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Management of wastes from primary resource processing: identification, environmental evaluations

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Management of wastes from primary resource processing: identification, environmental evaluations

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MANAGEMENT OF WASTES FROM PRIMARY RESOURCE PROCESSING: IDENTIFICATION, ENVIRONMENTAL EVALUATIONS

MSP-REFRAM D2.4

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1. INTRODUCTION

The objective of Task 2.5 and subsequently of this deliverable was to present the waste management current practices for the five refractory metals and to state the required actions for future recovery of the five refractory metals from mining streams. The registry of the waste management practices at the mining boundaries of the refractory metals will address the possible environmental risks. The initial vision in the proposal preparation was to utilize LCA studies for each of the five refractory metals, in order to state those processes in the mining value chain that cause the main environmental burden. However, this proved to be an ambitious objective, mainly due to the lack of data availability.

The complexity of the raw materials value chains and the demand on inventory data over input and output flows within this chain is challenging for the sector. Given that refractory metals industry is even restricted in compiled production data per year in some cases makes evident the fact that a LCA analysis was not feasible within this study.

The focus of the study is to present the mining waste management for the refractory metals in a qualitative manner and to depict those cases where valorization of mining wastes occurs and highlight the good practises. In addition, LCA studies per refractory metal are analysed with aggregated results for the mining boundaries.

2. MINING WASTES

The type, amount, and properties of mine waste produced at different mines vary depending on the resource being mined, process technology used, and geology at the mine site. While many mine wastes are benign, mining companies manage their waste in order to deal with the large volumes of waste produced and to prevent the release of contaminants into the environment. Waste management plans are developed as part of the mine approval process in Canada, and consist of waste storage area selection and design, strategies to address problematic waste, and long-term stabilization of waste as part of mine closure.

ORIGINS OF WASTE AT MINE SITES

Like the majority of human activities, mining operations produce waste materials. “Waste” is a general term for material which currently has little or no economic value¹. The soil and rock which is removed to gain access to buried ore, and the material (water, solids, and gases) left behind after the ore has been processed to remove the valuable commodities, are considered to be waste materials. However, the difference in mineral content between ore and waste rock can change depending on market conditions and available extraction technology, and there are a number of cases where material that was once considered waste has become a resource for modern mining operations².

TYPES OF MINE WASTE

There are different types of mine waste materials which vary in their physical and chemical composition, their potential for environmental contamination, and how they are managed at mine sites. Types of mine waste include:

- **Overburden:** Overburden includes the soil and rock that is removed to gain access to the ore deposits at open pit mines. It is usually piled on the surface at mine sites where it will not impede further expansion of the mining operation – moving large volumes of material is expensive. Overburden generally has a low potential for environmental contamination, and is often used at mine sites for landscape contouring and revegetation during mine closure.
- **Waste rock:** Waste rock is material that contains minerals in concentrations considered too low to be extracted at a profit. Waste rock is often stored in heaps or dumps on the mine site, but may be stored underwater with tailings if it contains a lot of sulphide minerals and has a high potential for acid rock drainage formation. Waste rock dumps are generally covered with soil and revegetated following mine closure, although there are cases of waste rock being re-mined due to an increase in mineral market prices or improvements in extraction technology.
- **Tailings:** Tailings are finely ground rock and mineral waste products of mineral processing operations. Tailings can also contain leftover processing chemicals, and are usually deposited in the form of a water-based slurry into tailings ponds (sedimentation lagoons enclosed by dams built to capture and store the tailings), although offshore tailings disposal has been successful in some cases. Tailings dams are discussed in further detail below.
- **Slags:** Slags are non-metallic by-products from metal smelting, and were historically considered to be waste. Slags are largely environmentally benign, and are being used increasingly as aggregate in concrete and road construction.

¹ Hudson-Edwards, K.A., H.E. Jamieson, and B.G. Lottermoser. Mine Waste: Past, Present, Future. 2011

² Rankin, W.J., Minerals, metals and sustainability : Meeting future material needs. 2011, Collingwood, Vic.: CSIRO Pub.

- **Mine water:** Mine water is produced in a number of ways at mine sites, and can vary in its quality and potential for environmental contamination. Water at mine sites is frequently monitored and various water management strategies have been developed to reduce the amount of mine water produced, and treat the water before it is discharged to the environment.
- **Water treatment sludge:** Sludge is produced at active water treatment plants used at some mine sites, and consists of the solids that had been removed from the water as well as any chemicals that had been added to improve the efficiency of the process. Although ways of recycling the sludge are being explored, the majority of sludge has little economic value and is handled as waste. Disposal of water treatment residues in underground mine workings is the least expensive option where it is permitted and environmentally safe. In extreme cases where the sludge is rich in cadmium or arsenic, it may be classified as hazardous waste and require special handling and disposal³.
- **Gaseous wastes:** Gaseous wastes include particulate matter (dust) and sulphur oxides (SO_x). The majority of emissions to the atmosphere are produced during high-temperature chemical processing such as smelting, and vary in their composition and potential for environmental contamination. Environmental control technologies such as gravity collectors, cyclones, and electrostatic precipitators are capable of removing up to 99.7% of dust and fumes, and wet scrubbers typically remove 80-95% of sulphur oxide emissions^{4, 5}. In Canada, the atmospheric sulphur dioxide emissions from metal smelters have decreased by 37% between 2003 and 2010⁶.

ENVIRONMENTAL IMPACTS OF MINE WASTE

The environmental impact of mine waste depends on its type and composition, which vary considerably with the commodity being mined, type of ore, and technologies used to process the ore. For instance, where waste rock and tailings contain significant quantities of sulphide minerals and are exposed to air and water, acid rock drainage (ARD) can occur⁷. As a result, every mine requires its own waste characterization, prediction, monitoring, control, and treatment⁸. Many mine wastes are environmentally benign, and can be used for landform reconstruction, vegetation covers, and road and dam construction.

The major environmental impacts from waste disposal at mine sites can be divided into two categories: the loss of productive land following its conversion to a waste storage area, and the introduction of sediment, acidity, and other contaminants into surrounding surface and groundwater from water running over exposed problematic or chemically reactive wastes.

MANAGEMENT OF MINE WASTES

Mine wastes require careful management to ensure the long-term stability of storage and disposal facilities, and to prevent and minimize air, water, and soil contamination. The inappropriate or unsafe management of wastes at mining operations continues to generate opposition from local communities, the general public, and non-government organizations, and has contributed to the negative public perception of the mining industry. Technological advances and changes in regulations have resulted in significant changes in waste management

³ Younger, P.L., S.A. Banwart, and R.S. Hedin, *Mine Water: Hydrology, Pollution, Remediation*. 2002, Dordrecht, The Netherlands: Kluwer Academic Publishers.

⁴ Vallero, D.A., *Fundamentals of Air Pollution*. 2007, Amsterdam: Elsevier.

⁵ U.S. Environmental Protection Agency. Module 6: Air Pollutants and Control Techniques -- Sulfur Oxides -- Control Techniques. Basic Concepts in Environmental Sciences 2010 .

⁶ Canada, Environment Canada. National Pollutant Release Inventory. 2012 Available from: <http://www.ec.gc.ca/inrp-npri/default.asp?lang=En&n=4A577BB9-1>.

⁷ Rajaram, R. and R.E. Melchers, Chapter 6: Waste Management, in *Sustainable Mining Practices -- A Global Perspective*, V. Rajaram and S. Dutta, Editors. 2005, A. A. Balkema Publishers, a member of Taylor & Francis Group: Leiden, The Netherlands. p. 193-230.

⁸ Lottermoser, B., *Mine Wastes: Characterization, Treatment and Environmental Impacts*, 2012, Springer: New York. p. 400.

practices over the last 10 to 20 years, and mine wastes at modern mines are generally better managed than they have been in the past^{9,10}. Waste management plans are frequently developed before a mine is constructed, and the reclamation of waste rock dumps and tailings ponds are increasingly incorporated into the designs of new mines. In addition, in many parts of the world authorities require a proper waste management plan before they will issue a mining permit.

Mine waste management practices and storage facilities used at different mines are based on common design principles, but are optimized by mine engineers depending on specific site conditions. These designs take into account the potential for extreme events, such as earthquakes and floods¹¹. Guidelines on waste management and mine closure have been developed at international, national, and regional levels, and provide an advisory framework for best practices in mine waste management.

The usual approach to managing wastes is to contain and collect them at the point of production, treat the wastes to make them environmentally safe if necessary, and dispose of them to the land, water, or air. The waste management method used at a particular mine depends mainly on an evaluation of cost, environmental performance, and risk of failure¹². Successful management of tailings and waste rock is based on selecting appropriate waste storage locations, and proper material characterization, including the accurate prediction of long-term chemical behaviour. Solid mine waste (overburden, waste rock, solidified tailings, slag, dust) can be used as backfill in underground or open pit workings, stored in piles on site or underwater to prevent ARD from occurring in the case of problematic wastes, used in construction of roads and dams at the mine, or recycled. Water can be recycled and reused for dust suppression and mineral processing, or treated and discharged into the environment.

TAILINGS MANAGEMENT

Because tailings are composed of fine particles (sand, silt, and clay-sized material), and often have a high water content, they have been particularly troublesome to manage. In the past, tailings were deposited directly into rivers or wetlands, which would introduce sediment and contaminants into those water bodies and in many cases adversely affect aquatic life. Tailings are currently used as backfill in underground mines, stored in open pits, dried and stacked, or pumped into tailings ponds on site.

Although there have been a number of incidents where the dams securing tailings ponds have been breached, mining engineers have been learning from the enquiries into tailing dam failures, and have improved tailings dam design and execution. A compilation of worldwide tailings dam failure statistics between 1909 and 1999 shows an improving trend as mining companies have learned from past mistakes and as regulators have imposed more stringent regulations and conducted more inspections. In the 1970s, there were 44 tailings dam failures, in the 1980s, 27 failures, and in the 1990s, only 7 failures. Modern tailings dam design is very technical, and takes a number of site-specific factors into consideration, such as rainfall and flooding predictions, earthquake response, seepage control, tailings discharge method and rate, and changes over the lifetime of the dams. Non-critical structures are typically designed to withstand a 1-in-100-year flood, while more critical structures are designed for a 1-in-1000-year event or above¹³.

⁹ Van Zyl, D., et al. Mining for the Future. 2002 .

¹⁰ Lottermoser, B.G., Recycling, Reuse and Rehabilitation of Mine Wastes. Elements, 2011. 7: p. 405-410.

¹¹ Caldwell, J. Mine Closure: The Basics of Success. [Online course] 2011 Version: 11 May 2011 Available from: <http://www.edumine.com/xutility/html/menu.asp?category=xcourse&course=Xclosure>.

¹² European Commission. Reference Document on Best Available Techniques for Management of Tailings and Waste-Rock in Mining Activities. 2009 Available from: http://eippcb.jrc.ec.europa.eu/reference/BREF/mmr_adopted_0109.pdf.

¹³ Robertson, A. and S. Shaw. Mine Closure. InfoMine E-book 2002 Available from: <http://www.infomine.com/publications/docs/E-Book%202%20Mine%20Closure.pdf>.

In response to concerns over tailings dam failures and water contamination, some mines are opting to produce thickened tailings, which are pressed or have chemicals added to remove excess water. Thickened tailings can be mixed with cement and used in construction or as backfill in underground mines. Although producing thickened tailings is often more expensive than storing the tailings in a pond, the use of thickened tailings is increasing, especially in arid areas where water availability is an issue.

TURNING MINING WASTES INTO A RESOURCE

The large volumes of waste produced at mining operations are expensive to manage, and are frequently cited as an obstacle in the environmental sustainability of mining. The mining industry plays a leading role in waste management, and is one of few industries that recycles its own waste. Uses of mine waste include:

- **Waste rock:** Can be reprocessed to extract minerals and metals, used as backfill, landscaping material, aggregate in road construction, or feedstock for cement and concrete
- **Manganese tailings:** Manganese tailings have been used in agro-forestry, buildings and construction materials, coatings, resin, glass, and glazes
- **Clay-rich tailings:** Clay-rich tailings have been used for making bricks, floor tiles, and cement
- **Slag:** Slag is often used for road construction, and in concrete and cement
- **Red mud:** Bauxite red mud is solid alkaline waste produced in aluminium refineries. Red mud has been used as a soil amender, in waste water treatment, and as a raw material for glass, ceramics, and bricks
- **Mine water:** Mine water is used for dust suppression and mineral processing, industrial and agricultural uses, as a coolant, and as a source of drinking water
- **Water treatment sludge:** Sludge from ARD treatment, which is high in iron, has been sold commercially for use in pigments
- **Sulphur oxide emissions:** Many smelters have installed acid plants to convert sulphur dioxide to sulphuric acid, a useful industrial chemical

MANAGEMENT OF WASTE FOLLOWING MINE CLOSURE

Despite the recycling and reuse of many wastes at mine sites, the majority of waste produced is still placed into storage facilities, and the reclamation and long-term management of these facilities has become an important part of modern mine development and mine closure. Regulators may require any waste storage structures to remain stable for a minimum of 100 to 200 years, which means they must withstand extreme events such as floods and earthquakes. Mine closure activities often involve containing and covering tailings to prevent their escape into the environment; minimizing the amount of water seeping from the tailings into surface or groundwater; covering waste rock piles and exposed materials with topsoil and planting vegetation to prevent erosion; and designing the final land formation to minimize erosion and post-closure maintenance. Plans for mine closure and site cleanup are required as part of the mine permitting process in Canada and these plans are updated after additional study¹⁴. It is also common in Canada for government agencies to issue a new permit on shutdown to cover mine closure.

¹⁴ Canada, Natural Resources Canada. 4. Mine Closure, Mining Sequence: Mining Information for Aboriginal Communities, 2011

3. EUROPEAN FRAMEWORK FOR WASTE MANAGEMENT

RAW MATERIALS INITIATIVE – EIP SIP

In view of the instability of prices in commodity markets and unreliability of political and economical developments in key raw material supplying countries, European institutions as well as national governments have sought to hedge against these risks by encouraging action on raw material security. These actions have included the creation of new or support for the growth of existing markets, specifically waste re-use and recycling markets. Indeed, one of the three pillars of the Raw Materials Initiative, launched in 2008 and led by the European Commission, is greater resource efficiency and promotion of recycling so as to reduce the EU's consumption of primary raw materials and in effect reduce its dependence on imports from outside the EU¹⁵. The European Innovation Partnership, which developed out of the Raw Materials Initiative, will among other things focus on promoting innovation in such areas as:

- Technologies to improve the recovery from waste, including e.g. red mud and abandoned or closed mining waste facilities;
- Turning wastes into valuable secondary raw materials by developing more efficient recycling/recovering processes (e.g. metals recycling from municipal waste, thermochemical phosphorous recovery from incinerated sludge, rare metals recovery from waste electric and electronic equipment, advanced recycling methods for the construction and demolition waste, multi-material cartons and paper waste etc.);

Furthermore, the European Commission in a 2012 communication stated that more ought to be done to help reduce the wastage of materials throughout their life cycle¹⁶. It is thus clear that existing and future policy will support a comprehensive approach to waste management.

MINING WASTE DIRECTIVE

In the EU, wastes deriving from the extraction and refining industries are regulated under the so-called Mining Waste Directive (2006/21/EC)¹⁷ (MWD). In this Directive, extractive waste is described as:

“Waste resulting from the prospecting, extraction, treatment and storage of mineral resources and the working of quarries but does not cover:

- waste which does not directly result from such activities;
- waste which results from offshore activities; and
- *injection/re-injection of groundwater as defined by the Directive 2000/60/EC¹⁸.*”

Extractive waste includes waste rock, which is unused extraction product, and mine tailings, which are defined in the MWD as:

¹⁵ European Commission, Brussels (2008) Communication from the Commission to the European Parliament and the Council – The raw materials initiative – meeting our critical needs for growth and jobs in Europe

¹⁶ European Commission, Brussels (2012) Communication from the Commission of the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions making raw materials available for Europe's future well being – Proposal for a European Innovation Partnership on Raw Materials.

¹⁷ Directive 2006/21/EC of the European Parliament and of the Council of 15 March 2006 on the management of waste from extractive industries and amending Directive 2004/35/EC; OJ L 102, 11.4.2006, p.15

¹⁸ Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy, OJ L 327, 22.12.2000, p. 1–73

“waste solids or slurries that remain after the treatment of minerals by separation processes (e.g. crushing, grinding, size-sorting, flotation and other physico-chemical techniques) to remove the valuable minerals from the less valuable rock”.

According to Eurostat statistics, the mining and quarrying industry produced 671,810,000 tonnes of waste in 2010, in the EU-27¹⁹. This is equivalent to around 30% of the total waste generated in the same countries. Mining waste is a substantial part of secondary raw materials and has the potential for becoming a mineral resource. This is particularly true for older facilities where previous technologies may have not been able to recover certain materials that may now be recoverable due to advances in processing techniques.

The MWD does not specifically refer to secondary raw materials and excludes ‘waste resulting from offshore’ activities. It is principally focussed on ‘waste management’ to reduce the environmental and socio-economic impacts of extraction and processing of mineral resources, rather than the recovery of secondary raw materials or determining their stocks.

LANDFILL DIRECTIVE

Council Directive 99/31/EC of 26 April 1999 on the landfill of waste (the ‘Landfill Directive’ (LFD)) entered into force on 16 July 1999. The deadline for implementation of the legislation in the Member States was 16 July 2001. The objective of the Directive is to prevent or reduce as far as possible negative effects on the environment from the landfilling of waste, by introducing stringent technical requirements for waste and landfills.

The Directive is intended to prevent or reduce the adverse effects of the landfill of waste on the environment, in particular on surface water, groundwater, soil, air and human health. It defines the different categories of waste (municipal waste, hazardous waste, non-hazardous waste and inert waste) and applies to all landfills, defined as waste disposal sites for the deposit of waste onto or into land. Landfills are divided into three classes:

- landfills for hazardous waste;
- landfills for non-hazardous waste; and
- landfills for inert waste.

The Directive sets up a system of operating permits for landfill sites. Applications for permits must contain amongst others the following information:

- a description of the types and total quantity of waste to be deposited;
- the capacity of the disposal site; and
- a description of the site.

In respect of the Minventory project, the Directive has relevance as far as it stipulates certain basic characterising data for landfills must be available within Member States, even if it is not publicly available or sufficient for waste stock estimation.

¹⁹Accessed via Eurostat Mining & Quarrying Waste landing page
http://epp.eurostat.ec.europa.eu/portal/page/portal/waste/waste_generation_and_management/generation/mining_quarrying

4. LIFE CYCLE ASSESSMENT & MATERIAL FLOW ANALYSIS

LIFE CYCLE ASSESSMENT

Among the tools available to evaluate environmental performance, LCA has gained recognition as the most powerful tool for the comparison of environmental impacts of products, technologies or services with a view to their whole life cycle (cradle to grave) or to a targeted part of that life cycle (cradle to gate, gate to gate or gate to grave). LCA is a process of evaluating the effects that a product has on the environment over the entire period of its life, thereby increasing resource-use efficiency and decreasing liabilities. LCA provides an instrument for environmental decision support.

According to ISO 14044 an LCA is carried out in four distinct steps as illustrated in Figure 1. These steps are often interdependent, meaning that the results of one step are used as necessary data for other steps. The methodology is characterized by a stepwise approach, being:

- **Step 1:** Goal and Scope Definition;
- **Step 2:** Life Cycle Inventory Analysis;
- **Step 3:** Life Cycle Impact Assessment;
- **Step 4:** Life Cycle Interpretation.

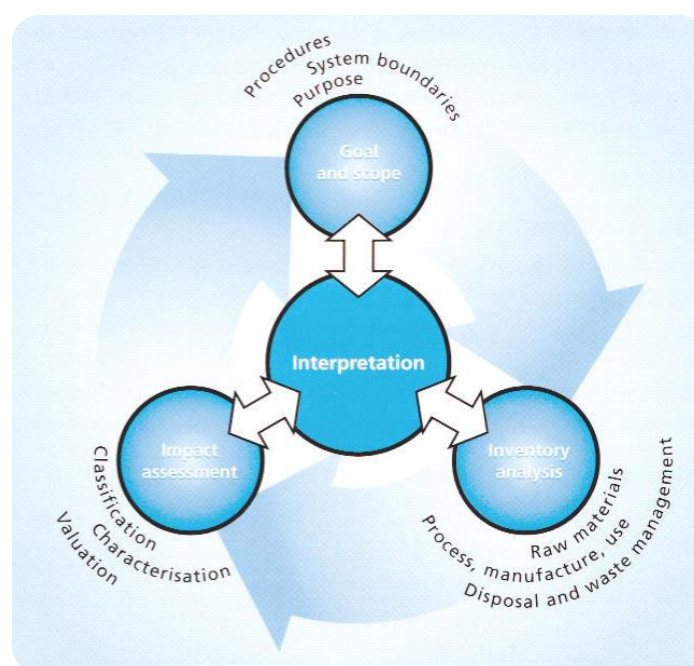


Figure 1. Schematic representation of Life Cycle Assessment Methodology

The initial scope of this report has been the evaluation of the mining production of the refractory metals in environmental terms with the utilization of LCA methodology. However, this proved to be ambitious since the limitation of data in mass and energy balances per unit process in the mining production of the refractory metals is evident and restricted only to LCA software companies and respective mining companies.

The complexity of the raw materials value chains (Figure 2) and the demand on inventory data over input and output flows within this chain is challenging for the sector. Given that refractory metals industry is even

restricted in compiled production data per year in some cases makes evident the fact that a LCA analysis was not feasible within this study.

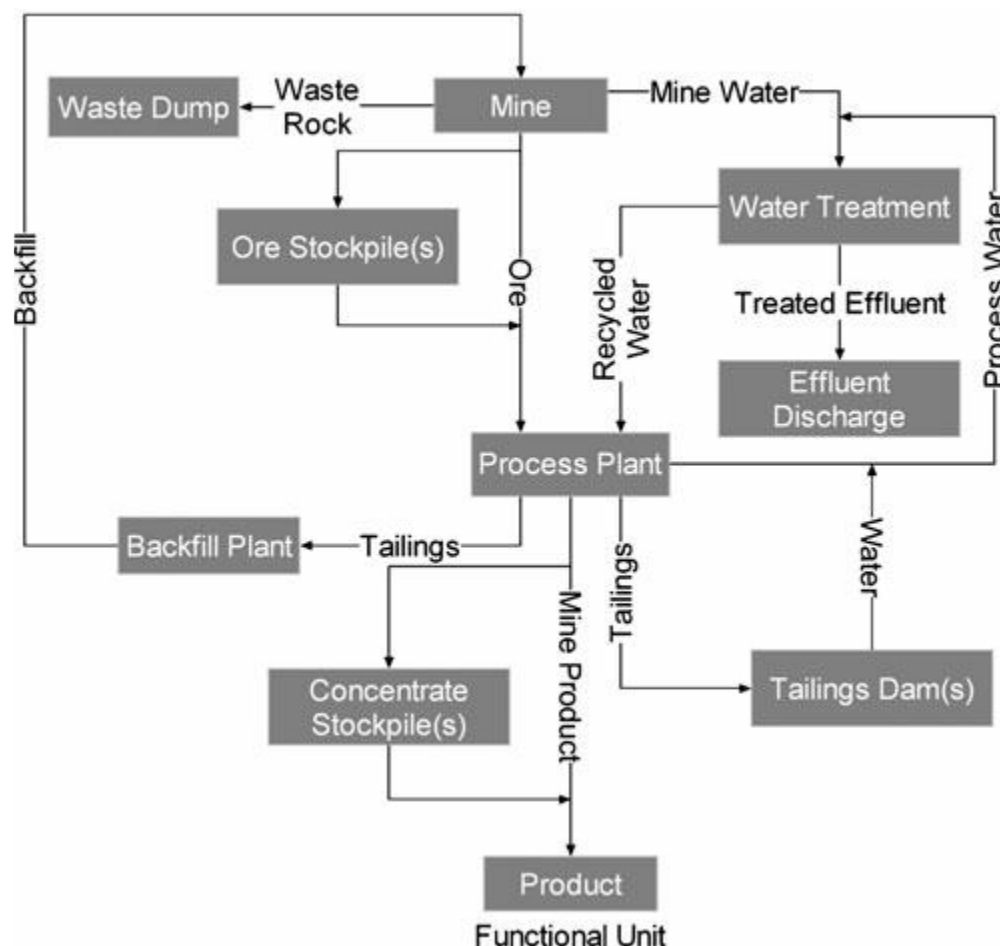


Figure 2. Indicative Raw materials value chain

One of the studies that provides LCA aggregated data for all the refractory metals is the “Life Cycle Assessment of Metals: A Scientific Synthesis”, where environmental impact data for five different LCIA categories are available. The comparative Table 1 does not lead to a single aggregated result on which metal is followed by the most environmental burden but is rather a category to category comparison. This is common in LCA studies and the overall result depends on the predefined goal and scope of the study and the assigned weighting factor for each LCIA category.

Table 1. Comparison of environmental data

IMPACT CATEGORY	UNITS	Ta	W	Re	Nb	Mo
Global warming potential	(kg CO ₂ eq / kg)	260	12.6	450	12.5	5.7
Cumulative energy demand	(MJ eq / kg)	4,360	133	9,040	172	117
Terrestrial acidification	(kg SO ₂ eq / kg)	1.7	0.29	11	0.053	0.16
Freshwater eutrophication	(kg P eq / kg)	0.15	9.3E-6	0.35	3.7E-03	0.54
Human toxicity	(CTUh/kg)	1.2E-04	3.4E-05	0.059	6.4E-06	9 E-04

In this case, Rhenium is causing the heaviest environmental impact in GWP and is followed by Tantalum with about 36% less GWP. Tungsten, Niobium and Molybdenum are causing almost 10 times less GWP compared to Rhenium. The same pattern is observed in the CED and Acidification LCIA. In Freshwater eutrophication and in Human Toxicity LCIA categories the impact is different with Molybdenum and Rhenium causing the heaviest environmental impact followed by Tantalum, Tungsten and Niobium.

In Figure 3, Figure 4, Figure 5, Figure 6 and Figure 7 the above mentioned LCIA categories are depicted in the periodic table for all the metal elements for comparison.

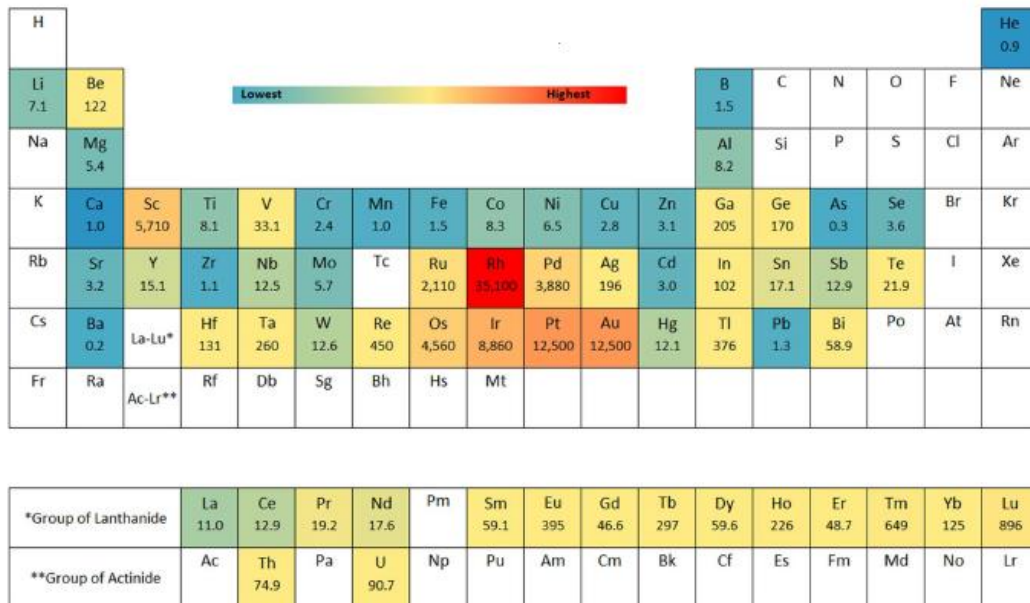


Figure 3: Global warming potential (kg CO2-eq per kg)

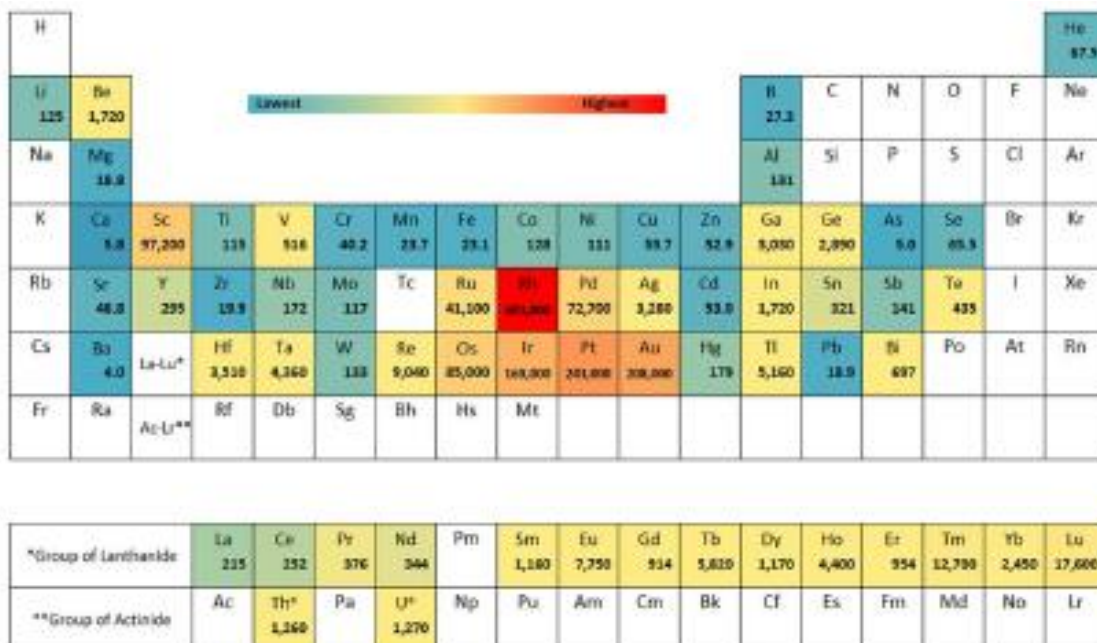


Figure 4: Cumulative energy demand (MJ-eq/kg)

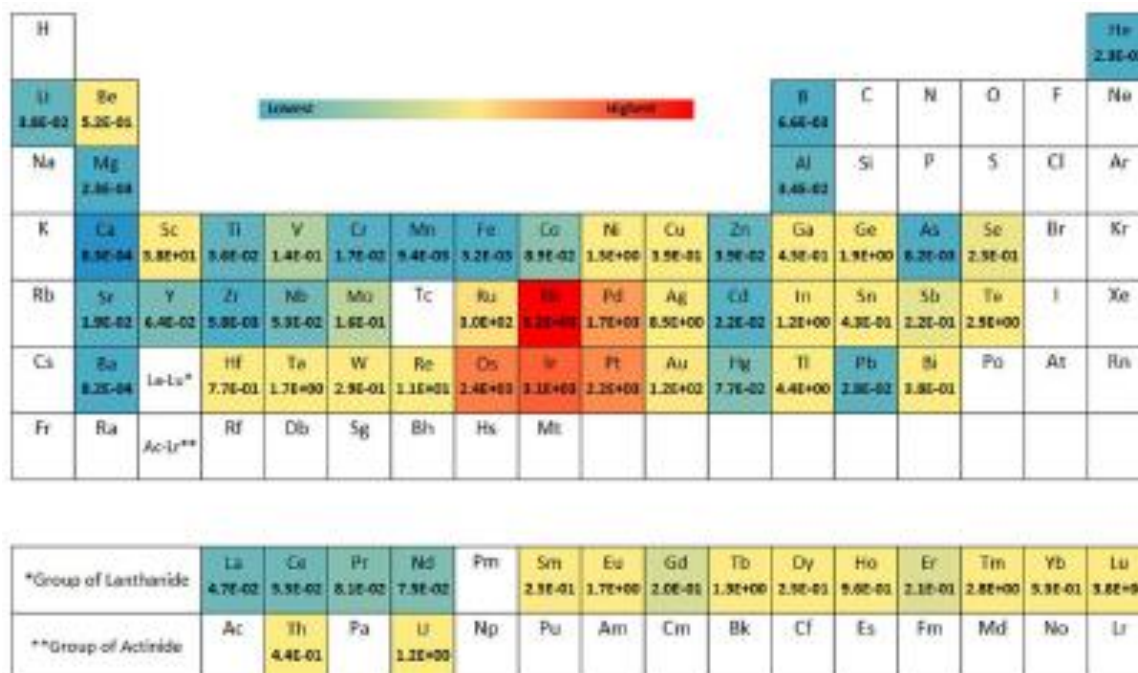


Figure 5: Terrestrial acidification (kg SO₂-eq/kg).

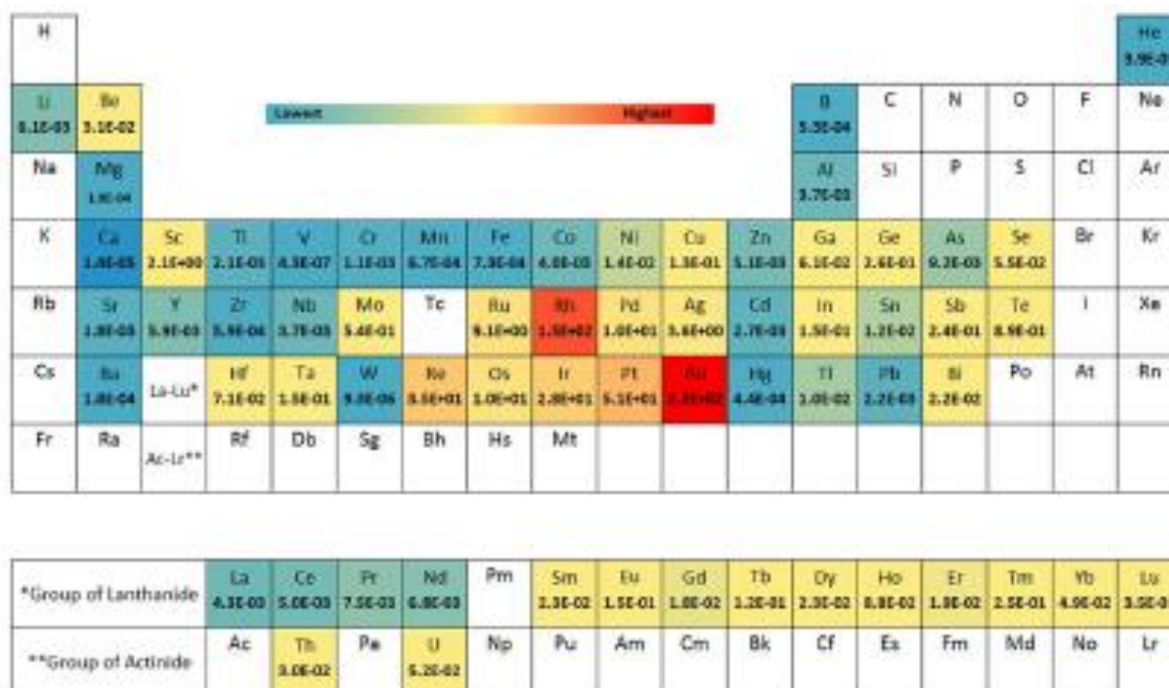


Figure 6: Freshwater eutrophication (kg P-eq/kg).

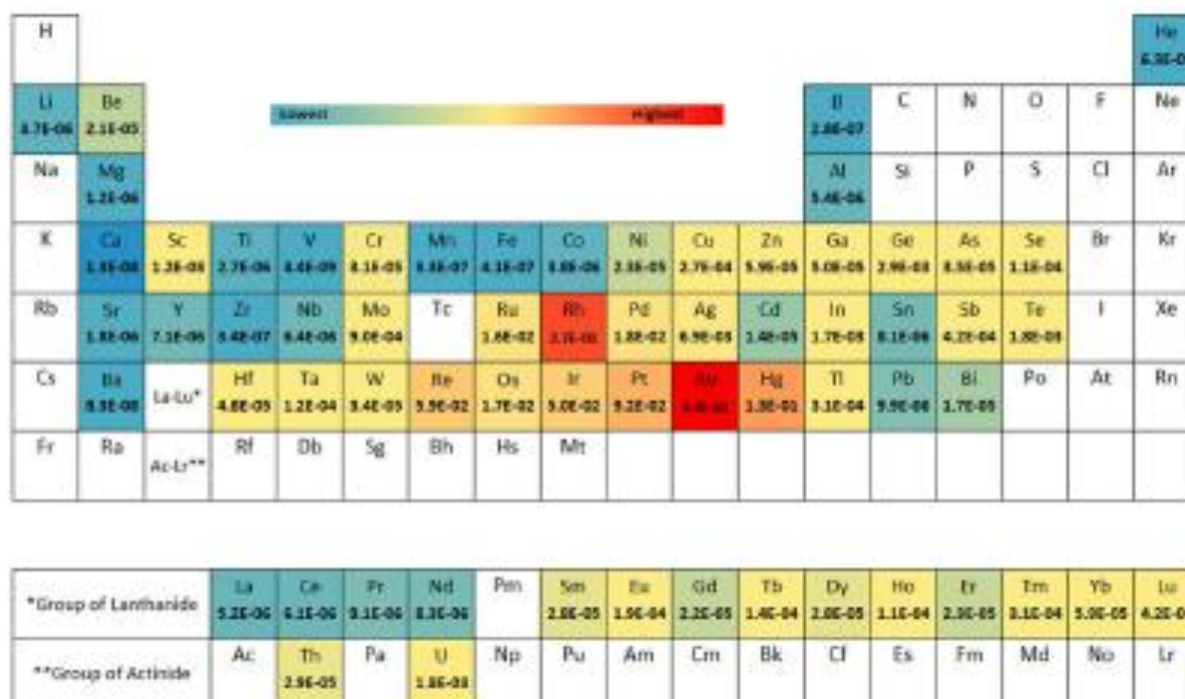


Figure 7: Human toxicity (Cancer & Non-cancer) (CTUh/kg).

MATERIAL FLOW ANALYSIS

Material Flow Analysis (MFA) is an analytical tool that maps physical flows of natural resources and materials into, through and out of the economy. According to OECD (2008), the term MFA refers to a family of tools which includes a wide variety of analytical approaches and measurement tools which can range in scope from economy-wide to substance or product-specific analyses. A study²⁰ has attempted to compile what OECD (2008) terms a material system analysis and focused on some refractory metals. A material system analysis is defined by OECD (2008)²¹ as follows:

“Material system analysis (MSA) is based on material specific flow accounts. It focuses on selected raw materials or semi-finished goods at various levels of detail and application (e.g. cement, paper, iron and steel, copper, plastics, timber, water) and considers life-cycle-wide inputs and outputs. It applies to materials that raise particular concerns as to the sustainability of their use, the security of their supply to the economy, and/or the environmental consequences of their production and consumption.”

The flowcharts that follow provide a simplified overview of the flows of each of the refractory materials in a recent year for which data are available and with a specific focus on the EU. The flowcharts are complemented by a brief overview of the structure of the relevant sectors and potential future trends. Information in the flowcharts is colour coded as follows:

- green colour indicates that data are largely available

²⁰ DG Enterprise and Industry (2012), Study on Data Needs for a Full Raw Materials Flow Analysis

²¹ OECD (2008): Measuring Material Flows and Resource Productivity Volume 1, available at www.oecd.org/dataoecd/46/48/40485853.pdf

-
- orange indicates that some (little) data are available (e.g. global use patterns instead of EU specific data); and
 - red indicates that insufficient information is available.

The flowcharts aim to primarily present information for the EU which is given within the black boundary and interactions with regions outside the EU are presented by means of an arrow at relevant stages in the lifecycle. Where information is available, the thickness of the arrows has been adapted to reflect the magnitude of the flows. However, the size of the boxes is standardised throughout, mainly reflecting paucity of information necessary for their differentiation.

The available MFA for Tungsten, Tantalum and Niobium clearly demonstrates the lack of available data for these refractory metals to cover the aspect of a life cycle approach not only in terms of environmental management in mining sites, but for the whole value chain as whole. The lack of data in both LCA and MFA forms a clear challenge for the stakeholders of the refractory metals and needs to be addressed.

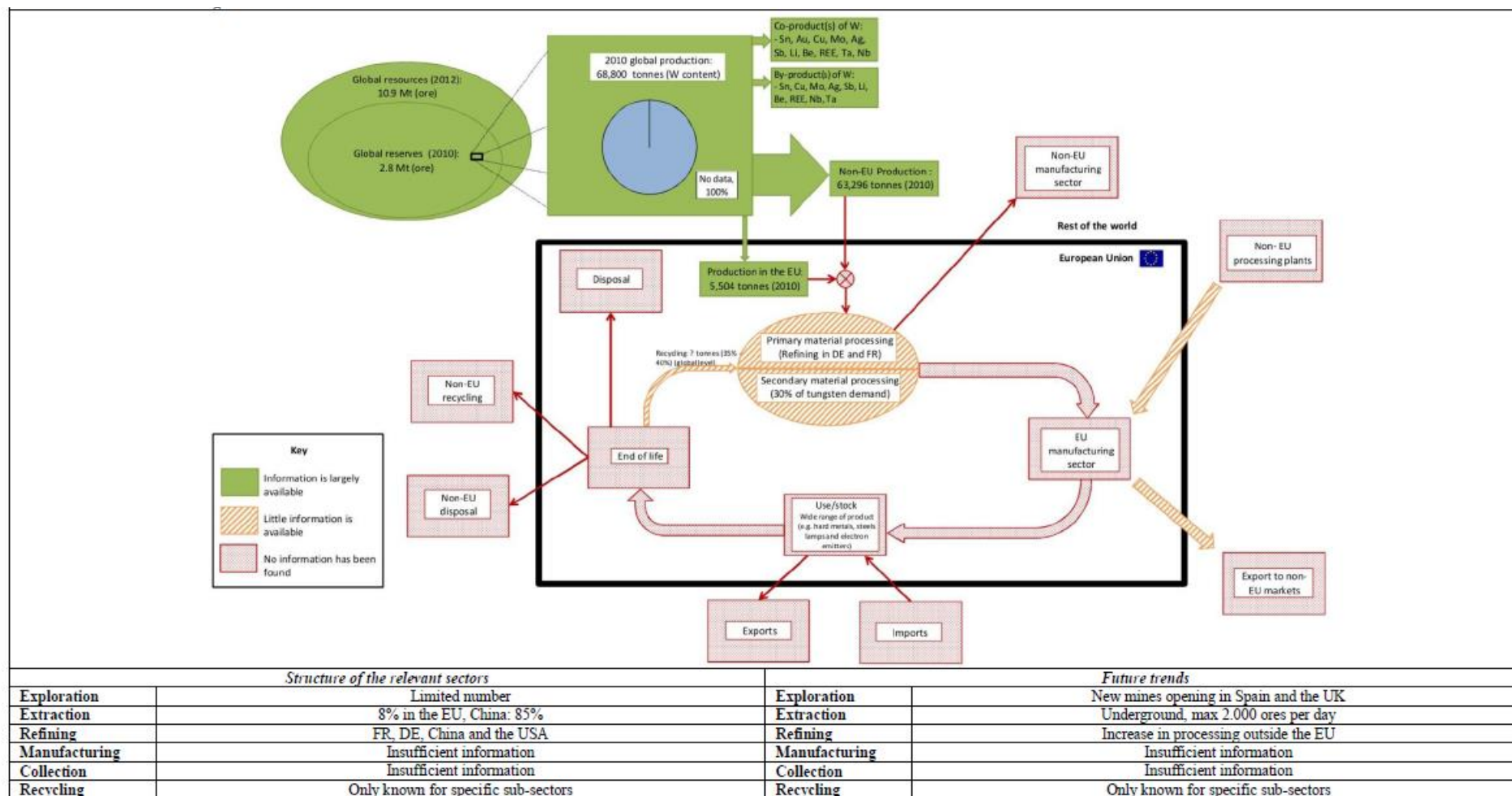


Figure 8. MFA for Tungsten

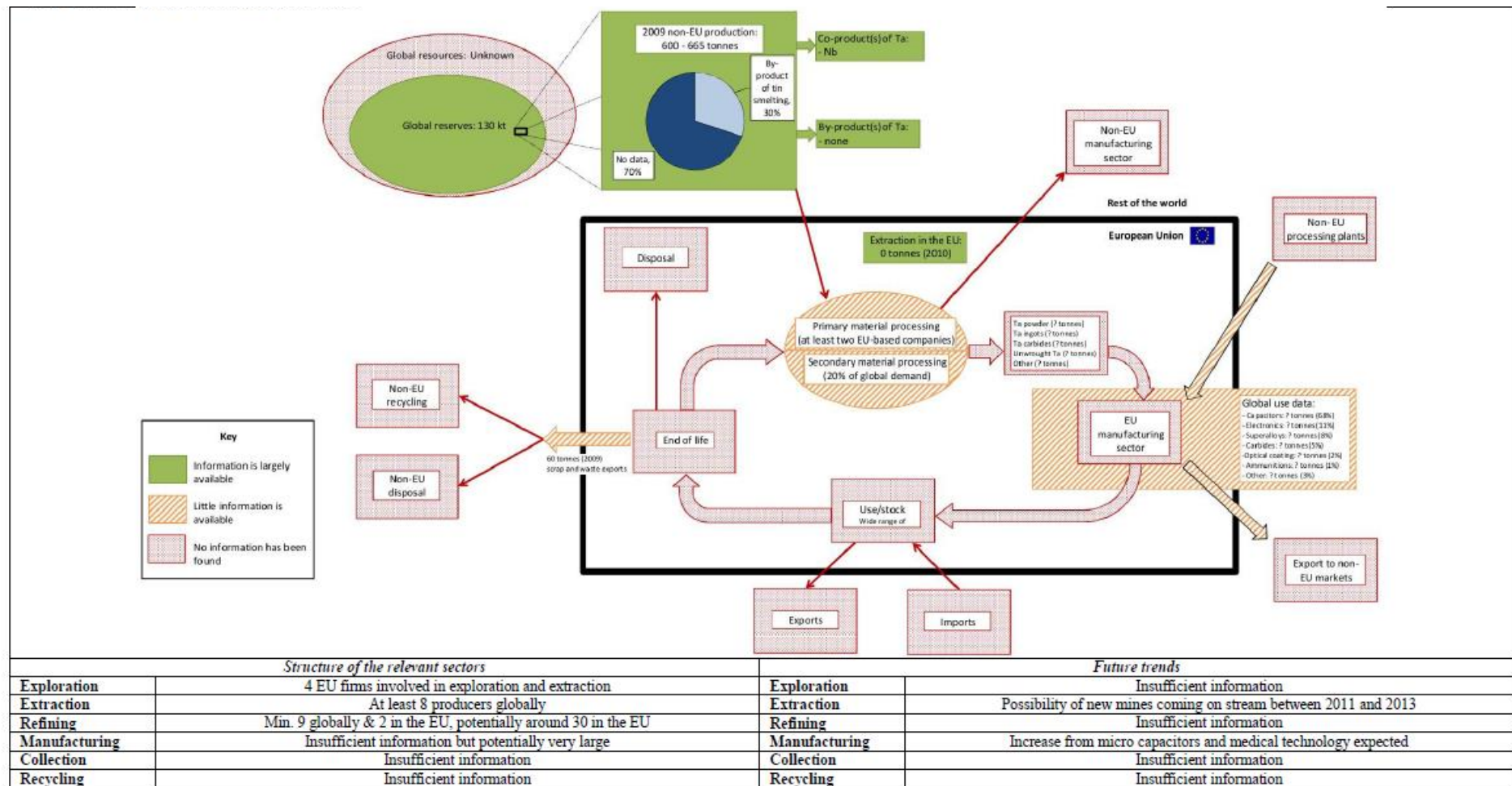


Figure 9. MFA for Tantalum

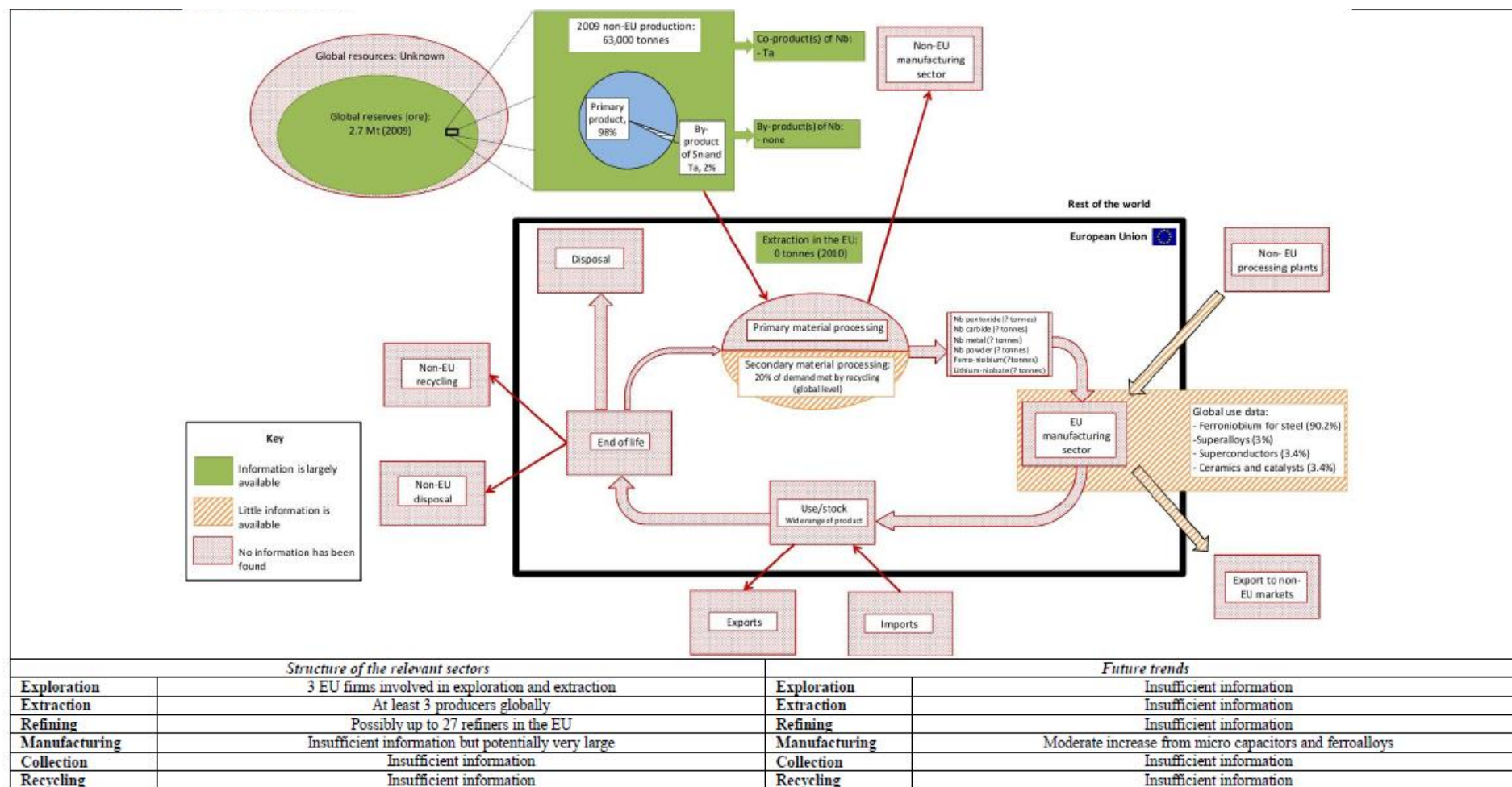


Figure 10. MFA for Niobium

5. TUNGSTEN

Tungsten (W) has been characterized by the EU as critical metal (European Commission, 2014) due to its high economic importance stemming from its wide range of applications, its lack of viable substitutes and the EU's dependence on imports and trade concerns arising from China's dominant market position.

According to the most recent US Geological Survey (USGS) report²² on the metal, world tungsten production reached 87,000 metric tons in 2015, an increase over 2014's 86,800 metric tons. Top 10 production countries in 2015 are China (71,000 metric tons), Vietnam (5,000 metric tons), Russia (2,500 metric tons), Canada, Bolivia (1,200 metric tons), Rwanda (1,000 metric tons), Austria (870 metric tons), Spain (730 metric tons), Portugal (630 metric tons) and UK (600 metric tons)²³.

The general flowsheet of tungsten production including mining, mineral processing and extractive metallurgy is shown in the Figure 11, while in Figure 12 a Sankey diagram is depicting the global mass flow of tungsten.

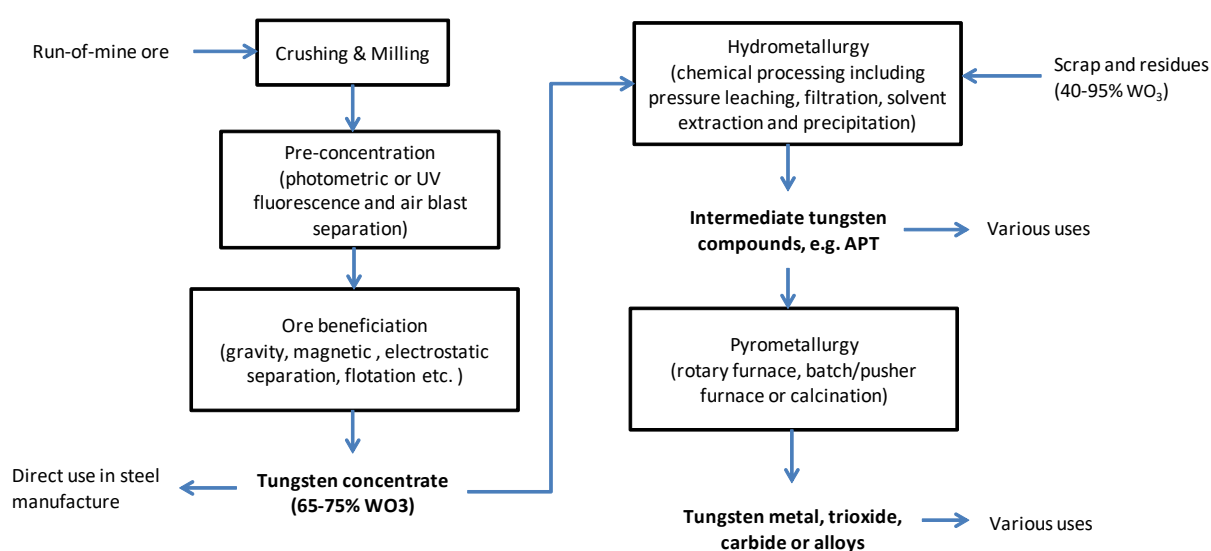


Figure 11. The general flowsheet of tungsten production

²² USGS, Mineral Commodity Summaries, 2016.

²³ A brief overview of the 10 countries that produced the most tungsten in 2015. Available from : <http://investingnews.com/daily/resource-investing/critical-metals-investing/tungsten-investing/top-tungsten-producing-countries-china-russia-canada>.

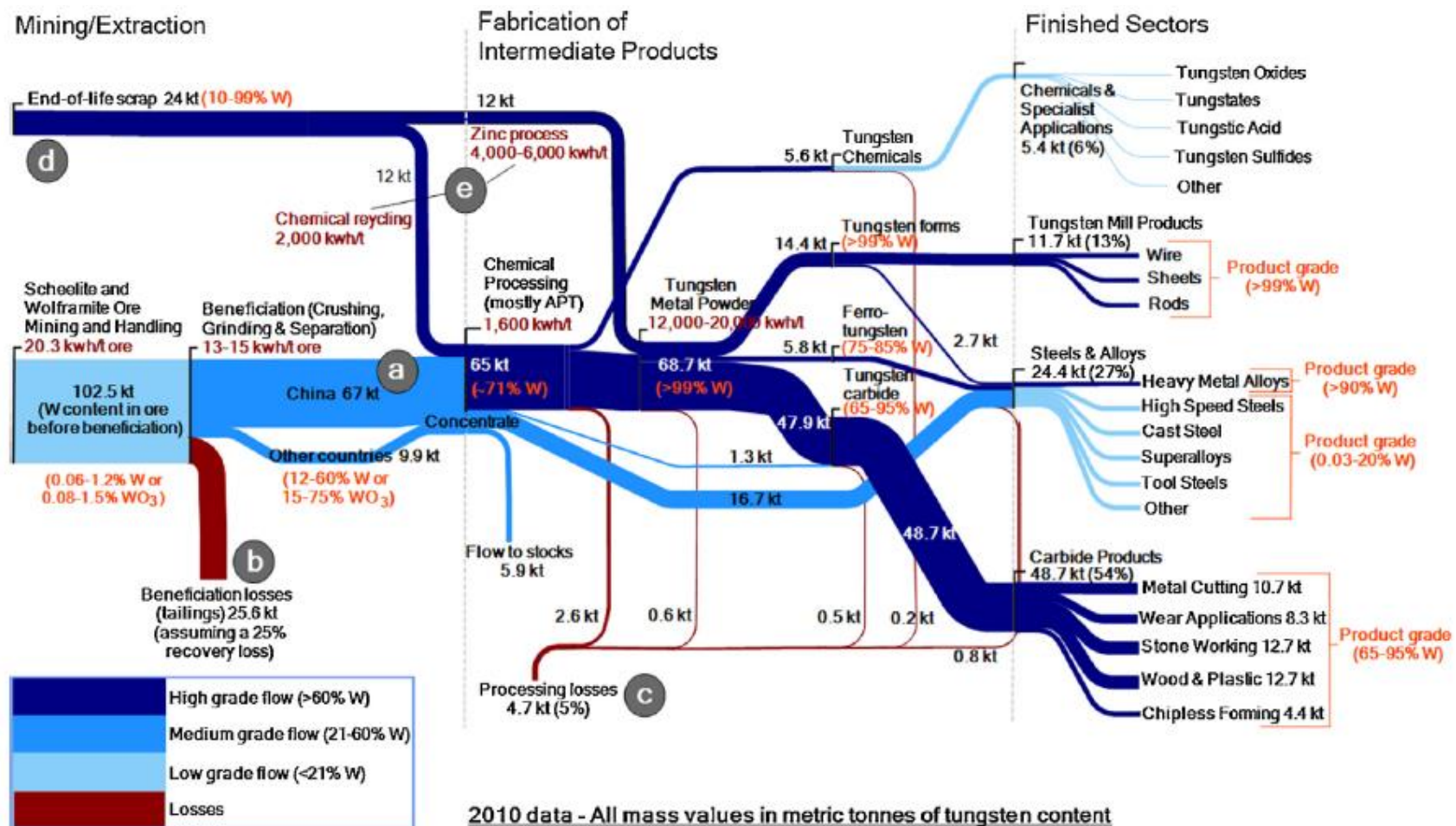


Figure 12. Global mass flow of tungsten²⁴

²⁴ David R. Leal-Ayalaa, Julian M. Allwooda,*, Evi Petavratzib, Teresa J. Brownb, Gus Gunnb, Mapping the global flow of tungsten to identify key material efficiency and supply security opportunities, Resources, Conservation and Recycling 103 (2015) 19–28.

MINING PRACTISES

There are numerous tungsten minerals, but only scheelite (CaWO_4) and wolframite ($(\text{Fe,Mn})\text{WO}_4$) are mined commercially^{25,26}. Wolframite accounts for about 70% of the total tungsten resources and scheelite accounts for about 30%. Wolframite mainly occurs in quartz veins and pegmatites associated with granitic intrusive rock. Scheelite occurs in contact metamorphic skarns, in high-temperature hydrothermal veins and greisens, and less commonly in granite pegmatites.

The beneficiation process generally consists of a pre-concentration step after crushing and grinding of the run-of-mine ore, followed by processing the pre-concentrate, concentrate cleaning or up-gradation step, and a final purification stage to meet the market specifications²⁷. Only scheelite is readily amenable to flotation. Wolframite, in contrast to scheelite, is paramagnetic. Thus, beneficiation techniques focus on gravity concentration and flotation for scheelite ore, and gravity and/or magnetic separation for wolframite. In addition, pre-concentration methods are usually used to discard a portion of the run-of-mine ore and increase the head grade prior to traditional beneficiation methods.

ENVIRONMENTAL CHALLENGES

As with any mining operation, tungsten mining is likely to have a significant environmental footprint, and environmental management plans have to be put in place to minimise the impact. Closure plans and environmental bonds are typically required from the onset of mining to ensure that the mine site is adequately cleaned up and rehabilitated once the ore deposit is exhausted.

Beside the mining operation itself (buildings and in the case of open pitting the “hole in the ground”), the most significant impacts are waste rock dumps and disposals of tailings (mill rejects). Tungsten deposits have typically a grade of less than 1% WO_3 and together with the swell factor (blasted rock takes up a far larger volume than in-situ material), tungsten mines produce volume-wise more waste than has originally been mined – in addition to the waste rock that has to be removed to access the tungsten ore.

Landscaping of waste piles is a common approach, and there have been examples where the original landscape has been enriched by the heritage of mining. However, in many cases, at least a part of the waste material needs to be backfilled into the void created by mining. In the case of underground mines, this can be a continuous process, while for open pits, adequate funding has to be kept to complete this task after mining has been completed.

Tailings of many tungsten projects are benign as they do not contain chemical reagents (or just minor quantities of fatty acids) and low levels of heavy metals. This allows projects being classified as non-class A facilities in the context of the EU Mining Waste Directive. Still, these tailings facilities constitute large engineered structures containing often millions of tonnes of fine-grained material and require adequate supervision and long-term stability planning. Many underground mining methods allow or require backfilling of voids, and depending on the grain size distribution and other physical properties, tailings may constitute a significant portion of the backfill material. However, the high amount of slimes in many tailings need to be

²⁵ Steffen Schmidt, P. Geo, Wolfram Bergbau & Hütten AG, Austria, From Deposit to Concentrate: The Basics of Tungsten Mining. Part 2: Operational Practices and Challenges, ITIA, Tungsten, Newsletter_Tungsten Mining, Dec.2012.

²⁶ Steffen Schmidt, P. Geo, Wolfram Bergbau & Hütten AG, Austria, From Deposit to Concentrate: The Basics of Tungsten Mining. Part 1: Project Generation and Project Development, ITIA, Tungsten, Newsletter_Tungsten Mining, June 2012.

²⁷ Krishna Rao N., Beneficiation of tungsten ores in India: A review, Bull. Mater. Sci., vol 19, April 1996, pp. 201-265.

removed, if stability of the backfill is of concern, especially if consolidated backfill is generated by mixing of the tailings with a binder such as cement and /or fly-ash.



Figure 13. Continuous rehabilitation and re-vegetation of a tailings pond, Mittersill tungsten mine, Austria.

As much as mining operations impact on their environment, the natural environment can also pose extraordinary challenges for the mine itself. In remote areas, infrastructure might be totally absent and the mine operator might find it challenging (or very costly) to attract qualified personnel. In contrast, in densely populated areas, there might be virtually no place for the mine, or it would need to be completely concealed to be accepted.



Figure 14, Figure 15, Figure 16: Challenges of remote and sensitive locations:

Top left: Pasta Bueno in the foothills of the Andes, Peru, where tailings placement on the steep slopes is particularly challenging.

Bottom left: Cantung, a fly-in fly-out operation in the Canadian North-West Territories.

Top right: At Mittersill, in the heart of the Austrian Alps, thousands of hikers on route to the Hohe Tauern National Park pass each year one of the biggest underground mining operations in Central Europe without hardly noticing it. All infrastructure is located underground (arrow indicates the portal) and the mill is located 3km further away in a far less sensitive location along a main highway. Ore is transported by conveyor through a tunnel to the mill.

TAILINGS RETREATMENT

Some tailings ponds of historic tungsten operations contain significant tungsten grades and appear an attractive target for re-treatment. Yet, the remaining grades are often a function of very high feed grades of the original plant, grain sizes are largely reduced, and “the best is gone”. There is normally a valid reason for the tailings grades being high, thus only if a clearly advanced or new beneficiation method is available, re-treatment is likely to return good results. If treatment was originally aiming for coarse mineralisation only, but the deposit contains also a significant portion of fine-grained mineralisation, or in the case of “primitive” artisanal to semi-industrial first-pass treatment, retreatment with more sophisticated methods will be successful. Weathering, oxidation and/or coating with reagents might be further challenges.

Tailings retreatment is currently undertaken for example in Russia (Zakamensk), NE Brazil (area around Currais Novos) and Australia (historic Mt Carbine mine).

On the other hand, tailings re-treatment might go hand-in-hand with the reclamation of abandoned mines and lead to an improved environmental performance.



Figure 17. : Tailings Retreatment: Rehandling and homogenisation of tailings at the historic Sritorrane mine near Chiang Mai ahead of transport to the flotation plant at Lampang Mineral and Metal (Thailand) Ltd.

MANAGEMENT OF TUNGSTEN MINING WASTES

A significant cause of environmental hazard in case of tungsten mining is the presence of high arsenic concentrations in the W deposits. Arsenopyrite-rich wastes from abandoned tungsten exploitations were studied to determine the composition and characteristics of the secondary phases formed under natural weathering conditions so as to assess their potential environmental risk²⁸. In some cases, W mining districts (for example in China) are located in close distance to communities and agricultural lands. In an extensive environmental study²⁹, field samples, including soil, water, rice, vegetable, fish, human hair and urine, were collected at an abandoned tungsten mine in Shantou City, southern China. Results showed that arsenic (As) concentration in agricultural soils ranged from 3.5 to 935 mg kg⁻¹. In addition, As concentration reached up to 325 µg L⁻¹ in the groundwater, and the maximum As concentration in local food were 1.09, 2.38 and 0.60 mg kg⁻¹. Health impact monitoring data revealed that As concentrations in hair and urine samples were up to 2.92 mg kg⁻¹ and 164 µg L⁻¹, respectively, indicating a potential health risk among the local residents.

Tungsten mining localities are characterized by intense arsenic (As⁺³ and As⁺⁵) pollution due to the geochemistry of W deposits. The As contamination can be easily spread to the soil of neighboring cultivation lands. The As-resistivity of specific bacteria in contaminated soils has been studied³⁰. Firmicutes (mainly *Bacillus* spp.) was found out that are tolerant in As⁺³ and As⁺⁵ contaminated soils (concentrations between 100 and

²⁸ Murciegoa, E. Álvarez-Ayusob, E. Pelliteroa, M.A. Rodríguezc, A. García-Sánchezb, A. Tamayod, J. Rubiod, F. Rubiod, J. Rubine, 2011, Study of arsenopyrite weathering products in mine wastes from abandoned tungsten and tin exploitations, *Journal of Hazardous Materials*, Volume 186, pp. 590–601.

²⁹ Chuan-ping Liua, Chun-ling Luo, Yun Gao, Fang-bai Li, Lan-wen Lin, Chang-an Wu, Xiang-dong Li, 2010, Arsenic contamination and potential health risk implications at an abandoned tungsten mine, southern China, *Environmental Pollution*, Volume 15, pp. 820–826.

³⁰ Angel Valverde, María González-Tirante, Marisol Medina-Sierra, Ignacio Santa-Regina, Antonio García-Sánchez, José M. Igual, Diversity and community structure of culturable arsenic-resistant bacteria across a soil arsenic gradient at an abandoned tungsten–tin mining area, *Chemosphere* 85 (2011) 129–134.

1000 mg/Kg). The above detection is promising concerning the bio remediation of W mining wastes rich in As content however further investigations should be performed.

Over the last decade, W mining wastes management has attracted the attention of scientists due to its high toxicity to living organisms. Ore tailings, metal dust, and other remnants of the exploitation of W may affect vegetation that has not previously been exposed to a high concentration of metals^{31, 32}. Below some innovative insights for the W mining wastes management are presented including phyto and bio remediation of the dumps or used of the rock wastes for construction applications.

In the recent study of Erdemir et al. (2015) is studied the behavior of flora near to an abandoned W mining district in Uludag mountain, Turkey (Figure 18)³³. The plant species tested were *Anthemis cretica* and *Trisetum flavescens* which are grown in this area and they are pioneer species on these contaminated sites. W levels in soils were found up to 1378.6 ± 672.3 mg/kg dry weight in contaminated areas. The leaf W contents of the selected plant species were found 41.1 ± 24.4 and 31.1 ± 15.5 mg/kg dry weight for *A. cretica* and *T. flavescens*, respectively. The results indicate that the elemental composition of species changed by the increased tungsten and some element concentrations in soil without detrimental effect. Consequently, the above species could potentially be used for the phyto-remediation of W in contaminated mining localities. Similar results concerning the significant retention of W amounts by plants were documented in case of Panasqueira mine, Portugal. Several plant species were examined while the highest W concentration was about 80 mg per kg of wet plant³⁴.

A major problem resulted by the W mining activity is the large amount of waste-rock tailings. Currently, several efforts have been performed for the valorization of this kind of wastes. It deserved be mentioned the example of Panasqueira, mine which consist and major worldwide tungsten mine locality. Panasqueira mining site have produced approximately 10 million m³ of mine wastes, over a period of more than 120 years (Figure 19), which clearly justifies the interest in their reuse³⁵. It has been proved that rocks wastes from Panasqueira mine can be used for construction applications due to their chemical stability and mechanical durability. Among to potential application has been proposed a new polymer-based construction material in technical-artistic applications, particularly as terrazzo tiles for outdoor use, fulfilling CE marking requirements. Coarse waste fractions from Panasqueira mining are highly suited as a component in the polymer-based construction without any prior treatment. Sculpture and architecture applications present an important potential interest (Figure 20).

³¹Koutsospyros A, Braida W, Christodoulatos C, Dermatas D, Strigul N (2006) A review of tungsten: from environmental obscurity to scrutiny. *J Hazard Mater* 136:1–19

³²Ernst WHO (1996) Bioavailability of heavy metals and decontamination of soils by plants. *Appl Geochem* 11:163–167

³³Umrhan Seven Erdemir, (2015). Hulya Arslan, Gurcan Guleryuz, Seref Gucer, Elemental composition of plant species from an abandoned tungsten mining area: Are they useful for biogeochemical exploration and/or phytoremediation purposes?, *Proceedings of the 14th International Conference on Environmental Science and Technology*.

³⁴ Sara C. Pé-Leve Santos, Mariana Eloy Cruz, António M. E. Barroso, Catarina P. S. Fonseca, Mauro Guerra, Maria Luísa Carvalho, José Paulo Santos, Elemental characterization of plants and soils in Panasqueira tungsten mining region, *J Soils Sediments* (2014) 14:778–784

³⁵ J.P. Castro-Gomes, Abílio P. Silva, Rafael P. Cano, J. Durán Suarez, A. Albuquerque, Potential for reuse of tungsten mining waste-rock in technical-artistic value added products, *Journal of Cleaner Production* 25 (2012) 34–41.



Figure 18: Investigation of flora behavior in an abandoned W mining locality.



Figure 19. : Partial view of Barroca Grande tailings (waste-rock and mud lagoon), in Panasqueira



Figure 20. : Prototype of urban furniture (outdoor bench) framed in a historical centre of a Portuguese city

PRIMARY SOURCES RECYCLING

The huge volumes of industrial waste produced today represent one of the world's greatest environmental problems and the recycling has emerged as a very important environmental issue nowadays due to the diminishing nature resources and the increasing amount of solid wastes. Tungsten tailing, as a tailing from the tungsten mine waste, also has brought some environmental problems, like contaminating soil, water and air in the surrounding areas. Several studies have shown that tungsten mine wastes can be used as geopolymeric binders or as a substitution material for cement^{36, 37, 38}. On the other hand, it deserves to be investigated the metallurgical treatment of the W tailings for the recovery of metallic tungsten. superconducting separation could be a promising technique for the tailings enrichment in W. The technique has been laboratory examined in case of uranium and gold and its application has been also proposed in case of tungsten mine tailings from England³⁹.

LCA IN TUNGSTEN

LCA studies in Tungsten are focused mainly on the post-mining fragment of the value chain and mainly connected to the production of Tungsten metal or Tungsten Carbide powder. Thinkstep company, owner of the Gabi LCA software has made a LCA study for the Tungsten mining, but is not available in commercial package. It is formed as data on demand with extra cost and with no information of the mine sites covered and if all the unit processes are included.

The available LCA study on the boundaries of mining site is limited and the only available data are derived from "Life Cycle Assessment of Metals: A Scientific Synthesis", where the LCIA results are depicted in Table 2.

³⁶ Yun Wang Choi, Yong Jic Kim, Ook Choi, Kwang Myong Lee, Mohamed Lachemi, Utilization of tailings from tungsten mine waste as a substitution material for cement, *Construction and Building Materials* 23 (2009) 2481–2486.

³⁷ Weizhen Liu, Ting Wu, Zhuo Li, XiaoJun Hao, Anxian Lu, Preparation and characterization of ceramic substrate from tungsten mine tailings, *Construction and Building Materials* 77 (2015) 139–144.

³⁸ Fernando Pacheco-Torgal, Joa~o Castro-Gomes, Said Jalali, Properties of tungsten mine waste geopolymeric binder, *Construction and Building Materials* 22 (2008) 1201–1211.

³⁹ J.H.P. Watson, P.A. Beharrell, Extracting values from mine dumps and tailings, *Minerals Engineering* 19 (2006) 1580–1587.

Table 2. Tungsten environmental data

IMPACT CATEGORY	VALUE	UNITS
Global warming potential	12.6	(kg CO ₂ eq / kg)
Cumulative energy demand	133	(MJ eq / kg)
Terrestrial acidification	0.29	(kg SO ₂ eq / kg)
Freshwater eutrophication	9.3E-6	(kg P eq / kg)
Human toxicity	3.4E-05	(CTUh/kg)

Another study performs an energy consumption per unit process in the mining of tungsten and in Table 3 the distribution is depicted during several steps of tungsten mining production. It is evident that Materials handling, Grinding and Beneficiation are the most energy intensive processes, while no data is depicted on the handling of the mining wastes.

Table 3. Energy consumption (per step and per t of W ore) during the tungsten production ⁴⁰.

PROCESSING STEP	ENERGY (kWh/ t ore)	COMMENTS
Ore mining & extraction		
Drilling	0.4	USA best practice across the whole metals sector
Blasting	2.2	
Digging	1.5	
Ventilation	1.3	
Dewatering	0.2	
Materials handling	14.7	
Beneficiation & processing		
Crushing	0.4	USA best practice
Grinding	14.4	USA best practice
Beneficiation general	12.8	Wolframite ore in India
Ore mining & extraction plus beneficiation & processing in Mittersill Mine, Austria	31.7	Scheelite concentrate production from ore in Mittersill, Austria

⁴⁰ David R. Leal-Ayalaa, Julian M. Allwooda,*, Evi Petavratzib, Teresa J. Brownb, Gus Gunnb, Mapping the global flow of tungsten to identify key material efficiency and supply security opportunities, Resources, Conservation and Recycling 103 (2015) 19–28.

6. TANTALUM & NIOBIUM

Niobium and tantalum usually occur together in the same type of mineral deposits and in minerals of similar characteristics. Very often, these metals are found in solid solutions⁴¹, as it is the case of columbite – tantalite (columbite series, also known as coltan), with the formula $(\text{Fe, Mg, Mn})(\text{Nb, Ta})_2\text{O}_6$, or the minerals from the pyrochlore group.

The mineral deposits sourcing niobium and tantalum are associated to some very specific types of igneous rocks. There are three main types of rocks that can contain profitable contents of these metals⁴²: Carbonatites and associated rocks, alkaline to peralkaline granites and syenites, and pegmatites.

Niobium is almost completely produced by 3 mines in the world, two of them in Brazil (Araxá and Catalão), accounting for the 90% of the total production, and one in Canada (Niobec). Although other countries can produce niobium, the world reserves of this metal are in these two countries.

Regarding tantalum, the largest reserves are located in Brazil and Australia. However, the combination between demand, lack of control on the production and commerce and the small-scale mining (and the association of both Nb and Ta to conflict minerals), lead to countries in the Great Lakes Region of Africa to dominate the tantalum production in the last years.

At present, there are no mines obtaining niobium or tantalum in Europe. There are some exploration projects, but none of them passed from the exploration status. These projects are mainly associated to the carbonatites and syenites from Finland and Greenland and the pegmatite deposits from Spain and Portugal.

Another potential source of Ta and Nb could be associated to tin deposits, which are also under investigation in Europe.

TANTALUM AND NIOBIUM MINING WASTES PROCESSING

Recent economic and technological changes in mineral processing techniques have enabled the processing of old dumped tailings of tantalum and niobium and more specifically tailings rich in columbite. This mineral contains oxide of niobium (Nb_2O_5) and oxide of tantalum (Ta_2O_5) in different proportions. Tailings from Rayfield (Nigeria) tailings dump was collected⁴³. Their enrichment in Ta and Nb was studied via different separation methods. The initial material contains 12.5 wt% columbite. The results showed that tailing has been successfully beneficiated to a higher columbite content of 69.6% and lower silica, zirconia, iron contents of 4.51%, 1.13% and 11.18% in that order using magnetic and gravity concentration methods. Recovery and separation efficiency using these concentration methods or process route are established to be 77.95% and 77.88% respectively.

The processing of mining tailings rich in Ta consists a subject with a high interest the last few years. It worth's be mentioned the case of Moolyella mines in Australia. Lithex Resources Ltd. company reported 1.9 Mt of

⁴¹ Černý, P.; Ercit, T.S. (1989) Mineralogy of Niobium and Tantalum: Crystal chemical relationships, paragenetic aspects and their economic implications. In: Lanthanides, Tantalum and Niobium. P. Möller, P. Černý and F. Saupé (Eds.). Special Publication of the Society for Geology Applied to Mineral Deposits, Vol. 7, Springer – Verlag Berlin Heidelberg. p.370.

⁴² BGS (2011) Niobium – tantalum. Mineral profile series. Minerals UK, BGS, p.26.

⁴³ Ayeni, F.A, Madugu, I. A, Sukop, P, Ibitoye, S. A, Adeleke, A. A, Abdulwahab, M, Secondary Recovery of Columbite from Tailing Dump in Nigerian Jos Mines Field, 2012. Journal of Minerals & Materials Characterization & Engineering, Vol. 11, No.6, pp.587-595.

inferred resources containing 20 g/t tantalum in tin mine tailings stockpiles at its Moolyella project. The tailings were generated between 1898 and 1986 and the company aims in the processing of the total amount⁴⁴.

The recycling of Ta and Nb mining wastes is currently applied in **industrial level** in Yichun mine, China. Yichun tantalum-niobium mine is located in Yuanzhou district, Yichun city, it has 7km² mining area, is one of the largest rare-metals mine in China⁴⁵. The explored reserve of Ta₂O₅ and Nb₂O₅ 18,500 and 14,900 tons respectively. 1500 tons of mine waste per day are processed. The enrichment technique which is applied comprises the following procedure: washed mineral is crushed by three open stages, the primary slurry is single selected, the qualified mineral is proceeded by stage grinding and stage separation, the fine tantalum and niobium is obtained by spiral chute and gravity separation. Despite the successful mine waste recycling further improvements should be done concerning the increase of the Ta and Nb recovery yield.

ENVIRONMENTAL CHALLENGES

The majority of niobium and tantalum deposits are correlated either (a) with pegmatite intrusions, where Nb-Ta contained in tantalite (Fe, Mn)Ta₂O₆ and columbite [(Fe,Mn)(Nb,Ta)₂O₆], or (b) with carbonatites (carbonate-silicate igneous rocks) contained in pyrochlore [(Na,Ca)₂Nb₂O₆(OH,F)] and euxenite [(Ca,Ce,U,Th)(Nb,Ta,Ti)₂O₆]. The above-mentioned minerals, in both cases, are known for their significant content in naturally occurring radioactive materials (NORMs) and especially in ²²⁶Ra, ²³⁸U, ²³²Th and ⁴⁰K. NORMs after the raw materials processing are converted to TENORMs (technologically enhanced natural radiation materials). The existence of TENORMs in waste-processing Ta-Ni ores has been described in Brazil^{46, 47} and in Nigeria⁴⁸. The environmental hazard is extremely intense in case of Nigeria where generated large quantities of tailings that are rich in these radioactive minerals and are mostly dumped haphazardly in the environment. Radiation monitoring in the area and at some processing mills shows high levels of dose rate with values as high as 100 aSv per hour for processed zircon. The in situ dose rate measurements for the public and workers showed that exposures significantly higher than the recommended values of 1 and 20 mSv/year, respectively.

Niobium ore deposits frequently contain a number of radionuclides at elevated concentrations. The release of radionuclide such as uranium and thorium could have an important impact on the neighboring environment and on the health of the workers. The exposure of miners to uranium, thorium, niobium has been investigated in case of a niobium mine located in Amazon forest⁴⁹. In this mine the minerals are extracted from the bed of small rivers using a floating river plant and from an open pit mine by mechanical techniques. Urine samples of miners were analyzed before and after their entrance in the working place. It was found out that Nb and U concentrations were significantly increased after the end of the working day.

⁴⁴ Lithex Resources Ltd., 2012, Maiden inferred mineral resource Moolyella project: Perth, Western Australia, Australia, March 12, 2 p.

⁴⁵ Yue-Long LIU^{1,a} and Jia LIU, The technical reconstruction for the tantalum-Niobium tailing mine in Jiangxi province, Advanced Materials Research, Vol. 1035, pp. 190-194.

⁴⁶ Anselmo Paschoa, José Godoy, 2002, The areas of high natural radioactivity and TENORM wastes, International Congress Series, Vol. 122, pp. 3–8.

⁴⁷ Anselmo S. Paschoa, 1998, Potential environmental and regulatory implications of naturally occurring radioactive materials (NORM), Applied Radiation and Isotopes, Vol. 49, pp. 189-196.

⁴⁸ I.I. Funtua, S.B. Elegba, 2005, Radiation exposure from high-level radiation area and related mining and processing activities of Jos Plateau, central Nigeria, International Congress Series 1276, pp. 401 – 402.

⁴⁹ L'gia M. Q. C. Juliao, Dunstana R. Melo, Wanderson O. Sousa, Maristela S. Santos, Paulo Ce'sar Fernandes and Maria Luiza D. P. Godoy, Exposure of workers in an mineral processing industry in Brazil, Radiation Protection Dosimetry (2007), Vol. 125, No. 1–4, pp. 513–515.

LCA IN NIOBIUM & TANTALUM

LCA studies in Niobium and Tantalum are restricted as well and open sources are those focused mainly on the post-mining fragment of the value chain and mainly connected to the processing stages for the metal production or alloys. Thinkstep company, owner of the Gabi LCA software has made a LCA study for the Tantalit Extraction, but is not available in commercial package. It is formed as data on demand with extra cost and with no information of the mine sites covered and if all the unit processes are included. In addition, Ecoinvent Database has data for the production of Tantalum Powder, but not for mining.

The available LCA study on the boundaries of mining site is limited and the only available data are derived from “Life Cycle Assessment of Metals: A Scientific Synthesis”, where the LCIA results are depicted in Table 4 and Table 5.

Table 4. Tantalum environmental data

IMPACT CATEGORY	VALUE	UNITS
Global warming potential	260	(kg CO ₂ eq / kg)
Cumulative energy demand	4,360	(MJ eq / kg)
Terrestrial acidification	1.7	(kg SO ₂ eq / kg)
Freshwater eutrophication	1.5E-01	(kg P eq / kg)
Human toxicity	1.2E-04	(CTUh/kg)

Table 5. Niobium environmental data

IMPACT CATEGORY	VALUE	UNITS
Global warming potential	12.5	(kg CO ₂ eq / kg)
Cumulative energy demand	172	(MJ eq / kg)
Terrestrial acidification	0.053	(kg SO ₂ eq / kg)
Freshwater eutrophication	3.7E-03	(kg P eq / kg)
Human toxicity	6.4E-06	(CTUh/kg)

In addition, an energy consumption flow for all the incorporated processes required to produce 1 tonne of Niobium is depicted in Table 6, where the mining contribution is only 10% compared to total and is equal to 37.5GJ/t.

Table 6. Energy consumption for the production of Niobium metal

Niobium production process	GJ/t	%	Probable energy type
Mining	37.5	10.17	Diesel Fuel
Beneficiation	15.7	4.26	Electricity
Chemistry	87.2	23.65	Coal
Reduction	151.8	41.17	Coal
Refinery	76.5	20.75	Electricity
Total	369	100.00	

7. MOLYBDENUM

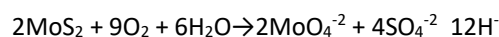
Molybdenum is mined as a principal ore and is also recovered as a byproduct of copper and tungsten mining. Molybdenum is contained in various minerals, but only molybdenite (MoS_2) is suitable for the industrial production of marketable molybdenum products. Molybdenite can occur as the sole mineralization in an ore body, but is often associated with the sulphide minerals of other metals, notably copper. The Mo content of viable ore bodies ranges between 0.01 and 0.25%⁵⁰.

According to the International Molybdenum Association (IMOA), molybdenum production reached a new high of 245 million kilograms in 2013⁵¹. The ten largest molybdenum producers accounted for over 60 percent of this total. In Europe only small number of molybdenum mines or projects were found. Munka mine in northern Sweden with the reserves of 1.7 Mt ore at 0.156% Mo. In Turkey North Aegean Copper Enterprises produced Cu concentrate 55,000 mt/y at 25-30% Cu and Mo concentrate 2,500 mt/y at 55-57% Mo in 2007 and started Havran Tepeoba molybdenum project in 2010 in Balıkesir Turkey^{52, 53}.

Generally, the ores are crushed and ground to fine particles and reported to flotation to separate the metallic minerals including molybdenite from the gangues, and in the case of copper/ molybdenum ores molybdenite is further separated by flotation from copper sulphide. The resulting concentrate contains between 85% and 92% MoS_2 . Further treatment by acid leaching can be used to dissolve impurities like copper and lead if necessary. Roasting in air at temperatures between 500 and 650°C converts MoS_2 concentrate into roasted molybdenite (MoO_3) concentrate. The resulting roasted molybdenite concentrate typically contains a minimum of 57% molybdenum, and less than 0.1% sulfur. Some of the by-product molybdenite concentrates from copper mines contain small quantities (<0.10%) of rhenium. Molybdenum roasters equipped to recover rhenium are one of the principal commercial sources for this rare metal.

ENVIRONMENTAL CHALLENGES

Leaching of metals during sulfide oxidation reactions in mining waste rock dumps presents a global environmental challenge. Molybdenum consist a metal which can be released at elevated concentrations during weathering of sulfidic waste rock while it can cause toxic effects at elevated environmental concentrations. Molybdenum is particularly harmful to ruminants which are susceptible to molybdenosis. Mo is released from mine wastes during the oxidative weathering of the sulfide ore mineral molybdenite (MoS_2) creating the anionic molybdate species (MoO_4^{2-})⁵⁴: Molybdate (MoO_4^{2-}) is strongly mobile in neutral to alkaline pH conditions.



⁵⁰ Molybdenum mining & processing Available from :<http://www.imoa.info/molybdenum/molybdenum-mining-processing.php>.

⁵¹ The 10 Biggest Molybdenum Producers 2013. Available from :<http://metals.about.com/od/Top-10-Producers/tp/The-10-Biggest-Molybdenum-Producers-2013.htm>.

⁵² E&MJ Engineering and Mining Journal, Global Business Reports, Turkey's mining industry. May 2014. Available from :http://gbreports.com/wp-content/uploads/2014/08/Turkey_Mining2014.pdf

⁵³ Özdoğan. Available from :<http://www.ozdogu.net/main.asp>.

⁵⁴ E.K. Skierszkan, K.U. Mayer, D. Weis, R.D. Beckie, 2016, Molybdenum and zinc stable isotope variation in mining waste rock drainage and waste rock at the Antamina mine, Peru, Science of the Total Environment 550, 103–113.

LCA IN MOLYBDENUM

LCA studies in Molybdenum are more vast and open compared to the other refractory metals. However, they are restricted mainly on the post-mining fragment of the value chain and mainly connected to the processing stages for the metal production. In the Mo case, Ecoinvent Database has data for the production of Molybdenum mining (concentrate), but the mass and energy balances for the unit processes are not open, which leads to aggregated results of the mining production as a whole. In addition, the International Molybdenum Association (IMOIA)⁵⁵ has an ongoing initiation over a life cycle assessment (LCA) program performing cradle-to-gate life cycle inventories (LCIs) of three molybdenum metallurgical products, followed by LCIs of eight molybdenum chemicals and an update to the metallurgical LCIs. From 2012 to 2014, IMOIA participated in a multi-metal industry initiative to harmonize the methodological approach to metal-related LCAs.

In the study of “Life Cycle Assessment of Metals: A Scientific Synthesis” The Mo environmental burdens are derived using inventory data of molybdenum metal, molybdenum concentrate (main product), and molybdenum concentrate (couple production from Cu ores) and lead to the results of Table 7 for the mining production.

Table 7. Molybdenum environmental data

IMPACT CATEGORY	VALUE	UNITS
Global warming potential	5.7	(kg CO ₂ eq / kg)
Cumulative energy demand	117	(MJ eq / kg)
Terrestrial acidification	0.16	(kg SO ₂ eq / kg)
Freshwater eutrophication	0.54	(kg P eq / kg)
Human toxicity	9 E-04	(CTUh/kg)

Rio Tinto has published a LCA study for the Molybdenum Oxide Environmental Profile and described the whole value chain of the oxide production⁵⁶. The Kennecott LCA project included a complete cradle to gate LCA study for copper cathode, gold, silver, molybdenum oxide and sulfuric acid produced by the mining operation. The results of the study are analysed in the following for the selected LCIA categories.

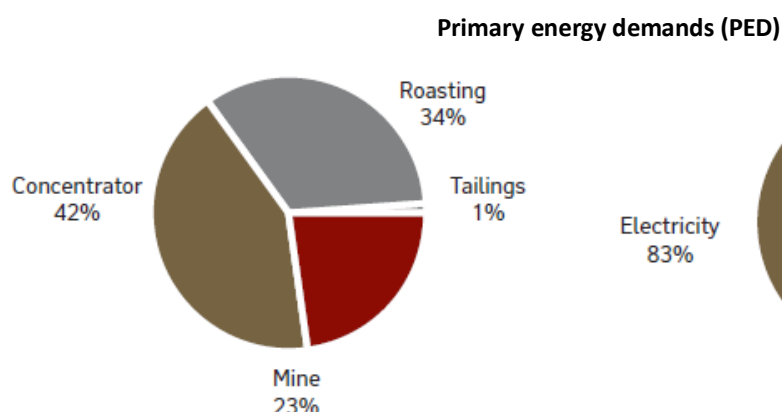


Figure 21: Breakdown of PED by process group for molybdenum

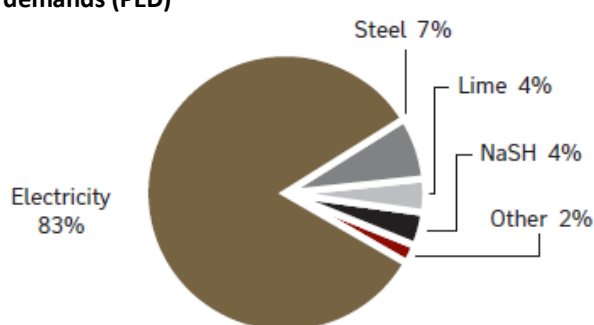


Figure 22: Breakdown of PED in concentrator process for molybdenum processing

⁵⁵ Anne Landfield Greig & Sandra Carey (2016), International Molybdenum Association (IMOIA) life cycle assessment program and perspectives on the LCA harmonization effort

⁵⁶ Rio Tinto (2006), Molybdenum Oxide Environmental Profile

In molybdenum oxide production, the concentrator contributes most to PED, drawing most of its energy for the milling process. The mining accounts for 23% of the total burden, while tailings only for 1%.

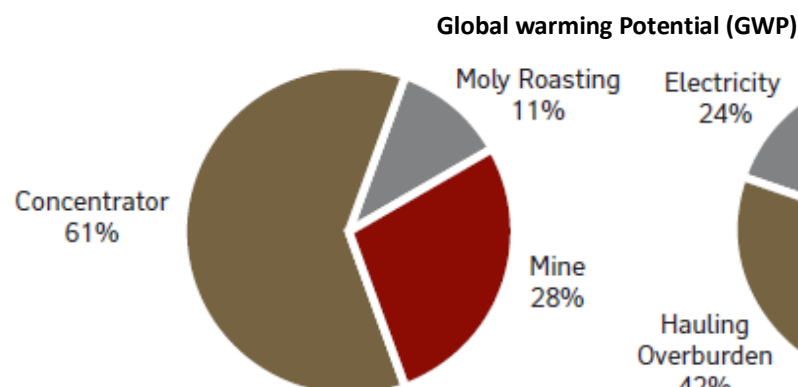


Figure 23: Breakdown of GWP by process group for molybdenum

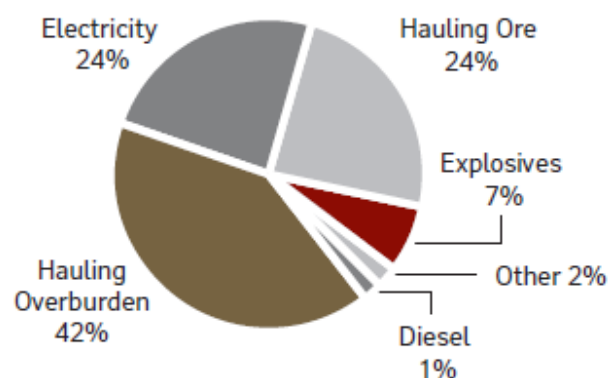


Figure 24: Breakdown of GWP in the mining process for molybdenum

Consistent with the analysis for PED, the concentrator dominates the GWP results for molybdenum oxide production system. Emissions associated with the concentrator are the result of greenhouse gases emitted through on-site and off-site electricity production. Diesel combustion and electricity consumption at the mine is second largest contributor of greenhouse gases in the molybdenum production system. Because the GWP breakdown for the concentrator is similar to the PED breakdown on the previous figures, the breakdown for the next most significant contributor, mining is shown.

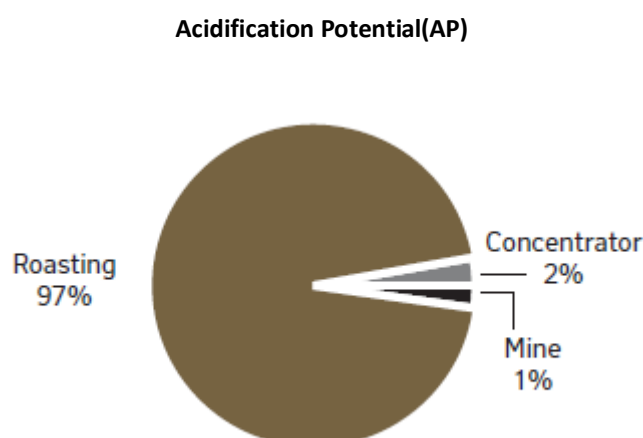


Figure 25: Breakdown of AP by process group for molybdenum

The majority of AP emissions are generated during the off-site roasting process. This is a result of Sox emissions from roasting facility, which are created by the removal of sulfur from the molybdenum sulfide in the roasting process and the combustion of natural gas. A breakdown of emissions within the roasting process has not been provided because detailed data beyond what was made available by IMoA was not available for this process.

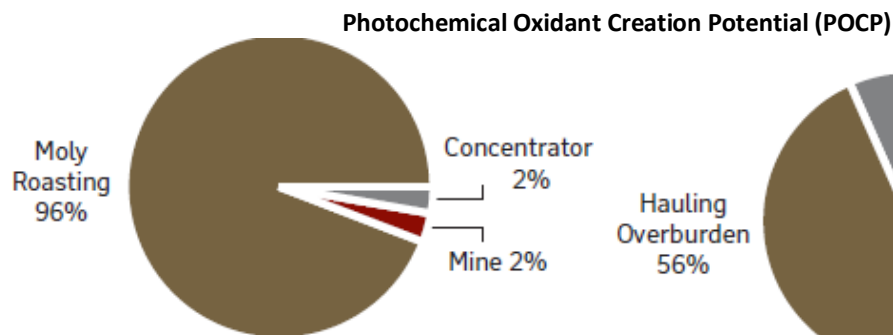


Figure 26: Breakdown of POCP by process group for molybdenum

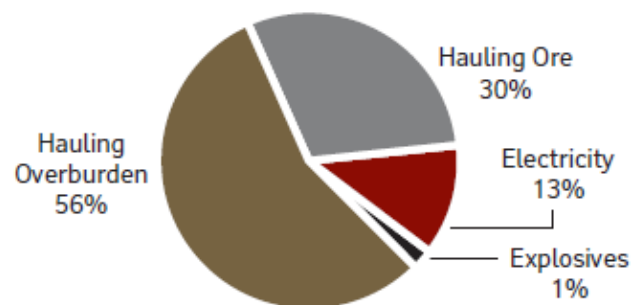


Figure 27: Breakdown of POCP in the mining of molybdenum

The majority of POCP emissions are generated during the off-site roasting process. This is a return of nitrogen oxide emissions generated at the roasted facilities as a result of the combustion of natural gas in the roasting furnaces. As with AP, a breakdown of emissions within the roasting process is not available because of the lack of Kennecott-generated data on this process and the resulting need to use IMoA data for the off-site roasting model. However, emissions attributed to mining are shown.

8. RHENIUM

Rhenium is the rarest element in the Earth's crust. Rhenium is probably not found free in nature, but occurs in amounts up to 0.2% in the mineral molybdenite, the major commercial source. Some molybdenum ores contain 0.001% to 0.2% rhenium. Most extracted rhenium is a byproduct of copper mining, with about 80 percent recovered from flue dust during the processing of molybdenite concentrates from porphyry copper deposits⁵⁷. Molybdenite, which commonly contains between 100 and 3,000 parts per million rhenium, is the principal source of rhenium in porphyry copper deposits. Porphyry copper ores typically contain less than 0.5 grams per metric ton rhenium, but rhenium production is feasible because of the large ore tonnage processed (hundreds of millions to billions of metric tons, the presence of sufficient molybdenite to make its recovery economically practical, and the presence of specialized facilities that allow rhenium recovery from molybdenite).

Worldwide mine production of rhenium in 2012 was 52,600 kilograms (kg) and about 27,000 kg were produced from porphyry copper mines in Chile⁵⁸. Molybdenite from porphyry-type deposits of Mo and Cu-Mo ores located in Chile, USA and Peru, where rhenium content is in the range 0.025 to 0.07%, is the most important source of rhenium. Rhenium can be also found as an accompanying element in sedimentary sulfide deposits of copper ores in Kazakhstan, Uzbekistan, Armenia, Russia, Iran, Mongolia, Congo/Kinshasa (Cu-Co ores) and China.

It should be pointed out that rhenium is a metal which is not independently produced from primary resources. It is a so called accompanying metal for copper or molybdenum ores and is recovered during their production.

ENVIRONMENTAL CHALLENGES

Rhenium extraction is usually performed as a byproduct in large scale sulfide polymetallic mines. The main environmental impact of sulfide deposits is the existence of drainage phenomena. Island Copper mine in Canada is a polymetallic ore deposit containing also rhenium. Island Copper Mine is located on northern Vancouver Island⁵⁹. The mine began production in 1971, and was the third largest copper mine in Canada when it was closed in 1995 due to resource depletion. An estimated 1.3 million tonnes of copper, 31,000 tonnes of molybdenum, 31.7 tonnes of gold, 336 tonnes of silver, and 27 tonnes of rhenium were extracted over the lifetime of the mine. More than a billion tonnes of material was excavated, which produced an oval-shaped pit with a depth 400 metres below sea level. During mining operations, the excavated ore was ground up and processed in a slurry by floatation to remove the copper and molybdenum. Waste rock was dumped in piles on site and along the shore, and the tailings produced from the copper processing operations were placed on the seabed⁶⁰. However, in 1986, acid rock drainage (ARD) from the waste rock dumps was observed, and considerable effort was put into monitoring and evaluating stream flow volumes and dissolved metal content⁶¹.

⁵⁷ USGS Mineral Resources Program, Rhenium—A Rare Metal Critical to Modern Transportation. Available from :<http://pubs.usgs.gov/fs/2014/3101/pdf/fs2014-3101.pdf>.

⁵⁸ Polyak, D.E., 2013, Rhenium [advance release], in Metals and minerals: U.S. Geological Survey, Minerals Yearbook 2012, v. I, 5 p., accessed August 12, 2014. Available from : <http://minerals.usgs.gov/minerals/pubs/commodity/rhenium/myb1-2012-rheni.pdf>.

⁵⁹ Welchman, B. and C. Aspinall. A Sustainable Legacy: Utilizing Mine Assets Post-Closure Island Copper Mine, Proceedings of the 24th Annual British Columbia Mine Reclamation Symposium, 2000, The Technical and Research Committee on Reclamation.

⁶⁰ Rescan. Island Copper Mine, Projects, 2011

⁶¹ Horne, I.A. The Development of a Closure Plan for Island Copper Mine, Proceedings of the 17th Annual British Columbia Mine Reclamation Symposium, 1993, The Technical and Research Committee on Reclamation.

LCA IN RHENIUM

The LCA studies performed on Rhenium mining is limited. The only available data are derived from “Life Cycle Assessment of Metals: A Scientific Synthesis”, where the Rhenium is considered to be recovered primarily from the roasting of molybdenite (MoS_2) from porphyry copper. The LCIA results are depicted in Table 8.

Table 8. Rhenium environmental data.

IMPACT CATEGORY	VALUE	UNITS
Global warming potential	450	(kg CO ₂ eq / kg)
Cumulative energy demand	9,040	(MJ eq / kg)
Terrestrial acidification	11	(kg SO ₂ eq / kg)
Freshwater eutrophication	3.5E+01	(kg P eq / kg)
Human toxicity	5.9E-02	(CTUh/kg)

9. CONCLUSIONS

The initial scope of this report has been the evaluation of the mining production of the refractory metals in environmental terms with the utilization of LCA methodology. However, this proved to be ambitious since the limitation of data in mass and energy balances per unit process in the mining production of the refractory metals is evident and restricted only to LCA software companies and respective mining companies.

The complexity of the raw materials value chains and the demand on inventory data over input and output flows within this chain is challenging for the sector. Given that refractory metals industry is even restricted in compiled production data per year in some cases makes evident the fact that a LCA analysis was not feasible within this study. However, throughout this deliverable LCA studies for the refractory metals on the mining boundaries have been described, but the approaches are in the logic of a black box. In such a way, the environmental assessment of the incorporated unit processes of the mining operation including waste creation and management is not possible. This clearly leads to a challenge for the refractory metals sector

- **Challenge 1.** Creation of LCI datasets for the mining boundaries of the refractory metals with specific focus on waste management.

The available Material Flow Analysis for Tungsten, Tantalum and Niobium clearly demonstrated the lack of available data for these refractory metals to cover the aspect of a life cycle approach not only in terms of environmental management in mining sites, but for the whole value chain as whole.

- **Challenge 2.** The lack of data in both LCA and MFA forms a gap in a Life Cycle Thinking approach and in a Circular Economy mindset. This is a clear challenge for the stakeholders of the refractory metals and needs to be addressed.

A significant cause of environmental hazard in case of **tungsten** mining is the presence of high arsenic concentrations in the W deposits. Tungsten mining localities are characterized by intense arsenic (As^{+3} and As^{+5}) pollution due to the geochemistry of W deposits. The As contamination can be easily spread to the soil of neighboring cultivation lands. In an extensive environmental study, field samples, including soil, water, rice, vegetable, fish, human hair and urine, were collected at an abandoned tungsten mine in Shantou City, southern China. Results showed that arsenic (As) concentration in agricultural soils, in the groundwater, and in local food were high indicating a potential health risk among the local residents. The As-resistivity of specific bacteria in contaminated soils has been studied, where Firmicutes was found out that are tolerant in As^{+3} and As^{+5} contaminated soils. This is promising concerning the bio remediation of W mining wastes rich in As content however further investigations should be performed. This leads to two challenges:

- **Challenge 3.** Tungsten waste management to prevent arsenic pollution and development of actions/technologies to remediate W mining waste rich in As.
- **Challenge 4.** Environmental regulations in low developed countries, where W mines operate to meet EU standards and avoid causing bad examples that cause bad name for the RM sector.

A major problem and prospect opportunity resulted by the W mining activity is the large amount of waste-rock tailings. Currently, several efforts have been performed for the valorization of this kind of wastes. It deserved be mentioned the example of Panasqueira, mine which consist and major worldwide tungsten mine locality. Panasqueira mining site have produced approximately 10 million m^3 of mine wastes, over a period of more than 120 years (Figure 19), which clearly justifies the interest in their reuse⁶². It has been proved that rocks

⁶² J.P. Castro-Gomes, Abílio P. Silva, Rafael P. Cano, J. Durán Suarez, A. Albuquerque, Potential for reuse of tungsten mining waste-rock in technical-artistic value added products, Journal of Cleaner Production 25 (2012) 34-41.

wastes from Panasqueira mine can be used for construction applications due to their chemical stability and mechanical durability. Among to potential application has been proposed a new polymer-based construction material in technical-artistic applications, particularly as terrazzo tiles for outdoor use, fulfilling CE marking requirements. Coarse waste fractions from Panasqueira mining are highly suited as a component in the polymer-based construction without any prior treatment. Sculpture and architecture applications present an important potential interest.

- **Challenge 5.** Tailings and mining waste valorization of W primary production.

The majority of **niobium and tantalum** deposits are correlated either (a) with pegmatite intrusions, where Nb-Ta contained in tantalite $(\text{Fe, Mn})\text{Ta}_2\text{O}_6$ and columbite $[(\text{Fe, Mn})(\text{Nb, Ta})_2\text{O}_6]$, or (b) with carbonatites (carbonate-silicate igneous rocks) contained in pyrochlore $[(\text{Na, Ca})_2\text{Nb}_2\text{O}_6(\text{OH, F})]$ and euxenite $[(\text{Ca, Ce, U, Th})(\text{Nb, Ta, Ti})_2\text{O}_6]$. The above-mentioned minerals, in both cases, are known for their significant content in naturally occurring radioactive materials (NORMs) and especially in ^{226}Ra , ^{238}U , ^{232}Th and ^{40}K . NORMs after the raw materials processing are converted to TENORMs (technologically enhanced natural radiation materials). The existence of TENORMs in waste-processing Ta-Ni ores has been described in Brazil and in Nigeria. The environmental hazard is extremely intense in case of Nigeria where generated large quantities of tailings that are rich in these radioactive minerals and are mostly dumped haphazardly in the environment. Radiation monitoring in the area and at some processing mills shows high levels of dose rate with values as high as 100 aSv per hour for processed zircon. The in situ dose rate measurements for the public and workers showed that exposures significantly higher than the recommended values of 1 and 20 mSv/year, respectively.

Niobium ore deposits frequently contain a number of radionuclides at elevated concentrations. The release of radionuclide such as uranium and thorium could have an important impact on the neighboring environment and on the health of the workers. The exposure of miners to uranium, thorium, niobium has been investigated in case of a niobium mine located in Amazon forest. In this mine the minerals are extracted from the bed of small rivers using a floating river plant and from an open pit mine by mechanical techniques. Urine samples of miners were analyzed before and after their entrance in the working place. It was found out that Nb and U concentrations were significantly increased after the end of the working day.

- **Challenge 6.** Waste management of hazardous tailings in niobium-tantalum primary production.

Leaching of metals during sulfide oxidation reactions in mining waste rock dumps presents a global environmental challenge. **Molybdenum** consist a metal which can be released at elevated concentrations during weathering of sulfidic waste rock while it can cause toxic effects at elevated environmental concentrations. Molybdenum is particularly harmful to ruminants which are susceptible to molybdenosis. Mo is released from mine wastes during the oxidative weathering of the sulfide ore mineral molybdenite (MoS_2) creating the anionic molybdate species

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seabed. However, in 1986, acid rock drainage (ARD) from the waste rock dumps was observed, and considerable effort was put into monitoring and evaluating stream flow volumes and dissolved metal content.