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**Innovation potential in the recovery of refractory metals from urban mines**

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Summary

Innovation potential in the recovery of refractory metals from urban mines

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## DELIVERABLE 4.3 INNOVATION POTENTIAL IN THE RECOVERY OF REFRACTORY METALS FROM URBAN MINES

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## INTRODUCTION

Barriers to metal recycling in general are mainly of thermodynamic character, this because is the processes involved to decrease the entropy from the widespread waste products back to the metal resources are energetically and economically very demanding. Already in 1981, Stumm and Morgan [1] presented the thermodynamic limits of recycling in a very clear manner, see Figure 1.

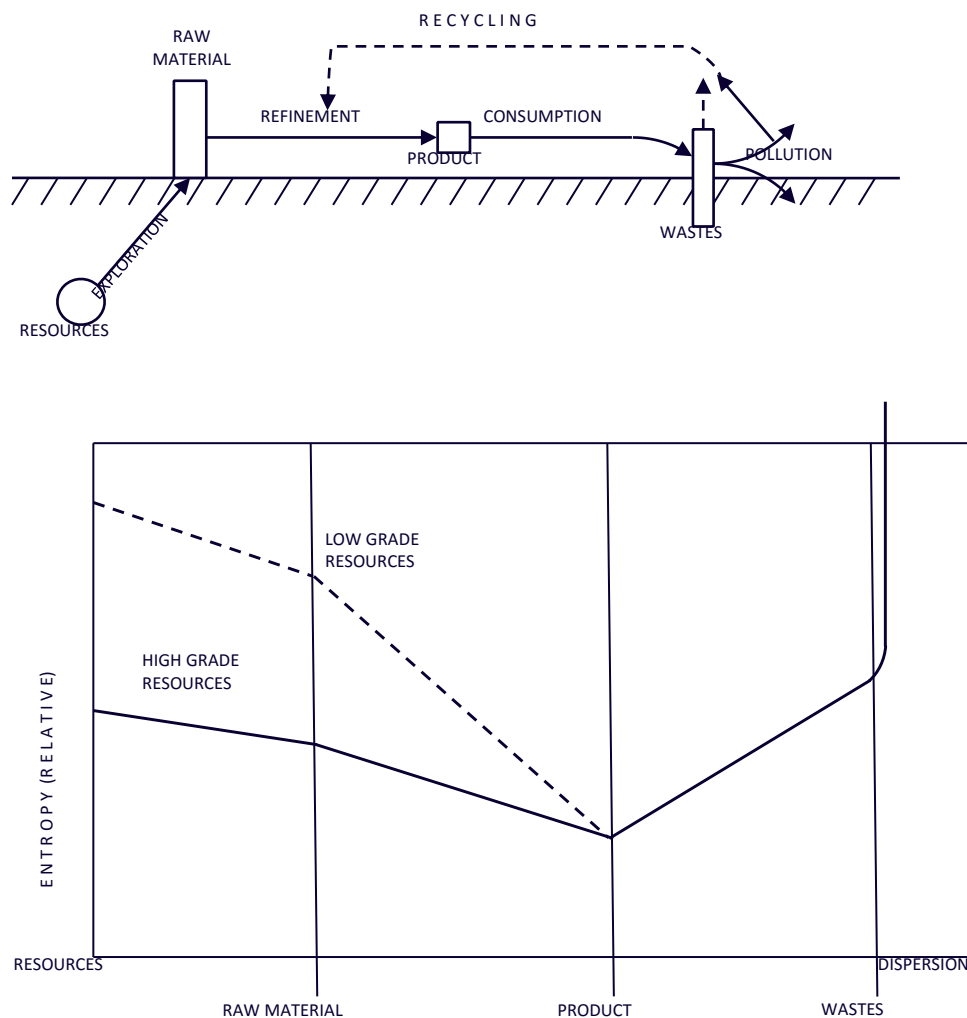


Figure. 1 Thermodynamic limits of recycling

The main limitation in metal recycling is thus connected to the dispersion of the target metals in the waste. In this connection one of the key innovation measures is to decrease dispersion by efficient metal collection in the waste streams.

In 2011 Graedel et al (2011) [2] pointed out what they consider the main factors that hinder higher metal recyclability:

- Product design that makes disassembly and material separation difficult or impossible
- A high product mobility across the globe, which has a tendency to move products from countries with higher recyclability to countries with lower recyclability.
- A lack of social and economic awareness of the loss of resources due to the low intrinsic value of products by unit
- Lack of recycling infrastructure
- Recycling technology has not kept pace with the complexity and diversity of modern products

One of the main recyclability barriers is also connected to the fact that little is known about the real potential for recyclability, what Hanada and other Japanese scientists define as the “artificial stock” or stock in the anthroposphere. The prejudice is that these stocks are small compared to ore deposit stocks.

Another aspect to be discussed as potential barrier is the fact that we normally believe that the resource usage involved in metal recycling is larger than the one used in processing natural ores.

In this respect Yamasue et al (2009) [3] performed an interesting study in which they compared the Total Materials Requirement (TMR) to extract the element from a Natural Ore (NO) by smelting with the TMR of recycling the same element from an Urban Ore (UO). The concept of TMR was developed by Halada (2007) in a publication where he showed that there is a linear logarithmic correlation between the TMR and the elemental concentration in the natural ore. Yamasue et al extended the TMR concept to Urban Mines (urban ore) and they calculated the UO-TMR for a number of metals, including Ta, and compared to the NO-TMR. As one can see in Figure 2, the estimated UO-TMR of Ta is smaller than the NO-TMR.

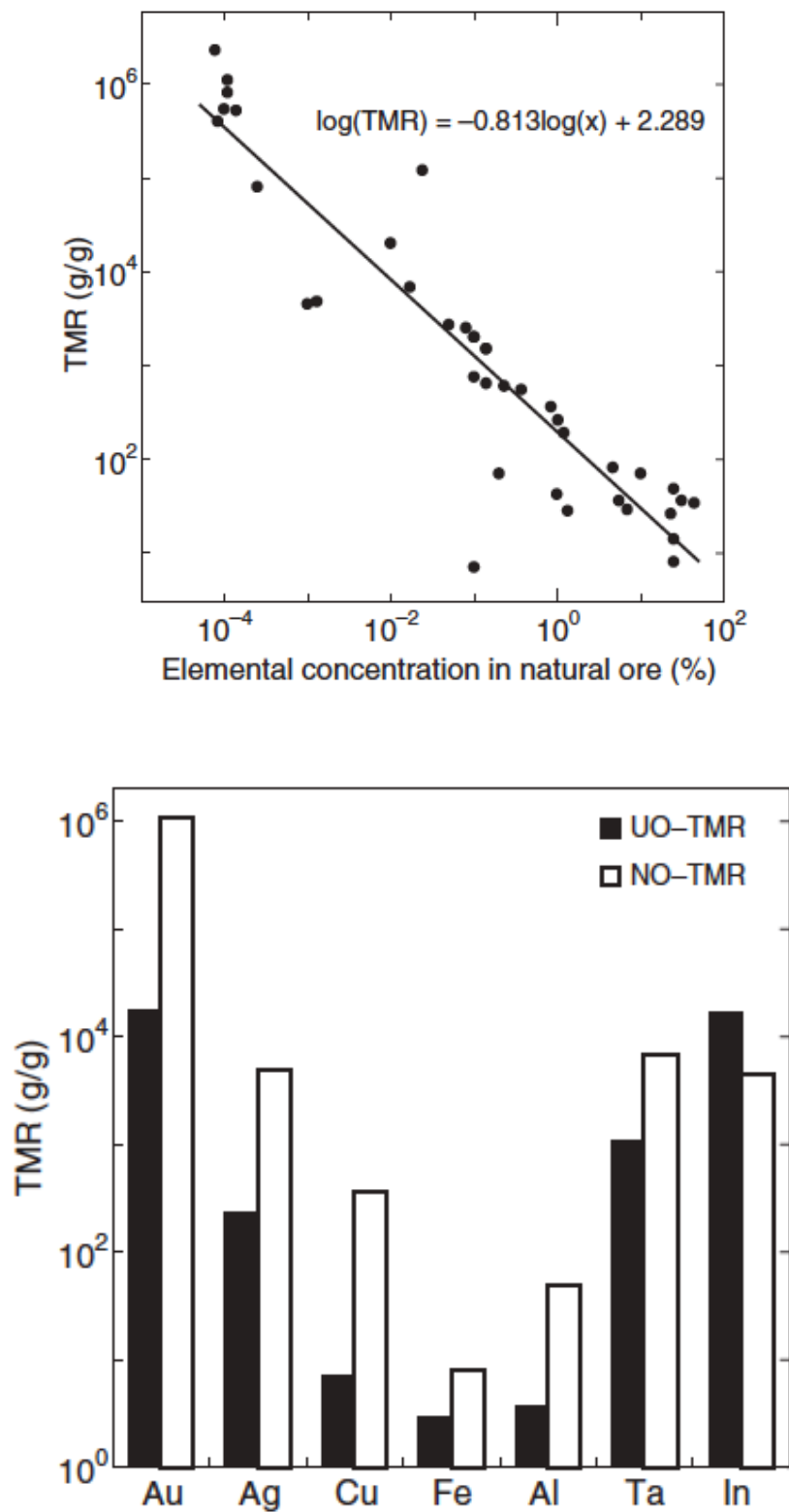


Figure 2 Total Materials Requirement (TMR) vs elemental concentration in the natural ore (top) ; comparison of Total Materials Requirement for natural Ore and Urban Ore (bottom)

So, if the urban ore potential is there which are the barriers that hinder the full deployment of a recycling industry?

Nakamura and Halada (2015) [4] have looked upon these questions in Japan which has a similar degree of social and economic development than the EU with similar rates of usage of WEEE, 20 kg/person/year with similar collection ratios also, less than 50% of the total amount. They indicate that there are both problems of the social system and technological problems. According to these authors, the biggest hurdle is constructing an economical collecting system for WEEE and it seems to apply also for other metal containing waste streams. Another big obstacle is the absence of recovery technologies to dismantle the parts containing the refractory metals which normally have low metal content and irregular shapes.

Concerning the technological issues, Nakamura and Halada have investigated the barriers by looking into the Urban Mines in a similar way as we do for the processes in Natural Ore Mining. The process analogy is depicted in Figure 3.

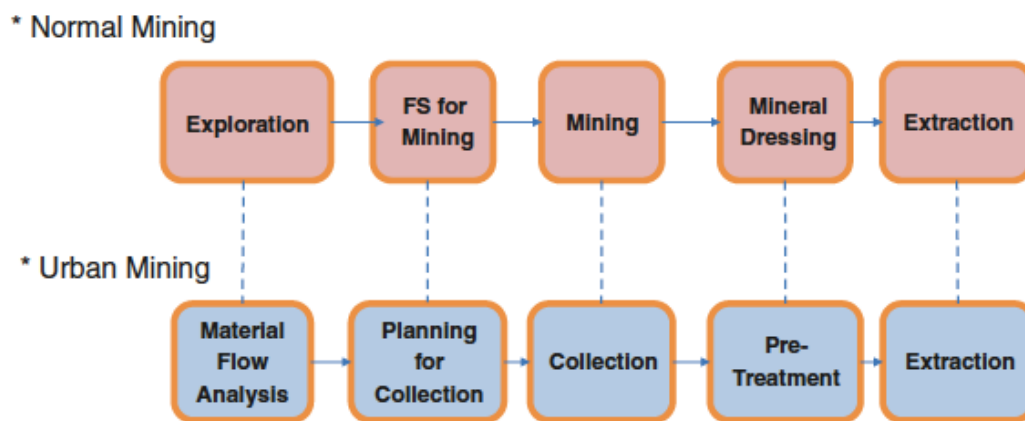


Fig. 3 Barriers in Urban Mines and Natural Ore Mining

The authors have developed a flow chart for the processing of electronic metal scrap which illustrates the technological difficulties (Figure 4)

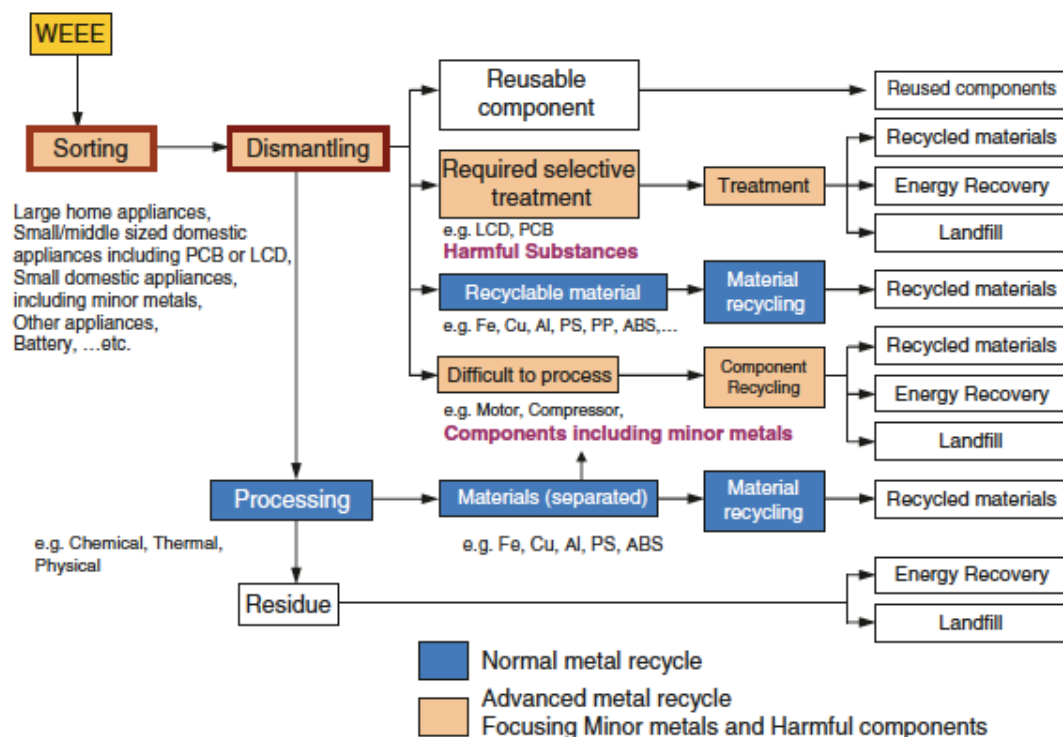


Fig. 4 Processing of electronic metal scrap and related technological difficulties

## TANTALUM

### BARRIERS TO RECYCLING AND POTENTIAL REMEDY MEASURES

The key applications of tantalum include capacitors (~40 % of Ta consumption), sputtering targets used in semiconductors and other electronic components (~20%), hard metal tools (~12%), superalloys (~14%) and different metallurgical products: sheets, plates, rods, wires etc. (8-11%) and other products. All these components and materials are further used in several different types of industrial and consumer products ending into different waste streams. In addition, Ta is used in different forms: pure Ta in powder, wire or other metallurgical product, Ta alloyed with other metals, Ta carbides, Ta oxides or nitrides, etc.

The diversity of applications and products containing Ta is a barrier of recycling, because Ta is dispersed to different end-of-life wastes produced by different industries and consumers and collected by different types of actors, and finally ending to different recycling and treatment plants. This leads to low volumes, the treatment of which is not feasible for individual recycling actors. Recycling is further complicated by the fact that the concentration of Ta/product may especially in case of capacitors and other electronic components be very low.

#### Capacitors and electronic components

Ta capacitors can be found especially in ELV (end-of-life vehicles), WEEE (Electronics waste, especially portable electronics, computers, TVs, components from telecom infra), aerospace and military applications and



demanding health applications. Capacitors are integrated to electronic circuits/printed circuit boards by soldering. Usually only a small part of capacitors used per application contains Ta.

The recycling rate of Ta from end-of-life electronic components is low, probably <1%. Recycling is mostly carried out outside Europe, e.g. in China. In Europe H.C. Starck (Germany) informs that they have facilities for recovery of Ta from capacitors. However, the key challenge of recycling is collection and separation on Ta containing capacitors from diversified material flows.

Most of old scrap is recycled in the form of tantalum bearing cemented carbide and super alloys. Jet engines are estimated to have a 20 year life span; discarded or obsolete parts can be recycled to the same alloy type or downgraded to applications with lower requirements. Recycling from discarded tantalum-containing electronic equipment has not been developed to a significant degree. Ongoing miniaturization of electrical conductors in electronic devices leads to dissipative problems. Each conductor contains less tantalum, but the whole number of produced conductors increases constantly. A major source for old tantalum-bearing scrap is seen in here, collection and recovery is economically difficult.

Technically it's problematic to recover tantalum from old scrap (low Tantalum concentrations). Due to chemical characteristics Ta oxidizes easily and moves during pyro-metallurgical processes into the slag phases

The barriers of recycling include:

- Inefficient management and monitoring of certain waste flows (WEEE, ELV) leading to insufficient knowledge about the fate of end-of-life waste containing Ta capacitors, and illegal export. Only a part of the WEEE (30%) and ELVs (~50 %) ends into the compliant collection systems. The statistical data covers only the compliant collection, and therefore it is impossible to be sure where the rest of the products ends up. It is estimated that from WEEE almost 30 % is exported from EU, mostly illegally.
- No economically feasible commercial scale technology exists for automatic identification and separation of Ta capacitors from end-of-life electronic circuits and printed circuit boards (PCBs) to which they are joined. Potential solutions have been studied in laboratory and pilot scale, for example by RWTH Aachen University, but also by several researchers outside Europe. Currently expensive manual separation is the only solution used.
- Technology used for joining of components to PCBs. To separate capacitors, the soldered joints need to be broken up using heat, strong mechanical force or chemicals.

The potential measures for improvement of recycling rates include legislative and administrative measures for improvement of efficiency and monitoring of WEEE and ELV collection systems, development of efficient technology for identification and separation of components from electronic circuits/printed circuit boards. Due to the very low quantities of Ta/product, it is difficult to develop economically feasible system for separation and recovery of Ta capacitors alone. However introduction of equipment for separation of several kinds of electric components could be more feasible.

Another possibility would be to develop joining technology that enables quick and easy separation of components from PCBs.

Ta capacitors have already been substituted in lower-voltage applications, but the substitutes are not very well suitable for applications requiring higher-performance. Further development of substitutes for Ta capacitors or development of new kinds of PCBs (e.g. printed electronics) could be an opportunity to reduce Ta use in future. However, reduction of Ta use in capacitors most probably further complicates recycling.

### **Cemented carbides**

Tantalum carbide is used as a minor component in hard metal tools, mostly in association with WC and TiC. There is no exact data about recycling rates of hard metal waste in Europe, but there are several companies

competent in hard metal recycling. Estimated recycling rates are relatively high, 60-70 %. Tantalum is mostly recycled as a component of the W-Co powder or as a separate metal.

Likely, the recycling rates could be further increased by reducing losses of hard metal waste in collection and pre-treatment stage, for example by giving more information about recycling opportunities to waste producers, collectors and pre-treatment companies.

### **Ta superalloys**

Ta used in nickel based superalloys ends mostly to the waste from aerospace sector, and also to the turbine waste from energy sector. Very little information was found about recycling rates of this waste, but it can be estimated that the recycling rates are reasonably good.

### **Ta alloys**

Ta alloys are used in industrial reactors and other applications requiring high temperature and/or high corrosion resistance. The alloys end up to industrial waste. Typically Ta is alloyed with a few per cent of tungsten. In addition, Ta is used as a metal or coating in medical applications, such as pacemakers, surgical implants, etc. ending to crematorium or medical waste. The information about recycling rates of Ta alloys is defective, but it can be estimated that a significant part of the industrial waste is recycled. Also recycling of metals from crematorium waste is growing. Recycling schemes exists in over 15 European countries. Dutch company Ortho Metals is specialized in recycling of crematorium waste [5].

## **APPLICATIONS WHERE RECYCLING MAY PRESENT SIGNIFICANT OPPORTUNITY**

The organisation of collection and recycling of Ta containing industrial waste (alloys, superalloys, hard metal tools) is significantly easier than that of electronic components which are scattered to different complex products. This reflects in significantly higher recycling rates of industrial Ta containing waste, which probably can further be somewhat increased. The data currently available does not enable estimation of the quantities that are currently not recycled in EU.

However, the most significant opportunity is to increase recycling of Ta from electronics waste (WEEE) and end-of-life vehicles (ELV) and other applications where Ta containing electronic components are used. In practice development of economically viable recycling system is challenging and requires development actions in several parts of the collection and recycling chain.

The following actions could result in increased recycling of Ta in electronics:

- Development and introduction of alternative solutions for joining/fixing of electronic components into printed circuit boards, enabling easy disintegration of the components. In addition to increased recycling, easy disassembly could also enable reuse of electronic components. The methods studied include replacement of solders with conductive adhesive (not very easy to separate) or use of polymer latex from which the parts can be separated by dipping to hot water [6].
- Improved management and monitoring of WEEE collection leading to increased amounts of WEEE and ELV to end to compliant collection and management.
- Development of an efficient technology for automatic identification and separation of the different components assembled to printed circuit boards [7]. In order to be economically feasible, the technological solution should be capable for separation of several different components simultaneously [8].

In addition, there is a need to produce better data about the quantities and qualities as well as recycling rates of different tantalum containing waste types. This data would enable estimation of actual recycling potential and need of further actions to increase recycling

## PROMISING NEW APPROACHES AND SOLUTIONS

### Electronic Waste

As mentioned in the deliverable D4.2, recycling of Ta from post-consumer electronic waste is facing several technical bottlenecks:

- In electronic devices, Ta is concentrated in components dispersed into PCBs and consequently is difficult to selectively recover and concentrate.
- Ta compounds are covered by several layers of minerals (manganese dioxide,  $MnO_2$ ) and plastics (carbon). This intimate mixing between parts of different chemical composition impedes recycling process to efficiently separate Ta.
- In addition, during the widely-developed pyro-metallurgical copper route used by e-waste recyclers in Europe (such as Boliden and Umicore), Ta easily oxidizes and migrates into the slag phases.

A capacitor consists of a metal terminal (Cu, Fe or Ni), a packing made of epoxy resin, and a tantalum electrode [9]. Several studies are currently undertaken in order to develop processes for recycling Ta contained in capacitors. In particular, recycling tantalum from the capacitors in PCBs needs a mechanical separation of these capacitors from the PCBs, something that has not been done so far.

Some examples of innovative projects on Ta recycling are presented hereinafter. The French project SILEXE aims to develop an effective method for extraction and purification of strategic metals such as indium, tantalum and gold from printed circuit boards [9]. The process is based on the use of ionic liquids at room temperature uses in the same time as extractants containing either the chelating ligands, or of ionic liquids to specific task (TSILs) that have a strong affinity and/or selectivity with the target metal and as purification by selective electrodeposition process. So few studies on the separation of ions by hydrometallurgical processes liquid / liquid involving chelating agents or TSILs in ionic liquid media are already described, just as studies of electrodeposition in organic solvents, the combination of the two techniques is so far not addressed in the recycling industry.

The REMETOX project fits also into the context of the recycling of waste electrical and electronic equipment (WEEE) [11]. This project proposes to study the potential of an alternative technology to recovery, based on the oxidation of printed circuit boards (PCBs) by water placed in conditions of pressure and temperature corresponding to its supercritical state. PCBs contain gold, silver, platinum, tantalum, copper and tin. This technology is designed to allow a total recovery of metals, say 100% of the total of metals contained in the rich electronic device, in particular metals such as tantalum are not today recovered by conventional technologies. It must improve the profitability of the recycling of electronic waste, while reducing its environmental footprint. The Remetox process consists of elimination of organic part in PCBs by supercritical water, followed by physical separation to separate the silicon fibers from metals. These metals are subjected to hydro-metallurgical/ pyro-metallurgical techniques to recover all metals selectively.

The recovery of Ta from capacitor scraps using an oxidation process followed by mechanical and chemical treatment was investigated by several authors [9, 10]. In these studies, sintered Ta electrodes inside the capacitor scraps are collected mechanically after the oxidation of the scraps in air and by combination with chemical treatment; tantalum oxide powder ( $Ta_2O_5$ ) with high purity was recovered by reducing the  $Ta_2O_5$  obtained through magnesiothermic reduction (Figure 5).

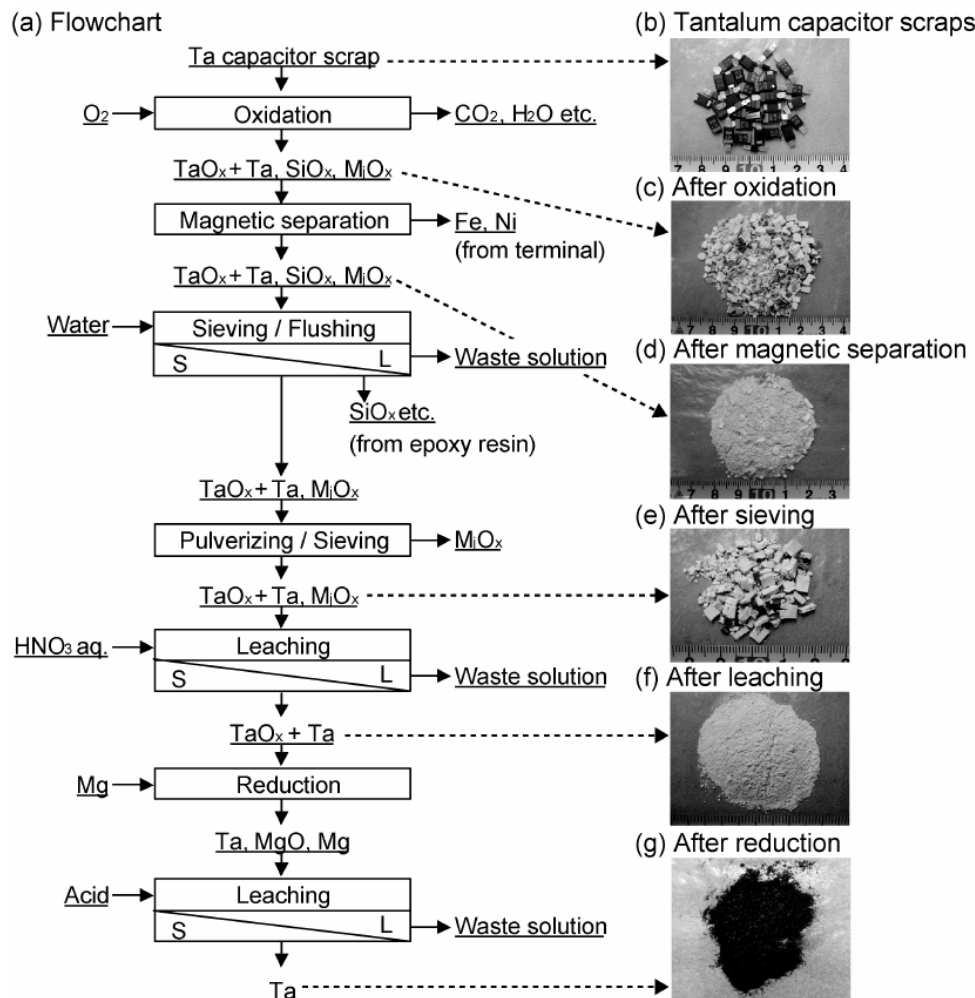


Figure 5. Flow-sheet of Ta recovery from Ta capacitor scrap [1]

Chlorination is another possibility to recover tantalum powder. Tantalum compounds are reacted with chloride wastes such as  $\text{FeCl}_x$ . It was found that tantalum was effectively separated and purified when tantalum powder is reacted with  $\text{FeCl}_x$  at  $830^\circ\text{C}$  under an argon atmosphere.

According to Katano et al. [12], the recovery of tantalum sintered compact can be performed by using steam gasification with sodium hydroxide at  $530^\circ\text{C}$  under nitrogen atmosphere to destroy mold resin and stabilize the halogenated compounds in sodium hydroxide to prevent exhausting halogenated gas. Mold resin can be decomposed by steam gasification with  $\text{NaOH}$  to recover the sintered compact of tantalum. Furthermore, most halogen gas generated from decomposition of mold resin can be trapped in  $\text{NaOH}$  not in exhaust halogen gas. These results suggested that recovery process of tantalum sintered compact from the used condenser using steam gasification with sodium hydroxide is expected as a feasible way to recycle the rare metal in electric equipment. The process is described in Figure 6:

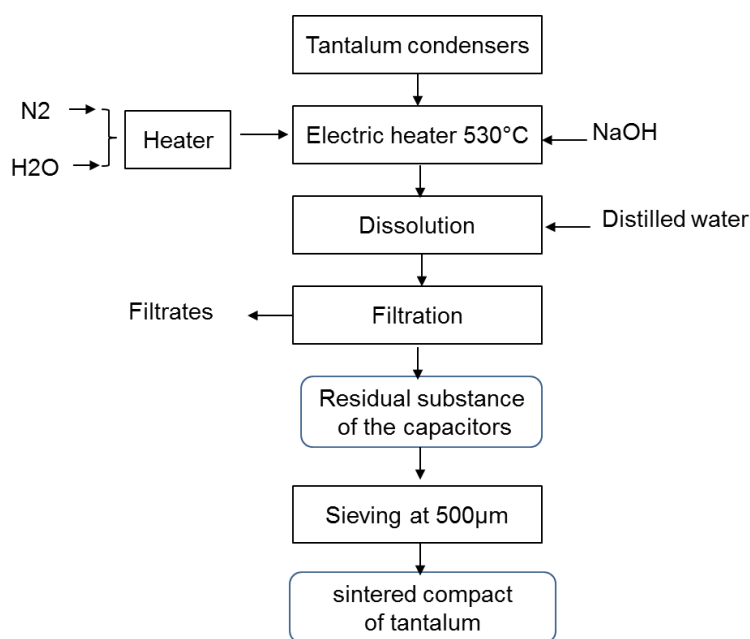


Figure 6. Innovative process to recover sintered compact of tantalum from used condensers

Several metals can be recovered from Tantalum Capacitors with Ionic Liquids [13]. The dissolution of the whole tantalum capacitors can be performed in acidic AlCl<sub>3</sub> based ionic liquids. Except the tantalum core, all capacitor components such as polymer housing and the contacts composed of silver and tin are dissolved in the ionic liquid. The tantalum core with some residues of MnO<sub>2</sub> might be used as a pre-concentrate for metallurgical refining of tantalum. Additionally, tin and silver can be directly recovered from the ionic liquid by electrodeposition, and maybe also manganese. Multi-element recovery approach has the potential to be applied in the recycling of other electronic equipment.

It is also worth mentioning that there is a patent dealing with the recovery of high-content tantalum from tantalum sintered compact collected from a tantalum capacitor [14]. The method combines the acid and alkali treatments, thereby recovering tantalum. The acid treatment is performed using HCl and the alkali treatment is performed using NaOH or KOH.

### Non-electronic waste

As mentioned in deliverable D4.2, metallurgical products (alloys and superalloys) and cemented carbides tools are the two main tantalum urban mines resources, apart from WEEE, which are considered worth to recover. For both types of products, the physical methods, which consist in a direct re-use of the materials after specific treatments (see D4.2) are the only options available on a large scale. However, in both cases, the full re-use of the material is often limited due to the contamination caused by usage and/or the high energy cost of the physical methods.

Another option is thus the chemical separation of the elements composing the materials, with is aim of the recovery of abundant and/or valuable elements such as Ta. Some options are presented in this section.

### Metallurgical Products and Superalloys

As presented in deliverable D4.2, the only industrialized method for reprocessing Ta-containing alloys consists in a direct remelting, without separation of its elements.

However, the chemical separation of superalloys components seems attractive, and alloys with Ta contents of up to 8% is sometimes claimed to have economic and strategic sense under the pure tantalum aspect [15]. A number of pyro- and hydrometallurgical approaches exists, but they are not all suitable because of their cost-intensive complexity or release time. The common difficulty related to the chemical processing of superalloys is indeed that these alloys are used for their chemical and mechanical resistance, which makes them resistant to grinding and leaching. According to patents issued in 2008 and 2009 [15-16], one of the main challenges consists in the dissolution of the superalloys, prior to their chemical separation.

One of the patented methods [15] relates to a process for the digestion of superalloys, wherein both electrodes of an electrochemical cell are composed of superalloy. The considered superalloys contain as the main component 50 to 75 wt.% nickel, 3 to 15 wt.% of at least one of the elements cobalt, chromium, and 1 to 10 wt.% of one or more of the elements tantalum, niobium, tungsten, molybdenum, rhenium, platinum and hafnium. Direct current electrolysis in aqueous solutions is not possible, since a superficial passivation layer is formed after a short electrolysis time, which brings the electrolysis current to a standstill. The electrolysis current is thus reversed at a frequency of about 0.1-1 Hz. An oxygen-free inorganic acid is used as the electrolyte-containing solution, such as hydrochloric acid, and the process is operated at about 60 to 80°C. As a result of the electrochemical decomposition, the elements Co, Ni and Cr are obtained as salts dissolved in the electrolysis brine and the elements Ta, W, Hf and Pt are obtained as filterable oxides, so that essentially quantitative separation of the two element groups can be carried out by filtration of the electrolysis brine.

Another patented method [8] consists in digesting the superalloy in a salt melt. The salt melt contains 60-95 wt% of NaOH and 5-40 wt% of Na<sub>2</sub>SO<sub>4</sub>, and an additional oxidizing agent (e.g. NaNO<sub>3</sub> or K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>). The process is operated at 900-1050°C with a mixture of air and oxygen passed into the salt melt. Several further steps are described in Figure 7. At the end of the process, the nonmagnetic residue, which contains up to 15% of tantalum, can be used as raw material in tantalum-metallurgy.

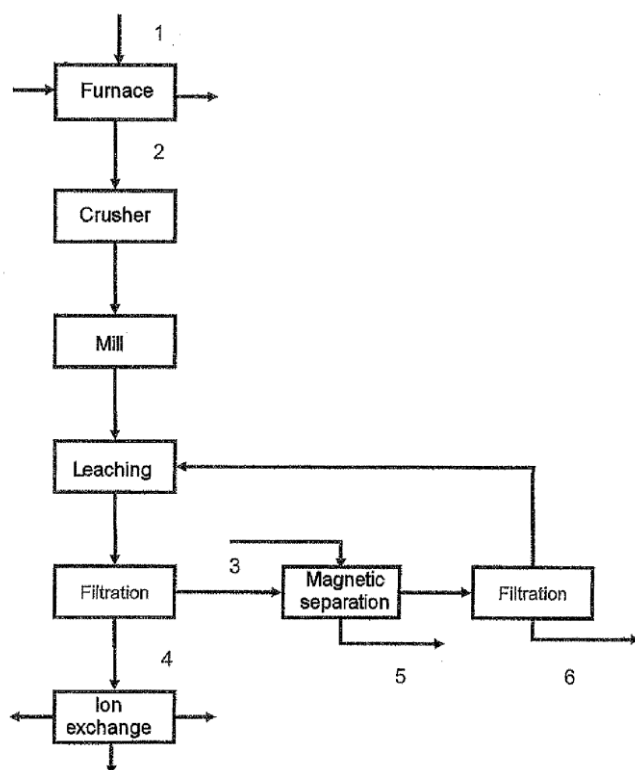


Figure 7. Innovative process for digestion of superalloys (1) and further separation of its elements (2-6), including Ta [16]

### Cemented Carbides

In the chemical processes, carbide scraps with different content of various metals, including tantalum, are treated chemically to extract tungsten and cobalt values first. The chemical process involves the recovery of tungsten oxide or ammonium paratungstate through an oxidation process combined with a purification process. The oxidation process can be one of many types, including thermal oxidation, chemical oxidation, mechanochemical oxidation, and electrochemical processes [17-18]. All these techniques are at laboratory scale development. Depending on the process, the contained tantalum is collected under various forms, like, for instance, an oxide sludge, which is suitable as source material for the tantalum extraction plant.

## MOLYBDENUM

### BARRIERS TO RECYCLING AND POTENTIAL REMEDY MEASURES

Recycling of molybdenum-bearing scrap will continue to be dependent on the markets for the principal alloy metals of the alloys in which molybdenum is found, such as iron, nickel, and chromium. While large quantities of molybdenum will continue to be consumed in downgraded form in steelmaking, molybdenum will continue to be recycled in this manner. As long as the value of molybdenum remains relatively low, scrap metal is not likely to be sought for its molybdenum content. Therefore, recycling rates and efficiency are not likely to change significantly in the near term [19].

### APPLICATIONS WHERE RECYCLING MAY PRESENT SIGNIFICANT OPPORTUNITY

#### Innovative potential in recycling of Mo-containing steel scrap

Similar to other steel scrap, Mo-containing steel scrap is normally recycled by re-melting in the EAF. During re-melting, molybdenum in the scrap is transfer to the melt, which is used to produce new products. Alloy steels (with 0.5-9 wt.% Mo) and stainless steels (with 1-6.1 wt.% Mo) have the highest percentage of molybdenum among the Mo-containing steels, while the carbon steels (with 0.2-0.5 wt.% Mo) has the highest production volume [20]. During re-melting recycling, the Mo may be downgraded into the new steels in a tolerant level without using or considering its Mo contents due to inability in sorting Mo-containing steel scrap from other steel scrap. Due to the miscellaneous sources, the Mo-containing steel scrap contains contaminate elements, such as copper and zinc, which should be effectively removed from the scrap before charging into the EAF. The innovative potential in recycling Mo-containing steel scrap in the future may involve the following two aspects:

- (i) Improving the sorting of Mo-containing steel scrap into various grades from its miscellaneous sources;
- (ii) Improving the impurity control.

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### **Innovative potential in recycling of Mo-containing spent catalysts**

The innovative methods for extracting molybdenum from Mo-containing spent catalysts generally include the following three processes [21-22]:

- (i) Pyro-metallurgical process. In this process spent catalyst is directly smelting-reduced in the furnace (e.g. electric arc furnace). The extracted Mo and other elements are present in the alloy product, while the other materials (such as  $\text{Al}_2\text{O}_3$ ) are present in the slag. The processing capacity of the process is very large. However, the process required large amount of energy and the recycled Mo can only be used for alloying steels.
- (ii) Hydro-metallurgical process. In this process molybdenum in the spent catalysts are converted into soluble compounds, which are consequently obtained by leaching. To facilitate the conversion of compounds, pyro-metallurgical steps are normally required. By applying hydro-metallurgical process it is possible to extract molybdenum as the element with high purity. However, the process is quite complex and generates large amount of hazardous wastes in many cases.
- (iii) Bio-metallurgical process. In bio-metallurgical process the spent catalysts are treated by the bacteria in the aqueous solution. The molybdenum from the leaching solution can be used to extract molybdenum, as that in the hydro-metallurgical process. The process is an environment-friendly and low-cost process; however, the process is too slow to be applied industrially so far.

A summary of the above mentioned processes is shown in Figure 8. The best processing strategy of spent catalyst is expected to be the combination of hydro- and pyro-metallurgical process. However, bio-metallurgical process with pyro-metallurgical steps can be the trend for the future.



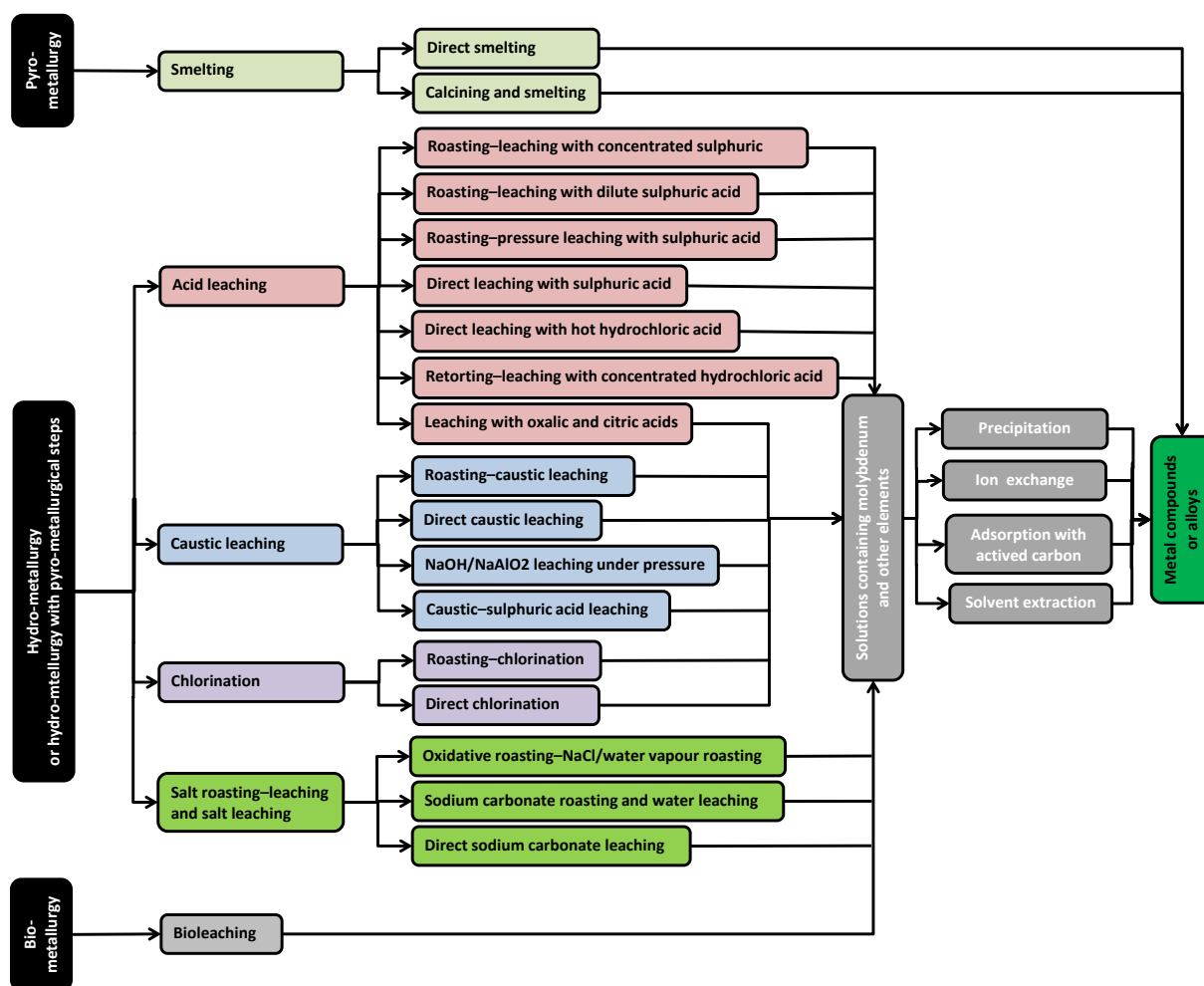


Figure 8. An overview of innovative methods for extracting Mo from spent catalysts (the information in the figure is derived from [21, 22])

## PROMISING NEW APPROACHES AND SOLUTIONS

### Recycling of Molybdenum in Iron-Potassium Catalysts

A technique for recycling of molybdenum in manufacture of iron potassium catalysts for dehydrogenation of isoamylenes [23]. The iron-potassium catalysts are complex oxide systems mostly composed of iron oxides with addition of various activators or promoters and, in particular, molybdenum and cerium compounds. The catalysts are used in the stage of dehydrogenation of isoamylenes in manufacture of isoprene from isopentane by the double-stage scheme, as well as in the dehydrogenation of ethylbenzene to styrene. The influence of the following factors on the extraction selectivity and yield of molybdenum was examined: nature and concentration of a leaching agent, extraction temperature, calcination mode, agitation rate, extraction duration, and liquid-to-solid phase ratio. It was shown that the method developed for recovery of molybdenum from a spent catalyst for dehydrogenation of isoamylenes to isoprene is valid and enables selective recovery of no less than 95% of molybdenum from the catalyst. It was found that the catalysts formed using the molybdenum-containing product from spent catalysts have no adverse effect on the reaction of dehydrogenation of isoamylenes and exhibit a high catalytic activity and selectivity in synthesis of isoprene, which suggest that the recycling of a spent catalyst is possible.

## End-of-life vehicles (ELVs)

The recycling of end-of-life vehicles (ELVs) not only significantly affects the recycling of iron, steel, but also the recycling of alloying elements (AEs) such as molybdenum. The environmental and economic benefits of alternative ELV recycling schemes, which allow more efficient utilization of AEs found in ELV-derived steel scrap (ELV-dSS) was evaluated by using Japanese data [24]. This study consists of two parts: first, the AE contents in automobiles and ELV-dSS were estimated by extending the waste input–output material flow analysis model (WIO-MFA model); second, the efficiency of ELV-dSS sorting was evaluated. Conclusions are from this study:

- 1) Efficient utilization of ELV-dSS by sorting will play an important role in resource dissipation pre-vention and conservation. It was found that the introduction of a rather simple sorting scheme for ELV-dSS, containing three parts (suspension parts, exhaust parts, and others), can be beneficial for the environment and the economy. This finding gives an alternative option for ELV recycling that focuses on the use of the AE content, which differs from previous recycling schemes that regard ELV-dSS as an iron source.
- 2) Appropriate ELV-dSS utilization, based on sorting, has significant potential for cost savings and virgin material import reduction. This may motivate ELV treatment stakeholders and EAF (the electric-arc furnace) steel makers to use appropriately sorted ELV-dSS. However, this form of ELV treatment has rarely been implemented in practice. The potential obstacles for the implementation of scrap sorting were identified [25] as gaps in knowledge and the attitude between steel production companies and ELV recyclers, and the absence of affordable efficient sorting technologies.
- 3) Another obstacle identified was the problem of the steel scrap market, which poses a challenge to the implementation of the scrap sorting methodology proposed in this study. In the current market, scrap is classified and traded almost exclusively based on its shape with almost no consideration of the value of its alloy content.

## Recovery of Mo from alloy scrap

A leaching process combined with multi-stage solvent extraction has been studied for recovery of Mo from recycled alloy scrap [26]. The concept is outlined in Fig. 9. The ground scrap containing 10 % Mo was leached with 8-9 M HCl (initial concentration) and the PLS contained 87.50, 32.5, 20.3 and 6.65 g/L of Ni, Cr, Co and Mo, respectively. Total acid and chloride concentrations were 2.0 M and about 300 g/L. Sequential extraction with Alamine 336 gave three metal fractions and the last one was relatively pure Mo solution for further processing to  $\text{MoO}_3$ .

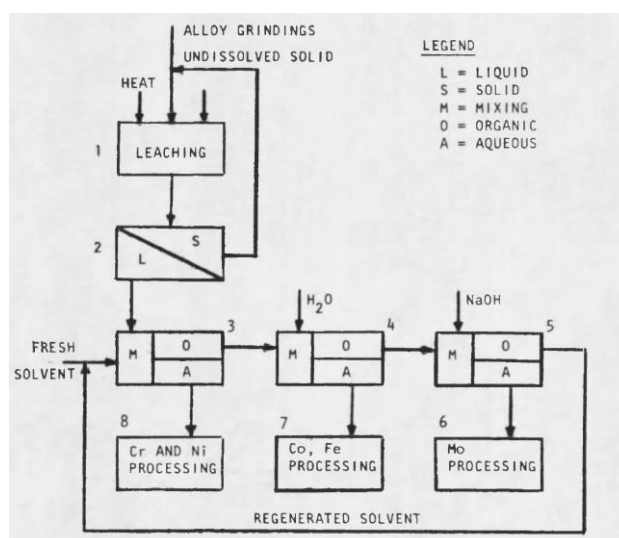


Figure 9. Recovery of Mo from alloy scrap [26]

## NIOBIUM

### BARRIERS TO RECYCLING AND POTENTIAL REMEDY MEASURES

Niobium is an element that is currently not functionally recycled. Most of the element is present in stainless steel and HSLA steel. One of the main barriers for improving the current recycling rate is that not much attention is paid to the composition of steel scrap during the recycling. This causes that a lot of niobium is diluted into lower grade steel or is lost in the slag phase. The most important source of Nb containing steel at the moment are ELV's. Recycling of this material is well organized in Europe with recycling rate over 80% and increasing. Efficiency for the functional recycling of Nb can be improved on short term by better sorting of the steel scrap from car shredders by, for example, separating the exhaust system from the other steel fractions. In the near future it is likely that more scrap becomes available from other sources, including pipe-lines but also steel from building and other applications that use HSLA steel. More niobium can be recovered by improving the sorting of steel scrap.

The European Union already has directives for the collection and recycling of ELVs and WEEE. The EU would surely benefit if guidelines and criteria of steel scrap were to be updated and would also include the presence of alloying elements.

After steel scrap superalloys are an important source and they are usually recycled by re-melting. New processes are being researched and the hydrometallurgical route can be used to process super alloy scrap and produce high-quality end products. Also on this topic more research is required as the recycling is difficult due to the variety of elements that are present in the alloy. This makes the process also expensive and uneconomical. Technologies are available to produce other high quality end products but only one company is known to do that in Europe. Recovery from WEEE is not done at the moment as the process is very complicated and at the moment uneconomical. To improve recycling from this type of waste also more research is required. The best option would be to design a process that recovers more of the valuable and critical elements and also turns them into pure end products.

### APPLICATIONS WHERE RECYCLING MAY PRESENT SIGNIFICANT OPPORTUNITY

The biggest source of niobium at the moment is in stainless and HSLA steel. For the recovery of Nb end-of-life vehicles are most important as they have a relative short life span compared to other applications that use this type of steel [27]. The EU 27 produced 6,430,000 tons of waste from end of life vehicles in 2013 but the amounts vary a lot as can be seen from Table 1 [28]. There is however an increasing trend in the percentage of material that is recycled.

**Table 1: EU-27 ELV waste produced and recycling and reuse (Eurostat, 2016)**

Year	ELV waste (Tonnes)	% recycling and reuse
2006	5,780,000	78,4
2007	6,030,000	82,1

2008	5,940,000	82,7
2009	8,370,000	82,1
2010	7,200,000	83,3
2011	6,700,000	84,2
2012	6,200,000	84,5
2013	6,430,000	85,4

Besides cars another very important end-user of HSLA steel is for the construction of pipe-lines for the oil and gas industry. These type of steels have a lifetime of approximately 60 years and have been introduced in the 1970, meaning they may provide a substantial source of niobium bearing scrap in the near future [27]. The demand in energy is expected to grow in the coming decades and to meet the demand, the transportation capacity for oil and gas also needs to be increased. It is fair to assume that pipe-line construction is going to remain a big user of HSLA steel. Besides the construction of more pipe lines, there has also been an ongoing trend in the increasing of the operating pressure of pipes. This requires higher strength steel which is generally coupled with an increase in Nb content [29]. Another trend that is mentioned by Heisterkamp and Carneiro was a increasing preference of the use of high strength steel. In general it is expected that niobium remains a very important alloying element and as no substitutes are available it is expected that niobium will continue to play an important role in the future.

After the HSLA and stainless steel, the superalloys are the largest consumer of Nb. These materials are used for their excellent mechanical strength, creep resistance at high temperatures, corrosion and oxidation resistance. The most important alloy is nickel-based alloy Inconel 718 which contains around 5% niobium. Recycling of super alloys is more difficult than recycling steel scrap, as their properties also makes it technically difficult to convert them. Of the total superalloy scrap processed in the world in 1996, around 70% was recycled into the same alloy while 20% was being downgraded and 10% sold to nickel refineries [27]. Nickel-based superalloys are responsible for roughly 28% of the total world's alloy production. The aerospace industry is the biggest consumer of these types of alloys followed by the power generation industry with respectively 55 and 20% and demand in superalloys is forecasted to grow with 3-4% a year. Super alloys have an expected lifetime of 20 years [27] and mainly because of their high Nb content they will represent also an important secondary source in the near future.

The waste from electrical and electronic equipment contains only minor amounts of Nb, nevertheless it is becoming an increasingly important source. Waste streams of electrical and electronic equipment are growing fast with 3-5% each year. The niobium content is also slightly increasing. Niobium oxide capacitors are becoming more common as they have a higher life expectancy as aluminum based capacitors. Especially new technologies as LCD and plasma screens contains more NbO capacitors (Zednick, n.d.). The expected lifetime of these devices is around 5 to 10 years.

## PROMISING NEW APPROACHES AND SOLUTIONS

### Recycling from steel scrap

Niobium is mostly recovered from steel scrap that is recycled. Recovery from other sources is only minor [31]. Exact amounts of how much niobium is recovered this way is not available but according to the USGS [32] it might be as much as 20% of the apparent consumption. A study done in 2011 by the British Geological Survey (BGS) showed that there was no evidence for the recycling of niobium in either the UK or Europe, besides from the recycling of steel scrap. Although a method was developed for the recovery of niobium from hard metal scrap, it was not known whether it is employed in Europe.

Because most niobium is used in HSLA steel, most niobium is also eventually brought back to the steel making process, which makes the recycling of niobium relatively easy. This is also demonstrated by the recycled content which describes the fraction of recycled material contained within the total metal flow metal production [33]. Niobium is one of the three elements that have a recycled content higher than 50%, the other two being lead and ruthenium [34]. This does not mean however, that niobium is also functionally recycled.

Niobium that enters the electric arc furnace is easily oxidized and goes to the slag phase. If this is not recovered in a later stage the metal is lost. Furthermore, in the current market steel scrap is classified and traded almost exclusively based on the shape with almost no consideration of the value of its alloy content [35]. In the upgrading process in a shredder plant, the steel scrap is normally only sorted in a ordinary steel fraction and a stainless steel fraction. Sorting based on the content of the alloying elements is very uncommon in the manufacturing industry. When steel is produced of a different (lower) grade, elements that are normally added to enhance the steel's properties can then be seen as contaminants. The steel is in that case diluted or the process is done in very oxidizing conditions which causes the trace metals to go into the slag phase where it is lost if not recovered in a later stage [33].

In 1998 most of the niobium scrap came in the form of steel scrap, about 70% of the total amount. The remaining 30% consisted out of super alloy scrap [27]. To improve the functional recycling of alloying elements in steel, a better knowledge is needed on where different types of alloys are used, how different elements are distributed in end-of-life products and where does it go in the recycling process. Some recent studies were done for scarce metals in end of life vehicles [36]. Most notably for Ni, Cr, Mo, platinum group metals and also REE. While for some metals, measurements are done in the waste flow, most elements are not traced throughout the entire recycling system.

The automotive industry is a large user of different types of steel to which all sort of alloying elements are added, including Cr, Nb, Mn and Ni. Although these elements are added during the steel production, they are often seen as contaminant during the recycling process and dissipated into the steel or lost in the slag [35]. This is caused by the lack of information about the composition of the scrap and the mixing of different types of steel.

Using a waste input-output material flow analysis model, the unintentional flows of alloying elements (Ni, Cr and Mo) were quantified using data for the Japanese automotive recycling industry. This showed that 7 to 8% of the annual consumption of alloying elements is brought unintentionally into the electric arc furnaces [35]. To improve material use a new approach was proposed by Ohno et al.(2015) to recycle ELV's by separating suspension parts and the exhaust parts from the rest of the ferrous metal. Although this study focused primarily on chromium, nickel and molybdenum it is very likely that also for niobium much can be improved. The steel used for exhaust normally contains 0.03 to 0.3% niobium as it deals with higher temperatures [37]. Steel used for the vehicle body contains less, 0.02 to 0.05% of niobium [38].

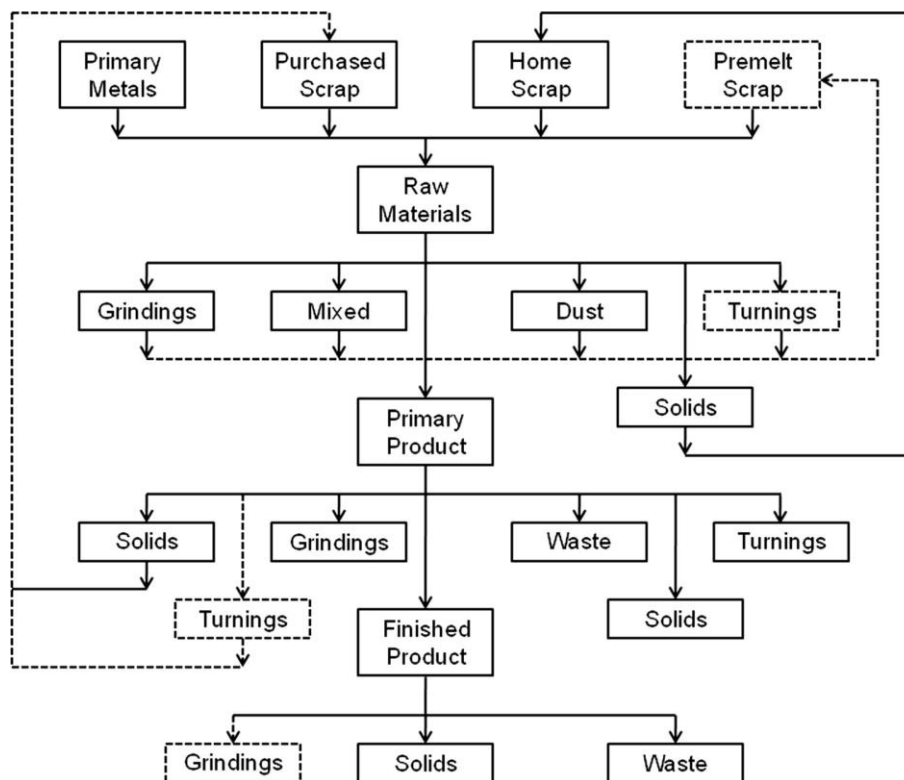
Recycling technologies that allow for functional recycling of ELV's on an industrial scale is at the moment lacking more for most metals [36]. While functional recycling is possible for some metals, such as gold silver and platinum, a long-term strategy would be the storage of relevant component and processed materials concurrent with the development and implementation of new recycling technologies. As possible candidates (permanent magnets) and audio systems were mentioned but also LCD displays which can also contain niobium and also dashboard control circuits and airbag controllers [30]. These applications are likely to play an increasingly big role in the future as electrical cars become more common.

### Recycling from superalloys

The recycling of super alloy scrap is difficult as the determination of the alloy's composition and purity is difficult. In the U.S. about a dozen scrap recyclers are certified by engine makers to process super alloy solids and only four can process turnings. Material that arrives at a site is first identified and tagged and sorted for alloy designation. Then the scrap is tested in the lab on trace elements down to ppb using an atomic absorption unit. Finally the scrap is reduced in size and cleaned before being sent to the melter [39].

Because the quality of the scrap is so important, most recycling of these alloys is done by the manufactures that recycle the scrap that is generated during the manufacturing process. Scrap alloy is then re-melted together with primary material. A typical flow sheet of materials is shown in Figure 10. The most used technique is re-melting of the metallic constituents together with fresh primary material. A problem with this method is that it can cause up to 20% loss of alloying elements due to oxidation losses. For this reason new routes have also been investigated [40]. Methods for the reprocessing of superalloy scrap can be divided into pyrometallurgy, hydrometallurgy and a combination of the two.

For the pyrometallurgical route, the scrap is then re-melted in an electric arc furnace followed by vacuum refining. Volatization losses are minimized by the addition of lime and fluorspar and smelting was done at 1600°C. Impurities such as Al, Ti, Zr and Hf were oxidized by sparing oxygen into the melt. The final melt yielded 93% non-oxidized metals that could be cast as an ingot. Further purification by recharging in a vacuum induction furnace.



**Figure 10: Flowsheet for the recycling and production of superalloys [40]**

The hydrometallurgical route involves the dissolution of the super alloy with for example hydrochloric acid. After the dissolution the leach liquor is subjected to further processing to obtain pure metallic constituents. A new topic that is currently being investigated is electro dissolution which can be used for the recovery of rare metals such as Re, Pt, Ta and Hf. In this process the super alloy is both used as a cathode and an anode and polarity of the electrolysis current is reversed with a frequency ranging from 0.005 to 5 Hz. [41]. This method was tested for super alloys that contain 50-75% nickel by weight, around 3-15% of at least one of the elements Com Cr and Al and 1-10% of one or more of the elements Nb, Mo, Re, Pt and Hf. The reversing of the polarity makes that the super alloy can be dissolved. As electrolyte an inorganic acid is used and the electrolysis is best conducted with e current density ranging from 80 to 600 mA/cm<sup>2</sup> at 60-80 degrees Celsius. After the dissolution stage the filtrate and the residue is treated further to reclaim the separate metal species. The exact route depends on the composition of the super alloy and no specific route was given for alloys that contain niobium.

Currently a combination of pyro- and hydrometallurgy is investigated. Examples include the melting of the scrap and feeding it into an air induction furnace. This removes the oxidizable metals first. Subsequently, the metals that are left in the melt are carburized to form insoluble carbides of, for example, tungsten and molybdenum. The metal carbides can then be leached with hydrochloric and sulphuric acid to recover the metals. Another method involves the conversion of the alloy in a sulphide matte, followed by controlled acid leaching in the presence of chlorine.

Redden and Greaves [42] developed a flow sheet and also did an economic analysis of the process. The flowsheet is presented in Figure 11. In the pretreatment the superalloys are first melted and carburized and turned into anodes. These anodes are then brought to a double membrane electrolytic cell (DEMCC). This cell consists out of three compartments, separated by two anionic membranes. The anode is dissolved in the anodic compartment and the anolyte is then brought to a series of treatment steps to recovery the different metals. These steps include cementation, carbon treatment and solvent- extraction. When the anolyte is purified, it is brought to the cationic compartment where pure metal is deposited at the cathode. The flowsheet demonstrated in Figure 4 treats a superalloy with Ni and Co and also extracts Cu, Cr and Mo. Although this flowsheet doesn't separate niobium, it should be possible to expand the process with a Nb recovery stage. It was calculated in 1999 that a process treating 16,800 kg of superalloy scrap a day could produce 1,535 kg of Co and 4,935 kg of Ni a day and would require a capital investment of 22.6 million US dollars [40].

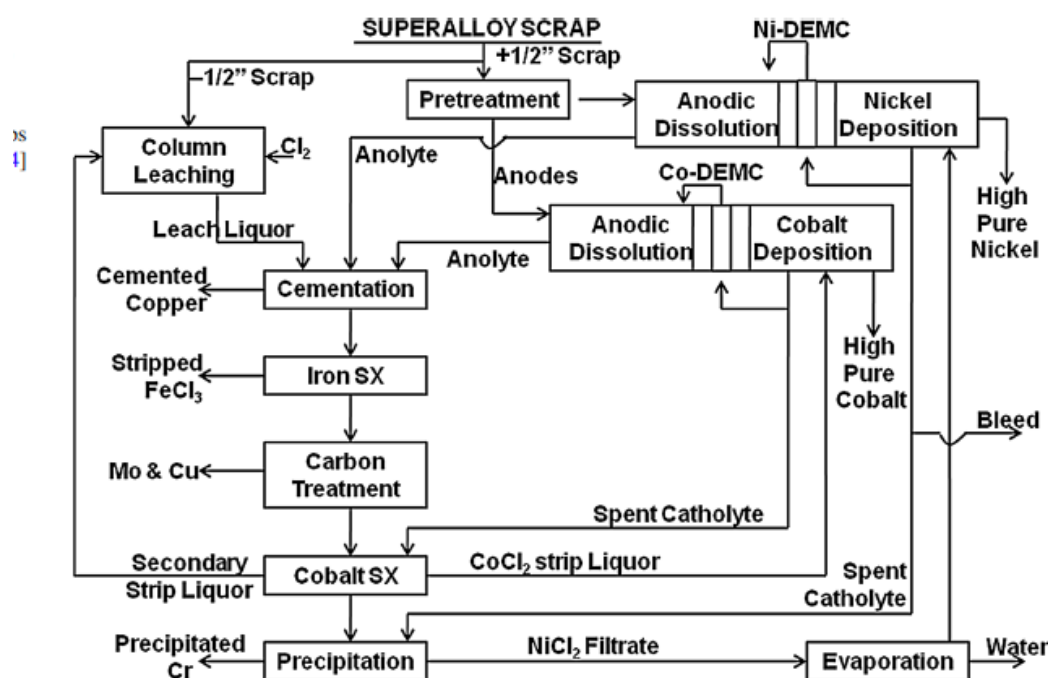


Figure 11: Flow diagram for the recycling of superalloy scrap using double membrane electrolytic cells [40]

Overall super alloys are an important source for critical metals including niobium. Effective recycling at the moment is however difficult and mostly done by re-melting of the scrap in the same alloy or in some cases by down grading. The combination of pyro- and hydrometallurgy might be effective but this needs to be done on a larger scale to make it cost effective. For the recovery of individual elements the hydrometallurgical route would be a good option but more research is needed. Although it is technically possible to retrieve separate elements, the re-melting method is now the most used as is it easier and more cost-effective.



One company that is known to produce niobium from waste material including super alloy is the German company H.C. Starck which treats scraps from niobium and nioboxide with Nb content ranging from 1 to 99%. Products include high quality end products including pure metals and oxides and nickel niobium. The internal processes are not shared but include the following processes:

- Thermal Treatment; Production of metal ingots. Metal powders as well as scraps are melted by electro-beam, followed by solidification of the material in a skillet. Through chemical processing the material can then be adopted into products such as  $\text{Nb}_2\text{O}_5$
- Chemical processing; Includes dissolution of oxidic material in acids and caustic solutions followed by the cleaning and removal of impurities.
- Mechanical Separation; includes the removal of unrequested component by milling and subsequent division using varying separation procedures.

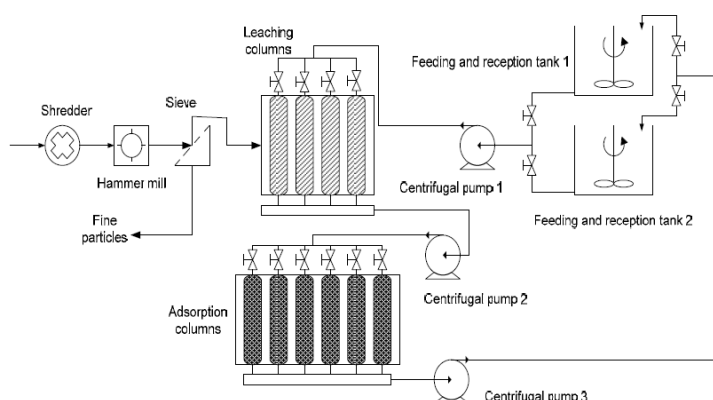
### **Recycling of niobium from other wastes**

Niobium is also found in WEEE in the form of alloys, abrasion and corrosion resistant coatings and structural ceramics. It can also be encountered as an oxide in camera's, computer screens and TV receivers. Lithium niobate is used in touch screen technology [31]. Recycling of the element from WEEE is not well established.

A computer can contain 0,0002% niobium by weight in the welding alloy and in the housing and the potential amount of niobium in waste computers might be up to 1.2 tonnes in the European Union. Also according to EMPRI [43] a typical computer weighing 32 kg would contain 0.000064 kg of niobium or 2 ppm. Most of the niobium is present in the printed circuit board which can contain up to 36 ppm of Nb [44]. Recycling of niobium is difficult in terms of economic viability as the metal is distributed in very small amounts into a large number of user end objects [45]. Storage devices, such as USB sticks, can contain up to 0.25 wt.% of Niobium or 2500 ppm. Although the amounts are small, recycling here is relatively easy since disassembly is not needed [46].

A method to retrieve niobium along with Au, Ag and Cu from printed circuit boards was discussed in [44] using column leaching with a sodium cyanide solution. First a manual separation process was used to remove heat sinks (aluminum scrap) from the PCBs. Then the rest is crushed using a hammer mill and sieved. The oversize was crushed again until 0.5 kg of PCB was collected, with a particle size range from 3.33 mm to 0.42 mm. The material was then brought into a column containing 10 liters of sodium cyanide solution at 4 g NaCN/L. The PCB were leached for 15 days at pH 11. After each day, the pregnant leach solution was passed through a column with activated carbon to complete the closed loop. The flux hereby was 20 L/d kg PCBs and active carbon to PCBs mass ration 3:1. Every day after the adsorption process, concentrations of Au, Ag, and Cu in the solution were measured by AAS. The Nb content was analyzed by SEM in the fire assay core. A flow sheet of the process can be seen in Figure 12.





**Figure 11: Flowsheet for Nb recovery from PCB using column leaching method [44]**

Niobium leaching rates were not measured on a daily base as the aqueous concentration was lower than the detection limit for AAS. The recovery was determined by calculating the difference between the starting concentration (unleached PCBs core bead) and the final concentration. For the experiment 48.1% of the niobium was recovered into the aqueous solution. 98.2% of the niobium in the solution was recovered by the activated carbon. Recovery into the leach solution was 77.2, 47.9 and 51.7% for copper, gold and silver respectively with active carbon recoveries similar to niobium.

The flow sheet proposed contains two size reductions stages which would produce a product also with a particle size range from 3.33 mm to 0.42 mm. Leaching solution is fed from a storage tank and passes through the crushed PCBs bed where it becomes enriched in dissolved metal. After the leaching the pregnant leach is fed through the columns with activated carbon where the niobium as well as gold, silver and copper is recovered. Finally the leach solution is brought back into a storage/conditioner tank where the NaCN concentration is restored before it is returned to the leaching column.

It was calculated that a small scale recycling plant with a monthly supply of 1,000 kg of raw material and an operation time of 10 years would give a financial yield of 27% internal rate of return and a net present value of roughly 100,000 US dollars. This calculation is based on a recycling plant in Latin-America and the solid waste still contained 319 g/t Au and 733 g/t Ag.

## RHENIUM

### BARRIERS TO RECYCLING AND POTENTIAL REMEDY MEASURES

In the recent years, 80-90% of rhenium have been produced from primary sources and waste from the processing of ore concentrates of copper and uranium, and only 10-20% comes from recycling [47-51]. Although in the recent years there has been a continuous upward trend in the production scale of rhenium recycling it still is too low in relation to the amount of demand for rhenium.

Only in a few countries in Europe, mainly in Germany, Estonia, France and Poland, exist narrow, specialized groups of scientists that deal with the processes of rhenium recycling [47-51]. The main reason for such low

number of specialized units dealing with the rhenium recycling and relatively insignificant amount of rhenium recovered from secondary production is the hermetic character of petrochemical, aircraft and energy industries. Rhenium recovered from spent catalysts from reforming processes, or waste from the production of superalloys remains within a closed loop including manufacturers and consumers. Spent catalysts return directly to the manufacturers, omitting the secondary market, where are subjected to regeneration and sold back to the refineries.

Until recently, spent parts of alloys and rhenium containing superalloys, as production waste, didn't enter the open market, they returned directly to the manufacturer. This situation is changing, presently more and more spent catalysts and scrap are available, which increases rhenium recovery from secondary market. However, there is a lack of an effective logistic system of rhenium containing spent materials. They randomly finish on various scrap-heaps, they are not segregated, which hampers their further processing. Their quantity and regularity of delivery is random and uncertain. Also, the unique properties of rhenium result in increasing applications and a wider range of specialized products on one hand while on the other make the recycling very difficult.

This makes it hard to plan processing and recycling of rhenium and other valuable components. Large companies do not want to implement the recycling technology of such wastes without providing a constant source of rhenium waste and their permanent character. Only small and medium companies have a chance to implement such technology. This technology would have to be flexible enough to adapt to the changing amount of supplies of waste and scrap and their great variety.

Presently, the main sources of secondary materials for rhenium recovery are spent Pt-Re catalysts, Mo-Re and W-Re alloys scrap, used turbine blades of aircraft engines, and also - until recently regarded as useless - waste and scrap from the production of alloys and superalloys based on nickel or cobalt. A small amount of rhenium is also being recovered from the medical equipment [52].

## APPLICATIONS WHERE RECYCLING MAY PRESENT SIGNIFICANT OPPORTUNITY

Despite the already wide range and diversity of the applications of rhenium in various fields of industry, new possibilities of using the specific properties of the metal are still discovered, and hence also new sources of rhenium wastes are generated. The catalysis supported with rhenium and its compounds is continuously developing; there are new catalyst systems of rhenium, new alloys and coverings containing rhenium being produced, which in the future may become a potential source for recovery of this metal. In the future, the rhenium catalyst systems will not only be in a form of catalysts with alumina or silica carriers, or in combination with platinum or palladium catalysts, but will be represented by the whole range of both hetero- and homogeneous catalysts, in which the amount of rhenium may vary over a wide range from several percent to just a few ppm. Rhenium therein may be combined with other metals exhibiting catalytic properties, e.g. Mo, Ir, Ru, Rh, Os.

There are also new rhenium alloys with metals that until now were not components of superalloys (Cu, Fe). The addition of rhenium should provide much higher resistance under load conditions, and also at the higher temperature. Rhenium as an alloy compound with boron forms a compound of hardness higher than diamond. These coatings applied even in a thin layer on large surfaces have the potential to revolutionize the abrasive and drilling tools industry.

Not only the technologies for creating the superalloys are developing, but also the technologies of deposition of a thin layer coating with rhenium on alloys. There are various techniques: powder, spray, plasma, PVD, CVD. In all of these methods, as well as in the surface treatment of alloys and coatings, the high amount of wastes is created, which not always can be directed back to the production cycle. The new electrochemical methods to

produce rhenium alloys which contain nickel or cobalt, but also molybdenum or tungsten are being developed [53-55]. These alloys can be employed as master alloys to produce superalloys, but also as thin coatings deposited on various surfaces to make them more resistant to grinding or to enable them to operate at high temperatures.

A new application of rhenium is also observed in its addition to tungsten-cobalt-rhenium heavy sinters used e.g. for production of armor-piercing and KEP bullet cores [54].

Such a large variety of materials, so difficult to process (very high chemical and thermal resistance, high hardness and abrasion resistance) and decreasing amount of rhenium contained therein are the main factors which initiate the search for new methods of recycling, which would enable to recover not only rhenium, but also other valuable components. It is also important for new technologies to be cost-effective, efficient and environmentally friendly. To make it possible it is required to apply hybrid technologies: both pyro- and hydrometallurgical, new leaching agents, systems of selective separation of metals – ion-exchange with ion-exchange resins or solvent extraction. It is also important to produce compounds of high purity, so that they can be not only directly re-used at the current production cycles, but also to prepare pure, useful commercial reagents and, preferably, new, more processed compounds.

Due to high cost of rhenium production from primary sources or tailings from processing of rhenium containing ores the rhenium recycling is economically justified, despite the current lowering price of rhenium. In the processing of rhenium containing waste and scrap also other valuable metals are recovered, often being recognized as strategic, and even critical. It seems highly important for the future research to develop new, ecological, innovative and flexible technologies to extract rhenium from secondary sources, especially from the waste and scrap of superalloys and then processing of produced commercial compounds into more processed compounds and materials, e.g. electrochemically obtained rhenium alloys with nickel or cobalt. Due to difficulties with collecting of the end-of-life rhenium components and the logistics involved, the highest potential for implementation of these technologies can be seen in small and medium enterprises which are not so strongly influenced and limited by the scale and diversity of raw material supply in their production operations.

## PROMISING NEW APPROACHES AND SOLUTIONS

There are many technologies that make recovery of rhenium from waste from the production of superalloys and used turbine engines blades, W-Re scrap, or spent catalysts possible. Generally they are based on dissolution in  $\text{H}_2\text{SO}_4$  or HCl solution, a mixture of HCl and  $\text{HNO}_3$ , or in aqueous acidic solution of sodium bicarbonate (catalysts). The process could be preceded by preliminary roasting of the material in oxidizing atmosphere or with application of molten salts of NaOH,  $\text{Na}_2\text{CO}_3$ , and  $\text{Na}_2\text{SO}_4$  with addition of oxidizing agents. The produced  $\text{Re}_2\text{O}_7$  is then dissolved in aqueous solution of ammonia until receiving  $\text{NH}_4\text{ReO}_4$ , or in water, and then precipitated as  $\text{KReO}_4$  by addition of e.g. KCl. To separate rhenium from other metals and to obtain pure rhenium compound, the ion-exchange method with appropriately selected ionites can be used. For the recovery of rhenium from superalloys the electrolysis in HCl solution is applied, with proper current intensity, frequency and higher temperature established. From the resulting solutions rhenium and other valuable components are recovered using ion-exchange method [47, 51, 56 - 58]. In Poland, the Innovator company has started the rhenium recovery in the form of ammonium perrhenate from waste from production of superalloys and spent blades. It is estimated that this installation would produce around 500kg of ammonium perrhenate each year [59-61].

Also new technologies are being developed aimed at production of new, more processed rhenium containing compounds or materials, e.g.  $\text{Cu}(\text{ReO}_4)_2$ ,  $\text{Ni}(\text{ReO}_4)_2$ ,  $\text{Co}(\text{ReO}_4)_2$ ,  $\text{Fe}(\text{ReO}_4)_3$ , complex rhenium compounds:  $[\text{Co}(\text{NH}_3)_4](\text{ReO}_4)_2$ ,  $[\text{Co}(\text{NH}_3)_6](\text{ReO}_4)_3$ ,  $[\text{Ni}(\text{NH}_3)_4](\text{ReO}_4)_2$  [53, 62].

The existing technologies are also optimized and perfected, e.g. for production of superalloys. Currently, there is a tendency to reduce the amount of alloying elements inside them, including rhenium. The amount in the first superalloys produced was up to 6% , then it was lowered to 3%, and now often oscillates in low ranges.

Process of leaching at elevated pressures and temperatures represents a very promising direction while increasing the share of recycling of rhenium in its total production, especially with such a large variety of materials, so difficult to process, and small amount of rhenium contained in them. The processes carried out at elevated temperature and elevated pressure, with the addition of strong oxidants or strong reducing agents, would increase the efficiency of leaching with a substantial reduction of processing time and reduction of the consumption of leaching reagents.

There is a large application potential in dissolving of superalloys and rhenium containing alloys scraps with application of an electrolyser of a special design [63]. Such diaphragmatic electrolyser with membranes separating the anode space from cathode space provide possibility for simultaneous dissolution of scrap and obtaining of a metal – nickel or cobalt in a form of a pure metal at the cathode. This process should be carried out from chloride solutions, which would allow to use the evolved at the anode chloride for dilution of the anode. Application of sulphate or nitrate solutions is also possible. The use of membrane techniques for concentration and purification of obtained solutions would also improve the process of recovery of rhenium in the form of pure useful commercial compounds and can significantly reduce the amount of sewage and waste [64-66]. By application of the membrane electrodialysis it is possible to produce perrhenic acid of high purity and concentration over 180g/dm<sup>3</sup> [67].

In the process of recycling of rhenium-containing wire scrap the W-Re wire scrap containing 3.27 % Re has been subjected to high-temperature oxidation to volatilize Re as Re<sub>2</sub>O<sub>7</sub> [68]. The oxide was then leached with dilute NH<sub>4</sub>OH solution and NH<sub>4</sub>ReO<sub>4</sub> was obtained by crystallization (Fig. 13).

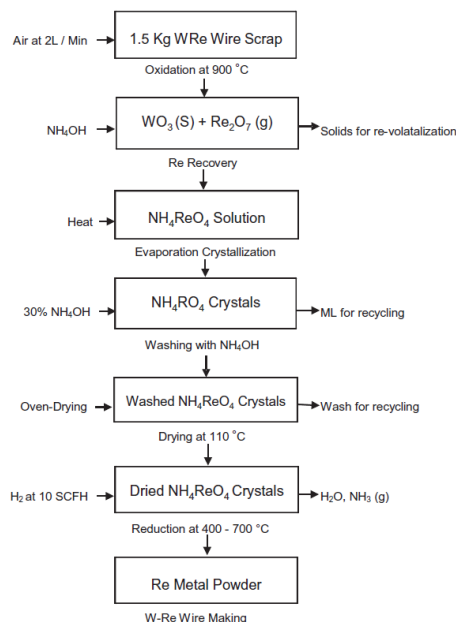


Figure 13. Re recovery from W-Re wire scrap [68].

The oxidation step can be also carried out by fusing the scrap with NaOH in the presence of an oxidant, such as NaNO<sub>3</sub> [69]. After the treatment, the metals are in the form of oxoanions that can be leached with water. WO<sub>4</sub><sup>2-</sup> and ReO<sub>4</sub><sup>-</sup> were separated using a strong base anion exchanger and Re was eluted from the resin using a mixture of tributylphosphate (TBP) and HCl. Only rhenium was reported to adsorb on the resin and its concentration in

the raffinate was very low. The rhenium was recovered from the resin as perrhenic acid dissolved in the organic phase that was subsequently stripped with aqueous  $\text{NH}_4\text{OH}$  to recover the ammonium perrhenate in aqueous solution.

Recovery from Ni-based super-alloys is possible by oxidative leaching with  $\text{HCl-HNO}_3$  mixtures and by sulfide precipitation, adsorption or solvent extraction [70]. In the presence of nitric acid, nearly complete dissolution of Ni and Re was achieved at 70-80 °C. A finely ground sample is claimed to be completely leached during 6 hours, while large particles needed 4 days for 99% extraction of Re. During leaching, large amounts of nitrogen oxides are formed but not  $\text{H}_2$  as in the case of  $\text{HCl}$  leaching. No details were given on the separation methods but a strong base anion exchanger is claimed to be suitable for Re recovery from the leaching liquor. However,  $\text{NH}_4\text{SCN}$  rather than  $\text{NH}_4\text{OH}$  was needed for Re desorption and, therefore, weak anion exchangers applied elsewhere should be more suitable.

Even though the main technologies address rhenium recovery from catalyst and alloys essentially by the classical hydrometallurgical approach: leaching-separation (solid-liquid, precipitation) usually combined with high temperature stages, also some newer approaches can be identified such as:

- Electrodialyse Ion exchange [71]
- Magnetically functionalized particles [72]
- Biologically based approaches [73, 74, 75]
- Poly electrolyte assisted membrane filtration [76]

These developments were not specifically prepared for treatment of urban waste but show high potential for their application in this field.

Bioleaching represents an interesting approach to reduce the number of stages leading to a simplified process. The use of Brown Algae gels as solid-liquid separation support was tested and can be used as bio sourced extractant for Re recovery (Fig 14).

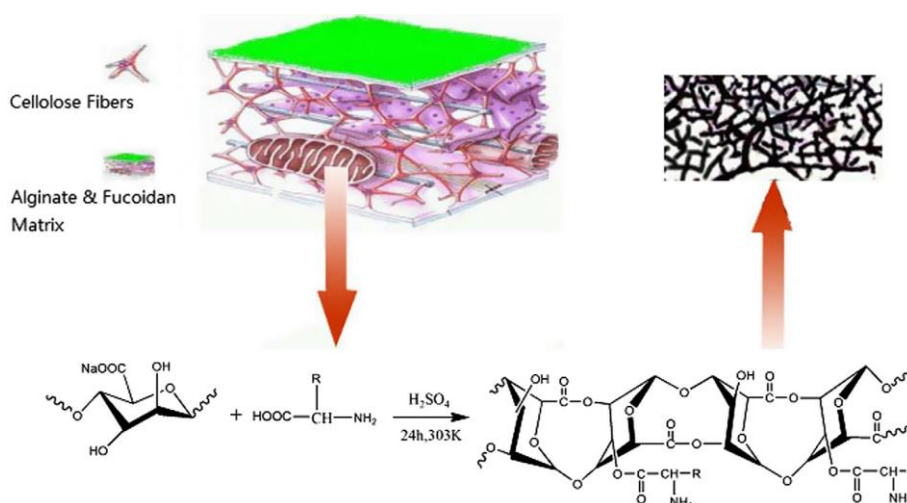


Figure 14: Bio-sourced material for Re recovery from solutions [74]

In the precedent work, the innovation lies in the low ecological impact as there are less chemicals used as in conventional processes.

Some work done in the field of catalyst treatment was based on the use of micro-organism (bacillus megaterium) for selective leaching of Re (98% recovery) vs noble metals (12 % recovery) [75]. Based on the production of cyanides, however, this approach shows ecological issues.

## TUNGSTEN

### BARRIERS TO RECYCLING AND POTENTIAL REMEDY MEASURES

The recycling of Tungsten is well established and 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. Most common used methods are direct methods in which the scrap is directly processed into a useable product. These methods are most often used for the recycling of cemented tungsten carbides, which comprises 70% of the tungsten usage in Europe. The downsides of these methods is that the purity cannot be controlled and further treatment is necessary if the quality of the product is important. New technologies are being developed that can also process a wider variety of wastes including scrap of lower quality.

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. Additionally, for example 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.

At the moment, most of tungsten-bearing metal scrap is withdrawn from the European value chain and exported to China, where scrap recyclers and tungsten producers offer better prices. Especially at the beginning, political regulatory procedures might be a useful tool to prevent the export of valuable scrap and support local recycling initiatives.

Generally, the recycling of tungsten is well established, especially the recycling of tungsten carbide scrap material. The biggest barriers are securing a steady supply of scrap. 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.

### APPLICATIONS WHERE RECYCLING MAY PRESENT SIGNIFICANT OPPORTUNITY

Besides methods for the recycling of tool 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. 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.

According to the experience of the Swerea MEFOS, oxidation-wet chemical treatment process will continue to be the trend for efficient recycling of tungsten carbide (both soft and hard scrap) in the future. Finding an optimized oxidation/roasting procedure is believed to be the challenge.

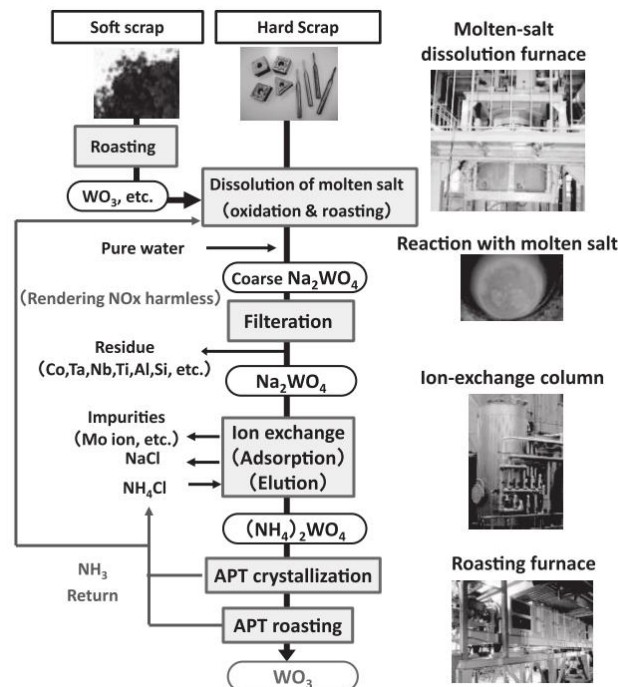


Figure 15. Flow sheet of new oxidation-wet chemical treatment process [77]

There is some potential in electrolytic process [78] for recycling of hard tungsten carbide scrap; however that process still needs development. The technology combines hydrothermal and electrolytic processes and is better described in the following subsection.

Also biosorption [79] can be seen as the method is feasible for industrialization process of WC recycling and can provide a more environmental friendly alternative to the recycling of WC scrap and also possibly less expensive.

## PROMISING NEW APPROACHES AND SOLUTIONS

### 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 [80]. 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 analyzed 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.

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 (Figure 16). 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.



**Figure 16: Digestive solution with immersed sample, blue colour indicates digestion of binder material**

### **Recycling scrap tungsten carbide roll collars**

Y.T. Liao, T. Wu and T.Chou [81] have reported a research on the recycling of scrap tungsten carbide rollers. Tungsten carbide rollers are being used in the steel industry in metal forming processes. Because of their high wear resistance, tungsten collars are very commonly used. Tungsten carbide content can be 85% in weight and in order to reduce costs steel mills are looking into ways to improve recycling of scrap WC collars as well as to reduce the tungsten content. A new method was developed that includes three mayor steps:

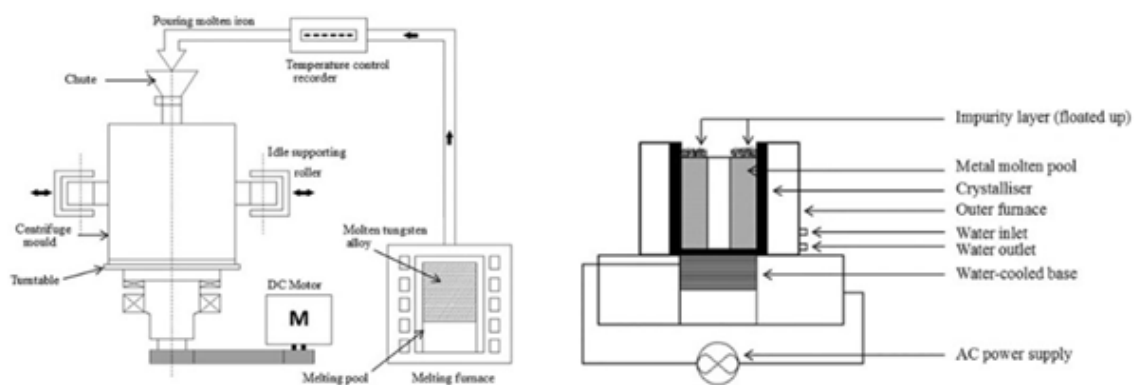
- (1) Crushing of scrap WC collars with high tungsten content into crystallites
- (2) Melting of crystallites together with other tungsten scrap and metal material to produce a mix of a specific chemical composition.
- (3) Re-melting of the mixture followed by electroslog refining.

After the electroslog refining roll collar ingots are produced that are brought to a heat treatment process which include quenching and annealing. The final product is a tungsten alloy roll collar containing 20% tungsten. The product produced has the same performance but tungsten consumption is greatly reduced by the recycling of scrap material and reducing the tungsten content of the new material.



The new process requires two major pieces of equipment, namely a centrifuge machine and an electroslag re-melting furnace (Figure 17). The tungsten scrap is first crushed by high pressure into a variety of crystallites with diameters of 0.1 - 0.15 mm. The crystallites are mixed with swarf material from the rolling and regrinding process of tungsten carbide roll collar and other metal to get a target chemical composition. The material is then placed into a melting furnace at a temperature of 1200°C. The temperature is then raised to 1300-1350°C in 15 minutes to maintain the Co and Ni in a semi-molten state. This is needed in the centrifuge state to ensure that the crystallites can be totally covered by the semi-molten Ni and Co to form a high density microstructure of the alloy. By centrifuging at 1300-1350°C the steel ingot will not segregate during the process.

The molten metal mixture was then poured into the centrifuge which rotates at 600 rpm. The tungsten crystallites would gather towards the outer layer to form a perfect centrifugal surface. After the centrifugal process, the outer mold has to be taken off within 24 hours. Next the original cast blank of the roll collars is rough machined and turned into a semi-finished product. The recycled tungsten alloy collar ingot was complete and sent for electroslag re-melting.

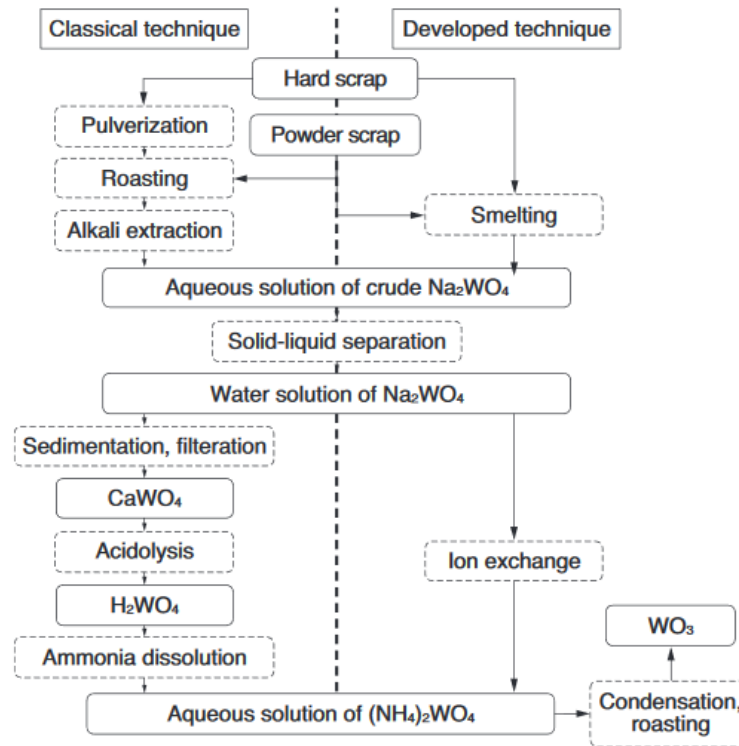


**Figure 17: Centrifuge machine and re-melting furnace [81]**

Electroslag melting is then used to improve the structure and properties of the collar. For this purpose a special melting furnace was designed. The design had a hollow centre and the product from the centrifuge process would fit around the hollow core. The outer part of the furnace was cooled with water. After the alloy roll collar ingot was placed into the furnace a consumable electrode was inserted at one end. The ingot was then melted from the bottom to the top by electrification, causing impurities to form an impure layer along the top. The bottom was cooled by water at the same time. The alloy was then instantly solidified to create a pure alloy collar with a dense microstructure. The new product was tested and showed to have the same performance but the costs to produce it were much less and also tungsten consumption was significantly lowered.

### Recycling of tungsten using molten slag

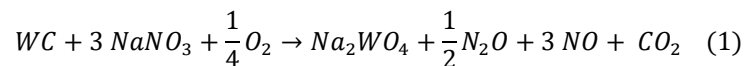
A new technique reported by Ishida et al. [82] uses a molten salt solution to obtain an aqueous solution of  $\text{Na}_2\text{WO}_4$  from cemented carbide. After this treatment the aqueous solution is then converted into a solution of  $(\text{NH}_4)\text{WO}_4$  by an ion exchange treatment. The flow sheet is presented in Figure 18.



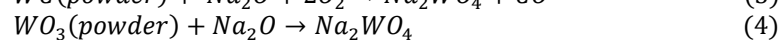
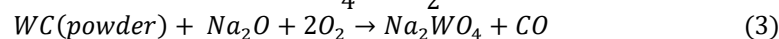
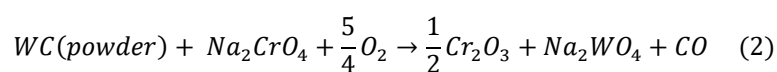
**Figure 18: flowsheet of recovery of tungsten from carbides using molten salt solution process with ion exchange [82]**

#### Molten salt solution treatment

In the molten salt solution the WC-Co cemented carbides react with the  $\text{NaNO}_3$  to produce  $\text{Na}_2\text{WO}_4$ . This then forms an aqueous solution with the  $\text{Na}_2\text{WO}_4$ . The process is performed at 720 degrees Celsius and is a fast reaction that release heat so that external heating is not required. To control the reaction a method is used were a fixed quantity of  $\text{NaNO}_3$  was dosed to the carbide scrap. The WC is then converted by the following reaction:



The oxidizing power of the molten salt solution is strong enough to also oxidize impurities such as Co, Ni, Ti, Ta, Ni, Cr and V up to the maximum oxidation state.  $\text{Na}_2\text{CrO}_4$  and  $\text{NaVO}_3$  are also soluble and will enter the aqueous solution, together with unreacted  $\text{NaNO}_3$ . To convert the chromium to an insoluble oxide, as well as removing any remaining  $\text{NaNO}_3$ , WC powder is added. This causes reactions 2 to 4 and produces soluble  $\text{Na}_2\text{WO}_4$ .



Vanadium is difficult to remove completely and is further removed during an ion exchange treatment.

### Ion exchange treatment

The purpose of the ion exchange treatment is to obtain an aqueous solution of  $(\text{NH}_4)_2\text{WO}_4$ . This is done by passing the solution through a resin tower filled with ion exchange resin (see Figure 19). Ion species supplied to the ion exchange resin carry out ion exchange reaction with the ion species originally captured by resin, and are adsorbed by the resin. The reaction is governed by the concentration of ionic species in the solution; adsorption selectivity; and ion sizes. In this case the  $\text{WO}_4^{2-}$  anions are adsorbed and  $\text{Cl}^-$  anions are discharged. Desorption is done by passing through a  $\text{NH}_4\text{Cl}$  solution, which results in a  $(\text{NH}_4)_2\text{WO}_4$  solution which can be used to produce APT.

Current problems with this method include the formation of polyacids, such as  $\text{W}_{12}\text{O}_{41}^{10-}$ , if the pH is below 7. Also heteropolyacids ions of tungsten and vanadium can be formed. By forming these polyacid ions it is possible to adsorb three times as much tungsten per unit volume of ion exchange resin. However, this also results in the formation of solid  $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$  which would clog the resin tower. To prevent this the ion exchange needs to be performed in basic conditions. Under these conditions it was possible to pass a  $(\text{NH}_3+\text{NH}_4\text{Cl})$  solution at high speed through the resin tower which improved the process three times more efficient compared to the conventional technique, without depositing any solid material.

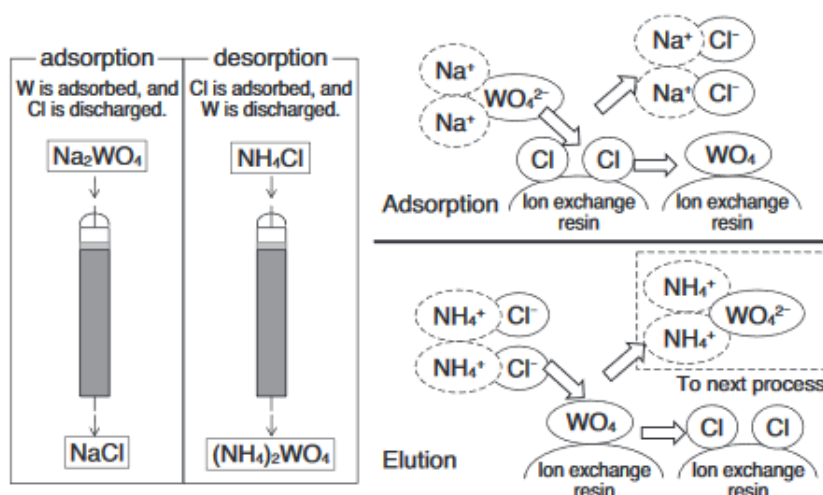


Figure 19: Diagram ion exchange, (Ishida et al., 2012)

### Direct recycling of cemented carbide tool scraps

A new method was developed by Wongsisa, Srichandr and Poolthong [78] for the direct recycling of cemented carbide tool scraps, combining the hydrothermal and electrolysis process (CHEP). The objective of was to use the advantages of both methods while minimizing their limitations. Objectives of the research were:

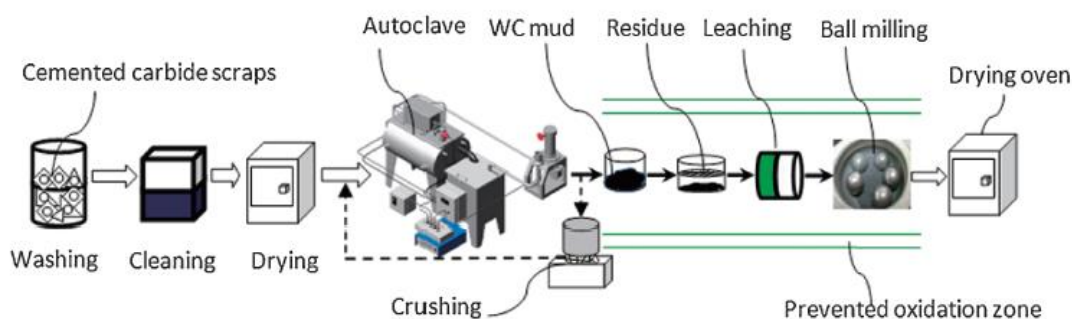
- (1) Determine feasibility of the process.
- (2) If feasible, determine performance and output characteristics in terms of process efficiency and environmental friendliness and product characteristics.

### Method

For the study cemented WC-Co scrap parts were used with dimensions of 12,75x12,75x3,75 mm and 94% WC and 6% Co by weight. The scraps were first washed and cleaned to remove dirt and other contaminants. After being dried the parts were put into a binder phase removal apparatus (autoclave). The autoclave removed the

binder and produces as an output a tungsten carbide mud. This mud was then crushed and washed to remove residue and contaminants. The product was then milled and dried in an oven to obtain a WC powder as final product.

The autoclave employs an electrolytic process to remove the binder phase at an elevated temperature. The apparatus consisted out of a barrel from Teflon in which the scrap parts were placed in an electrolyte. The electrolyte could move freely through holes that were made in the barrel. As a cathode curved titanium plates were used and the anode was made out of titanium rods that were placed in the center of the barrel. Hydrochloric acid was used as electrolyte and was circulated continuously to maintain the pH at a constant level. Also the temperature could be controlled. The entire construction was housed in a stainless steel tank. The barrel rotates during the process to improve contact. The WC particles that are released after removing the binder can go through the holes of the barrel and can settle on the bottom of the tank where they can be collected as a WC mud. The mud was then dried and crushed to produce the final product. A schematic diagram of the entire process is shown in Figure 20.



**Figure 20: Schematic diagram of the direct recycling process [78]**

#### Feasibility and performance

The process developed proved to be successful in the recycling of cemented WC. scrap. The binder phase removal sequence can be seen in Figure 21. The optimal conditions were at electrolyte concentration of 7N, at 80 degrees Celsius and at 0.6V operating voltage. The average power consumption was 4 kWh/Kg of scrap. The quality of the WC recovered in this experiment were found to be comparable to that of virgin WC.



**Figure 21: Binder phase removal sequence (a) WC scraps remaining after initial binder phase removal, (b) WC mud after binder phase removal, (c) ball milling (d) dried powder[78]**

In Table 2 the performance of the new method is compared to other methods. It can be seen that the CHEMEP process has a lower energy consumption than other methods and performs very well at a similar economy of scale. At the moment the technology is still under development. On a small scale (< 50 kg) this method could prove to be a very efficient way of recycling tungsten carbide scrap, especially for small entrepreneurs in

developing countries on a short term. The next step in the research is to investigate the usability of the process on a larger industrial scale so higher volumes of scrap can be processed.

**Table 2: Process for recycling WC powder from cemented carbide scraps [78]**

Recycling process	Tungsten carbide recovery (%)	Complete removal of cobalt (Hours)	HCl Loss (%)	WC Leached (%)	Energy consumption (kwh/kg)	Economies of scale (L-M-S)
Zinc process	98	<36 Depended on scrap input	—	<2	2–4	<i>L</i>
Electrolysis process (room temp.)	98	840	1.50	1.40	12	<i>S,M</i>
Electrochemical process~1-2 bar 80°C	97.5	144	19.00	2.50	6–9	<i>S,M</i>
Electrochemical process >5 bar 80°C	97.5	<u>36</u>	17.00	4.25	6–9	<i>S,M,L</i>
CHEP process	<u>99</u>	<u>36</u>	<u>1.00</u>	<u>1.00</u>	<u>4</u>	<i>S</i>

Note: Specimens indexable insert tools scraps WC-6%Co Economies of scale: *L* = production volume more than 300 kg, *M* = 50–299 kg, *S* = <50 kg.

### Selective recovery of tungsten from PCB recycling unit wastewater by emulsion liquid membrane process

Tungsten is also found in minor quantities in printed circuit boards (PCB). A new method is discussed by Lende and Kulkarni [83] to recover tungsten present in the wastewater from PCB recycling units. Tungsten is used in the wiring, electrode emitters, in contacts and also in heat sinks (ITIA, 2011). Printed circuit boards are mostly recycled to recover the copper and other precious metals such as gold and silver. The recycling of PCB can be done by thermal or non-thermal method. The latter one uses leaching as one of the main stages (Lende and Kulkarni, 2015). After the targeted metals are recovered the wastewater still contains some metals. The water that was used in this research contained around 600 ppm W and 150 ppm Pb, as well as Cu, Mn, Zn, Co, Ca, Na, K and Mg. The concentration of the latter metals was below 5 ppm.

The emulsion liquid membrane (ELM) process is a method that is extensively used for the separation of metal ions but also hydrocarbons and biological compounds. An ELM is the resultant emulsion membrane phase consisting of a homogeneous mixture of surfactant, extractant and inside to which contain an aqueous strip phase. As a surfactant, sorbitanmonooleate was used and Aliquat 336 was used as extractant.

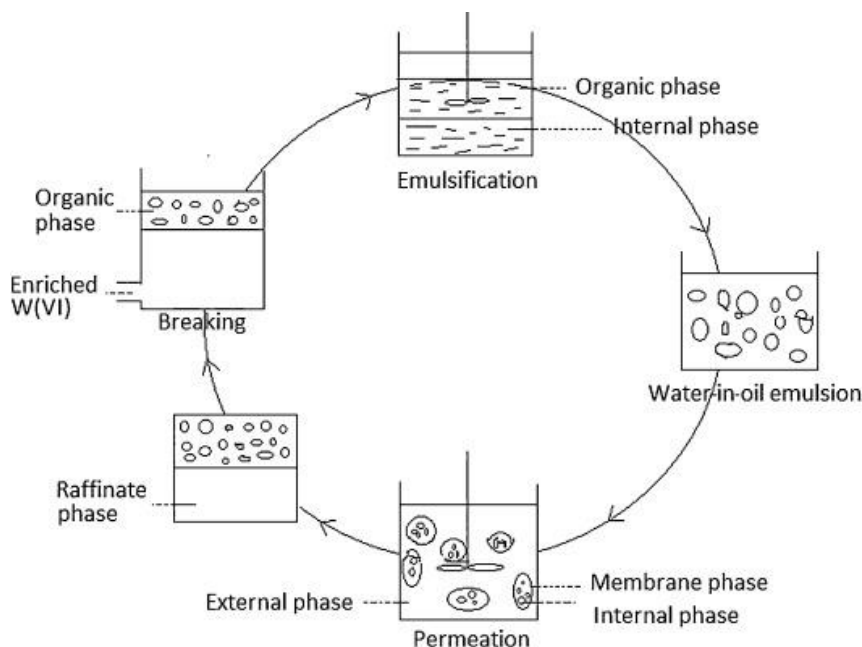
The emulsion was prepared by adding the extractant and surfactant with an organic diluent (hexane). This mixture was combined with the aqueous stripping agent containing 0.1-1 M NaOH and stirred at 6000 rpm for 15 minutes using high speed homogenizer.

The mixture of the emulsion and feed phase (waste water) was performed at 300 rpm using an overhead stirrer. Later the emulsion phase was separated from the raffinate phase and broken by heating it at 80°C. The extractant reacts as an anion- exchanger, forming an ion-pair with the metal oxyanions from the aqueous solution. In the waste water that was used only tungsten is present as  $WO_4^{2-}$  and it is exchanged very fast with the carrier. A schematic overview is shown in Figure 22.

Optimum recovery of the solute is achieved by establishing a proper contact and residence time between the feed and emulsion phase. Different contact times were tested and it was observed that the extraction efficiency of the metals increase at higher contact times.

Multiple parameters were tested and maximum recovery was achieved at extraction concentration of 0.6 M, feed phase pH 5, treat ratio 1:10, contact time 6 minutes and internal phase concentration of 0.5 M. The selected components of ELM has achieved 80% recovery of W and 4 times of enrichment of W from the wastewater.

The current technology is still under development in India and is in a very early stage. It has been showed that it is possible to separate and enrich the tungsten from the wastewater. The next step would be to use the technology in a flow sheet and determine the economic feasibility.



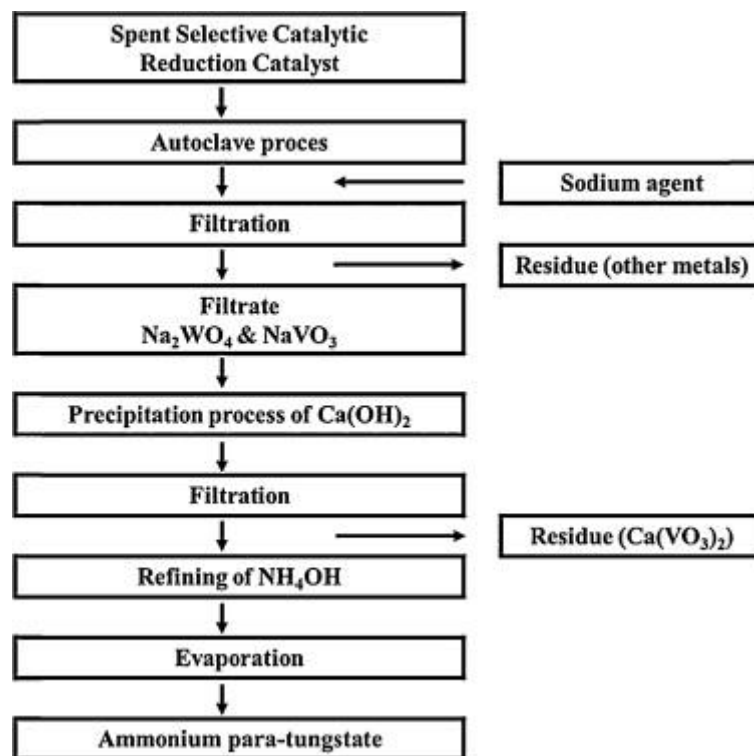
**Figure 22: A schematic overview of ELM process [83]**

#### **Recovery of tungsten from spent selective catalytic reduction catalysts - pressure leaching**

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) [84]. These catalysts are used to convert  $\text{NO}_x$  to  $\text{N}_2$  and  $\text{H}_2\text{O}$  in a selective reduction process. The catalysts are mainly composed of  $\text{TiO}_2$  but also smaller amounts vanadium and tungsten. These small amount 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. In Figure 23 a flowsheet is presented of the process. As a leaching agent  $\text{NaOH}$  was used. Tests were done at different temperatures,  $\text{NaOH}$  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  $\text{Ca}(\text{OH})_2$  to form  $\text{Ca}(\text{VO}_3)_2$ . The tungsten is converted to APT with a reaction by  $\text{NH}_4\text{OH}$ . Maximum recovery was achieved at 2 M  $\text{NaOH}$  solution at 300 degrees Celsius  $\text{L/S}=20$  and 0.2 M  $\text{Na}_2\text{CO}_3$  as additive which gave a W recovery of 99,9% and 86,8% for V.

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.



**Figure 23: Flowsheet for process for the recovery of V and W from spent SCR catalysts [84]**

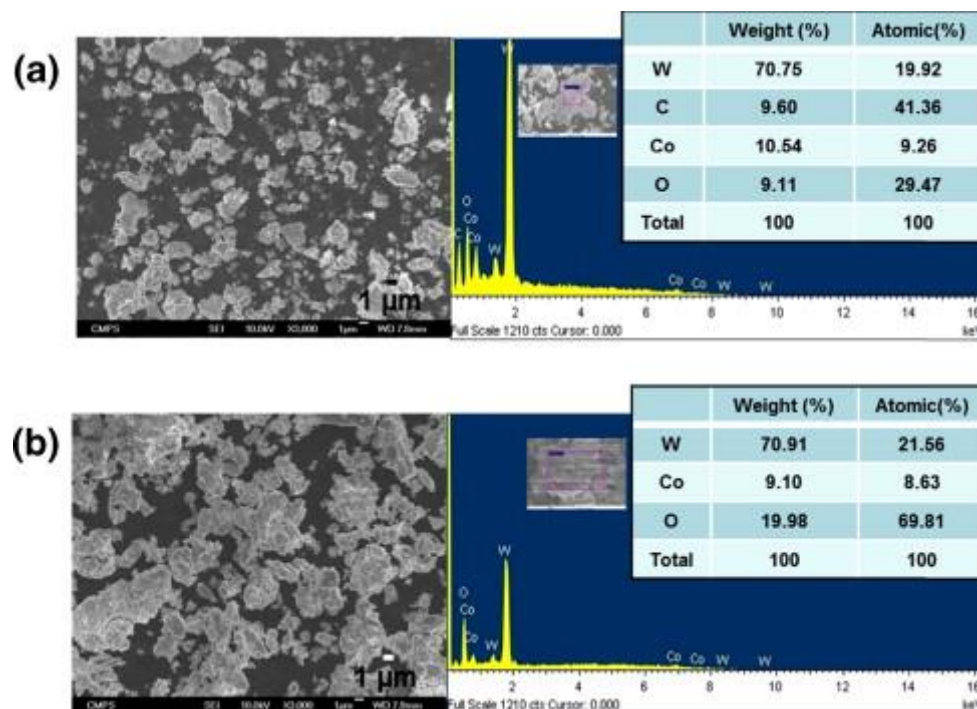
#### Recovery of tungsten carbide from hard material sludge - oxidation and carbothermal reduction process

During the manufacturing of cutting tools, the grinding of WC-Co cermets results in the formation of a very fine sludge. A variety of hydrometallurgical processes have been employed to treat this type of scrap and the most common one involves the separation of the carbides from the binder phase or by oxidation followed by alkali leaching. Some shortcomings of this method are the formation of coarse powders, high treatment cost and it requires large amounts of chemicals.

A new method was reported by Jung [85] 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  $\text{WO}_2$ ,  $\text{WO}_3$  and  $\text{CoWO}_4$ . In Figure 14 the SEM and EDS analysis results are shown for the dried sludge and the sludge after the oxidation stage. It can be seen that during the oxidation all the carbon is removed and the oxygen content increases as the tungsten is converted into oxides.

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. Figure 24 shows the change of the sludge for the morphology and chemical composition before and after oxidation.





**Figure 24: SEM and EDS analysis (a) dried sludge (b) sludge after oxidation [85]**

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.

#### Selective biosorption and recovery of tungsten

A new method was investigated to recover tungsten from wastewater using selective biosorption [79]. Normally W is recovered by other hydrometallurgical means such as solvent extraction and ion-exchange. However, these methods use a lot of reagents and energy and also generate waste that can be harmful to the environment. Biosorption might be useful as an alternative that is more environmental friendly and also cost-effective.

The study was done using a waste solution containing W, Mo and V ions and E. Coli and beer yeast. Two types of solution were tested. A real W waste solution from used WC scrap that was supplied by Kyocera Corp. It was prepared through alkali extraction of used WC scrap. After the extraction, the tungsten filtrate was dried and the dried powder was diluted in a prescribed volume of ultrapure water. The bulk solution a representative metal solution containing W, Mo and V that was prepared by dissolving corresponding weights of tungstate(IV) dihydrate, sodium molybdate(V) dihydrate and vanadium(V) oxide in distilled water. The pH was adjusted using 1 M HCl solution to get the required pH.

For the real waste solution, 5 ml of E.Coli suspension or beer yeast was added to 30 ml of solution. The pH was adjusted to 1.03 using the HCl solution. The experiments were conducted at 25°C at a cell concentration that ranged from  $2 \times 10^8$  to  $2 \times 10^{10}$  cells/mL. The number of E.Coli sells in the solution was determined by a Petroff-Hausser counting chamber. To follow the time course of the microbial adsorption, aliquots of the solution were periodically withdrawn and the concentration was determined using ICP-AES. After tungsten concentrate was prepared through a stage heating process. The E.Coli cells were then centrifuged and dried in an oven at 120°C for 4 hours. Then the sample was heated in a furnace of 1000°C for 2 h.

For the three component system the tests were conducted at a pH of 1.03 and the E.Coli cell concentration was maintained at  $8.7 \times 10^9$  cells/mL. After 4 hours 99.5% of the tungsten was removed as well as 91.2% of the Mo. The vanadium ions only showed a 18% decrease. This was however, higher than for the single component system

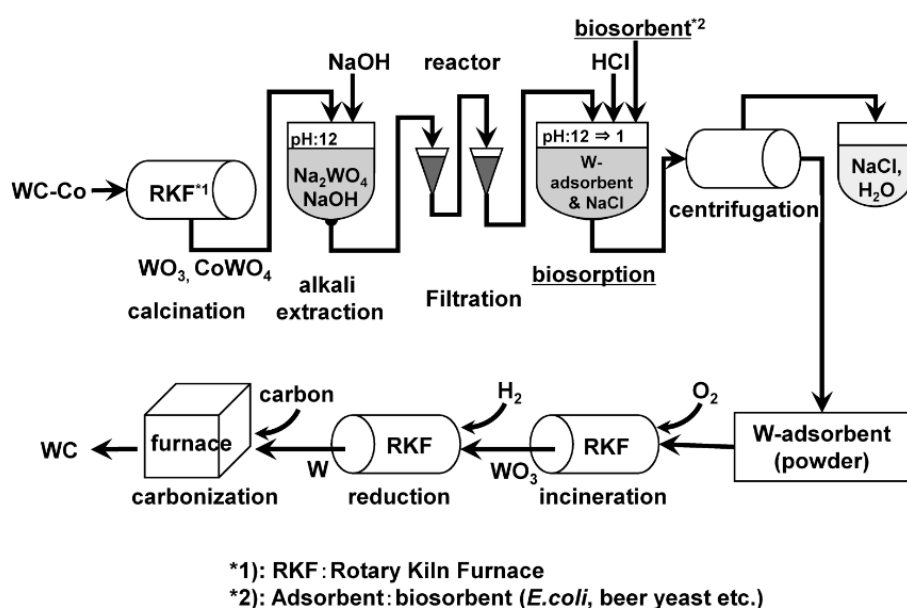


it is likely that the V ions in the three component system are in a different state and may have formed heteropolyacid with tungsten which can be adsorbed, thus increasing the removal ratio of the vanadium in the solution. For selective adsorption the study focused on the effect of cell concentration. At  $2.58 \times 10^8$  cells/mL there was no adsorption of V ions. This indicates that there is a preferential adsorption for W and Mo.

For the real waste solution, E.Coli concentration was kept at  $2.4 \times 10^9$  cells/mL. After 4 hours 93.1% of the Tungsten was removed, 6.0% of the Mo and 0.9% of the V. This showed that selective recovery of W ions by biosorption is applicable. The maximum sorption capacity of the W ions was calculated to be  $5.7 \times 10^{-16}$  mol wt/cell for the E. Coli cell. which is comparable to the adsorption properties of anion-exchange resin (SA-10A).

The dried sample had a W concentration that was 535 times higher than in the original solution. To prepare the W concentrate a calcination step was used. The W-adsorbed biosorbents were heated at  $800^\circ\text{C}$  for two hours. This resulted in the creation of  $\text{WO}_3$  crystals. The powder that remained contained 77% W by weight, and had a concentration that was 837 times higher than of the initial solution. Impurities that were present were likely sodium and phosphate.

For the recovery of tungsten from WC scrap, a theoretical flowsheet was created which can be seen in Figure 25. In this flowsheet beer yeast was used which has a adsorption performance of  $0.29 \text{ g}_w/\text{g}_{\text{beer yeast}}$ . The first part of the process is the heating of the WC scrap to 950 degrees Celsius for 12 hours in a dioxygen atmosphere to produce  $\text{CoWO}_3$  powders. This is then treated with an alkali extraction using NaOH solution to obtain  $\text{Na}_2\text{WO}_4$  solution. Beer yeast is then added and pH is adjusted with HCl solution to a pH of 1. By centrifugation the W-adsorbed beer yeast is separated and dried in an drying oven. The beer yeast was then removed by calcination at 800 degrees Celsius for four hours. Finally the  $\text{WO}_3$  powder was converted to WC by hydrogen reduction and carbonization. The final products was a WC tip.



**Figure 25: Theoretical flowsheet for the recycling of WC scrap using beer yeast biosorption [79]**

The product that was created was analyzed and compared to a commercially available WC powder and no significant differences were detected. The final part of the study was a feasibility study in which the costs of equipment and material was evaluated. Costs for growing, centrifuging and harvesting E. Coli were not taken into account but should be. A cost analysis showed that beer yeast was a better option than E.Coli bacteria which would need very large tank volumes to make it work. When compared to ion-exchange resin, beer yeast is also more expensive and also bring minor impurities such as sodium and phosphate originating from the

proteins in the biomass. The metals need to be removed further by heating processes. An advantage of the method was that the required amount of chemicals and displacement from the total process were relatively small compared to the ion-exchange resin. Although more research is needed to apply biosorption to the industrialization process of WC recycling, it was shown that the method is feasible and can provide a more environmental friendly alternative to the recycling of WC scrap and also possibly cheaper.

### Recycling of tungsten in the alloy scrap as carbide by the 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. The melt is granulated and then charged into titanium baskets. Diaphragm type electrolytic cells are used for anodic dissolution of the granulate. Fe, Co, Ni and small amounts of Cr are brought into a  $\text{CaCl}_2$  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  $\text{Cl}^-$ , 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 26. 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.

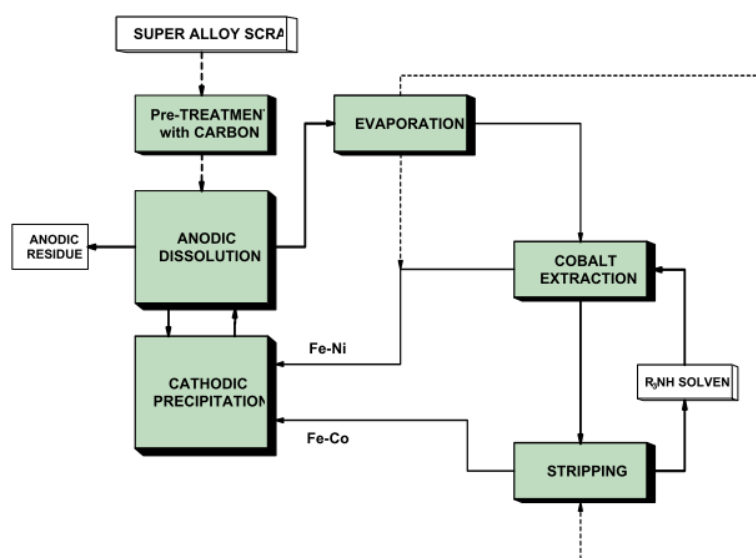
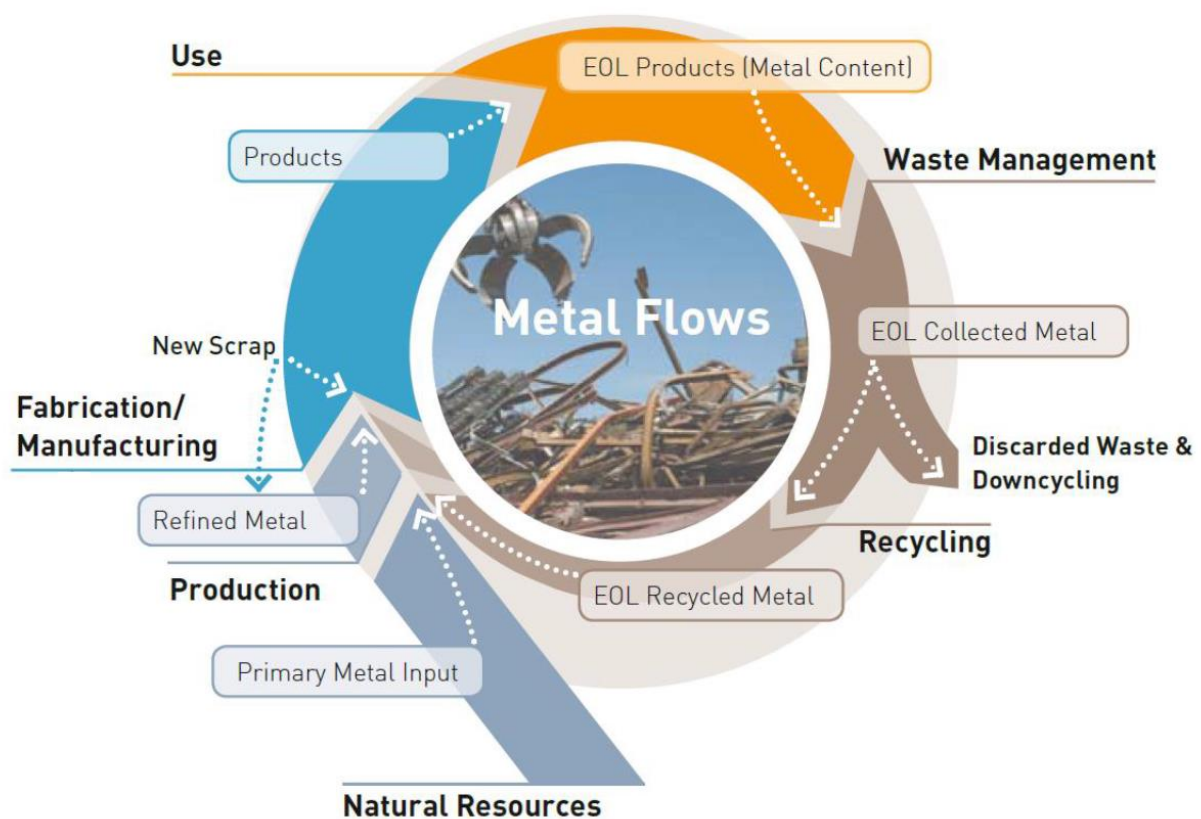


Figure 26. Flow sheet of the separation of iron, cobalt and nickel from super alloy scrap by a solvent extraction – electro-chemical procedure (Guspang process) [86].

## CONCLUSIONS



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Figure 27: Metal and production life cycle [34]

### The circular economy is a key answer

End-of-life recycling rates are disappointing at first glance – currently a large share of the secondary metal resources are lost. For only eighteen metals (aluminum, cobalt, chromium, copper, gold, iron, lead, manganese, **niobium**, nickel, palladium, platinum, **rhodium**, rhodium, silver, tin, titanium, and zinc) is the very important EOL-RR above 50 % at present. But the better results for some traditional and important metals like steel, aluminum, copper, and lead prove that there is a learning curve for recycling. In the 21st century this learning curve needs acceleration, because the variety and complexity of applications which embed metals (in a mobile phone at least 60 elements) is increasing. Furthermore, more and more countries in the world face rapidly growing waste flows for which they have no appropriate recycling infrastructure. Therefore, enhanced technology transfer and international cooperation should be decisively accelerated by international recycling conferences, technological implementation programs in emerging economies and developing countries, and specific scientific exchange programs.

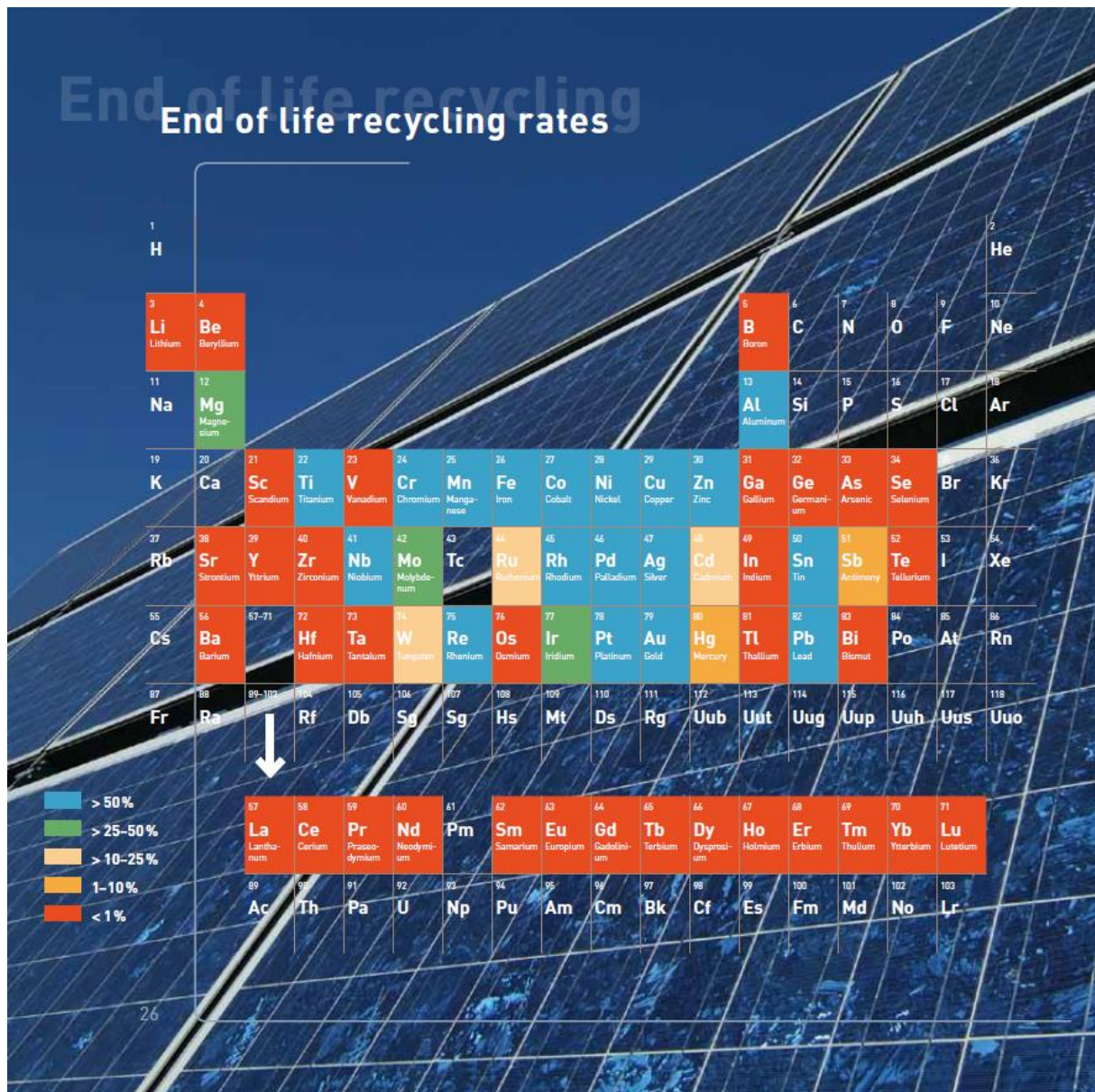


Figure 28. Recycling rates of metals [34]

### Stop illegal waste transport and grey recycling practises

Despite existing regulations like the Basel Convention the shipment of waste to countries without basic waste treatment and recycling infrastructure is an increasing global problem. The export is often incorrectly declared as export of second-hand goods. Therefore, international organizations like UNEP and OECD have to multiply their engagement in the monitoring and controlling of illegal scrap exports, which often contain metals with long-term supply concerns.

One of the biggest challenges for all collecting/recycling SMEs and probably, the main cause for the low recycling rates in some metals, is the so-called “grey recycling”, the informal collection sector consisting of individual garbage collectors who pick up metal bearing wastes and appliances left the formal system and sell them to scrap dealers, into a “black” market. On average only 35% of all European WEEE are collected and treated by the formal sector, the remaining 65% is split between “grey-recycling” and landfill disposal. Grey



recycling is today practiced, in different extent, in all EU countries and in some cases has escalated to a globalized waste trading network. Illegal trade of WEEE to non-EU countries continues to be identified at EU borders, with prominent destinations China, Ghana, Egypt, and Nigeria. There, backyard recyclers employ “family workshops” with primitive tools and methods to recover saleable materials and components from WEEE with little or no safeguards to human health and the environment. In summation, grey recycling contributes to environmental pollution, promotes illegal labor, reduces the “operational space” and the financial incentive for the formal collection and recycling e-waste sector, and deprives the European industry of “domestic” refractory metals resources.

### **Identify the current and future potential European refractory metals waste stream**

Refractory metals logistic chains should be identified and quantified across Europe, mapping net availability, consumption and demand, as well as potential supply gaps and expanded to circular economy mindset including end of life recycling aspects.

### **Develop a novel business model for the enlargement of the SME e-waste refractory metals recycling in targeted regions of Europe.**

Development of region specific business plans for the enlargement of the SME e-waste refractory metals recycling along with the SMEs as well as with local authorities and recycling networks should be pursued. Innovative region specific ways of increasing e-waste collection rates should be studied and set the guidelines for the rest.

### **Propose new directives and BATs for collecting and processing of refractory metals bearing wastes in the EU.**

The growth of global metal demand is currently faster than the adaption of legislation concerning recycling. Continuous improvements of the legislative systems in the industrialized countries are urgently needed in order to enable better recycling rates for many metals and post-consumer goods. The more developed countries should reinforce their attempts to help the less developed countries install appropriate legislative systems and ensure their enforcement in order to take advantage of metal stocks in society.

With emphasis on realigning the various waste directives from a mass focused quota to a metal focused quota, a new waste categorizations will be performed, while the existing legislative framework should be reviewed and improvements should be proposed to European policy making authorities.

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## ANNEXES