



# A review on extractive metallurgy of tantalum and niobium

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## ABSTRACT

On-going technological developments, especially in the field of microelectronics and communication have reflected in concomitant increase in the demand for strategic metals such as tantalum (Ta) and niobium (Nb). The extraction of these two metals from ore deposits and secondary resources is based on the generic extractive metallurgical techniques known from the non-ferrous metals value chains. However, their operational particularities and especially the downstream refining remain a particular challenge. To this end, the existing and emerging processes for preparation of raw materials of Ta and Nb, leaching and recovery of pure metals are reviewed. The upstream operations and the downstream extractive metallurgical processes are discussed. The different sub-processes making part of the hydrometallurgical processing of the two metals, including leaching and solvent extraction are described, with their advantages and limitations highlighted. The selective recovery of Ta and Nb from the leachates is most commonly realized by solvent extraction and stripping which are therefore extensively covered. In the same context, the most widely used and promising extractants are compared in the light of their separation efficiency and level of handling hazard.

## 1. Introduction

Tantalum (Ta) and niobium (Nb) are two refractory metals which have an undisputed technological significance for our modern society. Their intrinsic properties such as corrosion resistance, superconductivity, high electrical capacity and biocompatibility are the reasons behind their growing importance as strategic metals. These two metals frequently occur together in various minerals and in combination with oxide impurities that impede their metallurgical processing (Ungerer et al., 2014). Both metals are also similar in terms of chemical and physical properties which renders their separation and purification difficult (Ayanda and Adekola, 2011). However, their abundance in the earth's crust is quite low, Ta being found around 2 ppm (Bose and Gupta, 2002; Soedarsono et al., 2018; Yang et al., 2018) and Nb - around 24 ppm (Makanyire et al., 2016; Allain et al., 2019). This limited availability is driving the need to valorise secondary raw materials containing Ta and Nb, among them tin slags, but also metallic scraps and by-products.

Pyrochlore and columbite are known as the major mineral sources for Nb. Pyrochlore contains exclusively Nb, while columbite bearing ores contain also significant amount of Ta which can be economically converted to pure metal. Colombo-tantalite (coltan) mineral is the

largest natural resource of Ta that is found in ore deposits with appreciable reserves in central Africa, especially in the Democratic Republic of Congo (Cunningham, 2000; BGS, 2011). Both pyrometallurgical or hydrometallurgical routes are used to recover these metals from their ores following appropriate pre-treatment steps. Pyrometallurgical processing is commonly used to convert Nb from pyrochlore into ferroniobium alloy through aluminothermic or carbothermic reduction. The hydrometallurgical methods are commonly employed to recover both Ta and Nb from colombo-tantalite (Ungerer et al., 2014). The approach consists of several sequential steps involving tantalum and niobium leaching, solutions purification, precipitation, calcination and final recovery of high purity metals as oxides. However, since these leaching practices operate always in the presence of fluoride ions, frequently a mixture of HF and H<sub>2</sub>SO<sub>4</sub>, they pose operational challenges at the industrial scale production of Ta and Nb (Zhu and Cheng, 2011). Due to the harmful environmental effects of HF, several alternative processes have been tried to leach Ta and Nb. Even though studies on Ta and Nb leaching being attempted at various scales, a systematic fundamental and applied approach on the metallurgical extraction of these two metals virtually do not exist. Same is valid for the separation of Nb and Ta from the productive solutions, which nowadays remains still a major task accompanied by several

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technological and economical challenges.

Very few detailed studies are reported on the hydrometallurgical recovery of niobium and tantalum from their minerals (Agulyanski, 2004; Ayanda and Adekola, 2011; Zhu and Cheng, 2011; Nguyen and Lee, 2019). Agulyanski (2004), investigated the chemistry of Ta and Nb fluoride-based extraction in view of developing new materials for modern applications. Ayanda and Adekola (2011), focused on various extraction and separation processes involved in the treatment of Nb and Ta primary resources. Zhu and Cheng (2011), extensively reviewed the solvent extraction technology for separation and purification of Nb and Ta. Nguyen and Lee (2019) reviewed the extraction and separation of Nb and Ta from leach liquors via acidic and neutral extracting agents and amines in the presence and absence of hydrofluoric acid.

All these studies focused more on the separation of tantalum and niobium from acidic solutions, with neither discussing alkaline-based leach options nor the upstream and downstream operations accompanying Ta and Nb hydrometallurgy.

The present review aims to fulfil the identified missing gaps and to contribute towards the lack of information on the metallurgy of Ta and Nb. To this end, the existing information on the hydrometallurgical methods for leaching of tantalum and niobium has been systematically collected and described, together with the extractive and purification processes that deliver Ta and Nb as oxides or as pure metals. Furthermore, the common operations belonging to the upstream processing of the colombo-tantalite, such as magnetic and gravimetric separation and flotation are briefly reviewed.

## 2. Tantalum-niobium mineral resources

Three main types of Ta and Nb deposits exist (Linnen et al., 2013; Melcher et al., 2017) which could be grouped as: (i) carbonatites and associated rocks (pyrochlore: rich in Nb), (ii) alkaline to peralkaline granites and syenites (rich in Ta, Nb and rare earth elements), and (iii) granites and pegmatites of the lithium, caesium and tantalum (LCT) family. More than 150 minerals of Ta and Nb are known to accompany these deposits (Nete, 2009; Theron et al., 2011). However, only two mineral groups (titano-niobates and tantalum-niobates) are considered as economically feasible for extraction of tantalum and niobium. The titano-niobates group is the largest source of niobium and tantalum. Within this group, a pyrochlore subgroup with predominating niobium presence (40–65% Nb<sub>2</sub>O<sub>5</sub>) in the mineral matrix and microlite subgroup, when Ta predominates, could be distinguished (Nete, 2009; Nguyen and Lee, 2019; Linnen et al., 2013). High grade tin slags (containing about 3% Ta<sub>2</sub>O<sub>5</sub>) are also viewed as economically exploitable resources for Ta and Nb. When the market is favourable, lower grade slags (e.g. 1–3% Ta<sub>2</sub>O<sub>5</sub>) are also used as raw materials for Ta and Nb production. Table 1, summarises the most economically important minerals of Ta and Nb, and Fig. 1 illustrates the global distribution of the ore deposits containing these minerals.

Apart from that, Table 2 outlines the major deposits of Ta and Nb ores, as well as the corresponding companies exploiting them. The Ta–Nb ores are often concentrated through wet gravity techniques, magnetic separation and flotation. Generally, the concentrate from the pyrochlore flotation is used as ferroniobium feedstock. For this purpose, the concentrate is mixed with iron oxide and aluminium and Nb<sub>2</sub>O<sub>5</sub> is reduced by an aluminothermic reaction to niobium which reacts with and joins iron oxide to form a ferroalloy, commonly referred as ferro-niobium. The latter is purified by electron-beam melting for further alloying high quality steel.

Table 3 presents the principal industries manufacturing high purity (99.99%) Ta and Nb end materials such as: pure Ta and Nb metals, oxides as Ta<sub>2</sub>O<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub> and Ta and Nb carbides. As could be seen from the summarized data, the Ta–Nb concentrates used commonly as feed material, are generally leached with a mixture of hydrofluoric and sulfuric acids and the resulting leachates are purified and concentrated through solvent extraction with MIBK and rarely with TBP.

**Table 1**  
Overview of the economically important Ta and Nb minerals.

Minerals	Chemical formula	Characteristics	Location	References
Microlite	(Na, Ca) <sub>2</sub> (Ta, Nb) <sub>2</sub> (O,OH,F)O <sub>6</sub>	Contains a proportion of rare earths and iron oxides. Color: pale yellow to brown; density: 6.3 to 6.4; association of tantalite, columbite and ilmenite. Structure: cubic isomorphous.	Norway, Sweden, Zimbabwe, U.S.A, Brazil Australia, Madagascar	(Alfonso et al., 2016)
Colombo-tantalite	(Fe, Mn)(Nb, Ta) <sub>2</sub> O <sub>6</sub>	The proportions of Nb and Ta vary. They have orthorhombic structure, black to red brown color; are present in syenitic and granitic pegmatites (beryl pegmatites). Density: 5.2 to 8.2 kg/dm <sup>3</sup> (depending on Ta content).	France, Norway, Finland, Russia, Australia, U.S.A, Brazil, DRC, Japan, Madagascar, Ethiopia, Nigeria	(Alfonso et al., 2016)
Pyrochlore	(Na,Ca) <sub>2</sub> (Nb,Ta) <sub>2</sub> O <sub>6</sub> (O, OH, F)	The most important source of niobium, its density ranges from 4.3 to 5.8 g/cm <sup>3</sup> ; it consists essentially of calcium niobate containing large amounts of iron, Mn, fluorine and other alkaline metals. It has an octahedral structure.	Brazil, Canada, DRC, Norway	(Papp, 2015; Schulz et al., 2017)
Taptolite Mossite	Fe (Nb, Ta) <sub>2</sub> O <sub>6</sub>	Tetragonal structure minerals. Taptolite: contains less Nb than Ta. Mossite contains more Nb than Ta.	Morocco	(Papp, 2015)
Fergusonite	(Y,Er,Ce,Fe)(Nb,Ta,Ti)O <sub>4</sub>	Mineral of granitic pegmatites rich in rare earths; monodimic structure; brown to yellow color; density: 5.6 to 5.8 (g/cm <sup>3</sup> ); up to 6 in tantaliferous varieties.	Norway, Sweden, Russia, Rhodesia, Sri Lanka, U.S.A, Australia, Madagascar	(Alfonso et al., 2016)
Samaraskite	(Y, Er, Ce, Fe, U, Ca, Pb, Th)(Nb, Ta, Ti, Sn) <sub>2</sub> O <sub>6</sub>	Orthorhombic crystal of density 4.2 to 6.2 g/cm <sup>3</sup> . Highly radioactive mineral.	U.S.A, Canada, India, DRC	(Llorens González et al., 2017)

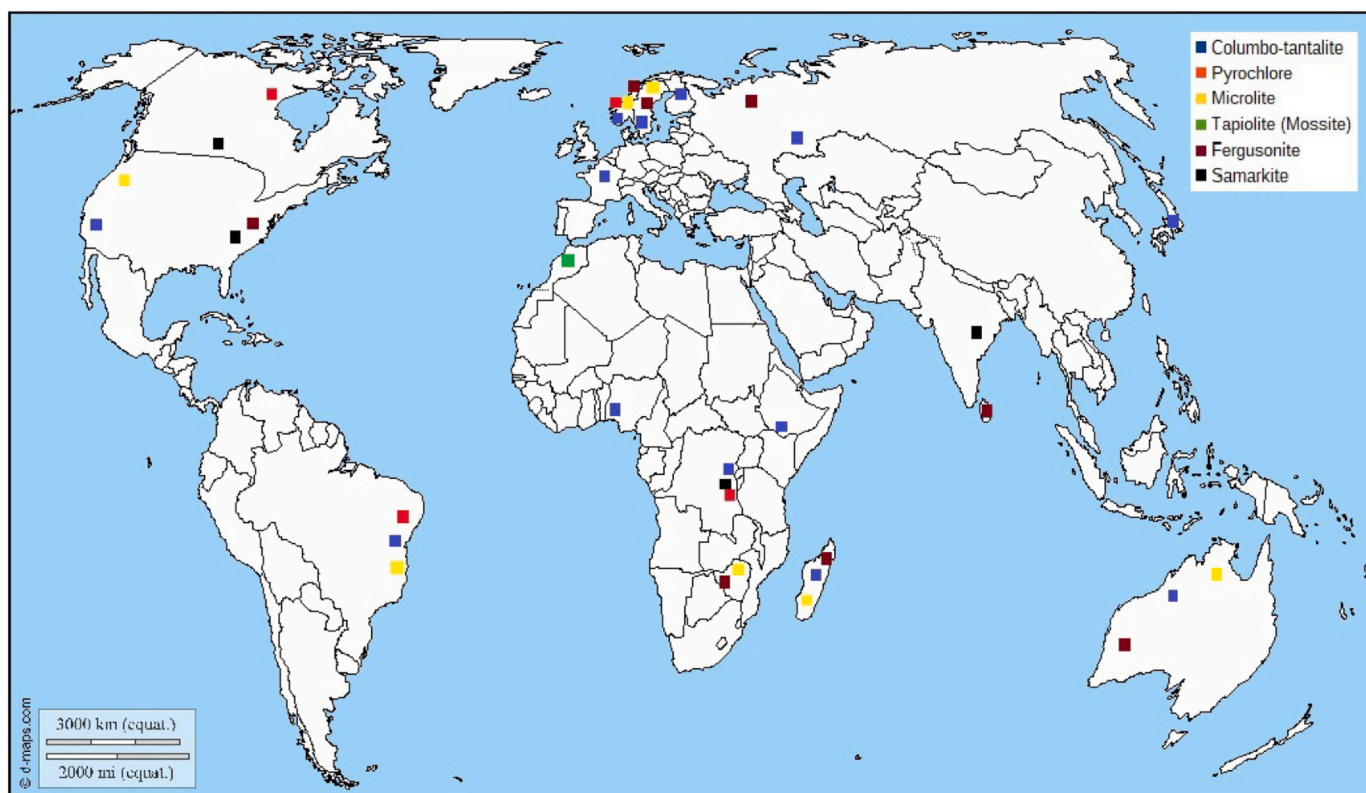


Fig. 1. Global distribution of the economically important Ta and Nb bearing deposits with the respective main minerals (image developed based on <http://www.d-maps.com>).

### 3. Metallurgy of Ta–Nb mineral resources

#### 3.1. Ore pre-treatment

The choice of an appropriate pre-treatment step is often considered as a key factor to establish an economically viable process for extraction. The pre-treatment of colombo-tantalite ores involves common size reduction operations such as crushing and grinding coupled with size classification. The targeted final granulometry by each of these operations is mainly dictated by the subsequent down-stream operations and the need for an early stage elimination of deleterious elements. If the following operation is a gravimetric or magnetic separation, it is strongly advised to perform relatively coarse grind in order to avoid material losses as fine particulates. When the subsequent operation is leaching, fine grinding is required in order to liberate the targeted minerals and facilitate the exposure of mineral phases to leaching agents.

#### 3.2. Physical pre-concentration

The physical methods involved in the colombo-tantalite beneficiation (gravimetric and magnetic separation) allow to concentrate the colombo-tantalite fraction from the other accompanying minerals (Gerôme and Gerôme and Charlier, 2017). The density of a coltan bearing ore is dictated by the tantalum grade and is generally between 5.3 and 7.8 g/cm<sup>3</sup> (Mirji et al., 2016). However, when the tantalum content is low, other minerals being present, such as cassiterite and wolframite could possess densities close to that of colombo-tantalite. Therefore, the density difference becomes negligible and gravimetric concentration inefficient.

Magnetic separation is useful not only for the iron ores but is also efficient in treating colombo-tantalite ores (Heizmann and Liebetrau, 2017). The method is based on the magnetic susceptibilities of the

different minerals to be separated. In most of the cases, coltan is accompanied by other useful minerals such as wolframite, cassiterite, ilmenite, rutile, and gangue minerals like magnetite, hematite, muscovite and quartz. Coltan and wolframite are paramagnetic, while cassiterite, muscovite and quartz are non-magnetic. Magnetite is the mineral with the highest magnetic susceptibility and therefore a low magnetic field (< 0.5 T) would allow magnetite to be separated from the remaining non-magnetic part. This resulting fraction can then be subjected to high intensity magnetic separation (> 0.5 T) to separate coltan and other minerals like cassiterite, quartz and muscovite.

Fig. 2 describes the sequence of magnetic separation steps to efficiently separate coltan from the remaining accompanying minerals.

#### 3.3. Flotation

The recovery of Ta and Nb from coltan bearing ores by flotation is in its early stages. The only exception to this, is the flotation of Nb<sub>2</sub>O<sub>5</sub> from pyrochlore which is already in practice on industrial scale (Burt, 2016). The flotation takes place at acidic pH (2.5–3.5) (Gibson et al., 2015), using an amine based cationic collector and oxalic acid as dispersant. The pH of the pulp is generally maintained at 3 by using dispersants such as fluorosilicic, oxalic and hydrochloric acids. During the process, most of the gangue minerals contained in the pyrochlore are leached out and removed. The end concentrates from this method are generally graded 55–65% in Nb<sub>2</sub>O<sub>5</sub> (Gibson et al., 2015).

At some industrial operations, such as those practiced in the Niobec (Canada) and Catalao (Brazil) mines, the ore is firstly subjected to reverse flotation of the gangue minerals followed by direct flotation of the Nb oxides. The reverse flotation is carried out with fatty acid as collectors in a similar way to the flotation of phosphates, spodumene and rare earth minerals. The most commonly used fatty acids are the oleic acid, causticized sodium oleate, synthetic fatty acids, tall oil and some oxidized petroleum derivatives (Gibson et al., 2015).

**Table 2**  
Principal deposits of Ta and Nb ores.

Deposit	Mining company	Country	Types of ore	Reserves (Mt)	Mean head grade, (%)		Ore processing	References
					Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub>		
Araxá	CBMM	Brazil	Carbonatite	462	2.48		aluminothermic reduction, flotation	Papp, 2008
Catalão mine	China Molybdenum	Brazil	Carbonatite	42	1.2		Flotation, aluminothermic reduction	Linnen et al. (2013)
Niobec mine	Magris Resources Inc.	Canada	Carbonatite	630	0.42		Flotation, Aluminothermic reduction	(BRGM, 2012)
Aley	Taseko Mines Ltd.Corp	Canada	Carbonatite	84	0.5		Aluminothermic reduction	Mackay and Mackay and Simandl (2014)
Greenbushes mines	Global Advanced Metals	Australia	Pegmatite	68	0.023	0.026	Ore concentration	(BRGM, 2012)
Wodgina mines	Global Advanced Metals	Australia	Pegmatite	28		0.042	Ore concentration	(Mackay and Mackay and Simandl, 2014)
Volta Grande Mine	Advanced Metallurgical Group	Brazil	Pegmatite	6	0.009	0.038	Flotation	(Papp, 2015)
Mt Cattlin	Galaxy Resources Ltd.	Australia	Pegmatite	10		0.015		(BRGM, 2012)
Tanco	Cabot Corporation	Canada	Pegmatite	2		0.22		(BRGM, 2012)
Pitinga Mine	Mineracao Taboca	Brazil	Peralkaline granite	267	0.22	0.027	Aluminothermic reduction	(Melcher et al., 2017)
Kenicha Mine	Elonilo Mining	Ethiopia	Pegmatite	116		0.02	Tantalite concentration	(Kiester et al., 2009)
Tabba Tabba	Pilabara Minerals	Australia	Pegmatite	0.318		0.095		(BRGM, 2012)
Abu Dabbab	Gippsland Ltd.	Egypt	Granite	32		0.027	Flotation	(BRGM, 2012)
Yichun mine	Ningxia Non-ferrous Metals	China	Peraluminous granite	75		0.025	Physical concentration	Linnen et al. (2013)

**Table 3**  
Major industrial players and employed processes leading to Ta–Nb end products.

Ta–Nb plant	Location	Feed materials	High purity end products	Process	Reference
Ningxia Non-ferrous Metals	China	Ta–Nb concentrate	Ta metal, Ta <sub>2</sub> O <sub>5</sub> and Nb <sub>2</sub> O <sub>5</sub>	HF–H <sub>2</sub> SO <sub>4</sub> leaching, SX with MIBK	(He et al., 1997; Papp, 2008; BRGM, 2012)
Conghua Tantalum and Niobium Smeltery (CTNS)		Ta–Nb concentrate	Ta <sub>2</sub> O <sub>5</sub> and Nb <sub>2</sub> O <sub>5</sub>	HF–H <sub>2</sub> SO <sub>4</sub> leaching, SX with MIBK	
F and X Electro-Materials Limited		Ta–Nb concentrate	Ta <sub>2</sub> O <sub>5</sub> and Nb <sub>2</sub> O <sub>5</sub> , Ta and Nb metals	HF–H <sub>2</sub> SO <sub>4</sub> leaching, SX with MIBK	
Fogang Jiata Metals		Ta–Nb concentrate	TaF <sub>5</sub> , K <sub>2</sub> TaF <sub>7</sub>		
Ningxia orient		Ta–Nb concentrate	TaF <sub>5</sub> , TaCl <sub>5</sub> , K <sub>2</sub> TaF <sub>7</sub>	HF–H <sub>2</sub> SO <sub>4</sub> leaching, SX with MIBK	
Global Advanced Metals	Australia	Ta ore	Ta powder, Ta <sub>2</sub> O <sub>5</sub>	HF leaching, SX	<a href="http://www.globaladvancedmetals.com">www.globaladvancedmetals.com</a>
Cabot Corp.	USA	Ta–Nb ore	Ta <sub>2</sub> O <sub>5</sub> , Nb <sub>2</sub> O <sub>5</sub> , Ta and Nb metal, Ta and Nb carbide.		(BRGM, 2012)
HC Start Inc.		Ta–Nb concentrate	Ta and Nb metal, Ta capacitor powder	HF–H <sub>2</sub> SO <sub>4</sub> leaching, SX with MIBK	(BRGM, 2012)
Wah Chang		Pyrochlore concentrate	Nb metal, Fe–Nb alloy, and K-salt		(Papp, 2008)
Niotan Inc.		Ta <sub>2</sub> O <sub>5</sub>	Ta powder	Aluminothermic reduction	(BRGM, 2012)
Companhia Industrial Fluminense (CIF)	Brazil	Ta–Nb ore	Ta <sub>2</sub> O <sub>5</sub> and Nb <sub>2</sub> O <sub>5</sub>	HF–H <sub>2</sub> SO <sub>4</sub> leaching, SX with MIBK	(BRGM, 2012), <a href="http://www.cif.ind.br">www.cif.ind.br</a>
Soilikamsk Magnesium works	Russia	Loparite minerals	Ta metal and Ta <sub>2</sub> O <sub>5</sub>	HF–H <sub>2</sub> SO <sub>4</sub> leaching, SX with TBP	(Papp, 2008; BRGM, 2012)
Ulba Metallurgical	Kazakhstan	Ta–Nb concentrate	Ta metal and Ta <sub>2</sub> O <sub>5</sub>	HF leaching, SX	(Papp, 2008), <a href="http://www.ulba.kz">www.ulba.kz</a>
Irtys Chemical and Metallurgical Works		Nb concentrate	Nb metal and Nb <sub>2</sub> O <sub>5</sub>	N.A.	(Papp, 2008)
Mitsui Mining and Smelting Co	Japan	Ta–Nb concentrate	Nb <sub>2</sub> O <sub>5</sub> and Ta <sub>2</sub> O <sub>5</sub> , Nb and Ta metal, Ta carbide	HF + H <sub>2</sub> SO <sub>4</sub> leaching, SX with MIBK	(BRGM, 2012), <a href="http://www.mitsui-kinzoku.co.jp">www.mitsui-kinzoku.co.jp</a>
H.C. Starck GmbH and Co. KG	Germany	Ta–Nb concentrate	Nb <sub>2</sub> O <sub>5</sub> , Ta <sub>2</sub> O <sub>5</sub> , Ta and Nb metal, Ta carbide, K-salt, Fe–Nb alloy	HF–H <sub>2</sub> SO <sub>4</sub> leaching, SX with MIBK	(Papp, 2008), <a href="http://www.hcstarck.com">www.hcstarck.com</a>

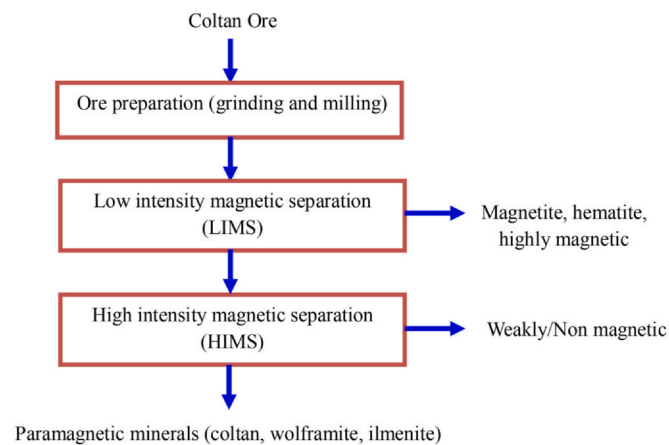


Fig. 2. Generic magnetic separation sequence applied for coltan bearing ores.

### 3.4. Leaching practices

Following a pre-treatment step, which will largely depend on the physical characteristics of the ore (grindability, apparent density) and its mineralogy, the feed material is generally subjected to acidic or alkaline leaching aiming to leach Ta and Nb. The productive solutions are

further directed to solvent extraction and stripping of the Ta and Nb complexes, followed by their precipitation as hydroxides. Fig. 3 provides a glance of the processes being practiced at the pre-treatment stage and the sequence of extractive metallurgical steps (metals leaching and purification). The most commonly practiced unit operations are discussed in more details further.

#### 3.4.1. Hydrofluoric acid leaching

The highly aggressive hydrofluoric acid was found to be the most efficient lixiviant for leaching of Ta and Nb from colombo-tantalite ores (He et al., 1997; Nete et al., 2012; Nete, 2013; Deblonde et al., 2016a). It was reported that a 40–48% hydrofluoric acid could bring up to 90% of Ta and Nb in solution (Agulyanski, 2004). The reason behind is that Nb(V) and Ta(V) are highly soluble in fluoride medium and readily form distinct complexes depending on pH and metal concentration. The complexes formed, generally are of two types:  $\text{TaF}_7^{2-}/\text{TaF}_6^-$  and  $\text{NbOF}_5^{2-}/\text{NbF}_6^-$  - Eq. (2) (Agulyanski, 2004; Zhu and Cheng, 2011; Toure et al., 2018). Eqs. (1) and (2) are not balanced.



The  $\text{TaF}_6^-$  and  $\text{NbF}_6^-$  complexes are the mostly desired ones due to their stability in the organic phase. In order to obtain these complexes, many studies recommend that the reaction should be carried out under

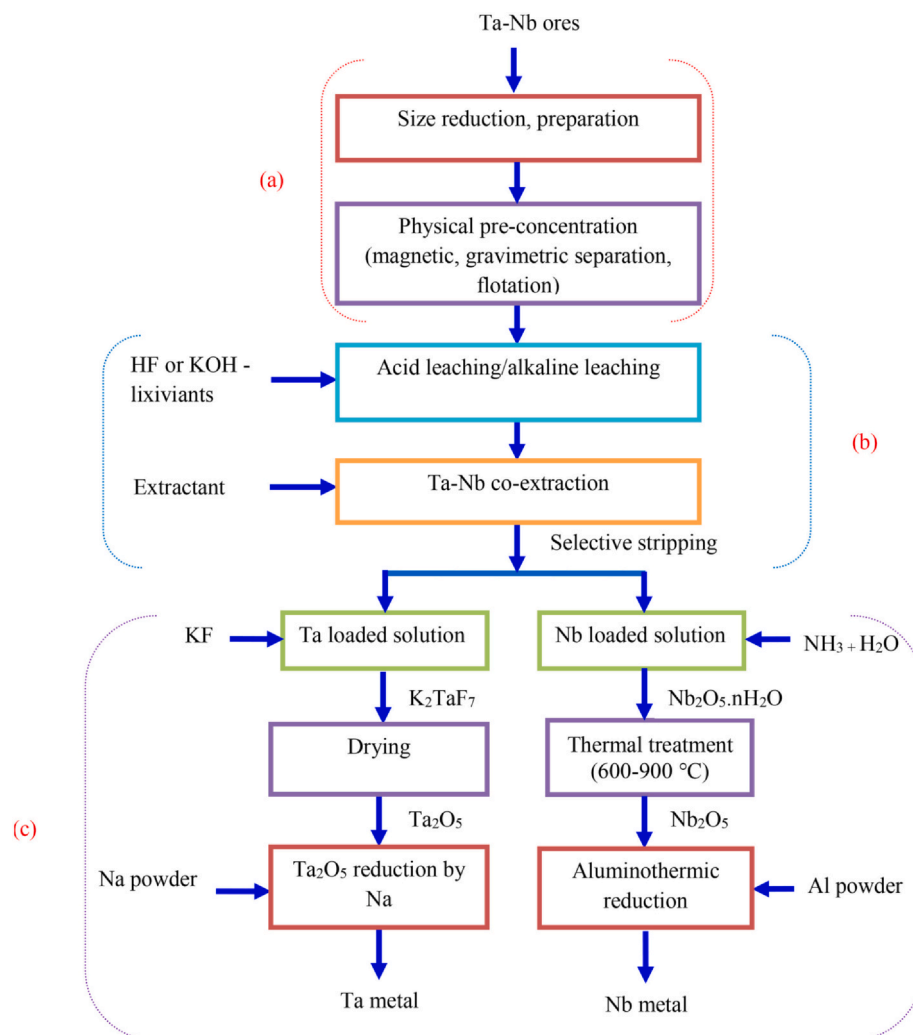


Fig. 3. Overall metallurgical paths for Ta and Nb primary ores: (a) upstream operations, (b) Ta and Nb hydrometallurgy, (c) downstream processing of metal laden solutions.



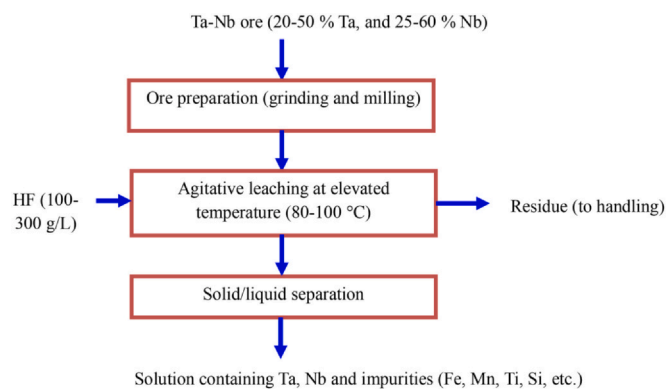


Fig. 4. Process sequence of hydrofluoric acid leaching of Nb and Ta bearing mineral resources.

high temperatures (80–100 °C) and with elevated acid concentrations (up to 20% HF) (F. Taylor, 2002; Rodriguez et al., 2004; Htwe and Lwin, 2008; Ungerer, 2012; Irfan et al., 2018; Purcell et al., 2018). The basic flow chart of the HF leaching route is shown in Fig. 4. It has to be noted, that the resulting phases after the leaching are separated by filtration and the filtrates are subjected to solvent extraction. The resulting pregnant leach solutions (PLS) could contain between 10 and 50 g/L Ta and 15–65 g/L Nb.

The hydrofluoric acid mediated leaching has however several drawbacks. Firstly, it is only appropriate for high grade tantalum-niobium ores, while for low grade ores (typically less than 20% Ta and 20% Nb) it causes practical issues (El-Hussaini and Madhy, 2002; Zhou et al., 2005b; Deblonde et al., 2016a, 2016b; Berhe et al., 2018b), since hydrofluoric acid dissolves too much of the gangue. Secondly, the use of hydrofluoric acid is accompanied by mass losses of about 6 to 7% due to volatilization (He et al., 1997; Kabangu and Crouse, 2012; S. Ayanda and A. Adekola, 2012; Berhe et al., 2018). These gas emissions are notoriously known as harmful to the environment, toxic to humans (Zhou et al., 2005a; Theron et al., 2011; Irfan et al., 2014; Berhe et al., 2018b; Yang et al., 2018) and corrosive to industrial equipment (Wang et al., 2010; Irfan et al., 2014). Moreover, the leaching process with HF is leading to wastewaters containing fluoride ions that require prior treatment before final disposal (Wang et al., 2009; Kabangu and Crouse, 2012; Deblonde et al., 2016a).

### 3.4.2. Leaching based on combination of hydrofluoric and sulfuric acids

In a way to address the application constraints provoked by the harmful effects from HF, an alternative process was developed in China at plant scale - high purity Nb<sub>2</sub>O<sub>5</sub> production capacity of up to 20 t/year. It is based on a mixture of hydrofluoric acid doped by another strong mineral acid, a sulfuric acid being the most widely used for this purpose. The sulfuric acid lowers the partial pressure of HF, reduces the volatilization losses and in such a way reduces the overall acid consumption that facilitates also the environmental foot-print of the process (He et al., 1997). The sulphates in the leachates could be eliminated together with the fluoride ions by precipitation through alkaline agents such as lime. Zhu and Cheng (2011), indicated that the mixture of HF-H<sub>2</sub>SO<sub>4</sub> also enhances the digestion of Ta/Nb better than HF-alone mediated leaching. In addition, for calcium-rich minerals, it is preferable to use the HF-H<sub>2</sub>SO<sub>4</sub> to keep calcium in the form of a non-soluble calcium sulphate. The solubilization of Nb and Ta in fluoride form, thus decreases the overall consumption of HF.

The operational temperature of colombo-tantalite leaching in HF-H<sub>2</sub>SO<sub>4</sub> media is usually kept around 100 °C (Htwe and Lwin, 2008; El-Hazek et al., 2012). When parameters such as particle size, HF/H<sub>2</sub>SO<sub>4</sub> ratio, digestion time and stirring rate are maintained close to their optimal values, high dissolution degrees could be obtained. The leaching reaction scheme of colombo-tantalite in the HF-H<sub>2</sub>SO<sub>4</sub> media is complex. It has been noted, that sulfuric acid most probably dissolve iron and manganese, while hydrofluoric acid converts Ta and Nb into soluble fluorides (Agulyanski, 2004).

### 3.4.3. Leaching using molten ammonium difluoride

Agulyansky et al. (2004), and Kabangu and Crouse (2012) proposed another approach based on fusion of colombo-tantalite with ammonium difluoride followed by water leaching. The process starts with fusion of a mixture between colombo-tantalite and ammonium difluoride (NH<sub>4</sub>HF<sub>2</sub>) at temperatures between 200 and 400 °C resulting in a calcine consisting of (NH<sub>4</sub>)<sub>2</sub>TaF<sub>7</sub> and (NH<sub>4</sub>)<sub>3</sub>NbOF<sub>6</sub>. The leaching of calcine with water or hydrofluoric acid of low concentration gives filtrate (after adjusting the pH of the solution) which is suitable for either direct purification or concentration by solvent extraction. The principal flow chart of this process is illustrated in Fig. 5 in where more than 90% leaching efficiency was achieved using NH<sub>4</sub>HF<sub>2</sub> as an agent to decompose colombo-tantalite minerals.

The main advantage of using ammonium bifluoride is that the HF is entirely excluded from the process. The amount of fluoride needed for

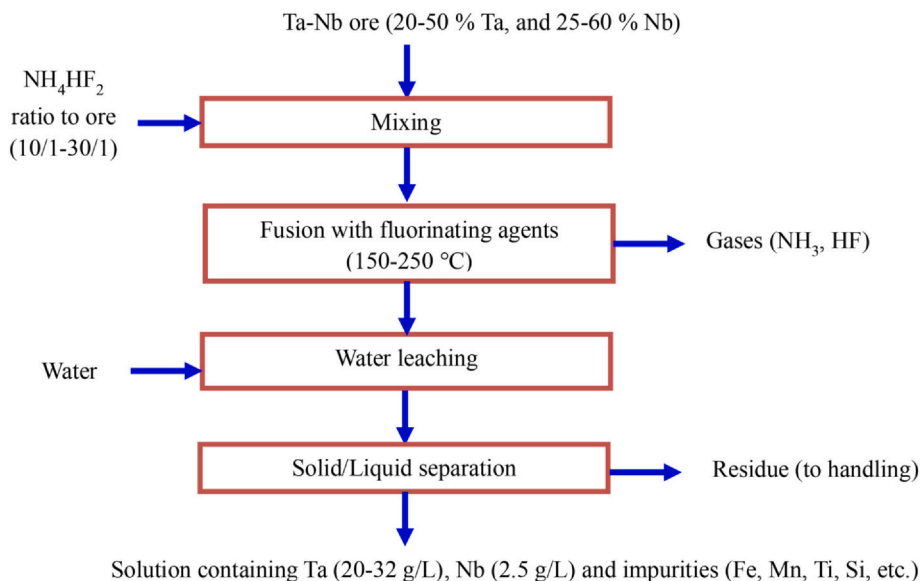


Fig. 5. Process sequence of ammonium difluoride based processing of Ta and Nb mineral resources.

**Table 4**  
Summary of available laboratory-scale leaching practices for Ta–Nb ores based on fusion with ammonium difluoride.

Raw materials	Ratio ore/ NH <sub>4</sub> HF <sub>2</sub>	Recovery (%)		References
		Ta	Nb	
Ta and Nb low grade loparite	1:1.7	> 90	> 90	(Krysenko et al., 2016)
Ta <sub>2</sub> O <sub>5</sub> and Nb <sub>2</sub> O <sub>5</sub>	1:10	> 90	> 90	(Nete et al., 2016)
Tantalite	1:30	98.7	97	(Kabangu and Crouse, 2012)
Ta <sub>2</sub> O <sub>5</sub> and Nb <sub>2</sub> O <sub>5</sub>	1:10	100	100	(Nete, 2013)
Tantalite	1:30	98.5	95	(Kabangu, 2014)
Ferro-columbite	1:10	91	96	(Purcell et al., 2018)

the raw materials decomposition can be calculated and adjusted as close as possible to the stoichiometric requirement (Kabangu and Crouse, 2012). Since the leaching of the calcine is performed in aqueous media, the resultant leachate has a low acidity (Agulyansky et al., 2004; Kabangu and Crouse, 2012). This opens the opportunity to use solvent extraction to recover the dissolved Ta and Nb in a collective or selective manner. In addition, the NH<sub>4</sub>F·HF is about 70% less expensive, much safer, easier to handle and to store than HF (Nete, 2013). However, the main drawback of this process is the toxic gas emissions that contain NH<sub>3</sub> and HF. Table 4, summarises the studies that deal with molten ammonium difluoride mediated leaching.

Alternative processes using acids other than the fluoride-based ones were also studied for the recovery of Ta and Nb from low grade ores or tin slags, but they have mostly been limited to laboratory or pilot scales. The most important developments in the non-fluoride lixiviants are summarized in Table 5.

#### 3.4.4. Alkaline leaching

Various chemical compounds such as caustic soda, potassium hydroxide, potassium carbonate or their mixtures have been proposed for alkaline leaching of Ta and Nb. These lixiviants can also be used in combination with oxidizing agents such as sodium nitrate and sodium peroxide to leach Ta and Nb from natural ores (Ayanda and Adekola, 2011). The alkaline-based leaching operates either by fusion or by direct dissolution via concentrated alkaline solutions. In the case of fusion, the process is combined with leaching using diluted alkaline solutions or water. This technique consists the earlier approaches being adopted at industrial scale. In this case, the first stage is designed to leach out iron, manganese, tin, titanium and silicon and produce columbite and tantalite concentrates which are then subjected to Ta and

Nb leaching (Ayanda and Adekola, 2011). However, this route has only been tested on low-grade Ta and Nb mineral ores (Nguyen and Lee, 2019). On the other hand, direct alkaline leaching of colombo-tantalite requires large amount of reagents which need to be evaporated and recycled back into the system (Wang et al., 2009; Berhe et al., 2018b).

The dissolution of Ta and Nb oxides in alkaline solutions leads to formation of hexaniobate and hexatantalate ion complexes (Nb<sub>6</sub>O<sub>19</sub><sup>8-</sup> and Ta<sub>6</sub>O<sub>19</sub><sup>8-</sup>). The dissolution rate of accompanying elements increases according to the following order: Li<sup>+</sup>Na<sup>+</sup>K<sup>+</sup>Rb<sup>+</sup>Cs<sup>+</sup> (Zhou et al., 2005b). The alkaline leaching mechanism of Ta and Nb bearing minerals revealed that when Nb<sub>2</sub>O<sub>5</sub> or Ta<sub>2</sub>O<sub>5</sub> react with potassium oxide, K<sub>3</sub>NbO<sub>4</sub> (K<sub>3</sub>TaO<sub>4</sub>) or KNbO<sub>3</sub> (KTaO<sub>3</sub>) were formed (Wang et al., 2010). The nature of the reaction products depends on the molar ratio of K<sub>2</sub>O to Nb<sub>2</sub>O<sub>5</sub> (or Ta<sub>2</sub>O<sub>5</sub>). At molar ratio ≤ 1:1, the reaction product is mainly KNbO<sub>3</sub> (KTaO<sub>3</sub>); when the molar ratio is higher or equal to 4:3, the principal reaction product is K<sub>3</sub>NbO<sub>4</sub> (K<sub>3</sub>TaO<sub>4</sub>). While KNbO<sub>3</sub> (or KTaO<sub>3</sub>) is insoluble in water, K<sub>3</sub>NbO<sub>4</sub> (K<sub>3</sub>TaO<sub>4</sub>) is hydrolysable to produce K<sub>8</sub>Nb<sub>6</sub>O<sub>19</sub> (K<sub>8</sub>Ta<sub>6</sub>O<sub>19</sub>) which can be leached out by water. These reactions take place according to the following equations, 3 and 4

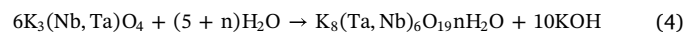
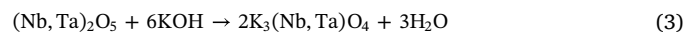


Table 6, summarises the various processes proposed for the alkaline leaching of Ta and Nb. But mostly they are confined to leaching alone and selective recovery of Ta and Nb from the leachates was not attempted. Fig. 6 depicts the principal leaching practices for the Ta–Nb low-grade resources based on both acidic (non-fluoride) and alkaline routes. The process conditions and the reported metallurgical results are presented for the sake of comparison.

Fig. 6 reveals that the selection of lixiviant route (either non fluoridic or alkaline) and optimum process parameters (concentration and type of leaching or roasting agent, process temperature), inevitably reflects in quite variable Nb and Ta recovery figures with a corresponding large differences in metal grades of the productive solutions. It could be assumed that both mineralogy and resources quality dictate the choice of the leaching route and determine process economics. Also it can be observed that Ta extraction is comparatively lesser than Nb, thus confirming the fact that Ta is more refractory than Nb.

Although the various alkaline-based systems prove efficient for leaching Ta and Nb, the approaches to separate both metals from the accompanying impurities are less elaborated. Wang et al. (2009) developed a process for the recovery of Nb and Ta as oxides from alkaline leachates described in Fig. 7. It involves initial addition of a certain amount of Nb<sub>2</sub>O<sub>5</sub> to the ore. The enriched ore is fused with potassium

**Table 5**  
Summary of other than fluoride-based lixiviants used for leaching Ta and Nb resources being tested at laboratory scale.

Raw materials	Lixiviant	Concentration/ parameters	Results obtained	References
Columbite ore	HCl	4 M	15.4% of columbite leached	(Ayanda and Adekola, 2012)
Columbite rich ilmenite ore	H <sub>2</sub> SO <sub>4</sub>	2 M	60.2% of columbite leached	(Baba et al., 2018)
Tantalite ore	HNO <sub>3</sub>	8.06 M	81.3% of columbite leached	(Baba et al., 2007)
Tin slag containing 14.1% Nb <sub>2</sub> O <sub>5</sub>	NaOH/HCl	Conc. NaOH Conc. HCl	Up-graded concentrate with 78.8% Nb <sub>2</sub> O <sub>5</sub>	(Odo et al., 2014)
Tin slag containing 15% (Ta,Nb) <sub>2</sub> O <sub>5</sub>	NaOH/HCl	1.2 M HCl 2 M NaOH	Up-graded concentrate with 63% (Ta,Nb) <sub>2</sub> O <sub>5</sub>	(Allain et al., 2019)
Nb-Ta as euxenite, samarskite and fergusonite minerals	H <sub>2</sub> SO <sub>4</sub> + HNO <sub>3</sub>	10.5 M H <sub>2</sub> SO <sub>4</sub> + 5.3 M HNO <sub>3</sub> solid/liquid ratio - 1:3	Recovery: 93.4% Ta and 99.5% Nb	(El-Hussaini and Mahdy, 2002)
Tin slag containing 1.56% Ta <sub>2</sub> O <sub>5</sub> and 1.11% Nb <sub>2</sub> O <sub>5</sub>	Double leaching with NaOH followed by HCl leaching of residue	5 M NaOH 5 M HCl	concentrate with 60% (Ta, Nb) <sub>2</sub> O <sub>5</sub>	(Soedarsono et al., 2018)
Mangano-tantalite ore	H <sub>2</sub> SO <sub>4</sub> + NH <sub>4</sub> F	50% H <sub>2</sub> SO <sub>4</sub> NH <sub>4</sub> F/ore - 0.8:1 Solid/liquid - 1:5	Recovery: > 93% Ta; > 96% Nb	(Yang et al., 2018)
TiO <sub>2</sub> residue containing Nb	HCl	4 M HCl	Recovery: 90% Nb	(Makanyire et al., 2016)

**Table 6**  
Summary of the main alkaline-based processes for Ta and Nb leaching tested at laboratory scale.

Raw materials	Decomposition technique	Fusion agent/ore ratio or concentration	Recovery, (%)		Reference
			Ta	Nb	
Nb <sub>2</sub> O <sub>5</sub> and Ta <sub>2</sub> O <sub>5</sub> (synthetic ore; pure oxides a.g.)	Alkaline fusion with KOH followed by acid leaching	5:1	95	95	(Wang et al., 2010)
Ta-Nb low grade ore	Alkaline fusion with KOH followed by water leaching	2:1	94	95	(Wang et al., 2009)
Ta-Nb low grade ore	Alkaline leaching with KOH	7:1	100	100	(Zhou et al., 2005b)
Colombo tantalite ore	Direct dissolution in KOH	4:1	81.7	92.2	(Wang et al., 2018)
Mangano-tantalite ore	Alkaline fusion with KOH followed by water leaching	5:1	75.8	94.7	(Berhe et al., 2018)
Nb-Ta low grade concentrates	Alkaline leaching using NaOH	400 g/L NaOH	65	65	(Deblonde et al., 2016b)
Low grade polymineralized Ta-Nb-Lanthanides ore	Alkaline fusion with KOH followed by water leaching	1:2	93.7	95	(El et al., 2019)
Nb low grade ore	Alkaline leaching with KOH	7:1		95	(Irfan et al., 2018)
Columbite and tantalite ores	Alkaline fusion (with K <sub>2</sub> CO <sub>3</sub> )/water leaching	2.5:1	45	65	(Matorov et al. (2011))

oxide at about 400 °C and the obtained products are subsequently leached with water. After filtration, the leachates containing niobium and tantalum are treated by evaporation and crystallization to obtain K<sub>8</sub>(Ta,Nb)<sub>6</sub>O<sub>19</sub> salt. This salt is finally transformed into high purity Nb and Ta oxide (Nb,Ta)<sub>2</sub>O<sub>5</sub> by means of a dilute acid solution. The main drawback of this process is that Ta and Nb are not separated, but recovered as oxide mixture.

### 3.5. Downstream processing of leach solutions containing Ta and Nb

#### 3.5.1. Solvent extraction

The most renowned downstream processing of the acidic leachates derived from processing of colombo-tantalite ores is based on solvent extraction (SX). This process achieves efficient separation of Ta and Nb from the leachates while eliminating the unwanted accompanying impurities. The mechanisms of solvent extraction when applied to recovery of Ta and Nb from HF-based leachates, largely depend on the chemical nature of the Ta and Nb complexes (Mayorov and Nikolaev, 2002). The two most common forms of Ta(V) and Nb(V) complexes are the TaF<sub>7</sub><sup>2-</sup>/NbOF<sub>5</sub><sup>2-</sup> complex, at low pH (3–5), and TaF<sub>6</sub><sup>2-</sup>/NbF<sub>6</sub><sup>-</sup>, at high pH. The NbF<sub>6</sub><sup>-</sup> complexes are extremely stable and hence require high acidity to be extracted by the organic solvents. On the other hand, TaF<sub>7</sub><sup>2-</sup> can be easily extracted from the leachates by either low or high acidity. This particular difference observed between these two Lewis acids offers the possibility of their separation by solvent extraction (Agulyanski, 2004). The stripping of Ta and Nb from the loaded organics to the aqueous phase will take place in the reverse order (Ungerer, 2012). Among the studies for downstream separation of the two metals from their accompanying impurities one should note the work done by (Zhou and Tokuda, 2000; Deblonde et al., 2019) illustrating the possibility of extracting Nb and Ta from alkaline leachates using a quaternary ammonium salt as an extractant. The salt is based on methyltriocetylammmonium chloride diluted in toluene. Niobium is then selectively stripped out using oxalic acid and nitrate ions, while Ta is stripped by nitric acid.

There are two existing methods for the separation of Ta and Nb by solvent extraction, namely collective and selective extraction. The first one is based on the co-extraction of Ta and Nb, while the second relies on selective recovery of Ta and Nb by adjusting the pH. Nevertheless, the collective extraction of Ta and Nb is the most widely used one, since the leaching using highly concentrated fluoric acids logically generates leachates with elevated acidity.

#### 3.6. Commonly used extractants for Ta and Nb

Nowadays, several commercial extracting agents and amines are subject of intensive testing. Among them, methyl isobutyl ketone (MIBK), tributyl phosphate (TBP), cyclohexanone (CHO) and octanol (OCL) are mostly used on industrial scale (Zhu and Cheng, 2011). These extractants are reported to be most suitable for processing fluoride containing leachates (Irfan et al., 2014).

The extractant MIBK is often the preferred choice for Ta and Nb extraction (Ayanda and Adekola, 2011; Sanda and Taiwo, 2012; Yang et al., 2013; Nguyen and Lee, 2019). This is because it has low density (0.802 g/mL), low viscosity (0.58 mPa.s at 20 °C), low solubility in water (1.91 g/100 mL) and high selectivity (Agulyansky et al., 2004; Zhu and Cheng, 2011). However, MIBK is highly volatile and possesses low flash point (14 °C) rendering it easily flammable and requiring special handling (Micheau et al., 2019). In addition, it can be lost in the raffinate at concentrations of up to 1.7% (w/w) thus requiring a complicated and expensive systems for its recovery (Kabangu and Crouse, 2012).

The solvent extraction with MIBK ends in organic phase rich in Ta and Nb, and an aqueous phase, rich in impurities. The tantalum bearing organic phase is stripped out with water to obtain a fluorotantallic acid solution (Bose and Gupta, 2002). Further on, the niobium is stripped



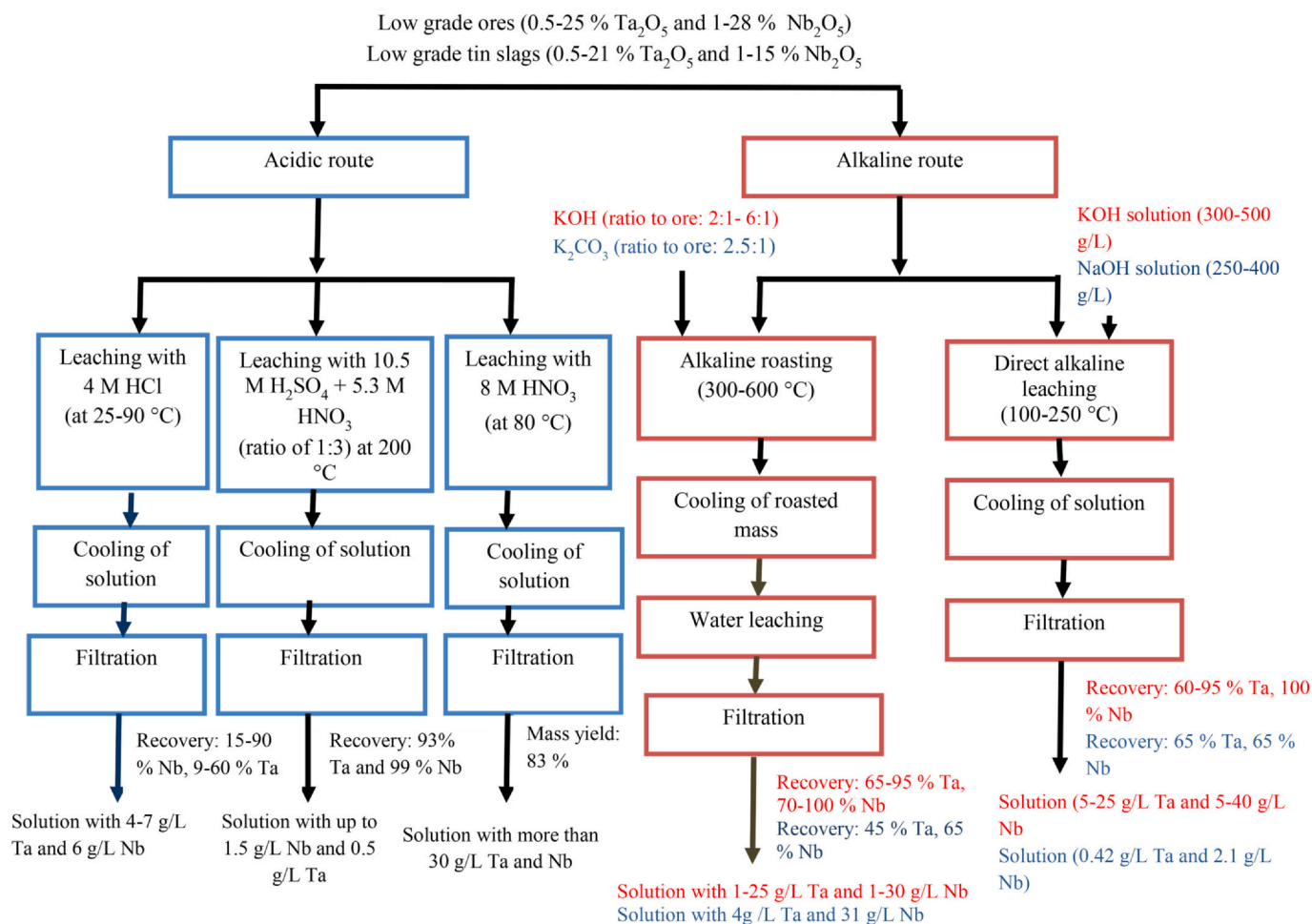


Fig. 6. Summary of non-fluoride acidic and alkaline leaching practices and down-stream steps when processing of Ta–Nb low-grade resources with associated metallurgical data (for the alkaline route, same color denotes process/stream data).

and recovered with a diluted HF-H<sub>2</sub>SO<sub>4</sub> mixture (Bose and Gupta, 2002) or diluted sulfuric acid (Zhu and Cheng, 2011).

The solubility of TBP in water is lower than that in MIBK (0.606 mL/100 mL). It also has a higher flash point (193 °C) which renders it less dangerous. However, its intrinsic density of 0.973 g/mL poses difficulties during the separation of the resultant phases, thus imposing the need for using extraction equipment with large volumes (Nguyen and Lee, 2019). Moreover, TBP is unstable in highly concentrated acidic solutions, especially in the presence of hydrofluoric acid (Toure et al., 2018). The resulting hydrolysis products such as phosphorous acids, might provoke contamination, resulting in end products with reduced purity (Mayorov and Nikolaev, 2002; Ungerer, 2012). Tantalum(V) and niobium(V) can be extracted into the TBP phase either at high or low HF acidity. During extraction, HNbF<sub>6</sub>·3TBP and HTaF<sub>6</sub>·3TBP complexes are generally produced. Tantalum and niobium are selectively stripped out from these loaded organic phases into the aqueous phase by ammonia.

Cyclohexanone (CHO) is known by its high solubility in water (16 mL/100 mL), which is the reason for its quite marginal use as an extractant in the separation and purification of Nb and Ta (Gupta and Suri, 1994; Toure et al., 2018). The main advantage of CHO compared to MIBK, is its superior degree of Ta extraction even when solutions with very low acid concentrations are processed. Tantalum can be stripped with water, whereas niobium stripping needs a diluted acid.

Octanol is the commonly used alcohol-based extractant. It is characterized by low solubility in water (0.1 mL/100 mL) and high flash point (81 °C) (El-Hazek et al., 2012). Two octanol-based extractants are

commercialized for Ta and Nb extraction. The extractant 1-octanol has been used for quite a long time to prevent formation of a third phase while using a second supplementary extractant. The reagent 2-octanol has shown higher selectivity against Ta than the 1-octanol and the other aliphatic alcohols (Kabangu and Crouse, 2012). It has been also reported that the 2-octanol possesses a separation coefficient ( $\beta_{Ta/Nb}$ ) of 238 compared to 97 for 1-octanol (Agulyansky et al., 2004). However, it has a disadvantage of having a relatively high viscosity (8.10<sup>-3</sup> Pa.s) which requires appropriate dilution.

There were few studies that report on separation of Ta and Nb using octanol (C<sub>18</sub>H<sub>18</sub>O) diluted in kerosene (Mayorov and Nikolaev, 2002; Agulyansky et al., 2004; El-Hazek et al., 2012; Kabangu and Crouse, 2012). The extraction process consists of collective extraction of Ta and Nb and their subsequent selective stripping from the loaded octanol. Kabangu and Crouse (2012) studied extraction of Ta and Nb by octanol. At the first stage, tantalite bearing minerals were subjected to fusion with NH<sub>4</sub>HF<sub>2</sub> followed by leaching with water. Sulfuric acid was then added to the initial solution to adjust the acidity before extraction.

The operation relevant properties of the most commonly used extractants for Ta and Nb are shown in Table 7. It should be noted, that cyclohexanone is less expensive and possesses higher solubility in aqueous solution than the other three extractants. Although tributyl phosphate has high cost, it also has a higher selectivity and comparatively lower fire hazard. Methyl isobutyl ketone has higher fire hazard but greater stability compared to other extractants, while octanol is known as the least expensive extractant. Table 8 presents the type of the solutions being subjected to solvent extraction and the reported degree

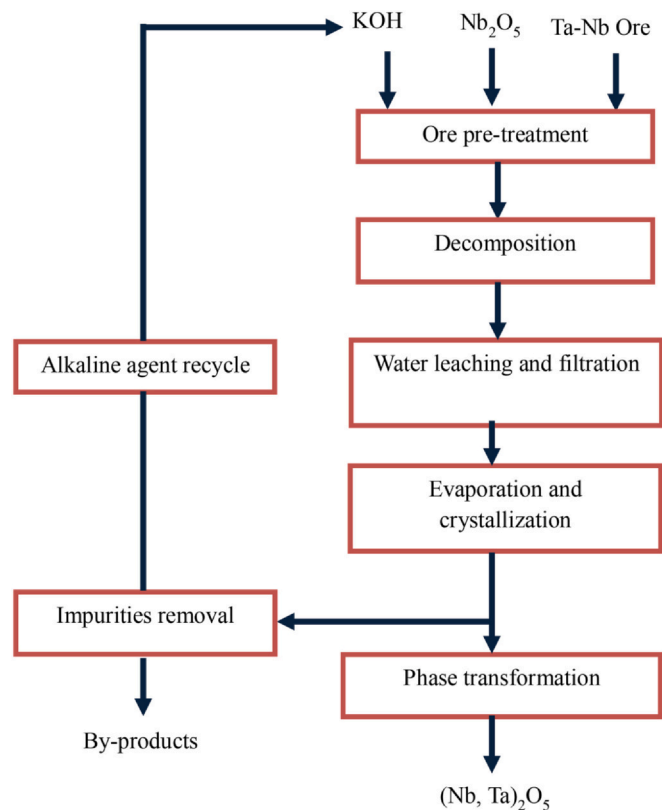


Fig. 7. Flow chart of an alkaline route for producing Ta and Nb oxide sources (adapted from Wang et al., 2009).

Table 7

Comparison of properties of common commercial Ta and Nb extractants (Nikolaev and Nikolaev and Maiorov, 2007).

Properties	Order of significance
Fire hazard	MIBK > CHO > OCL > TBP
Extraction power	TBP > CHO > MIBK > OCL
Selectivity	TBP > OCL > CHO > MIBK
Cost	TBP > MIBK > CHO > OCL
Water solubility	CHO > MIBK > OCL > TBP

(efficiency) of recovery for Ta and Nb with different extractants described above.

### 3.7. Amine-based extractants

Wide commercial application of amines has not been documented

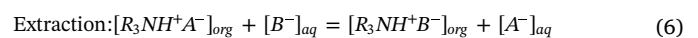
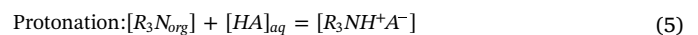
Table 8

Summary of the commonly used extracting and stripping agents for Ta and Nb tested at laboratory scale.

Targeted solution	Extracting agent	Recovery, (%)		Stripping agent	Reference
		Ta	Nb		
HF + H <sub>2</sub> SO <sub>4</sub>	MIBK	94	88	Water for Ta and H <sub>2</sub> SO <sub>4</sub> < 8 M for Nb	(Purcell et al., 2018)
HF + H <sub>2</sub> SO <sub>4</sub>	MIBK	98		Water	(Yang et al., 2013)
Sulphate solution pH 2 for Ta and pH 0.7 for Nb	2-octanol (100%, A/O = 1)	100	100	6 M H <sub>2</sub> SO <sub>4</sub> + 7 M HF for Nb, and water for Ta, ratio 1:1	(El-Hazek et al., 2012)
Sulphate solution (2.5–3.5 M) + HF	2-octanol (100%, A/O = 1–1.2: 1)		100	3 M H <sub>2</sub> SO <sub>4</sub> and water, ratio 3:1	(Agulyansky et al., 2004)
HF + H <sub>2</sub> SO <sub>4</sub>	2-Octanol	100	100	Water and H <sub>2</sub> SO <sub>4</sub>	(Kabangu and Crouse, 2012)
HF	1-Octanol	95.6	90	Water for Ta and H <sub>2</sub> SO <sub>4</sub> for Nb	(Mayorov and Nikolaev, 2002)
HF + H <sub>2</sub> SO <sub>4</sub>	Cyclohexanone	96	97	H <sub>2</sub> SO <sub>4</sub> for Nb and water for Ta	(Gupta and Suri, 1994)
HF (150 g/L) + H <sub>2</sub> SO <sub>4</sub> (100 g/L)	TBP (0.3: 1)	> 80	> 70	H <sub>2</sub> SO <sub>4</sub> for Nb and water for Ta	(Mayorov et al., 2015)

on industrial scale so far, but they have been extensively studied and have shown promising potential (Zhu and Cheng, 2011). Alamine 336 and Aliquat 336 are the two most widely used amines. Both are insoluble in water, making them ideal for solvent extraction purposes (Ungerer, 2012). Although, Alamine 336 and Aliquat 336 have high flash points, 179 °C and 132 °C respectively, their main disadvantage lies in their tendency to generate a third phase and form emulsion (Ungerer, 2012; El-Hazek et al., 2012). The addition of a modifier, for example a 1-octanol, has been suggested to prevent these drawbacks (El-Hazek et al., 2012).

Since Alamine 336 contains a basic nitrogen atom, it typically reacts with variety of inorganic complexes to form amine salts, which are undergoing ion exchange reactions with other anions (Friess, 2014). The principal reaction consists of a two-step sub-reactions, being protonation and ion exchange extraction respectively, as shown below with B representing Ta or Nb complex (Eqs. (5) and (6)).



The extent to which B<sup>−</sup> will exchange for A<sup>−</sup> is a function of the relative affinity of the two anions for the organic cation and the relative solvation energy of the anions by the aqueous phase (Friess, 2014). When used as a reagent in solvent extraction, the Alamine 336 first extracts Ta and Nb compounds from the aqueous solution and then it has to be stripped for recovery of the targeted species and reused again after stripping.

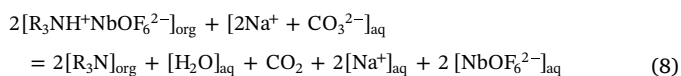
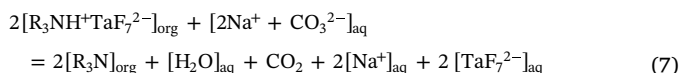
Aliquat 336 was found to be a suitable reagent for the extraction of Ta and Nb from alkaline solutions (Zhou and Tokuda, 2000; Deblonde et al., 2016a; Deblonde et al., 2019). Recently, Deblonde et al. (2019) proposed an innovative solvent extraction process for Ta and Nb from alkaline solutions (pH 12), using Aliquat 336 dissolved in an organic diluent. However, for scaling up this process to industrial application, it needs to be improved for tantalum extraction.

#### 3.7.1. Stripping and separation processes

The stripping stage principally aims at two objectives: (i) recovery of the metal values from the organic phase and (ii) regeneration of the extractant for its reuse. Stripping agents differ according to the nature of their extraction mechanisms, that are either ion-pair transfer or ion exchange (Friess, 2014). Currently, tantalum is stripped from the loaded organic phases by back washing of the organic phase with demineralized water (Mayorov and Nikolaev, 1996, 2002; Agulyansky et al., 2004; Zhu and Cheng, 2011). In contrast, niobium is stripped by a weak HF or H<sub>2</sub>SO<sub>4</sub> solution (Mayorov and Nikolaev, 2002). The Nb(V) and Ta(V) stripped from the organic phase, produce NbOF<sub>6</sub><sup>2−</sup> and TaF<sub>7</sub><sup>2−</sup> in the aqueous phase, respectively. It is obvious that these complexes are explicitly found in solutions of low acidity.

Amine based extractants could be stripped by wide variety of

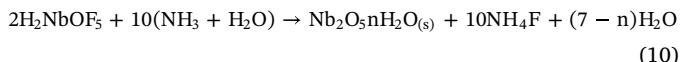
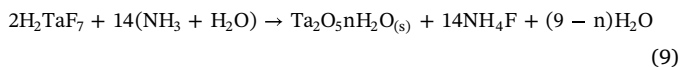
inorganic salt solutions, such as NaCl, Na<sub>2</sub>CO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (Friess, 2014). The type of the employed stripping agent depends on the overall recovery process. In general, basic stripping agents which can reverse the amine protonation (Eq. (5)), give the best stripping degrees within fewest stages (Friess, 2014). Eqs. (7) and (8), depict the stripping action of Na<sub>2</sub>CO<sub>3</sub> on the amine salt.



According to Deblonde et al. (2019), Nb can be selectively stripped from alkaline leachates containing Nb and Ta using a mixture of diluted nitric and oxalic acids followed by Ta stripping with a diluted nitric acid.

### 3.7.2. Precipitation of Ta and Nb

The precipitation of Ta and Nb from the leachates allows to generate highly pure Ta and Nb intermediates. These intermediates are mostly oxides (Nb<sub>2</sub>O<sub>5</sub> or Ta<sub>2</sub>O<sub>5</sub>) or potassium salts (K<sub>2</sub>TaF<sub>7</sub> or K<sub>2</sub>NbF<sub>7</sub>). The oxides are obtained from fluoro-tantalate (H<sub>2</sub>TaF<sub>7</sub>) and oxyfluoro-niobic (H<sub>2</sub>NbOF<sub>5</sub>) acids through precipitation using basic solutions (such as ammonia or ammonium carbonate). Potassium salts are obtained by precipitation of the Ta and Nb bearing acidic leachates via potassium fluoride. Ammonia is the most widely used agent in industry for the precipitation of Ta and Nb in the form of hydroxides (Mirji et al., 2016; Yan and Tang, 2018). Its advantage over KF is the removal of fluoride already taking place at this earlier stage of the process, which enables to bring end products containing as less fluoride as possible. The ammonia precipitation is realized via reaction between tantalate or oxyfluoro-niobic acids and ammonia solution according to Eqs. (9) and (10):



The equilibrium of the above reactions depends on the amount of ammonia used, meaning the higher amount of ammonia, the higher precipitation level of Ta and Nb achieved. Generally, the most favourable regions for precipitation are around pH 8–9 (Ayanda and Adekola, 2011; Mirji et al., 2016; Yan and Tang, 2018). However, the resulting precipitates may be contaminated with up to 20% (g/g) of fluoride (Yan and Tang, 2018). It was reported, that the most important parameter affecting the amount of fluoride in the precipitate is the dose level of ammonia added to the stripped solution. Therefore, highly alkaline pH is recommended in order to avoid the presence of fluoride which could ultimately affect the quality of the end products.

### 3.7.3. Removal of hydroxides

The removal of the accompanied hydroxides is an important step in the production of high-purity oxides. The step is commonly accomplished by dissolving the impurities that are co-precipitated with Ta or Nb in a way to avoid contamination of the end products with fluoride. Yan and Tang (2018), recommended the use of 2% NH<sub>3</sub>/H<sub>2</sub>O to obtain dry hydroxides containing less than 2% fluoride. Washing is therefore a crucial step which has to be repeated as long as possible to remove all the impurities until no fluoride traces are detected in the precipitate.

### 3.7.4. Thermal treatment

The washed and filtered precipitates contain two types of water inside their structure. The first one is known as intrinsic moisture and can easily be removed by drying at 100–200 °C. The other type of water incorporated within the Ta(V) and Nb(V) hydroxides themselves can be

removed at elevated temperatures (700–900 °C). In practice, the step consists of calcination of the obtained hydroxides resulting in yielding high-purity oxides. Additionally, this step leads to elimination of the volatile substances such as fluoride and ammonium being entrained in the precipitates. The removal of water according to the above described path could be presented in a simplistic way by the equations below (eqs. 11 and 12):

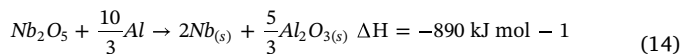


## 3.8. Production of metallic Ta and Nb

The way to yield Ta and Nb as pure metals is ultimately dictated by the form under which they are found in the respective intermediates. The refining of Ta from the potassium heptafluorotantalate is commonly achieved by the reduction of the latter with sodium (Eq. (13)). To obtain high-purity tantalum, it is recommended that both the salt and the sodium bearing reducing reagent are of high purity. The reaction takes place at about 1200 °C inside a reactor operating under inert atmosphere (or vacuum) to avoid accumulation of oxygen during the reduction process. This reaction is exothermic and is known to release 2985 kJ kg<sup>-1</sup> of energy (Mirji et al., 2016).



Niobium metal is obtained by reduction of its intermediates Nb<sub>2</sub>O<sub>5</sub> or K<sub>2</sub>NbF<sub>7</sub> using reducing agents such as calcium, aluminium, magnesium, sodium, hydrogen or suitable electron donors (Mirji et al., 2016). The most widely practiced approach is based on aluminium and is known as aluminothermic process. It consists of reaction between Nb<sub>2</sub>O<sub>5</sub> and pure aluminium at temperatures above 1100 °C according to Eq. (14):



## 4. Conclusions

The important developments in the leaching and recovery practices of tantalum and niobium from their primary ores are reviewed. Upstream methods (magnetic separation, gravimetric concentration or flotation) are important to pre-concentrate Ta and Nb from accompanying gangue, remove deleterious elements from the coltan bearing ores prior to leaching and optimise reagent consumption during leaching. The choice of the given pre-treatment method will largely depend on the mineralogy of the ore. In the specific case of coltan bearing ores, magnetic separation is the most suitable method for primary beneficiation. The extractive metallurgy of Ta and Nb involves leaching, solvent extraction and stripping of Ta and Nb complexes and their precipitation as hydroxides. Current industrial practice use leaching of colombo-tantalite ores by a mixture of concentrated hydrofluoric and sulfuric acids. Due to the harmful environmental effects of the hydrofluoric acid, HF-free hydrometallurgical alternatives are also proposed. However, the low recovery and inferior selectivity of the emerging alternatives render their application limited to laboratory or pilot scales only. Among the promising alternatives, the following two deserve a mention: use of fluorohydric salts such as NH<sub>4</sub>F or NH<sub>4</sub>F·HF, and an alkaline leaching after a molten pre-treatment of coltan with alkaline reagents such as KOH and NaOH.

The solvent extraction of Ta and Nb allows their co-extraction followed by selective stripping. Tantalum and niobium contained in the acidic leachates could be co-extracted by commercial extractants such as MIBK, OCL, and TBP or by promising amines such as Alamine 336 and Aliquat 336. The selective stripping of tantalum from the loaded extractants by sulfuric acid could be realized at near neutral pH (6–7)

and niobium stripping is favoured at relatively acidic pH of 1–3. Highly concentrated ammonia solutions (50–100 g/L) are needed if the intention is for complete precipitation of Ta(V) and Nb(V) as hydroxides. High temperature treatment is then used to obtain Ta(V) and Nb(V) oxides of sufficient purity to serve further as intermediates for the production of Ta and Nb as pure metals.

Future work should focus on leaching of Ta and Nb by concentrated acids such as sulfuric, hydrochloric or nitric doped in advance with fluoride salts such as  $\text{NH}_4\text{F}$  or  $\text{NH}_4\text{FHF}$ . The resulting solid residues and process water (the latter carrying fluoride ions) need to be managed in an environmentally sound manner.

### Author statement

A. Shikika contributed to experiments execution, data compilation and writing the initial draft.

M. Sethurajan contributed in manuscript editing and data presentation.

F. Muvundja contributed in background supply and conceptualisation.

M. Mugumaoderha contributed in background data supply and conceptualisation.

St. Gaydardzhiev contributed in experiments planning, formulation of research aims and paper concept as well as in final paper polishing.

### Declaration of Competing Interest

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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