

## Article

# Simulation to Recover Niobium and Tantalum from the Tin Slags of the Old Penouta Mine: A Case Study

Ricardo Magdalena <sup>1,\*</sup>, Alicia Valero <sup>1</sup>, Guiomar Calvo <sup>1</sup>, Francisco J. Alguacil <sup>2</sup> and Félix Antonio López <sup>2</sup>

<sup>1</sup> Campus Rio Ebro. C/Mariano Esquillor Gómez, CIRCE Institute, Universidad de Zaragoza, 15, 50018 Zaragoza, Spain; aliciavd@unizar.es (A.V.); gcalvose@unizar.es (G.C.)

<sup>2</sup> Centro Nacional de Investigaciones Metalúrgicas (CENIM), Consejo Superior de Investigaciones Científicas (CSIC), Avda. Gregorio del Amo, 8, 28040 Madrid, Spain; fjalgua@cenim.csic.es (F.J.A.); f.lopez@csic.es (F.A.L.)

\* Correspondence: rmagdalena@unizar.es

**Abstract:** Demand for niobium and tantalum is increasing exponentially as these are essential ingredients for the manufacture of, among others, capacitors in technological devices and ferroniobium. Mine tailings rich in such elements could constitute an important source of Nb and Ta in the future and alleviate potential supply risks. This paper evaluates the possibility of recovering niobium and tantalum from the slags generated during the tin beneficiation process of mine tailings from the old Penouta mine, located in Spain. To do so, a simulation of the processes required to beneficiate and refine both elements is carried out. After carbothermic tin reduction, the slags are sent to a hydrometallurgical process where niobium oxide and tantalum oxide are obtained at the end. Reagents, water, and energy consumption, in addition to emissions, effluents, and product yields, are assessed. Certain factors were identified as critical, and recirculation was encouraged in the model to maximise production and minimise reagents' use and wastes. With this simulation, considering 3000 production hours per year, the metal output from the tailings of the old mine could cover around 1% and 7.4% of the world annual Nb and Ta demand, respectively.

**Keywords:** coltan; niobium; tantalum; critical raw materials; technological metals; mineral processing; tailings



check for updates

**Citation:** Magdalena, R.; Valero, A.; Calvo, G.; Alguacil, F.J.; López, F.A. Simulation to Recover Niobium and Tantalum from the Tin Slags of the Old Penouta Mine: A Case Study. *Minerals* **2021**, *11*, 1123. <https://doi.org/10.3390/min11101123>

Academic Editors: Bohdan Křibek, Ondřej Šrámek and Grzegorz Gzyl

Received: 16 September 2021

Accepted: 7 October 2021

Published: 13 October 2021

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

The 20th century has been characterised by a drastic increase in global material extraction, and this trend is far from changing in the 21st century [1,2]. In the last decades, we have seen a considerable increase in the demand for certain metals, especially intended for the manufacture of electric and electronic components [3,4].

Electric and electronic equipment (EEE) allow for increased efficiency and better experiences in technological devices, the Internet of Things (IoT), Machine Learning (ML), or Artificial Intelligence, among others [2]. They are also crucial in the development of clean technologies. Indeed, digital technologies need to be combined with clean technologies to mitigate climate change. In the “Mission Innovation” signed in Paris in 2015, 20 countries agreed to promote the acceleration of innovation on clean energies to make them more affordable and accessible to all, and achieve the goals of the Paris Agreement and pathways to net-zero [3]. This, in turn, increased the investment of governments and deployment of renewable energies, a type of technology that requires a considerable amount of critical materials in the manufacturing process [4,5].

In short, the use and applications of electric and electronic equipment (EEE), both in renewable energies and in other fields, is steadily growing as innovation has made devices more efficient [6,7]. This development usually implies an increase in the number and variety of the metals used [8,9], improving the capabilities of electronic devices [10].

The abovementioned is the case of niobium (Nb) or tantalum (Ta), both crucial for EEE and renewable energies. Niobium is an essential metal for manufacturing ferroalloys, such as ferroniobium, containing between 60%–70% niobium [11]. It also forms part of high-strength low alloy (HSLA) steels [12]. Tantalum is used almost entirely in electronic devices, specifically in capacitors and in different parts of smartphones such as lenses, batteries, microprocessors, etc. Both metals were discovered centuries ago; still, they have only begun to be used in the last decades. However, even if they are included in small quantities on each device, the total amount used at the world level is considerable. Moreover, their future availability could be dangerously compromised as the primary sources, meaning the places where they are mined are limited [13]. They are considered critical by many countries and institutions, as their current and future availability, or the concentration of supply, could put many economies at risk [14–16].

Therefore, securing a stable supply of certain raw materials including Nb and Ta is essential for many governments, such as the European Union, which promotes the so-called circular economy [17]. Unfortunately, current technologies are not designed to recover all the components and valuable metals from the waste of electric and electronic equipment (WEEE) [18]. This could be eventually solved following eco-design guidelines [19].

Alternatively, a stable supply of raw materials can be secured by resorting to domestic production. Yet, this is not free of difficulties, as there is much opposition to the opening of new mines due to the social and environmental issues that this may entail [20].

In this respect, the long mining tradition has left many abandoned facilities and discarded materials such as tailings, which are also a source of concern. If the remediation process is insufficient, it can cause a series of environmental impacts. Tailings can contain certain elements whose mobility and dispersion may pose an environmental hazard for soils, water, ecosystems, and people [21,22].

That said, particular mining wastes may include considerable amounts of valuable elements discarded during the initial mining process for not being economically profitable at the moment of exploitation. These wastes could become a relevant source of raw materials in the future, thereby increasing the domestic supply of metals that are currently almost only imported. However, the metallurgical processes to recover valuable metals from tailings usually involve the use of toxic substances. Therefore, the processes that can be applied have to be studied in depth, analysing how the use of reagents could be minimised to avoid further impacts.

This paper explores the potential recovery of niobium and tantalum from the zinc tailings of an abandoned mine in Spain. To that end, a virtual pilot plan modelled with HSC chemistry was set and optimised to maximise its efficiency and identify costs of chemicals, water, electricity, and emissions.

## 2. Niobium and Tantalum Production and Availability

According to the United States Geological Survey (USGS), Brazil is the largest niobium producer at the world level, and this trend has been maintained over the last few decades (Figure 1). Only in 2020, this single country was responsible for 91% of the niobium world production, followed by Canada (8%) [23]. Niobium reserves are also mainly concentrated in Brazil (95%) and Canada (3.5%), while the remaining are located in Angola, Australia, and South Africa, among others [24].

As for tantalum, one of the most valuable ores from which this metal is extracted is coltan. Coltan is a mixture of two minerals: tantalite, where tantalum predominates, and columbite, where niobium predominates. For this reason, coltan is also an important source of niobium.

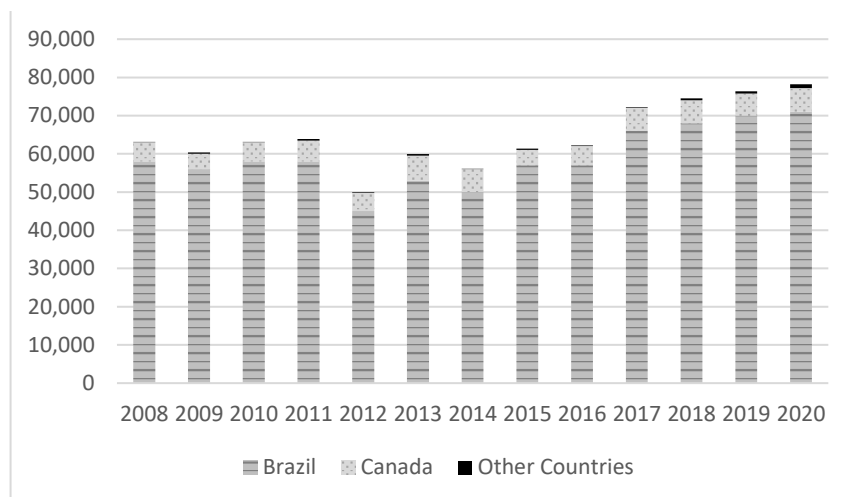


Figure 1. Historical production of niobium in metric tons, adapted from [23].

More than 60% of tantalum reserves are hosted in the Democratic Republic of Congo (DRC), while the remaining are in Brazil and Australia [25]. DRC alone was responsible for 40% of the total world production in 2020 [23]. Historical tantalum production can be seen in Figure 2, clearly showing the predomination of Africa over other regions of the world.

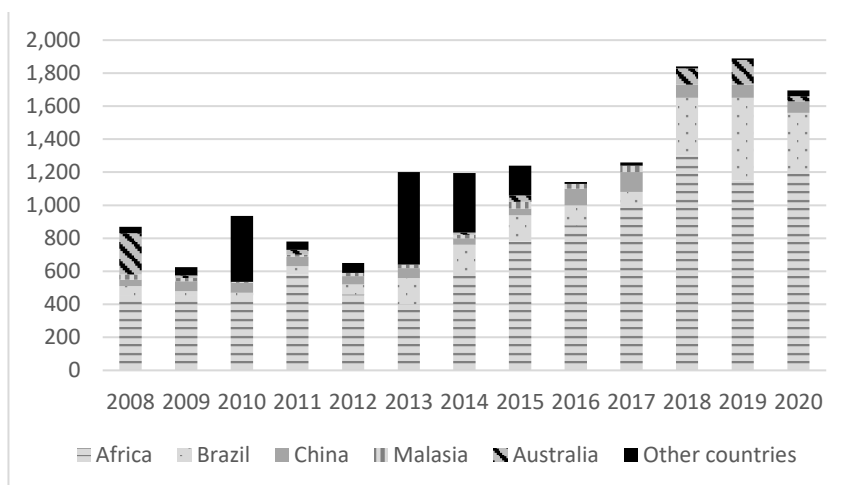


Figure 2. Historical production of tantalum in metric tons, adapted from [23].

Africa plays, thus, a key role in tantalum production since it has been responsible for more than 60% of the global production on average in the last years. Before 2008, Australia had an important market share, reaching almost 50% of the total world production [26]. However, with the worldwide crisis that occurred in 2008, some of the biggest mines in Australia suspended their activity due to financial difficulties, reducing their production share in the global market in the following years [27].

The concentration of supply in DRC and Rwanda, countries that arguably do not respect human and work rights, is a global concern [28,29]. Some of the most powerful companies agreed to obtain every metal used in their devices from a trustworthy resource [30]. To that end, a certificate can be provided to the end-user, claiming that the device has been manufactured by companies that respect human and work rights, from the extraction of the mineral until the device is sold [28].

Another alternative to overcome this situation of supply concentration is to find new ways to obtain niobium and tantalum or new sources. For this endeavour, the slags generated during the tin beneficiation process in the Penouta mine (located in Spain) will

be analysed as a future source for both metals. Different geological studies were carried out, but the mine ceased its activity in the 1980s due to a decrease in tin price and depletion of higher ore grade zones.

#### *Penouta Mine*

The history of the Penouta mine goes back to the beginning of the 20th century when the area was first exploited, and small amounts of cassiterite were extracted. Mining activity was then resumed in the 1960s and until 1971, becoming one of the most important tin mines in Europe. During the last years of activity, around 1,600,000 t of rock were extracted, containing around 640 t of cassiterite and 170 t of tantalite concentrate [31]. This deposit consists of a greisenised, altered and kaolinised granite mass enclosed in metamorphic rock, with disseminated cassiterite and columbo-tantalite [32]. In the 21st century, new studies were carried out. Between the two zones analysed, estimated resources add up to 11,910,402 t of ore, with a Sn and Ta content of 428 and 35 ppm, respectively. In 2020, Strategic Minerals Spain resumed the mining activities in the area, becoming again the only mine in Europe in which concentrates of Nb and Ta are recovered, but not yet refined.

### **3. Methodology and Data Availability**

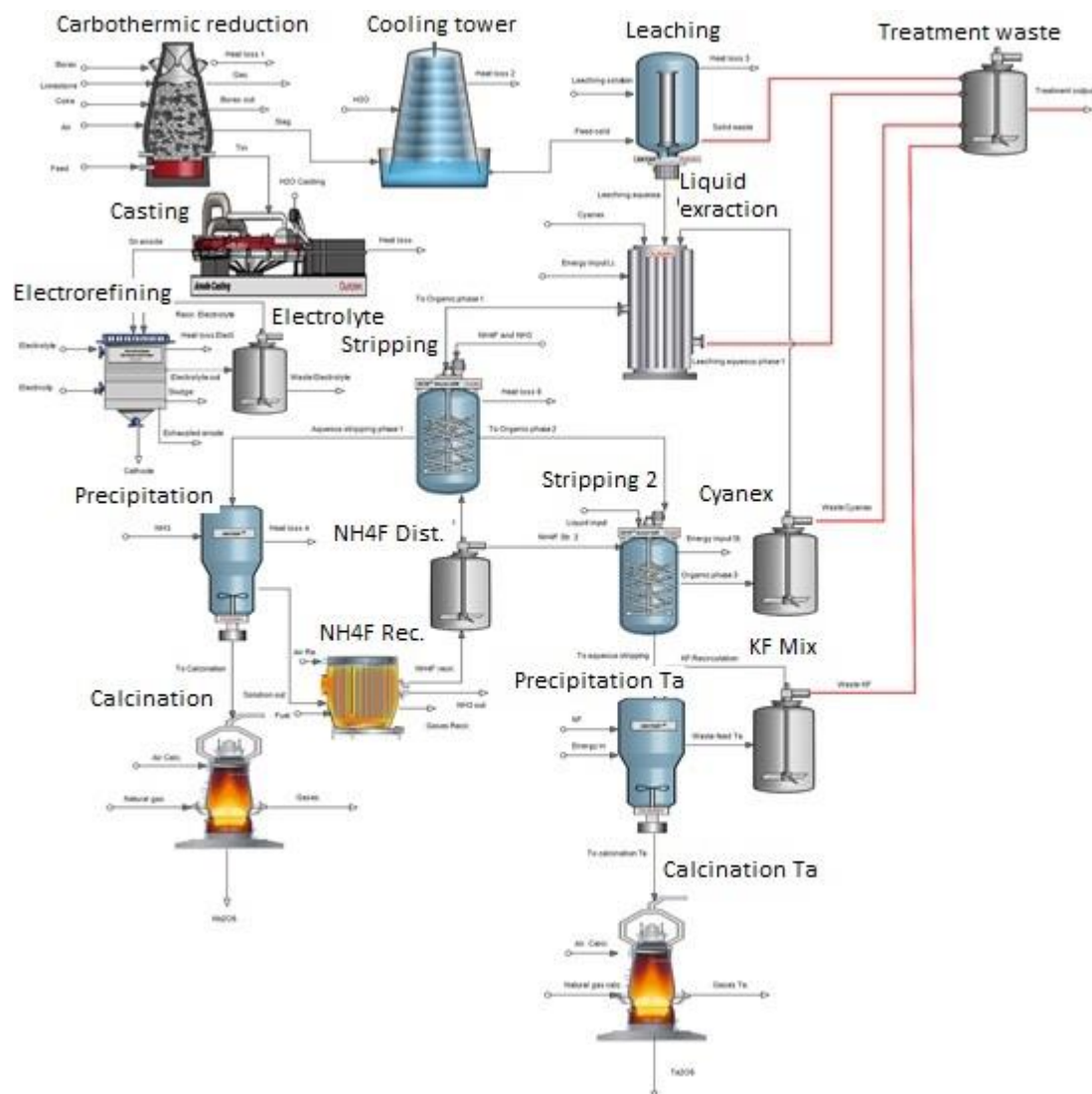
#### *Model for Recovering Nb and Ta from Slags*

The aim of this study is to analyse the possibilities of the recovering process of Nb and Ta from tin slags using a simulation of a metallurgical plant. Similar simulations using the same software to recover metals from common rocks, such as iron, lead, zinc, and gold, have been carried out in previous studies [33–35].

As stated before, the Penouta tin mine was selected for the case study. Tin was initially obtained from cassiterite ( $\text{SnO}_2$ ), containing important concentrations of Nb and Ta that could be economically profitable to recover [36]. The slags obtained after the first metallurgical process still have an important concentration of Nb and Ta. Until now, they had remained in the tailings as they could not be beneficiated when the mine was operating, yet they constitute a valuable source of such commodities.

The processes required for niobium and tantalum recovery were already studied by different authors in previous studies, establishing the initial concentration for the three metals considered [36–39]. As niobium and tantalum have similar chemical and physical properties, their separation and purification processes are considerably difficult [38]. Still, they can be recovered from the slags generated after a carbothermic reduction [39,40]. Additionally, recent investigations driven by research groups at CSIC developed a process at lab scale to recover Nb and Ta by solvent extraction from Sn-Ta-Nb mining tailings which has also been the seed of this study [40].

Figure 3 shows the flowsheet of the processes used to recover the three metals generated with HSC Chemistry. The process starts with the tailings coming from a particular mine with Sn-Nb-Ta, in our case, Penouta. It is important to mention that before the beginning of the process, comminution is needed to reduce the rock coming from the tailings; for this, jaw crushers and ball mills are used. The particle size is then reduced to 200  $\mu\text{m}$  and sent to the feed of the metallurgical process. Next, it is necessary to proceed with pre-concentration in the industrial plant. After mixing the minerals of the feed with some additives, they are sent to the carbothermic reduction to start the purification of metals [39]. Carbothermic reduction is applied to separate Sn from other oxides.



**Figure 3.** Flowsheet of the process used to recover Sn along with Nb and Ta from the slags.

At this point, Sn is obtained with a concentration higher than 96%, while the slags contain a significant concentration of Ta and Nb, 25% and 21%, respectively [39]. As the final product should be 99.99% Sn, it is necessary to apply an electrorefining process in order to increase its concentration. To that end, an electrolyte of  $\text{H}_2\text{SO}_4$  is prepared in order to separate impurities from Sn, increasing its concentration to the desired value [39].

On the other hand, slags are sent to different units to extract Nb and Ta. The feed is first sent to the leaching unit, obtaining solid wastes and another output in an aqueous phase, which ends in the liquid-liquid extraction unit. It is then mixed with organic additives, discarding the leaching aqueous phase and redirecting the organic phase output into the stripping unit. Additionally,  $\text{NH}_3$  and  $\text{NH}_4\text{F}$  are added since this is the unit where Nb and Ta will be separated. By using these additives, a new enriched Nb aqueous phase is formed, finishing in the precipitation unit. Meanwhile, the other output, still in the organic phase, is sent to a new stripping unit to convert it into an aqueous phase, too. It follows precipitation for both feeds, aiming at eliminating any impurities before continuing with the last phase of the process, calcination. Calcination is used to eliminate the undesired water and humidity, recovering at the end of the whole process, Nb with a concentration close to 99% and Ta with a concentration of 78%.

It is important to mention that there are also several recirculation units and that a vast number of reagents are needed for this whole process. To reduce the total use of chemicals,

feeds are recirculated and introduced again in the units when possible. One example is the “mixing Cyanex 923” unit, where 95% of the total Cyanex 923 is recirculated in order to maximise its use. Another one is the “mixing KF” unit. It is not possible to use 100% of this reagent due to the conditions needed in the extraction of tantalum. For that reason, a recirculation of 65% is assumed, thereby re-using it as many times as possible.

This process has been widely studied by different authors [41,42] as coltan has become one of the most important minerals in industry. Additionally, its scarcity and concentration of supply are also well known. Hydrometallurgy processes used to recover these two elements are based on strong acids, which are economically and environmentally challenging. One of these studies considers a greener approach for the selective dissolution of the amorphous slag matrix, obtaining a concentration similar to commercial grade [41]. This same study reflects the high mass losses produced by sequential acid and alkaline leaching, while the sequential Acid-Basic-Acid leaching is the most favourable, with concentrations of 63% [41]. One of the main disadvantages of this process is the high amount of chemicals needed to purify the metals. Another study analyses the availability to purify Nb and Ta from tin slags with a very low ore grade [42]. Although the recovery ratio of the metals is very high and the results are very promising, a vast number of processes, time, and a high amount of chemicals are required [42]. As a result, the environmental impact is very high, and with the reagents applied, it makes this process less cost-efficient compared with the process proposed in this paper.

In this study, alternative chemicals as those proposed in the literature are used during the leaching process, thereby reducing material losses as well as increasing the metal yields. In that same line, in our case study, the aim is to reuse reagents as much as possible to decrease the environmental impact of the whole process.

Once the initial model of the treatment plant is ready, a preliminary analysis of the different inputs needed to purify the three main metals present in this mine (Sn, Nb, Ta), as well as a thermodynamic analysis for a future set up of the metallurgy plant, is undertaken.

#### 4. Results

The process validated at lab scale, is upscaled with a specialised software called HSC Chemistry. This software allows to assess costs and optimise processes [43]. In particular, for this paper, it has been applied for thermodynamic and mineral processing calculations, such as mineral extraction, beneficiation, and mineral refining [33].

The first step is to determine the amount of rock per hour to be treated, selected as 1 ton per hour (tph). This number is in accordance with the size and capacity of the mine. After setting up all equipment, flows, and reactions taking place, the amounts of reagents needed for the whole process (and for each unit) as well as outputs of metals and electricity used, among other factors, were obtained, as described in the next sections.

##### 4.1. Reagents and Water Used

Table 1 shows information about the flow rates of the different reagents introduced in the system.

**Table 1.** Amount of reagents introduced (in t/h).

Borax	Limestone	Coke	HF	H <sub>2</sub> SO <sub>4</sub>	Cyanex 923
0.14	0.20	0.23	0.49	2.03	0.07
Solvesso	NH <sub>4</sub> F	NH <sub>3</sub>	KF	Natural gas	
0.12	0.11	0.66	0.03	0.03	

A significant number and amount of chemicals are used in the aforementioned process to recover Sn, Nb, and Ta. Nonetheless, sulphuric acid is the most used reagent, with 2.03 t/h. This is something that is consistent with the beneficiation process used, as an

electrolyte is needed to process more than 0.5 t/h of Sn in order to increase its concentration to 99.99%.

The type of reagents used in each metallurgical unit have also been analysed (Figure 4). This way, it is possible to compare which reagents are used on each specific part of the whole process and their share with respect to the total use on each unit.

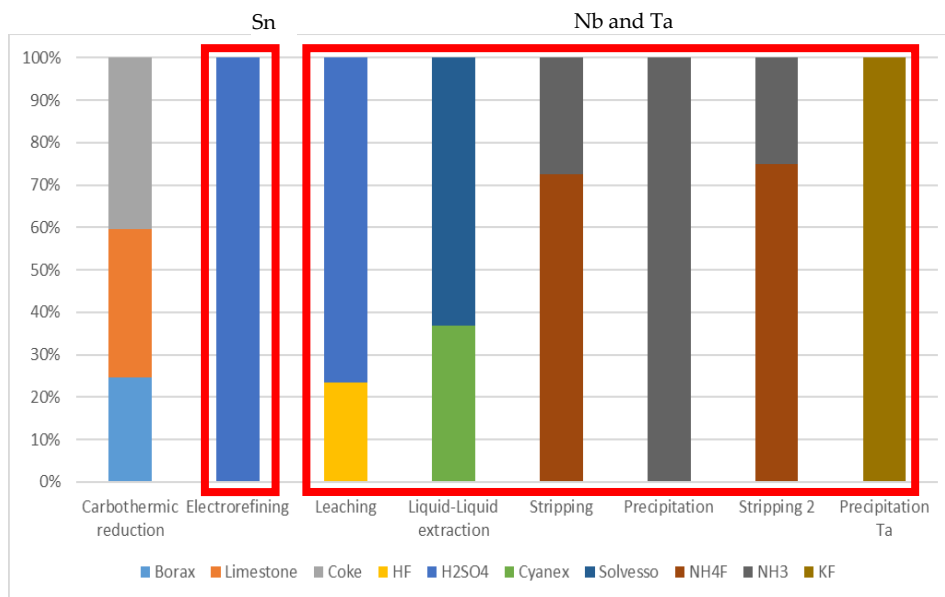


Figure 4. Share of reagents needed in each unit of the treatment and beneficiation process of Sn, Nb, and Ta.

In this case, it is also possible to see how the carbothermic reduction is the unit where a greater number of different reagents are introduced (borax, limestone, and coke). Moreover, the liquid-liquid extraction process also stands out as a crucial unit since the phase changes from aqueous to organic. Specifically, it is the only unit that uses Solvesso (solvent) and Cyanex 923(extraction agent). Additionally, HF is only used in the leaching unit and KF in the precipitation of tantalum, while NH<sub>3</sub> is used in three different units, stripping 1 and 2, and precipitation.

Among the materials used during the beneficiation process, water is the largest input in the system with almost 12 t/h, which is a common rate used in metallurgical processes [44].

Of these 12 t/h of water needed, almost half (5.12 t/h) are used in the electrorefining unit (Figure 5). The second unit, where more water is required, is in the stripping because of the high volumetric relation between the organic and the aqueous phase.

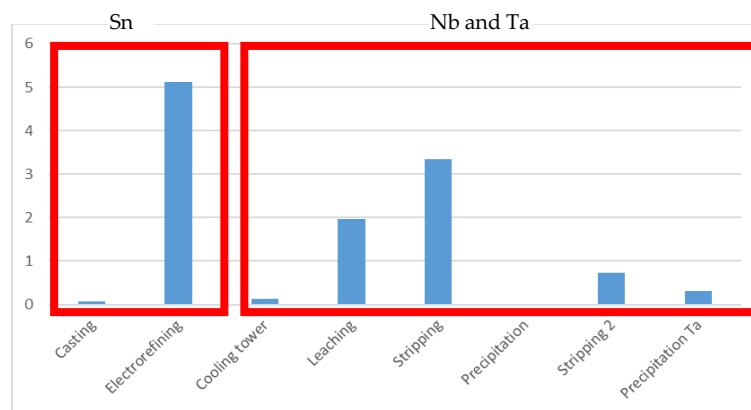


Figure 5. Water requirements in the beneficiation process of Sn, Nb, and Ta (in t/h).

#### 4.2. Metal Output

At the end of the process, the metals obtained are tin, niobium, and tantalum. Table 2 shows how much metal is recovered with a feed of 1 t/h of ore. The main difference between these metals is that tin is recovered after two metallurgy processes using a very small number of reagents. A total of 0.50 tons of tin are recovered per hour and considerably lower amounts of Nb and Ta. Besides, niobium and tantalum are recovered as by-products. Their initial concentration is very small, and a higher number of processes and chemicals are needed to purify them.

**Table 2.** Metal output (in t/h).

Metal	Amount
Sn	0.45
Nb	0.03
Ta	0.05

#### 4.3. Electricity Consumption and Gas Emissions

The electricity required for the hydrometallurgy processes, as well as the gases generated during them, are also considered in the study.

Electricity is needed during the process to move the blades that are in charge of mixing the reagents with the feed [45]. During the simulation with HSC, it is not possible to directly obtain figures on electricity consumption as this parameter is related to the feed introduced and the size of the units. However, some authors state that an average value could be between 0.05 and 0.1 kW/m<sup>3</sup> [46].

Since the volume of every hydrometallurgy unit is known, it is then possible to calculate the electricity needed for our process, choosing the highest electricity consumption value (see Table 3).

**Table 3.** Electricity needed on each unit.

Unit	Electricity (kW)
Electrolyte mix	1.062
Leaching	0.416
Liquid-Liquid extraction	0.842
Stripping	0.959
Precipitation	0.515
Mixing reagents	0.428
Stripping 2	0.858
Mixing Cyanex 923	0.421
Precipitation Ta	1.31
Mixing KF	1.301

The highest energy values correspond to the units that precipitate and recirculate Ta. This is in line with the results obtained during the simulation since the volumetric relation between H<sub>2</sub>O and the reagent used to precipitate Ta is very high. Consequently, recirculation units must be similar to the previous units since the amount of feed introduced is within the same order of magnitude, and therefore, it will have a high energy consumption.

According to some studies, the electricity needed to send tin to electrorefining could be between 150–200 kW/t/tin [47]. Therefore, with the amount of pure Sn obtained in our simulation, the electricity needed would be in the range of 75–100 kW.

As for gaseous emissions, mainly CO and CO<sub>2</sub> are generated predominantly in three units: carbothermic reduction, Nb calcination, and Ta calcination (Table 4). In the carbothermic reduction, as it is necessary to increase the temperature to 1200 °C so that the process can occur, 0.23 t/h (around 24% of the feed) of coke is introduced, producing 0.84 t/h of CO<sub>2</sub> emissions to the atmosphere. Additionally, both Nb calcination and Ta calcination



also need a temperature of 1200 °C to eliminate the humidity from the feeds. In these cases, 0.02 t/h and 0.01 t/h of natural gas are introduced in the Nb calcination unit and Ta calcination unit, respectively. Compared to the emissions of the carbothermic reduction, they have almost negligible gas emissions to the atmosphere.

**Table 4.** Gases emissions per unit (in t/h).

Output Gases	Carbothermic	Calc. Nb	Calc. Ta
CO	0.06	0.003	0.005
CO <sub>2</sub>	0.84	0.05	0.013

#### 4.4. Analysis of the Results

After processing one ton of ore coming from the Penouta mine, around 0.5 tons of metals are recovered, the vast majority corresponding to tin.

As mentioned, several metallurgical processes are needed to purify Nb and Ta from that ore. Various reagents must be mixed with the feed to produce changes in the phases and separate them so that they finally end up precipitating in the form of almost pure metal. At the end of the simulation, to obtain 30 kg of Nb and 50 kg of Ta, more than 3000 kg of chemicals were used to reach full separation. Moreover, the amount of water needed in the process is not negligible either. Around 12,000 kg of water has to be used to process one ton of ore, of which around 6000 kg are needed in the electrorefining process to purify tin. The rest is used in the remaining processes to concentrate Nb and Ta.

As seen in Figure 3 and after analysing the costs associated with the reagents, it was determined that different recirculation units should be incorporated. Particularly, we introduced five units that recirculate reagents and water. These units are crucial as the requirements of chemicals could increase up to 50% if there were no recirculation.

Additionally, a final unit named “treatment waste” was included in the simulation. All the undesired outputs are recirculated to this unit to proceed with further treatment and decrease the overall environmental impact of the plant. Table 5 shows the most abundant reagents that reach this unit. This can be used to better understand the importance of waste treatment as more than 8000 kg/h of water is discarded and mixed with other substances.

**Table 5.** Certain reagents that end in the treatment waste unit (in kg/h).

Variable	Amount
H <sub>2</sub> O	11,510
HF	370
H <sub>2</sub> SO <sub>4</sub>	2030
CaF <sub>2</sub>	80

According to the results obtained during the simulation, the percentage of recovery at the end of the process from the rock is 45%, 3%, and 5% for Sn, Nb, and Ta, respectively. However, if only tin slags are considered, values for Nb and Ta increase significantly, reaching values close to 50% for niobium and more than 56% for tantalum. These values are considerably higher than those that can be found in the literature [48].

## 5. Discussion and Conclusions

The results obtained from the simulation are very promising since the recovery of niobium and tantalum after tin beneficiation has been demonstrated to be possible. Furthermore, even if the Penouta mine was mainly aimed at obtaining tin, both metals could also be extracted from the slags as by-products with currently available technology. Considering that the current demand of pure Nb in 2017 was 6400 tons while the demand of Ta was 2079 tons, according to our simulation, the metal output from the mine could represent more than 1% and 7.4% of the annual market share for Nb and Ta, respectively, assuming 3000 production hours in a year. These values represent a moderate scenario

since the input introduced could be higher than 1 t/h of rock, depending on the capacity of the mine and ore quality. Additionally, this 3000 production hours in a year could also increase, depending on different factors such as different working shifts, working days in the year, etc.

The main disadvantage found in the simulated process is the number of chemicals that are required, as well as the use of water in the process. This issue could affect the cost-effectiveness of a future processing plant. Additionally, the environmental impacts related to all the reagents discarded should also be closely monitored and find ways to reduce or mitigate them. An example is the Ta precipitation unit. Despite water humidity and KF being recirculated at a 65% rate, high amounts of water are still needed, and a large part of this humidity is discarded and hence lost. The “Liquid-Liquid extraction” unit is also a critical one. This is because an organic phase is introduced in this unit, and an important amount of water and other elements in the water phase end up being discarded.

Until now, in Penouta, Nb and Ta ended up in tailings, but we have proved that there are ways to recover a very significant amount of these elements annually. Looking for new and more sustainable paths to get the most out of the mines and recover metals more efficiently could be a way to overcome future shortages of elements, mineral depletion, and decreasing ore grades without compromising the environment.

**Author Contributions:** Conceptualisation, F.A.L.; data curation, F.A.L. and F.J.A.; formal analysis, R.M.; investigation, R.M.; methodology, R.M.; writing—original draft, R.M.; writing—review and editing, G.C.; funding acquisition, A.V.; supervision, G.C., A.V., and F.A.L. All authors have read and agreed to the published version of the manuscript.

**Funding:** This paper has received funding from the Spanish Ministry of Science and Innovation (PID2020-116851RB-I00 and RTC-2017-6629-5).

**Acknowledgments:** Thanks to Alejandro Abadías of Helmholtz Institute Freiberg for Resource Technology for the revision of the first draft of the paper. We acknowledge support towards the publication fee by the CSIC Open Access Publication Support Initiative through its Unit of Information Resources for Research (URICI).

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Calvo, G.; Valero, A.; Valero, A. Material flow analysis for Europe: An exergoecological approach. *Ecol. Indic.* **2016**, *60*, 603–610. [[CrossRef](#)]
2. Kumar, V.; Ramachandran, D.; Kumar, B. Influence of new-age technologies on marketing: A research agenda. *J. Bus. Res.* **2020**, *125*, 864–877. [[CrossRef](#)]
3. Jung, S.H.; Feng, T. Government subsidies for green technology development under uncertainty. *Eur. J. Oper. Res.* **2020**, *286*, 726–739. [[CrossRef](#)]
4. Calvo, G.; Valero, A. Strategic mineral resources: Availability and future estimations for the renewable energy sector. *Environ. Dev.* **2021**, 100640. [[CrossRef](#)]
5. Stegen, K.S. Heavy rare earths, permanent magnets, and renewable energies: An imminent crisis. *Energy Policy* **2015**, *79*, 1–8. [[CrossRef](#)]
6. Kitajima, T.; Sawanishi, H.; Taguchi, M.; Torihara, K.; Honma, O.; Mishima, N. A Proposal on a Resource Efficiency Index for EEE. *Procedia CIRP* **2015**, *26*, 607–611. [[CrossRef](#)]
7. Ikhlayel, M. An integrated approach to establish e-waste management systems for developing countries. *J. Clean. Prod.* **2018**, *170*, 119–130. [[CrossRef](#)]
8. Parajuly, K.; Habib, K.; Liu, G. Resources, Conservation and Recycling Waste electrical and electronic equipment (WEEE) in Denmark: Flows, quantities and management. *Resour. Conserv. Recycl.* **2017**, *123*, 85–92. [[CrossRef](#)]
9. Valero, A.; Valero, A.; Calvo, G.; Ortego, A. Material bottlenecks in the future development of green technologies. *Renew. Sustain. Energy Rev.* **2018**, *93*, 178–200. [[CrossRef](#)]
10. Xie, F.; Zhang, T.A.; Dreisinger, D.; Doyle, F. A critical review on solvent extraction of rare earths from aqueous solutions. *Miner. Eng.* **2014**, *56*, 10–28. [[CrossRef](#)]
11. Gasik, M.I. Technology of Niobium Ferroalloys. In *Handbook of Ferroalloys*; Butterworth-Heinemann: Dnipropetrovsk, Ukraine, 2013; pp. 411–419. [[CrossRef](#)]
12. Patel, J.; Wilshire, B. The challenge to produce consistent mechanical properties in Nb-HSLA strip steels. *J. Mater. Process. Technol.* **2002**, *120*, 316–321. [[CrossRef](#)]

13. Grandell, L.; Lehtilä, A.; Kivinen, M.; Koljonen, T.; Kihlman, S.; Lauri, L.S. Role of critical metals in the future markets of clean energy technologies. *Renew. Energy* **2016**, *95*, 53–62. [CrossRef]
14. European Commission. *Study on the EU's list of Critical Raw Materials (2020)*; Final Report; Joint Research Centre: Brussels, Belgium, 2020.
15. Department of Industry, Science, Energy and Resources. *Australia's Critical Minerals Strategy*; Australian Government: Canberra, Australia, 2019.
16. U.S. Department of Commerce. *A Federal Strategy to Ensure Secure and Reliable Supplies of Critical Minerals*; Executive Order 13817; U.S. Department of Commerce: Washington, DC, USA, 2019. Available online: <https://www.commerce.gov/data-and-reports/reports/2019/06/federal-strategy-ensure-secure-and-reliable-supplies-critical-minerals> (accessed on 6 October 2021).
17. European Commission. Critical Raw Materials. Government World's Mineral Resources. Raw Material. Available online: [https://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical\\_en](https://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_en) (accessed on 6 October 2021).
18. Ortego, A.; Valero, A.; Valero, A.; Iglesias, M. Downcycling in automobile recycling process: A thermodynamic assessment. *Resour. Conserv. Recycl.* **2018**, *136*, 24–32. [CrossRef]
19. Russo, D.; Spreafico, C. TRIZ-Based Guidelines for Eco-Improvement. *Sustainability* **2020**, *12*, 3412. [CrossRef]
20. Temper, L.; del Bene, D.; Martinez-Alier, J. Mapping the frontiers and front lines of global environmental justice: The EJAtlas. *J. Political Ecol.* **2015**, *22*, 254–278. [CrossRef]
21. González, J.C.A.; Rivero, V.C. Evaluación de la movilidad de metales pesados en residuos mineros de flotación de minería metálica en la provincia de Huelva. *Bol. Geol. Min.* **2011**, *122*, 203–220.
22. Guzmán-Martínez, F.; Arranz-González, J.C.; Ortega, M.F.; García-Martínez, M.J.; Rodríguez-Gómez, V. A new ranking scale for assessing leaching potential pollution from abandoned mining wastes based on the Mexican official leaching test. *J. Environ. Manag.* **2020**, *273*, 111139. [CrossRef] [PubMed]
23. U.S. Geological Survey. *Mineral Commodity Summaries 2021: U.S. Geological Survey*; Federal Source for Science about the Earth; U.S. Geological Survey: Washington, DC, USA, 2021. Available online: <https://pubs.er.usgs.gov/publication/mcs2021> (accessed on 6 October 2021).
24. Dutta, S.K.; Lodhari, D.R. Niobium and Tantalum. Chapter M of Critical Mineral Resources of the United States. Available online: <https://pubs.usgs.gov/pp/1802/m/pp1802m.pdf> (accessed on 6 October 2021).
25. Salazar, I.P.; Valdés, D.A.; Bustamante, N. Análisis descriptivo del coltán en Colombia y sus posibles mercados potenciales. *Trab. Grado* **2010**, *9*, 43.
26. Schütte, P.; Näher, U. Tantalum supply from artisanal and small-scale mining: A mineral economic evaluation of coltan production and trade dynamics in Africa's Great Lakes region. *Resour. Policy* **2020**, *69*, 101896. [CrossRef]
27. Bleischwitz, R.; Dittrich, M.; Pierdicca, C. Coltan from Central Africa, international trade and implications for any certification. *Resour. Policy* **2012**, *37*, 19–29. [CrossRef]
28. Nathan, D.; Sarkar, S. Blood on your mobile? *Econ. Political Wkly.* **2010**, *45*, 22–24.
29. Group of Experts on the Democratic Republic of the Congo. *Final Report 2010.pdf*; United Nations Security Council: New York, NY, USA, 2010; Volume 61506, p. 191.
30. Van Bockstael, S. The emergence of conflict-free, ethical, and Fair Trade mineral supply chain certification systems: A brief introduction. *Extr. Ind. Soc.* **2018**, *5*, 52–55. [CrossRef]
31. Calvo, M. *Minerales y minas de España. Volumen IV: Óxidos e hidróxidos*; Prames: Zaragoza, Spain, 2009.
32. Marina, E.F.; Guzmán, V.F. *The Mining Industry in Spain*; IGME: Madrid, Spain, 1987.
33. Magdalena, R.; Valero, A.; Valero, A.; Palacios, J. Mining energy consumption as a function of ore grade decline: The case of lead and zinc. *J. Sustain. Min.* **2021**, *20*, 109–121. [CrossRef]
34. Palacios, J.-L.; Abadías, A.; Valero, A.; Valero, A.; Reuter, M.A. Producing metals from common rocks: The case of gold. *Resour. Conserv. Recycl.* **2019**, *148*, 23–35. [CrossRef]
35. Palacios, J.-L.; Fernandes, I.; Abadías, A.; Valero, A.; Valero, A.; Reuter, M.A. Avoided energy cost of producing minerals: The case of iron ore. *Energy Rep.* **2019**, *5*, 364–374. [CrossRef]
36. López-Moro, F.J.; Polonio, F.G.; González, T.L.; Contreras, J.L.S.; Fernández, A.F.; Benito, M.C.M. Ta and Sn concentration by muscovite fractionation and degassing in a lens-like granite body: The case study of the Penouta rare-metal albite granite (NW Spain). *Ore Geol. Rev.* **2017**, *82*, 10–30. [CrossRef]
37. Ghorbani, Y.; Fitzpatrick, R.; Kinchington, M.; Rollinson, G.; Hegarty, P. A Process Mineralogy Approach to Gravity Concentration of Tantalum Bearing Minerals. *Minerals* **2017**, *7*, 194. [CrossRef]
38. Shikika, A.; Sethurajan, M.; Muvundja, F.; Mugumaoderha, M.; Gaydardzhiev, S. A review on extractive metallurgy of tantalum and niobium. *Hydrometallurgy* **2020**, *198*, 105496. [CrossRef]
39. López, F.A.; García-Díaz, I.; Largo, O.R.; Polonio, F.G.; Llorens, T. Recovery and purification of tin from tailings from the Penouta Sn-Ta-Nb deposit. *Minerals* **2018**, *8*, 20. [CrossRef]
40. Rodríguez, O.; Alguacil, F.J.; Baquero, E.E.; García-Díaz, I.; Fernández, P.; Sotillo, B.; López, F.A. Recovery of niobium and tantalum by solvent extraction from Sn-Ta-Nb mining tailings. *RSC Adv.* **2020**, *10*, 21406–21412. [CrossRef]
41. Allain, E.; Kanari, N.; Diot, F.; Yvon, J. Development of a process for the concentration of the strategic tantalum and niobium oxides from tin slags. *Miner. Eng.* **2019**, *134*, 97–103. [CrossRef]

42. Subramanian, C.; Suri, A.K. Recovery of Niobium and Tantalum from Low Grade Tin Slag—A Hydrometallurgical Approach. In *Environmental & Waste Management in Non-Ferrous Metallurgical Industries*; NML Jamshedpur: Jamshedpur, India, 1998; pp. 100–107.
43. Outotec. Outotec HSC Chemistry Software. 2020. Available online: <https://www.outotec.com/> (accessed on 4 December 2019).
44. Valero, A.; Valero, A.; Martínez, A. Inventory of the exergy resources on earth including its mineral capital. *Energy* **2010**, *35*, 989–995. [[CrossRef](#)]
45. Valero, A.; Valero, A. *Thanatia: The Destiny of the Earth's Mineral Resources*; World Scientific Publishing: Zaragoza, Spain, 2014.
46. Latva-Kokko, M.; Hirsi, T.; Ritasalo, T.; Tiihonen, J. Improving the process performance of gold cyanide leaching reactors. In *Proceedings of the World Gold Conference, Johannesburg, South Africa, 27 September–1 October 2015*; pp. 1–11.
47. Christie, T.; Brathwaite, B. Mineral Commodity Report 6—Lead and Zinc. *N. Z. Min.* **1995**, *16*, 22–30.
48. Odo, J.U.; Okafor, W.C.; Ekpe, S.O.; Nwogbu, C.C. Extraction of Niobium from Tin Slag. *Int. J. Sci. Res. Publ.* **2014**, *4*, 1–7.