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RECOVERY OF TANTALUM FROM DIFFERENT RESOURCES

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Abstract
Tantalum is a chemical element with important properties. It is used in industry and its numerous branches for instance in jewelry and watchmaking products. As a result, it is not uncommon for this metal to become an object of interest for a variety of buyers. After it has been bought back from the customers, tantalum can be recycled and, as a result, its full content can be retrieved. In economy, tantalum has become a 'technology-critical element' which is increasingly used in new technologies. This has led to a need to evaluate potential environmental impacts, which, in turn, requires knowledge of its concentration in the natural and industrial environment. This paper will present secondary sources of tantalum extraction and recycling, which makes it possible to limit the use of this raw material from natural sources, which are in increasing exhaustion. The analysis also includes the case study of the old Penouta mine, and processing of tailings from waste-rock heaps and ponds on these area. It is located in the innermost part of the Iberian Variscan Belt in Galicia in northwest Spain where two main formations crop out: the Viana do Bolo Series (high-grade metamorphic rocks) and the Ollo de Sapo Formation.

Keywords: **Tantalum; Recycling; Critical raw material; Mine waste; Tailings; Capacitors.**

1. INTRODUCTION

Tantalum is used in the electronics industry to produce electrolytic capacitors, which are found in every electronic device, defense and space equipment. It is used in the production of chemical equipment due to its resistance to most acids and bases. On the one hand, it is widely used in industry and its numerous branches and on the other hand in jewelry or watchmaking products [1]. As a result, it is not uncommon for this metal to become an object of interest for a variety of buyers. After it has been bought back from the customers, tantalum can be recycled and, as a result, its full content can be retrieved [2].

The major use for Tantalum, as the metal powder, is in the production of electronic components, mainly capacitors and some high-power resistors [3]. Tantalum electrolytic capacitors exploit the tendency of tantalum to form a protective oxide surface layer, using tantalum powder, pressed into a pellet shape, as one "plate" of the capacitor, the oxide as the dielectric, and an electrolytic solution or conductive solid as the other "plate" [4]. Tantalum is used in a variety of alloys to add high strength, ductility and a high melting point. When drawn into a fine wire, it's used as a filament for evaporating metals such as aluminum. More than half of tantalum's use is for electrolytic capacitors and vacuum furnace parts.

The exceptional properties of Ta have led to a high demand for these metal for highly specialized applications (Fig. 1). The main application as already was mentioned is capacitors. In addition, there are super alloys or sputtering targets [5].

Capacitors are, and are expected to remain, the largest single market but the increasing functionality of smartphones, and ongoing changes in capacitor size, are the main limitations on growth of these sector because the Ta content required for manufacturing is decreasing in natural resources [6].

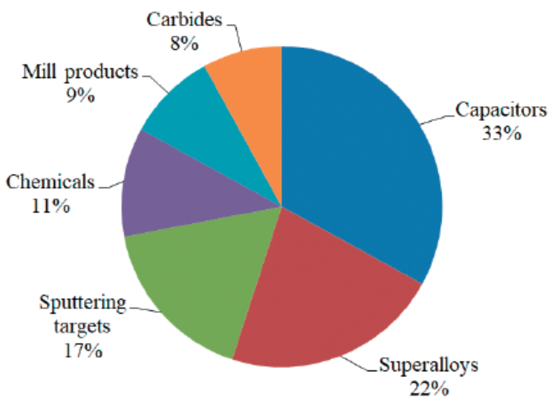

Figure 1.
Main applications of Ta [4]

2. SECONDARY SOURCES OF TANTALUM RECEIVING FROM RECYCLING

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 [7]. Tantalum is extracted from cassiterite placer middling using shaking tables, and magnetic and electrostatic separation methods [8, 9]. Tin smelter waste typically contains 8 to 10 per cent tantalum oxide, although exceptionally this may rise to 30 per cent [10]. Low grade smelter waste can be upgraded by electro thermic reduction yielding a synthetic concentrate with up to 50 per cent tantalum and niobium [11].

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 [12]. According to the "Tantalum-Niobium International Study Center" (TIC) the production from secondary resources has grown considerably between 2008 and 2012. The best quality slags have been found in Brazil, Thailand and Malaysia, which are most important producers of slag based Ta. Due to reduction of tin mining, the most interesting sources are old slag dumps [13].

The potential of old tin slags and other waste areas has also been studied in Europe. Table 1 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 [5, 12, 14].

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 [15]. It has been estimated that about 5% of WEEE ends up to municipal landfills or incineration plants [16]. 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 [17]. 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 [6, 18]. 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 [19]. These means that both manufacturing and end-of-life is available in Europe. The different waste tantalum sources are listed in Tab. 1.

Table 1.
Secondary resources of Tantalum

Material type	Size of source	Location/Owner	Comments	Physical Properties – particle size	Chemical properties – main component
Municipal landfills MSW containing WEEE [17]	Estimated Ta concentration in MSW about 1 mg/kg 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/ Municipalities	Low concentrations mixed into large amounts of MSW. Very little information and no data about Ta concentration 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

Disposal areas of incineration slags. MSW incinerations slags [2]	About 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
Industrial landfills containing waste from WEEE processing [17]	Not applicable	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	Not applicable
Mine waste [9]	Not available	Echassieres, France		Not applicable	Not applicable
Mine waste [10]	Closed pegmatite mine	Hagenforf, Germany		Not applicable	Not applicable
Tin mining residues tantalite Albite-, Amblygonite-, Arsenopyrite-, Beryl- Cassterite-, Columbite-, Muscovite-, Pyrite-, Quatrz [12]	Not known, surface storage areas	Vieiros Canadelo, Porto Region, Portugal	Closed tin mining area	Not applicable	Ta concentrations not available
Tailings and waste from tin mining [9]	Tailings 5Mt and waste dump 6.8 Mt	Penouta, Spain/Aprovecha mineto Mineiro	Closed tin mining area, tailings and waste studied for recovery of Ta	Not applicable	Tailings 48 g/t; waste dump 27 g/t
Mine waste and tailings [9]	Not known	Bessa, Portugal		Not applicable	not applicable
Slag [22]	About 1 000 t of radioactive slag from Nb production Larger amounts of light waste Apatite-Calcite-Mica, deposited to the sea	Sove, Norway	Small quantity, due to radioactivity will be either transported to a waste area or contained	Not applicable	Containing Ta (1.34% Ta_2O_5), Th, Zircon
Waste from uranium mining [12]	not applicable	Straz, Czech republic		Not applicable	Not applicable
Mine tailings, pegmatite-granite 12]	Cosed Be-Ta mine	Rosendal, Finland			Li-Nb-Ta
Tin slag [22]	Not know	Golbejas, Salamanca Spain	Tin and Ta mine closed in early 1980s, potential to start mining again has been studied. Waste areas have been at least partly reprocessed in 1980's	Not applicable	Not applicable
Tailings of china clay extraction [18]	Ta, Nb, Ti, Sn Columbite-tantalite, cassterite, 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

There are many methods of tantalum recycling from waste electrical and electronic equipment (WEEE). Acknowledged practice is mechanical separation of tantalum by breaking and milling [20]. Otherwise, it is possible to burn the epoxy resin in 500÷10000°C for 1÷5 hours. Oxidation is also obtained Ta_2O_5, which can be reduced most commonly with Na, Mg or Ca. Tantalum capacitors can be leached e.g. in aqua regia, concentrated HCl, NaOH or KOH [21]. The leaching capacitors by using iron chlorides (FeClx) tantalum chloride is obtained, which is then reduced with Mg [22].

3. RECOVERY OF TANTALUM FROM TAILINGS – CASE STUDY OF THE OLD PENOUTA MINE

The Penouta Sn-Ta-Nb deposit is located in the Central Iberian Zone, in the innermost part of the Iberian Variscan Belt in Galicia in northwest Spain where two main formations crop out: the Viana do Bolo Series (high-grade metamorphic rocks) and the Ollo de Sapo Formation, characterized by a volcanogenic sequence which mainly consists of augen gneisses [23]. Fig. 2 show the areas of Penouta Mine.

The following areas may be differentiated on the old tailings of the Penouta Mine (Fig. 2):

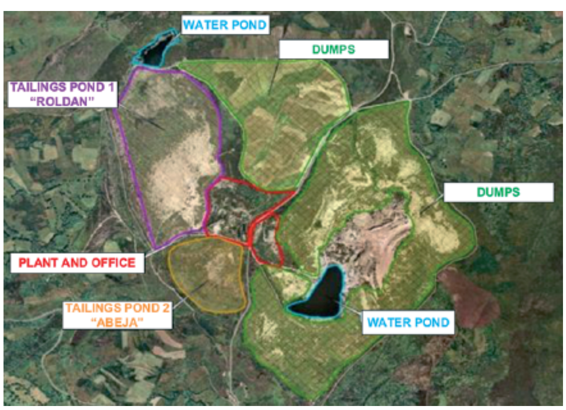

Figure 2.
The areas of Penouta Mine [9]

- Tailings Pond 1 –"Roldan": 4.8 Mt, average grades of 387 ppm Sn and 48 ppm Ta (Indicated resources),
- Tailings Pond 2 "Abeja": 0.2 Mt, average grades of 421 ppm Sn and 26 ppm Ta (Inferred resources),
- Waste-rock heaps: 6.8 Mt, average grades of 428 ppm Sn and 27 ppm Ta (Inferred resources) [9].

The processing of tailings from waste-rock heaps and ponds of the old Penouta mine leads to the obtaining of tantalum and niobium minerals [24]. It should be noted that Ta and Nb are known as rare metals because of their scarcity in nature. Thanks to their exceptional properties, they are elements that today have important applications in new technologies, medicine, and science [25].

The biggest tantalum reserves in the world are located in South America (40%) and also in Australia (21%), but only 1% being found in Europe. With the exception of small quantities of tantalite that are obtained as a by-product from the exploitation of kaolin in France, there is no production of primary origin in the EU. There are only a few processors in the EU, that is, in Estonia, Austria, Germany, and UK (mainly secondary materials).

In Europe there are known deposits of niobium and tantalum in Finland and Norway, but they cannot be economically exploited using conventional processes. There are some deposits of niobium and tantalum in Spain that could be exploited in satisfactory economic conditions [26].

Tantalite and columbite are the main sources of tantalum and niobium in the Penouta mine. Thanks to the development of new technologies and the evolution of old mineral separation techniques, it is possible to recover the metals of interest contained in these tailings and waste-rock heaps of the former Penouta mine [27].

During the processing of tailings from waste-rock heaps and ponds of the old Penouta mine, around 1% of tin, tantalum, and niobium concentrate is obtained, which is sold to international companies that process the raw material to generate intermediate compounds that serve to produce highly specific components. In this process 99% of mining tailings are generated, which are mainly composed of silicate minerals that can be reprocessed, obtaining around 70% of industrial minerals, namely quartz, mica, feldspar, and kaolin. The aim of the overall process is to achieve approximately 80% revalorization of mining wastes [28].

The Penouta mine scheme could also be applied to other mining deposits not only in Spain but also in the rest of the Europe, which contain Sn associated with various CRMs such as Ta, Nb, or W. There are numerous ore deposits here that have been previously exploited and, as in Spain, were mostly abandoned after the fall in metal prices. Therefore, there are many abandoned waste-rock heaps and ponds with a certain degree of mineralization that should follow this example [26, 27].

The minerals consisting of these elements react to separation by density in a similar way, which is the principle on which the gravimetric separation performed in Penouta is based. This fact is an advantage in replicating this model of utility in other mining wastes, but it is also an obstacle because each deposit has its own characteristics mineral associations. The market situation can also define whether or not a low grade mining waste is profitable or not at a given moment, in addition to the regional distribution (there are serious energy supply limitations in some mining areas), and the political and regulatory conditions in each region [27, 28].

4. CONCLUSIONS

Metals, minerals and natural materials are part of our daily life. Raw materials, which are the most important from an economic point of view and whose supplies are subject to high risks, are called critical raw materials. Critical raw materials are essential for the functioning and integrity of many different industrial ecosystems. The new industrial strategy for Europe proposes to strengthen Europe's open strategic autonomy, warning that a transformation of Europe leading to climate neutrality could replace the current dependence on fossil fuels by dependence on raw materials, a large part of which Europe obtains abroad and for which there is increased global competition. The EU's open strategic autonomy in these sectors will therefore have to continue to be based on diversified and undistorted access to global raw material markets. At the same time, in order to reduce dependence on external factors and environmental pressures, the fundamental problem of rapidly growing global demand for resources must be addressed by reducing material consumption and reuse before recycling [29].

Tantalum is also included in the list of critical raw materials due to its important use in various technologies. Its primary deposits are currently depleted, so it is important to look for secondary sources of its occurrence as well as methods of its recovery depending on its source. The described example of the old Penouta mine is a great case study on which the methods of searching for tantalum can be based. Moreover, it is also worth to focus on end-of-life products, which are one of the best secondary sources for recycling and recovery of tantalum. Nowadays it is the capacitors that are the best source of this raw material [3, 5, 6].

Access to resources and sustainability are key to the EU's resilience in the area of raw materials. Achieving resource security requires action to diversify supplies from both primary and secondary sources, reduce dependency and improve resource efficiency and closed-loop circulation, including sustainable product design. This applies to all raw materials, including base metals, industrial minerals, aggregates and biotic raw materials, but is even more necessary for raw materials that are critical for the EU [30]. In addition, the COVID-19 crisis has revealed how quickly and how deeply global supply chains can be disrupted, making it all the more necessary to search for new, secondary sources.

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