT by evaporation.

In a new study of Zhang et al. (2016) [370] this direct solvent extraction from alkaline medium has been optimized to promote the application in commercial scale. Therefore, pilot (multi-stage mixer-settler system) and industrial (multi-stage annular centrifugal extractor) test plants were run over a longer period of time. Trioctyl methyl ammonium chloride was transformed into quaternary ammonium carbonate and used as extractant.

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The extraction rate reaches 98 %. Molybdenum is coextracted and needs to be removed in a consecutive precipitation step. Other impurities like P, As, Si and Sn are almost removed quantitatively. A flowsheet of the overall process is shown in **Figure 93**. The organic and the aqueous phase form closed cycles in the leaching-solvent extraction process, as well as Na_2CO_3 and NaOH .

There is no consumption of acid and the precipitation of P, As and Si by precipitation is not necessary. Compared with the traditional technology, this technology shows the advantages of a shorter process, a high recovery rate, a low consumption of chemicals, and dramatically reducing the amount of waste water with obvious economic and environmental benefits, producing a final product which meets the quality standards. It is reported, that the overall costs can be reduced by about US\$ 400 per ton APT) [370].

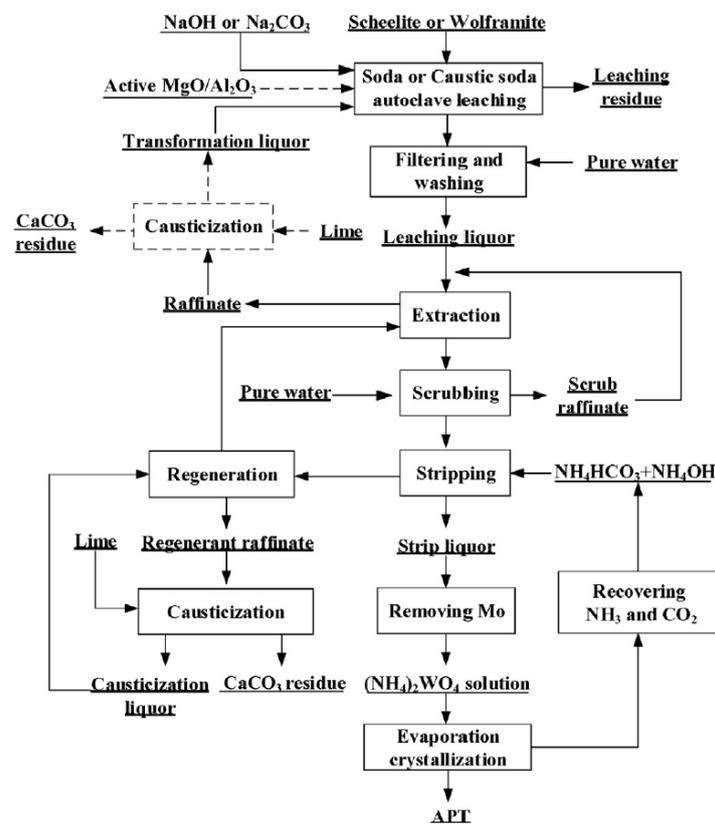


Figure 93. Flowsheet of tungsten hydrometallurgy based on direct solvent extraction from alkaline medium. [370]

ALLOY SCRAP

Guspang process (MEAB, Sweden)

In this process [86] the alloy scrap is pretreated in a furnace with graphite to transfer the high-melting-point metals (Mo, W etc.) into carbides [371], [344]. The melt is granulated and then charged into titanium baskets. Diaphragm type electrolytic cells are used for anodic

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dissolution of the granulate. Fe, Co, Ni and small amounts of Cr are brought into a CaCl_2 solution by the current. The metal carbides are not dissolved and recycled as anodic residue in the baskets. The anolyte, containing about 50 g/l Cl^- , is fed to a solvent extraction operation for separation of the metals, based on their tendency to form metal chloride complexes in the solution. The flow sheet of the proposed process is shown in Figure 94. The Guspang process has been running in pilot plant scale for about half a year, and the claimed advantages include low consumption of energy and environment-friendliness.

In conclusion, the application electro-chemical procedure in extracting refractory metals, such as tungsten, is very attractive, as normally low energy is required. A combination of the electro-chemical procedure with other hydro- or pyro-metallurgical steps can be the trend for effective recycling of tungsten from its carbide, from its alloys, etc.

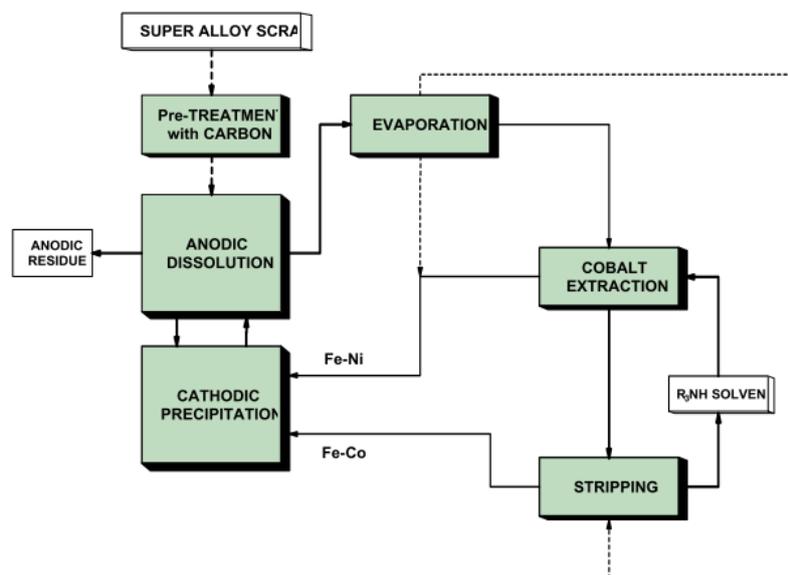


Figure 94. Flow sheet of the separation of iron, cobalt and nickel from super alloy scrap by a solvent extraction – electro-chemical procedure (Guspang process).

GRINDING SLUDGE

During the manufacturing of cutting tools, the grinding of WC-Co cermets results in the formation of a very fine sludge.

A new method was reported by Jung [372] [344] and involves a two-step process. First the material is oxidized followed by the reduction of the powder by carbothermic reaction. The scrap used in the experiment contained 77% W, 9,94% Co 5.34% C, and 0.38% Cr, 0.24% Fe and 6,90% O. The chromium and iron are impurities that enter during the manufacturing process. The WC-Co hard alloy sludge was first dried and oxidized in air at 973 K in a muffle

furnace. The oxidized powder was then ball-milled for 24 hours. This converts the tungsten and cobalt into WO_2 , WO_3 and $CoWO_4$.

In the next stage, carbon powder was added, and the mixture was ball-milled again for 24 hours. The mixed powder was then reduced in an alumina crucible at temperature 1073-1273 K for 6h in a stream of argon. This resulted in the formation of WC and Co metal. Optimal conditions were at 300% mixing of carbon powder and a reduction temperature of 1000°C.

The current technology is still in the experimental phase. The method worked but more research is needed to optimize all parameters and develop a flowsheet.

DRILL BITS

Another research that is being done by the laboratory is the recycling of drill bits that are used in the oil and gas industry. These consist of a complex alloy of copper, manganese, nickel, zinc and tungsten. This waste cannot be effectively processed by the zinc process that only effectuate the disintegration without separation of impurities.

Globally around 1,000 tons of tungsten is lost each year in the value-added chain. These drill bits can thus prove a valuable secondary source of tungsten if a suitable recycling method can be developed.

At the moment tests are done for the selective chemical digestion of the binder alloy. Different digestion solutions are combine with oxidizing or complexing agent and tested on their efficiency on dissolving the binder material while leaving the WC intact. The laboratory is also looking for ways to recover the other metals from the solution to bring additional value. This research is still in a very early stage and not much technical details are available. [344]

3.2 POST-CONSUMER RECYCLING (OLD SCRAP)

Main barriers to post-consumer recycling are [373]:

- 1) Dispersion or dilution in the material/structure (low-grade material)
- 2) Lack of appropriate post-consumer collection systems for open-loop recycling.
- 3) Poor economic viability. Although tungsten recycling is less energy intensive than primary production, tungsten recycling is not necessarily cheaper than buying ore concentrate, due to the high cost of tungsten scrap.

E WASTE

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Emulsion liquid membrane (ELM) techniques have been extensively investigated for the separation of metal ion, hydrocarbons and other biological compounds. ELM combines the two consecutive steps extraction and stripping within one single operation [374]. Therefore, the emulsion membrane phase (w/o emulsion) consists of a homogeneous mixture of extractant, organic diluent, an internal aqueous stripping phase and a surfactant for stabilizing the emulsion. The solute species from the external feed phase gets dissolve in the organic phase and diffuses into the internal strip phase. Finally, the enriched solute can be recovered by breaking of the emulsion (electro-coalescer, temperature) [375]. This transport of the solute through the liquid membrane is coupled with counter-transport of ions (H^+ or OH^-) from the internal stripping phase to the external feed phase, which is the main driving force and allows high enrichment concentrations. On the other side, this driving force triggers an osmotic water flow and results in swelling or shrinking of the internal stripping phase and hence a loss of performance. Safety issues are another problem for an industrial application, where plant for zinc recovery in Austria burnt down due to a malfunction in the electro-coalescer [376]. Lende & Kulkarni (2015) [377] investigated the ELM technique for the selective recovery of W from a multi-component waste stream of printed circuit boards (PCB) in a stirred tank. Under optimized conditions, the extraction efficiency was found to be 80 % with 4 times enrichment in the stripping phase. The separation factor for W(VI) vs. other co-ions was found to be very high thereby indicating selective recovery of W(VI) from the wastewater by using ELM process. The basic properties of ELM operations such as low-solvent inventory and high surface area make them ideal for the separation of solutes from dilute aqueous streams

SPENT NI-W WASTE CATALYSTS

Tungsten is used in the chemical industry as catalysts. A method was investigated to recover and purify the tungsten from honeycomb- type spent selective catalytic reduction catalysts (SCR) [344] [378]. These catalysts are used to convert NO_x to N_2 and H_2O in a selective reduction process. The catalysts are mainly composed of TiO_2 but also smaller amounts vanadium and tungsten. These small amounts are however 40% of the total price. Methods are available to extract these metals. These include soda roasting and acid leaching.

The pressure leaching reaction was conducted with the soda digestion process. As a leaching agent NaOH was used. Tests were done at different temperatures, NaOH concentration, leaching time and liquid/solid ratio. The solution that is obtained contains both V and W. The vanadium is separated by a precipitation reaction with $Ca(OH)_2$ to form $Ca(VO_3)_2$. The tungsten is converted to APT with a reaction by NH_4OH . Maximum recovery was achieved at 2 M NaOH solution at 300 degrees Celsius $L/S=20$ and 0.2 M Na_2CO_3 as additive which gave a W recovery of 99,9% and 86,8% for V.

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The method proved to be successful in the recovery of Tungsten and Vanadium. The APT that is produced at the end of the flow sheet is a sellable product. The process itself is relatively easy and does not require a lot of equipment. The biggest challenge would be the supply of sufficient amount of catalysts. Further analysis would be required to investigate the logistics (supply of tungsten) and the economic feasibility.

4. LIFE CYCLE ASSESSMENT DATA

Tungsten mining and beneficiation processes often account for high losses (10 – 40 %) and high amounts of waste rock and landfill. Although primary production cannot be entirely substituted by recycling, because the demand is growing year by year recycling methods require lower processing energies, and hence, produce lower carbon emissions and avoid waste rock, waste water and leachates from mining operations. Additionally, many of the mentioned innovative technologies lead towards a greener tungsten processing industry by reducing the amount of reagents needed and/or reducing the production of harmful or useless by-products (e.g. salts from neutralization reactions) [352], [342].

4.1 MINING AND METALLURGICAL WASTES

Mining wastes can affect the environment through one or more of the following intrinsic criteria: chemical and mineralogical composition; physical properties; volume and surface occupied, and waste disposal method [342].

Mansour Edrakia et al, 2014 reviewed alternative tailings management methods to improve environmental, social and economic outcomes [379]. Three approaches in particular were highlighted: paste and thickened tailings; tailings reuse, recycling and reprocessing; and proactive management (e.g. the integration of sulphide flotation with cemented paste backfill). In the future, models could be constructed to optimize environmental, social and economic outcomes of tailings management across the value chain through integrated orebody characterization, mine planning, processing, disposal, re-processing, recycling and reuse. On the viewpoint of economics, avoiding of tailings was considered the most preferable and reducing, reusing, recycling, recovering, treatment and disposal of the tailings are less preferable in sequence [380]. Innovations in all these items are the most important.

The increase in demand (quantity and diversity) and metal prices leads to a renewed interest in the historical mining waste which can be considered as potential source of base metals and critical metals. One major difficulty regarding mining waste reprocessing concerns the quantification and distribution of elements and minerals on all scales from the nano-scale to the macroscale in space and time (for example considering the oxidation of sulphide). Developing predictive tools and reliable, field-tested modelling of long-term mining waste

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behaviour are among the greatest challenges. Such data and tools are needed to establish the recycling and reuse potential of these materials; geochemists and mineralogists have a significant role to play in this endeavour [381].

Any operation will require a cost and benefit approach to ensure its feasibility, which should take into account restocking of the remaining mining wastes after their reprocessing including to ensure their long term safe disposal, and to prevent or at least minimize any long term negative effects for example attributable to migration of airborne or aquatic pollutants from the mining waste facility. This new approach should consider the following strategy: engage the operation if the economic value of the recovered metal is superior to the reprocessing costs and the final disposal of the remaining mining wastes; If not, include the long term environmental and social benefits (especially regarding ground water and surface water impact reduction) of the remaining materials long term safe disposal [381].

4.1 NEW/OLD SCRAP

Tungsten recycling is less energy intensive than virgin production [342]. According to [352], virgin production results in roughly 10,000 kWh/t of tungsten (Mittersill, Austria), depending on the grade and cut-off (usually 0.2 %), whereas tungsten from recycling (zinc process) accounts for < 6,000 kWh/t. Despite these energy savings, recycling is not necessarily cheaper than buying ore concentrate, depending on the market conditions, the costs of tungsten scrap may even be higher.

The above mentioned innovative processes are usually (still) more expensive than the conventional tungsten recovery processes, but further research initiatives or developments might lead to economically more competitive processes. For example, if biosorbents are used as waste products from other fermentation processes or other, cheaper ones were found, the main cost driver for that technology will be significantly reduced. Basically, all the innovative concepts aim to reduce the energy or reagent consumption (e.g. acid, base, stripping solution etc.) or waste (water) amount, which is often outweighed by a consumption of other reagents or a lower yield. Only an overall and detailed analysis of the specific production costs and yield will judge, if the specific technology is competitive enough [342].

Waste flows containing tungsten such as grinding sludges, floor sweepings or mill scale are only recycled internally as raw material in big plants, but in small plants, they are often sent to landfills. Big recycling plants are only economically operable, if a continuous supply of metal scrap can be guaranteed in sufficient amounts. Therefore, centralized waste collection centers might provide continuously those recycling plants with fresh feed material by channeling those waste streams of different waste-types and grades. Practical initiatives like take back schemes between manufacturers and end-users have already been reported.

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Additionally, some companies of the tungsten industry e.g. H.C. Starck (Germany) and Wolfram Bergbau und Hütten AG (Austria) buy scrap (powder, grinding sludges or WC hard scrap etc.) from end-users and mix them into their production process.

From a political point of view, special incentives might reward those tungsten producers or processors, who maintain a recycling management system in order to increase the recycling rates. These potential benefits should provide incentives to investors and companies, who are willing to explore and develop new tungsten resources and re-evaluate known resources outside China and reduce the dependence on Chinese exports and prices. In the opposite direction, tungsten producers or processors are fined, if they don't implement a recycling management system into their value chain or exceed an assigned contingent (similar to emission contingents) [352], [342].

5. SUMMARY

In hard metal applications, tungsten included in monocarbides can be relatively easily recycled with established technologies. In turn, in steels and in other applications where tungsten is diluted in the material, its recycling is problematic, and tungsten cannot really be recovered.

To increase tungsten recycling rates, a reliable identification and estimation of available secondary resources is required. Although large tungsten-bearing tailings in Europe have been identified, various other potential feed streams remain undiscovered, especially various kinds of industrial waste (mill tailings, grinding sludge, dust, sweepings) which are withdrawn from the value chain of recycling.

More complex hydrometallurgical routes are being developed that can treat a wider variety of scrap. One of the biggest challenges is making the process profitable as these methods are very energy intensive and require a lot of reagents. Solutions might be to develop processing plants that can recover multiple metals and can turn them into high quality end-products. Another issue is that these plants produce a lot of effluents and waste. New technologies might also be needed to reduce the environmental impact of these type of recycling plants.

Besides methods for the recycling of scrap, new technologies are also being developed to recycling tungsten from other sources such as drill bits, roller collars, catalysts and e-waste. Recycling technologies for these types of waste are still in an early stage of development.

Main barriers to post-consumer recycling are dispersion or dilution in the material/structure (low-grade material); lack of appropriate post-consumer collection systems for open-loop recycling and poor economic viability.

VANADIUM

1. THE SECONDARY RESOURCES

Vanadium production is mainly obtained from the titaniferous magnetite and being substantially used to produce HSLA steels. Vanadium can be directly extracted from titaniferous magnetite by the roast-leach process or extracted from titaniferous magnetite by producing the V-rich slag first and then by the roast-leach process. The overall vanadium yield from the direct roast-leach process is around 82% and the yield from the indirect roast-leach process is around 58%. The other vanadium is lost in the solid wastes and in the slag, respectively. The recycling of vanadium from HSLA steels is very rare due to the low contents of vanadium and the oxidation of vanadium during the scrap re-melting. The recycling of vanadium from spent catalyst is common due to the toxic property of vanadium as well as the existence of other valuable elements in the spent catalyst. Vanadium is a moderately rare metal, especially in the form of commercially exploitable deposits. It is very widely used as an alloying metal and catalyst. Its abundant use in alloys, including tool steel, means that it is very amenable to recycling.

According to the value chain of vanadium shown in D4.1 [382], 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. [383] [384]

Thus, applications and related products with potential for recycling are reported in Table 22:

Table 22. applications and related products with potential for recycling

Application	Identified products (potential recyclables)
Alloys	Steel scrap
Catalysts	Spent chemical process catalysts

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Fossil fuel processing	Ash, slag, residues
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2. EXISTING PROCESSING ROUTES – GAPS & BARRIERS

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.

a) Vanadium from steel/alloy scrap:

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. Recycling processes referring to this category are described in the chapter “new scrap” and “post-consumer recycling (old scrap).

b) 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 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). [385]

c) 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% aluminum (Al_2O_3), 2.5– 24.8% silicon (SiO_2), 2–30% sulfur and 1–54% for carbon [386]. Due to the high vanadium content in the fly ash, it is considered as one of the important secondary resources of vanadium.

2.1 MINING AND INDUSTRIAL WASTES

As reported before there are no current processes to obtain Vanadium from mining tails or metallurgical wastes. Currently various processes are applied in the recovery of vanadium from oil fly ashes and spent catalysts coming from the fuel industry.

According to the literature the vanadium extraction from the fly ash can be implemented either by hydrometallurgical processing or pyro-metallurgical processing. [386] [387], [388]. 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 [387]. In the process described in [386] 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 includes a drying stage at moderate temperatures of about 150 oC, 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%.

Vanadium from spent catalysts:

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.

In Table 23, commercial processes for the recycling of spent catalysts by different companies are shown:

Table 23. commercial processes for the recycling of spent catalysts

Company	Key processing steps
Gulf Chemical and Metallurgical Corporation	Soda roasting + water leaching + precipitation + smelting
CRI-MET	Two-stage caustic pressure leaching

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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 ₂ O 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)	Hydro- and pyro-metallurgical methods (specific methods are not clear)
Nippon Catalyst Cycle Co.	Roasting + leaching + solvent extraction

2.2 NEW SCRAP

Vanadium in the special steel scrap and vanadium alloy scrap are possible to be recycled, if these scraps are processed under reducing condition (such as in the Electric arc furnace with addition of strong reducing agent) or recycled by melting under vacuum condition [389]. 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. Such considerations are applicable to both new and old scrap.

2.3 POST-CONSUMER RECYCLING (OLD SCRAP)

Vanadium from steel/alloy scrap:

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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 [390], [391]); 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.

3. INNOVATIVE PROCESSING ROUTES – GAPS & BARRIERS

3.1 MINING AND INDUSTRIAL WASTES

The project EXTRAVAN [392] developed technical innovations to recuperate Vanadium from two resources: BOF-slag and V-slag. Such developments allow vanadium recovery from many resources in Europe. Two technics have been studied:

- i) Carbo-oxy-chloruration aims to the extraction of vanadium from BOF-slag. The process is used to recover chlorine and vanadium released by PVC waste incineration. Such selective process produces water-soluble vanadium chlorides from the chlorine released by thermal decomposition of PVC. The laboratory results show a 95% vanadium recovery.
- ii) A second technic developed by EXTRAVAN is a high-temperature roasting (HTR) used to recover vanadium from V-slag. Such process optimizes leaching procedure, processing time, pH, temperature, as well as precipitation condition. The result was a 97% vanadium recovery.

The traditional practice to extract vanadium from v-slag has a vanadium recovery of 80% and chromium recovery of 5%, as a result the leaching residue presents high contents of chromium and vanadium constituting an environmental problem. The solution would be to increase the vanadium and chromium recovery rate. The following studies provide some interesting solutions:

In [393] a coextraction of vanadium and chromium from high chromium containing vanadium slag was studied. Such process proposes a low-pressure leaching using NaOH solution to extract vanadium and chromium. NaOH concentration and leaching temperature have proved to be determining factors for the process. Optimal conditions were found to be a temperature of 200° C and a NaOH concentration of 50%, under these conditions a recovery of 98.3% and 93.3% of, respectively, vanadium and chromium was achieved.

In the study [394] an innovative NaOH-added pellet was applied. During the roasting process at 700°C such pellet increased its volume by 144% and many cavities were formed. Inside the pellet a three-phase reaction occurred constituted by dry slag minerals, molten liquid drops

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of NaOH and O₂. The formed cavities provided good kinetic condition for the reaction. Optimal condition for temperature, time and ratio Na/Cr have been found at, respectively, 700^o, 15 min and 7.67. With such conditions a vanadium recovery of 99.2% was achieved.

Vanadium Recovery from Oil Fly Ash:

In the study [395] a vanadium recovery process from oil fly ash by carbon removal and roast-leach was studied. The oil fly ashes contained 85% and 2.2% by weight of, respectively, carbon and vanadium. The first step consisted in a carbon removal process to obtain a vanadium enriched product with 19% by weight. Subsequently the obtained product was roasted with sodium carbonate to convert vanadium oxides to water-soluble sodium metavanadate. Finally, the roasted sample was leached with 60^oC water to achieve a 92% vanadium extraction by weight.

Recovery of vanadium from spent catalyst:

In [396] a bioleaching process of vanadium-rich spent refinery catalysts using sulfur oxidizing lithotrophs was studied. For the process chemo-lithotrophic sulfur oxidizing bacteria were used to recover several valuable metals. Two bioleaching processes have been studied and compared. Prior to both processes the spent catalyst was pretreated with acetone as a solvent. The first process was a one-step process during which bacteria were grown in the leaching medium in the presence of up to 50 g/L of spent catalyst on a substrate of elemental sulfur. The spent catalyst concentration was varied to establish the optimal conditions. Such conditions have been found for a concentration of 15 g/L at pH 2-3. The metal yield was 88.3% Ni, 58.0% Mo and 32.3% V. The second process was a two-step process in which the bacterially produced acid medium at pH 0.9-1.0 was used as the leaching agent. In this case the concentration of the spent catalyst was 50 g/L and a 88.3% Ni, 46.3% Mo and V 94.8% recovery was achieved after 7 days. Nevertheless, in both processes, a significant amount of MoO₃ was lost in the solid phase.

3.2 NEW SCRAP

N.a.

3.2 POST-CONSUMER RECYCLING (OLD SCRAP)

In [397] a process for recovery of tungsten and vanadium from a leach solution of tungsten alloy scrap was described. The sodium tungstate solution was prepared in the Japan New Metal Co. production plant in Akita, Japan. The solution was prepared by roasting the tungsten alloy scrap at temperatures ranging between 500^o and 700^oC, followed by caustic soda dissolution at 200^oC, 8 × 10⁵ Pa pressure, 3 h of delay time and 15 wt.% concentration of Na₂CO₃. The recovery process consists of three phases. The first one is the purification and

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separation of tungsten and vanadium; the other two steps are the recovery phases of tungsten and vanadium. Relatively to the vanadium, purification was carried on using $MgCl_2$ and ammonia solution which precipitated vanadate and impurities. Acetic acid was then used to dissolve the vanadium and leave the impurities in the residue. At the end NH_4OH was added to precipitate NH_4VO_3 and achieve a vanadium recovery of 88.28%. During tungsten recovery, after the purification of the sodium tungstate solution, sodium salt is converted to calcium salt. Subsequently, $CaWO_4$ is converted to H_2WO_4 using a HCl solution, which is then dissolved in a NH_4OH solution with final crystallization of APT. Such process allowed an over 85% tungsten recovery.

4. LIFE CYCLE ASSESSMENT DATA

The main challenge for ensure a circular economy of vanadium lies in the difficulty in recycling vanadium from the HSLA steels. This is on one hand due to that in quite many cases HSLA steels are not carefully sorted from the others in the steel scrap. On the other hand, this is due to the oxidation and thereafter the loss of vanadium in the slag during the re-melting of the steel scrap. A circular economy of vanadium will reply on the improvement in the recycling logistics of the V-containing HSLA steel scrap as well as the scrap re-melting strategy.

Vanadium occurs naturally in soil, water, and air. Natural sources of atmospheric vanadium include continental dust, marine aerosol, and volcanic emissions. Releases of vanadium to the environment are mainly associated with industrial sources, especially oil refineries and power plants using vanadium rich fuel oil and coal [398]. The toxicity of vanadium is dependent on its oxidation state. The pentoxide form is more toxic than the elemental form. Vanadium can cause a variety of toxic effects such as hematological and biochemical changes. Inhalation of vanadium may cause rhinitis, pharyngitis, chronic productive cough, tracheobronchitis, and bronchopneumonia. Moreover, the most often observed side effects include loss of appetite and significant reduction of body weight, often leading to anorexia, weakness, and nose bleeding, vomiting, diarrhea, dehydration, pulmonary hemorrhage, or death. [399]

5. SUMMARY

Vanadium can be found in several residues deriving from mining, metallurgy, fuel industry and EoL products. Such residues constitute, from one hand, a significant environmental risk and from the other an exploitable resource which can contribute reducing the criticality of such material. The main obstacle, nowadays, is its recovery from HSLA steels. Several studies have been conducted and several projects are active in the research of processes and technologies which will facilitate the recovery of vanadium from metallurgical residues, scraps, spent catalysts and oil fly ashes.

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