

NIOBIUM AND TANTALUM

SHORT DESCRIPTION

NIOBIUM

Niobium is a soft silvery-grey metal that resembles fresh-cut steel. It neither tarnishes nor oxidizes in air at room temperature because of a thin coating of niobium oxide. It does readily oxidize at high temperatures (above 200°C), particularly with oxygen and halogens. Niobium is not attacked by cold acids but is very reactive with several hot acids such as hydrochloric, sulphuric, nitric, and phosphoric acids. It is ductile and malleable [23]. The European Union has recently identified Niobium as critical raw material.



Fig. 1. Niobium metal

TANTALUM

Tantalum (Ta) is a dense, tough and ductile element with very high melting point of 3017°C. It is also highly corrosion-resistant to most acids below 150°C and, in most cases, chemically inert. It has good thermal and electrical conducting properties and is easy to machine [16]. Tantalum has not been placed on the critical raw materials list as of yet, but it is strategically important in several industries.



Fig. 2 Tantalum metal

APPLICATIONS

NIOBIUM

The main application of Niobium is in high-strength low-alloy steels (HSLA), where Niobium is added as Ferro-Niobium. This market accounts for 90% of Niobium usage and is responsible for most of the increase in overall consumption. The next table shows the main Niobium applications [1] [2]:

Form of Nb	Applications	Principal markets	Nb grade
HSLA FeNb	HSLA steels	Automobiles, gas linepipe, construction, heavy engineering	~0.1%
	Stainless and heat resistant steels	Automobiles, petrochemical and power plants	0.04-0.08%
Vacuum grade FeNb and NiNb	Superalloys	Aircraft engines, electricity generation, petrochemicals	3-5%
Nb metal and alloys	Superconductors	Particle accelerators, magnetic resonance imaging, various small tonnage uses	45-89%
Nb chemicals	Functional ceramics and catalysts	Optical, electronics	21-66%

Table 1. Main Nb applications

Ferro-Niobium and Nickel-Niobium are applied in super-alloys used in the aerospace industry, particularly in commercial aircraft engines, as well as in land-based gas turbines for electricity generation, and in corrosion-resistant alloys. Titanium and Zirconium Niobium alloys are used in aeronautics, superconductors and nuclear energy.

Niobium chemicals are applied in many fields such as catalysts and functional ceramics, but information concerning the Niobium grades that are employed in specific individual applications is scarce.

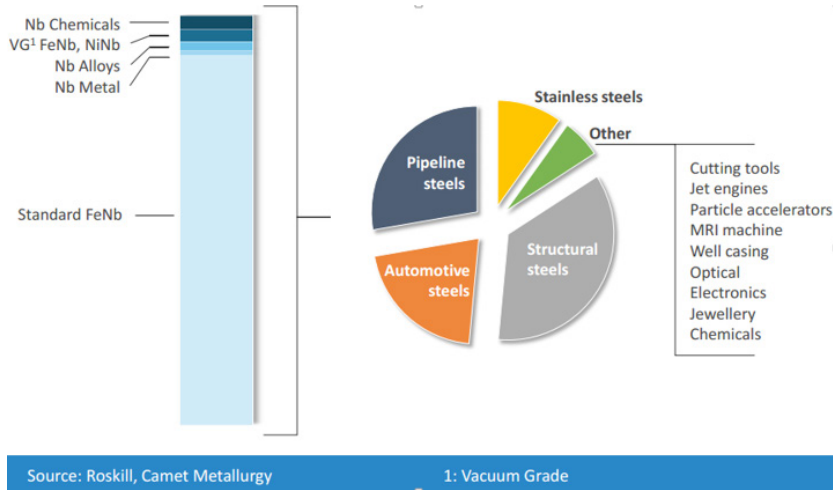
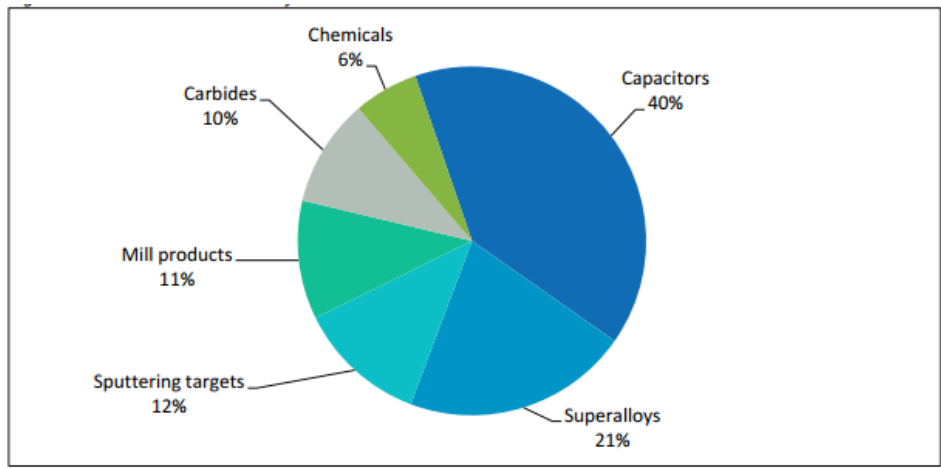


Fig. 3 Niobium applications

TANTALUM

Tantalum is used in different sectors of the industry thanks to its corrosion-resistant qualities and its applicability as capacitor, the latter being the most important application, with billions of units produced every year. Other applications in electric and electronic equipment (EEE) are sputtering targets (Ta metal, Ta₂O₅, TaN) and surface acoustic wave filters, of which the applications are cellular and wireless telephones, television sets, video recorders, tire pressure control and keyless entry systems [5]. Tantalum is also used for high temperature applications, e.g. aircraft engines, in the form of super alloys based on nickel and cobalt. Tantalum carbide is used for the fabrication of cemented carbides. Tantalum oxide is used for manufacturing of special types of glass.



Source: Roskill 2013 in Minor Metals Conference

Fig. 4 Tantalum applications, Source: Roskill 2013 in Minor Metals Conference

EU SUPPLY AND DEMAND: CURRENT AND FUTURE

NIOBIUM

90% of the world's Niobium is produced by three mines, two of which are in Brazil (the Araxá and Catalao mines) and the other in Canada (the Niobec mine). The vast majority of the world's Niobium reserves are in these countries and there are currently no Niobium-mining operations in Europe.

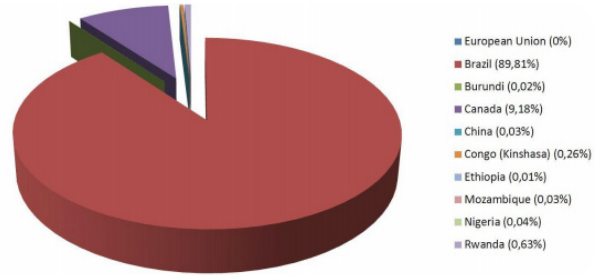


Fig. 5 Niobium production worldwide

Statistics on imports to the EU EU of Niobium and Tantalum-containing slags, ashes and residues from 2011 to 2015 are shown in Fig. 6 [4].Exporting flows and importing and exporting wastes containing Niobium in this period were almost zero.

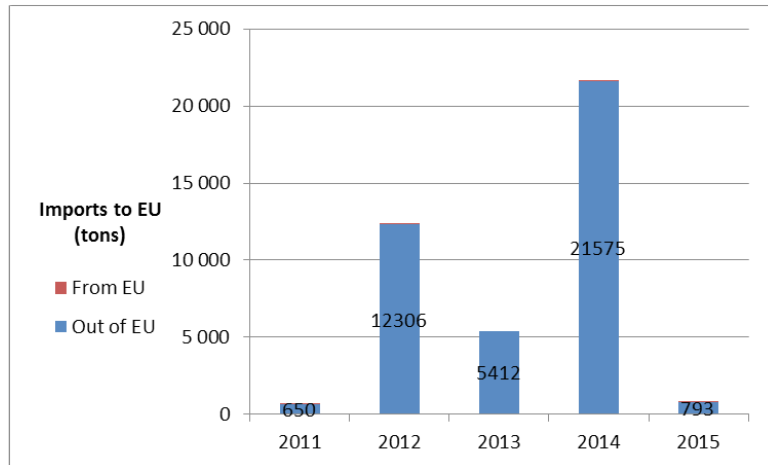


Fig. 6 Imports to the EU of Nb- and Ta-containing materials

Niobium is mainly imported and exported as Ferro-Niobium:

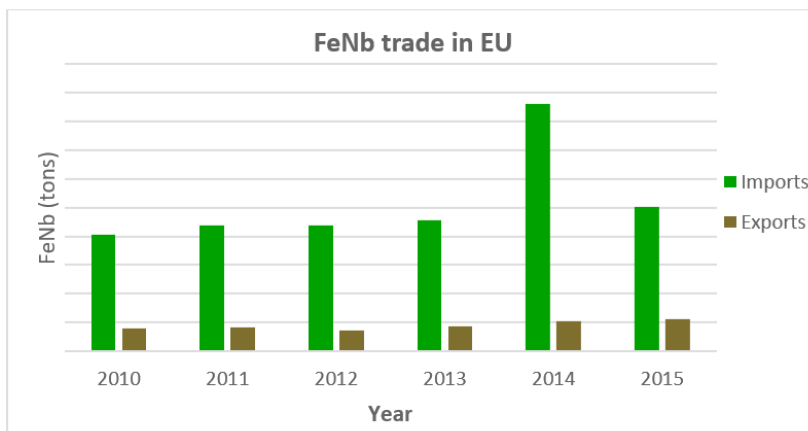


Fig. 7. EU FeNb imports and exports, 2010-2015

	2008	2009	2010	2011	2012	2013	2014
Total production	85984	53520	83895	88918	57532	54574	59700
Total EU imports	22871	12107	20249	21902	21960	22774	43016
% EU	26.6	22.62	24.14	24.63	38.17	41.73	72.05

Table 2. EU import quantities as a percentage of total FeNb production

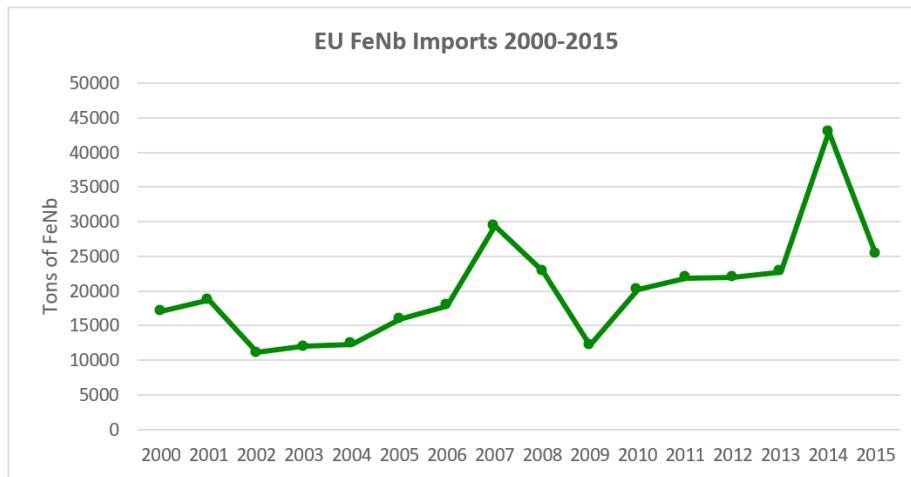


Fig. 8 EU FeNb imports 2000-2015 (BGS Statistics)

Ferro-Niobium imports to the EU have risen every year since 2009, after the decrease recorded between 2007 and 2009, which probably occurred as a result of the poor economic situation which led to a fall in demand for automobiles and structural steel for the construction industry. Ferro-Niobium imports to the EU rose considerably in 2014, mainly as a result of the large quantities of Ferro-Niobium imported by Spain (20,093 tons). If Spain's imports had not been taken into account, total EU demand would have been 22,923 (based on data from the previous years) and would have increased in 2015.

Sharp growth in demand is expected between now and 2020 for Ferro-Niobium (over 8% per year), driven by a global demand for steel in construction, infrastructure and automotive applications, and a trend towards increased use of HSLA steels. Increasing demand for natural gas is also expected to result in increased demand for pipeline steel [26]. ArcelorMittal, whose headquarters are in Luxembourg, is the world's leading steel maker (96.1 million tonnes of crude steel production in 2013). ThyssenKrupp in Germany is also among the world's leading steel makers (15.9 million tonnes of crude steel production in 2013). Therefore, it is clear that, given the current economic situation, the demand for Ferro-Niobium in the EU will remain high. The graph below shows annual Ferro-Niobium demand projections based on an average increase in demand of 8% per year ([27]):

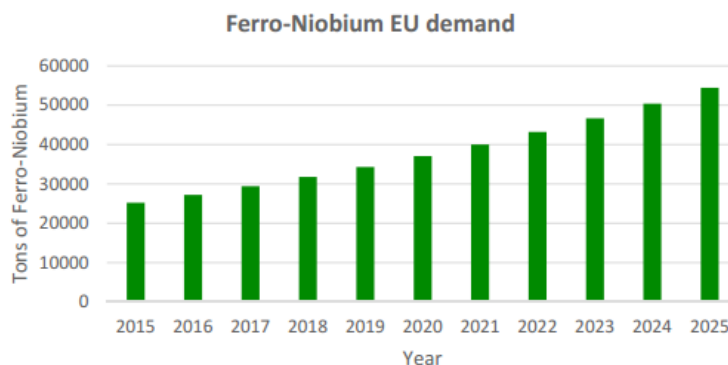


Fig. 9 Estimated FeNb demand from 2016 to 2025

TANTALUM

Rwanda provided almost 50% of 2013 worldwide production of concentrate. Other countries, such as Congo and Brazil, played lesser but still significant roles (16.56% and 12.58%, respectively). The European Union's contribution to the world production of Tantalum concentrate was low. The only primary production of Tantalum came from the Echassières kaolin quarry (in France), which in 2011 produced 55 tonnes of Sn-Ta-Nb concentrate at 10% Ta₂O₅, i.e. around 4.5 tonnes of Ta [5].

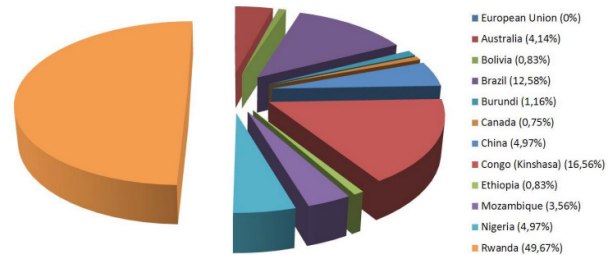


Fig. 10 Tantalum production worldwide

In 2014, 375 tons of capacitors were imported by the EU, and 415 tons were exported. The EU 28 export more wastes and scraps than they import (+ 94 tons) but they import huge amounts (21,575 tons) of slag, ash and residues containing mainly Tantalum and Niobium, mainly from Malaysia (20,862 tons in 2014).

There is currently no data available on EU production or transformation of Tantalum. Roskill does not make any assessment for Europe in its market reviews and the Tantalum-Niobium International Study Center (TIC) states that there are no figures for the EU market, as its members are “unable to provide this level of information”. This lack of transparency could be related to the fact that Europe imports Tantalum extracted in conflict-affected countries in Central Africa, which underscores the fact that it is a very fragile and small market with very few actors [27].

EU Tantalum consumption is roughly estimated to lie between a quarter and a third of total worldwide production, i.e. between 250 and 330 tons [Hocquard ,2016], if a global production figure of 1,000 tons is assumed for 2015 [27].

So far, Europe has not encountered any supply problems, but as demand for Tantalum is expected to grow, different options could be studied to improve supply chain security [27], including:

- Improving recycling rates, focusing not only on old scraps (cemented carbides and alloys) but also on end-of-life products containing high-grade Tantalum (electrolytic capacitors: 36.7%, wavefilters: 33%, semiconductors: 28.6%).
- Exploitation of old tin tailings containing Tantalum (or Niobium) in metal extraction procedures, using new technologies.
- Exploitation of new deposits, especially in Australia which had 49% of estimated Tantalum reserves in 2015. There are also resources to be exploited in the EU, among which Treguennec in France represents a potential source of 1,600 tons of Tantalum.

Substitution of Tantalum in the manufacture of capacitors is simple and could mitigate Tantalum supply-and-demand issues in the future. There is no real supply risk for EU industries, but the situation could change if tighter regulations are placed on importation of supplies from conflict-affected regions and countries with poor working conditions and if environmental concerns are fully addressed. Finally, more transparency among EU processors will be required if the EU's needs and weaknesses are to be properly assessed [27].

MAIN PRIMARY AND SECONDARY RESOURCES

PRIMARY RESOURCES

Tantalum usually occurs together with Niobium in the same type of mineral deposits and in minerals of similar characteristics. These metals are often found in solid solutions, as is the case with columbite-tantalite, represented by the formula (Fe,Mg,Mn)(Nb,Ta)₂O₆, or minerals from the pyrochlore group. Mineral deposits from which Tantalum is extracted are associated with specific igneous rocks: Carbonatites and associated rocks, alkaline with peralkaline granites and syenites, and pegmatites. The weathering of these deposit types can result in other types of Niobium – Tantalum

mineral deposits, as laterites concentrating pyrochlore, and alluvial deposits (placers). This is the case with the Araxá deposit, which is managed by CBMM (major worldwide Niobium producer).

- Carbonatites and associated rocks: rarely contain profitable concentrations of Tantalum, neither as a by-product. They are mainly sources of Niobium.
- Alkaline granite and syenites: Tantalum can occasionally be obtained as a by-product.
- Pegmatites: more widespread throughout the world. The main Niobium and Tantalum minerals in this type of deposits are columbite-tantalite series.

Although the largest Tantalum reserves are located in Brazil and Australia, the combination of demand issues, lack of control over production and sale, and small-scale mining has led to continued domination by the countries in Africa's Great Lakes Region in recent years.

The main economical ores for Tantalum and Niobium production are:

Mineral	Formula	Ta ₂ O ₅ Content	Nb ₂ O ₅ Content
Tantalite	(Fe,Mn)(Ta,Nb) ₂ O ₆	40-80% Ta ₂ O ₅	2-30% Nb ₂ O ₅
Wodginite	(Ta,Nb,Sn,Mn,Fe,Ti) ₁₆ O ₃₂	45-75% Ta ₂ O ₅	1-15% Nb ₂ O ₅
Microlite	(Ca,Na) ₂ (Ta,Nb) ₂ (O,OH,F) ₇	50-79% Ta ₂ O ₅	1-10% Nb ₂ O ₅
Columbite	(Fe,Mn)(Ta,Nb) ₂ O ₆	1-40% Ta ₂ O ₅	30-75% Nb ₂ O ₅
Stueverite	(Fe,Mn)(Ta,Nb,Ti) ₂ O ₆	5-26% Ta ₂ O ₅	7-17% Nb ₂ O ₅
Euxenite	(Y,Ca,Ce,U,Th)(Ta,Nb,Ti) ₂ O ₆	2-12% Ta ₂ O ₅	22-30% Nb ₂ O ₅
Samarskite	(Fe,Ca,U,Y,Ce) ₂ (Ta,Nb) ₂ O ₆	15-30% Ta ₂ O ₅	40-55% Nb ₂ O ₅

Table 3 Main economical ores for Ta and Nb production

The natural co-occurrence of Tantalum and Niobium in Ta-bearing ores explains their co-production from primary resources. Tantalite is the primary mineral for industrial production of Tantalum (being called ferrotantalite or manganotantalite depending on the presence of Fe or Mn). Tantalum-free Niobium can be found in the mineral pyrochlore (NaCaNb₂O₆F).

SECONDARY RESOURCES

Niobium

Niobium can be extracted as by-product of tin smelter waste or extracted from sludge from the cemented carbide tool industry or from mill scrap from alloyed and unalloyed metal fabrication and scrap from industrial alloys and superalloys.

Concerning end-of-life products, Niobium is found in [3]:

- Waste electric and electronic equipment (WEEE). It was estimated that a computer can contain 0.0002% of Niobium. The amount of Niobium recovered from collected IT and telecommunications equipment could be as high as 1.2 tonnes, and the grade of Niobium in PCB is about 36 g/t.
- End-of-life Vehicles. The grade of Niobium in ELV can be estimated thanks to the grades of Niobium used in stainless steels, which is in the range of 0.04-0.08%.

Potential sources for Niobium recovery are mostly steels, but the Niobium content is low (<0.5% in weight).

Among the companies in Europe that have been identified as Niobium recyclers are: Buss&Buss Spezialmetalle GmbH, Innova Recycling GmbH, Jean Goldschmidt International SA, Metherma KG, ELG Utica Alloys Ltd, Metallum Metal Trading AG (Minor Metal Trade Association, Ta-Nb international study centre).

Tantalum

Tantalum can be extracted as a by-product of tin smelter waste. Tin smelter waste typically contains 8 to 10 per cent tantalum oxide, but can sometimes be as high as 30%. Low grade smelter waste can be upgraded by electrothermic reduction yielding a synthetic concentrate with up to 50% Tantalum and Niobium. In the EU, potential tailings and slags



can be found in Spain, Portugal, France, the UK, Germany and the Czech Republic. Tantalum can also be found in waste from uranium mining operations.

Tantalum can also be extracted from municipal waste landfills, industrial landfills (WEEE recycling companies) and incineration slags.

Other potential sources are scrap from manufacturing of Tantalum powders and ingots as well as manufacturing of Tantalum-containing products and end-of-life scrap containing Tantalum. Fig. 4 shows Tantalum sources in 2011 (%Ta₂O₅).

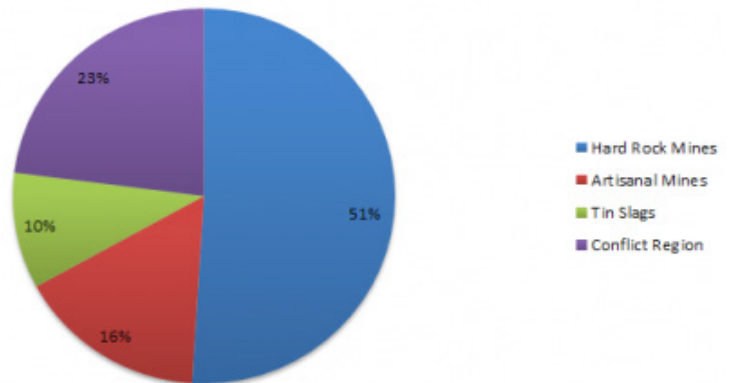


Fig. 6. Primary Tantalum Supply 2011

MAIN PROCESSING AND EXTRACTING TECHNIQUES

PRIMARY RESOURCES

Mining technology

The size and grade of the ore, the depth and the distribution of the ore minerals (disseminated or concentrated) and the geotechnical properties of the rock, are the main factors taken into account for the type of mining: open pit or underground. Almost all mines in carbonatites and other steeply-dipping intrusive rock structures are mined in open pits. The Araxá mine starts mining in the most surficial weathered part of the deposit, whereas the Niobec mine employs only underground mining techniques. Underground mining is restricted to deep deposits (the Tanco mine in Canada, the Greenbushes mine in Australia, for example, for Tantalum extraction).

Processing technologies

Industrial beneficiation of the ores on an industrial scale relies upon the combination of:

- Crushing (jaw, cone or impact crusher) to say <15-20 mm
- Grinding (ball or rod milling) and classification (screens and hydrocyclones) in closed circuit to <1mm
- Conventional (jig, shaking table), centrifugal (spiral) and enhanced gravity separation (MGS, Falcon concentrator), depending on the size of the liberated particles.
- Selective reverse flotation in order to concentrate the finest material, normally at controlled pH. The high consumption of additives is a significant cost factor for the flotation processing of Ta-Nb fines, and represent a pollution issue as well.
- Regular and high magnetic separation to remove companion magnetic phases.
- Thickening circuit to recycle the process water.

Extractive Metallurgy

- Hydro-metallurgy
 - o **Leaching:** Acid digestion of ores in a mixture of hydrofluoric acid with other mineral acids, generally sulphuric acid.
 - o **Fractional Crystallization:** Separation should preferably be conducted at an acid concentration of about 1 to 7% HF, where the solubility of Niobium complex is nearly 10 to 12 times that of Tantalum. Apart from acidity, many other factors, such as temperature and the presence of other ionic species, affect the solubility of the complex species. The separation of Niobium and Tantalum by fractional crystallization is achievable due to their double fluoride complexes with potassium.

As the solubility of potassium fluotantalate (K_2TaF_7) is low, it crystallizes out. The crystalline solid is redissolved and recrystallized. The process is conducted in several stages. The process works quite satisfactorily and relatively easily as far as the preparation of pure tantalum complex K_2TaF_7 is concerned. The process flow sheet is shown to the right.

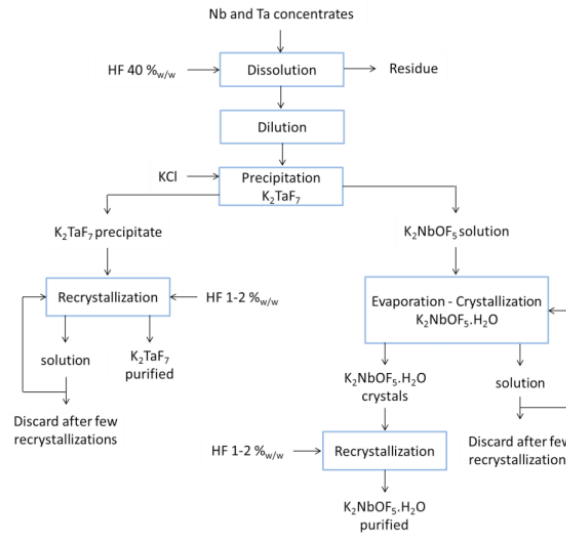


Fig. 11 Crystallization process for Nb and Ta production

o **MIBK extraction:** The key parameter is H^+ concentration, which controls the degree of separation as well as the recovery of the two metals. Normally, operated mixer-settlers are used. Niobium and Tantalum remain in the organic phase, in which they are cleaned with concentrated sulphuric acid and re-extracted with water or dilute sulphuric acid to obtain Niobium. Niobium oxide hydrate is then precipitated using gaseous or aqueous ammonia and is subsequently filtrated, dried and calcined at up to $1100\text{ }^\circ\text{C}$. The precipitation, drying and calcination parameters can be modified to obtain different particle sizes of the oxides, depending on the desired application. Impurities are not extracted and are left in the raffinate. Very pure Ta and Nb products are obtained. The process flow sheet is shown to the right:

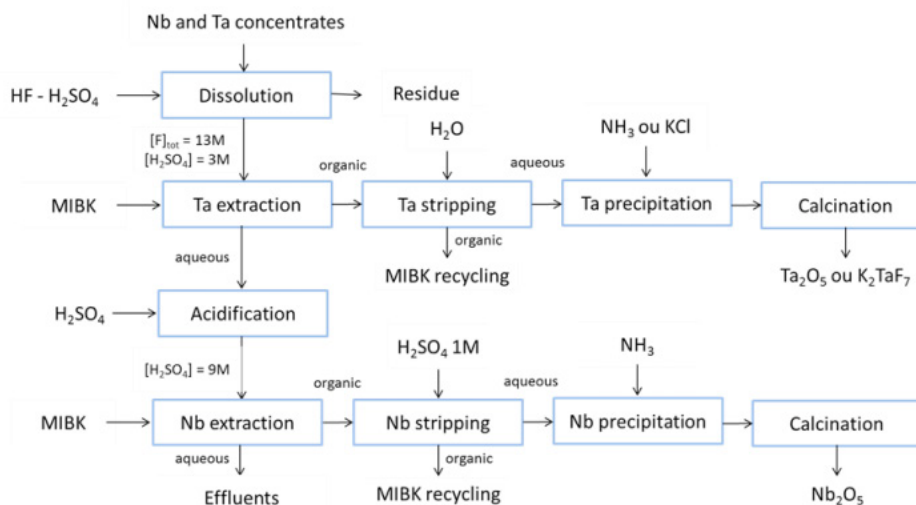


Fig. 12 MIBK extraction process for Nb and Ta production

o **Pyro-metallurgy:** The pyrochlore concentrate obtained after physical beneficiation followed by chemical leaching to remove impurities is of the right specification and it can be used directly for the production of Ferro-Niobium through an aluminothermic reduction process.

One of the simplest methods for breakdown treatment of Niobium concentrates is direct reduction with aluminium and carbon, with or without the addition of iron and iron oxides. In aluminothermy, all the oxides that have free energy of formation which are less negative than that of alumina are reduced to the metallic state and form ferroalloys, particularly Ferro-Niobium alloys. In carbothermic reduction, Niobium reacts with excess carbon and forms carbides, which in turn form an alloy carbide. This process is usually performed in a smelting electric arc furnace.

However, if the objective is to separate Tantalum from Niobium, a selective reduction of the chlorides can be applied. Niobium pentachloride is more readily reduced by hydrogen (or by metals such as aluminium) to the lower chlorides. $NbCl_5$ reduction is then performed at 450-550°C to form a trichloride. $TaCl_5$ is not reduced under these conditions.

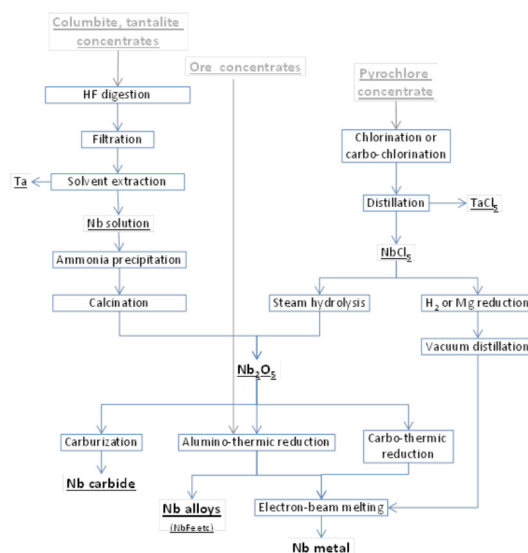


Fig. 13 Pyro-metallurgy process for Nb and Ta extraction from concentrates

EXTRACTION OF TANTALUM FROM SECONDARY RESOURCES:

Mineral processing

- **Municipal and Industrial Landfill waste:** The first stages include crushing and separation of fines from larger particles using a rotary screen, for example. The typical methods employed are the magnetic, density and ballistic separation methods or, in some cases, the eddy current method is used.
- **Incineration bottom ash:** Usually the slag is treated at the incineration plant. Before treatment, the slag is stored at least one day for integration of CO_2 and to make it less wet and sticky. Metal pieces and particles are separated by several mechanical processing stages: sieving, crushing and mechanical separation (magnetic, eddy current). Sensor separators are also used.
- **Tin slags and silt-like tailings:** Strong chemical digestion or electro-thermic reduction are usually required.

Extractive metallurgy

- **Hydrometallurgy:** the organic solvents than can be used in Niobium and Tantalum extraction are of two categories: 1) neutral oxygen-containing extractants, such as ketones, TBP, TOPO or octanol, and 2) anion exchangers, such as trioctylamine (TOA). Industrially, MIBK, cyclohexanone, TBP and 2-octanol are used. Generally, the extraction and refining of Tantalum is accomplished through hydrofluoric and sulphuric acid leaching at high temperatures, which produces complex fluorides. After filtration and solvent extraction (MIBK) or ion exchange (amine extractant in kerosene), highly purified solutions of Tantalum and Niobium are produced. Tantalum values in the solution are generally converted into potassium tantalum fluoride or tantalum oxide.
- **Pyrometallurgy:** Tantalum oxidizes easily and moves into the slag produced in pyro-metallurgical processes. By using electrothermic reduction process, the slag is upgraded to a Tantalum-oxide content as high as 50%. Carbothermic, metallothermic, and hydrogen reduction can be applied to extract Tantalum. Molten salt electrolysis is also applied. After being subjected to these processes, Tantalum metal can be refined by molten salt electro-refining, vacuum sintering, electron beam or plasma processes.

EXTRACTION OF NIOBIUM FROM SECONDARY RESOURCES:

Mineral processing

Tin smelting slags are generally upgraded by a pyrometallurgical process, involving the production of ferroalloy called block metal, which acts as a collector for Niobium and Tantalum. The block metal is further upgraded through simple acid leaching or by a combination of oxidative smelting followed by acid leaching of the slag derived from the second smelting. The upgraded slag is used for the extraction of Niobium and Tantalum using hydrofluoric acid.

Extractive metallurgy

Well-classified metal scrap can be reused by pulverizing it after hydriding, applying acid leaching to remove iron contamination, if there is any, and then reusing it in the fabrication stream. Similarly, well-classified scrap of cemented carbide tools consisting primarily of a low carbide cemented with a cobalt binder can be reused in the fabrication plant after separating the carbides from the cementing material. This can be achieved by a simple process involving treatment of the scrap with molten zinc. Cobalt and zinc form an alloy which has a higher specific volume, which disintegrates the cemented carbide shapes. The carbide powder can thus be reused and cobalt can be recovered through vacuum distillation of zinc.

Niobium and Tantalum separation by solvent extraction is normally performed in the presence of fluorides. Sulphuric and hydrochloric acid solutions are characterized by association and polymerization of complexes of these elements, which prevent their selective isolation.

Niobium extraction processes from tin slags can be divided into the following process types:

1. Upgrading the Niobium content of the slag: separating some of the constituents by leaching (acid leaching of slag with 2% sulphuric acid at 50°C).
2. Preparing synthetic concentrate.
3. Recovering Niobium directly from medium-grade slags.

Recycling of iron and steel scrap

Scrap is collected by scrap dealers and processed into a physical form and chemical composition that can be consumed by steel mills in their furnaces. Baling presses are used to compact the scrap into manageable bundles. Scrap dealers sort scrap materials, and steelmakers carefully purchase scrap that does not contain undesirable elements that exceed acceptable levels. The scrap is mainly melted in basic oxygen and electric arc furnaces (BOF and EAF). In the recycling of high-strength low-alloy steel, one must be aware that about 0.05% of Niobium will most likely be oxidised to the slag



phase and lost during recycling to EAF or BOF. In the fabrication of new steel products, new steel scrap with a known chemical composition is produced. Preparation of the new scrap for recycling is usually limited to cutting, cleaning and baling prior to shipment back to the steel maker [28].

ENVIRONMENTAL AND SOCIAL IMPACTS OF THEIR EXPLOITATION

Niobium and Tantalum do not represent any special risk. The solid forms of Tantalum and Niobium do not pose any particular environmental problems. There is no reported information on toxicity of the metals and alloys, and the only associated health hazards stem from the powders, which, like any other powder, can be irritants. Flotation reagents are generally biodegradable and the tailings are not very hazardous, as occurs for example in mine drainage[29]. The life-cycle analysis performed by Nuss & Eckelman in 2014 shows 260 kgCO₂eq/kg of global warming potential for Tantalum (considered to be a medium degree of impact), whereas for Niobium, the figure is 12.5 kgCO₂eq/kg (lower impact). However, Niobium has 133 MJ eq/kg of cumulative energy demand compared to 4,360 MJ eq/kg for Tantalum. As for terrestrial acidification, Niobium would have low impact compared to other metals on the periodic table, while Tantalum would be in the middle. The same occurs for freshwater eutrophication and human toxicity.

The minerals from which Nb and Ta are extracted are known for their significant content in naturally occurring radioactive materials (NORMs), especially in the cases of 226Ra, 238Ru, 232Th and 40K. NORMs. Afterwards, the raw materials are processed they are converted into TENORMs (technologically enhanced natural radiation materials). The environmental hazard is extremely intense in the case of Nigeria, where large quantities of generated tailings rich in these radioactive minerals are disposed of haphazardly into the environment. Radiation monitoring in the area and at some processing mills has revealed high dose rates with values as high as 100 aSv per hour for processed zircon. The in situ dose rate measurements for workers and the public at large indicated 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 radionuclides such as uranium and thorium could have an important impact on the local environment and on worker health.

Tantalum concentrates from pegmatites generally contain minute quantities of natural thorium and uranium, but pose a very low radiological risk during transport, and the regulations are designed so that safety is provided through passive safety inherent in the package. Moreover, generation concentrates, especially those produced from alkaline and peralkaline deposits, will almost certainly have higher levels of these radioactive elements, and some type of on-site processing prior to shipment may well be required [29].

Ferro-Niobium production is not hazardous as on-site safety precautions are adequate [29]. Pyrochlore concentrates used to produce Ferro-Niobium also contain thorium and uranium, which are present in the Ferro-Niobium slag. This slag contains elevated levels of thorium and uranium and is generally stored on site. Despite its thorium and uranium content, FeNb is not included in the Best Available Techniques Reference Document for the Non-Ferrous Metals Industries, where it is only commented that the dust generated from the furnace is discharged to a landfill except for a certain amount of FeNb, and that 1.9 tons of slag is generated per ton of alloy.

As the key to increased Tantalum capacitor efficiency is the fineness of the powder, care must be taken to ensure a static and ignition-free environment as, as in the cases of many other very fine powders, they are pyrophoric and may explode if handled improperly. Comprehensive regulation of materials is now in place in the European Union, under a protocol known as REACH (registration, evaluation, authorisation and restriction of chemicals). All companies wishing to produce substances in the EU or import them into the EU must ensure they meet their registration obligations if they are to continue with their activities; further guidance can be obtained from the European Chemical Agency website (ECHA, 2011) or from national authorities [29]. A life cycle analysis was performed as part of the MSP-REFRAM EU Project, comparing Tantalum primary extraction and the Ta secondary recovery. The results indicate that, in all categories considered, (global warming, cumulative energy demand, terrestrial acidification, freshwater eutrophication and human toxicity) there is an important gap between the impact of the secondary recovery process and the primary extractive process, with the effects of secondary process representing only about 15 % of primary process activities. As there is currently no primary production of Ta or Nb in Europe, secondary production is a good opportunity in terms of environmental impact.



SUBSTITUTION POSSIBILITIES

Table 4 shows substitutability scores for Tantalum presented by Oakdene Hollins and Fraunhofer ISI in their report entitled Critical Raw Materials at the EU Level in 2013. A score of “0” means the material is easily substitutable at no additional cost or loss in performance, while a score of “1” represents substitutable, but with an increase in cost and loss in performance:

Material	Application	Share	Megasector	Substitutability
Tantalum	Capacitors	40%	Electronics	0.3
Tantalum	Superalloys	21%	Metals	0.7
Tantalum	Sputtering targets	12%	Electronics	1.0
Tantalum	Mill products	11%	MechEquip	0.7
Tantalum	Carbides	10%	MechEquip	0.3
Tantalum	Chemicals	6%	Chemicals	1.0

Table 4. Tantalum substitutability in different applications [30]

Thus, Tantalum substitutability according to the scores shown in Table 4, is quite simple due to the low costs of capacitors and carbides. In superalloys and mill products, substitutability is possible, but at a higher cost and/or with a loss in performance. In sputtering targets and chemicals, Tantalum is still not substitutable. Thus, Tantalum can be substituted by other materials but most substitutes have either higher costs or adverse properties. Distribution of end-uses and corresponding substitutability assessment for tantalum is presented in the figure below:

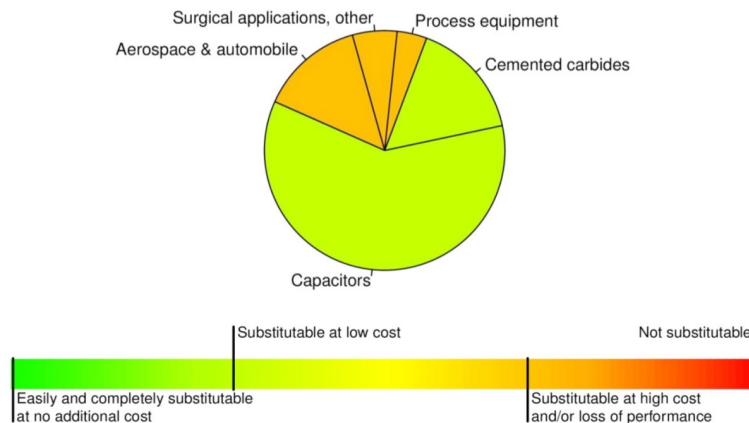


Fig. 14 Substitutability of Tantalum in its major applications [31]

Niobium was listed as one of the 21 critical raw materials for the EU in a December 2015 study conducted by Oakdene Hollins Research & Consulting and Fraunhofer ISI. Table 5 provides a breakdown of Niobium applications with their respective substitutability levels:

Application	Share	Megasector	Value (GVA)	Substitutability
Steel: Structural	31	Construction	104.4	0.7
Steel: Automotive	28	Transport – Road	147.4	0.7
Steel: Pipeline	24	Oil	50.0	0.7
Superalloys	8	Metals	164.6	0.7
Others	6	Other	63.3	0.5
Steel: Chemical	3	Mechanical Eqpt.	182.4	0.7

Table 5 End uses, megasector assignment and substitution values [30]

Figure 15 shows the distribution of Niobium uses and their substitutability levels. The manner and scaling of the assessment is compatible with the work done by an ad-hoc group on the definition of critical raw materials (2010):

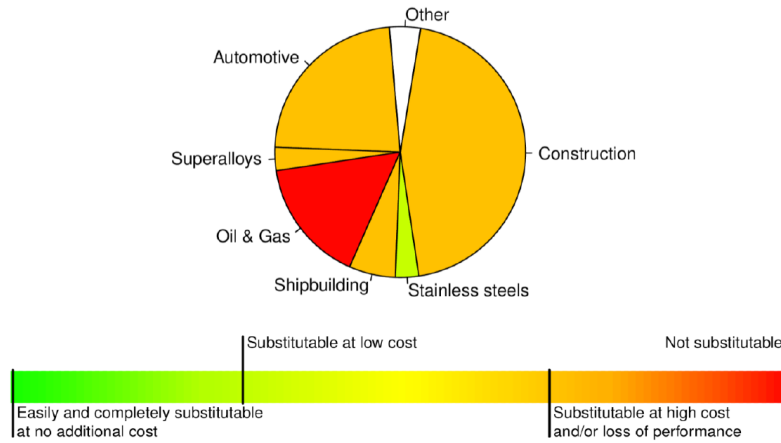


Fig. 15 Distribution of end-uses and corresponding substitutability assessment of Niobium [31]

As seen, the substitution of Niobium and Tantalum is possible depending on the applications they are used for. The following table outlines several possibilities [16-24][25]:

Metal	Application	Substitutes
Nb	HSLA Steels	Titanium, Vanadium, Molybdenum
Nb	Stainless Steels	Titanium, Tantalum, High Nitrogen steels
Nb	Superalloys	Ceramic Matrix Composites, Molybdenum, Titanium, Tantalum
Nb	Superconductors	Vanadium-Gallium alloys, BSSCO alloys
Ta	Capacitors	Niobium oxide, Aluminium, Ceramic
Ta	Cemented carbides	Niobium, Tungsten, Titanium carbides, Titanium nitride (some CRM)
Ta	Steels super-alloy	Vanadium, Molybdenum
Ta	Super-alloys for high T applications	Hafnium, Iridium, Molybdenum, Niobium, Rhenium, Tungsten (some CRM)
Ta	Process equipment, resistance to corrosion, high-T environment	Niobium (CRM), Glass, Platinum (CRM), Titanium, Zirconium
Ta	SAW filters and SAW resonators in electronic applications in cellphones, TV sets, video recording	Lanthanum gallium silicate (CRM)
Ta	Orthopaedic applications	Titanium and ceramics in some cases
Ta	Surgical equipment	Chromium/Nickel steel alloys
Ta	Optic/lenses	Niobium in some cases
Ta	Hard disk drives	Niobium

HEADING TOWARDS THE FUTURE: RECENT RESEARCH ACTIVITIES

Innovative improvements in hydrometallurgical technology for processing Niobium and Tantalum concentrates is expected in the following areas [4]:

- The application of **more robust extractants with higher stability and lower water solubility**. A process for extracting Nb and Ta from a fluorinated leach liquor with Alamine 336, using kerosene and xylene as diluents and n-decanol as a modifier has been proposed. Ta extraction was higher than that of Nb [6]. High purity Tantalum and Tantalum-free Niobium (99.99-99.99%) can be obtained using quaternary ammonium salts as extractants from a hydrofluoric acid solution [12] containing various metallic impurities (alkaline or alkaline-earth metals such as cobalt, manganese, iron, nickel, copper, etc.). This patented process can be applied to ore concentrates as well as scrap containing Nb and Ta, or Ta-rich tin slags.
- **Less HF or no HF used for the digestion of concentrates and metal separation using SX**. Using ammonium bifluoride as an alternative to hydrofluoric acid, the leaching process is performed with water and large amounts of impurities are precipitated in the form of insoluble compounds that can be separated from the solution through filtration. Optimum digestion conditions were determined: a tantalite-to-bifluoride mass ratio of 1:30, a reaction temperature of 250 °C and a reaction time of 3 h. Under these conditions, the leach recoveries of Niobium and Tantalum were 95% and 98.5% respectively [11].
- **Recycling reagents used as much as possible to reduce liquid and solid wastes**

More specifically, Niobium and Tantalum extraction techniques for secondary resources research has been done on:

- **Extraction of Niobium and Tantalum from Tin slag**: chlorination at 1000°C has allowed the extraction of about 84% and 65% of the Nb and Ta compounds, respectively. Carbochlorination at 500°C has allowed complete extraction and recovery of both compounds [7].
- **Niobium and Tantalum from Copper Smelting slag**: physical separation by froth flotation is widely used. Hydroxamates are powerful collectors in flotation due to their ability to selectively chelate on the surfaces of minerals that contain Niobium [8].
- **Tantalum extraction from concentrates**: a novel hydrometallurgical process was developed to selectively extract Nb and Ta from Nb-Ti-Fe raw concentrates, by forming a sodium hexaniobate through a reaction between the initial concentrate and concentrated NaOH at atmospheric pressure [9]. After caustic conversion, the sodium hexaniobates are selectively dissolved in water.
- **Tantalum from alloy scrap**: iodization of alloy scrap produces volatile tantalum (V) iodides that can be reduced in a plasma furnace to produce high surface area tantalum metal powder precursors, which, after being annealed, yield high-purity nano-powders with uniform particle size distribution, low oxygen content, and high surface area and capacitance [10].
- **Tantalum from electronic waste**: use of ionic liquids at room temperature concurrently with the extractants, containing either the chelating ligands or task-specific ionic liquids (TSILs) that have a strong affinity and/or selectivity with the target metal and as purification agents through a selective electrodeposition process [13]. Also, oxidation in the air of the scraps followed by a mechanical collection of the sintered Ta electrodes inside the scraps in combination with chemical treatment allows high purity Ta₂O₅ recovery, by reducing the Ta₂O₅ obtained through magnesiothermic reduction [14].
- **Niobium from steel scrap**: Niobium has a recycled content higher than 50%. Niobium is eventually reintroduced into the steel-making process, which makes the recycling of Niobium relatively easy [15].



EUROPEAN RELATED PROJECTS

- **OptiMore:** optimizes the crushing, milling and separation ore processing technologies for Tungsten and Tantalum mineral processing, by means of improved, fast and flexible fine tuning production process control based on new software models, advanced sensing and a more thorough study of the physical process, which increases by 7-12% over the best current production processes, increasing energy savings by 5% compared to the best available techniques.
- **E4-CritMat (Marie Curie programme):** Engineering of Energy Efficient Extraction of Critical Materials – Application to the Processing of Niobium and Tantalum Minerals.



REFERENCES

- [1] Roskill, THE ECONOMICS OF NIOBIUM, Eleventh Edition, 2009
- [2] D. Arcos, AMPHOS 21, Nb_Ta_mining_state of the art D_Arcos-V1.pptx, presentation from WS1 in Barcelona, May, 30-31st, 2016
- [3] S. Casanovas, AMPHOS, Mapping_of_secondary_Nb_resources_(EOL_products) S_Casanovas_V1.pptx, presentation from WS1 in Barcelona, May, 30-31st, 2016
- [4] Extraction from Eurostat databasis "EU Trade Since 1999 by HS2,4,6 and CN8 (daily updated)" website, based on CN8 codes, <http://epp.eurostat.ec.europa.eu/newxtweb>
- [5] Audion A.S., Piantone P., Panorama 2011 du marché du tantale (in French), report BRGM/RP-61343-FR, 2012
- [6] El hussaini O. M.; Rice N. M. (2004) Liquid-liquid extraction of niobium and tantalum from aqueous sulphate/fluoride solutions by a tertiary amine, *Hydrometallurgy*, 72, 259-267.
- [7] I. Gaballah, E. Allain, and M. Djona, Extraction of Tantalum and Niobium from Tin Slags by Chlorination and Carbochlorination, *Metallurgical and Materials Transaction B*, volume 28B, June 1997—359-369.
- [8] S. Roy, A. Datta et S. Rehani, Flotation of copper sulphide from copper smelter slag using multiple collectors and their mixtures, *International journal of mineral processing*, vol. 143, pp. 43-49, 2015.
- [9] Gauthier J.-P. Deblonde, Valérie Weigel, Quentin Bellier, Romaric Houdard, Florent Delvallée, Sarah Bélaïr, Denis Beltrami, Selective recovery of niobium and tantalum from low-grade concentrates using a simple and fluoride-free process, *Separation and Purification Technology* 162 (2016) 180–187
- [10] Joseph D. Lessard, Leonid Shekhter, Daniel Gribbin, Larry F. McHugh. A new technology platform for the production of electronic grade tantalum nanopowders from tantalum scrap sources. *International Journal of Refractory Metals and Hard Materials* 48:408-413 · January 2015
- [11] Kabangu, M. J. and P. L. Crouse (2012). "Separation of niobium and tantalum from Mozambican tantalite by ammonium bifluoride digestion and octanol solvent extraction." *Hydrometallurgy* 129: 151-155.
- [12] Niwa, K.; Ichikawa, I.; Motone, M. (1987). "Method of separating and purifying tantalum and niobium-containing compounds." Patent JP82487/86; EP0241278.
- [13] Matsuoka, R., Mineta, K., & Okabe, T. H. (2004). Recycling process for tantalum and some other Reactive Metal Scraps. In the *Minerals, Metals & Materials Society [TMS] (Ed.), Proceedings of the Symposium on Solid and Aqueous Waste from Non-ferrous Metal Industries* (pp. 689-696). Charlotte: TMS.
- [14] <http://www.agence-nationale-recherche.fr/?Projet=ANR-13-CDII-0010>
- [15] Worrel, E. & Reuter, M., 2014, "Handbook of Recycling: State of the art for Practitioners, Analysts and Scientists", Newnes, pp 74-75
- [16] RPA, 2012. Study on data needs for a full raw materials flow analysis. Prepared for Directorate – General Enterprise and Industry. London, UK Risk and Policy analysis limited.
- [17] BGS 2011. Mineral profile: Tungsten
- [18] Argus 2016. An overview of downstream Tungsten markets. Argus Metal Pages Forum, Tokyo.
- [19] EUROSTAT DATABASE <http://ec.europa.eu/eurostat/data/database>
- [20] European Commission 2014. Report on critical raw materials for the EU. Report of the Ad-hoc working group on defining critical raw materials. European Commission.
- [21] BGS 2012. Risk list 2012- Current supply risk for chemical elements or element groups which are of economic value.
- [22] BGS 2015. Risk list 2015- Current supply risk for chemical elements or element groups which are of economic value.
- [23] Krebs, Robert E. *The history and use of our earth's chemical elements: a reference guide*. Greenwood Publishing Group, 2006. ISBN: 9780313334382
- [24] Chapman, A., et al. "Study on Critical Raw Materials at EU Level." Oakdene Hollins: Buckinghamshire, UK (2013).
- [25] CRM_InnoNet: Substitution of Critical Raw Materials. "Critical Raw Materials Substitution Profiles". September 2013. Revised May 2015. Accessed Online: October 2016. Link: <http://www.criticalrawmaterials.eu/wp-content/uploads/D3.3-Raw-Materials-Profiles-final-submitteddocument.pdf>
- [26] E. Commission, "Report on Critical Raw Materials for the EU," European Commission, 2015.
- [27] D1.1 "Current and future needs of selected refractory metals in EU" MSP REFRAM EU H2020 project
- [28] D4.2 "State of the art on the recovery of refractory metals from urban mines" MSP-Refram project EU H2020.
- [29] *Critical Metal Handbook, First Edition*, Edited by Gus Gunn. Chapter 15 "Tantalum and Niobium" by Robert Linnen, Dave Trueman and Richard Burt. 2014
- [30] Chapman, A., et al "Study on Critical Raw Materials at EU Level" Oakdene Hollins: Buckinghamshire, UK (2013)
- [31] CRM_InnoNet: Substitution of Critical Raw Materials. "Critical Raw Materials Substitution Profiles". September 2013. Revised May 2015. Accessed Online: October 2016. Link: <http://www.criticalrawmaterials.eu/wp-content/uploads/D3.3-Raw-Materials-Profiles-final-submitted-document.pdf>

