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Gauthier J.-P. Deblonde, David Bengio, Denis Beltrami, Sarah Bélair, Gérard Cote, et al.. A fluoride-free liquid-liquid extraction process for the recovery and separation of niobium and tantalum from alkaline leach solutions. *Separation and Purification Technology*, 2019, 215, pp.634-643. 10.1016/j.seppur.2019.01.052 . hal-02182966

HAL Id: hal-02182966

<https://hal.univ-lorraine.fr/hal-02182966>

Submitted on 8 Aug 2019

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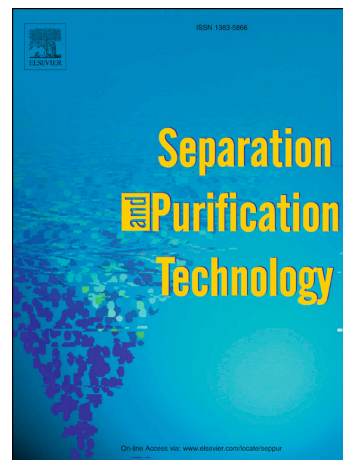
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PII: S1383-5866(18)34427-7
DOI: <https://doi.org/10.1016/j.seppur.2019.01.052>
Reference: SEPPUR 15282

To appear in: *Separation and Purification Technology*

Received Date: 14 December 2018
Revised Date: 21 January 2019
Accepted Date: 21 January 2019



Please cite this article as: G.J. Deblonde, D. Bengio, D. Beltrami, S. Bélair, G. Cote, A. Chagnes, A fluoride-free liquid-liquid extraction process for the recovery and separation of niobium and tantalum from alkaline leach solutions, *Separation and Purification Technology* (2019), doi: <https://doi.org/10.1016/j.seppur.2019.01.052>

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A fluoride-free liquid-liquid extraction process for the recovery and separation of niobium and tantalum from alkaline leach solutions.

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ABSTRACT

The production of high purity niobium (Nb) or tantalum (Ta) compounds still relies on processes that require highly acidic conditions and concentrated HF or NH₄F solutions. Recent progress in the chemistry of group V elements, along with the evolution of the environmental concerns, call for the development of more sustainable industrial processes for these strategic elements. In sharp contrast with the historical fluoride approach chosen by the Nb and Ta refining industry, there has been a recent surge in the literature concerning the chemistry of these elements in diluted alkaline or oxalate media. We here propose an innovative liquid-liquid extraction process that is amenable to separate Nb and Ta from alkaline feed solutions, can be operated at low acidity and that does not require any fluoride-based chemical. The developed strategy is as follows: first, Nb and Ta are co-extracted from their alkaline solution (pH 12) using a quaternary ammonium salt (Aliquat® 336) dissolved in an organic diluent; then, Nb is selectively back-extracted in a mixture of diluted nitric and

oxalic acids; and finally, Ta is stripped in a diluted nitric media. The process also affords purifying Nb from Ti, Fe and Na. Following an optimization at laboratory scale, the full process has been validated during continuous running tests (160 h at 1.4 L.h⁻¹) using industrial Nb-Ta caustic solutions coming from the development of the so-called Maboumine process. The developed process works at room temperature, low acidity ($[H^+] < 1 \text{ M}$), exhibits high recovery yields, and allows producing Nb₂O₅·nH₂O with purity higher than 99.5 %. The process also yields a tantalum product (Ta₂O₅·nH₂O with >20 wt% Ta) even when starting from a diluted feed (39 ppm Ta). The proposed strategy paves the way for new Nb and Ta hydrometallurgical processes operating under mild chemical environments and represents a concrete alternative to the current fluoride-intensive industrial methods.

Introduction

Niobium (Nb) and tantalum (Ta) have become incredibly important to a broad variety of industries, going from the automobile, aerospace, and construction sectors, to the defense, nuclear, electronic, and chemical companies. Due to their unparalleled properties, their monopolistic and sometimes volatile markets, as well as the absence of cost-effective alternatives, Nb and Ta are often labeled as “critical” or “strategic raw materials” [1,2]. For instance, Nb is a key component of the high-strength low-alloy (HSLA) steels used by numerous industries because the addition of a few parts per million of Nb strengthens the steels without impairing their ductility. The manufacture of HSLA steels represents nearly 90 % of the Nb usage worldwide [3,4], and owing to its relatively low cost compared to the final value of these high-end materials, the substitution risk for Nb is essentially non-existent. The rest of the Nb market [1,2,5,6] consists of some high-value niche markets such as the supra-conducting magnets, nuclear fuel claddings, medical implants, electronic components, optical lenses, etc. The worldwide production of Nb is about 100,000 tons per year whereas

that of Ta is only 500 to 2,000 tons per year due to its lower natural abundance [7]. The main application of Ta is the production of electronic components and specialty alloys for cutting tools, military projectiles, and aircraft parts. Despite their essential role in several strategic applications, Nb and Ta are still obscure materials from the general public's perspective and little attention is paid to the way they are produced.

The high-tech applications using Nb typically require starting materials with a minimum purity of 99.5 wt% whereas the Ta concentrates can be commercialized as long as the Ta content is at least 20 wt% thanks to their higher market value [7]. Nb and Ta are usually found together in natural deposits and their almost identical chemical properties (both are group V elements with identical ionic radius...) render their separation one of the most challenging of the periodic table. Nb and Ta also have very peculiar chemistries as they have very low solubility in classical acidic media compared to other d-block elements (1.4×10^{-5} M for Nb and 7.8×10^{-5} M for Ta in 1 M HNO_3 at room temperature) [8]. Due to this fact, the main option for processing Nb and Ta concentrates remains the solutions with high concentrations of HF or NH_4F , *i.e.* highly corrosive and highly toxic media, where both metals form the soluble complexes NbOF_5^{2-} , NbF_6^- , TaF_6^- , and TaF_7^{2-} [9,10]. The development of the Nb and Ta hydrometallurgical industry started with the so-called Marignac's process which operates in HF media and dates back to the 19th century [11] but the current processes are still based on a similar philosophy. Currently, all the commercialized solvent extraction processes for the Nb–Ta separation are operated in fluoride media and an intensive effort is still being made to improve the Nb–Ta separation by liquid-liquid extraction in such media. These processes typically require an aqueous phase composed of a mixture of HF or NH_4F and a mineral acid such as H_2SO_4 or HCl in the range of 1 to 10 mol.L⁻¹ [9,10,12–18]. Moreover, the fluoride processes are only appropriate for high-grade Nb–Ta concentrates [19]. Another drawback of these fluoride-based methods is

that the extractants are sometimes also harmful such as the methylisobutyl ketone derivatives. Hence, these hydrometallurgical processes represent a serious health hazard for the operators and the generated wastes are inherently toxic, both for humans and the environment.

In light of these observations, there is a growing interest for developing more sustainable Nb-Ta purification methods that could be operated under milder chemical conditions and, if possible, without any fluoride-based chemical. We here propose to fill the gap between this need and the recent progress in the chemistry of Nb and Ta in fluoride-free media. Over the past few decades, the chemistry of Nb and Ta has experienced a revival in two types of fluoride-free environments: the basic media and the oxalate media [20–40]. Recent studies have also shown that the extraction of Nb and Ta from natural ores is possible and economically sound if performed in alkaline media [19,41–46]. Nonetheless, separation methods for the two elements in these media have not been developed yet.

Herein, we developed the first Nb-Ta separation process amenable to use an alkaline feed solution. The selected strategy consists of a three-step liquid-liquid extraction process: 1) co-extraction of Nb and Ta from alkaline media using a quaternary ammonium diluted in an aliphatic diluent, 2) selective back-extraction of Nb in a diluted solution of oxalic acid and nitrates, and 3) total stripping of Ta in diluted nitric media. The process also affords purifying niobium from titanium, iron and sodium. The treatment of the Nb and Ta stripped solutions and subsequent recycling of the oxalate are detailed in a follow-up publication [47]. The Nb-Ta separation detailed in the present study has been optimized at laboratory scale and then validated by pilot scale testing. The process operates at room temperature, at relatively low acidity ($[H^+] < 1 \text{ M}$), and does not require any fluoride-based chemical.

Experimental

Materials and methods. All synthetic solutions were prepared with deionized water ($R > 18.2$ Mohm). Nb_2O_5 (Sigma Aldrich, 99.9% purity), Ta_2O_5 (Sigma Aldrich, 99.99% purity), Aliquat® 336 (Sigma Aldrich), standard NaOH solutions (Prolabo Normadose), HNO_3 (6M, VWR), NH_4NO_3 (VWR, ACS grade), $NaNO_3$ (VWR, ACS grade), H_2SO_4 (10 M, VWR), HCl (6M, VWR), $HClO_4$ 70% (ACS grade, VWR), H_3PO_4 85% (VWR), $H_2C_2O_4 \cdot 2H_2O$ (VWR, 99.5% purity), isotridecanol (BASF) were used as received. Elixore 205, a 100% aliphatic diluent ($C_{11} - C_{14}$) offering a good balance between low viscosity, high boiling point range (199 – 237°C) and high flashpoint (76°C), was provided by Total Special Fluids. The solvent extraction was prepared by diluting Aliquat® 336 and isotridecanol in Elixore 205 (a classical phase modifier used to avoid third phase formation). During extraction, Aliquat® 336 was used in its chloride form and was pre-equilibrated with an alkaline solution at pH 12. $Na_7HNb_6O_{19} \cdot 15H_2O$ and $Na_8Ta_6O_{19} \cdot 24.5H_2O$ were synthesized from Nb_2O_5 and Ta_2O_5 as starting materials using previously reported synthesis [8,48,49]. The synthetic aqueous solutions of $Na_7HNb_6O_{19} \cdot 15H_2O$ and $Na_8Ta_6O_{19} \cdot 24.5H_2O$ were prepared by direct dissolution in water and used within a few hours. The industrial alkaline solutions containing Nb and Ta were provided by the mining group ERAMET (ERAMET IDEAS, Trappes, France). The alkaline solutions come from the development of the so-called Maboumine process which aims at recovering the valuable elements (Nb, Ta, rare earth elements, uranium) from the Mabounié deposit located in Gabon. The upstream part of the process that led to the raw Nb-Ta alkaline solution has been described previously [45,46,50–53].

Table 1. Typical composition of the industrial solution used during the tests.

Composition	Nb	Ta	Ti	Fe	Na
(mg/L)	1917	39	5.1	1.2	1160

pH measurements were performed with a 827 pH-lab (Metrohm) pH-meter and a low alkaline error combined electrode (Unitrode, Metrohm). The Fe, Ti, Ta, and Nb concentrations were determined by ICP-OES using an ICP 720-ES spectrometer (Varian). Quantitative ICP analyses were performed at 238.204 nm (Fe), 334.188 nm (Ti), 268.517 nm (Ta) and 313.078 nm (Nb) spectral emission lines. Na concentrations were determined by flame absorption spectroscopy using an AA 220 spectrometer (Varian) at 589.6 nm.

Experimental procedures. The volume phase ratios, $V_{\text{organic}}/V_{\text{aqueous}}$, given in this study were determined based on measurements of the mass and density of each phase. In a typical experiment, the organic phase and the aqueous phase were put in contact in a plastic tube (15 mL, Falcon). The samples were shaken at 300 rpm at room temperature (22 °C) for at least 30 min as kinetic experiments showed that equilibrium was reached after less than 5 min (data not shown). The samples were then centrifuged for 5 min at 3000 rpm and separated before analysis. The organic phases corresponding to the batch experiments were filtered with Whatman 1 PS filters before analysis. This was done systematically in order to remove eventual micro droplets of aqueous phase although tests with and without filtration revealed no variation (meaning that the phase separation was naturally effective). The aqueous phases were analyzed by ICP or flame absorption spectroscopy after dilution. For analytical purposes, the organic phases were totally stripped using an equal volume of a mixture of 3 % H_2O_2 and 5 % HNO_3 at 50 °C. The use of H_2O_2 ensures the complete removal of Ti from the organic phase as Ti is known to form stable species with extractant molecules [54]. The stripped solutions were then analyzed by ICP to check the mass balance. The distribution ratio, $D(M)$, of a given metal, M, is defined as follows:

$$D(M) = \frac{[M]_{\text{organic}}}{[M]_{\text{aqueous}}} \quad \text{Eq. (1)}$$

$[M]_{\text{organic}}$ represents the total concentration of M in the organic layer whereas $[M]_{\text{aqueous}}$ represents the total concentration of M in the aqueous layer after extraction. The separation factor, SF , between two metals, M_1 and M_2 , is defined as follows:

$$SF_{M_1/M_2} = \frac{[M_1/M_2]_{\text{final}}}{[M_1/M_2]_{\text{initial}}} \quad \text{Eq. (2)}$$

The extraction yields were calculated as follows:

$$\% \text{Extraction} = \frac{[M]_{\text{organic}}}{[M]_{\text{aqueous initial}}} \times \frac{V_{\text{organic}}}{V_{\text{aqueous}}} \times 100 \quad \text{Eq. (3)}$$

The back-extraction yields were calculated as follows:

$$\% \text{Back extraction} = \frac{[M]_{\text{aqueous}}}{[M]_{\text{organic initial}}} \times \frac{V_{\text{aqueous}}}{V_{\text{organic}}} \times 100 \quad \text{Eq. (4)}$$

Continuous running test. A continuous running test was performed at ERAMET's research center (ERAMET IDEAS, Trappes, France). The pilot campaign was performed for 160 hours at steady-state conditions. About 225 L (11 drums of ~20 L) of alkaline solution ($\text{pH} \approx 12$) containing Nb and Ta were processed during this campaign. The liquid-liquid extraction process was operated in counter-current mode. The extraction battery contained two mixer-settler stages, the Nb back-extraction battery five stages, and the Ta stripping battery two stages. The mixer volume was 200 mL whereas the settler volume was 400 mL. Pictures of the pilot installation are given in Figure S 1. The liquid streams were circulated via peristaltic pumps. The flow rate of each stream was controlled by weight and density measurements at least once per work shift. Each stream was analyzed by ICP (Nb, Ta, Ti, Fe) and flame absorption spectroscopy (Na) at least once per work shift.

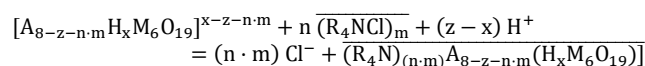
Speciation considerations

Due to the peculiarity of Nb and Ta chemistries and since several equilibria are involved in the developed hydrometallurgical process, a summary of the relevant data on the speciation

of Nb and Ta in basic, and oxalate media, as well as, in the presence of Aliquat® 336 is given hereafter. In alkaline aqueous solutions, Nb and Ta form the hexameric species $M_6O_{19}^{8-}$ (also called the Linqvist ions) and are subject to protonation reactions. As recently demonstrated by Nyman et al. [21], these highly charged clusters also interact with the alkaline counter-ions and form ion pairs. More recently, the intermetallic substitutions Nb-Ta has also been observed in alkaline aqueous solutions containing the Nb and Ta Linqvist ions [55–57]. The ion pairing behavior and the intermetallic substitutions are specificities of the chemistry of Nb and Ta in alkaline media but have to be taken into account when developing hydrometallurgical processes for these two elements.

Table 2. Speciation data available on Nb and Ta, in media relevant to the developed process.

Media	References
Alkaline pH > 9	Protonation: $H_3Nb_6O_{19}^{5-} = H_2Nb_6O_{19}^{6-} + H^+$ pKa = 9.35 to 9.39 [48,58–60] $H_2Nb_6O_{19}^{6-} = HNb_6O_{19}^{7-} + H^+$ pKa = 9.92 to 10.88 $HNb_6O_{19}^{7-} = Nb_6O_{19}^{8-} + H^+$ pKa = 12.6 to 13.8
	$H_3Ta_6O_{19}^{5-} = H_2Ta_6O_{19}^{6-} + H^+$ pKa = 9.28 [61–64] $H_2Ta_6O_{19}^{6-} = HTa_6O_{19}^{7-} + H^+$ pKa = 9.3 to 12.2 $HTa_6O_{19}^{7-} = Ta_6O_{19}^{8-} + H^+$ pKa = 11.5 to 13.89
	Ion pairing: $H_xM_6O_{19}^{x-8} + nA^+ = [A_nH_xM_6O_{19}]^{n+x-8}$ [21,23] A = Li, Na, K, Rb, Cs. M = Nb or Ta.
	Intermetallic substitution: [55–57] $(6-y)Nb_6O_{19}^{8-} + yTa_6O_{19}^{8-} = 6Nb_{(6-y)}Ta_yO_{19}^{8-}$ Protonation omitted for clarity. $1 \leq y \leq 5$.
Oxalate	Nb complexes observed: [29,30,33,65–68] $[NbO(C_2O_4)_2(H_2O)_2]^-$ $[NbO(C_2O_4)_3]^{3-}$ $[NbO(OH)(C_2O_4)_2H_2O]^{2-}$
	Ta complexes observed: [69–71] $[TaO(C_2O_4)_3]^{3-}$ $[TaO(C_2O_4)_2(H_2O)]^-$ $[Ta_4O_4(C_2O_4)_3]^{2-}$
Aliquat® 336	Ion-exchange: [72,73] $R_4NCl + X^- = R_4NX + Cl^-$ X = NO_3^- , SO_4^{2-} , CO_3^{2-} , HO^-
	Extractant self-association: $mR_4NCl = (R_4NCl)_m$
	Hexametallate extraction:



A = alkali ion. $0 \leq x \leq 3$. $0 \leq z \leq 7$. $1 \leq n \cdot m \leq 8$. M = Nb or Ta.
Overlined symbols indicate species that are in the organic phase.

Results and discussion

Solvent extraction of Nb and Ta from alkaline media. Building on the recent report that Aliquat® 336 is a suitable and efficient extractant to transfer polyoxoniobate anions (*i.e.* the species formed by Nb in alkaline media) into an organic solvent [72], the extraction of polyoxotantalate ions was then investigated. Table 3 gives the extraction profiles for equimolar mixtures of hexaniobates and hexatantalates at constant pH and for various organic-aqueous volume ratios. As expected from the well-known similarities between Nb and Ta chemistries, extraction of Ta by Aliquat® 336 with a high efficiency was also observed. More interestingly, the extraction yields for Nb were found to be systematically higher than that of Ta, with separation factors of about 4 (Table 3), indicating that the quaternary ammonium extractant has a much higher affinity for the polyoxoniobate ions compared to their polyoxotantalate counterparts.

Table 3 : Extraction yields of Nb and Ta by Aliquat® 336 using a synthetic solution containing both the hexaniobate and hexatantalate ions. Initial aqueous solutions: $[Ta_6O_{19}] = [Nb_6O_{19}] = 1.8$ mM, $[NaOH] = 10$ mM. $pH_{equilibrium} = 11.9 \pm 0.1$. Organic phase: $[Aliquat® 336] = 8.9$ mM + isotridecanol 42 mM diluted in Elixore 205. One contact. T = 25°C, t = 30 min.

V_{org}/V_{aq}	% Extraction Ta	% Extraction Nb	D(Ta)	D(Nb)	SF Nb/Ta
0.8	14.7	40.9	0.221	0.880	4.0
1.0	20.3	47.7	0.261	0.934	3.6
1.5	36.7	66.7	0.391	1.350	3.5
2.0	54.0	80.0	0.590	2.007	3.4
3.0	86.7	96.1	2.195	8.368	3.8

In basic aqueous solutions ($pH > 9$), the speciation of Nb and Ta is remarkably similar, with the two elements forming exclusively the stable hexanuclear species $H_xNb_6O_{19}^{x-8}$ and $H_xTa_6O_{19}^{x-8}$ ($0 < x < 3$) [20,23,48]. Based on the reported pKa values (Table 2), the major species for niobium at $pH \sim 12$ is the mono-protonated hexaniobate ion [48]. In the case of

tantalum, three different groups have investigated the acid-base equilibria of $H_xTa_6O_{19}^{x-8}$ and, as previously reviewed [48], there is a large discrepancy among the reported pKa values. Nonetheless, the most recent study shows that the mono-protonated and fully deprotonated hexatantalate ions coexist at pH 12 [64]. We recently demonstrated that the extraction reactions involved during the extraction of the hexaniobate ions by quaternary ammonium salts, like Aliquat® 336, are the protonation of $H_xNb_6O_{19}^{x-8}$, the competitive co-extraction of other anions (HO^- , Cl^- , NO_3^- , CO_3^{2-} , SO_4^{2-} ...), the co-extraction of alkali cations and water molecules, and the self-association of the extractant in the organic layer [72].

The higher extraction yields for Nb compared to Ta could tentatively be ascribed to a slight difference between the averaged protonation states of the hexametallate species as the most recent studies [48,64] show a higher degree of protonation for $H_xNb_6O_{19}^{x-8}$ compared to $H_xTa_6O_{19}^{x-8}$ in the pH range 10-13. Another hypothesis to explain the observed selectivity Nb/Ta is the difference in the ion-pairing behavior that exhibit $H_xNb_6O_{19}^{x-8}$ and $H_xTa_6O_{19}^{x-8}$. We recently showed that the speciation of the hexaniobates and hexatantalates can be influenced by the alkali cations present in the media, including modification of their solubility as well as electrophoretic mobilities [8,57,74]. Furthermore, Nyman et al. previously established that the hexaniobates form contact ion-pairs with alkali cations whereas the hexatantalates form solvent-shared or solvated-separated ion-pairs [21,23]. The presence of water molecules around the hexatantalates may render them more hydrophilic than their hexaniobate analogues and subsequently less prone to be transferred into the organic phase by the hydrophobic extractant. These two hypotheses need further investigations to be confirmed and the origin of the Nb/Ta selectivity goes well beyond the scope of the present study. Nonetheless, the surprisingly high selectivity observed upon liquid-liquid extraction of polyoxometalates represents an opportunity, with a technique that

has been rather underused in this field, and could be leveraged to probe subtle differences between the chemistries of polyoxoniobates and polyoxotantalates.

The selective extraction of Nb over Ta in alkaline media using Aliquat® 336 would also represent a major step forward for the hydrometallurgy of these two elements since such a process would be fluoride-free and rather simple to operate compared to the current processes that require highly corrosive and concentrated HF or NH₄F solutions. Encouraged by the apparent selectivity of Aliquat® 336, separation of Nb and Ta was attempted on an industrial alkaline solution containing ~2 g/L of Nb and ~50 mg/L of Ta at pH 12. Experiments were also performed with the same solvent, under the same acidity conditions, but using freshly prepared synthetic mixtures of hexaniobates and hexatantalates instead of the industrial solution. The Nb and Ta extraction yields for both synthetic and industrial samples are compared in Figure 1.

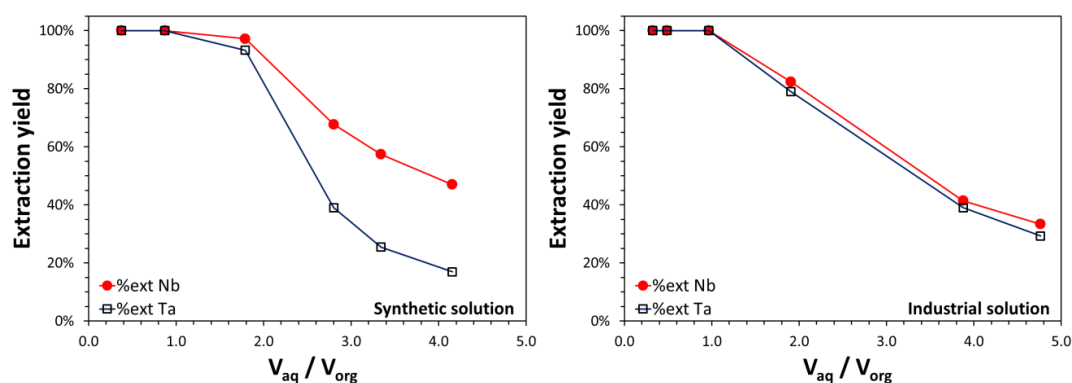


Figure 1. Extraction yields of Nb and Ta obtained from a synthetic mixture of hexaniobates and hexatantalates (Left) or from an industrial solution (Right) at various volume phase ratios. Initial synthetic aqueous solutions: [Ta] = 0.3 mM, [Nb] = 21 mM. $pH_{equilibrium} = 11.9 \pm 0.1$. Initial industrial aqueous solutions: [Ta] = 0.28 mM (50 mg/L), [Nb] = 21.5 mM (2.0 g/L). $pH_{equilibrium} = 11.9 \pm 0.1$. Organic phase: [Aliquat® 336] = 45 mM + isotridecanol 105 mM diluted in Elixore 205. One contact. $T = 25^\circ C$, $t = 30$ min. Synthetic solution used within 8 h of its preparation. Squares: Ta. Circles: Nb.

The selectivity of Aliquat® 336 was again confirmed when starting from synthetic mixtures containing the equivalent of 2,000 mg/L of Nb and 50 mg/L of Ta in the form of hexaniobates and hexatantalates and the separation factors are in the same range as those

given in Table 3. Surprisingly, a total loss of selectivity is observed when using the industrial Nb-Ta solution and both elements are extracted with identical extraction yields (within the experimental uncertainty). We previously showed by UV-vis spectrophotometry that the speciation of Nb in industrial solutions mainly consists of hexaniobate ions [45,48]. More recently, we demonstrated by capillary electrophoresis that $H_xNb_6O_{19}^{x-8}$ and $H_xTa_6O_{19}^{x-8}$ ions undergo intermetallic substitutions when present in the same solution and naturally form mixed polyoxometalates, $H_xNb_{6-y}Ta_yO_{19}^{x-8}$ ($1 \leq y \leq 5$), after a several hours or upon heating [55–57]. Taking these observations into account, given the high ratio Nb/Ta in the studied industrial samples, and due to the process by which they have been produced [45,51] it is very likely that Ta is entirely present as $H_xNb_{6-y}Ta_yO_{19}^{x-8}$ instead of pure $H_xTa_6O_{19}^{x-8}$ ions in industrial samples. Even if Aliquat® 336 seems capable of making the distinction between pure and freshly prepared hexaniobates ions and hexatantalates ions, it seems very unlikely to find an extractant selective enough to separate pure hexametallate species from the mixed Nb-Ta species as, for example, $Nb_6O_{19}^{8-}$ against $Nb_5TaO_{19}^{8-}$. The industrial processing of Nb-Ta raw materials in basic media inherently implies that the resulting hexametallate streams contain Nb-Ta substituted species due to the presence of both metals during the synthesis (or alkaline conversion), and also because of prolonged residence times and, sometimes, heating [19,42–45]. As a consequence, even if the formation of the mixed polyoxoanions $H_xNb_{6-y}Ta_yO_{19}^{x-8}$ seems rather anecdotic in the context of industrial applications, it actually has a primordial importance since it stands in the way of developing Nb-Ta separation processes solely based on a selective extraction step from alkaline solutions.

Selective back-extraction of niobium. Despite the lack of selectivity observed with industrial alkaline solutions, the co-extraction of Nb and Ta using Aliquat® 336 remains attractive as it allows recovering both elements from alkaline industrial streams. Going one step further, a selective back-extraction step, following the co-extraction of Nb and Ta by

Aliquat® 336, has been developed. Nb and Ta are soluble in only a handful of aqueous media. The most studied ones are the fluoride-based or alkaline-based solutions but Nb and Ta are also highly soluble in the presence of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) due to the formation of monomeric niobium oxalate or monomeric tantalum oxalate complexes such as $[\text{NbO}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$, $[\text{NbO}(\text{C}_2\text{O}_4)_3]^{3-}$, and $[\text{TaO}(\text{C}_2\text{O}_4)_3]^{3-}$ (Table 2). The oxalic media therefore represents the only fluoride-free and polymetallic species-free media in which Nb and Ta could be separated. Unfortunately, oxalic acid alone is not capable of stripping Nb or Ta from Aliquat® 336 (Figure 2). This is due to the fact that the extraction of hexaniobates by Aliquat® 336 is mainly an anion exchange mechanism (Table 2) whereas solutions of oxalic acid do not provide enough anions to exchange owing to the high pKa's of this acid. A screening experiment was consequently performed with combinations of oxalic acid, which plays the role of Nb and Ta complexant, and several strong acids which provide anions for the back-extraction. The screening was performed at constant oxalic acid concentration and with variable concentrations of nitric, perchloric, hydrochloric, sulfuric, or phosphoric acid (Figure 2). As expected, the back-extraction efficiency of Nb and Ta increases with increasing acid concentration (and its conjugated anionic base) due to the anion exchange mechanism. The back-extraction yield trend for both Nb and Ta is as follows: $\text{HClO}_4 > \text{HNO}_3 > \text{HCl} > \text{H}_2\text{SO}_4 > \text{H}_3\text{PO}_4$. Interestingly, we previously reported that the extraction yield of hexaniobates by Aliquat® 336 in basic media follows the trend $\text{NO}_3^- < \text{Cl}^- < \text{SO}_4^{2-}$ [72] and this trend is also observed for the back-extraction step *i.e.* Aliquat® 336 has a higher affinity toward NO_3^- relative to Cl^- and SO_4^{2-} .

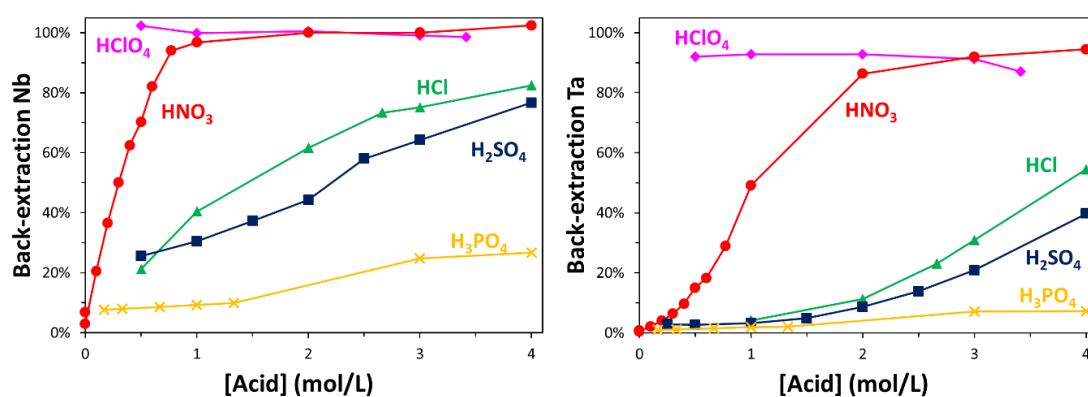


Figure 2 : Back-extraction yields for Nb and Ta in oxalic acid as a function of the total acid concentration. Aqueous phase: $[\text{H}_2\text{C}_2\text{O}_4] = 0.50 \text{ M}$ + mineral acid; HClO_4 (diamonds), HNO_3 (circles), HCl (triangles), H_2SO_4 (squares), or H_3PO_4 (crosses). Initial organic phase: 45 mM Aliquat® 336 + 105 mM isotridecanol diluted in Elixore 205, $[\text{Nb}] = 15.4 \text{ mM}$ (1,435 mg/L), $[\text{Ta}] = 0.17 \text{ mM}$ (31 mg/L). $[\text{Ti}] = 0.065 \text{ mM}$ (3.1 mg/L). $V_{\text{org}}/V_{\text{aq}} = 1/4$. $T = 20 \text{ }^\circ\text{C}$, $t = 15 \text{ min}$.

The back-extraction in the presence of ClO_4^- ions affords very high yields for a low concentration of acid but the $\text{H}_2\text{C}_2\text{O}_4/\text{HClO}_4$ system exhibits no selectivity at all as both metals are almost totally stripped from the organic phase. Beside $\text{H}_2\text{C}_2\text{O}_4/\text{HClO}_4$, the other four systems show a selective stripping of Nb relative to Ta throughout the entire acidity range investigated (Figure 2 and Figure 3). Phosphoric acid appears selective but moderately effective with only 27 % of Nb and 7 % of Ta stripped from the organic phase even while using 4 M H_3PO_4 . The back-extraction systems based on $\text{H}_2\text{C}_2\text{O}_4/\text{H}_2\text{SO}_4$ and $\text{H}_2\text{C}_2\text{O}_4/\text{HCl}$ offer relative high yields but the best solution in terms of stripping efficiency, Nb/Ta selectivity and acid consumption is the combination of $\text{H}_2\text{C}_2\text{O}_4$ and HNO_3 . A similar trend was also observed for the separation of Nb against Ti, although this element was only a minor and non-valuable component of the initial solution (Figure S 2).

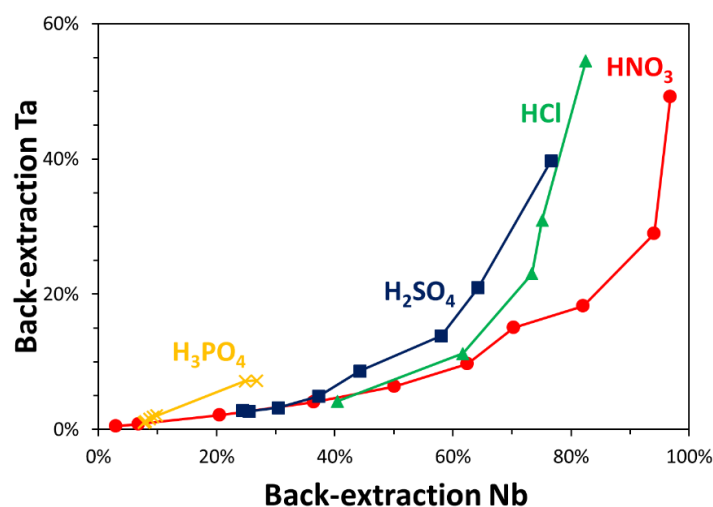


Figure 3. Comparison of the selectivity of different mixtures of oxalic acid and mineral acid for the back-extraction of Nb and Ta from an Aliquat® 336 organic phase. Aqueous phase: $[\text{H}_2\text{C}_2\text{O}_4] = 0.50$ M, $[\text{Mineral acid}] = 0$ to 4 M, H_3PO_4 (crosses), H_2SO_4 (squares), HCl (triangles), or HNO_3 (circles). See Figure 2 for other conditions.

The selectivity for Nb over Ta during the back extraction step was found to slightly increase with the oxalic acid concentration (Figure 4). The Nb yield is almost independent of the oxalic acid concentration whereas a higher oxalic acid concentration significantly reduces the back extraction of Ta. The optimal $\text{H}_2\text{C}_2\text{O}_4$ concentration was fixed at 0.50 M because higher concentrations created oversaturated solutions at room temperature, probably due to the presence of HNO_3 in the media.

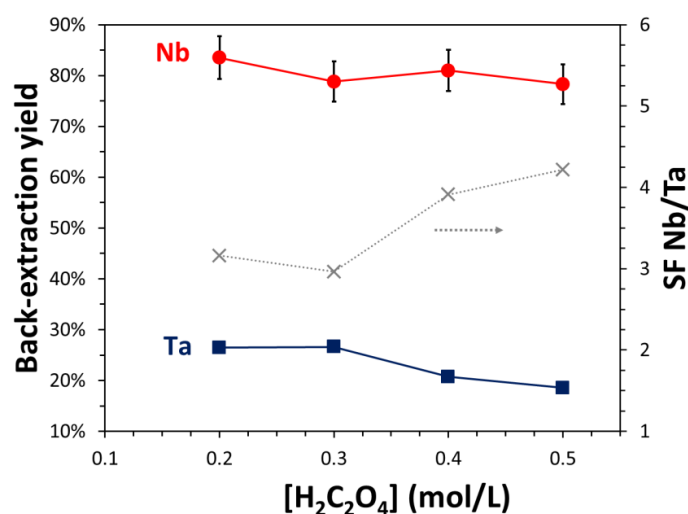


Figure 4. Back-extraction yields for Nb (circles) and Ta (squares), and separation factor Nb/Ta (crosses) as a function of the oxalic acid concentration. Aqueous phase: $\text{H}_2\text{C}_2\text{O}_4 + 0.50 \text{ M HNO}_3$. Initial organic phase: 45 mM Aliquat® 336 + 105 mM isotridecanol diluted in Elixore 205, $[\text{Nb}] = 14.9 \text{ mM (1,383 mg/L)}$, $[\text{Ta}] = 0.17 \text{ mM (31 mg/L)}$. $V_{\text{org}}/V_{\text{aq}} = 1/4$. $T = 20 \text{ }^\circ\text{C}$, $t = 15 \text{ min}$.

The stripping solution for the selective back-extraction of niobium was finally optimized by fixing the total concentration of nitrates and using mixtures of $\text{H}_2\text{C}_2\text{O}_4$, HNO_3 , and NH_4NO_3 . Indeed, reducing the acidity of the solution by replacing HNO_3 by NH_4NO_3 not only reduces the operating costs related to the reactant consumption but also decreases the cost of the downstream process if the Nb stripped solution needs to be neutralized. Figure 5 gives the back-extraction yields for Nb and Ta in $\text{H}_2\text{C}_2\text{O}_4/\text{HNO}_3/\text{NH}_4\text{NO}_3$ media as a function of the acidity. The Nb stripping efficiency is almost independent of the acidity of the solution with a slight increase from 72 to 77% after one contact when the proton concentration increases from 0 to 0.45 M. On the opposite, the stripping yield for Ta decreases from 26 to 19% as the acidity increases so that the selectivity Nb/Ta is improved at higher acidity. The highest improvement in terms of selectivity happens between 0 and 0.30 M HNO_3 whereas a higher HNO_3 concentration only marginally improves the selectivity of the process. Therefore, the best compromise between minimizing the acid consumption and maximizing the selectivity Nb/Ta is to use a stripping solution composed of 0.50 M $\text{H}_2\text{C}_2\text{O}_4$, 0.30 M HNO_3 , and 0.15 M NH_4NO_3 . Substitution of NH_4NO_3 by NaNO_3 also gives similar results both in terms of selectivity and efficiency (Figure 6 and Table S 1) although the presence of sodium may be an issue for final processing and purity of the niobium stripped solution.

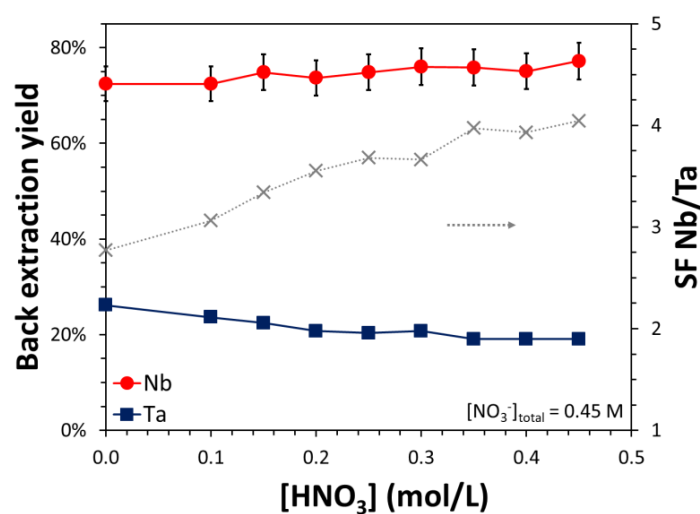


Figure 5. Back-extraction yield of Nb (circles) and Ta (squares), and separation factor Nb/Ta (crosses) at constant oxalic acid and nitrate concentration and as a function of the acidity. Aqueous phase: 0.5 M H₂C₂O₄ + HNO₃ + NH₄NO₃ with [NO₃⁻] = 0.45 M. Initial organic phase: 45 mM Aliquat® 336 + 105 mM isotridecanol diluted in Elixore 205, [Nb] = 18.4 mM (1714 mg/L), [Ta] = 0.22 mM (40 mg/L). V_{org}/V_{aq} = 1/6. T = 20 °C, t = 15 min.

Separation experiments at various volume ratios definitely confirmed the selectivity of Aliquat® 336 for Ta over Nb in oxalic media. Figure 6 shows that the selectivity of the extractant is maintained across a wide range of operating conditions which may ease the process control. Nb concentrations higher than 10 g/L were obtained in the Nb stripped solution and the separation factor Nb/Ta increases with the volume ratio (Table S 1). The surprising selectivity of this system, with Nb initially extracted from basic media and back-extracted in slightly acidic media, suggests that the hexametallate ions are stripped and that Ta is selectively re-extracted in the form of an oxalate species since the hexatantalate and hexaniobate ions are not stable below pH ~9 [8,20,64]. Direct re-extraction of Ta from the acidic Nb stripped solution shows that Aliquat® 336 is also selective towards Ta in oxalic/nitric media (Table S 2) and corroborates the possible re-extraction of Ta as an oxalate species.

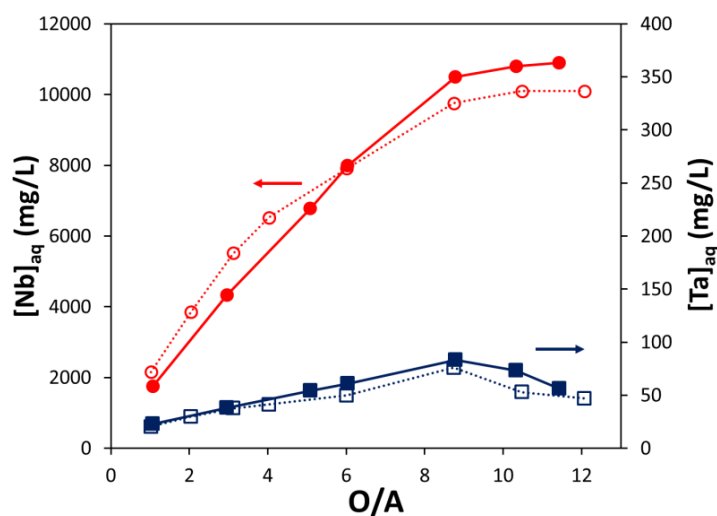


Figure 6. Concentration profile for Nb (circles) and Ta (squares) in the aqueous phase after back-extraction as a function of the phase volume ratio. Solid lines: 0.50 M $\text{H}_2\text{C}_2\text{O}_4$ + 0.30 M HNO_3 + 0.15 M NH_4NO_3 . Dotted lines: 0.50 M $\text{H}_2\text{C}_2\text{O}_4$ + 0.30 M HNO_3 + 0.15 M NaNO_3 . Initial organic phase: 45 mM Aliquat® 336 + 105 mM isotridecanol diluted in Elixore 205, $[\text{Nb}] = 19.6 \text{ mM}$ (1,820 mg/L), $[\text{Ta}] = 0.39 \text{ mM}$ (70 mg/L). $T = 20 \text{ }^\circ\text{C}$, $t = 15 \text{ min}$. See Table S 1 for corresponding separation factors.

Tantalum stripping. Since Ta exits the Nb back-extraction battery through the organic stream, a final stripping step is necessary in order to recover the purified Ta fraction. The speciation of Ta being partially unknown after the Nb back-extraction step, stripping tests were performed on an organic phase that underwent the following sequence: i) co-extraction of Nb and Ta in basic media, ii) selective back-extraction of Nb in oxalic-nitric media. The stripping isotherms for Ta in different acidic media are displayed in Figure 7.

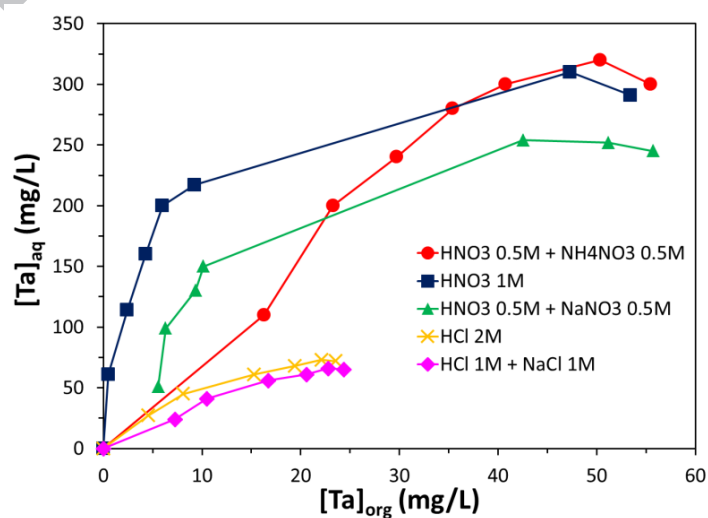


Figure 7. Stripping efficiency for Ta following, a co-extraction Nb-Ta by Aliquat® 336 and a selective back-extraction of Nb in $\text{H}_2\text{C}_2\text{O}_4/\text{HNO}_3/\text{NH}_4\text{NO}_3$ media. Ta stripping solution: 0.5 M HNO_3 + 0.5 M NH_4NO_3 (circles), 1M HNO_3 (squares), 0.5 M HNO_3 + 0.5 M NaNO_3 (triangles), 2 M HCl (crosses), or 1 M HCl + 1 M NaCl (diamonds). Initial organic phase: 45 mM Aliquat® 336 + 105 mM isotridecanol diluted in Elixore 205, $[\text{Nb}] = 1.0$ mM (90 mg/L), $[\text{Ta}] = 0.17$ mM (31 mg/L). $T = 20$ °C, $t = 15$ min. Results obtained by varying the phase volume ratio from 1 to 20.

Similar to the Nb back-extraction step, the stripping efficiency for Ta is higher in nitrate-based media than in chloride-based media. This is due to the ion exchange mechanism and the better affinity of Aliquat® 336 for nitrate ions compared to chlorides. The highest Ta stripping efficiencies were obtained in 1 M HNO_3 or a mixture of 0.5 M HNO_3 and 0.5 M NH_4NO_3 . Concentrations up to 320 mg/L of Ta at room temperature were reached in these nitric media and about 70 mg/L in chloride media which is much higher than the reported solubility of Ta(V) in HNO_3 or HCl [75,76]. This strongly suggests that Ta is complexed by oxalates at this stage and is stripped as an oxalate species. Titration of the Ta stripped solution by manganometry revealed the presence of up to 0.02 M of oxalates which is enough to chelate the totality of Ta (and Nb) under these experimental conditions. This confirms that the separation mechanism during the selective Nb back-extraction step is at least a two-step process with, first, the transfer of Nb and Ta hexametallates from the organic phase to the acidic aqueous phase, and then, the selective re-extraction of Ta into the organic phase, most likely as an oxalate species.

Continuous running test. In order to demonstrate the viability of the proposed strategy, the different steps described above (*i.e.* Nb-Ta extraction, selective back-extraction of Nb, stripping of Ta) were tested in continuous operation at pilot scale. The full process was operated for 160 hours at steady-state conditions and about 225 L of alkaline Nb-Ta solution were processed. The average composition of the industrial Nb-Ta feed solution is given in Table 4. Liquid-liquid extraction batteries were operated in counter-current mode and the flow-rate of the organic phase was fixed at $1.4 \text{ L}\cdot\text{h}^{-1}$. The solvent was recirculated for the entire duration of the test which corresponds to about 60 cycles. No loss of performance was

observed which confirmed the suitability of commercial Aliquat® 336 for this type of process. The process was operated at room temperature (20 ± 2 °C) and was comprised of two extraction stages, five Nb back-extraction stages, and two Ta stripping stages, each stage being a mixer-settler assembly (Figure 8).

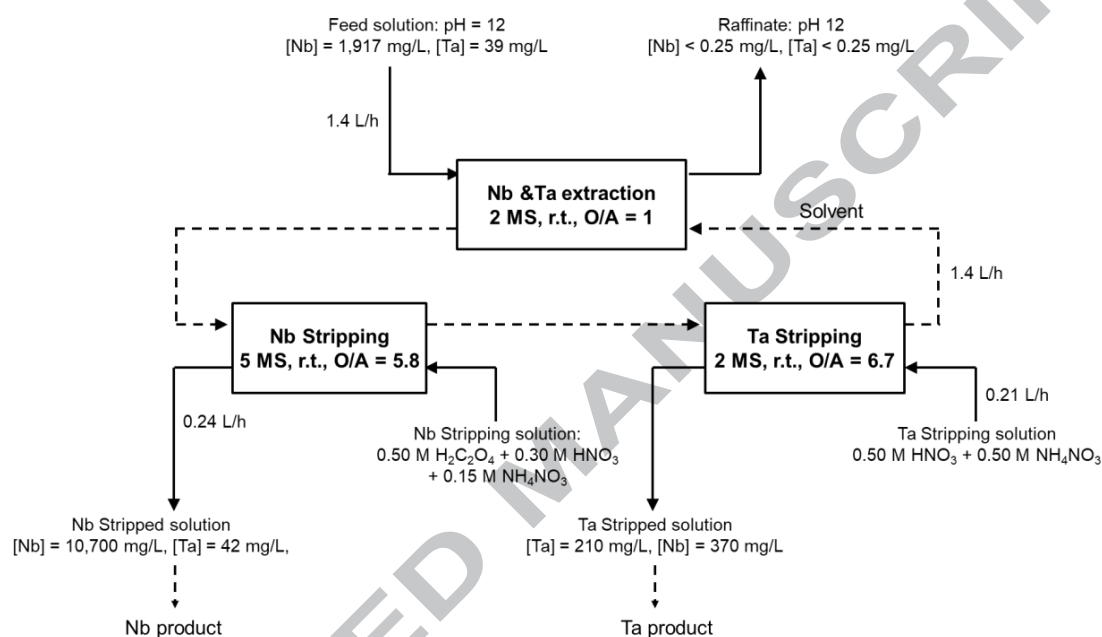


Figure 8. Typical flowsheet tested for the fluoride-free process and results obtained during the continuous running test. Organic phase: 45 mM Aliquat ® 336 (2.5 % v/v) + 105 mM isotridecanol (2.5 % v/v) diluted in Elixore 205 (95 % v/v). MS: mixer-settler, r.t. = room temperature (18-22°C).

The Nb-Ta co-extraction battery was operated with a flow rate ratio of 1 as extraction isotherm measurements showed that this setup was enough to quantitatively extract Nb. The extraction yield for Nb was higher than 99.9 % throughout the campaign whereas that of Ta was higher than 99.3 % (limit of detection reached).

Table 4. Composition of the feed solution, Nb and Ta stripped solutions, Nb product, and Ta product obtained during the pilot campaign. a: Limit of detection. b: Analysis given for solids dried at 110 °C.

	Nb	Ta	Ti	Fe	Na	Nb / Σ elements	SF Nb/Ta	SF Nb/Ti	SF Ta/Nb
Feed (mg/L)	1917	39	5.1	1.2	1160	61.4%	/	/	/
Raffinate (mg/L)	< 0.25 ^a	< 0.25 ^a	< 0.05 ^a	< 0.05 ^a	1160	/	/	/	/
Nb stripped solution (mg/L)	10700	42	2.6	3.1	/	99.6%	5.2	10.9	/
Ta stripped	370	210	25	0.1	/	/	/	/	/

solution (mg/L)										
Nb	product	56.3	0.23	0.015	<0.026 ^a	< 0.026 ^a	99.6%	5.0	10.0	/
	(wt%)^b									
Ta	product	20.3	20.8	1.48	< 0.026 ^a	< 0.026 ^a	/	/	/	50.4
	(wt%)^b									

The selective back-extraction of Nb was performed with 0.50 M H₂C₂O₄ and 0.45 M HNO₃ for the first part of the pilot campaign and a mixture of 0.50 M H₂C₂O₄, 0.30 M HNO₃ and 0.15 M NH₄NO₃ during the second part of the test. The performances of the two solutions were similar. As mentioned above, the use of a H₂C₂O₄/HNO₃/NH₄NO₃ mixture decreases the operating expenses of the process since the downstream neutralization of the Nb stripped solution requires less reactant. The flow rate ratio for the Nb back-extraction battery was maintained between 4.5 and 6.5. In accordance with the Nb back-extraction isotherm determined prior to the pilot test (Figure S 3), the stripping yield for Nb reached 98 % ± 5 throughout the campaign. During this step, 15-20 % of Ta was also back-extracted. Due to the presence of about 5 ppm of Ti and 1 ppm of Fe in the feed solution, these two minor impurities were also followed during the pilot test. The back-extraction yield of Ti was around 10 % throughout the campaign indicating that the process also exhibits a good selectivity Nb/Ti. In the case of Fe, this impurity was totally co-stripped with Nb but this impurity is removed during downstream treatment of the Nb stripped solution [47]. The purity of the final Nb product was higher than 99.5 wt% (Table 4) which is enough to use it as starting material in the HSLA steels manufacture or for the high-end applications described in the introduction. It should be pointed out that this continuous pilot test was the first attempt for this type of process and that the results reported here do not represent the best performances of this type of processes. For example, increasing the number of mixer-settlers and the flow rate ratio in the Nb back-extraction battery would certainly give a higher selectivity Nb-Ta. The addition of a single re-extraction step on the Nb stripped solution is also a possible way for increasing the overall selectivity Nb/Ta of the process (Table S 2).

The Nb stripped solution was quantitatively converted to niobium oxide by a neutralization-precipitation procedure which also affords recovering the oxalates and nitrates. This procedure is detailed in a follow-up paper [47]. The final stripping of the organic phase was performed with different solutions during the campaign. The flow rate ratio was limited to 7 for technical reasons (mainly equilibration time versus duration of the pilot campaign). Stripping with 2 M HCl or a mixture of 1 M HCl and 1 M of NaCl only gave stripping yields of about 80 % for Ta. In accordance with the batch extraction tests performed prior to the pilot campaign (Figure 7), stripping with 1 M HNO₃ or a mixture of 0.50 M HNO₃ and 0.50 M NH₄NO₃ yielded a quantitative recovery of Ta. Similar to the Nb stripped solution, the purified Ta stripped solution were converted to Ta oxide by neutralization-precipitation [47]. The overall Ta/Nb separation factor of the process reached 50 (Table 4). The final Ta product contained up to 20 wt% of Ta after drying at 110 °C which is significant given the low Ta concentration in the feed solution (< 40 mg/L). A higher Ta content is expected upon drying at higher temperatures since Nb and Ta oxides are known to remain hydrated up to 300 °C [77].

Conclusion

A new separation method for niobium and tantalum was developed. In contrast with the current industrial processes, the proposed liquid-liquid extraction process does not require any fluoride-based chemical. The process can be used to recover and separate Nb and Ta from alkaline feed solutions. The developed strategy is a three-step process: first, Nb and Ta are co-extracted from their alkaline solution using a long chain quaternary ammonium salt dissolved in an organic diluent; then, Nb is selectively back-extracted in a mixture of 0.50 M H₂C₂O₄, 0.30 M HNO₃ and 0.15 M NH₄NO₃ (or 0.50 M H₂C₂O₄ and 0.45 M HNO₃); and finally, Ta is back-extracted in 0.50 M HNO₃ and 0.50 M NH₄NO₃. The three steps of the process were optimized using batch experiments and then validated during a continuous

running test at pilot scale (160 h – 225 L of Nb-Ta alkaline solution) with the production of high-purity Nb oxide (>99.5 wt%) and a Ta oxide product (> 20 wt%) even starting from a diluted feed (1,917 mg.L⁻¹ Nb and 39 mg.L⁻¹ Ta). This study represents the first demonstration of a fluoride-free separation process for Nb and Ta and paves the way for a new type of liquid-liquid extraction processes for purifying Nb and Ta raw materials. As shown in Figure 9, the combination of this liquid-liquid extraction process and the previously reported hydrometallurgical processing of Nb and Ta from natural ores in alkaline media [19,44–46] could afford a complete fluoride-free route for the recovery and purification of Nb and Ta.

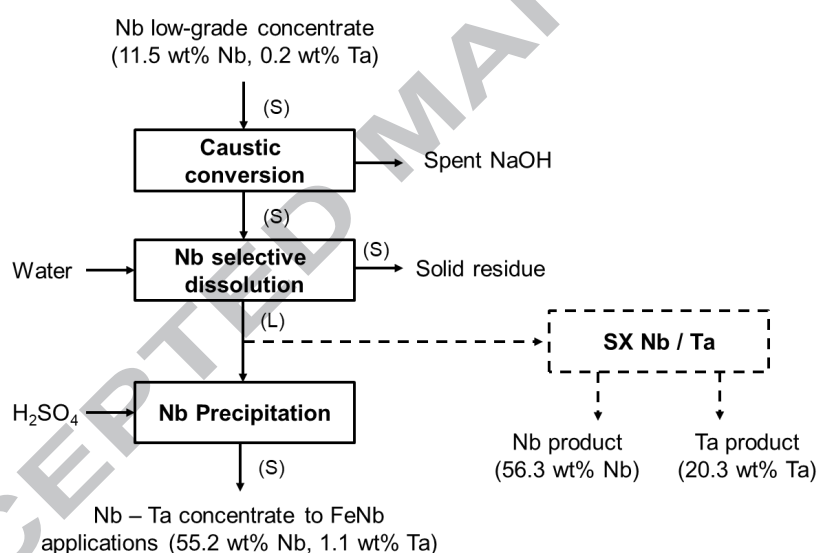


Figure 9 : Simplified flowsheet for a fluoride-free route allowing the recovery and purification of Nb and Ta from natural ores. Details of the caustic conversion and its application to a Gabonese Nb-Ta deposit have been published elsewhere [45].

Acknowledgements

Financial support for this work from the company ERAMET (France) is gratefully acknowledged. The authors would like to thank Valérie Weigel, Eric Tizon, Farid Arbouche, Thomas Héroult, and Antoine Fournier for their support and help with the experimental part of this study.

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Supporting information

A fluoride-free liquid-liquid extraction process for the recovery and separation of niobium and tantalum from alkaline leach solutions.

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Figure S 1 : Pictures of the Nb-Ta separation pilot campaign. (A) Alkaline feed solution containing Nb and Ta. (B) Mixer-settlers corresponding to the Nb-Ta co-extraction step. (C) Purified Nb oxide. (D) and (E) Views of the process.

Table S 1. Separation factors Nb/Ta and Nb/Ti obtained by back-extraction with 0.50 M H₂C₂O₄ + 0.30 M HNO₃ + 0.15 M NH₄NO₃ or 0.50 M H₂C₂O₄ + 0.30 M HNO₃ + 0.15 M NaNO₃. Initial solution: [Nb] = 1,820 mg/L, [Ta] = 70 mg/L, [Ti] = 6.9 mg/L. See Figure 6 for details.

H ₂ C ₂ O ₄ /HNO ₃ /NH ₄ NO ₃			H ₂ C ₂ O ₄ /HNO ₃ /NaNO ₃		
V _{org} / V _{aq}	SF Nb/Ta	SF Nb/Ti	V _{org} / V _{aq}	SF Nb/Ta	SF Nb/Ti
1.1	2.93	3.02	1.0	4.05	3.70
3.0	4.38	4.56	2.0	4.97	4.79
5.1	4.83	5.14	3.1	5.62	5.59
6.0	5.04	5.22	4.0	6.07	6.19
8.8	4.87	4.98	6.0	6.11	5.53
10.3	5.69	6.50	8.7	4.94	5.21
11.4	7.49	7.51	10.5	7.33	8.90
			12.1	8.27	6.72

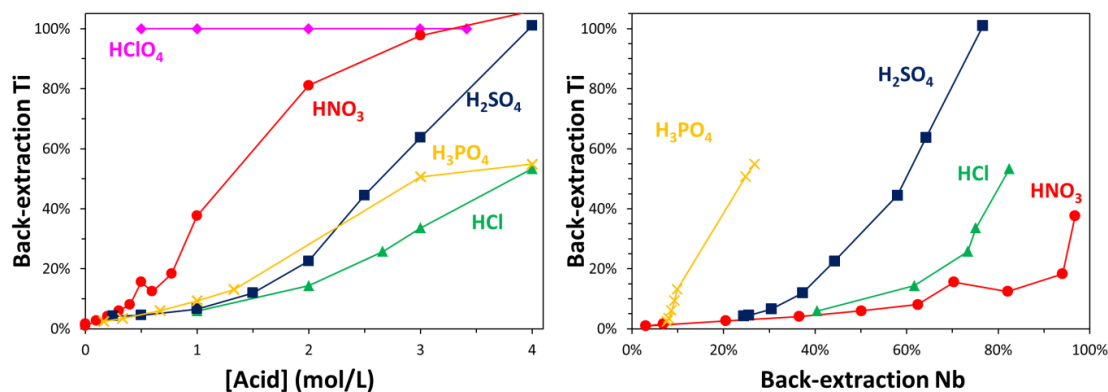


Figure S 2. Ti back-extraction corresponding to Figure 2 and Figure 3. Initial solution: [Nb] = 15.4 mM (1,435 mg/L), [Ta] = 0.17 mM (31 mg/L). [Ti] = 0.065 mM (3.1 mg/L).

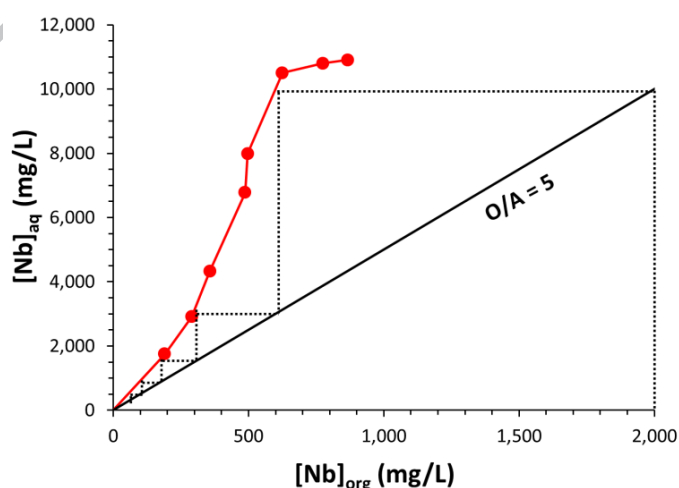


Figure S 3. Nb back-extraction isotherm corresponding to Figure 6. Aqueous phase: 0.50 M H₂C₂O₄ + 0.30 M HNO₃ + 0.15 M NH₄NO₃). The McCabe-Thiele construction is given for an organic feed containing 2 g/L of Nb and a volume ratio O/A of 5.

Table S 2. Re-extraction of Ta from the acidic Nb stripping solution raffinate. Media: 0.50 M $\text{H}_2\text{C}_2\text{O}_4$, 0.45 M HNO_3 . One contact using different phase volume ratios. Organic phase: 45 mM Aliquat 336 + 105 mM isotridecanol in Elixore 205. T = 20 °C.

	[Nb] mg/L	[Ta] mg/L	[Ti] mg/L	% Ext. Nb	% Ext. Ta	% Ext. Ti	Nb/Ta g/g	Nb/ (Nb+Ta+Ti) g/g
Initial solution	10 700	50	3.6	/	/	/	213	99.50 %
$V_{\text{org}}/V_{\text{aq}}$								
1/5	10 600	42	3.0	0.9%	17%	18%	252	99.58 %
1/4	10 500	40	2.9	1.9 %	27 %	20 %	263	99.59 %
1/2	9 970	35	2.5	6.8 %	31 %	31 %	285	99.63 %
1	9 570	28	2.0	10.6 %	44 %	45 %	342	99.69 %
2	8 980	19	1.5	16.1 %	62 %	59 %	473	99.77 %
3	7 950	13	1.0	25.7 %	74 %	64 %	612	99.82 %

Highlights

- A new process for separating Nb and Ta in fluoride-free media is proposed
- High-purity Nb oxide (99.5 %) can be produced
- Nb and Ta can be recovered and separated starting from an alkaline feed solution
- The process works at room temperature and under mild chemical conditions

ACCEPTED MANUSCRIPT