

PRODUCTION OF NIOBIUM: OVERVIEW OF PROCESSES FROM THE MINE TO PRODUCTS

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Abstract

A number of industrial and technology sectors have been paying attention to a particular chemical element in recent years, namely niobium (Nb). There are many niobium deposits scattered around the world, and for each deposit different technologies are applied for extraction and processing due to the singular characteristics present at each site. In this paper, a review of the many technologies for niobium production will be presented starting at the mine, through techniques of niobium ore beneficiation and refining, technologies to produce ferroniobium alloy, oxides, special oxides, ammonium niobium oxalate, the separation of niobium from tantalum, and techniques to reduce and purify metallic niobium.

Key words: niobium production; pyrochlore concentration; metallic niobium; tantalum-niobium separation; ferroniobium; niobium oxides.

1. Introduction

Industrialization is the most important factor for the development of the wealth of nations, by increasing the production of goods and stimulating a consumer economy [1]. However, such consumerism is based on non-sustainable industries, along with the perception that natural resources are infinite, leading to cyclic environmental crisis and the generation of dangerous residues [2]. In this scenario, efficient solutions aimed at increasing quality and sustainability have been developed to minimize and/or eliminate environmental damage, while at the same time "green" products and clean technologies are introduced to markets and industries. As an example, the conversion of carbon dioxide into light olefins using a niobium pentoxide (Nb₂O₅) as catalyst can be cited [3]. The metallic element niobium (Nb) has attracted the attention of diverse industrial sectors, including steel and electronic equipment production, chemical inputs, and batteries [4–6]. This is due to the fact that Nb forms compounds

that are semiconductors, act as catalysts and can be used as additives for steel alloy production, and all of these are necessary for high-tech and sustainable products [7, 8].

Niobium can be found in deposits in many parts of the world (Figure 1) [9] and there are more than 90 types of niobium-containing minerals. However, in terms of economic viability for extraction, only two minerals are profitably obtained. These minerals are columbite-tantalite, presenting 76% as a maximum level of Nb₂O₅ and pyrochlores, presenting a maximum of 71% of Nb₂O₅ [10, 11]. Brazil has the largest concentration of exploitable Nb deposits, at >97% by mass [12] and in the first quarter of 2020 nearly 20.000 tons were commercialized, with US\$ 425.16 million in total [13]. In the region of Araxá, Minas Gerais State, an extensive pyrochlore deposit is located; it is the world's most important source of Nb, and the operations there are run by the Companhia Brasileira de Metalurgia e Mineração (CBMM) [14].

As stated, Nb can be obtained from various types of

ores. However, Nb ore is not found isolated in the nature, but with many types of impurities. As a result, in order to extract Nb, a beneficiation process is required, and that process depends on various factors such as the type of the ore and gangue, available power supply, and local labor force availability [15]. In addition to the beneficiation techniques, the conversion to Nb and Nb-containing products depends on many factors. The present article presents a brief review of the steps and processes involved in the production of Nb and its products. The paper will discuss the steps summarized in Figure 2. To the best of our knowledge, there are no comparable reviews in the literature that bring together several works involved in this theme: mining, ore concentration, ore concentrate refining, metallurgical process (ferroniobium production), niobium oxide, special oxides, metallic niobium, ammonium niobium oxalate, and tantalum-niobium separation techniques [12,14,16].

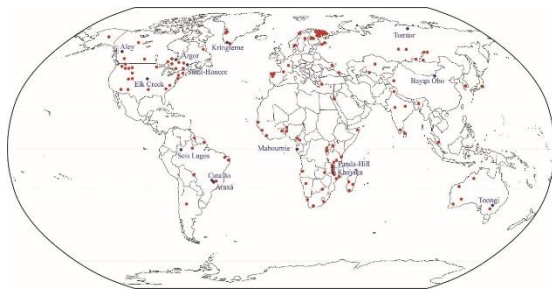


Figure 1 Resources of Nb around the world (red and blue spots). Blue spots are the localization of the largest deposits

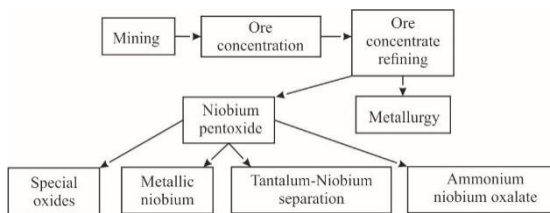


Figure 2 General process of Nb production

2. The mining operation

At the mine, trucks and tractors are used to remove large quantities of ore-containing material (rocks, earth, etc.). However, the ore-containing material contains a variable ore percentage; for example, in the barium pyrochlore mine localized in the city of Araxá (Brazil), the percentage of Nb_2O_5 varies from 1% to 7% (w/w)

[17] and this variation is not suitable for down-stream processing. To correct this variation, a blending step must be performed [18]. Figure 3 presents the most common system to perform this step by employing a chevron-type pile, which involves the positioning of various horizontal layers of mined material containing different ore percentages. The layers are deposited one upon the other by an ore stacker, forming a prismatic pile. After the pile has reached a certain height, the ore is recovered in a vertical cross-section by an ore reclaimer in such a way that a slice of all different ore percentages is removed at the same time; that slice is mixed, forming a homogeneous material which is sent to an ore concentration plant [19].

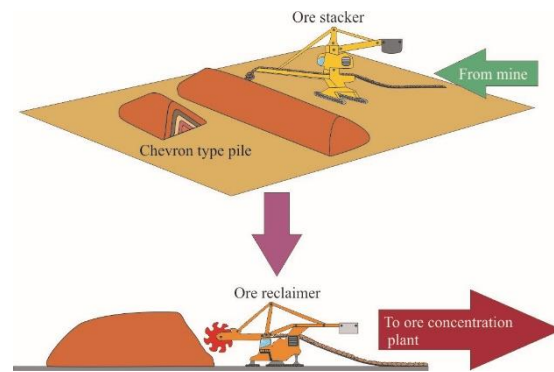


Figure 3 Ore blend using the chevron-type pile technique

3. Ore concentration

After the homogenization, the low concentration of the ore means that an operation to enrich it must be performed. In the literature, a number of enriching processes are reported, and the choice depends on the type of ore, its granulometry and gangue composition. In the following section, a number of processes that were used or are currently in operation will be discussed.

3.1. Pyrochlore from carbonatite rocks

In the case of pyrochlore, originated from the rocks that contain calcite and dolomite (carbonatites), the granulometry of the ore and efficiency in the removal of gangue are crucial to obtain an acceptable concentrate for downstream processing [20]. In practice, systems that process pyrochlore from carbonatites are or were used by the most important operations in the world, such as CBMM, Niobec, CMO, Oka (not in operation

today), and Mrima Hill complexes. All the cited operations have their simplified processes demonstrated in Figures 4 to 8 where some common mining equipment and reagents (flotation agents commonly used or assayed, as described in Table 1 and 2) are discussed.

Table 1 Calcite-dolomite flotation agents. Adapted from [20]

Calcite-dolomite collector	pH of Flotation	Pyrochlore depressant agents
Oleic acid	~8.3	Caustic corn starch and/or dextrin
Tall oil fatty acid		
Emulsified tall oil		
Xanthate		
Tall oil/Na ₂ CO ₃ /Na ₂ SiO ₃ (60:20:20)		
Tall oil/Na ₂ CO ₃ /Na ₂ SiO ₃ (65:15:20)		

Table 2 Pyrochlore floating agents. Adapted from [20]

Pyrochlore collector	Gangue depressant agents
Aliphatic monoamine	Oxalic acid, HF, H ₂ SiF ₆ , sodium hexametaphosphate and/or sodium pyrophosphate.
Aliphatic diamine	
Octanoic acid	
8-quinolinol	
2-methyl 8-quinolinol	
4-methyl 8-quinolinol	
6-methyl 8-quinolinol	
Burner oil (co-collector)	
Furnace oil (co-collector)	
Ortho-dihydroxybenzene	

In the first beneficiation process (Figure 4) used by CBMM, the ore is first submitted to a closed circuit composed by a sieve and a crusher until it passes through a 50 mm mesh. The underflow is directed to ball mills, and afterwards the ore is separated in 508 mm hydrocyclones with the underflow returned to the mills for the size adequation. The overflow fraction is then passed to magnetic separators to remove magnetite while the non-magnetics are directed to 381 mm hydrocyclones. In this step the underflow is treated in scrubbers and deslimed using another 381 mm hydrocyclones having the overflow returned to the feed

of the first battery of 381 mm. The overflow of first 381 mm hydrocyclones is directed to a group of 45 102 mm hydrocyclones, where the underflow is also treated using scrubbers and deslimed by another 102 mm battery. The overflow of 102 mm and 381 mm are combined forming the main rougher flow. The overflow of the 102 mm hydrocyclones are directed to a desliming circuit composed of 400 25mm hydrocyclones to recover pyrochlore. The main flow described previously is treated in conditioner tanks with diamine acetate (T50 – Quimikao) as pyrochlore collector, H₂SiF₆ or Na₂SiF₆ as pyrochlore activator, and MC553 (etoxilated fatty acids – Henkel) as gangue depressors with this being floated in 8 flotation cells and then directed to a thickener to adequate the percentage of solids. The thickener underflow is treated again in a conditioner tank and directed to the cleaner circuit flotation composed of 21 cells. The underflow of 25 mm hydrocyclones is now treated in a conditioner tank, cleaned in a circuit composed of 14 flotation cells and combined with the clean ore from the 21-cell battery. The cleaned ore is then thickened and filtered in 6 disk filters, presenting a concentration of Nb₂O₅ between 55-60% [21–23].

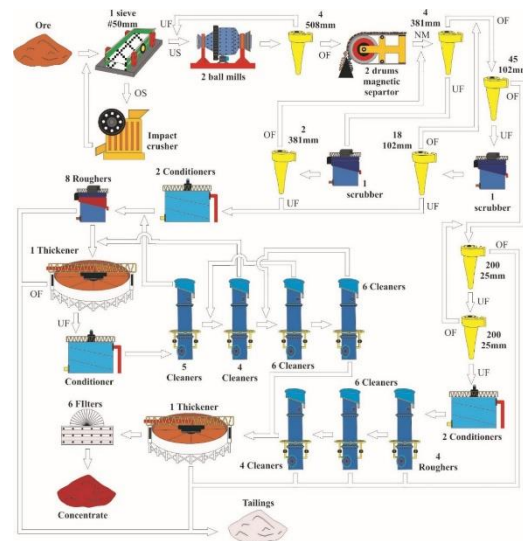


Figure 4 Simplified process used by CBMM (Araxá).

UF: overflow, US: undersize, OS: oversize, OF: overflow, NM: non-magnetic. Adapted from [21]

In the operation ran at CMOC, demonstrated in Figure 5, the ore with approximately 1.2% of Nb₂O₅ is crushed and passed through the grizzly feeder where the first classification is realized. The particles 1" or

under are milled and classified using the rod, ball mills, 1" and 4" hydrocyclones, and magnetic separators. The coarse fraction with the granulometry between $-100 \mu\text{m} + 15 \mu\text{m}$, is directed to the battery of silica flotation, followed by desliming and Nb cleaners using etheramine as silicate collector and starch as pyrochlore depressor. The fine fraction (granulometry between $-15 \mu\text{m}$ and $+5 \mu\text{m}$) suffers a similar beneficiation process like the coarse, composed of desliming, silica flotation, and Nb cleaners. The clean ore from coarse and fine fractions is then combined and directed to filters; the filtercake is treated with NaOH, thickened, filtered and calcined, reaching a final grade of approximately 64% of Nb_2O_5 [23].

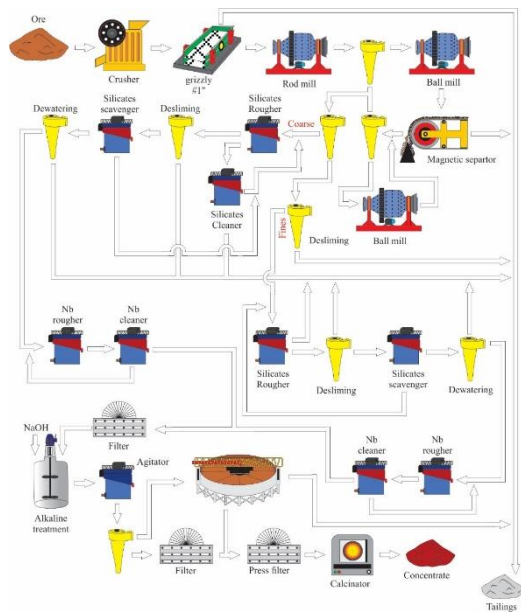


Figure 5 Simplified process used by CMOC (Catalão). Adapted from [23]

At Niobec's beneficiation plant (Figure 6), the ore feed has Nb_2O_5 between 0.55% and 0.71%, being initially crushed, then milled, and classified by 230 μm sieves. After desliming, carbonates are removed using emulsified tallow diamine acetate as pyrochlore collector, oxalic acid and H_2SiF_6 as pyrochlore activator, potassium amyl xanthate as pyrite collector, and copper sulphate as pyrite activator in a series of flotation cells and cleaners, then deslimed again before the magnetic separation stage. The non-magnetic fraction is now submitted to a new series of flotation operations in order to clean Nb ore and remove sulphides. Further, the

resultant pulp is thickened and directed to leaching tanks to remove apatite using HCl before being treated in a second sulphide cleaner step. Upon exit, the pulp is then filtered and dried having a composition of $\sim 58\%$ of Nb_2O_5 [22, 23].

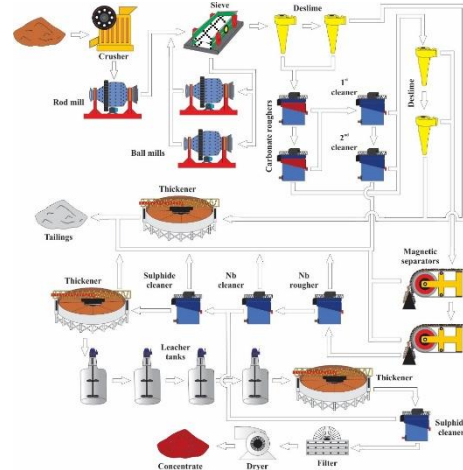


Figure 6 Simplified process used by Niobec (Saint-Honoré). Adapted from [23] and [22]

Although it is no longer in operation today, the simplified process used at Oka is demonstrated in Figure 7. After mining and homogenization, the ore with 0.4-0.5% of Nb_2O_5 is crushed and classified in a closed circuit composed by rod mills and sieves, followed by stages of desliming, pyrite flotation, and magnetic separation. Afterwards, new stages of pyrochlore rougher flotation are realized using amines as pyrochlore collector and HF as gangue depressor pyrochlore activator, deslimed again, cleaned and processed using magnetic separators. Gravity tables were also used to remove mica and diopside followed by flotation on cells to remove sulphide and silica. The final concentrate is then filtered and dried containing about 50% of Nb_2O_5 [23].

The Mirna Hill ore processing (Figure. 8) starts with an ore containing about 2.4% (w/w) of Nb_2O_5 , being passed through three sieves and a grinding circuit, until the granulometry of the ore reaches ≤ 65 mesh. After sieving and grinding, the ore is treated with apatite/barite floating agents (Table 3) in conditioning tanks and floated in a four-cell floating circuit. The resulting pulp is deslimed, the magnetic fraction is separated in a low intensity magnetic separator and then treated with a pyrochlore floating agent in conditioning tanks before being floated in a 7-cell

floating circuit. The pyrochlore floating agent in this case is a mixture composed of 60% ortho-dihydroxydebenzene, 30% low molecular weight acrylic acid, and 10% of hexametaphosphate (w/w). At the end of this process, the final concentrate contains about 43.2% (w/w) of Nb₂O₅ [20].

Table 3 Apatite/Barite floating agents from carbonatite rock. Adapted from [20]

Apatite/Barite collector	Gangue depressant agents
Tall oil fatty acid	Na ₂ SiO ₃ and/or caustic
Sulphonates	starch

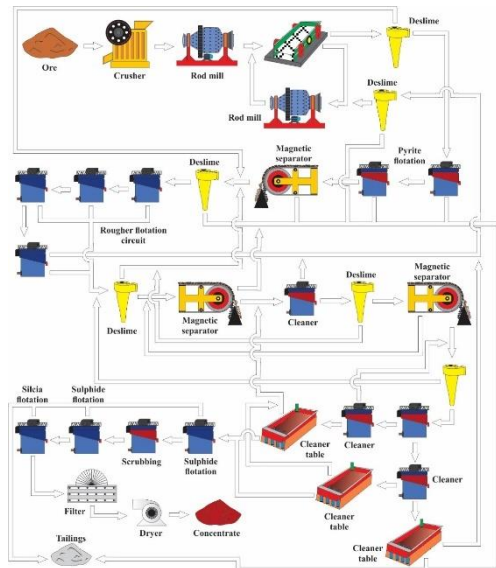


Figure 7 Simplified process used at Oka (not in operation today). Adapted from [23]

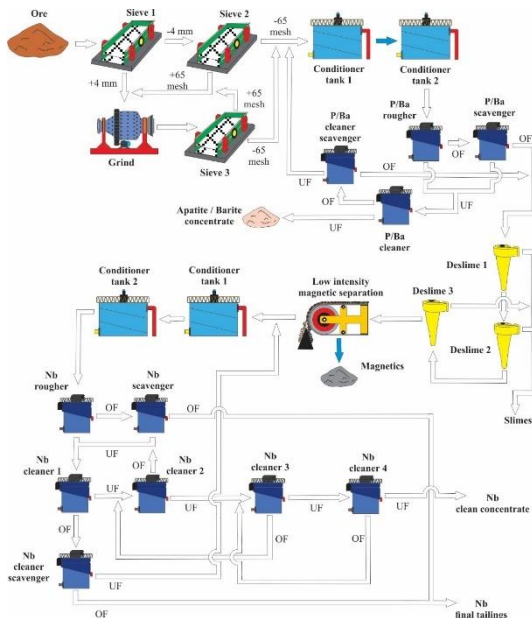


Figure 8 Process used in Mirna Hill complex. UF: underflow, OF: overflow. Adapted from [20]

3.2. Gravimetric (or densimetric) concentration

This technique consists of exploiting the difference in the specific gravity of niobium ore and the gangue using inclined vibrating tables. On the industrial scale, this technique is applied in the Green Bushes (Australia) and Bernic Lake (Canada) operations, following the scheme presented in Figure 9. As demonstrated, the ore is initially ground and passed through a sieve circuit composed by three units (6, 48, and 100 mesh). Subsequently, all three oversized outflows are treated on gravity tables and the undersize flow of the 100-mesh sieve is deslimed and mixed with the oversize from the same sieve. The concentrate from the first and second gravity table are mixed and directed to a second grinding operation. Exiting the mill, the ore is sieved and the oversize flow is mixed with the concentrate from the third gravity table and then directed to be processed by a further two gravity tables. The first concentrate outs after the last gravity table until the combined tails and slimes are directed to an ore recovery circuit. In this circuit the material is sieved and grinded until it passes through a 100 mesh, deslimed and transferred to a conditioner tank to receive oxalic acid and Na₂SiF₆ as gangue depressor and a mixture of phosphoric esters, alkyl sulphate, and mineral oil as ore floating agent. The pulp is then floated in a circuit composed of six floating cells and the material is then treated with NaOH to be separated in a final gravity table, producing then a second concentrate [20].

3.3. Concentration of ores contaminated with Zr

Pyrochlore, yttrio-pyrochlore, and columbite can associate with Zr in some deposits, such as the Ghurayyah mine in Saudi Arabia. In this case, the process to concentrate niobium ore also concentrates Zr due its chemical nature, and to separate both further treatments must be performed. Figure 10 demonstrates the complete process, which starts with a grind and sieves circuit to adequate the ore particle size under 200 mesh. After, the bulk is treated in a conditioner tank with

some agents to be deslimed. The resultant pulp is directed to conditioner tanks to receive ore floating agents (a blend of succinamate and phosphoric acid esters) and gangue depressing agents (oxalic and H_2SiF_6 mixed with low molecular weight acrylic acid and condensation product of disulfonic acid).

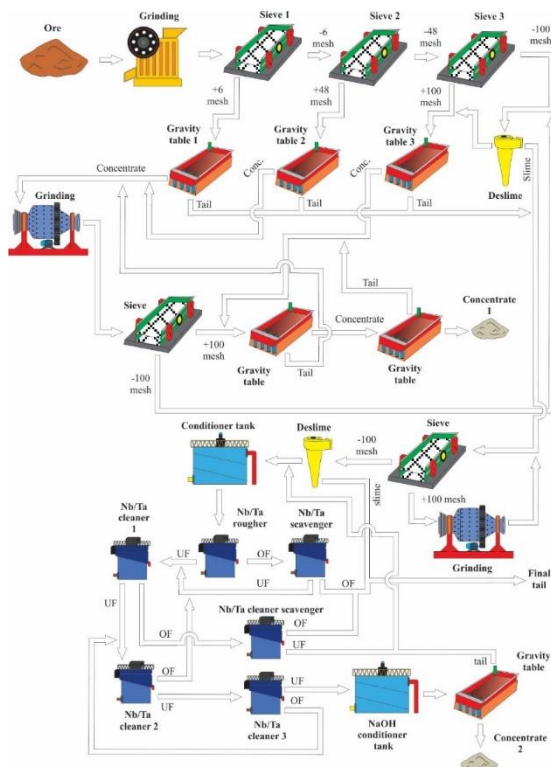


Figure 9 Process used in Green Bushes and Bernic Lake mine complex for columbite-tantalite concentration. UF: underflow, OF: overflow, Conc.: concentrate. Adapted from [20]

Once received these floating and depressant agents, the pulp is then floated in an eight-cell flotation circuit, producing a bulk concentrate. In the next circuit, the bulk undergoes further grinding until it passes through a 100-mesh sieve and is then deslimed and treated with a mixture of NaOH and AQ4 (mixture of 60% ortho-dihydroxybenzene, 30% low molecular weight acrylic acid and 10% hexametaphosphate) deslimed three times to remove the iron in the form of hydroxide. After iron removal, the pulp is then treated with Na_2SiF_6 , thickened and treated with caustic starch. Finally, the pulp is floated in a four-cell flotation circuit to separate Nb from Zr [20].

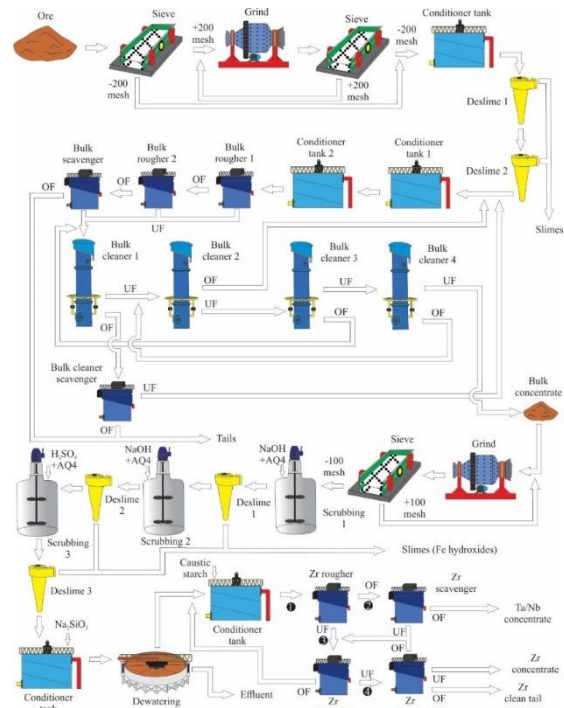


Figure 10 Process used in Ghurayyah mine complex for columbite-tantalite concentration: In points 1 and 2, a mixture of primary and secondary amines is added. In points 3 and 4, caustic starch is added. UF: underflow, OF: overflow. Adapted from [20]

3.4. Concentration of mixture of pyrochlore and columbite-tantalite contaminated with Zr

In some deposits such as the Malawi operations (Africa), Nb ore can be compounded of a mixture of pyrochlore and columbite and Zr. In this case, the ore concentration process is slightly different to the previous technique (3.3). As shown in Figure 11, the deslimed ore is directed to the conditioning tanks to receive gangue depressors (oxalic acid and H_2SiF_6) and next, ore floating agents (mixture of alkyl sulfosuccinamate and ester phosphates modified with sodium alkylsulfate, called PLV28). The pulp is then directed to an eight-cell flotation circuit with some additions of gangue depressors and ore floating agents during the process. At the end of this stage, a bulk concentrate is produced, and as such processed in the flowsheet presented in Figure 10, the bulk needs subsequent treatment to remove Fe and separate Zr from Nb ore [20].

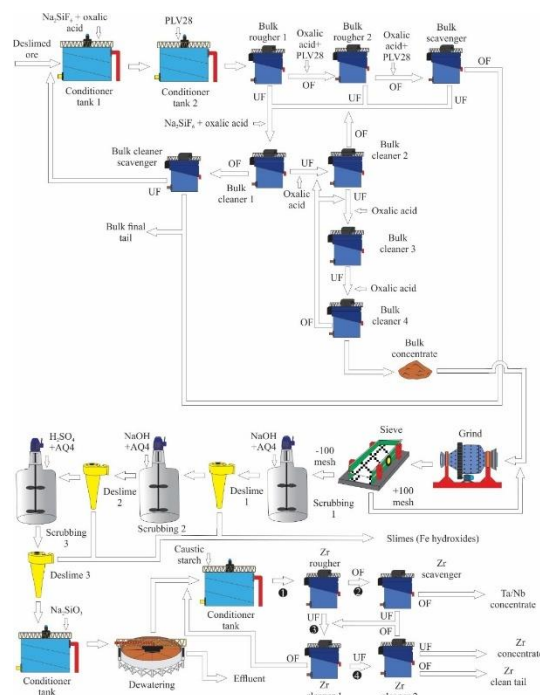


Figure 11 Process used in Malawi Nb operations for pyrochlore columbite-tantalite mixture concentration: In points 1 and 2, a mixture of primary and secondary amines is added. In points 3 and 4, caustic starch is added. UF: underflow, OF: overflow. Adapted from [20]

4. Ore concentrate refining

Most ores contain impurities like phosphorus, sulfur, tin, and lead. These elements are not appropriate to produce ferroniobium and other products and must be

reduced to the levels described in ASTM A550 (Table 4) [24, 25]. The techniques used to remove these impurities are chemical or pyrometallurgical refining and will be described below.

Table 4 Maximum impurity content in ferroniobium (% w/w). Adapted from [25]

Element	Low alloy steel	Stainless steel	High purity alloy
Sulfur	0.10	0.05	0.02
Phosphorus	0.10	0.05	0.02
Tin	0.25	0.15	0.02
Lead	0.25	0.01	0.01

4.1. Pyrometallurgical refining

In this step there are two techniques to refine the concentrate. However, both techniques use a carbon source (coal or petroleum coke) and binding agents such as sugar, carboxymethylcellulose or tar oil to pellet the concentrate to produce spherical particles with a maximum 10 mm of diameter.

For Technique I (Figure 12), in the first circuit after being pelletized, the particles are sintered in a sintering oven where sulfur is removed as SO₂ or SO₃. Subsequently, the sintered mass is melted in an electric arc furnace at 1300°C with another load of carbon source. In this phase the Pb, Sn and P are reduced forming a metallic phase while the Nb oxide and other oxides form the slag phase. The metallic phase is leaked, cooled and stored while the slag phase is granulated by water jets to form the refined ore concentrate [25, 26].

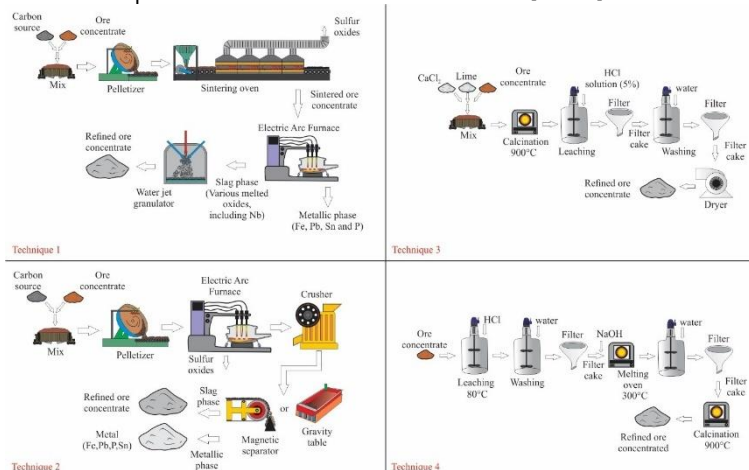


Figure 12 Ore refining using pyrometallurgical and chemical techniques. Adapted from [25, 26] and [24]

In the case of Technique II (Figure 12) the second circuit, after being pelletized, the mass is directly carried to a refractory vessel and transferred to a furnace (such as a Lurgi or mobile hearth furnace) and heated until all the mass is melted. Sulfur is also removed in this step, again as SO_2 or SO_3 . After the reaction is completed, the resultant bulk is composed of a metallic phosphorus aggregate with Sn and Pb scattered in an Nb ore matrix. To separate the metallic phase from the Nb ore, all mass is crushed and the metallic phase is separated from the Nb ore by a magnetic separator or a gravity (density) table [24].

4.2. Chemical refining

In chemical refining, such as pyrometallurgical refining, two circuits are also used to treat the ore concentrate. In the first (Figure 12 – Technique III), the ore concentrate is mixed with lime and CaCl_2 , and calcined at 900°C . After the calcination step, the material is leached with a 5% solution of HCl and then filtered. The filter cake is washed with water and filtered again. The refined resultant (ore concentrate) is then dried using a blower [25].

In the second circuit (Figure 12 – Technique IV), the ore concentrate undergoes leaching with hot HCl. After the leaching, the material is washed with water, filtered, and the filter cake is mixed with NaOH before going to the melting step. After melting, the mass is cooled and leached with water. The resultant pulp is filtered in the next step, and the filter cake calcined at 900°C resulting in the refined ore concentrate after cooling [24].

5. Metallurgy

The ferroniobium production process (Figure 13), the most widely used Nb product, starts with mixing the refined ore concentrate with Al or an Fe-Al alloy, a source of Fe such as hematite or iron scrap, and some fluxing agents like lime or fluorite to produce a product according to the composition presented in Table 5. This mixture is transferred to an electric arc furnace and is heated until all the mass melts.

The molten mixture separates in two phases: a slag phase that contains mainly Al_2O_3 and a metallic phase containing the melted ferroniobium. The slag phase is syphoned off, cooled and stored, and the metallic phase is directed to molds and after cooling, is unmolded and crushed to an adequate size [27].

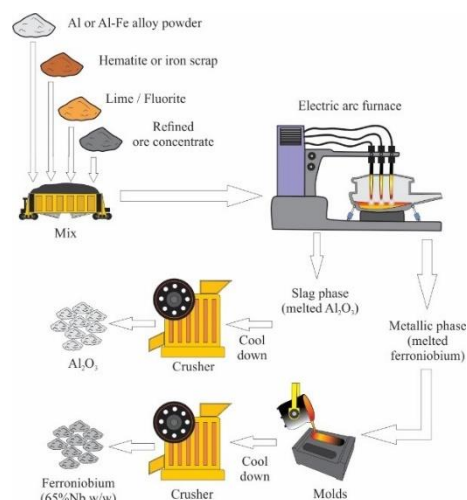


Figure 13 Ferroniobium production process. Adapted from [27]

Table 5 Composition of commercial ferroniobium (% w/w) according to the ABNT NBR 5910/1988 or ASTM A550 [24]

Element	Ferroniobium type 1	Ferroniobium type 2
Niobium	64.00 – 69.00	Minimum 63.00
Silicon	3.00	0.50
Carbon	0.20	0.10
Aluminum	2.00	2.00
Sulfur	0.10	0.05
Phosphorus	0.20	0.05

6. Niobium pentoxide

The refined ore concentrate is now submitted to a chemical treatment that extracts the Nb in the oxide form (Nb_2O_5) to be used as a final product or raw material for further processing. Currently, there are four ways to produce Nb_2O_5 which are described below.

6.1. Solvent extraction

In the Technique I, as demonstrated in Figure 14, the process starts with the digestion of the refined ore concentrate using H_2SO_4 at about 200°C for 1 h. The system is then cooled and the suspension is diluted with water until the acid concentration reaches a value between 40-45%. Afterwards, the suspension is filtered to remove the rougher particles and HF solution (48%) is added. This new suspension is mixed and centrifuged to remove small particles and the solution is then

directed to a solvent extraction step. In this step, the solution is vigorously mixed with methyl-isobutyl-ketone (MIBK), and the system is left to rest until two phases (organic and an aqueous) are formed. The aqueous phase is discarded and the organic phase is directed to another tank where NH_4F is added and also vigorously mixed. After mixing, the system is left to rest until it forms two phases: organic and an NH_4F extract. The

organic phase is treated in another tank to recycle the methyl-isobutyl-ketone, and the NH_4F extract is directed to a precipitator tank where the hydrated Nb_2O_5 is precipitated with NH_3 . Subsequently, the hydrated Nb_2O_5 precipitate is separated in the filter, dried and calcined at 900°C for 1 h to convert to Nb_2O_5 with 99.9% purity [28].

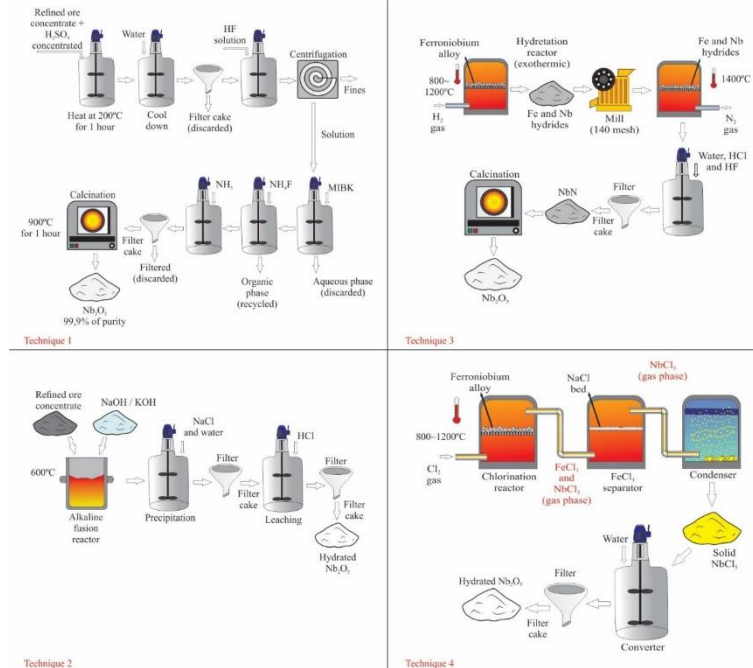


Figure 14 Nb oxide production techniques. Adapted from [28,29] and [30]

6.2. Alkaline fusion

This method (Figure 14 – Technique II) consists in a fusion of a mixture of refined ore concentrate and an alkali, such as NaOH or KOH , at $\sim 600^\circ\text{C}$. After the molten mixture has cooled, it is leached with a solution of NaCl to precipitate hydrated Nb_2O_5 . The hydrated Nb_2O_5 is then separated in a filter and the filter cake is leached with a solution of HCl to remove impurities. Subsequently, the hydrated Nb_2O_5 is separated in another filter to give the final product [29].

6.3. Alloy recovery

Nb_2O_5 can be produced by recovery of Nb from alloys by employing two techniques: the first consists of a hydration and nitriding and the second, similar to the first one, of chlorination.

As can be seen in Figure 14, in Technique III an Nb alloy (e.g. ferroniobium) reacts with H_2 gas in a high-temperature reactor ($800\text{--}1200^\circ\text{C}$) to form both Fe and Nb hydrides. These hydrides are then crushed and reacted with N_2 at 1400°C to form nitrides. These nitrides are then leached with a solution of HCl and HF , filtered, and the filter cake calcined to convert the bulk to Nb_2O_5 [30].

In the second process, showed in Figure 14 (Technique IV), a Nb alloy is chlorinated using Cl_2 gas in a high-temperature reactor ($800\text{--}1200^\circ\text{C}$), forming FeCl_3 and NbCl_5 , both in gas phase. The gases are then passed through an NaCl bed to remove the FeCl_3 and then passed through a condenser to produce a solid NbCl_5 . NbCl_5 is then converted to hydrated Nb_2O_5 by hydrolyzation with water, forming a suspension which is then separated by filtration [30].

7. Special niobium oxides

Nb oxides can be treated to modify certain properties such as surface acidity, particle shape and size, purity, and type of crystalline structure [31–34]. One treatment example is described by Okazaki et al [31] where H_3PO_4 is added to hydrated Nb_2O_5 to prevent the crystallization and acidity lost at high temperatures (500°C – 800°C), which is used as catalyst in alkylation of alcohols and ethylene hydrolyzation (Figure 15 – Technique I). Another example is the production of micro spherical Nb_2O_5 particles, as described by Behrens et al. [32], where a solution of NbF_5 is neutralized first with NH_3 until the pH reaches 6 and then with a saturated $(NH_4)_2CO_3$ solution until the pH reaches 9. After this, the precipitate is separated by filtration, washed with diluted NH_3 and water, dried, and calcined at 850°C (Figure 15 – Technique II).

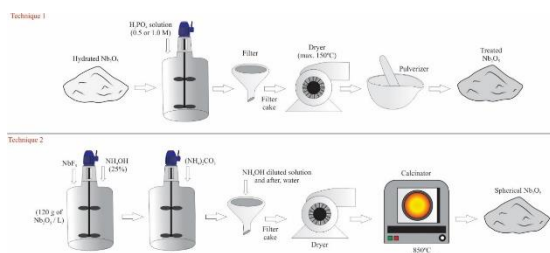


Figure 15 Special Nb oxides techniques. Adapted from [31, 32]

8. Metallic niobium

8.1. Reduction

Nb can be reduced to the metallic state by different methods. Currently, there are ten methods but not all of them are industrially viable. Technique I (Figure 16) is the most employed and is known as aluminothermic reduction. This technique consists of igniting a mixture of Nb_2O_5 and Al powder in a refractory vessel. This reaction, after initiated, is self-sustaining until all the reagents are consumed. After the reaction ceases, two phases are formed: a slag phase composed of Al_2O_3 and a metallic phase composed of molten Nb. The metallic phase is then transferred to molds and cooled forming ingots [15].

In the vapor plating technique (Figure 16 – Technique II), $NbCl_5$ vapor is mixed with H_2 gas in a hot chamber, which contains at its base a plate of an unreactive metal (e.g. Cu). After a while, metallic Nb is reduced by H_2 and deposited over the plate. This

reduction reaction must occur in a special chamber due the HCl formation in the process [15].

In the calcium bomb reduction (Figure 16 – Technique III), a mixture of Nb_2O_5 , iodine and metallic Ca is placed in a vessel coated with a layer of MgO. Subsequently, a cover with an Nb wire is screwed over the vessel and an electric current is passed through the wire, heating it. A fast reaction occurs, and after the reaction ceases, the molten mixture separates in two phases: a slag phase (upper) and a metallic Nb phase (bottom) which can be transferred and cooled in ingot molds [15].

In Technique IV (Figure 16), a mixture of K_2NbF_7 and Al powder is heated in a refractory vessel to reduce the Nb and yield an Al_3Nb alloy. In the next step, this alloy is melted with Cu powder to produce free metallic Nb suspended in a Cu-Al alloy matrix. To separate the Nb from alloy, the mass is crushed and leached with a strong acid, like HCl, to dissolve the Al-Cu alloy leaving metallic Nb [15].

For next method (Figure 16 - Technique V), called the Kroll process, $NbCl_5$ is placed over a grid localized in the middle of a stainless-steel reactor and in the bottom of the reactor, metallic Na or Mg-Na alloy is placed. After the reactor is closed, it is heated at 800°C to melt the alkaline metal and vaporize $NbCl_5$. The $NbCl_5$ vapor makes contact with melted alkaline metal reacting with it and producing metallic Nb and $NaCl/MgCl$. To separate Nb from salts, the mass is transferred to a high vacuum reactor where all mass is heated until the salts vaporize, leaving only Nb [15].

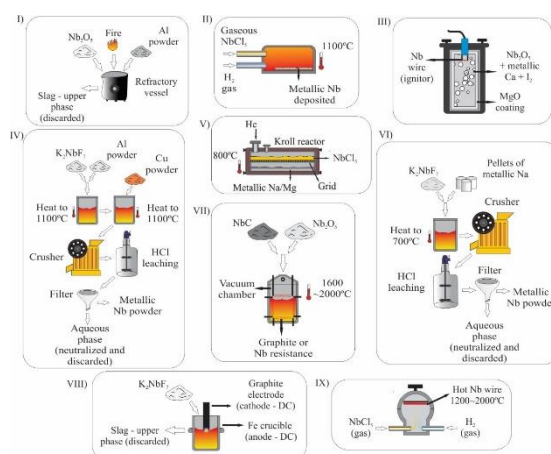


Figure 16 Nb reduction techniques. Adapted from [15]

In the VI technique (Figure 16 - Technique VI), pellets of metallic Na and K_2NbF_7 , are placed in a

refractory vessel and heated until 700°C. After the reaction, the mass is crushed and leached with an acid solution (such as HCl) to dissolve impurities. Subsequently, the metallic Nb powder is separated from the leachate by filtration [15].

In the carbon reduction technique (Figure 16 – Technique VII), Nb₂O₅ is mixed with NbC in stoichiometric proportions. After that, the mass is pressed into bars and then transferred to vacuum ovens which are heated by a graphite or Ta resistance. This initiates a reaction between Nb and carbon producing metallic Nb and CO₂/CO. The Nb produced is a porous mass and can be transformed into powder by grinding [15].

In the electrolysis reduction (Figure 16 - Technique VIII) K₂NbF₇ is melted in a conductive vessel (anode). After the mass is melted, a graphite electrode (cathode) is placed in the molten mixture and an electric current is passed, reducing the Nb to the metallic state forming fine crystal line aggregates. When no more crystals are produced, the system is left to cool and subsequently leached with strong acids to remove the impurities from the metallic Nb [15].

The IX technique (Figure 16 - Technique IX) is similar to the vapor plating technique (II). The only difference is that instead of Nb being deposited over a metal plate, it is deposited over a hot wire resistance, composed of metallic Nb [15].

The last technique is known as the nitriding process; NH₃ is used instead of using N₂ gas as in Figure 14 (Technique IV). In this process, crushed ferroniobium reacts with NH₃ in a high-temperature reactor, forming nitride compounds which are washed with a mixture of HNO₃ and HCl to remove Fe and other impurities. Following this, the solid material undergoes pyrovacuum treatment at 1825°C to remove nitrogen and impurities at pressure of 0.02 mtorr, producing a metallic Nb sponge [35].

8.2. Refining

Some applications of metallic Nb, such as nuclear reactors, require that the presence of impurities is maintained at minimum levels, as demonstrated in Table 6. In order to reach these levels, a step of refining must be performed.

Table 6 Maximum impurities content in metallic Nb, according to the ASTM B391 (% w/w) [36]

Element (each ingot)	Nb reactor grade type 1 (R04200)	Nb reactor grade type 2 (R04210)	Nb reactor grade type 3 (R04251)	Nb commercial grade (R04261)
Carbon	0.0100	0.0100	0.0100	0.0100
Nitrogen	0.0100	0.0100	0.0100	0.0100
Oxygen	0.0150	0.0250	0.0150	0.0250
Hydrogen	0.0015	0.0015	0.0015	0.0015
Zirconium	0.0200	0.0200	0.8-1.2	0.8-1.2
Tantalum	0.1000	0.3000	0.1000	0.5000
Iron	0.0050	0.0100	0.0050	0.0100
Silicon	0.0050	0.0050	0.0050	0.0050
Tungsten	0.0300	0.0500	0.0300	0.0500
Nickel	0.0050	0.0050	0.0050	0.0050
Molybdenum	0.0100	0.0200	0.0100	0.0500
Hafnium	0.0200	0.0200	0.0200	0.0200
Titanium	0.0200	0.0300	0.0200	0.0300
Boron	2 ppm	...	2 ppm	...
Aluminum	0.0020	0.0050	0.002	0.0050
Beryllium	0.0050	...	0.005	...
Chromium	0.0020	...	0.002	...
Cobalt	0.0020	...	0.002	...

In the literature, there are five techniques to refine Nb, with the most used being the electron beam method (Figure 17 - I). In this technique, melted Nb is leaked in ingots molds. After cooling, the ingots are placed in an

electron beam furnace, and melted by the electron beam which fuses the ingot and volatilizes impurities. The impurities are removed by vacuum system. The melted Nb is collected in a bottom chilled vessel forming a new

refined ingot [15, 37, and 38].

In the second technique (Figure 17 - II), Nb powder is placed in a copper chilled vessel (anode) and closed with a cover which contains a graphite or W electrode attached to a piston (cathode). After the chamber is evacuated, a current is passed and the piston moves the cathode into contact with the Nb powder, melting it and volatilizing the impurities. At the required end-point, the piston and electrode are removed and this turns off the reaction. After cooling, the refined Nb is then removed [15].

The third technique (Figure 17 - III), starts with pressing Nb powder to form ingots. Each ingot can then be refined by two ways: in the first, the ingot is heated in a vacuum (or under an inert gas flow) at temperatures between 2100 and 2600°C. This sinters the ingot and volatilizes impurities. In the second method, the Nb ingot is connected by two wires and a D.C. current is passed, producing heat which volatilizes impurities, while at the same time sintering the ingot [15].

The next technique (Figure 17 - IV), known as zone refining, starts with placing an Nb ingot in a kart. The ingot passes through an inductive coil, heating a small area. According to the direction of the movement, the impurities remain stationary and accumulate in a defined region. Finally, the region with impurities is removed, leaving refined Nb [15].

The final technique is called floating zone refining (Figure 17 - V), and is very similar to zone refining. The difference is that instead of the ingot being positioned horizontally, the ingot is in the vertical position, and the magnetic field is more intense, melting and levitating the region. The ingot is lifted while impurities remain at the bottom. After refining, the region that contains the impurities is removed [15].

9. Ammonium niobium oxalate

Ammonium niobium oxalate (ANO), a water soluble Nb compound, is a precursor for many catalysts and its production (Figure 18) starts dissolving an Nb precursor (e.g. hydrated Nb_2O_5) in a solution of oxalic acid and ammonium oxalate. After dissolution, a crystalline solution is formed, which is then diluted with water to reach to a density between 1090 and 1170 g/L. The solution is cooled to precipitate excess oxalic acid, which is removed by a filtration and recycled. The filtered solution is then heated to leave the density between 1150 and 1300 g/L and more ammonium salt is added to replace the ions lost in the evaporation step.

The solution is subsequently cooled to precipitate the ANO, which is separated by a filtration, followed by drying with compressed air [16].

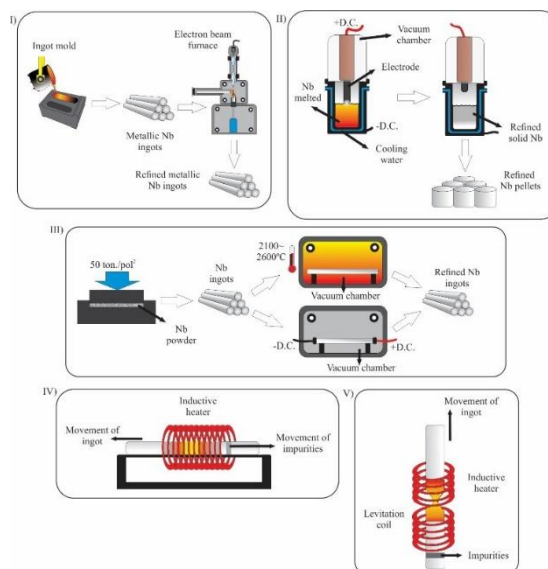


Figure 17 Metallic Nb refinement techniques. Adapted from [15]

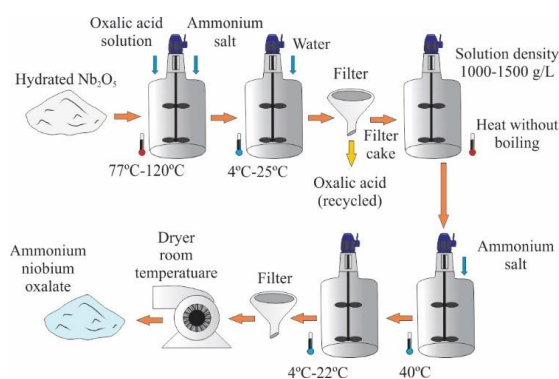


Figure 18 Ammonium niobium oxalate production process. Adapted from [16]

10. Niobium-tantalum separation

Nb and Ta have very similar chemical properties and this is reflected by the difficulty of separation [6]. However, in some cases, extremely pure Nb is required, with a minimum possible level of Ta. For example, in the fabrication of resonance cavities for particle accelerators, Ta can produce heat during operation and this is not beneficial as the cavities operate at ultra-low temperatures, breaking the superconducting effect [39].

To separate Nb and Ta, some techniques can be applied which are described below.

10.1. De Marignac's method

The first technique developed to separate Nb from Ta consists in exploring the difference in solubility in a HF solution between K_2TaF_7 and K_2NbOF_5 , or K_2NbF_7 where K_2TaF_7 precipitates first. However, this technique doesn't produce pure Nb due to K contamination; therefore, further purification is required [40].

10.2. Solvent Extraction - MIBK

This is the main method used to separate Nb from Ta [39]. This technique is similar to the process given in Figure 14 (Technique) with a few modifications. As shown in Figure 19, the refined ore concentrate is mixed with hot H_2SO_4 and HF. After the digestion, the pulp is filtered and the filtrate is sent to a new tank to be mixed with methyl-isobutyl-ketone (MIBK) and H_2SO_4 . After vigorous mixing, diluted H_2SO_4 is added and mixed again. Two phases are formed: an organic phase and an aqueous raffinate. The organic phase, containing Ta, is then treated with steam to separate MIBK, which is recovered and recycled. The Ta can be converted into oxide by addition of NH_4OH , and after calcination or it can be converted to K_2TaF_7 with crystallization using KCl. The aqueous raffinate contains Nb and it is mixed with NH_4OH to precipitate the hydrated Nb_2O_5 by filtration and calcination to convert to high purity Nb_2O_5 [41].

10.3. Solvent extraction - TBP

This is another solvent extraction technique to separate Nb from Ta, but instead of using MIBK, tributyl phosphate (TBP) is used. TBP is a safer option which is less soluble in water than MIBK. In this technique (Figure 20) the refined ore concentrate is mixed with concentrated HF in a special tank. The resultant slag is mixed with H_2SO_4 and then with TBP by shaking vigorously. The pulp separates into two phases: an organic phase which contains both Nb and Ta, and an aqueous phase which contains some impurities and other metals. The organic phase is transferred to another tank and receives a mixture of NH_4OH , H_2SO_4 and HF, also by vigorous mixing. The solution separates into another two phases: an organic phase and an aqueous phase. The organic phase is mixed with H_2SO_4

to remove the remaining Nb, and left to rest to form an aqueous phase which is mixed with the aqueous phase from the previous separation, and an organic phase which is mixed with NH_4OH to precipitate hydrated Ta_2O_5 , which is separated by filtration. The Nb-containing aqueous phase is then mixed with a mixture of TBP, H_2SO_4 , and HF, and left to rest to form two phases: an aqueous phase which contains impurities, and an organic phase which contains Nb. This solution is then mixed with NH_4OH to precipitate hydrated Nb_2O_5 , which is separated by filtration [42].

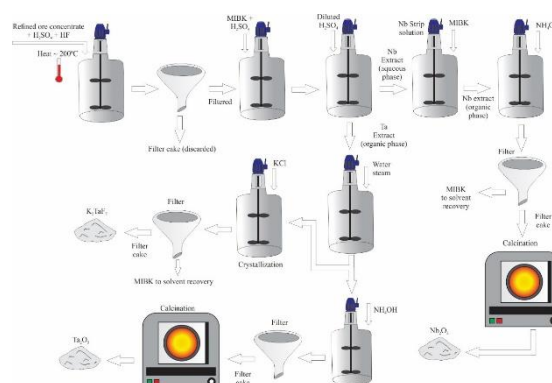


Figure 19 Nb-Ta separation: MIBK process. Adapted from [41]

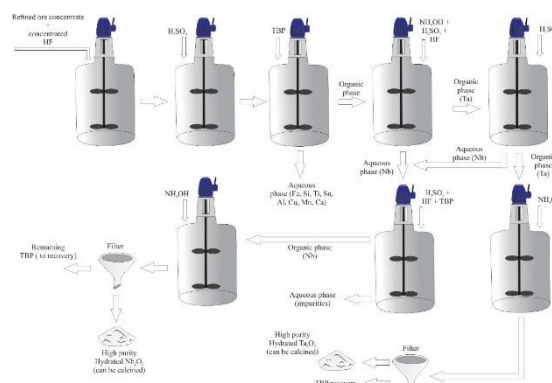


Figure 20 Nb-Ta separation: TBP process. Adapted from [42]

10.4. Solvent extraction - CHO

This method to separate Nb from Ta is very similar to the MIBK and TBP processes. However, instead of using methyl-isobutyl-ketone or tributyl phosphate it uses cyclohexanone (CHO), with some variations that are briefly described below.

In the first technique, Nb and Ta can be separated

from each other using a digestion solution (6 M HF and 2.5 M H₂SO₄), where Nb is extracted using water, while Ta is extracted using a solution of 4.75 M H₂SO₄ and 1.5 M (NH₄)₂SO₄ with small amounts of NH₄F [43]. In thesecond technique, a HF-free extraction can be performed with CHO using a digestion solution (2 M H₂SO₄ and 0.49 M SCN⁻) where H(H₂O)_p(CHO)_qNb(SCN)₄ and H(H₂O)_p(CHO)_qTa(SCN)₄ complexes are formed, with only the Nb complex being extractable in this form [43].

Finally, the third method, a study using a digestion solution composed of HF-HCl ranging from 0 to 5 M HCl and 2 to 10 M HF demonstrated that CHO is also compatible in this medium to separate both metals, reaching a 1700 separation factor of Ta over Nb [43]. However, despite the good results achieved with these techniques, CHO is not widely used because of its high solubility in water [44].

10.5. Solvent extraction - amines

In this technique (Figure 21), the refined ore concentrate is mixed with hot H₂SO₄. Following this, H₂O₂ is mixed with the resultant pulp at a slightly lower temperature, and is then mixed with HF at room temperature. In the next step, the leached liquor is separated and directed to another tank to be mixed with a mixture of trioctylamine (10%) in kerosene. The solution separates in two phases with the aqueous phase being discarded and the organic phase directed to another tank to be mixed with a solution of (NH₄)₂CO₃. After addition of (NH₄)₂CO₃, Ta precipitates and is separated in a filter. The remaining solution separates in two phases: an organic phase and an aqueous phase which contains Nb. The aqueous phase is directed to another tank and mixed with NH₃ to precipitate hydrated Nb₂O₅ which is separated by filtration [42, 45]. In this technique methyltrioctylammonium chloride (Aliquat 336) can be used as a substitute for trioctylamine in kerosene [42].

10.6. Solvent extraction – octan-2-ol

In this technique (Figure 22), refined ore concentrate is fused with KHSO₄ at 650°C. After cooling, the resultant material is leached with water and filtered to remove impurities. Following this, the filtrate is mixed with oxalic acid to precipitate rare earth elements (REE) and Ti, separated by filtration. The filtrate is then mixed with NH₄OH until the pH stabilizes between 2.5 and 4.0,

precipitating Fe and Al. The resultant filtrate is directed to a tank to be mixed vigorously with octan-2-ol and subsequently mixed with water and left to separate in two phases. The aqueous phase is treated with NH₄OH to precipitate Ta which is separated by filtration and calcined. The organic phase is further mixed with octan-2-ol and then mixed with a solution of H₂SO₄ and HF and left to rest. The Nb-containing aqueous phase is directed to another tank and mixed with NH₄OH to precipitate hydrated Nb₂O₅, which is separated by filtration and calcined, giving Nb₂O₅ [46].

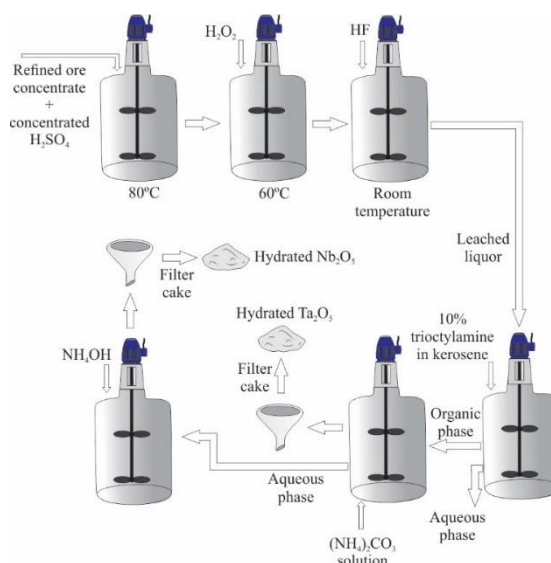


Figure 21 Nb-Ta separation - Trioctylamine process. Leached liquor composition: 11.5 g/L of Nb, 10.0 g/L of Ta, 0.5 M of H₂SO₄, 0.2 M of HF and 0.2 M of H₂O₂. Adapted from [45]

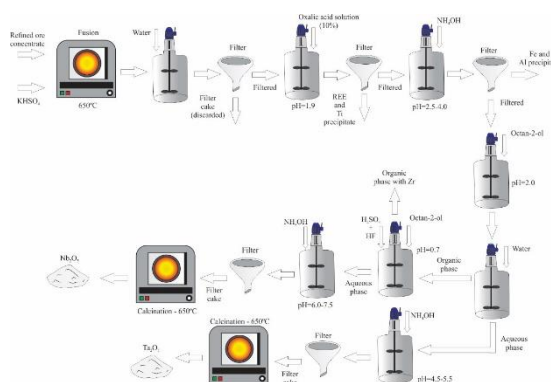


Figure 22 Nb-Ta separation: octan-2-ol processes. Adapted from [46]

10.7. Ion exchange separation

Ion exchange is mostly applied at laboratory scale and mainly in analysis. In the literature there are many methods using ion exchange, mostly varying the eluent (e.g. HCl, H₂SO₄, HF, NH₄Cl) and their combinations. Stationary phases are also varied, with resins such as Dowex-1, Amberlite IRA-900, Dowex Marathon, and Cellulose adsorbent being employed [47–49]. The ion exchange technique consists of firstly digesting the material for analysis (e.g. refined ore concentrate or mixed oxides) to convert Nb and Ta to a soluble state. Subsequently, the metal-containing solution is passed through in a pre-treated resin column and is collected at the bottom of the column in a flask. Subsequently, after resin re-treatment, a second eluent solution, different from the first, is also passed through the column and is collected in another flask. Both solutions can precipitate Nb and Ta by addition of NH₄OH [47–50]. Figure 23 presents a proposed industrial scale technique. First, the refined ore concentrate reacts with HF, and is then diluted with water. Afterwards, the aqueous phase is directed to pass through in two elution columns filled with Dowex-1 pre-treated resin. In sequence, one elution solution is passed through the column. For example, in Nb elution, a mixture of 3 M HCl -1 M HF is employed, with the solution being collected in a tank and mixed with NH₄OH to precipitate Nb. The second elution solution for Ta is composed by a mixture of 4 M NH₄F-1 M HF, and is also passed through the column and collected in another tank. This eluted solution can receive the same treatment as the Nb solution to precipitate Ta [48].

10.8. Chlorination

In the chlorination technique, there are three methods to separate Nb from Ta: solid-vapor, vapor-vapor and liquid-vapor. After the separation, all the produced compounds can be converted into their oxide forms via reactions with steam or NH₄OH, followed by being calcined [42].

In the solid-vapor method (Figure 24 - I), Nb and Ta oxides are heated in a reactor with Cl₂ or TaCl₅ at temperatures between 800 and 1200°C. In this reaction, Nb is preferentially volatilized over Ta in the chloride form, leaving Ta in the oxide form. Using AlCl₃ as chlorinating agent, NbOCl₃ and TaCl₅ are produced and when the temperature reaches 150°C, TaCl₅ sublims first, while NbCl₅ is formed in sequence, sublimating at

230°C [51]. A similar technique consists of submitting a mixture of NbOCl₃ and TaCl₅ to vacuum distillation, under a pressure of 0.1 mmHg [40].

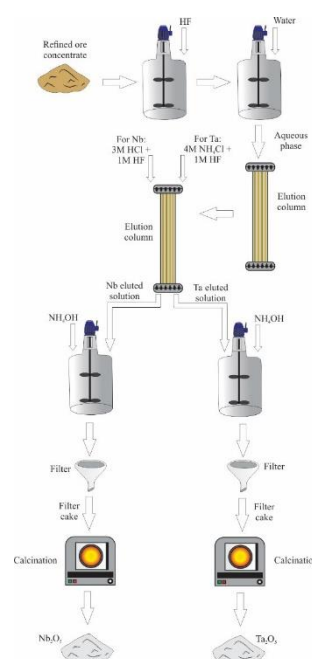


Figure 23 Nb-Ta separation: ion exchange process. Adapted from [48]

The vapor-vapor technique (Figure 24 - II), a mixed vapor of TaCl₅ and NbCl₅ can be separated using H₂ to reduce NbCl₅ to NbCl₃, at temperatures between 400 and 500°C. NbCl₃ is a non-volatile green-black solid, while TaCl₅ remains in the vapor phase at this temperature [51].

In liquid-vapor phase or distillation methods (Figure 24 - III), a mixture of melted NbCl₅ (melting point: 248°C) and TaCl₅ (melting point: 236°C) are directed to a fractional distillation column where these compounds are separated, followed by condensation [42, 51].

10.9. Alkaline extraction

This method is a fluorine-free Nb/Ta separation with low acid concentrations. In general, as reported by the authors, values of purity higher than 99.5% of hydrated Nb₂O₅ can be reached following this technique on a lab scale: a synthetic solution composed of 1.8 mM of [Ta₆O₁₉]⁸⁻ and [Nb₆O₁₉]⁸⁻ was prepared from the dissolution of the respective hydrated oxides using NaOH (pH=12). Following this, the synthetic solution

was mixed at a ratio between 0.8-3.0 (extraction solvent: synthetic solution) with an extraction solvent composed by 8.9 mM of Aliquat 336 (methyltrioctylammonium chloride) and 42 mM of isotridecanol diluted in Elixore 205 (phase modifier), at 300 rpm, room temperature, for 30 minutes. Following this process, centrifugation at 3000 rpm for 5 minutes is performed to separate the organic (Nb content) from the aqueous (Ta content) phase. Nb is stripped from the organic phase using a solution of 3% H₂O₂ and 5% HNO₃ while Ta was directly analyzed from the diluted aqueous phase [52].

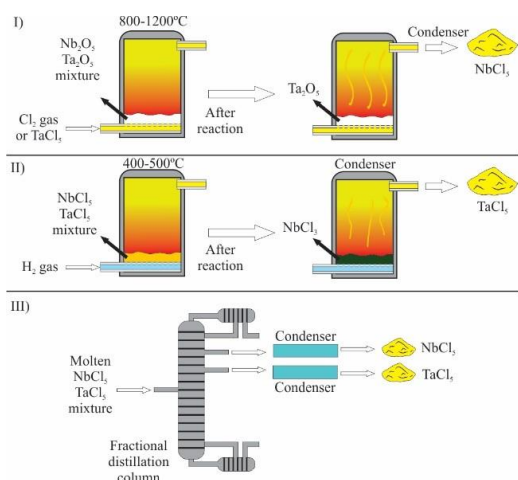


Figure 24 Nb-Ta separation: chlorination processes. Adapted from [51]

However, this method was applied for an industrial alkaline solution from Mabounié deposit (Gabon, Africa) (1917 mg/L of Nb, 39 mg/L of Ta) and the separation was not successful. This was despite the fact that the assays performed using a synthetic solution at the same Nb and Ta concentrations as industrial sample have displayed promising results. This difference can be attributed to the industrial steps as Nb and Ta were present in all previous processes (for example, concentration and alkaline fusion) which can promote an intermetallic replacement in niobate clusters [52].

Finally, with few modifications, the industrial alkaline solution can be processed for Nb/Ta separation: After the solvent extraction step, the organic phase is mixed with a solution composed of 0.50 M of oxalic acid, 0.30 M HNO₃ and 0.15 M of NH₄NO₃ for Nb stripping reaching purity similar to the lab assays. Furthermore, Ta can be extracted in the following step using an extractant composed of 0.50 M of HNO₃ and 0.5 M of NH₄NO₃ [52].

11. Conclusion

In general, there are many techniques developed in recent years to process Nb. However, choosing the best technologies depends on many factors, such as location, ore and gangue composition, particle size, reagents, application, and type of the product required. With continuous technology development, the demand for Nb will increase as the element is being increasingly incorporated into electronic components, batteries, catalysts and more efficient alloys, the components used in “green” products. This progress also can be reverted to the Nb chain production, developing newer, safer, and more environmentally friendly products, equipment and techniques to increase the efficiency of Nb recovery.

Declaration of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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PROIZVODNJA NIOBIJUMA: PRIKAZ PROCESA OD RUDNIKA DO PROIZVODA**P. Henrique do Nascimento Pereira¹, C. Marques Cury¹, A. Anastacio de Campos²,
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Izvod

U skorije vreme, veliki broj industrijskih i tehnoloških sektora sve više obraća pažnju na jedan hemijski element – niobijum. Ležišta niobijuma se nalaze širom sveta, i zbog osobenih karakteristika svakog ležišta primenjuju se različite tehnike za ekstrakciju i preradu. U ovom radu se daje prikaz mnogih tehnologija za proizvodnju niobijuma, počevši od rudnika, preko obogaćivanja rude niobijuma i rafinacije, tehnologija za proizvodnju feroniobijumske legure, oksida, specijalnih oksida, amonijum niobijumskog oksalata, izdvajanje niobijuma iz tantala, kao i tehnologije za redukciju i prečišćavanje metala niobijuma.

Ključne reči: proizvodnja niobijuma; koncentracija pirohlor; metal niobijuma; separacija tantala-niobijuma ; feroniobijum; oksidi niobijuma.
