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Report on potential innovation pathways to balance demand and supply of refractory metals in the EU

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Summary

Report on potential innovation pathways to balance demand and supply of refractory metals in the EU

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REPORT ON THE POTENTIAL INNOVATION PATHWAYS TO BALANCE DEMAND AND SUPPLY OF REFRACTORY METALS IN THE EU

MSP-REFRAM D1.4

December 2016

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CONTENT

CHAPTER 1 INTRODUCTION

This task will be performed by organizing a 3rd workshop where the various stakeholders have the possibility to discuss the proposed innovation pathways assessed in Task 1.3 and evaluate their viability. The Multi-Level Perspective (MLP) methodology will be used to describe these transition pathways.

In preparation with the workshop and based on the results of previous tasks (from this WP and others), the partners will analyse the need for an evolution of applicable standars and legal framework; this preliminary analysis will be presented to be enriched the workshop.

OBJECTIVES

Deliverable 1.4, "Report on the balance between demand and supply of refractory metals in the EU" aims to fulfil a series of objectives that are outlined throughout the document. Furthermore, it is stressed in objectives treated in last tasks, such as the proposed innovation pathways for each refractory metal. Given this, specific objectives of this Deliverable are the following ones:

- Design of future industrial value chains for refractory metals in contrast with the current ones.
- Discuss the proposed innovation pathways in Task 1.3, "EU reserve vs. EU demand: the supply chain" and evaluate their viability for each refractory metal.
- Analyse the need for an evolution of applicable standards and legal frameworks.
- Evaluate potential innovations.
- Describe new technologies and innovative process in relation to production and extraction in each refractory metal.
- Analyse and describe the transition pathways for each refractory metal according to the Multi-Level Perspective (MLP) methodology.

CHAPTER 2 TUNGSTEN: RE-DESIGN OF THE VALUE CHAIN

INPUTS AND CONCLUSION FROM OTHER DELIVERABLES AND TASK (SUMMARY TASK 1.2 AND TASK 1.3)

DEFINITION OF CURRENT VALUE CHAIN

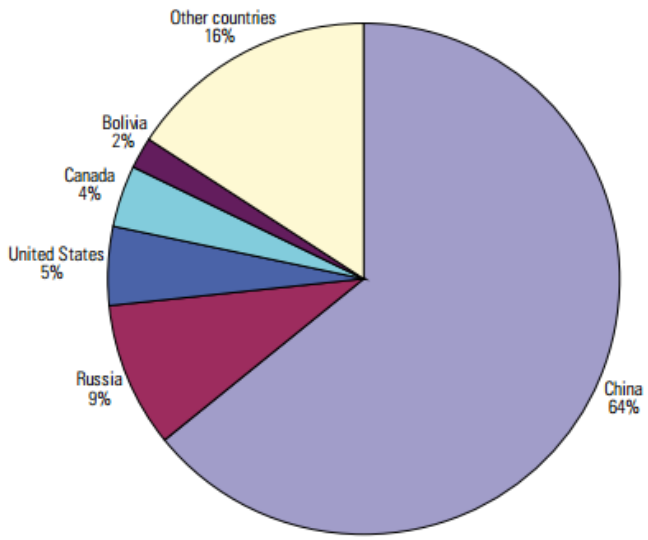
Primary Tungsten Producers – Raw material procurement becomes more difficult, due to lack of investments in new mines. Current mines in Europe are identified in the map below:

Main European Deposits. Source: SIEMCALSA.

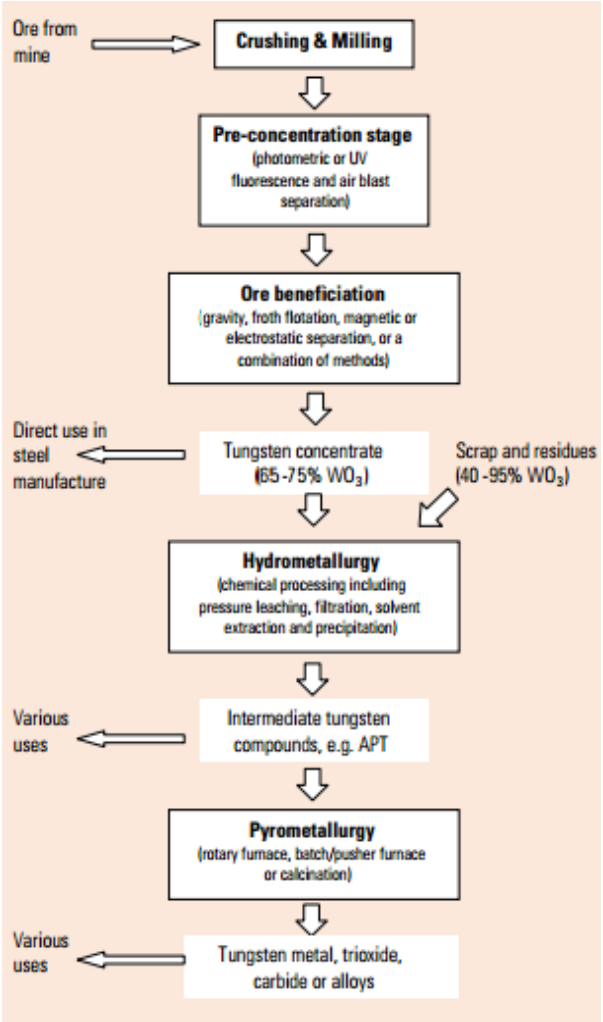
The expected tungsten production in Europe for this year 2016 is:

- **Spain**: 2,700 tonnes (38.6%)
- **United Kingdom**: 2,700 tonnes (38.6%)
- **Portugal**: 800 tonnes (11.4%)
- **Austria**: 800 tonnes (11.4%)

Regarding the global reserves of tungsten China clearly dominates the market provisions:



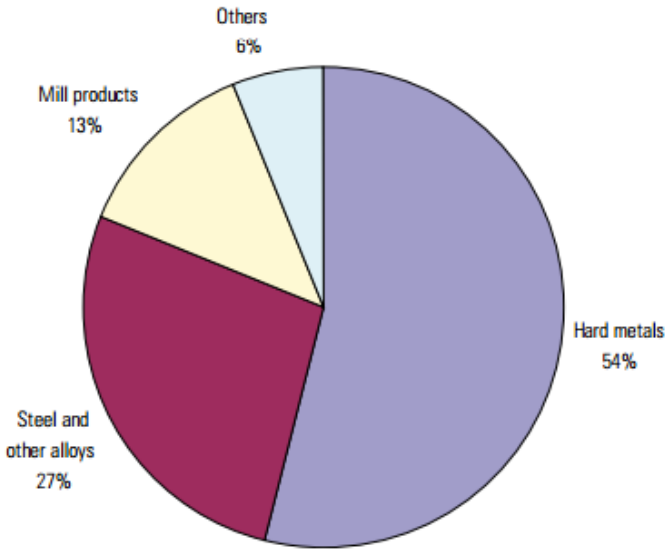
Global Distribution of tungsten reserves



Steps in processing tungsten

The main applications of tungsten are Hard Metals:

- Cemented Carbides: Tungsten Carbide and Cobalt; Machining; etc.
- Tungsten in steel: Tool Steel; High Speed Steel; etc.
- Special Applications: Stellites; Superalloys; Diamond Tools; etc.
- Lamp Industry.
- Electronic & Electrical Industries: X-ray Tubes; etc.
- Chemical Applications: Catalysts; Chemical Products; etc.
- Other Applications: Jewellery; Biology; etc.
- Future Applications: Deep Drilling; Medical Industry; etc.



End-use Products

SUMMARY/CONCLUSIONS

- The high melting point of Tungsten makes its recovery very difficult due to economic reasons (high associated energy cost).
- Classical European deposits such as the French of Anglade (Salau) or the Czech district of Krasno are not being investigated at this moment. Yxsjöberg´s deposit is being evaluated and there are no figures for its resources.
- Raw material procurement becomes more difficult, due to lack of investments in new mines and reduced secondary raw material availability.
- The majority of Tungsten primary raw material reserves are located in China or "politically instable"regions. China is the major producer of primary Tungsten.
- Lack of suitable recycling technologies.

Future demand on tungsten :

Future actions:

- Update Prospecting Guides.
- Recover Tailings.
- Recycling Tungsten scraps.

Innovative pathway:

1) To obtain more W from primary resources:
   1.1) New mines:
      - Exploration (H2020 projects for mining research on focus Critical Raw Materials, esif funds)
      - Other uses of the soil: coordination management, flexibility and calification.
      - Time to autorizathions.
      - SLO (sustainable mining certification). Spain is the only EU country – export.
   1.2) Tailings (≈35%) :
      - To convence the owner (business plan)
      - Pilot plant: replicability.
2) To improve mineral processing? Is it possible?
3) To improve metallurgy? Are there new methods?
4) To valorize co-products of W.

INNOVATION POTENTIALS FOR W VALORIZATION

When it comes to metals and materials that have a wide range of benefits and uses, it is hard to argue with the effectiveness of tungsten carbide. There is a great deal of benefits that come from using this reliable and very tough material and the number of different industries that rely on tungsten carbide indicates just how important it is. From its superior cutting skills making it of great value to mining and milling industries to the reliable yet stylish nature which makes tungsten carbide a natural choice for so many jewellers, there is no doubt that tungsten carbide is hugely important.

Like all metals, there is a business and demand for scrap tungsten carbide. The recycling of scrap metal is important for many reasons and whether you are looking to do your bit for the environment or you just want to be as cost effective as possible, there are strong arguments for taking the recycling of tungsten carbide very seriously.

One of the reasons why it is important to recycle tungsten carbide comes from the fact that it has been listed as a metal that is of great importance to the EU and the overall economy in Europe. It is believed that there are very few materials that can provide the quality and reliability of tungsten carbide, which makes it very difficult to find a notable substitute. There is also a lot of doubt over how much tungsten carbide supplies there are left in the world. This means that there is an increasing need to ensure that recycling of tungsten carbide scraps and reside take place. So, if there are large amounts of tungsten carbide scrap, it should be recycling them, as this will be of benefit to the overall economy.

There are several reasons for recycling tungsten scrap. First, most scrap materials are richer in tungsten than ore concentrations, making tungsten scrap a worthy material for recycling. Second, the demand for tungsten products is increasing; consequently, the demand for tungsten resources is rising. Companies can lower their raw material costs and make greater profits by recycling tungsten scrap. Third, recycling tungsten scrap has many environmental benefits, such as reducing land-filled waste, saving valuable and finite virgin raw materials and energy, as well as reducing pollution.

Methods for recycling tungsten can be broadly divided into two types: direct methods and indirect methods. Direct methods mean that tungsten scrap is transformed into powder of the same composition by either chemical or physical treatment, or a combination of both. A typical example of the direct methods is the zinc treatment method (*Clean cemented carbide inserts and compacts are converted to powder by the zinc process, i.e. molten zinc forms an alloy with the contained cobalt which disrupts the integrity of the cemented carbide. The zinc is then removed by distillation, leaving a spongy material which is easily crushed. This material is added to new, ready-to-press tungsten powder. This process not only allows tungsten carbide to be recycled but also carbides of cobalt, tantalum and other metals*). This method has many advantages, such as limited energy consumption and chemical waste, as well as low production costs. The disadvantages of this method are the restrictions on the recycled materials. The indirect methods, such as the wet chemical treatment method, are generally used in the ore refining process. This way of recycling has no restrictions on materials, but large quantities of chemicals and energy are needed.

The estimated increases in primary mine supply are predicted to be outpaced by the use of secondary recycled tungsten raw materials in the years to 2018. Tungsten recycling is expected to keep growing at about 8% per year over the next five years, increasing global production of recycled tungsten materials from 23% of total supply in 2012 to 28% of global supply in 2018. The main regions for growth in tungsten recycling are most likely to be Europe and Asia, as collection programs for tungsten products are improved and construction of new tungsten recycling facilities.

Lack of suitable recycling technologies.

Secondary resources include metals discarded in landfills, metals still in use, for example in long-lasting infrastructure systems, or metals in hibernating stocks. Although the relevance of these resources is increasing, so far only minor fractions of metals undergo high-quality recycling due to adverse economic conditions, insufficient infrastructure or technical limitations. Especially for the short to medium term, the quantity of material available for recycling may often meet only a modest proportion of future demand. The problem is the non-existence of an established economic technology for the recycling of end-of-life consumer products is considered as a criterion.

Tungsten is an outstanding element of technological metals. Their application is widespread and the substitution is only possible in few cases. While China has most tungsten in the world, notable deposits can also be found throughout Europe; however, the domestic industry is forced to process secondary raw materials in order to diminish dependencies on foreign raw material suppliers. The comprehensive analysis of material flow starts at the mining, followed by the processing of the ore and the reduction, goes beyond the further processing of diverse intermediate products up to the applications (end product). To find potential secondary resources for this metal it is very important to know their main as well as the minor application areas and accordingly the whole production cycles of the different products. The scrap, generated during the production (pre consumer scrap) represents an important secondary source of raw materials. Post-consumer scrap is also an attractive source but in many cases the lack of a recycling infrastructure hampers the use of it. Another complicacy is the dissipation of tungsten in the end products and so in the waste materials. In an economical view an extraction is not possible. If one metal is enriched in residuals of other recycling processes - e.g. indirect recycling of hard metal scrap - the recovering of tungsten could be an opportunity. Recycling in direction of this refractory metal is a balancing act between technological and economical feasibilities and sustainable use.

Of course, however, only at places where you want to feel it: concerning costs and environmental protection. That is where recycling refractory materials can be felt in an extremely positive way. Regarding the function of materials, there are no losses in view of quality. Hard metal tools made of recycled tungsten carbide, for example, work as precisely and steadily as before. This has been proven in motor construction as well as in other tungsten applications. After recycling is just like before recycling – without fail.

Three ways – on goal: Complete Recycling[1]

1. Thermal Treatment.

Metal powders, as well as scraps are melted by electro beam, followed by solidification of the material in a skillet. Then the ingots can be finished by forging, cutting and rolling. When metals and scrap pieces of single origin are provided, they will be also melted first. Finally, through chemical processing the material can be adapted into products.

2. Chemical Processing

Oxidised material, but also tungsten capacitor scraps are dissolved after corresponding preparation in acids or caustic solution, chemically cleaned of all impurities and further transformed to metal. It becomes then a "virgin" material, such as the metals we gain - through the same methods - directly out of ore or a concentrate.

3. Mechanical Separation

Whenever possible scraps are first mechanically reprocessed, that means recyclable material contained in secondary raw materials will be separated from unrequested components by milling and subsequent division using varying separation procedures. Often these recyclable materials can be directly integrated into the production process, which supports reduction of energy consumption and process materials, economically and environmentally efficient.

Others types of treatments[2]

4. Thermochemical Treatment – Technologies for Recovery

Dumping of hazardous waste on landfills or in abandoned mines is not sustainable from an ecological, economical and political viewpoint. The environmental impact of hazardous wastes and residues from industrial processes such as fly ashes, filter cakes, cast sands, metallurgical slags, grinding debris and so on must be kept as low as possible by applying advanced material separation technologies that can also facilitate extensive recycling, re-use and re-utilisation. The use of industrial waste products as secondary raw materials in metallurgical processes and the processes for the production building materials or other useful materials is being evaluated.

The arc furnace has reached broad application in the metallurgy and in the silicate industry, mainly as a heating and melting aggregate. Also, the arc furnace technology is applied for thermochemical materials separation. Thermochemical processes are well suited for the treatment of waste materials enabling a recovery of useful elements and products. Thermochemical treatment comprises a variety of processes over a wide temperature range: combustion and pyrolysis as well as partial oxidation, hydrogenation, hydrolysis, alcoholysis, special technologies and combinations of all these.

[1] H.C.Starck. High Tech Recycling for Refractory Metals. www.hcstarck.com

[2] Gerd Kley, Rudolf Brenneis, Burkart Adamczyk, Franz-Georg Simon. "Thermochemical Treatment-Technologies for Recovery and Utilisation of Materials". The Chinese Journal of Process Engineering. (2006)

Treatment of waste materials in an arc furnace displays a special technology. Usually applied for scrap smelting or the production of high temperature materials, the furnace enables a separation of materials by applying reducing conditions and high temperatures.

Substitutes

Because of the unique combination of properties of tungsten, there are limited options for substitution in many applications, especially where optimum performance is required at high temperatures. Unlike many other metals, there are no substitutes for tungsten that do not involve a considerable cost increase and compromise in product performance. In the aerospace and defence industries where product performance is paramount, substitution is generally avoided.

Potential substitutes for cemented tungsten carbides or hard metals include cemented carbides based on molybdenum carbide and titanium carbide, ceramics, ceramic- metallic composites (cermets), diamond tools, and tool steels. Potential substitutes for other applications are:

- molybdenum can replace tungsten in certain mill products;
- molybdenum steels can substitute for tungsten steels for some applications;
- lighting based on compact fluorescent lamps, low energy halogen light bulbs and light-emitting diodes (LEDs) are gradually replacing the traditional use of tungsten in light bulb filaments as inefficient incandescent light bulbs are being phased out;
- depleted uranium can be used in weights and counterweights instead of tungsten alloys or unalloyed tungsten, but generally it has been tungsten that has substituted for depleted uranium for health and environmental reasons;
- depleted uranium alloys can also be used in armourpiercing projectiles instead of cemented tungsten carbides or tungsten alloys.

Because of its perceived benign impacts on human and environmental health, tungsten alloys have been the preferred substitute for lead-based munitions since the mid-1990s. However, although the metal's toxicity is low compared with lead, there is some evidence that in certain forms tungsten may inhibit particular functions in some plant or animal species. Further research is required to evaluate the significance of these effects.

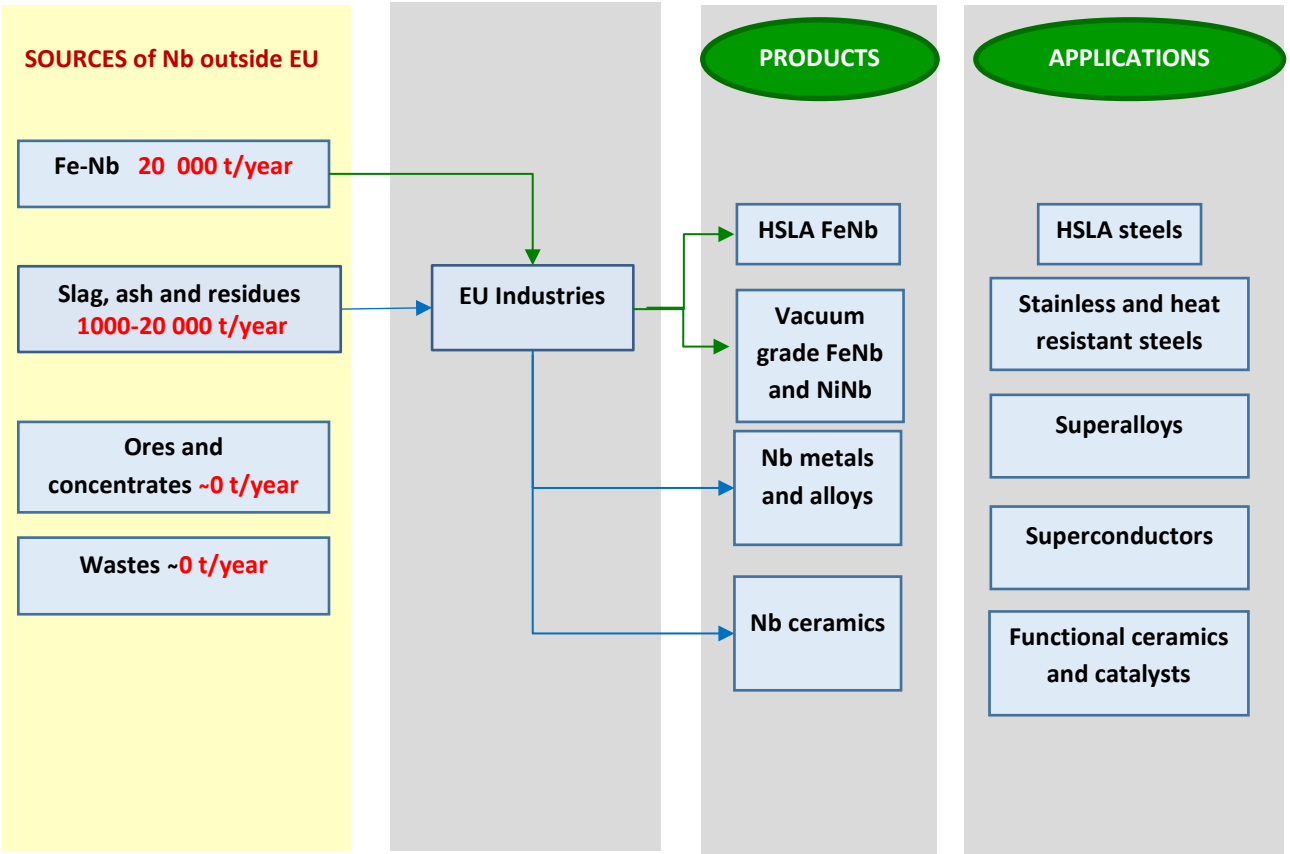
In some applications, substitution commonly results in a trade-off against the performance characteristics. For instance, silver/tungsten composites are widely used in protective switchgear but are plagued by the formation of a high resistivity surface layer caused by the propensity of tungsten to oxidise. Composites of silver with diborides (compounds containing two atoms of boron) of zirconium, hafnium and titanium are more oxidation-resistant than tungsten but have a higher erosion rate.

CHAPTER 3 NIOBIUM AND TANTALUM: RE-DESIGN OF THE VALUE CHAIN

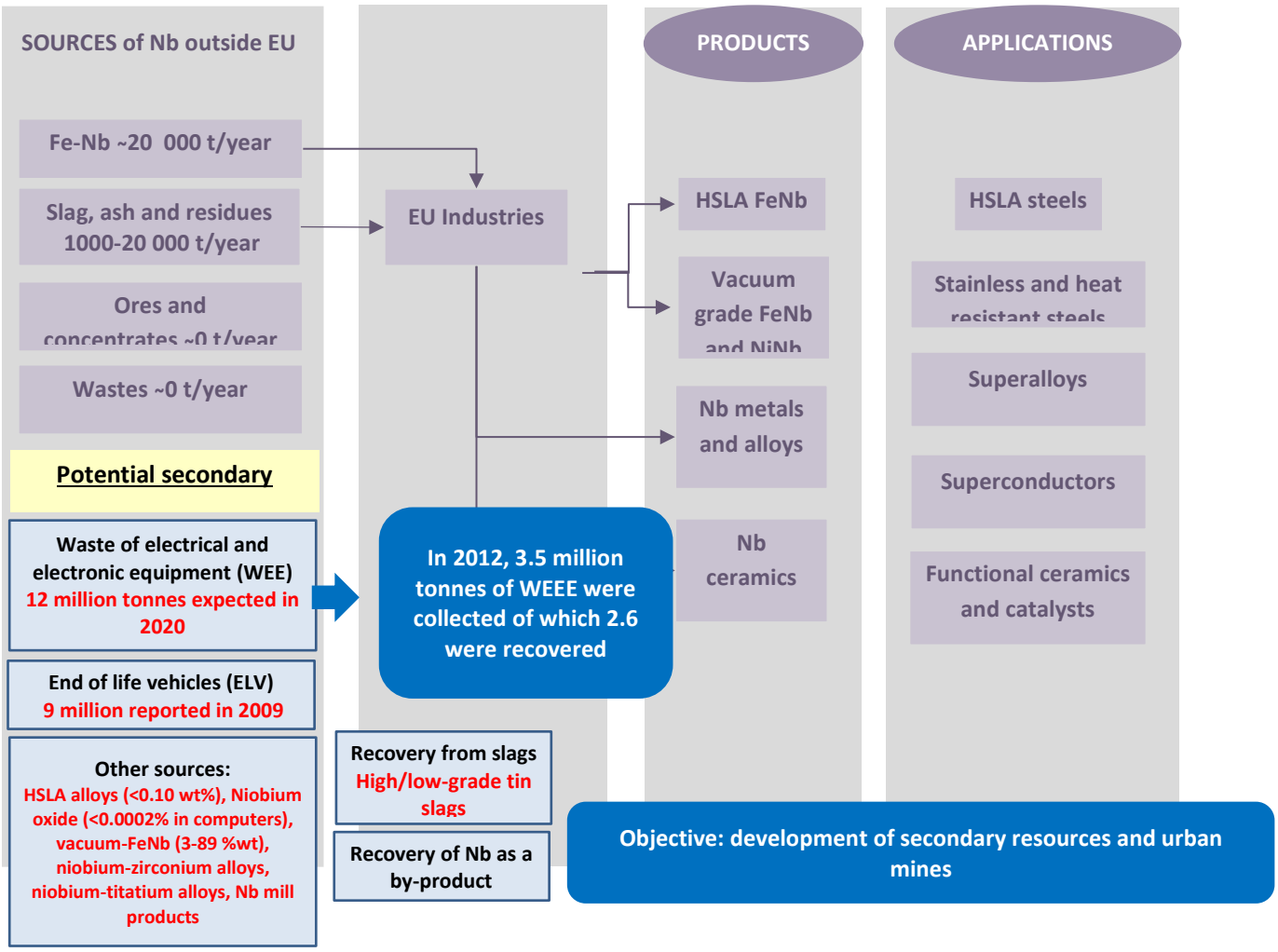
INPUTS AND CONCLUSION FROM OTHER DELIVERABLES AND TASK (SUMMARY TASK 1.2 AND TASK 1.3)

DEFINITION OF CURRENT VALUE CHAIN

The graphics below sumarize the current and future value chain for niobium.

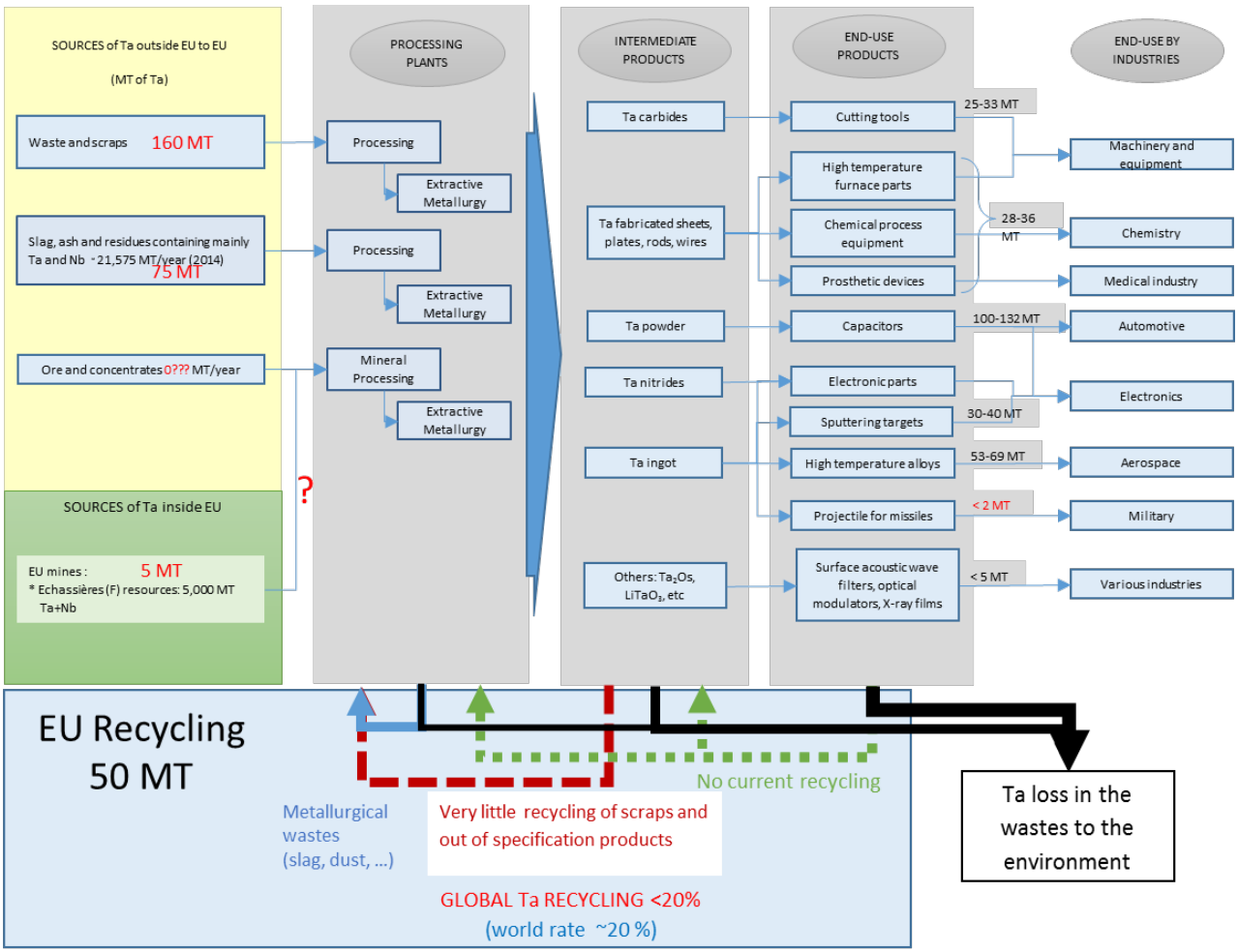


Current value chain for niobium



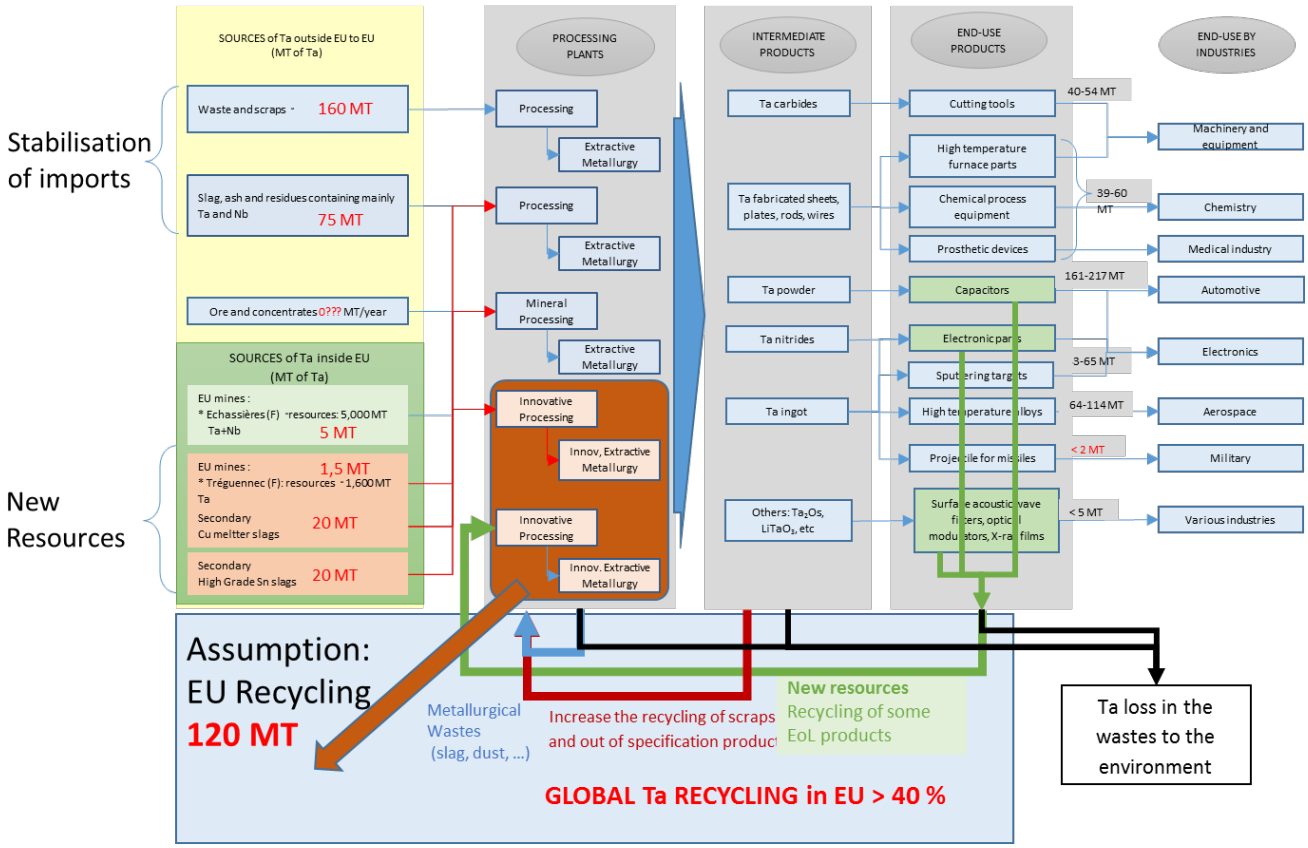
Future value chain for niobium

The graphics below sumarize the current and future value chain for tantalum.



Current value chain for tantalum

Future value chain of tantalum (based on 400 MT/year)



SUMMARY/CONCLUSIONS

Tantalum

Globally, it has been estimated that 10-20 % of the global Tantalum supply is produced from tin slags and 20-30% from different types of manufacturing and End-of-Life scrap. According to the Tantalum-Niobium International Study Center (TIC), the production from secondary resources has grown considerably between 2008 and 2012. The best quality slags have been found in Brazil, Thailand and Malaysia, which are most important producers of slag based Ta. Due to reduction of tin mining, the most interesting sources are old slag dumps.

The potential of old tin slags and other waste areas has also been studied in Europe. Based on the available information, potential tailings and slags can be found in Spain, Portugal, France, and UK (Tin belt reaching through these countries), but also in Germany and Czech Republic. Tantalum can also be found in waste from uranium mining, which usually contains radioactive thorium. Very little public data could be found available about the characteristics and Ta potential of the European mine waste areas.

In addition to mine waste areas, Ta can be found also from municipal waste landfills, industrial landfills (such as landfills of WEEE recycling companies) and from incineration slags. It has been estimated that about 5 % of WEEE ends up to municipal landfills or incineration plants. Because Ta containing components are mainly used in high-tech electronics, such as portable electronics, it is likely, that the Ta concentrations in MSW landfills and slags are very low.

Other potential sources are scrap from manufacturing of Ta powders and ingots as well as manufacturing of Ta containing products as well as end-of-life scrap containing Ta. The most important applications of Ta are capacitors and other electronic components, different Ta containing alloys and hard metal, where small percentage of Ta can be used in addition of W. Although for example the largest capacitor manufacturers are situated in USA and Asia, based on Eurostat Prodcom statistics there is still considerable manufacture of Ta containing products in Europe. These means that both manufacturing and end-of-life is available in Europe.

The Niobium world production in 2010 was 62,900 t in 2010 92% from Brazil Niobium does not occurred as free metal and commonly is grouped with Tantalum. The columbite-tantalite mineral group is the most common group of tantalum and niobium bearing minerals. The pyrochlore group is of great economic importance, particularly for niobium. This group has a wide compositional range, including some species rich in both niobium and tantalum. Pyrochlore is typically found as a primary mineral in alkaline igneous rock. There are some secondary deposits with niobium and tantalum bearing minerals, relatively close association with their primary sources. Major examples of secondary resources are in Brazil, Russia and Democatric Republic of Congo.

Niobium

The highest potential for Niobium recovery in Europe is addressed to Greek and Macedonian sites. Buchim Mine's potential (Macedonia) is related to the active plant for extraction of the minerals: Chalcocite, Chalcopyrite, Covellite, Cuprite, Galena, Hematite, Goethite (limonite), Magnetite, Pyrite, Sphalerite, Tenorite, Native metal. This high potential (up to 313 270 t) is linked to the mine waste dump (surface storage).

Greek potential is much lower but still reaches a national average sum of 65 440 tonnes of Nb that may eventually be recovered. This tonnage is distributed along 7 different locations in northern Greece. These wastes are associated to former smelter or refinery plants with smelting slag waste containing Nb.

INNOVATION POTENTIALS FOR Ta AND Nb VALORIZATION

Worldwide the Ta recycling rate is estimated aroud 20 %, but there is no figure available for the EU. The average value for the EU is probably lower, despite the German company H.C. STRACK has large-scale capabilities to produce synthetic concentrates "SynCon", which are reprocessed secondary materials containing Ta.

Some examples are quoted herafter to illustrate the opportunies that could be explored within the EU.

RECOVERY FROM SLAGS

- High-grade tin slags (>10% Nb+Ta)

  They are an interesting secondary Ta and Nb resource that should deserve the industry's interest. There are usually lly processed directly by hydrometallurgy (using HF) or carbochlorination at 500°C to allow complete extraction and recovery of pure Ta and Nb compounds (Gaballah 1997). Hydromettalurgy seems to be simplier and could be favoured because of many impurities to deal with; it could be developed in Europe with no further R&D efforts, excepting the use of HF which could be susbstituted by alkaline leaching to reduce chemical risks.

  At the opposite, low-grade tin slags (<10% Nb+Ta), which are generally upgraded by a pyrometallurgical process leading to ferroalloy, show no economic reason to be recycled.

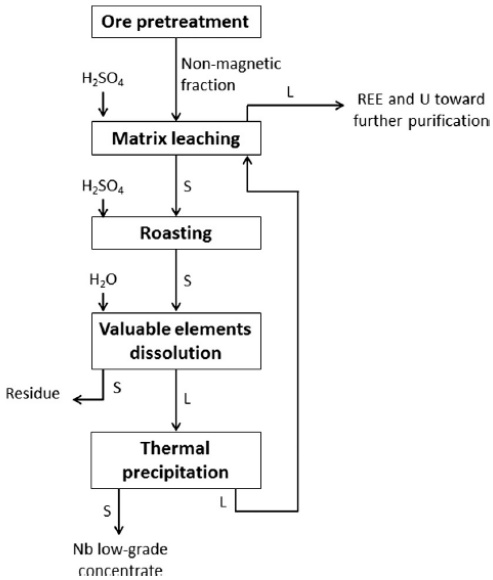
- Copper smelting slags

  They could be processed using froth flotation with alkyl hydroxamates as collectors (selective chelation to Ta or Nb-containing minerals) [Roy 2015]. If this new way can give a sufficient yield, they coul be treated by UMICORE, which is a coppermetallurgist.

  If so, a limited R&D scale-up programme could be proposed, including recovery of the different valuable metals in the EU.

RECOVERY OF NB AS A BY-PRODUCT

The example of the Mabounie ore (Gabon) has been suggested as an example. This polymetallic resource, beside U and REE, allows the production of a low-grade Nb concentrate (Nb= 10-15 %, Ta=0.25 %, Fe=6-10 %, Ti=8-12 %). A fluoride-free process using caustic conversion has been developed by ERAMET (Deblonde, 2016), leading to water-soluble sodium hexaniobate and hexatantalate, which are precipitated at pH 4 purified hydrated niobium or tantalum oxide. Global Nb and Ta recovery yields of 65% have been obtained during continuous pilot tests.



There are probably other secondary mining resources to be valorised using simpler separation processes, therefore being profitable at limited throughputs.

RECOVERY FROM TUNGSTEN CARBIDE SLUDGE

This is an important secondary resource for recycling Nb and Ta (average composition: [Nb] = 5.6 % [Ta] = 7.2 %) but no innovative processes have been found. There could be an economic opportunity to recycle several elements at the same time (W, Ta, Nb) but a suitablehas to be set up, in coordination with WC recycling actors.

INNOVATIVE SOLVENT EXTRACTION PROCESSES

Innovative improvements can be expected in the following items:

- Less or no HF used for digestion and SX metal separations, by using impregnation and maturing by $H_2SO_4$for leaching, like for some refractory ores;
- More robust extractants with higher stability and lower water solubility (the best results are obtained with phosphinic acid or D2EHPA as extractants)
- Increased recycling of reagents to reduce liquid and solid waste.

INNOVATIVE PYROMETALLURGICAL PROCESSES

Most of the pyrometallurgy of Ta and Nb goes through their fluorides or chorides, which complicates the whole process to obtain the metals. An improvement is clearly foreseeable if the transformation from the oxide to the metal could be done in one step.

Direct Electrolytic Reduction of Solid Ta_2O_5 to Tawith solid-oxide-oxygen-ion conducting membrane (SOM) Process [Chen 2016], which uses electrolysis in molten $CaCl_2$ or MgF_2-CaF_2 at higher potential than FCC Cambridge process, seems very promising.

Thetantalum powder preparation from Ta_2O_5 by calciothermic reduction [Ha 2012] at a molar ratio Ca/Ta_2O_5 > 10 (2*stoichiometry) and 900 °C leads to Ta with 1 % O_2.

References:

I. Gaballah, E. Allain, and M. Djona, Extraction of Tantalum and Niobium from Tin Slags by Chlorination and Carbochlorination, Metallurgical and Materials Transaction B, volume 28B, June 1997—359-369.

J.U Odo et al., Extraction of Niobium from Tin Slag, International Journal of Scientific and Research Publications, Volume 4, Issue 11, 2014

S. Roy, A. Datta et S. Rehani, Flotation of copper sulphide from copper smelter slag using multiple collectors and their mixtures, International journal of mineral processing, vol. 143, pp. 43-49, 2015

G.J.P. Deblonde et al., Selective recovery of niobium and tantalum from low-grade concentrates using a simple and fluoride-free process, Separation and PurificationTechnology 162 (2016) 180–187

C.Chen et al., Direct electrolytic reduction of solidTa_2O_5 to Ta with SOM Process, Metallurgical and Materials Transactions B 47(3), March 2016

J.W. Ha et al., Tantalum powder preparation from Ta_2O_5 by calciothermic reduction, Journal of the Korean Institute of Metals and Materials 50(11):823-828, November 2012

CHAPTER 4 MOLYBDENUM: RE-DESIGN OF THE VALUE CHAIN

INPUTS AND CONCLUSION FROM OTHER DELIVERABLES AND TASK (SUMMARY TASK 1.2 AND TASK 1.3)

DEFINITION OF CURRENT VALUE CHAIN

The current value chain starts from primary mine, which consists of mainly Mo ore and Cu-Mo ore. In EU the production of Mo ores is very limited. Due to the sharp gap between local supply and consumption, Mo are imported, mainly in the form of primary ore, molybdenum oxides and metals. The obtained primary Mo ore are metallurgically processed by roasting, reduction, etc. to produce various intermediate products. The produced intermediate products are further metallurgically processed/manufactured to produce various end-user products (mainly Mo-containing steels and catalysts). These products after ending their lives are regarded as urban mines of molybdenum. During mining and mineral processing, waste rock and tailings are generated; during metallurgical process, dust (such as steelmaking dust), slag (such as Mo-containing copper slag), etc. are generated as industrial residuals; during processing and manufacturing dust, mill scale, etc. are generatedas industrial residuals. These generated waste rock, tailings and industrial residuals are regarded as secondary mine of molybdenum. The secondary mine is believed to be partially recycled and the leftover being deposited as potential mines (such as historically dumped Mo-containing slag) for the future or lost in the environment for ever. The molybdenum from urban mines is partially recycled and the leftover is either lost to the environment due to wearing, corrosion, discard, etc., or down-graded into other steels without using its Mo content. The flow of molybdenum from primary mine to secondary mine, urban mine and the environment is well described by **Figure 1.**

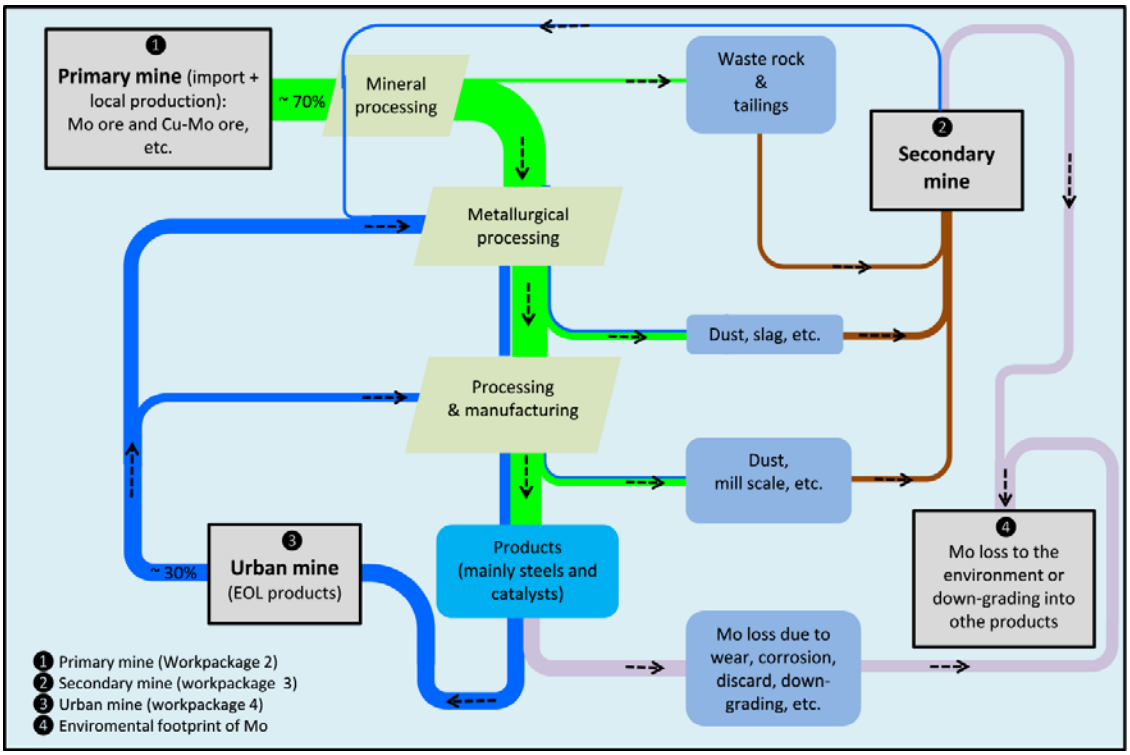


Figure 1 Flow of Mo amongprimary mine, secondary mine, urban mine and the environment.

SUMMARY/CONCLUSIONS

According to reported deliverables on Mo as well as the information shown in Figure 1, the key facts can be summaried as the following:

1) Production of Mo is mainly dependent on the primary Mo ore, which is largely imported from non-EU countries;
2) Oxidative roasting of primary Mo ore is an important technical step for producing technical grade MoO_3, which is an important intermediate product;
3) Molybdenum is largely used to produce steels and catalysts ;
4) Due to 3) mill scale and dust are regarded as an important secondary mine of molybdenum ;
5) Due to 3) steel scrap and spen tcatalysts are regarded as important urban mine of molybdenum.

INNOVATION POTENTIALS FOR Mo VALORIZATION

Barriers (technological and non-technological)

1) Roasting of molybdenum ore

Oxidative roasting of molybdenum ore is an industrialized process for processing molybdenum ore. The limitation of this process lies in the emmision of sulfurous gas and dust to the environment. Due to the strict environmental regulations, the roasting process is facing a challenge. There are innovative processes develpped in this aspect; however, the processes have not been industrially proved to be economic and/or efficient.

2) Mo loss from the secondary mine

As shown in **Figure 1**, molybdenum from the secondary mine can be partially recovered, however, quite a large portion islost or locked in the environment. The lost of Mo in EU are believed to bemainly in the form of Mo-containing copper slag, millscale and dust. According to the review of innovative technologies presented in D3.3, thereis no technical barriers to recover Mo from these materials. However, due to low economic incentive and immaturity of these technologies are not seen to be industrially implemented in the near future.

3) Mo lossfromurban mine

Mo is largely used to produce a bigvariety of steelproducts. During the application, Mo islost to the environment due to corrosion, wearing and discard. At the moment, there is no effective way to reduce this kind of Mo loss. Another kind of Mo loss is believed to be the down-grading of Mo to other steels without considering its Mo content. The main barriers for recover Mo in this aspect lies in the lack of efficient sorting and collection infrastructure.

In summary, thereis no technological barriers to recover Mo from various types of materials; however, some innovativete chonologies are difficult to be industrialized due to low economic incentives. New technological breakt hrough may make a change for the future.

- Market

Figure 2 shows the prices of molybdenum oxide since 2000 from the global market. It is seen that the prices of molybdenum oxide decreased sharply from mid of 2008 and stay in a lower level until now. The low prices of Mo result in the recycling of Mo from secondary mine and urban mine being less competitive.

Figure 2. Molybdenum oxide prices between 2000-2016 [1]

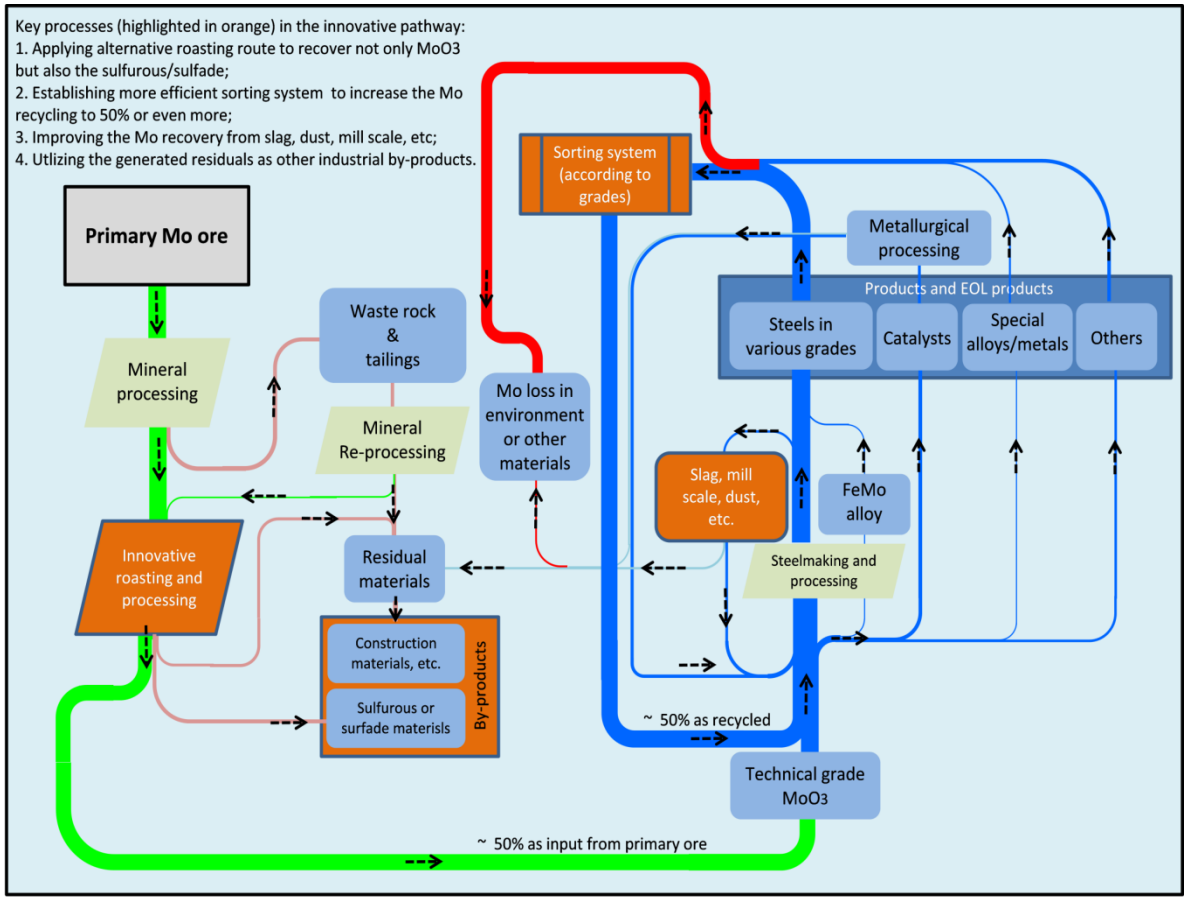
- Supplychain

As shown in D1.2 the recycled molybdenum amounts to 1/4 to 1/3 of the total molybdenum need, the others are mainly imported from non-EU countries in the form of molybdenum ore, oxide and metal.

- Critical transition steps to re-design the current value chain

According to the reported deliverables on Mo, the critical transions teps to re-design the current value chain include the following aspects:

1) Zero harzadous emission: development of more environment-friendly process to replace the present oxidative roasting process. This may change the present Mo industrial layout in EU and increase its competitiveness.
2) More recovery: establishing more efficient sorting and collection infrastructure for EOL products. This will reduce the dependence of EU on Mo supply from non-EU countries.
3) Higher integration of the processes. This will increase the competitiveness the Mo industry in EU.
4) No wastes: Increasing the added value of the generated wastes by using them as by-products. This will increase the competitiveness and sustainability of the Mo industry in EU.



References:

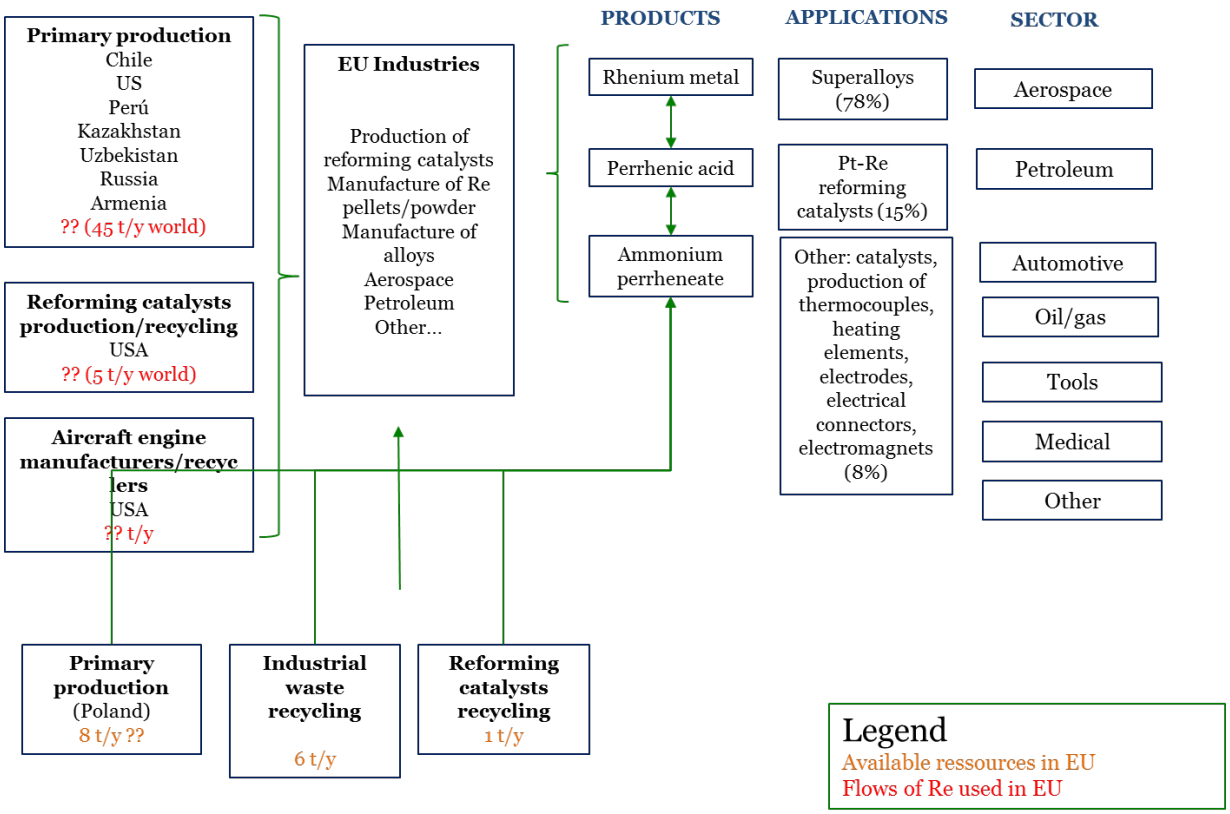
[1] "Historical molybdenum oxide prices." [Online]. Available: http://www.infomine.com/investment/metal-prices/molybdenum-oxide/all/.

CHAPTER 5 RHENIUM: RE-DESIGN OF THE VALUE CHAIN

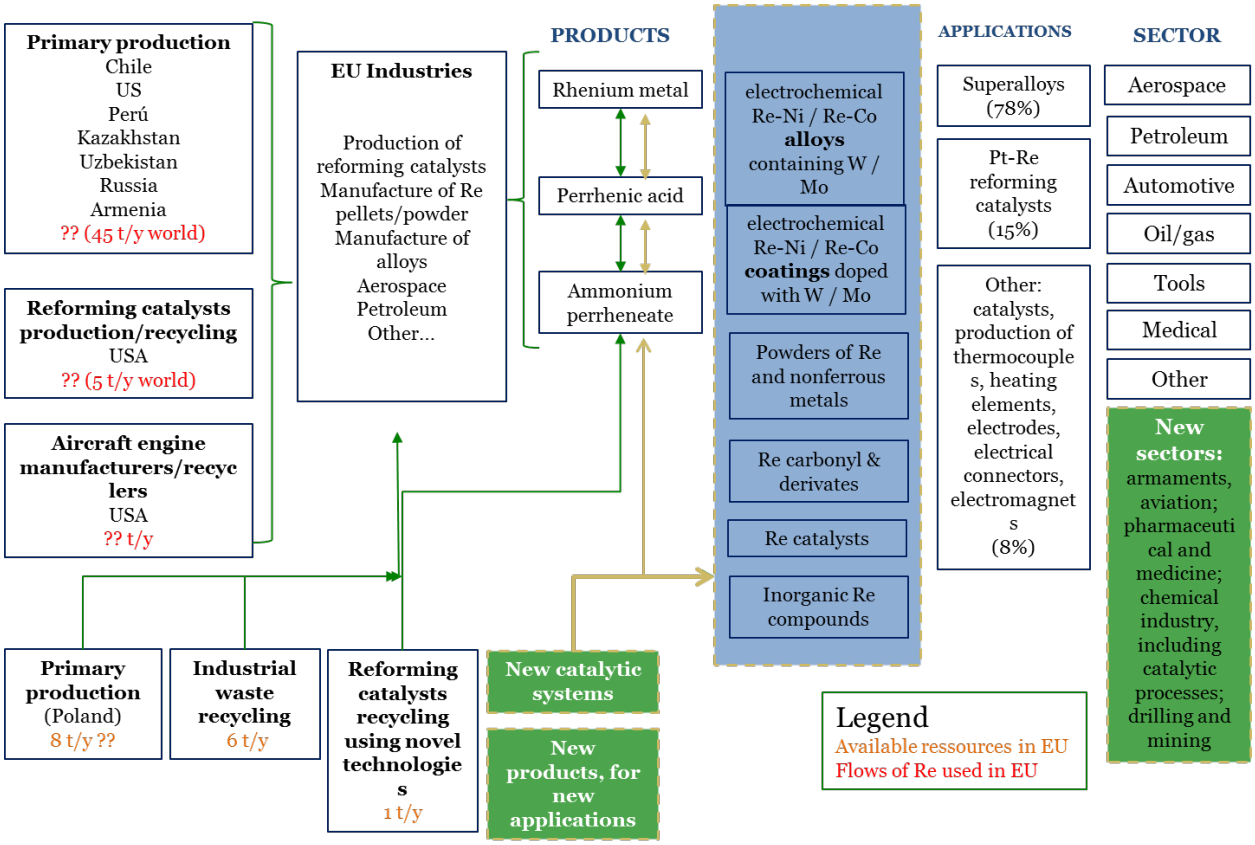
INPUTS AND CONCLUSION FROM OTHER DELIVERABLES AND TASK (SUMMARY TASK 1.2 AND TASK 1.3)

DEFINITION OF CURRENT VALUE CHAIN

The graphics below explain the current and future value chain for rhenium:



Rhenium current value chain

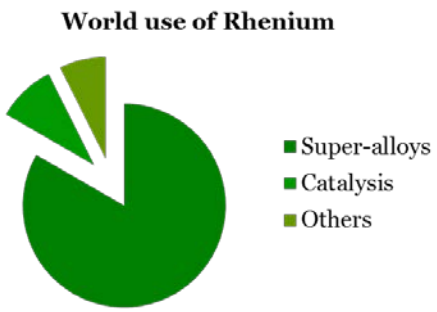


Rhenium future value chain

INNOVATION POTENTIALS FOR Re VALORIZATION

INNOVATION PATHS ON PROMOTION OF RE PRODUCTIONFROM PRIMARY ORES (GTK)

About 8 t of Re is produced annually from primary resources in Poland whichis the only country producing Re as by-product of the copper production process. Rhenium existing in domestic copper concentrates is processed in three smelters. Re contents in the ores are 1.22 to 1.68 g/t; and 8.26 to 12.5 g/t in the concentrates from three mines [1]. Promoting primary Re production by the increase of the recovery of Re in mining and enrichment and insmelting and refining, meanwhile, reprocessing Re-containing secondary wastes (tailings, residues) could be significant innovation paths.



INNOVATION PATHS ON PROMOTION OF RE PRODUCTION FROM RECYCLING (GTK)

Metal recycling has the environmental benefits comparing to recovery from primary resources. Recycling activities require capital and natural resources, but avoid the energy-intensive mining, concentrating, smelting, and refining activities required for primary materials. For this reason, metals can often be recycled or reprocessed for additional uses at environmental and economic costs that are much lower than those for primary metal. Estimates of energy savings are ranging from 55-98% depending on the metal. Similar reductions in water use, air and water emissions, and waste generation also accompany recycling compared to producing virgin materials [2].

Some 55-60 tons of Re are produced in the world of which the vast majority used in super-alloys, the remaining used in catalysts, medical anodes and filaments etc. For instance, In 2012, in the 54 t of Re production,45 t (83.3%) were used in super-alloys for the aerospace and industrial gas turbine industry; 5 t (9.3%) were used in catalysts; and 4 t (7.4%) used in others. The key to increase the recycling rate of Re is promoting the recycling of Re from super-alloys [1].

Because Re occurs in small quantities in the super-alloys the energy use, greenhouse gas (GHG) emissionsand economic cost associated with collecting, sorting, cleaning, and otherwise processing of the alloy scraps would be higher than most of other metals[3].

The following aspects would be important for implementation of a successful end-of-life Recyclingsystem of Re:

- Establishing database of Re containing product inventories, sales, product info of components, expected wastes (such as in the next 20 years, 40,000 aircraft will come out of service according to a study [3])
- Promoting sorting logistics and collection efficiency of Re containing end-of-life products, and establishing a stable supply source
- Promoting pre-processing efficiency by using innovative and scale-up technologies
- Innovating processing technologies by taking account of economic cost and environmental impact
- Scale-up market access and havelarge companies, suppliers and specialized groups engaging in Re recycling
- Encouraging manufacturers to improve design of products taking account of easy disassembly, reuse and recycling

References

[1] MSP-REFRAM Reports: D2.2, D3.2, D4.2 May 2016; D2.3, D4.2. Aug 2016.

[2] R.L.Moss et al., JRC Sceintific and Policy Reports, Critical metals in the Path towards the Decarbonisation of the EU Energy Srctor. 2013. https://setis.ec.europa.eu/sites/default/files/reports/JRC-report-Critical-Metals-Energy-Sector.pdf

[3] Eckelman, M.J. et al., Life Cycle Carbon Benefits of Aerospace Alloy Recycling. http://www.sciencedirect.com/science/article/pii/S0959652614005071

INNOVATION PATHS ON PROMOTING NEW APPLICATIONS OF Re (IMN)

Rhenium has a great innovative potential due to its application in numerous new products and materials. The following examples confirm that rhenium can present very high potential to be a metal applied in innovative solutions.

Firstly, depletion of natural resources and high metals demand force intensification of recyclable materials research and investigation on new, efficient, innovative, ecological technologies [1-6]. Therefore, it is important to address technological issues, which are important and innovative for world rhenium market, such as increase of the amount of rhenium-containing wastes coming from processing by large volume materials e.g. dross formed during superalloy smelting, scraped superalloy products and other wastes formed during superalloy products manufacturing [1-6]. Currently, rhenium is not recovered from such components. Moreover, there are not many companies in the world which are dealing with recycling of that metal. Nowadays, rhenium is recovered mainly from wastes formed during processing of superalloys of diameter ≤30 mm. Development of rhenium recovery method for materials of diameter >30 mm, which are not currently processed, will allow to increase ammonium perrhenate world production – it can present a breakthrough process innovation and will result in intensification of the small, hermetic and tough rhenium market [7-9].

Secondly, due to significantly decreasing rhenium prices, development of new, ecological and innovative technologies for conversion of commercially prepared rhenium compounds (mainly ammonium perrhenate) to more technologically advanced and processed functional compounds, materials or components seems to be future-oriented solution [9-11]. Within this part it is proposed to manufacture numerous compounds, materials and composites for application in developing economic sectors using rhenium products, like:

- armaments industry;
- aviation;
- pharmaceutical industry and medicine;
- chemical industry, including in particular catalytic processes;

as well as in economic sectors, where rhenium has never been applied:

- drilling industry;
- mining industry [2-5].

Innovative rhenium products include:

- electrochemical rhenium-nickel and rhenium-cobalt alloys containing tungsten and/or molybdenum;

- electrochemical rhenium-nickel and rhenium-cobalt coatings doped with tungsten and/or molybdenum;
- powders of rhenium and nonferrous metals;
- rhenium carbonyl and its derivatives – basic substrate for manufacturing of homogenous catalysts with rhenium as an active centre;
- homogenous and heterogenous rhenium catalyst;
- inorganic rhenium compounds with application properties to be used in many industrial branches [1-2. 11-13].

An important innovation in rhenium life-cycle should address utilisation of new, rhenium superalloyscontaing materials which are not currently processed due to the lack of appropriate technologies for production of ammonium perrrhenate and other rhenium compounds. Nowadays, recycling of rhenium from waste materials covers mainly spent catalysts, scrap from metallic rhenium production and wastes formed during mechanical processing of superalloy products. Only rhenium contained in catalysts is systematically recovered, but rhenium from this source is fully utilised for preparation of new catalysts and data covering production volume and recovery methods are not published. Relatively small rhenium amounts (3÷6 tonnes per annum) are recovered from shredded wastes or from the waste which may be easily comminuted using two basic methods. First one comprises material digestion in acid solutions. Second method covers oxidative roasting of material in order to separate volatile rhenium (VII) oxide, which is then absorbed in ammonia solutions. Defective and spent superalloys products are not process but only stored. Lack of effective reprocessing method is the main obstacle in their proper management. Additionally, their smelting and manufacturing of new elements is often limited by strict regulations that are applied e.g. in aviation industry - the main recipient of superalloys. That new rhenium source may be exploited thanks to a technological-technical innovation based on development of innovative electrodigestion technology using symmetric alternating current with a very small frequency. It presents a technological innovation, due to electrodigestion by alternating current, as well as technical one, because dedicated electrolyser and AC adapter are necessary. Development of new methods for production of catalytic systems which contain metal nanopreparations (including rhenium) using novel nanotechnologies (nanotransfer) can represent an example of a product innovation in rhenium applications area. New catalytic systems, which contain rhenium and/or its compounds, manufactured using nanotechnology are characterised by high repeatability of physical parameters and unique catalytic properties. Further innovation in rhenium application area can also be seen in industrial scale manufacture of rhenium carbonyl. The novelty of the method should result from new resources applied in the production. Another innovation may result from application of new polymetallic coatings used e.g. on drilling heads. The coatings novelty will be brought by combination of at least two refractory metals, like rhenium, molybdenum and tungsten, in one layer. These metals will be bound by one of VIIIB group elements i.e. nickel or cobalt. Such coatings are not manufactured nor used applied so far. Additional innovation in rhenium application area may also result from new drilling methods, which can be developed using new, more durable drilling heads. The new heads application may reduce drilling costs thanks to extension of the single head lifetime. Potential application of new rhenium compounds, powders and alloys in aviation and arms industry

can result in important innovation as it may significantly reduce production costs of superalloys and alloys used in these sectors.

References:

[1] http://europejskiportal.eu

[2] Roskill: The Economics of Rhenium, seventh ed., Roskill Information Service, London, 2006: 1-220.

[3] Colton R.: The Chemistry of Rhenium and Technetium, Wiley, London/New York/Sydney, 1965: 1–25.

[4] Gmelin: Rhenium and silver 70, 1967:152–154.

[5] http://minerals.usgs.gov/minerals/pubs/commodity/rhenium/ (21.03.2016)

[6] Snakowski T., Golas K., Lewicka E.: Mineral Yearbook of Poland, 2014.

[7] Benke G., Leszczyńska-Sejda K., Chmielarz A., Dubrawski: Recyklingkomponentówzłomównadstopówzawierającychren, Seminarium IMN, Zaawansowanemateriałyitechnologieichwytwarzania, 2015, Wisła- materiałykonferencyjne: 23-28.

[8] Benke G., Leszczyńska-Sejda K., Chmielarz A., Anyszkiewicz K.: Odzyskrenu z niezagospodarowanychpółproduktówiodpadów, Monografia: Nowetechnologieoraznowekonstrukcjemaszyniurządzeń do wzbogacaniaimetalurgicznegoprzerobusurowcówmineralnych POIG 01.03.01-24-019/08, pod red. A. Chmielarza, Gliwice, Instytut Metali Nieżelaznych, 2013: 154-162.

[9] Chmielarz A., Benke G., Leszczyńska-Sejda K., Anyszkiewicz K., Litwinionek K.: Recovery and production of rhenium in copper metallurgy, Conference Materials GDMB Copper 2010, Hamburg, Germany, Section 5 Hydrometallurgy, 2010: 1803–1814.

[10] Chmielarz A, Benke G., Śmieszek Z., Anyszkiewicz K., Leszczyńska-Sejda K.: Recovery and production of rhenium in copper metallurgy, Conference Materials GDMB Copper 2003, Chile, Section Hydrometallurgy 5, 2003: 667–676.

[11] Taylor P.R., Anderson C., Anderson C.: Extractive Metallurgy of Rhenium: A Review Minerals and Metallurgical Processing, 30, 1, 2013: 59-73.

[12] Millensifer, T.A.: Rhenium and rhenium compounds, Kirk Othmer Encyclopedia of Chemical Technology, John Wiley and Sons, 2010: 1-21.

[13] Churchward P.E., Rosenbaum J.B.: Sources and recovery methods for rhenium, United States Bureau of Mines, Report of Investigations, 1963: 6246 -6248.

CHAPTER 6 RELEVANT INFORMATION FROM WS1 AND WS2

RELEVANT INFORMATION FOR D1.4 FROM WS1 AND WS2

INTRODUCTION

Deliverable 1.4 aims to report the potential innovation pathways to balance demand and supply of refractory metals in the EU, in order to design of future industrial value chains for refractory metals. To that aim, information from workshops 1 and 2 has been reviewed in order to complete the deliverable with expert's opinion and additional information that may be relevant for this topic.

WS1 information was compiled from WS1 presentations and WS2 information comes from WS2 work package summaries. The information is presented per each work package.

WP1

There is a lack of reliable figures on EU value chains of refractory metals, and therefore the estimation of future consumption may be quite poor for the EU. More data is needed to be generated in EU for giving a consistent value chain.

WP2 – PRIMARY RESOURCES

There are some elements being produced entirely out of European Union. Niobium comes primarily from Brazil and a little part from Canada. Tantalum comes mainly from Rwanda, Congo and Brazil; and Molybdenum comes mainly from China, USA and Chile. European Union does not produce Niobium, Molybdenum and Tantalum, so it is important to search for new pathways to extract refractory metals from the available resources, which currently are secondary resources and urban mines. Really, there are deposits of Niobium and Tantalum of this metals in EU that are being investigated in Spain, Greenland and Finland, which if developed, could supply a part of the EU demand of these metals.

Tungsten and Rhenium are produced in European Union. Rhenium is only produced in Poland, which accounted for 17.02% of total Rhenium production in 2014. Tungsten is produced in Austria, Portugal and Spain (3.01% of total production in 2014).

An example of technological innovations in case of Tungsten, which is mined in EU, are presented:

1) New direct alloying steel with Tungsten by tungsten ore in pyro-metallurgy and improved acidic leaching and biosorption process in hydrometallurgy for Tungsten extraction, saving energy and decreasing process cost and chemical consumption.
2) Combined gravity-magnetic-flotation process for complex Tungsten ores processing, and novel molybdenum leaching methods of alkaline pressure leaching (oxidant additives leaching and bioleaching), thus increasing process efficiency, metal recovery and product quality.

3) There is a challenge to increase the leaching yield and/or to reduce the tungsten content in residues or tailings.

In general, the need of data is present in Tungsten innovative techniques, and much information is in Chinese and therefore difficult to translate.

WP3 – SECONDARY RESOURCES

It is found that secondary resources of tungsten, tantalum, niobium, rhenium and molybdenum are existent in Europe, sometimes some of these elements co-exist. In most cases, there are existing hydro-metallurgical and pyro-metallurgical methods which can be used but these methods need to be optimised and combined in a feasible way.

Niobium and Tantalum usually appear together and may be extracted from tin slags and copper smelting slags. Tin smelter waste usually contain 8 to 10 % Tantalum oxide, and when lower grade, an electrothermic reduction may allow up to 50 % Tantalum and Niobium. This represent a good pathway of Tantalum and Niobium recovery for EU industrial players smelting tin. Potential tailings and slags can be found in Spain, Portugal, France, Greece, Sweden, UK, Germany and Czech Republic. A potential source of Tantalum is also from capacitors manufacturing. There is considerable manufacture of Tantalum containing products in Europe.

Molybdenum can be found in Copper mines tailings, like Boliden Aitik or Garpenberg mine in Sweden or Legnica-Glogow copper basin in Poland. The main focus is on development of enrichment technologies (such as centrifugal separation and high gradient magnetic separation). Molybdenum can be extracted from mill scale from the hot metal working process of molybdenum-containing steels, and dusts from steelmaking process. In Europe there are several steelmakers, so there is a big opportunity here. However, Molybdenum price at the moment is low, so the main driver for its recovery may be environmental benefits, maybe incentivised by governments. There is no technical hinder for the recovery of molybdenum from secondary materials.

Tungsten is recovered from waste rock and tailings in mining sites. There are three mines in Europe: Austria, Portugal, Spain, where it can be recovered. For example, Panasqueira mining (Portugal) is currently generating almost 100 tonnes of waste-rock tailings per day, which tungsten content is about 2.4 mg/kg. Secondary resources of tungsten include waste rock/tailings, mill scale, grinding dusts/sludge, etc. Due to the high price of tungsten, some of the industrial residuals are recycled in-house directly by the processors. Economic studies of innovative processes should be developed to study the feasibility. Tungsten recycling is not restricted by technological availability. Main barrier is the lack of infrastructure and affordable collection route for the residuals that are not recycled.

Rhenium is recovered from Molybdenum and Copper sulphide concentrates (80%), so the same Copper mines for Molybdenum extraction are valid for Rhenium extraction. In Europe, the biggest quantity of Cu-Mo concentrates is found in Greece. The future development of the potential technology will be dependent on the availability of the secondary materials for EU production.

In general, more economic data are also needed, in order to incentive the recovery of refractory metals from secondary resources, and to study the availability of the recovery. Political decisions on allowance for intermediate storage or landfill as well as taxes may force this recovery. After recovery of refractory and other metals, the major bulk of residue could be used as construction materials, energy source, slag former, etc., thus enforcing the circular economy.

A general problem is that secondary resources are dispersed over many different locations, refractory metals often diluted and large volumes have to be treated for recovering a moderate amount of the metal. In addition, there is a lack of collection infrastructure.

WP4 - RECYCLING

Refractory metals can be recycled from:

- Tantalum: ELV, WEEE, metal scrap, hospital waste, crematories, hard metal tool waste, industrial metal screap. From 75 to 150 tonnes of Tantalum could be available. A capacitor contains 40-50% Tantalum.
- Niobium: Steel scrap, stainless steel scrap, superalloy scrap, WEEE (a computer can contain 0.0002% of Niobium), ELV. Information and technology gaps.
- Molybdenum: steel material (it is 100% recyclable), spent Ni-Mo catalyst, ELV.
- Rhenium: superalloys, catalysts. It is already being done in Germany (Starck company)
- Tungsten: spent Ni-W catalyst, WEEE,

The main problems related to refractory metal recycling can be summarised as follows: the design of products in which metals take part is more and more complex and therefore is very difficult to separate the material and there is not recycling technology to that aim. Moreover, as for secondary resources, the recycling material is dispersed. Finally, there is a lack of social and economic awareness of the loss of resources due to the low value of products by unit. Potential solutions is to enhance the technology available, for example by international recycling conferences. Moreover, there is a need to identify and quantify the logistic chains, mapping net availability, consumption and demand as potential supply gaps, fostering the circular economy concept. The cooperation with local authorities and recycling networks in the developing of business plans is essential. In addition, economic data are needed, and in case of not being feasible, some incentives or subventions could be helpful.

Some specific information gaps and R&D needs have been identified:

- Tantalum: no sufficient data available on its recovery.
- Niobium and Tungsten: data of their presence in electronics
- In general, identification of new applications of which refractory metals could be extracted.
- Development of cost effective, flexible hydro-processes for recovery from multicomponent alloys.
- Validate the new developed processes by upscaling.
- The task of Identifying economic incentives for better management and recovery of refractory metals from EoL was very limited.

WP5 - SUBSTITUTION

In the search of possible substitutes for refractory metals it is essential to set the major applications of each of them, and what properties do they have for that aim. In this line, a summary of main applications are:

Metal	Main application	Function	Industry	Potential substitutes
Nb	As FeNb in steels	Grain refinement, precipitation hardening (mechanical strength, toughness, corrosion resistance, temperature strength)	Automotive Construction Energy Aerospace	Titanium, Molybdenum, and Mo-Vanadium combinations
Ta	As powder or wire in capacitors	Temperature insensitive volumetric capacitance. High resistance to corrosion	Electronics	Aluminium and ceramics, maybe Nb. Corrosion resistants: glass, platinum, titanium, zirconium. High-T:Hafnium, Iridium, Mo, Re,W.
Re	Super alloys Catalysts	Creep Strength Operating at lower pressures and high temperatures Erosion resistance	Aviation Automotive Rocket engines and hot gas valves	-
Mo	As oxide in steels	Strength, hardness, electrical conductivity and resistance to corrosion and wear.	Automotive, mechanical engineering, building&construction, aerospace&defence.	B, Cr, Nb, Va
W	Cemented carbides, Steel alloys	Hardness and strength with good toughness	Aircraft engines, marine vehicle,…	TiC and TiN

Long term research (-10years) investment is needed for technology leap in new material development to develop sustainable substitutes for refractory metals.

CHAPTER 7 POTENTIAL PATHWAYS DISCUSSED AT THE WS3

The assessment of the five refractory metals' value chains has led the community to propose different actions to balance the needs for the EU industry in the future.

TUNGSTEN

Three ways should be explored:

* Update prospecting guides to open new mines in Europe

* Recover tailings

* Recycle tungsten scraps.

Among these possibilities, the most promising one seems to be the development of new mines in Europe because there is a real potential, but with eco-design thought from the beginning of the projects, including treatment of tailings in order to prevent pollution of the water table or rivers. These further treatments contributing to a sustainable mine concept need to be fostered by local or EU authorities, otherwise they will never compete with a Chinese supply.

As for the tungsten scraps, direct methods such as the zinc treatment method should be preferred.

TANTALUM AND NIOBIUM

The potential to find rich enough and profitable new mines in Europe is limited. During our 3rd workshop, we shared the viewpoint that high-grade tin slags and copper smelting slags are the best promising secondary resources. Copper metallurgists like UMICORE could be interested if they can adapt their processes to a variety of intrants.

Improvements in both hydrometallurgy and pyrometallurgy could be boosted from R&D to the industry to make processes simplier, safer and more profitable. The recovery of by-products could be also supported.

MOLYBDENUM

There is presently no lack of Mo in the EU but the increased need of special steels will make more recycling necessary.

The treatment of primary resources can be improved using alternative roasting routes, especially using sulfur absorber, such as Ca, Mn and/or their oxides to refrain the emission of sulfurous gas.

As for the secondary resources, the recycled Mo accounts for around 1/4-1/3 of the total inputs; this value could be enhanced by improving the Mo recovery mill scale, dust and slag. For example, ~ 5 wt. % mill scale can be charged into EAF with no operation problem, leading directly

to Mo-containing steels.Establishing more efficient sorting and recovery system can be also a good way to improve the economic interest to recover the different Mo containing wastes.

RHENIUM

Rhenium is a rare and strategic metal for the EU, with applications mainly in superalloys (83 % of the Re production) and Pt-Re reforming catalysts (15%). Most of the prospects that could be developed in the EU concern the valorization of Re in urban mines.

Several innovation pathways have been identified by the coworkers and specialists:

- Promoting sorting logistics and collection efficiency of Re containing end-of-life products, and establishing a stable supply source.
- Promoting the recycling of superalloys through the development of rhenium recovery methods for materials of diameter >30 mm, which are not currently processed.
- Encouraging manufacturers to improve design of products taking account easy disassembly to simplify the process of reuse and recycling.
- Fostering innovative technologies for conversion of commercially prepared rhenium compounds (mainly ammonium perrhenate) to more technologically advanced and processed functional compounds, materials or components.
- From a strategic viewpoint, encouraging large companies, suppliers and specialized groups to commit themselves in Re recycling.

CHAPTER 8 MULTI-LEVEL PERSPECTIVE

The transition in path-dependent system is a complex multidimensional societal change process, dealing with the co-evolution of technological, industrial, policy and social changes. A Multi-Level Perspective (MLP) framework has been developed first in the Netherlands (Geels 2005), in order to describe this complex process. The framework has also been developed and applied in UK (Foxon et. al. 2010). Geels has applied the MLP framework also to the transport system in his recent work as he has studied transitions towards low-carbon futures of automobile systems (Geels 2012).

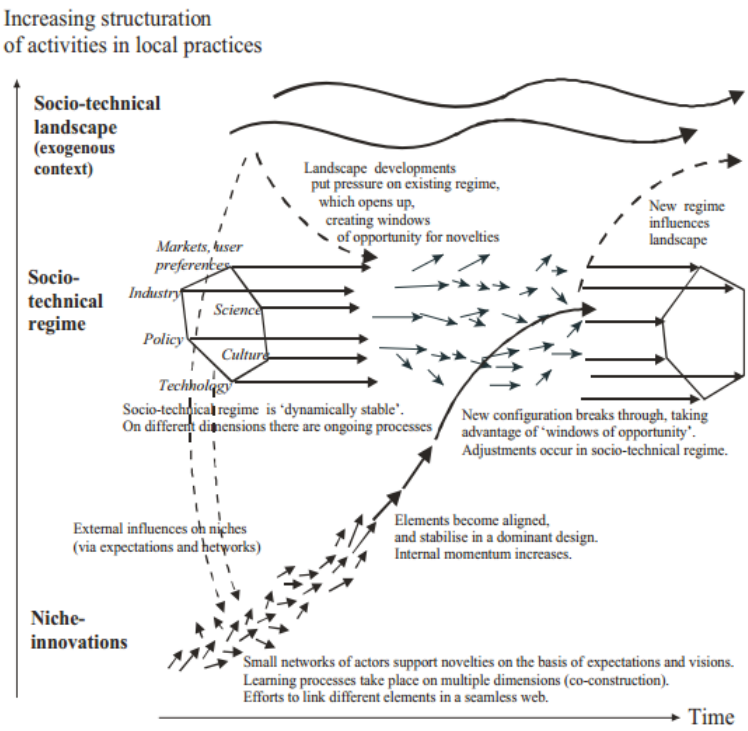
The MLP posits three levels to aid understanding transitions: a landscape (macro) level that encompasses the dynamics of deep cultural, economic and political patterns; a regime (meso) level that refers to the current practices, routines and dominant rules that prevail in a socio-technical system; and a niche (micro) level which represents the space where actors experiment with radical innovations that may challenge and break through into the prevailing regime:

• **Landscape level (macro)** is the overall socio-technical setting that encompasses the dynamics of deep cultural patterns, macro-economics and macro-political developments that make up the environment or context of socio-technical transition. It is the backdrop to the regime and niche levels, which stimulates and exerts pressure on the socio-technical regime and the technological niches and so plays an important role in stimulating socio-technical transitions. Landscape, forms an exogenous macro level environment that influences developments in niches and regimes. General developments in global operating environment, including economic, cultural or environmental factors compose the landscape level. The socio-technical landscape only tends to change very slowly since for example demographic changes, macro-economics, and cultural changes are slow, possibly over generation changes.

• **Regimes level (meso)** comprises the structures that represent current practices and routines, including the dominant rules and technologies that provide stability and reinforcement to the prevailing socio-technical systems. The regime is also a barrier to change, including new technological and social innovations. Regime refers to the existing structures and actions of the system. The specific form of the regime is mainly shaped and maintained through the mutual adaptation and coevolution of its actors and elements. Path dependent planning and innovations based on existing solutions direct the almost stable system. Hence, the prevailing system acts as a barrier to the creation of a new system.

• **Niches level (micro)** is the level in which space is created for experimentation and radical innovation. The niche level is more loosely structured than the regime and is less subject to market and regulation influences. There is much less co-ordination among niche actors than among regime actors, but this allows for the emergence of new interactions between actors that may support innovation. Niches, in turn, form the level where radical novelties emerge. Niches are local innovative solutions, experiments. Niches may, for instance, take the form of small-market niches, where selection criteria are different from the existing regime. Survival of such niches may be supported by public subsidies and act as incubators for new technologies or practices. Niches provide opportunities for learning and incubation of alternative solutions that may gradually become strong enough to challenge the existing regime or adopt and transform the regime towards new directions. Niche level solutions give alternatives and options by performing social experiments of energy related innovations.

The strength of the MLP approach is that transitions can be explained by the interplay of establishing mechanisms at the regime level, combined with destabilising pressure from the landscape and radical innovations at the niches. In particular, the breakthrough of innovations is dependent on multiple processes in the wider context of regimes and landscape.



Multi level perspective on transition

The following table highlights the MLP proposed for each of the refractory metals studied throughout this deliverable:

METAL	TARGET/OBJECTIVE	LANDSCAPE LEVEL (MACRO)	REGIMES LEVEL (MESO)	NICHES LEVEL (MICRO)
Ta	To promote the valorization of the secondary resources, and at a lower level, of the urban mines	• The price/value of tantalum escalates rapidly as it moves through the chain. the differential between raw material cost and finished product value is at least 100% • The production from secondary resources has grown considerably between 2008 and 2012. Due to reduction of tin mining, the most interesting sources are old slag dumps. • Recovery of Ta from secondary resources is not enough competitive for EU industry, metallurgical activities within the EU should be strengthened. • Potential tailings and slags can be found in Spain, Portugal, France, UK, Germany and Czech Republic. • Ta can be found also from municipal waste landfills, industrial landfills (such as landfills of WEEE recycling companies) and from incineration slags. • Other potential secondary sources: scraps from manufacturing of Ta powders and ingots	• Global Ta recycling <20%. • EU Ta recycling 50 MT. • Very little recycling of scraps and out of specification products (from intermediate products to processing plants). • Ta loss in the waste to the environment. • Important secondary resources such as copper smelting slags are not fully recovered. • Scrap containing Ta is not recovered in the EU.	In general, more R&D is needed; pilot scale trials should be carried out for the recovery of different valuable metals from copper smelting slags. All in all, niches level are to be focused on: • **Recovery from slags**: o High-grade tin slags (>10% Nb+Ta) by hydrometallurgy (using HF) or carbochlorination at 500°C. o Copper smelting slags using froth flotation with alkyl dydroxamates as collectors (selective chelation to Ta or Nb-containing minerals). • **Recovery from W arbide sludge**: o Important secondary resource but no innovative processes have been found. Need of coordination with WC recycling actors. • **Recovery of Ta from alloy scrap**. • **Innovative solvent extraction processes**. • **Innovative pyrometallurgical processes**: o Direct Electrolytic Reduction of Solid Ta_2O_5 to Ta with solid-oxide-oxygen-ion conducting mebrane (SOM) process, which uses electrolysis in molten $CaCl_2$ or MgF_2-CaF_2 at higher potential than FCC Cambridge process, seems very promising. o The Ta powder preparation from Ta_2O_5 by calciothermic reduction at a molar ratio Ca/Ta_2O_5> 10 (2*stoichiometry) and 900°C leads to Ta with 1% O_2.

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Re	To promote Re production from primary ores (evolution increasing the urban mines)	• Demand for rhenium is forecasted to continue to rise strongly over the next 20 years. • 55-60 tons of Re are produced in the world of which the vast majority used in super-alloys, the remaining used in catalysts, medical anodes and filaments etc.	• 8 ton/year are produced from primary resources in Poland (as by-product of the copper production process).	• Promoting primary Re production by the increase of the recovery of Re in mining and enrichment and insmelting and refining, meanwhile, reprocessing Re-containing secondary wastes (tailings, residues) could be significant innovation paths.
	To promote Re production from recycling	• Demand for rhenium is forecasted to continue to rise strongly over the next 20 years. • The gap between supply and demand is being rescued from rhenium to be wasted in the past. Thus, recycling of the metal has grown considerably over the past several years. • Recycling of superalloys and other metal containing wastes mostly takes place out of the EU. • Rhenium has a great innovative potential due to its application in numerous new products and materials	• Re occurs in small quantities in the super-alloys. Hence, the energy use, GHG emissions and economic cost associated with collecting, sorting, cleaning, and otherwise processing of the alloy scraps would be higher than most of other metals. • Lack of effective logistic system of Re containing spent materials. They are not segregated, which hampers their further processing. • Rhenium superalloys containing materials are not currently processed due to the lack of appropriate technologies for production of ammonium perrhenate and other rhenium compounds.	The key to increase the recycling rate of Re is promoting the recycling of Re from super-alloys. For this purpose, niches level are to be focused on: • Establishing database of Re containing product inventories, sales, product info of components, expected wastes. • Promoting sorting logistics and collection efficiency of Re containing end-of-life products, and establishing a stable supply source. • More efficient collection, sorting logistics and cleaning infrastructure for EoL products, establishing a stable supply source. • Promoting pre-processing efficiency by using innovative and scale-up technologies. • Innovative processing technologies by taking account of economic cost and environmental impact. • Scale-up market access and havelarge companies, suppliers and specialized groups engaging in Re recycling/recovery. • Encouraging manufacturers to improve design of

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				products taking account of easy disassembly, reuse and recycling. • More R&D and innovating technologies are needed; pilot scale trials should be carried out to verify the economic, environmental and technological feasibilities of the process.
W	To increase the supply of W from the primary	• Demand for tungsten products is estimated with a moderate but permanent use growth in steels and alloys. • China has the majority of material reserves and rules the tungsten market and prices. • Notable deposits can also be found throughout EuropeH2020 projects on mining research focusing on Critical Raw Materials. • Administrative barriers: Time to autorizathions for opening a new mine, SLO (sustainable mining certification) and Pilot plant.	• Lack of investments in new mines and reduced secondary raw material availability. • The expected tungsten production in Europe for this year 2016 is: 2,700 tonnes in Spain, 2,700 tonnes in United Kingdom, 800 tonnes in Portugal and 800 tonnes in Austria.	• Promote exploration at EU level (H2020, ESIF, etc.) • Update Prospecting Guides • Future Applications in: o Deep Drilling o Medical Industry • More R&D is needed; pilot scale trials should be carried out to improve the economic, environmental and technological feasibilities of mineral processing.
	To create new method for Tungsten recycling	• Demand for tungsten products is estimated with a moderate but permanent use growth in steels and alloys. • The quantity of material available for recycling tungsten	• Lack of suitable recycling technologies. • The high melting point of Tungsten makes its recovery very difficult due to economic reasons (high associated energy cost).	• There are limited options for W substitution.In few occasions, it could be substituted for another metal (e.g. molybdenum carbide and titanium carbide) or for another application (e.g. LEDs are gradually substituting light bulb filaments). • Recovery of tungsten from Tailings and recycling of

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		may often meet only a modest proportion of future demand. • W has been listed as a metal that is of great importance to the EU and the overall economy in Europe.		tungsten scraps. • More R&D is needed; pilot scale trials should be carried out to improve the economic, environmental and technological feasibilities of metallurgical processes.
Mo	To conclude that there is no hurry to change the current situation.	• Strict environmental regulations in EU: the roasting process lies in the emission of sulfurous gas and dust to the environment.	• Prices of molybdenum oxide decreased sharply from mid of 2008 and stay in a lower level until now.The low prices of Mo result in the recycling of Mo from secondary mine and urban mine being less competitive.	• There are innovative processes developed in the enviromental aspect; however, the processes have not been industrially proved to be economic and/or efficient.
Nb	Options for improving secondary and developing urban mines	• There is no primary production on Nb in Europe; the only possible sources are the secondary ones.	• Wastes associated to former smelter or refinery plants with smelting slag waste containing Nb. • Very little recycling of scraps and out of specification products (from intermediate products to processing plants). • Nb loss in the waste to the environment. • Important secondary resources such as copper smelting slags are not fully recovered.	• Recovery of Nb as a by-product. A fluoride-free process using caustic conversion has been developed.Global Nb and Ta recovery yields of 65% have been obtained during continuous pilot tests.There are probably other secondary mining resources to be valorised using simpler separation processes, therefore being profitable at limited throughputs. • Innovative Pyrometallurgical Processes of Ta and Nb: An improvement is clearly foreseeable if the transformation from the oxide to the metal could be done in one step. • **Recovery from** slags: o High-grade tin slags (>10% Nb+Ta) by hydrometallurgy (using HF) or carbochlorination at 500°C. o Copper smelting slags using froth flotation with alkyl

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				dydroxamates as collectors (selective chelation to Ta or Nb-containing minerals). • Innovative solvent extraction processes: More robust extractants with higher stability and lower water solubility or Increase recycling of reagents to reduce liquid and solid waste.

MLP provides useful analytical structures for developing innovation and transition policies and strategies. The innovation systems approach and the multilevel frameworks have both been applied for the study of radical innovation and transformation processes. They are based on common theoretical roots and offer promising complementarities, reviewing the state of the art and, on the basis of a comparison, identified similarities, conceptual overlap, strengths and weaknesses. This led us finally to outline an overarching conceptualization which would build on promoting their strengths. After developing MLP for each refractory metal we can conclude that:

- **Tantalum:** the existence of a large number of niches levels bring to the forefront that a major investment in R&D is need, as there are multiple applications that still need further development. Pilot scale trials should be carried out for the recovery of different valuable metals from copper smelting slags. In addition, metallurgical activities within the EU should be strengthened and competitiveness enhanced.
- **Niobium:** This metal is closely linked to tantalum, so we may come to the same conclusions.
- **Molybdenum:** Due mainly to economic barriers in regimes level (from 2008 prices of molybdenum are not competitive), environmental politicies in landscape level (Molybdenum roasting procces is considered as harmful to the environment) and lack of innovative solutions in niches level, there is not urgently need to change the current situation.
- **Tungsten:** Limited substitution of tungsten, along with a great number of novel applications, make a large number of niches levels and make increase the necessity of investment in R&D in substitution, recycling and extracting fields.
- **Renium:** Niches level are focused on the increase of recycling rate of Re by promoting the recycling of Re from super-alloys and improving extracting process. Rhenium also has a great innovative potential due to its application in numerous new products and materials.

We can conclude that tantalum, niobium, tungsten and rhenium need more R&D, providing each of them alternatives and options by performing social experiments of energy related innovations. In tungsten case, a deep study of innovative processes in the enviromental aspect is needed with the aim of improve its economic and/or efficient aspect.