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Mapping the secondary resources in the EU (mine tailings, industrial waste)

Authors : Dr. SANTIAGO CUESTA-LOPEZ (ICCRAM) Rocío Barros (ICCRAM), Mroueh Ulla-Maija (VTT), Stefan Willersinn (UNIKL), Yang Xiao Sheng (GTK)

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| Author(s) | Dr. SANTIAGO CUESTA-LOPEZ Rocío Barros (ICCRAM), Mroueh Ulla-Maija (VTT), Stefan Willersinn (UNIKL), Yang Xiao Sheng (GTK) |
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Summary

Deliverable 3.1 'Mapping the secondary resources in the EU (mine tailings, industrial waste)' has been produced in the context of WP3 'Secondary Resources (industrial waste, tailings)', Task 3.1 'Mapping'. The main purpose of deliverable 3.1 is to map important waste streams from mining, processing and extraction that contains tungsten, tantalum, rhenium, molybdenum and niobium in Europe.

Approval

| Date | By |
|---------------------|--------------------------------------|
| 2016-05-16 16:39:21 | Mrs. Lena SUNDQVIST OEQVIST (Swerea) |
| 2016-05-17 07:36:14 | Mr. BOURG STÉPHANE (CEA) |

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1 INTRODUCTION

Mining waste can be defined as a part of the materials that result from the exploration, mining and processing of substances governed by legislation on mines and quarries. It may consist of natural materials without any modification other than crushing (ordinary mining waste, unusable mineralised materials (see definition in glossary) or of natural materials, processed to varying degrees during the ore-processing and enrichment phases, and possibly containing chemical, inorganic and organic additives [1].

Mineral processing wastes are referred to in the Resource Conservation and Recovery Act (RCRA) as wastes that are generated during the extraction and beneficiation of ores and minerals. These wastes can be subdivided into a number of categories: waste rock, mill tailings, coal refuse, wash slimes, and spent oil shale [2].

- **Waste rock** generally consists of coarse, crushed, or blocky material covering a range of sizes, from very large boulders or blocks to fine sand-size particles and dust. Waste rock is typically removed during mining operations along with overburden and often has little or no practical mineral value. Types of rock included are igneous (granite, rhyolite, quartz, etc.), metamorphic (taconite, schist, hornblende, etc.) and sedimentary (dolomite, limestone, sandstone, oil shale, etc.). It is estimated that approximately 0.9 billion metric tonnes (1 billion tonnes) of waste rock are generated each year in the United States [3].
- **Mill tailings** consist predominantly of extremely fine particles that are rejected from the grinding, screening, or processing of the raw material. Typically, mill tailings range from sand to silt-clay in particle size, depending on the degree of processing needed to recover the ore. The basic mineral processing techniques involved in the milling or concentrating of ore are crushing, then separation by any one or more of the following methods including heavy media separation, gravity separation, froth flotation, or magnetic separation. About 500 million tonnes per year of mill tailings are generated from copper, iron, taconite, lead, and zinc ore concentration processes and uranium refining, as well as other ores, such as barite, feldspar, gold, molybdenum, nickel, and silver.
- **Coal Refuse** is the reject material that is produced during the preparation and washing of coal. Coal naturally occurs interbedded within sedimentary deposits, and the reject material consists of varying amounts of slate, shale, sandstone, siltstone, and clay minerals, which occur within or adjacent to the coal seam, as well as some coal that is not separated during processing.
- **Wash Slimes** are by-products of phosphate and aluminum production. These wastes are generated from processes in which large volumes of water are used, resulting in slurries having low solids content and fines in suspension. They generally contain significant amounts of water, even after prolonged periods of drying. In contrast, tailings and fine coal refuse, which are initially disposed of as slurries, ultimately dry out and become solid or semi solid materials.
- **Spent Oil Shale** is mined as a source of recoverable oil. Spent oil shale is the waste by-product remaining after the extraction of oil. It is a black residue generated when oil shale is retorted (vaporized and distilled) to produce an organic oil-bearing substance called kerogen.
- The study “Management of mining, quarrying and ore-processing waste in the European Union” [2] describes **slags** as waste produced from the burned ore or concentrate to remove certain components in order to produce a purer marketable product. These products are found either accumulated near the mine, if smelting was conducted nearby, or often stacker in heaps near the smelter.

Waste rock and mill tailings from mineral processing could be major secondary sources of metals including tungsten, tantalum, molybdenum, niobium and rhenium. Large amounts of waste rock are produced from surface mining operations, such as open-pit copper, phosphate, uranium, iron, and taconite mines. Small amounts are generated from underground mining.

1.1 PREVIOUS RESEARCH

Antropogenic concentrations related to the mining and metallurgical industries such as mine wastes and unprocessed products (run-of-mine ore, unprocessed ore stockpiles, mine waste dumps, barren overburden), ore processing wastes (cobbing wastes, wash tailings, flotation tailings, leach residues, magnetic separation tailings) and treatment wastes (smelter wastes, flue dusts, roasting residues, chemical treatment wastes, leach tailings, ashes, coke plant residues, etc.) are compiled in the Project “PROMINE” [4]. This project focuses on those commodities with the highest potential in terms of volume / tonnage content for recovery.

The table below shows a quantitative summarize of the most promising sites for recovery in Europe regarding its potential (volume / tonnage).

Table 1. Potential sites for recovery in Europe (Source: PROMINE)

| Commodity | Total number of sites | Number of sites with calculated potential | Potential Summatory |
|-----------|-----------------------|---|---------------------|
| Mo | 65 | 28 | 7737 |
| Nb | 18 | 8 | 379 |
| Re | 7 | 1 | 13.9 |
| Ta | 11 | 0 | 0 |
| W | 127 | 24 | 25 382 |

2 TUNGSTEN

Figure 1 represents the flowchart of production of tungsten products.

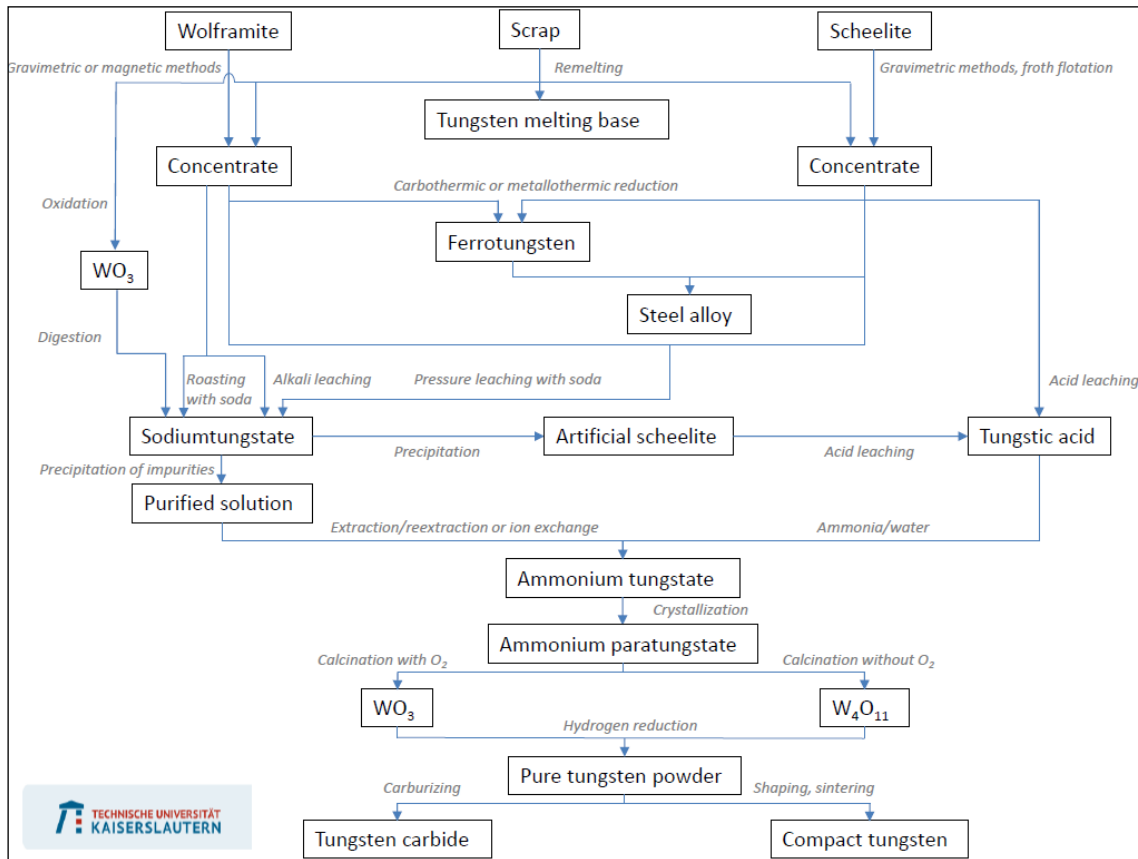


Figure 1. Tungsten flowchart

The global mass flows tungsten in 2010 was reported in the paper [5]. In 2010 the total 102.5 million tonnes tungsten mass was contained in the mined ore from which 76.9 kt was produced in the tungsten concentrate. Total 30 300 WO_3 tonnes were lost in the waste streams in which 25 600 t WO_3 was lost in the mine tailings and 4700 WO_3 t in the processing residues. In 2010 WO_3 about 24% of the total tungsten production was from the end-of-life scrap. But the recovery of lost tungsten in the mine tailings and the processing residues has not been statistically reported.

Historical tungsten mine tailings contain slimes (ultrafine grain size) in which tungsten minerals are difficult to be recovered such as in Panasqueira mine (a large tungsten mine) in Portugal. Currently, Panasqueira mining generates almost 100 tonnes of waste-rock per day. Mineral extraction and processing produce, primarily, two main types of mine tailings, accordingly to its grain size: coarse waste-rock tailings (sterile material) derived from rock blasting and waste-mud tailings from crushing and milling conveyed by pipelines into lagoons (mud dams), amounting to several million tonnes. In the 1980's Panasqueira mining was generating of about 300 tonnes of waste-rock tailings per day; currently, it is still generating almost 100 tonnes per day [6].

Avila et al. reported the geochemistry and mineralogy of mill tailings from Panasqueira mine [7]. The total tailing volume of was around 1.9 million m³. The average metal content in the tailings is presented in Table 2.

Table 2. Average metal content in tailings

| Metal | Concentration in mg/kg |
|-------|------------------------|
| Ag | 40 |
| As | 4.7 |
| Ba | 182 |
| Cd | 79 |
| Co | 5 |
| Cu | 3.5 |
| Mn | 641 |
| Ni | 34 |
| Pb | 171 |
| Sn | 702 |
| V | 81 |
| W | 2.4 |
| Zn | 460 |

The Panasqueira deposit consists of a series of stacked, sub-horizontal hydrothermal quartz veins intruding into the Beira schists and shales. The mineralogy of these tailings was found to be mainly quartz and muscovite, determined by XRD diffraction. Kaolinite, illite-montmorillonite, montmorlo-nite-vermiculite, and chlorite and also arsenopyrite, wolframite, and natrojarosite are also present in the mineralogy of these tailings.

In Luanchuan mine in China the tailings of the Molybdenum flotation contain scheelite with grade 0.143% WO₃ [8] [9]. The chemical compositions of the Molybdenum flotation tailings and the particle size distribution and tungsten distributions in the size fractions are shown in Table 3 and Table 4

Table 3. The chemical compositions of the molybdenum flotation tailings in Luanchuan mine

| | Ore | Tailings |
|--------------------------------|-------|----------|
| Mo | 0.224 | 0.02 |
| WO ₃ | 0.148 | 0.143 |
| S | 1.87 | 0.64 |
| P | 0.24 | 0.18 |
| As | 0.059 | 0.049 |
| Fe ₂ O ₃ | 6.97 | 6.67 |
| SiO ₂ | 43.64 | 46.88 |
| Al ₂ O ₃ | 3.95 | 3.4 |
| CaO | 27.06 | 25.36 |
| CaCO ₃ | 6.73 | 5.24 |
| MgO | 1.77 | 1.46 |
| CaF ₂ | 4.76 | 5.02 |
| Cu | 0.038 | 0.02 |
| Pb | 0.035 | 0.024 |
| Au g/t | 0.96 | 0.56 |
| Ag g/t | 20.33 | 6.03 |

Table 4. Particle size distribution and tungsten distributions in the size fraction

| Size fraction, mm | Weight, % | WO ₃ grade, % | WO ₃ distribution, % |
|-------------------|------------|--------------------------|---------------------------------|
| +0.2 | 3.96 | 0.028 | 0.78 |
| -0.2+0.154 | 18.35 | 0.042 | 5.39 |
| -0.154+0.105 | 12.55 | 0.081 | 7.11 |
| -0.105+0.074 | 16.47 | 0.134 | 15.43 |
| -0.074+0.037 | 10.07 | 0.242 | 17.04 |
| -0.037+0.019 | 11.87 | 0.228 | 18.93 |
| -0.019+0.010 | 17.58 | 0.189 | 23.29 |
| -0.010 | 9.15 | 0.188 | 12.03 |
| Total | 100 | 0.143 | 100 |

The processing tungsten-bearing dumps and tailings produced from the Barruecopardo tungsten mine in Spain have the data in Table 3 [10]. The material in the western part in this mine has higher tungsten grades of 0.1% WO₃ and with a higher proportion of fine material amenable to direct spiral concentration.

Table 5. Contents of tungsten in the processing tungsten-bearing dumps and tailings produced from the Barruecopardo tungsten mine

| | Average WO ₃ % | | Average distribution | |
|-----------------|---------------------------|-------|----------------------|-------|
| | -1 mm | +1 mm | -1 mm | +1 mm |
| Tailings | 0.093 | 0.088 | 73% | 27% |
| Dumps | 0.044 | 0.022 | 38% | 62% |

The Bom-Gorkhon tungsten ore deposits are located in the Petrovsky-Trans-Baikal area of Chita region in Russia. The Vein deposit contains tungsten mainly in the form of hubnerite (74-95%), the rest is scheelite. From the explored reserves 13.4 thousand tonnes have relatively high grade (WO₃ 0.917%). The enrichment of Bom-Gorkhon ore by a gravity method hundred thousand tonnes of the tailings with WO₃ content from 0.1 to 0.35% were accumulated. Besides the main element (tungsten), there are associated components – bismuth and tin [11].

Tin tailings in Bolivia contains tungsten (grade of 0.64% WO₃), and also Cu (grade of 0.84%) and Sn (grade of 0.84%), Tungsten is predominately present in wolframite and tin in cassiterite [12].

In order to effectively utilize industrial wastes, ceramic substrates was successfully prepared by conventional ceramic sintering process using tungsten mine tailings from different production regions in China as the main raw material [13].

Tailings from Cantung Mine in Canada was reported by North American Tungsten Corporation Ltd [14]. The amount of the material accumulated from 1971-2007 reached 3.7 to 4.1 Mt (short tonnes) with the grade of 0.29-0.35% WO₃ and 0.24-0.28% Cu.

In La Parrilla mine (a tungsten mine) in Spain [15] the 7 Mt of ore was processed from which some 2 Mm³ of coarse tailings and 1.2 Mm³ of slimes were produced during the period 1968-1986 with a grade of 0.28% WO₃ (the assay result with a 1000kg composite sample collected in 1980-1982).

Los Santos mine (another tungsten mine in Spain) two different kinds of tailings are produced [16]: the coarse rejects from the thickening cyclones and dewatering screens and the fine rejects from the filter press.

In Kolar and Hutti gold fields in India [17], scheelite is associated with gold mineralization. The old tailing dumps of Kolar including Walker dump and Balaghat dump were tested for recovery of scheelite in 1986. The Walker dumps amounted to 17 tonnes at 0.18% WO₃, and the Balaghat dumps to 81 tonnes at 0.04%.

In Mittersill in Austria, 450 000 tonnes of ore are mined yearly in the underground mine with an average WO₃-content of 0.50 %. The host rock of the Mittersill deposit consists of quartz lenses, laminated quartzites, pyroxenites, orthogneisses, amphibolites, hornblendites and granites. The tungsten bearing mineral at Mittersill is scheelite (CaWO₄). The tailings stream at Mittersill site represent 99 % of the initial process feed. At the present throughput of 450 000 t/yr, a storage volume of 250 000 m³ is needed every year [18].

In addition, tungsten scrap is a very valuable raw material due to its high tungsten content (in comparison to ore [19]). In 2010 WO₃ about 24% of the total tungsten production was from the end-of-life scrap that was 24 000 t [5].

The tungsten containing waste rock and mill tailings from different sources are listed in Table 6.

Table 6. The tungsten containing waste rock and mill tailings from different sources

| Material type | Company/ Mine | Location | Grade of WO ₃ | Reserve, Mineralogy & Characterization | Ref. |
|--------------------------------|---|--|--|---|-------------|
| Waste-rock | Almonty Industries | Panasqueira mine, Portugal | | Producing 100 t/d Derived from rock blasting, coarse grain size, high content of arsenic in arsenopyrite contained | [6] |
| Waste-mud tailings (slimes) | Almonty Industries | Panasqueira mine, Portugal | 2.4 mg/Kg | Amounting to several million tonnes; Derived from crushing and milling processes, high content of arsenic; wolframite most below 25 microns in size and associated with a complex mixture | [6], [7] |
| Mo flotation tailings | China Molybdenum Company Limited | Luanchuan mine in China | 0.143% | Scheelite, grain size -0.074 mm 48.7%, over 71% WO ₃ distribution in fraction of -0.074 mm | [8], [9] |
| Tungsten- bearing dumps | Ormonde Mining | Barruecopardo tungsten mine, Spain | -1 mm: 0.044; +1 mm: 0.022 | Grain size distribution: -1 mm 38%, +1 mm 62% | [10] |
| Tungsten- bearing tailings | Ormonde Mining | Barruecopardo tungsten mine, Spain | -1 mm: 0.093% ; +1 mm: 0.088% | Grain size distribution: -1 mm 73%, +1 mm 27% | [10] |
| Milling tailings | | Bom-Gorhon tungsten ore deposits, Russia | >0.1% | hundred thousand tonnes accumulated; hubnerite and scheelite associated components – bismuth and tin | [11] |

| Material type | Company/ Mine | Location | Grade of WO ₃ | Reserve, Mineralogy & Characterization | Ref. |
|--|---|---|---|--|------|
| Tin milling tailings | | Bolivia | WO ₃ .64% (Cu 0.84%, Sn 0.84%) | Wolframite, cassiterite | [12] |
| Mine Tailings | North American Tungsten Corporation Ltd | Cantung Mine, Western Northwest Territories, Canada | 0.29-0.35% WO ₃ 0.24-0.28% Cu | Accumulated material from 1971-2007: 3.7 to 4.1 Mt | [13] |
| Coarse tailings and slimes | Tungsten Resources | La Parrila mine, Extremadura region of Southwest Spain | 0.28% WO ₃ | In the period 1968-1986 the 7 Mt of ore processed produced some 2 Mm ³ of coarse tailings and 1.2 Mm ³ of slimes | [14] |
| Old tailing dumps of Kolar (Walker dump and Balaghat dump) | | Kolar and Hutti gold fields in India | scheelite is associated with gold | 0.01% - 0.53% WO ₃ ; Walker dumps amounting to 17 tonnes at 0.18% WO ₃ , and Balaghat dumps with 81 tonnes at 0.04% WO ₃ | [17] |
| Tailings of coarse rejects (thickening cyclones and dewatering screens) | Almonty Industries | Los Santos mine, Spain | Scheelite | 2010-2012: 705 kt, 0.14% WO ₃ 2012-2013: 216 kt, 0.10% WO ₃ 2013-2015: 643 kt, 0.14% WO ₃ | [16] |
| Tailings of fine rejects (filter press) | Almonty Industries | Los Santos mine, Spain | Scheelite | 2010-2012: 309 kt, 0.24% WO ₃ 2012-2013: 114 kt, 0.20% WO ₃ 2013-2015: 76 kt, 0.14% WO ₃ | [16] |
| Mine Talings | | Milttersill, Austria | Scheelite | Volume of storage: 250 000 m ³ /year 0.50% of WO ₃ | [18] |
| (Smelting) Slag | Kiprianos Kavodokanos Komobil Ayia Paraskevi Neapoli Panormos Fougara | Greece | 3-76 ppm | Surface storage. 825 000 m ³ Former Smelter or refinery. | [20] |
| Flotation Tailings | Ylöjärvi | Finland | 0.02% | Surface storage. Former concentration – mill. Inactive plant. Minerals: Biotite, Chlorite, Epidote, Feldspar, Hornblende, Plagioclase, Quartz, Sericite | [20] |

| Material type | Company/ Mine | Location | Grade of WO ₃ | Reserve, Mineralogy & Characterization | Ref. |
|---|-------------------------------|-----------|-----------------------------|---|------|
| Mine Waste dump | Buchim Mine (waste dump) | Macedonia | 3-152 ppm | Surface storage. 46 409 630 m3 Minerals: Chalcocite-Chalcopyrite- Covellite-Cuprite-Galena- Hematite-Goethite (limonite)- Magnetite-Pyrite-Sphalerite- Tenorite-Native metal; | [20] |
| Slag | Veles Smelter (inactive) | Macedonia | 152 ppm | 716 656 m3 Galena-Sphalerite-Native metal | [20] |
| Slag | Zguri | Macedonia | 77.5 ppm | 625 000 m3 Native metal | [20] |
| Flotation tailings | Sasa | Macedonia | 655 ppm | Active plant 5769231 m3 Minerals: Arsenopyrite-Bismuthinite- Chalcopyrite-Epidote-Galena- Garnet-Ilvaite-Polybasite-Pyrite- Sphalerite-Bustamite | [20] |
| Mine products and waste (unprocessed) | Argozelo | Portugal | 268.5 ppm | Inactive plant Minerals: Arsenopyrite-Calcite- Cassiterite-Fluorite-Pyrite- Quartz-Scheelite-Wolframite | [20] |
| Mine products and waste (unprocessed) | Borralha | Portugal | 3.7 ppm | Inactive plant Minerals: Apatite-Arsenopyrite- Bismuthinite-Chalcopyrite- Galena-Molybdenite-Powellite- Pyrite-Quartz-Scheelite- Tourmaline-Marmatite (Fe Sphalerite)-Carbonates | [20] |
| Mine products and waste (unprocessed) | Campo Mineiro da Adória | Portugal | 94.5 ppm | Inactive plant Minerals: Arsenopyrite-Azurite-Blende (Sphalerite)-Chalcopyrite- Galena-Malachite-Pyrite- Pyrrhotite-Quartz | [20] |
| Mine products and waste (unprocessed) | Carris | Portugal | 26 000 ppm | Inactive plant Minerals: Cassiterite-Chalcopyrite- Molybdenite-Pyrite-Quartz- Scheelite-Wolframite | [20] |

| Material type | Company/ Mine | Location | Grade of WO ₃ | Reserve, Mineralogy & Characterization | Ref. |
|---------------------------------------|-----------------------------------|----------|-----------------------------|--|------|
| Mine products and waste (unprocessed) | Covas (Viana do Castelo district) | Portugal | 1864 ppm | Surface storage. Mine products and waste (unprocessed). Minerals: Apatite-Arsenopyrite-Ferberite-Goethite (limonite)-Marcasite-Pyrite-Scheelite-Wolframite | [20] |
| Mine products and waste (unprocessed) | Freixo de Numão | Portugal | 2500 ppm | Inactive plant Minerals: Arsenopyrite-Azurite-Blende (Sphalerite)-Chalcopyrite-Galena-Malachite-Pyrite-Pyrrhotite-Quartz | [20] |
| Mine products and waste (unprocessed) | Pintor | Portugal | 492 ppm | Inactive plant Minerals: Arsenopyrite-Blende (Sphalerite)-Chalcopyrite-Galena-Wolframite | [20] |
| Mine products and waste (unprocessed) | Ribeira | Portugal | 118.5 ppm | Inactive plant Minerals: Arsenopyrite-Cassiterite-Scorzalite-Pyrite-Triphylite-Wolframite | [20] |
| Mine products and waste (unprocessed) | Tarouca | Portugal | 1028 ppm | Inactive plant Minerals: Apatite-Blende (Sphalerite)-Cassiterite-Chalcopyrite-Feldspar-Fluorite-Galena-Garnet-Ilmenite-Pyrrhotite-Quartz-Scheelite-Wolframite-Zircon | [20] |
| Mine products and waste (unprocessed) | Vale das Gatas | Portugal | 123.5 ppm | Inactive plant Minerals: Arsenopyrite-Bismuthinite-Blende (Sphalerite)-Cassiterite-Stannoidite-Chalcopyrite-Galena-Pyrite-Pyrrhotite-Quartz-Wolframite-Carbonates | [20] |
| Mine products and waste (unprocessed) | Senhora da Guia | Portugal | 1028 ppm | Inactive plant Minerals: Arsenopyrite-Chalcopyrite-Marcasite-Pyrite-Pyrrhotite-Quartz-Scheelite-Wolframite | [20] |
| Mine products and waste (unprocessed) | Sarzedas | Portugal | 5 ppm | Inactive plant Minerals: Antimonite-Arsenopyrite-Gold-Pyrite-Wolframite | [20] |
| Inactive Plant | Laver | Sweden | 23.4 ppm | Surface storage. Flotetion tailings Minerals: Biotite-Chalcopyrite-Muscovite-Plagioclase-Pyrrhotite-Quartz | [20] |

3 TANTALUM

The flowchart of production of Tantalum products is presented Figure 2.

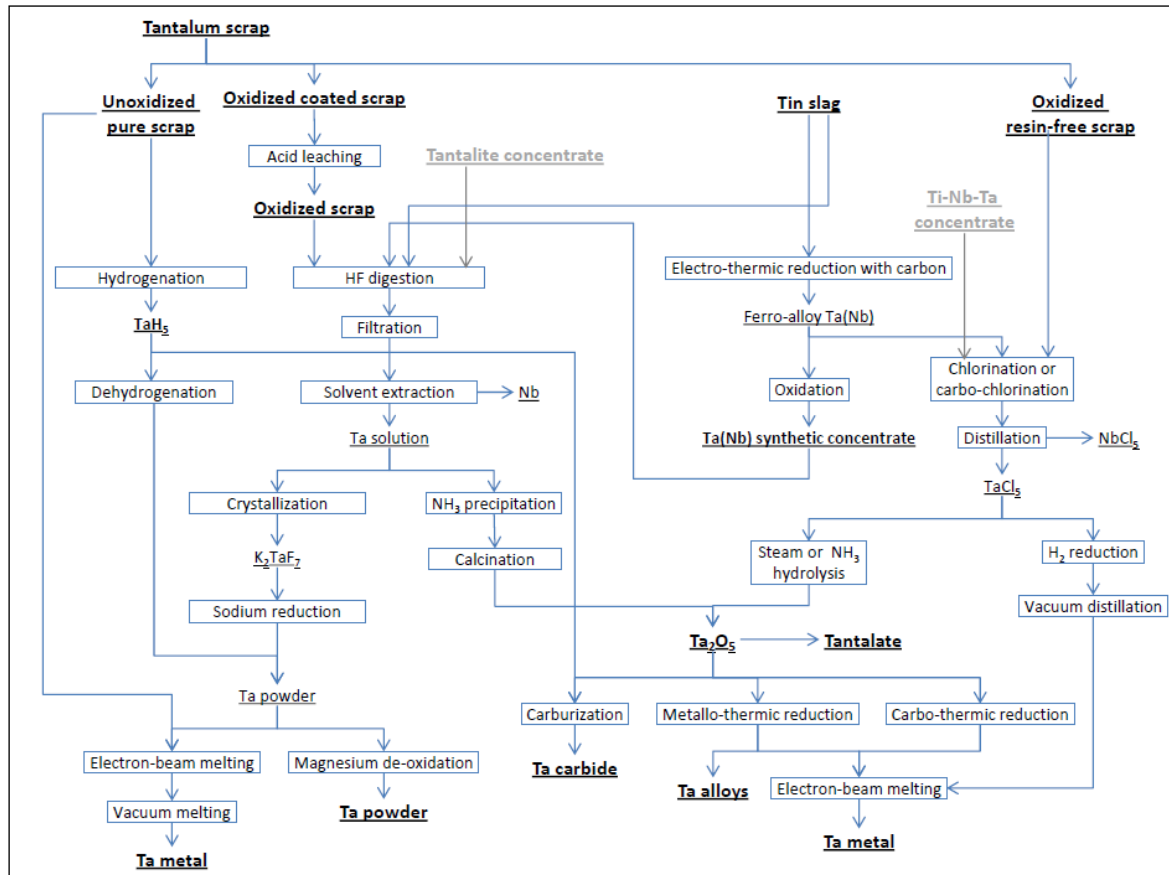


Figure 2. Tantalum flowchart

Tantalum can be extracted as a by-product of tin smelter waste. Tantalum produced in this way is around 14 percentage of total tantalum production. Tantalum is extracted from cassiterite placer middling using shaking tables, and magnetic and electrostatic separation methods. Tin smelter waste typically contains 8 to 10 per cent tantalum oxide, although exceptionally this may rise to 30 per cent. Low grade smelter waste can be upgraded by electrothermic reduction yielding a synthetic concentrate with up to 50 per cent tantalum and niobium.

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 [21]. According to the “Tantalum-Niobium International Study Center (TIC) [21] 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. Table 7 lists some of the identified sources. 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 different waste tantalum sources are listed in Table 7.

Table 7 Secondary resources of Tantalum

| Material type | Size of source | Location/ Owner | Comments | Physical Properties | | Chemical properties | | Impurities | Ref. |
|--|---|--|--|--|----------|---|------------------------|---|------------------|
| | | | | Particle size | Moisture | Main component | Content of Ta | | |
| Municipal landfills MSW containing WEEE | Estimated Ta concentration in MSW about 1 mg/kg (12) which is lower than the average concentration of Ta (2.4 mg/kg) in earths crust. | In countries where the share of landfilling has been significant in 2000's/ Municipalites | Low concentrations mixed into large amounts of MSW. Very little information and no data about Ta concentrations found. | Soiled small electronic devices or their components | | Capacitors and other electronic components mixed in large amounts of MSW and materials used for daily cover | | Mainly organic waste, plastics, fine particles. 3-4 % metals, mainly Al and Fe, smaller amounts of several other metals | [22], [23], [21] |
| Disposal areas of incineration slags. MSW incineration slags | ~61 000 t/d slags produced in EU, most of the Ta in the incinerator feed ends up to bottom ash | EU countries/ Municipalities, energy producers, etc. | Low concentrations, contains other metals, very little information from Europe | Mostly in >2mm particles | | Estimated 3-5 mg Ta/kg | Estimate 13->100 mg/kg | Minerals, molten slag, grit, unburnt organics; Fe, Al, Zn, Cu, Ni, minor metals | [23], [31], [32] |
| Industrial landfills containing waste from WEEE processing | n.a | In several EU countries/ Recycling companies | | Mostly crushed materials, particle sizes from very fine to over 10 cm, may contain also specimens that are not crushed | n.a | n.a | n.a | Plastics, mineral material, base (mainly Fe, Cu, Al, Zn), precious and critical metals | [34] |
| Mine waste | Not available | Echassieres France | | | n.a | n.a | n.a | | [20] |
| Mine waste | Closed pegmatite mine | Hagendorf, Germany | | | n.a | n.a | n.a | | [20] |

| Material type | Size of source | Location/ Owner | Comments | Physical Properties | | Chemical properties | | Impurities | Ref. |
|---|---|--|--|---------------------|----------|---------------------------------------|---------------|---|------------------------|
| | | | | Particle size | Moisture | Main component | Content of Ta | | |
| Tin mining residues tantalite Albite- Amblygonite- Arsenopyrite- Beryl- (Sphalerite)- Cassiterite- Columbite- Covellite-Goethite (limonite)- Muscovite-Pyrite- Quartz-Scorodite- Metatorbernite | Not known, Surface storage areas | Vieiros, Canadelo, Porto Region, Portugal | Closed tin mining area, | n.a | n.a | Ta concentrations not available | n.a | | [29] |
| Tailings and waste from tin mining | Tailings 5Mt and waste dump 6.8 Mt. | Penouta, Spain/Aprovechamiento Mineiro; Strategic Minerals Spain, Planning commercialization | Closed tin mining area, tailings and waste studied for recovery of Ta. | n.a | | Tailings 48 g/t; Waste dump 27 g/t | n.a | Tailings 390g Sn/t; Waste dump 29 g Nb/t, 460 g Sn/t | [24], [25], [26], [27] |
| Mine waste and tailings | Not known Cassiterite- Columbite- Feldspar-Quartz- Tantalite- Wolframite | Bessa, Portugal | | n.a | n.a | n.a | n.a | n.a | [20] |

| Material type | Size of source | Location/ Owner | Comments | Physical Properties | | Chemical properties | | Impurities | Ref. |
|--|--|---|--|---------------------|----------|---|---------------|--------------------------------------|------------|
| | | | | Particle size | Moisture | Main component | Content of Ta | | |
| Slag | About 1 000 t of radioactive slag from Nb production Larger amounts of light waste Apatite-Calcite-Mica, deposited to the sea | Söve, Norway | Small quantity, due to radioactivity will be either transported to a waste area or contained | n.a | n.a | Containing Ta (1.34 % Ta ₂ O ₅), Th, Zircon; | | Radioactive containing Th and Zircon | [20], [29] |
| Waste from uranium mining | n.a | Straz, Czech republic | | n.a | n.a | n.a | n.a | Radioactive | [20] |
| Mine tailings, pegmatite-granite | Closed Be-Ta mine | Rosendal, Finland | | | | | Li-Nb-Ta | REE, Sn, Zr | [20] |
| Scrap from Ta powder and castings manufacturing | | Manufacturing industries | | | | More information D4.1 | | | [30] |
| Waste from manufacturing of Ta capacitors, super alloys and alloy products, hardmetal products | | Several EU countries/Manufacturing industries | More information about applications in D4.1 | | | More information D4.1 | | | [30] |

| Material type | Size of source | Location/ Owner | Comments | Physical Properties | | Chemical properties | | Impurities | Ref. |
|---|---|--|---|---------------------|----------|-----------------------|---------------|------------|------|
| | | | | Particle size | Moisture | Main component | Content of Ta | | |
| Tin slag | Not known | Golbejas, Salamanca Spain | Tin and Ta mine closed in early 1980s, potential to start mining again has been studied (Goldtech) Waste areas have been at least partly reprocessed in 1980's | n.a | n.a | n.a | n.a | n.a | [24] |
| Tailings of china clay extraction | Ta, Nb, Ti,Sn Columbite-tantalite, cassiterite, Nb-Ta-rutile No info on concentration | St Austell, Cornwall | Gravity separation can be used for enrichment of Ta concentrate from fine grained waste | Fine particles | | Several locations | | Nb, Ti, Sn | [28] |
| End-of-life waste (capacitors, industrial applications of Ta alloys and superalloys, hard metal products) | | All European countries/ Consumers, several industrial sectors, medical sector | More information about applications and EoL-waste in D4.1 and D4.2 | | | More information D4.1 | | | |

4 MOLYBDENUM

Figure 3 shows the molybdenum flowchart.

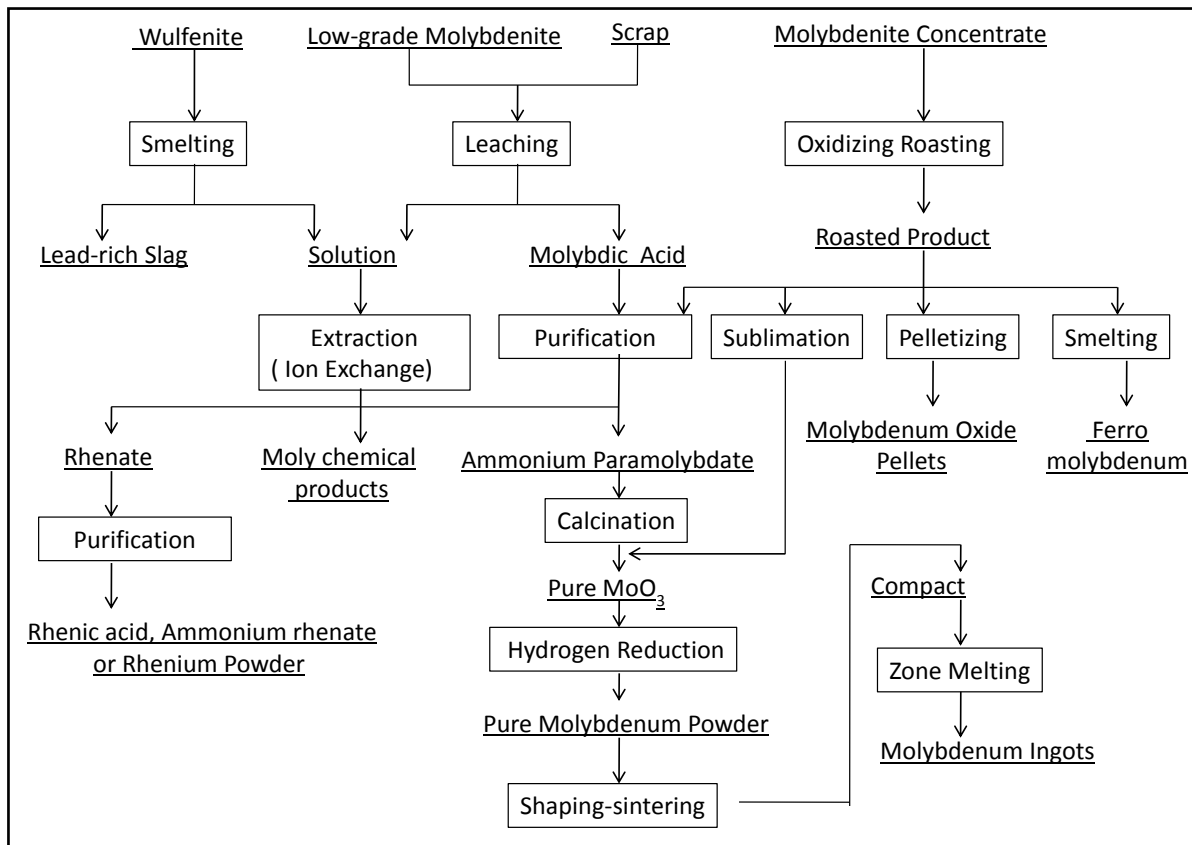


Figure 3. Molybdenum flowchart

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 [34]. The Mo content of viable ore bodies ranges between 0.01 and 0.25%.

Depending upon the minerals contained in the ore body and their quality, molybdenum mines are grouped in three classes:

- Primary mines, where the recovery of molybdenite is the sole objective;
- By-product mines, where the recovery of copper-bearing ores is the primary objective, and molybdenite recovery provides additional economic value; and
- Co-product mines, where the commercial viability of the mine requires that both molybdenite and copper-bearing minerals be recovered.

Very little public data could be found available about the characteristics and Mo potential of the European mine waste areas.

Boliden Aitik, is the largest copper mine in Sweden. The Aitik mine is a porphyry Cu-Au-Ag deposit. The deposit was discovered in 1932 and has been in production since 1968. Since then, over 632 Mt of ore has been mined averaging 0.35% Cu, 0.18 ppm Au and 3.4 ppm Ag. Molybdenite is sporadically observed in the ore zone and footwall of the deposit, usually in association with chalcopyrite and/or pyrite, in quartz veins of varying composition, and as coarse aggregates within pegmatite dykes [35]. The amount of tailing reaches 35 676 Kt with a percentage of 0.00027% of Mo. The results obtained from the study are presented in Table 8.

Table 8. Mass balance for molybdenum production at Aitik

| Product | Wight k Tonne | % Mo |
|-----------------------|---------------|---------|
| Ore Feed | 36 000 | 0.0025 |
| Cu Concentrate | 324 | 0.2479 |
| Mo Concentrate | 0.849 | 53 |
| Tailing | 35 676 | 0.00027 |

The Knaben Molybdenun mines in Norway, (1918-1973) left more than 8 million tonnes of tailings in ponds. Several sampling media of the surrounded are was analysed [36]. The Cu and Mo concentrations are presented below:

Table 9. Copper and Molybdenum concentration in Knaben Molybdenum mine

| Sampling media | Cu concentration | Mo concentration |
|---|------------------|------------------|
| Tailing pond | 215 | 51 |
| Natural sediment sources | 6.3 | 2.7 |
| Top section of ovebank sediments | 76 | 137 |
| Sandbars | 81 | 93 |
| Stream Sediments | 122 | 61 |

Garpenberg mine is located in Sweden and produces complex ores containing zinc, lead, silver, copper and gold. The current production is 1.4 million tonnes of ore per year and it is expect to reach 2.5 million tonnes per year. At Garpenberg mine in Sweden, the tailings were investigated with regard to composition and weathering characteristics. The tailings deposited in the tailings pond is around 500 000 tonnes of tailings/yr and the typical size distribution was $d_{50}=20 \mu\text{m}$, $d_{80}=64 \mu\text{m}$ [18].

Table 10. Average result of tailing analysis at the Garpenberg site

| Element | Concentration (mg/Kg) | Element | Concentration (mg/Kg) |
|---------|-----------------------|---------|-----------------------|
| As | 56.3 | Mn | 4163 |
| Ba | 338.8 | Mo | 2.9 |
| Be | 0.45 | Ni | 7.8 |
| Ca | 30 933 | P | 149 |
| Cd | 18.6 | Pb | 4011 |
| Co | 6.1 | S | 44 600 |
| Cr | 3.2 | Sn | <5 |
| Cu | 317.7 | Sr | 19.6 |
| Fe | 65 533 | V | 9.5 |
| Li | 4.6 | Zn | 7051 |

Legnica-Glogow copper basin is located in Poland. The production is 6808 kt/yr in Lubin mine, 10 436 kt/yr in Polkowice-Sieroszowice and 11 490kt/yr in Rudna mine. The mining method in the three mines is underground (room and pillar). At the Legnica-Glogow copper basin the tailings from all three mineral processing plants are pumped to a single tailings pond at 14-20% solids. The composition and particle size distribution are shown in the following tables (Table 11 and Table 12).

Table 11. Chemical analysis of tailings from the Legnica-Glogow copper basin

| Element | Unit | Mineral Processing Plant | | |
|--------------------------------|------|--------------------------|-------|-----------|
| | | Lubin | Rudna | Plokowice |
| Cu | % | 0.16 | 0.21 | 0.26 |
| Pb | % | 0.06 | 0.04 | 0.026 |
| Zn | % | 0.007 | 0.006 | 0.004 |
| Fe | % | 0.57 | 0.54 | 0.48 |
| S (total) | % | 0.27 | 1.12 | 0.66 |
| S (s2-) | % | 0.15 | 1.01 | 0.12 |
| C (total) | % | 2.80 | 4.14 | 9.26 |
| C (organic) | % | 0.48 | 0.32 | 0.54 |
| SiO ₂ | % | 68.03 | 53.05 | 18.42 |
| CaO | % | 5.43 | 12.14 | 26.25 |
| MgO | % | 3.15 | 5.72 | 6.88 |
| Al ₂ O ₃ | % | 3.09 | 4.11 | 4.58 |
| Mn | % | 0.094 | 0.153 | 0.190 |
| Na | % | 0.26 | 0.40 | 0.40 |
| K | % | 1.23 | 1.20 | 1.17 |
| As | g/t | 71 | 10 | 37 |
| Ag | g/t | 13 | 7 | 6 |
| Co | g/t | 39 | 10 | 21 |
| Ni | g/t | 27 | 16 | 42 |
| V | g/t | 72 | 38 | 110 |
| Mo | g/t | 15 | 12 | 8 |
| Au | g/t | 0.002 | 0.006 | 0.008 |

Table 12. Particle size distribution of tailings from the Legnica-Glogow copper basin

| Tailing type | Particle size | | |
|---|---------------|------------------|---------------|
| | >0.1 mm (%) | 0.1-0.045 mm (%) | <0.045 mm (%) |
| Sandstone-carbonate ore (processed at Lubin and Rudna) | 27-36 | 16-35 | 40-60 |
| Dolomite-shale ore (processed at Polkowice) | - | 8-11 | 89-92 |

The different waste materials containing molybdenum are listed in Table 13.

Table 13. Secondary resources of Molybdenum

| Type of Material | Company/ Mine | Location | Grade of Mo | Reserve, Mineralogy and Characterization | Ref |
|------------------------------|------------------------------|----------|--|--|---------------|
| Waste tailings Waste rock | Boliden Aitik | Sweden | 0.00027% | Aitik porphyry Cu-Au-Ag-(Mo) deposit Ore feed, 36 000 with a Mo concentration of 0.849 kt. Tailing produced of 17 700 000 and 26 000 Kt/year of waste rock | [35], [18] |
| Waste tailings | Knaben Molybdenumines | Norway | 40 ppm acid-soluble Mo Molybdenite and Molybdate (MoO_4^{2-}) Associate with fine-grained silicates or oxidates. Size particle: 0.2-0.9 | Inactive mine. 8 million tonnes of waste material produced and deposited in two ponds. 420000 tonnes have been washed and deposited sabdbars of the river. Chemical composition of tailing pond: Cu 215, Mo 51. Other materials: Ba, Cu, K, La, Li, Mg, Mn, Mo, S, Th, Y, Zn | [36] |
| Waste tailing | Boliden Garpenberg | Sweden | 2.9 mg/Kg | 500 000 tonnes of tailings/yr Other minerals: Pb, S, As, Ba, Fe, Ni, P, V, Zn, Cu. | [18] |
| Waste tailing | KGHM Lubin | Poland | 15 g/t | Underground mine Tailings: 27 000 000 kt/yr Other minerals: V, N, Co, Ag, As, K | [18] |
| Waste tailing | KGHM Polkowice-Sierszowice | Poland | 12 g/t | Underground mine Tailings: 27 000 000 kt/yr Other minerals: V, N, Co, Ag, As, K | [18] |
| Waste tailing | KGHM Rudna | Poland | 8 g/t | Underground mine Tailings: 27 000 000 kt/yr Other minerals: V, N, Co, Ag, As, K | [18] |
| Waste tailing | Kiruna and Svappavaarra Mine | Sweden | 15-11 ppm | Iron mine Other minerals: Cu, Nb, Ni, Pb, V, W, Zn... | [18] |

| Type of Material | Company/ Mine | Location | Grade of Mo | Reserve, Mineralogy and Characterization | Ref |
|-----------------------|---|-----------|---------------|--|------|
| Flotation tailing | Medet | Bulgaria | 17.49 g/t | Surface Storage | [20] |
| Mine Waste dump | Benkovski | Bulgaria | 0.01% | Surface Storage 62 000 000 m ³ | [20] |
| Recycled waste (slag) | Larmna | Greece | 0.15 g/t | Smelting (slag) | [20] |
| Mine waste dum | Ermioni-Karakasi/ Ermioni – Kapsospiti/ Ermino-Roros/ Ermioni-Aghios Dimitrios / Ermioni-Stoa | Greece | 5 – 45 ppm | Inactive Plant. Surface storage. Volume 1100 - 163 000 m ³ Actinolite-Ankerite-Azurite- Calcite-Chalcopyrite- Chlorite-Dolomite-Galena- Goethite-Hematite- Lepidocrocite-Pyrolusite- Maghemite-Magnetite- Malachite-Manganosite- Mica-Oligist iron-Pyrite- Quartz-Smithsonite- Sphalerite-Todorokite- Nsutite-Actinolite-Albite- | [20] |
| Slag | Kiprianos Kavodokanos Ayia Paraskevi Neapoli Panormos Fougara | Greece | 3 ppm – 9 ppm | Surface Storage. Former Smelter o refinery. 825000 m ³ | [20] |
| Mine Waste Dump | Buchim Mine | Macedonia | 5.5 ppm | Active plant Surface Storage. 46409630 m ³ Chalcocite-Chalcopyrite- Covellite-Cuprite-Galena- Hematite-Goethite (limonite)-Magnetite-Pyrite- Sphalerite-Tenorite | [20] |
| Mine Waste Dump | Lojane | Macedonia | 40 ppm | Inactive plant Surface Storage. 37500 m ³ Bravoite-Chromite- Cinnabar-Marcasite- Orpiment-Pyrite-Realgar- Stibnite | [20] |
| Slag (smelting) | Veles Smelter | Macedonia | 19 ppm | Surface Storage 716656 m ³ | [20] |
| Slag (smelting) | Zguri | Macedonia | 8.5 ppm | Surface Storage. Native metals. 62500 m ³ | [20] |

| Type of Material | Company/ Mine | Location | Grade of Mo | Reserve, Mineralogy and Characterization | Ref |
|--------------------------------|----------------------------|-----------|-------------|--|------|
| Flotation tailings | Sasa | Macedonia | 15.5 ppm | Surface Storage 5 769 231 m ³ Arsenopyrite-Bismuthinite- Chalcopyrite-Epidote- Galena-Garnet-Ilvaite- Polybasite-Pyrite-Sphalerite- Bustamite | [20] |
| Red muds from bauxite refining | Trzebinia | Poland | 53% | Inactive plant 160 000 m ³ | [20] |
| Mine products and waste | Carris | Portugal | 3924 ppm | Inactive plant Surface storage. Cassiterite-Chalcopyrite- Molybdenite-Pyrite-Quartz- Scheelite-Wolframite | [20] |
| Flotation tailings | Zlatna laz NR. 1 pr Sfarci | Romania | 42 ppm | Inactive plant Surface Storage 2 300 000 m ³ | [20] |
| Flotation tailings | Valea Cutii | Romania | 5 ppm | Inactive plant Surface Storage 1 620 000 m ³ | [20] |

5 NIOBIUM

The flowchart of production of different Niobium products is shown in Figure 4.

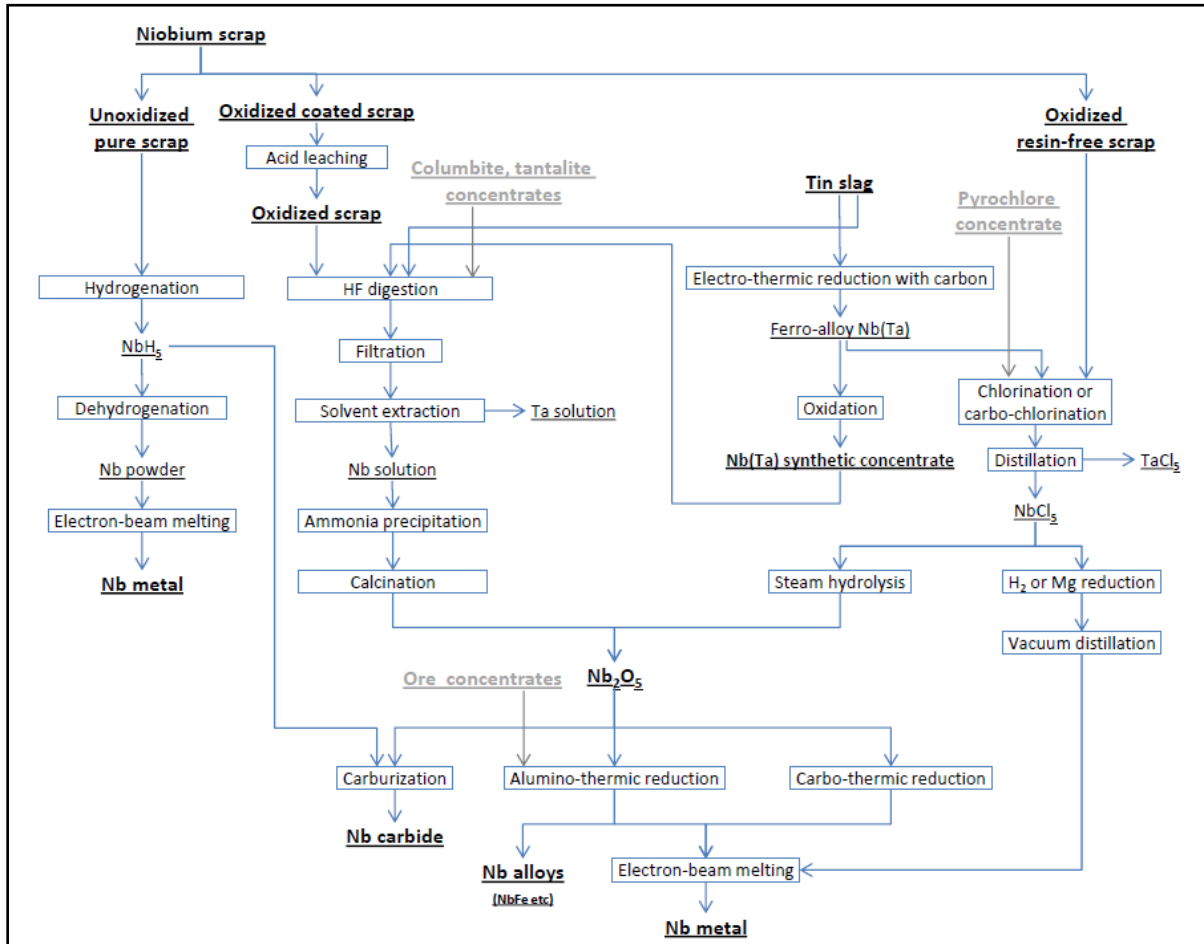


Figure 4. Niobium flowchart

The Niobium world production in 2010 was 62 900 t in 2010 92% from Brazil [37] Niobium does not occur 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 [38]. 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 Democratic Republic of Congo [38].

Niobium can also be extracted as a by-product of tin smelter waste. Niobium produced in this way accounts for less than two per cent of total global niobium production [38].

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 313.3 t) is linked to the mine waste dump (surface storage) [4].

Greek potential is much lower but still reaches a national average sum of 65.5 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.

Kiruna mine in Sweden is the largest underground iron ore mine in the world and is operated by LKAB. The characteristics of the tailings are included in Table 14 [18].

Table 14. Average trace element concentrations for wet-sorting tailings and other tailings material at Kiruna and Svappavaarra

| Element | Wet-sorted tailing (ppm) | Other tailings (ppm) |
|---------|--------------------------|----------------------|
| As | 3.7 | 18.1 |
| Ba | 168 | 205 |
| Be | 8.2 | 6.1 |
| Cd | 0.1 | 0.1 |
| Co | 94.2 | 67 |
| Cr | 13.4 | 23.5 |
| Cu | 356 | 211 |
| Hg | <0.0400 | 0.060 |
| La | 107 | 331 |
| Mo | 15.4 | 11.8 |
| Nb | 11.9 | <12.0 |
| Ni | 82.4 | 56.5 |
| Pb | 9.4 | 7.56 |
| S | 4990 | 4130 |
| Sc | 48.2 | 24.7 |
| Sn | 36.8 | 21.1 |
| Sr | 30.3 | 80.4 |
| V | 523 | 290 |
| W | 11.9 | <12.0 |
| Y | 40.6 | 170 |
| Yb | 7.78 | 15.4 |
| Zn | 56.5 | 42.5 |
| Zr | 114 | 161 |

The different waste materials containing niobium are listed in Table 15.

Table 15. Secondary resources of Niobium

| Type of Material | Company/ Mine | Location | Grade of Mo | Reserve, Mineralogy and Characterization | Ref |
|-------------------------|-----------------------------|-----------|-------------|---|------|
| Waste tailing | Kiruna and Svappavaara Mine | Sweden | 11.9 ppm | Iron mine Other minerals: Cu, Nb, Ni, Pb, V, W, Zn... | [18] |
| Slag | Kiprianos | Greece | 2.9 ppm | Surface storage 825 000 m ³ | [20] |
| Slag | Kavodokanos | Greece | 2.1 ppm | Surface storage 825 000 m ³ | [20] |
| Slag | Komobil | Greece | 3.8 ppm | Surface storage 825 000 m ³ | [20] |
| Slag | Ayia Paraskevi | Greece | 2.4 ppm | Surface storage 825 000 m ³ | [20] |
| Slag | Neapoli | Greece | 3.1 ppm | Surface storage 825 000 m ³ | [20] |
| Slag | Panormos | Greece | 5.4 ppm | Surface storage 825 000 m ³ | [20] |
| Slag | Fougara | Greece | 6.7 ppm | Surface storage 825 000 m ³ | [20] |
| Mine waste dump | Buchim Mine | Macedonia | 2.5 ppm | Active plant Surface storage. 46409630 m ³ Mineralogy: Chalcocite- Chalcopyrite-Covellite- Cuprite-Galena-Hematite- Goethite (limonite)- Magnetite-Pyrite-Sphalerite- Tenorite-Native metal | [20] |
| Mine product and waste | Chabanne | France | n.a. | Inactive plant Surface Storage | [20] |
| Mine product and waste | La Vedrenne | France | n.a. | Inactive plant Surface Storage | [20] |
| Ore processing waste | Søve | Norway | n.a. | Inactive plant Surface Storage Apatite-Calcite-Mica | [20] |
| Mine products and waste | Bessa | Portugal | n.a. | Inactive plant Surface Storage Cassiterite-Columbite- Feldspar-Quartz-Tantalite- Wolframite | [20] |
| Mine products and waste | Vieiros | Portugal | n.a. | Inactive plant Surface Storage Albite-Amblygonite- Arsenopyrite-Beryl-Blende (Sphalerite)-Cassiterite- Columbite-Covellite-Goethite (limonite)-Muscovite-Pyrite- Quartz-Scorodite-Tantalite- Metatorbernite Apatite-Calcite-Mica | [20] |

6 RHENIUM

Rhenium does not occur specially mineralized, being carried essentially by molybdenite (MoS_2). Accordingly, the world reserves of Re are primarily encircled in molybdenite from porphyry copper deposit, turning rhenium into a by-product of the copper mining industry. Some of the by-product molybdenite concentrates from copper mines contain small quantities (<0.1%) of rhenium. Molybdenum roasters equipped to recover rhenium are one of the principal commercial sources for this rare metal [34].

Recycling of the Pt–Re catalysts gives about 4 t/yr of Re (almost 0.1% of the global production). The largest enterprises are W.C. Heraes GmbH and H.C. Starck, a subdivision of the Bayer Group (Germany). CLAL, a subdivision of Metallore (Engelhand, France), and Gemini Industrials (United States) are also known [39]. The Kyshtym copper–electrolyte industrial complex (Russian Copper Company) also produced a pilot batch of ammonium perrhenate from used Pt–Re catalysts. In industry, 80% of sources of rhenium raw materials are molybdenum and copper sulfide concentrates. The remainder of this amount is obtained by recycling of Re–Pt catalysts.

The rhenium recovery process by liquid ion exchange and solid ion exchange is presented in Figure 5. A summary of the production of rhenium and products is presented in Figure 6 [40].

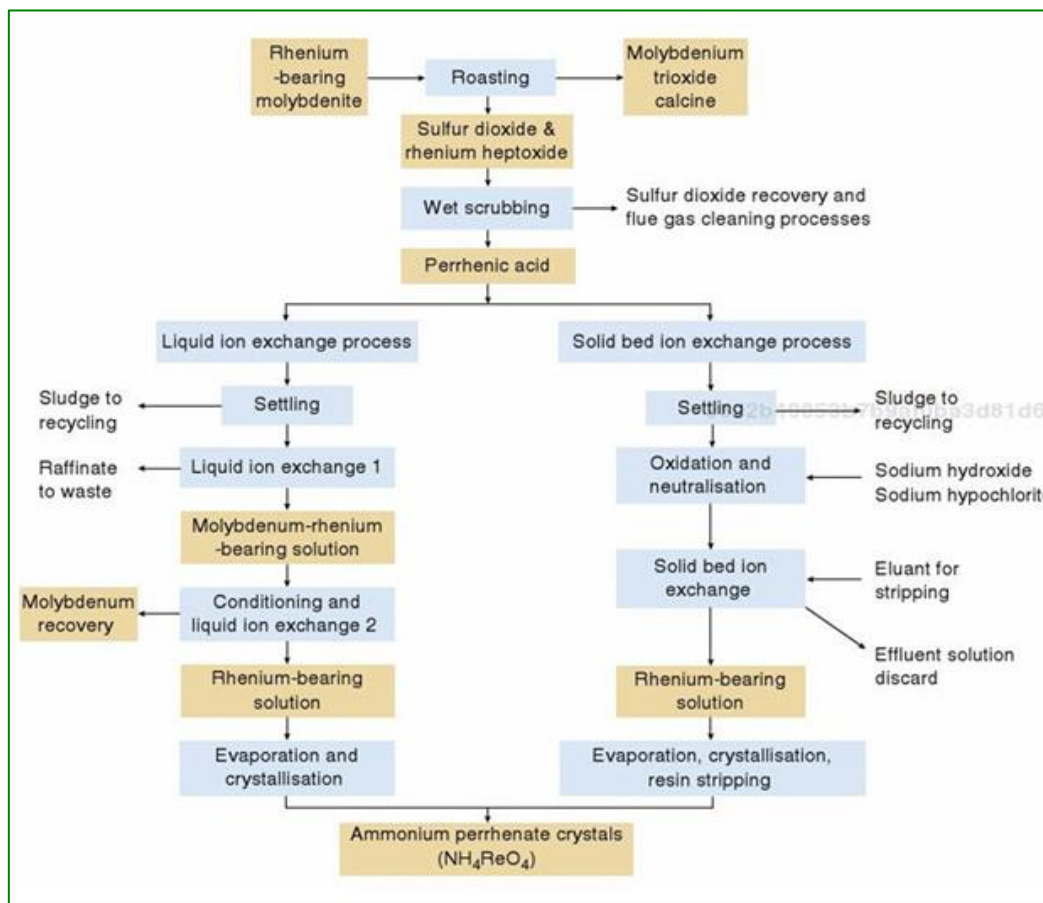


Figure 5. Rhenium recovery process by liquid ion exchange and solid ion exchange

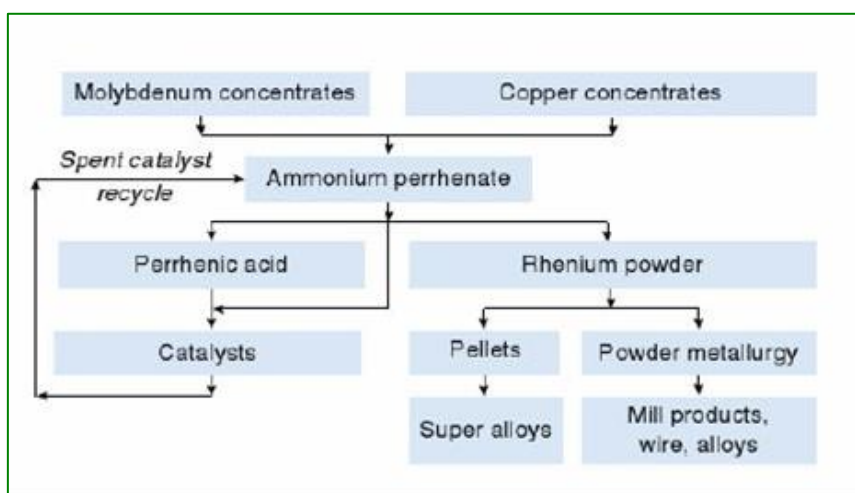


Figure 6. Summary of the production of rhenium and products

The São Domingos massive sulphide orebody is dominated by pyrite and located at the top of a Volcano Sedimentary Complex (VSC) sequence belonging to a giant volcanogenic massive sulphide deposit, the Iberian Pyrite Belt (IPB). This ore deposit extends from Portugal to Spain in the south of the Iberian Peninsula. The waste minerals of Sao Domingos abandoned pyrite mine (Iberian Pyrite Belt, souther Portugal) were analyzed. The Re content was 3.4 ppm, that is, thousand times higher than the assumed mean concentration in the Earth's crust [41]. Am study has showed that that the rhenium occurs in the stable molecular compound Re_2O_7 [42].

An study about the rhenium distribution in the vegetation of Asarel mine, a copper extracting and processing factory in Bulgaria [43]. The study provides information about the Re amount in the mine soil and tailings. The concentration of rhenium in the tailing mainly composed by ashes was $0.05 \mu\text{g/g}$ ash.

The Finnish mine of Nivala recently was a matter for examination for the discovery of a new mineral species of ideal composition $(\text{Cu,Fe})(\text{Re,Mo})_4\text{S}_8$, called tarkianite. Hitura is an active Ni–Cu–PGE mine in Nivala, western central Finland [44]. Hitura nickel mine has produced some 16 Mt of ore has been hoisted from the open pit, and since the late 1980's, from the underground mine. The mine produced 2,200 tonnes (4.9 million pounds) of nickel in concentrate per annum from underground operations. The Hitura Mill is capable of producing two sulphide concentrates. The grains of Tarkianite were found in a heavy-mineral concentrate containing pentlandite, chromite, pyrrhotite, and PGM (platinum-group minerals), consisting of sperrylite (81.1%), michenerite (6.6%), irarsite (1.9%), froodite (6.9%), hollingworthite (1.9%) and an undefined Rh–Ni–Co sulfarsenide. The average Re content of the PGE is 20 ppb.

At Ekojoki, southwestern Finland, the first Os-bearing rhenium sulphide enclosed in intercumulus pentlandite with numerous worm-like grains of mackinawite. It occurs as a single euhedral crystal in the early Proterozoic Ekojoki Ni Cu deposit in Finland, being enclosed by interstitial magmatic Fe–Ni sulphides. The Re–Os model age calculations indicate that approximately 2/3 osmium is "common" Os that was accommodated by the sulphide at the time of crystallisation, 1/3 being produced via post-crystallisation decay of ^{187}Re to ^{187}Os [45].

Aitik is one of Europe's largest open pit copper mines. Molybdenite in this deposit and its southern extension was studied through mineralogical/chemical analysis and laboratory flotation tests [35]. These studies certify that Molybdenite grains contain up to 1587 ppm Re, with an average of 211 ± 10 ppm in Aitik molybdenite and 452 ± 33 ppm in Salmijärvi molybdenite. Regarding the composition, higher Re concentrations were found in

molybdenite associated with sericite- and quartz-amphibole-magnetite altered rocks, whereas low Re values occur in rocks in which potassic alteration is prominent. Mineralogy of the host rock and the alteration grade slightly impact the Molybdenite recovery, which lower from flotation feeds with significant amounts of Mg-bearing clay-micas.

Different studies provide information about the Re content in Porphyry Cu-Mo-Au [35], [46]. The study case of Notheastern Greece refers to porphyry type occurrences in Sapes–Kirki–Esymi, Melitena and Maronia areas. Northeastern mines have proved to contain extremely Re-rich molybdenite. This occurs with pyrite in sodic–calcic, sodic–sericitic and sericitic-altered porphyritic stocks of granodioritic–tonalitic and granitic composition ores. In this area, molybdenite deposits are spatially associated with rheniite, as well as with intermediate (Mo,Re)S₂ and (Re,Mo)S₂ phases, with up to 46 wt % Re. P. Voudouris et al., includes a list of Rhenium content of molybdenite from porphyry-type deposit in Europe (Table 16).

Table shows the characterization of the rhenium sulfide from the Lukkulaivaara intrusion by electron-microprobe analyses [35]:

Table 16. Rhenium content in molybdenites (g/t) in different porphyry deposit in Europe

| Deposit | Type | Re in molybdenites (g/t) | | | | Cu/Mo | Au (g/t) |
|--------------------------|------------------|--------------------------|-------|--------|---------|-------|----------|
| | | n | Min. | Max. | Average | | |
| Greece | | | | | | | |
| <i><u>THRACE</u></i> | | | | | | | |
| Pagoni Rachi | Porphyry Cu–Mo | 175 | 379 | 46,900 | 16,318 | 22 | 0.57 |
| Konos | Porphyry Cu–Mo | 7 | 750 | 31,100 | 15,621 | 4.95 | 0.04 |
| Maronia | Porphyry Cu–Mo | 55 | 1,200 | 28,800 | 7,600 | 15 | 0.10 |
| Melitena | Porphyry Mo ± Cu | 49 | 2,100 | 17,400 | 7,900 | 0.2 | 0.16 |
| Myli | Porphyry Cu–Mo | 32 | 440 | 19,200 | 2,733 | 35 | 0.09 |
| Kimmeria | Porphyry Mo–W | 47 | 10 | 550 | 134 | - | - |
| <i><u>CHALKIDIKI</u></i> | | | | | | | |
| Skouries | Porphyry Cu–Au | 4 | 800 | 1,000 | 900 | 37 | 0.80 |
| <i><u>KILKIS</u></i> | | | | | | | |
| Axioupolis | Porphyry Mo–W | 9 | 10 | 1,000 | 344 | - | - |
| <i><u>AEGEAN SEA</u></i> | | | | | | | |
| Sardes, Limnos Isl. | Porphyry Cu–Mo | 7 | 1,100 | 5,200 | 3,785 | - | - |
| Fakos, Limnos Isl | Porphyry Cu | 5 | 910 | 2,220 | 1,396 | 69 | 0.03 |
| Stypsi, Lesvos Isl. | Porphyry Cu | 10 | 300 | 10,600 | 2,460 | 40 | 0.10 |
| Serifos | Porphyry Mo–W | 11 | 10 | 1,030 | 345 | - | - |
| <i><u>ATTICA</u></i> | | | | | | | |
| Lavrión | Porphyry Mo–W | 27 | 10 | 1,310 | 229 | - | - |
| Bulgaria | | | | | | | |
| Assarel | Porphyry Cu | 1 | - | - | 739 | 200 | 0.20 |
| Elastsite | Porphyry Cu–Au | 19 | 273 | 2,740 | 1,250 | 30–60 | 0.21 |
| Medet | Porphyry Cu | 22 | 565 | 1,163 | 905 | 37 | 0.10 |
| Serbia | | | | | | | |
| Bor | Porphyry Cu–Au | 3 | - | - | 1,520 | - | 0.84 |
| Majdnapek | Porphyry Cu–Au | 3 | 2,320 | 3,550 | 2,770 | 120 | 0.35 |
| Sweden | | | | | | | |
| Aitik | Porphyry Cu | 13 | 20 | 784 | 226 | 133 | 0.2 |
| Russia | | | | | | | |
| Aksug | Porphyry Cu–Mo | 1 | - | - | 460 | 70 | 0.06 |
| Zhireken | Porphyry Mo–Cu | 7 | 12 | 57 | 29 | 1 | 0.03 |
| Sora | Porphyry Mo–Cu | 9 | 6 | 18 | 14 | 15 | 0.02 |
| Tominskoe | Porphyry Cu | | - | - | 1,080 | 113 | 0.12 |

A summary of different waste materials containing rhenium are listed in Table 17.

Table 17. Secondary resources of Rhenium

| Type of Material | Company/ Mine | Location | Grade of Re | Reserve, Mineralogy and Characterization | Ref |
|---|------------------------|----------|------------------|--|------------|
| Flue dust (pyrometallurgical, electrochemical processes) | Mansfeld (smelter) | Germany | 63 g/t | Surface Storage 257 000 m ³ Anglesite-Galena- Quartz-Sphalerite- Wurtzite-Acanthite- Augite-Boléite-Bornite- Chalcopyrite-Digenite- Fayalite-Galena- Hardystonite-Melilite- Sphalerite-Djurleite | [20] |
| Tailing waste | Iberian Pyrite Belt | Portugal | 3.4 ppm | Abandoned pyrite mine | [41], [42] |
| Tailing and ash | Asarel Mine | Bulgaria | 0.05 µg/g ash | In operation. Cu extraction and processing factory | [43] |
| Waste tailings Waste rock | Aitik Mine | Sweeden | 1587ppm | 26 000 waste rock (65% deposited separately for alternative use) Tailing produced of 35 676 Ktonnes | [35], [18] |

7 CONCLUSION

This report is delivered in the context of MSP-REFRAM project, WP3 “Secondary resources”. The main objective of this WP is to address the recovery of refractory metals in metallic or oxide form existing in waste (old mine tailing and industrial waste) and reduce the amount of waste put in landfill. To reach this objective, and analysis of the available resources containing refractory metals has been identified and listed in this deliverable.

The waste rock, tailing mills, mine waste dump, ashes and slag generated in different mines in Europe has been identified. Information from PROMINE Project <http://promine.gtk.fi/> has been completed with further information of possible sources of secondary resources of W, Ta, Mo, Nb and Re in different countries in Europe.

Sites with secondary resources of Tungsten and Molybdenum are quite well described in the whole world. However, information related with Ta, Nb and Re is not fully available. Molybdenum and Rhenium are mainly related with porphyry Cu deposits. An evaluation of this deposit in Europe has been studied, however in some cases, there is not clear information about the tailing or waste rocks. Information available for niobium is very limited.

Information regarding the type of waste, company mine, location, grade of metal, reserve, mineralogy and characterization have been provided for each metal.

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