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Niobium and tantalum processing in oxalic-nitric media: $Nb_2O_5 \cdot nH_2O$ and $Ta_2O_5 \cdot nH_2O$ precipitation with oxalates and nitrates recycling

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ABSTRACT

Oxalate-based aqueous media represent one of the rare options for solubilizing macroscopic amount of niobium (Nb) and tantalum (Ta) without using toxic fluoride-based mixtures. Recent progress in the hydrometallurgy of Nb and Ta also highlighted the potential of oxalate-nitrate media for the separation of Nb and Ta. Nonetheless, the resulting purified aqueous solutions, containing Nb or Ta in HNO_3 - $H_2C_2O_4$ mixtures, need to be further processed in order to yield Nb and Ta solid products that can be commercialized. Furthermore, oxalic acid is relatively expensive in the frame of the hydrometallurgy of Nb and its recycling is necessary. In this study, the precipitation of Nb and Ta, as well as their usual minor impurities (Ti and Fe), from oxalic-nitric acid solutions has been investigated for the first time. Neutralization of Nb- HNO_3 - $H_2C_2O_4$ mixtures to pH 7-8 by concentrated NaOH or NH_4OH was found to be effective at decomposing the oxalate complexes ($[NbO(C_2O_4)_3]^{3-}$ and $[NbO(C_2O_4)_2(H_2O)]^-$) and precipitating Nb in the form of $Nb_2O_5 \cdot nH_2O$ while leaving the

oxalate ions in solution. Taking advantage of the solubility difference between nitrate and oxalate salts, the subsequent concentration of the filtrates yields to the recovery of the oxalates as $\text{Na}_2\text{C}_2\text{O}_4$ or $(\text{NH}_4)_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$ and a concentrated solution of sodium or ammonium nitrate. The developed method exhibits high precipitation yields ($>99.9\%$) for Nb and Ta and high recovery yields ($>99\%$) for the nitrates and oxalates. The process was optimized at the laboratory scale (~ 50 mL) and then validated on industrial Nb and Ta solutions (~ 225 L) with successful production of purified $\text{Nb}_2\text{O}_5\cdot n\text{H}_2\text{O}$ and $\text{Ta}_2\text{O}_5\cdot n\text{H}_2\text{O}$, recovery of the oxalates in the form of $\text{Na}_2\text{C}_2\text{O}_4$ or $(\text{NH}_4)_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$ and a concentration solution of nitrates. Taking together, the proposed precipitation method and the fluoride-free liquid-liquid Nb-Ta separation recently reported pave the way for more suitable hydrometallurgical processes for Nb and Ta.

1. Introduction

Niobium (Nb) and tantalum (Ta) materials play a central role in the manufacturing of various strategic goods such as electronic components, optical lenses, supraconducting magnets, military projectiles, and high-strength low-steel alloys [1]. Despite their economic and geopolitical importance, Nb and Ta are rarely studied and their chemistry is still poorly developed in comparison to the other elements of the periodic table such as the platinum group metals or the rare earth elements. Nb and Ta are both group V elements, are hard Lewis acids, and are essentially insoluble in classical aqueous acidic media such as HCl, H_2SO_4 , HNO_3 , HClO_4 , and H_3PO_4 [2–5]. For example, the solubility of $\text{Nb}_2\text{O}_5\cdot n\text{H}_2\text{O}$ and $\text{Ta}_2\text{O}_5\cdot n\text{H}_2\text{O}$ in 1–6 M HNO_3 is lower than $1.5\cdot 10^{-5}$ M and $1\cdot 10^{-4}$ M, respectively [2]. This renders the hydrometallurgical processing of Nb and Ta raw materials really challenging. Due to their high charge density (+V oxidation state and an ionic radius of 64 pm [6]) and their subsequent tendency to hydrolyze, weighable amounts of Nb and Ta can only be

solubilized in aqueous media containing strong complexing agents such as the fluoride ions [7]. As of today, all the industrial processes implemented for purifying Nb and Ta involve the use of hydrofluoric acid or other fluoride-based aqueous media [8]. The fluoride-based chemicals generate safety and environmental concerns since they are inherently highly toxic, both to humans and the environment. The fluoride routes for processing Nb and Ta raw materials started with the so-called “Marignac process”, proposed by Marignac in 1866 [9], and the fluoride-based processes are still in used today. Since the 1970’s, several Nb-oxalate and Ta-oxalate compounds have been reported in the literature (Table 1) but the development of Nb-Ta processes based on oxalate media never followed. Nb(V) and Ta(V) form a large variety hexa or heptacoordinated complexes with $C_2O_4^{2-}$ ions, with the coordination sphere often completed by an oxo or hydroxide ions, or water molecules. The most common motifs for Nb are $[NbO(C_2O_4)_3]^{3-}$, $[NbO(C_2O_4)_2(H_2O)_2]^-$, and $[NbO(OH)(C_2O_4)_2]^{2-}$ whereas Ta forms $[TaO(C_2O_4)_3]^{3-}$, $[TaOH(C_2O_4)_3]^{2-}$, and $[Ta_4O_8(C_2O_4)_3]^{2-}$ (Table 1).

Table 1. Oxalate compounds of Nb and Ta reported in the literature.

Compound	Synthesis	Reference
$[(C_6H_5)_4P]_3[NbO(C_2O_4)_3]$ $[(C_6H_5)_4As]_3[NbO(C_2O_4)_3]$	$H_2C_2O_4/Nb = 2.3$ + $(C_6H_5)_4PCl$ or $(C_6H_5)_4AsCl$	[10]
$Na_3[NbO(C_2O_4)_3] \cdot 4H_2O$	$2 < pH < 6$; $H_2C_2O_4/Nb > 3$	[11]
$(NH_4)_3[NbO(C_2O_4)_3] \cdot H_2O$	$Nb_2O_5 \cdot nH_2O$ dissolved in $H_2C_2O_4/(NH_4)_2C_2O_4$	[12]
$Rb_3[NbO(C_2O_4)_3] \cdot 2H_2O$	$Rb[NbO(C_2O_4)_2(H_2O)_2] \cdot 2H_2O$ + 1.5 equivalents of $H_2C_2O_4$. $pH = 4$	[13]
$(NH_4)_3[NbO(C_2O_4)_3] \cdot H_2O$	Same as reference [12]	[14]
$\{(Ba)_2(H_2O)_5[NbO(C_2O_4)_3]HC_2O_4\} \cdot H_2O$	$(NH_4)_3[NbO(C_2O_4)_3] \cdot H_2O$ + 2 equivalents of $Ba(NO_3)_2$	[15]
$Na_2[Nb_2O_3(OH)_3(C_2O_4)] \cdot 3H_2O$	$pH \sim 4$; precipitation with ethanol	[11]
$H_2[NbO(OH)(C_2O_4)_2H_2O] \cdot 4H_2O$	Synthesis not described	[16]
$H_2[NbO(OH)(C_2O_4)_2] \cdot nH_2O$ (n = 4 et 5) $KH[NbO(OH)(C_2O_4)_2] \cdot 4H_2O$ $RbH[NbO(OH)(C_2O_4)_2] \cdot 3H_2O$ $CsH[NbO(OH)(C_2O_4)_2] \cdot 3H_2O$ $MgH_2[NbO(OH)(C_2O_4)_2] \cdot 10H_2O$	Synthesis not described	[17]
$Cs[NbO(C_2O_4)_2(H_2O)_2] \cdot H_2O$	Synthesis not described	[18]
$NH_4[NbO(C_2O_4)_2(H_2O)_2] \cdot nH_2O$ (n = 2 et 3) $K[NbO(C_2O_4)_2(H_2O)_2] \cdot 3H_2O$ $A[NbO(C_2O_4)_2(H_2O)_2] \cdot 2H_2O$ (A = Rb, Cs) $Mg[NbO(C_2O_4)_2(H_2O)_2] \cdot 8H_2O$	$pH < 1$, recrystallized $[Nb] = 10^{-2} M$, $[H_2C_2O_4] = 5 \times 10^{-2} M$, $[NH_4] = 6 \times 10^{-3} M$ or $[A] = 2 \times 10^{-2} M$ or $[Mg] = 10^{-1} M$	[19]

$\text{NH}_4[\text{NbO}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$	Same as reference [20]	[21]
$\text{Na}[\text{NbO}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$	$0 < \text{pH} < 2$; precipitation with ethanol	[11]
$(\text{NH}_4)[\text{NbO}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$	$\text{H}_2\text{C}_2\text{O}_4/\text{Nb} \sim 4$; $\text{NH}_4/\text{Nb} \sim 0.3$	[22]
$\text{Na}_3[\text{TaO}(\text{C}_2\text{O}_4)_3] \cdot 4\text{H}_2\text{O}$	$2 < \text{pH} < 6$; $\text{H}_2\text{C}_2\text{O}_4/\text{Ta} > 3$	[11]
$\{(\text{Ba})_2(\text{H}_2\text{O})_5[\text{TaO}(\text{C}_2\text{O}_4)_3\text{HC}_2\text{O}_4]\} \cdot \text{H}_2\text{O}$	$\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ dissolved in $\text{H}_2\text{C}_2\text{O}_4$ and addition of $\text{Ba}(\text{NO}_3)_2$	[23]
$\text{Na}[\text{TaO}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$	$0 < \text{pH} < 2$; precipitation with ethanol	[11]
$[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{TaOH}(\text{C}_2\text{O}_4)_3]$ $[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{TaOH}(\text{C}_2\text{O}_4)_3]$	$\text{H}_2\text{C}_2\text{O}_4/\text{Ta} = 9 \text{ mol/mol} +$ $(\text{C}_6\text{H}_5)_4\text{P}\text{Cl}$ or $(\text{C}_6\text{H}_5)_4\text{As}\text{Cl}$	[10]
$\text{A}_2[\text{Ta}_4\text{O}_8(\text{C}_2\text{O}_4)_3] \cdot 2\text{H}_2\text{O}$ (A = Na, K, Rb, Cs) $\text{Ba}[\text{Ta}_4\text{O}_8(\text{C}_2\text{O}_4)_3] \cdot 2\text{H}_2\text{O}$	$[\text{Ta}] = 10^{-3} \text{ M}$, $[\text{H}_2\text{C}_2\text{O}_4] = 10^{-2} \text{ M} + \text{A}\text{Cl}$ ou BaCl_2 . $\text{pH} \sim 0.3$. $\text{T} < \text{Room temperature}$	[17]

Jehng & Wachs reported a solubility of about 30 wt% for “Nb oxalate” (stoichiometry not identified in the original paper [24]) in 1 M $\text{H}_2\text{C}_2\text{O}_4$ at room temperature. The combined high solubility of Nb in the presence of oxalate and very low toxicity of oxalic acid make oxalate-based media the perfect alternative to the fluoride-based media for the hydrometallurgical processing of Nb. Although no solubility data for Ta in oxalate media is available, a behavior similar to Nb is expected for the Ta oxalate species.

Building on these considerations, we recently developed a fluoride-free liquid-liquid extraction process for the separation of Nb and Ta [ref sepa NbTa]. The process is based on the selective back-extraction of Nb against Ta in an oxalate-nitrate media following co-extraction of the two metals into a solvent containing a long chain quaternary ammonium extractant (Figure 1). The process produces a purified stripped solution of Nb in an acidic oxalate-nitrate mixture (0.50 M $\text{H}_2\text{C}_2\text{O}_4$, 0.30 M HNO_3 , and 0.15 M NH_4NO_3), and a purified stripped solution of Ta in oxalate-nitrate media (Ta oxalates in 0.50 M HNO_3 , and 0.50 M NH_4NO_3). These purified solutions need to be converted into solid Nb oxide and Ta oxide before commercialization.

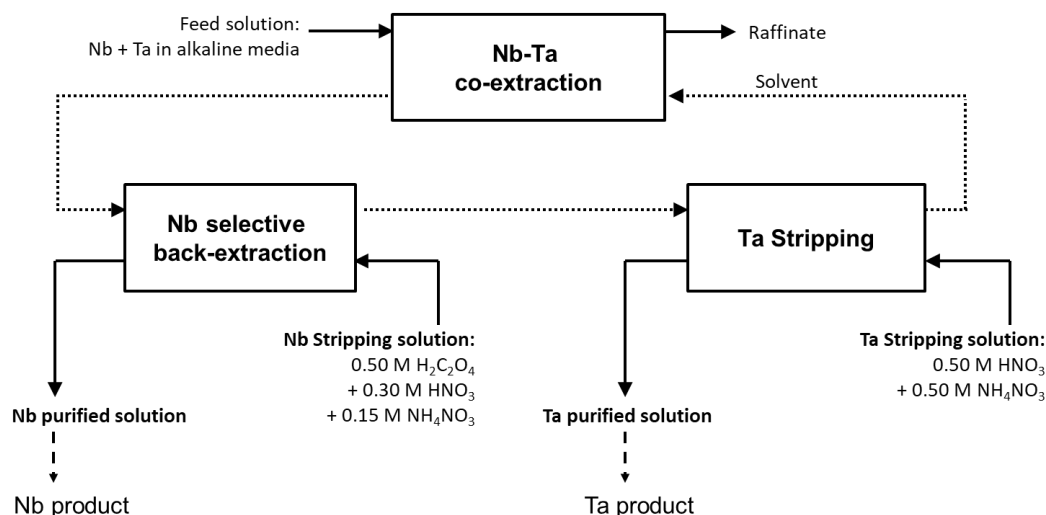


Figure 1. General flowsheet of the Nb-Ta separation process leading to the purified Nb and Ta solutions in oxalic-nitric media.

Herein, we report the first precipitation method for the recovery of Nb and Ta, in the form of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, from oxalate-nitrate solutions. In order to limit the environmental footprint of the process and to improve its economy, the recovery and separation of the oxalates and nitrates have also been developed.

2. Experimental

2.1. Materials and methods

All synthetic solutions were prepared with deionized water ($R > 18.2$ Mohm). TaCl_5 (Sigma Aldrich, 99.8% purity), Nb(V) oxalate hydrate ($\text{Nb}(\text{HC}_2\text{O}_4)_5 \cdot 2\text{H}_2\text{O}$, Alfa Aesar), TiOSO_4 (Sigma Aldrich, 99.99% purity), $\text{Fe}_2(\text{SO}_4)_3$ (VWR), standard NaOH solutions (Prolabo Normadose), 5 M NH_4OH (Sigma Aldrich), Na_2CO_3 (Acros, ACS grade), HNO_3 (6M, VWR), NH_4NO_3 (VWR, ACS grade), NaNO_3 (VWR, ACS grade), $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (VWR, 99.5% purity), 0.2 M KMnO_4 solutions (VWR, AVS Titrimorm). The industrial solutions containing Nb and Ta were provided by the mining group ERAMET (ERAMET IDEAS, Trappes, France). The Nb-Ta solutions come from the development of the so-called Maboumine process which aims at recovering Nb, Ta, the rare earth elements, and uranium

from the natural deposit of Mabounié located in Gabon. The upstream parts of the process have been described previously [25–30][+sepa Nb-Ta]. pH measurements were performed with a 827 pH-lab (Metrohm) pH-meter and a low alkaline error combined electrode (Unitrode, Metrohm). The concentrations of Fe, Ti, Ta, and Nb were determined by ICP-OES using an ICP 720-ES spectrometer (Varian). Quantitative ICP analyses were performed at 238.204 (Fe) nm, 334.188 (Ti) nm, 268.517 (Ta) nm 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. The concentrations of oxalates were determined by a standard titration procedure using KMnO_4 .

2.2. Precipitation procedure

Synthetic Nb-containing solutions were prepared by dissolving commercial Nb(V) oxalate (Mislabelled as $\text{Nb}(\text{HC}_2\text{O}_4)_5 \cdot 2\text{H}_2\text{O}$ by the providers) in aqueous solutions of 0.5 M nitric acid. Ta-containing solutions were prepared by dissolution of TaCl_5 in a hydrochloric acid solution. In both cases, synthetic solutions containing various amounts of impurities were prepared by adding TiOSO_4 and $\text{Fe}_2(\text{SO}_4)_3$. Typically, 50 mL assays of synthetic solution were sampled and precipitation of Nb or Ta was achieved by progressive addition of a base at room-temperature (NaOH , KOH , $\text{Ca}(\text{OH})_2$, Na_2CO_3 and NH_4OH were tested). The base reactant was added as a 4 M hydroxide or 2 M bicarbonate aqueous solution. pH was monitored throughout the test and the latter was stopped when the desired final pH value was reached. The obtained slurry was filtered using 0.45 μm Millipore filters. After filtration, the solid was washed with deionized water and dried before ICP-OES analyses. Nb, Ta, Ti and Fe concentrations in the filtrates were measured by ICP-OES and the oxalate concentration was determined by standard colorimetric titration with potassium permanganate at 50°C. Prior to titration, 2.5 mL of concentrated sulfuric acid were added to the solution in order to ensure quantitative oxidation of the oxalates by the permanganate ions.

2.3. Evaporation procedure

After neutralization by NaOH or NH₄OH, precipitation, and recovery of Nb₂O₅·nH₂O or Ta₂O₅·nH₂O, the filtrates containing sodium or ammonium ions and oxalates were evaporated in order to precipitate selectively Na₂C₂O₄ or (NH₄)₂C₂O₄ crystals. The evaporation set up included a round bottom flask with a heating-mantle, a distillation column and a condenser. The condensate was collected in a measuring cylinder to allow an instantaneous estimation of the evaporated volume. After evaporation, the mass of condensate was measured and the content of the balloon was filtered on a 0.45 μm Millipore filter. The crystals obtained were dried prior to analysis. ICP-OES and X-Ray Diffraction allowed confirming the nature of the crystals obtained and determining their purity.

2.4. Validation on industrial solutions.

A continuous running test was performed at Eramet's research center (Trappes, France). The pilot campaign was performed for 160 hours at steady-state conditions. The tested process is given in Figure 1. About 220 L (11 drums of ~20 L) of alkaline solution (pH ≈ 12) containing Nb and Ta were processed during this campaign. The process was operated at room temperature (20 ± 2°C). The average composition of the feed solution was as follows: 1917 ± 58 mg/L of Nb, 39 ± 1 mg/L of Ta, 5.1 ± 1.0 mg/L of Ti, 1.2 ± 0.5 mg/L, and 1160 ± 71 mg/L Na. The liquid-liquid extraction part of the process has been detailed previously [ref Sepa paper]. The purified Nb stripping solution and the purified Ta stripping solution were collected every 8 hours and further processed. Each stripped solution was neutralized in order to achieve Nb₂O₅·nH₂O or Ta₂O₅·nH₂O precipitation. Both NaOH and NH₄OH neutralization methods were tested during the pilot campaign. Each stream was analyzed by ICP-OES (Nb, Ta, Ti, Fe) and flame absorption spectroscopy (Na) at least once per work shift.

3. Results and discussion

3.1. Precipitation of Nb, Ta, Ti, and Fe from oxalate solutions

Nb and Ta are known to be almost insoluble in the pH range ~2 to ~8 if no strong chelators are present in the system [2,4,31] but fairly soluble in the presence of oxalate. Jehng & Wachs studied the speciation of Nb in acidic oxalate solutions (pH < 3) by Raman spectroscopy at various Nb and oxalate concentrations and proposed the presence of two complexes that are in equilibrium: $[\text{NbO}(\text{C}_2\text{O}_4)_3]^{3-}$ and $[\text{NbO}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]^-$ [24]. These aqueous species are in accordance with the solid state literature on Nb and Ta oxalates (Table 1). Above pH 3, Jehng & Wachs observed the hydrolysis of the oxalate complexes into $[\text{NbO}(\text{C}_2\text{O}_4)_2(\text{OH})_2]^{3-}$, $[\text{NbOC}_2\text{O}_4(\text{OH}_2)\text{H}_2\text{O}]^-$, $[\text{Nb}_2\text{O}_4(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$ followed by a decomposition into hydrous niobium oxide, $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$. Hydrous niobium oxide, sometimes called “niobic acid”, exhibits a very low solubility at near-neutral pH (less than 10^{-5} M of Nb at 25°C [2,3]) whereas simple oxalate salts, such as sodium or ammonium oxalate, are highly soluble in water (> 0.25 M at 25°C [32]). Therefore we investigated the potential one-pot precipitation of Nb and Nb/oxalate separation by neutralization of acidic Nb oxalate solutions. Figure 2 gives the fraction of Nb and oxalates left in solution as a function of pH following neutralization by NaOH. In line with Jehng & Wachs’ observations, the decomposition of the Nb oxalate species and formation of a white and amorphous Nb hydrous oxide were observed at pH higher than 4, with a quantitative precipitation of Nb at pH 7 or higher ($> 99.9\%$). On the opposite, the total concentration of oxalates in solution remains nearly constant throughout the pH range tested except between pH 5 and 7 where a small decrease is observed (~10 % lost). The results clearly indicate that Nb can be recovered as a solid material and separated from its chelating oxalates by a simple neutralization procedure.

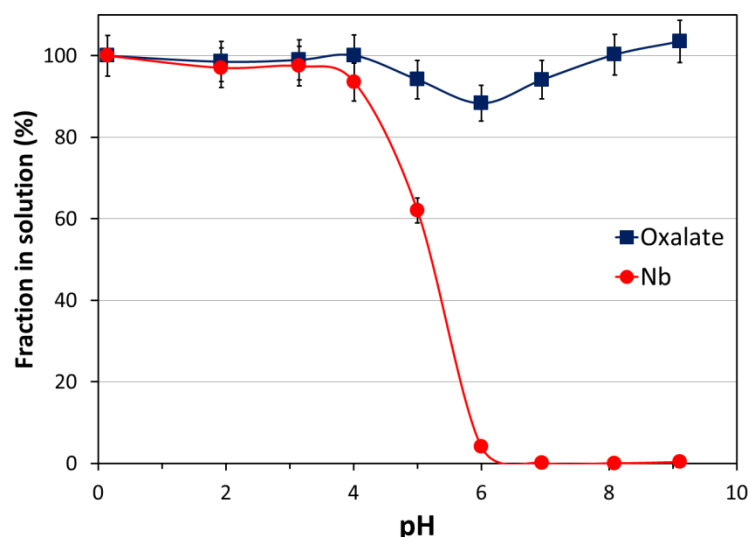


Figure 2. Fraction of Nb (circles) and oxalates (squares) remaining in solution as a function of pH following addition of 4 M NaOH into an acidic Nb oxalate solution. Initial solution: [Nb] = 13.2 g/L (0.142 M), $[C_2O_4]_{total} = 0.50$ M, $[HNO_3] = 0.50$ M. T = 20 °C. Yields are corrected for the dilution induced by NaOH additions.

Similar experiments were performed with other bases that are relevant to the hydrometallurgical industry such as $Ca(OH)_2$, Na_2CO_3 , and NH_4OH . The precipitation behavior of the Nb-oxalate system when using KOH was also studied even though this reactant is more expensive than the others mentioned above. Figure 3 shows the percentage of Nb and oxalate ions remaining in solution as a function of pH following neutralization of an acidic Nb oxalate solution by five different bases. As expected, NaOH, KOH, and NH_4OH give similar results and afford total precipitation of Nb above pH 7 while keeping the oxalates in solution owing to the relatively high solubility of the sodium oxalate, potassium oxalate, and ammonium oxalate salts [32]. This indicates that these three basic reagents can be used for the simultaneous precipitation of Nb and Nb-oxalate separation. In the case of $Ca(OH)_2$, precipitation of Nb is observed at lower pH relative to NaOH, KOH, and NH_4OH and it is concomitant with precipitation of the oxalates. The early precipitation of Nb is probably due to the formation of an insoluble calcium-niobium oxalate precipitate similar to the barium-niobium oxalate and magnesium-niobium oxalate compounds reported by Jurić et al. [15] and Brničević and Djordjević [17], respectively (Table 1). The precipitation of the

oxalates is also due to the low solubility of calcium oxalate salts [33] as $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}_{(s)}$ and $\text{CaC}_2\text{O}_4 \cdot 2.25\text{H}_2\text{O}_{(s)}$ which detected by XRD in the amorphous Nb precipitate (data not shown). Despite its low cost, the use of $\text{Ca}(\text{OH})_2$ for the separation of Nb from the oxalates is therefore impractical. More surprisingly, Na_2CO_3 also does not yield a practical separation between Nb and the oxalates ions as 68 % of Nb remain in solution at pH 7 and 35 % at pH 8. Based on the behavior of the Nb-oxalate system during the neutralization by NaOH, KOH, or NH_4OH , the Nb-oxalate complexes are not stable above pH 4. Hence, the precipitation profiles in the case of the neutralization by Na_2CO_3 clearly indicate the formation of Nb carbonate, or Nb hydrogen carbonate, or eventually Nb carbonate-oxalate soluble species in the pH range 4-8. To the best of our knowledge, the speciation of Nb (and Ta) in carbonate media has never been investigated. Further experiments showed that Nb exhibits long-term stability in carbonate media at pH 7 and that up to 2.5 g/L of Nb (0.027 M) can be solubilized at room temperature (Figure S 1). Although not practical for the purpose of the present study, the formation of carbonate water-soluble complexes could be another way of processing Nb and Ta without using fluoride-based chemicals.

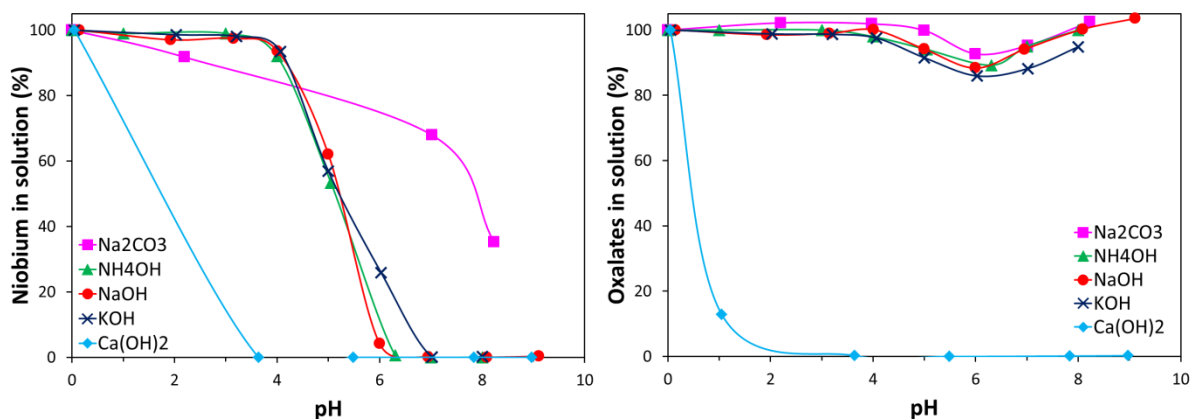


Figure 3. Fraction of niobium (left) and oxalates (right) remaining in solution as a function of pH following neutralization of an acidic Nb oxalate solution by 2 M Na_2CO_3 (squares), 4 M NH_4OH (triangles), 4 M NaOH (circles), 4 M KOH (crosses), and 2 M $\text{Ca}(\text{OH})_2$ (diamonds). Initial solution: $[\text{Nb}] = 14.0 \text{ g/L}$ (0.151 M), $[\text{C}_2\text{O}_4]_{\text{total}} = 0.50 \text{ M}$, $[\text{HNO}_3] = 0.54 \text{ M}$. $T = 20 \text{ }^\circ\text{C}$.

As detailed in recent studies [25,28,29,34][sepa Nb/Ta paper], the most common impurities found in Nb industrial streams are Ta, Ti, and Fe. Consequently, the precipitation behavior of

these three elements in oxalate media was also probed (Figure 4). The precipitation profiles for Ta and Ti are very similar to that of Nb except that they precipitate about 1 pH unit earlier. No practical practical separation Nb/Ta or Nb/Ti is expected from this precipitation method but it should be noted that the behavior of Ta is closer to that of Ti rather than Nb. The similarity Ta-Ti has also been observed in liquid-liquid extraction processes [ref Sepa]. In the case of Fe, its oxalate complexes seem more resistant toward hydrolysis and Fe(III) precipitates at higher pH compared to Nb(V), with about 50 % and 35 % of Fe still in solution at pH 6 and 7 respectively, so that Fe could be partially purged during the Nb precipitation step.

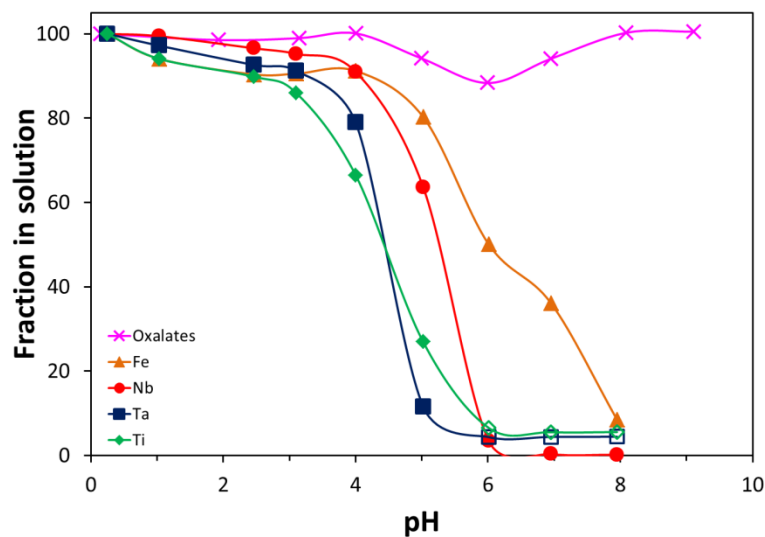
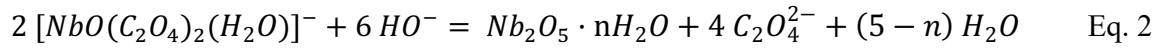
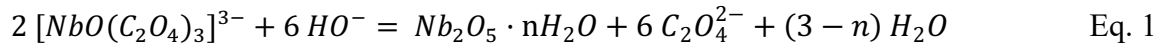


Figure 4. Fraction of oxalates (crosses), Nb (circles), Ta (squares), Fe (triangles), and Ti (diamonds) remaining in solution as a function of pH following neutralization of an acidic oxalate solution by 4 M NaOH. Initial solution: [Nb] = 12,7 g/L (0.137 M), [Ta] = 15 mg/L ($8.3 \cdot 10^{-5}$ M), [Fe] = 20 mg/L ($3.6 \cdot 10^{-4}$ M), [Ti] = 12 mg/L ($2.5 \cdot 10^{-4}$ M), $[C_2O_4]_{total} = 0.47$ M, $[HNO_3] = 0.45$ M. T = 20 °C. Open symbols indicate that the analytical limit of quantification was reached.

3.2. Base consumption and optimum concentration

In regards to the process development, the reactant consumption is often a critical parameter. Taking into account the two soluble Nb oxalate species proposed by Jehng & Wachs [24] and suggested by the solid-state literature (Table 1) and considering the pKa values of oxalic acid

(1.40 and 4.26 at 25 °C, I = 0 [35]), the following reactions are expected for a precipitation-neutralization process at pH 7:



For both Nb oxalate species, the reaction leading to $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ consumes 3 moles of hydroxide per mole of Nb. Since the literature data available on the speciation of Nb (and Ta) in oxalate media are relatively scarce, the precipitation reactions proposed above were checked by titrating synthetic solutions of commercially available Nb oxalate (often mislabeled $\text{Nb}(\text{HC}_2\text{O}_4)_5 \cdot n\text{H}_2\text{O}$ by the providers...) with NH_4OH . As shown in Figure 5, the quantity of base needed to precipitate an Nb oxalate solution is proportional to the initial Nb concentration. Experimentally, the precipitation of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ happens between pH ~3 and ~7. This corresponds to the two pH plateaus observed on the titration curves (Figure 5). The quantity of reactant required to reach the first plateau is about 1.5 mol of base per mol of Nb whereas the second plateau is reached after about 4.6 mol/mol. The difference corresponds to 3 mol of base per mol of Nb which is in accordance with the precipitation reactions proposed above (Eq 1. and Eq. 2). The initial 1.5 mol of base are thought to be due to the counter ions (probably H^+ or NH_4^+) of $[\text{NbO}(\text{C}_2\text{O}_4)_3]^{3-}$ and $[\text{NbO}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]^-$ as commercial Nb oxalate salts emit an ammonia smell. As expected, the addition of HNO_3 or $\text{H}_2\text{C}_2\text{O}_4$ in the initial Nb oxalate solution only shift the total base consumption by the amount require to neutralize HNO_3 or $\text{H}_2\text{C}_2\text{O}_4$ until pH 7 (Figure S 2). Consequently, the consumption of base for neutralizing an acidic solution of Nb in oxalic-nitric media is given by Eq. 3.

$$n_{\text{base}} = 3 \times n_{\text{Nb}} + 2 \times n_{\text{H}_2\text{C}_2\text{O}_4 \text{ free}} + n_{\text{H}^+} \quad \text{Eq. 3}$$

The validity of Eq. 3 was also confirmed on industrial solutions of Nb in oxalic-nitric media (Figure S 3).

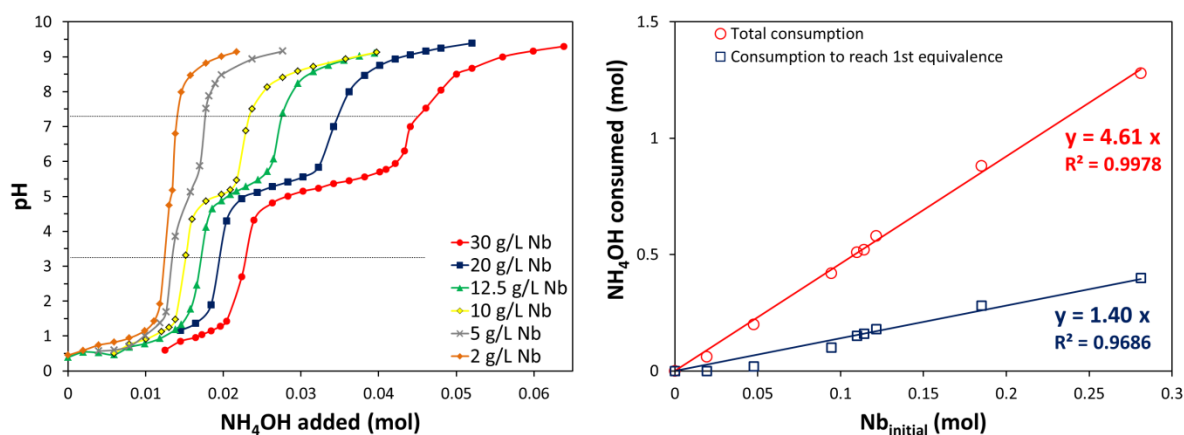


Figure 5. pH evolution observed during the neutralization of Nb oxalate solutions by NH_4OH (left) and consumption of NH_4OH for the two equivalence points as a function of the initial Nb quantity (right). Initial solution: $[\text{Nb}] = 2$ to 30 g/L as Nb oxalate. $V = 25$ mL. $T = 20$ °C.

Knowing the initial oxalate and nitrate concentrations in the Nb solution, as well as the solubilities of the oxalate and nitrate salts, the concentration of the base can be selected in order to prevent the co-precipitation of sodium or ammonium oxalate during the neutralization and precipitation of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$. Figure 6 gives the expected final concentrations for the sodium oxalate and ammonium oxalate systems.

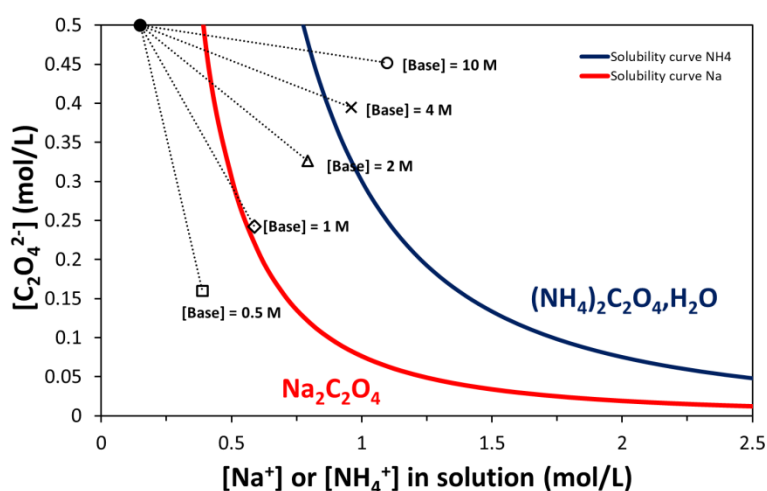


Figure 6. Solubility curves of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{C}_2\text{O}_4$ and calculated final concentrations after neutralization with different concentrations of bases (NaOH or NH_4OH 0.5 to 10 M). Initial solution: $[\text{Nb}] = 10$ g/L (0.108 M), $[\text{HNO}_3] = 0.30$ M, $[\text{ANO}_3] = 0.15$ M ($A = \text{Na}$ or NH_4), $[\text{Oxalate}] = 0.50$ M.

Solubilities taken from references [32,33]. Volume variations due to the precipitation of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ are neglected. $T = 25\text{ }^\circ\text{C}$.

Based on the solubility data available in the literature on $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{C}_2\text{O}_4$, co-precipitation of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ or $\text{Na}_2\text{C}_2\text{O}_4$ and $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ should be observed if the concentration of base used for neutralization is higher than 1 M. Nonetheless, experiments performed with 4 M NaOH and 4 M NH_4OH did not show any sign of co-precipitation (Figure 2 and Figure 3). This suggests that the systems are oversaturated. Experimentally, the precipitation of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ is instantaneous whereas that of the oxalate salts is extremely slow with still 84 % of the $\text{Na}_2\text{C}_2\text{O}_4$ solubilized after 24 h and 92 % for $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (Table S 1).

3.3. Processing of the oxalate-nitrate stream

As detailed previously [ref Sepa], Nb and Ta can be separated by liquid-liquid extraction in nitric-oxalic media (Figure 1). Therefore, the filtrates of the $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ (or $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) precipitation step detailed above will contain mixtures of oxalate and nitrate salts. Fortunately, oxalates salts are generally far less soluble than their nitrate counterparts. The reported solubilities of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (ammonium salt formed under normal conditions) and $\text{Na}_2\text{C}_2\text{O}_4$ in water at $25\text{ }^\circ\text{C}$ are 0.42 and 0.27 mol/kg, respectively, whereas that of NH_4NO_3 and NaNO_3 are 25 and 11 mol/kg, respectively [32,33]. Consequently, this solubility difference can eventually be leveraged for an effective oxalate-nitrate separation. The proposed oxalate-nitrate processing is summarized in Figure 7. Once $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ (or $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) is recovered (*vide supra*), the filtrates containing mixtures of oxalate, nitrate and sodium or ammonium ions are concentrated by evaporation in order to reach the solubility of the oxalate salt while keeping the nitrate ions in solution.

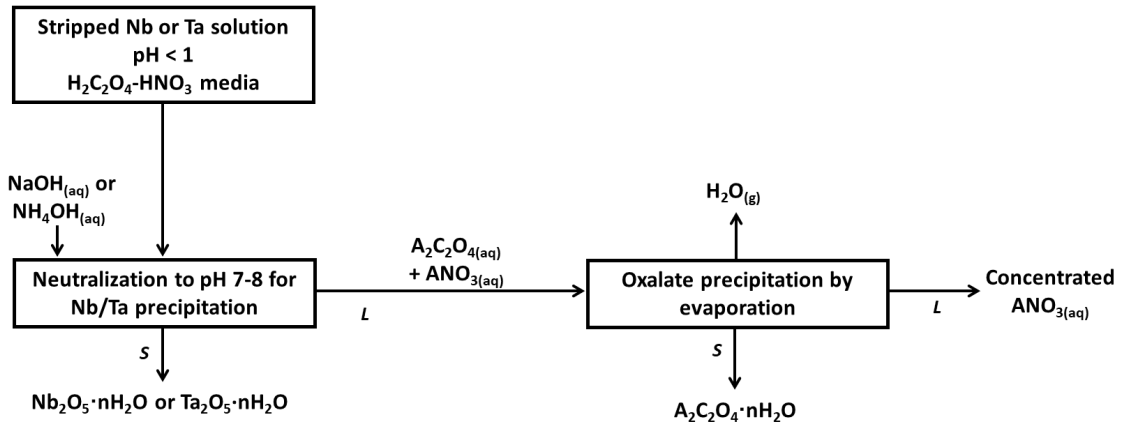


Figure 7 : General process flowsheet for the precipitation of Nb or Ta from oxalate-nitrate media and oxalate-nitrate separation. A = NH₄ or Na.

Oxalate precipitation experiments were performed on the Nb₂O₅·nH₂O precipitation filtrates by using an evaporation-concentration and cooling sequence. Figure 8 shows that nearly quantitative recovery of the oxalates can be obtained by concentrating the filtrates by a factor of about 10 followed by cooling to room temperature.

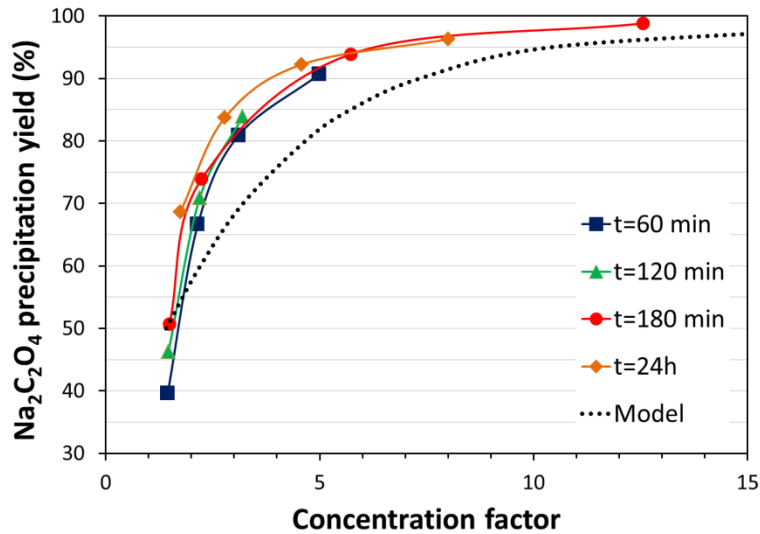


Figure 8. Precipitation yield of the oxalates in the Na-C₂O₄-NO₃-H₂O system as a function of the concentration factor. Initial solution: [Nb] = 10.0 g/L (0.108 M), [HNO₃] = 0.30 M, [NaNO₃] 0.15 M, [Oxalate] = 0.50 M. Neutralized to pH 7 by addition of 4 M NaOH. Nb₂O₅·nH₂O was removed and the filtrates were concentrated by evaporation at boiling point followed by cooling at 25°C. Concentration factor = V_{initial}/V_{final}. The dotted curve corresponds to the expected precipitation yield based on the solubility data available on Na₂C₂O₄ [32]. Analyses 60 min (squares), 120 min (triangles), 180 min (circles), and 24 h (diamonds) after precipitation confirmed the absence of oversaturation.

The obtained solids were highly crystalline and characterization by XRD and TGA-MS confirmed formation of Na₂C₂O₄ for the sodium route and (NH₄)₂C₂O₄·H₂O for the

ammonium route as well as the absence of nitrate salts (Figure S 5 and Figure S 5). Analyses of the precipitate by ICP-AES, TGA-MS, and titration by KMnO_4 evaluate the purity of the sodium or ammonium oxalate salts at 95 ± 3 %. Table 2 gives a summary of the performances for the Nb oxalate neutralization followed by the evaporation-precipitation of the oxalate-nitrate filtrates.

Table 2 : Summary of the optimized conditions for the two-step precipitation process for recovering niobium and separating the oxalates and nitrates.

	Neutralization and $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ precipitation	Filtrates concentration and oxalates precipitation
Conditions	4 M NaOH or 4 M NH_4OH Room temperature Final pH = 7-8	Concentration factor ≥ 10
Yields	Nb ≥ 99.9 % Oxalates ≤ 1 % Nitrates ≤ 1 %	$\text{Na}_2\text{C}_2\text{O}_4 \geq 95$ % $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O} \geq 95$ % Nitrates ≤ 5 %

3.4. Validation on industrial solutions

The developed precipitation method was tested during an industrial continuous running test. A pilot campaign was performed at ERAMET IDEAS pilot hall (France) using as feed about 225 L of Nb-Ta alkaline raw solution coming from the up-stream processing of a few tons of Gabonese ore sampled at the Nb-Ta deposit of *Mabounié* [25,28–30]. The process was operated for 160 h at steady-state conditions. Following recovery and separation of Nb and Ta by liquid-liquid extraction [ref Sepa], the purified stripped solutions were further processed for production of solid products and selective recovery of the oxalates and nitrates. The stripped solutions were treated by batches of 500 mL in order to facilitate the operations. Precipitation of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ or $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ was achieved by neutralization of the stripped solutions to pH 7.4-8.1 by 4 M NaOH for the first part of the pilot campaign and 4 M NH_4OH for the second part of the campaign. The averaged compositions of the Nb purified solution and corresponding solid $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ are given in Table 3. The precipitation yields for Nb

and Ta was higher than 99.9 % throughout the pilot test. The precipitation yields of the trace impurities were >99 % for Ta and >98 % for Ti. Only partial precipitation (~70%) is observed for Fe when NaOH for neutralization which is in line with the results obtained on synthetic solutions.

Table 3. Averaged composition of the Nb and Ta stripped solution and corresponding oxide products obtained during the pilot campaign by neutralization using 4 M NaOH or 4 M NH₄OH. Solid dried at 110°C before analysis.

		Nb	Ta	Ti	Fe	Na	Nb / Σelements
NaOH	Nb stripped solution (mg/L)	9,491 ±1,521	44.9 ±9.1	3.4 ±0.6	5.9 ±1.9	/	/
	Solid (wt%)	53.9 ±1.0	0.257 ±0.029	0.019 ±0.003	0.022 ±0.023	6.91 ±1.25	88.22 % ±1.93
NH ₄ OH	Nb stripped solution (mg/L)	10,209 ±1,130	44.8 ±4.9	3.6 ±1.1	5.2 ±3.3	/	/
	Solid (wt%)	55.3 ±1.6	0.251 ±0.038	0.019 ±0.005	< LoD	< LoD	99.51 % ±0.08
NaOH	Ta stripped solution (mg/L)	400 ±88	131 ±5.5	22.4 ±2.4	0.19 ±0.15	/	/
	Solid (wt%)	40.1 ±1.3	13.6 ±1.1	2.1 ±0.2	0.036 ±0.008	8.25 ±0.69	/
NH ₄ OH	Ta stripped solution (mg/L)	382 ±92	187 ±35	22.2 ±4.2	0.15 ±0.08	/	/
	Solid (wt%)	22.6 ±7.2	17.7 ±4.2	1.51 ±0.38	< LoD	< LoD	/

However, the oxalate fraction left in solution after precipitation of Nb₂O₅·nH₂O only reached 90 ±4%, which is lower than what was observed during the bench experiments (i.e. >95 %). This is thought to be due to the lower temperature of the hall where the process was operated compared to the laboratories (19 vs. 22°C). Na₂C₂O_{4(s)} was indeed detected in the amorphous Nb₂O₅·nH₂O product by XRD (Figure S 6). The sensitivity of the oxalate precipitation yield

corroborates the formation of an oversaturated solution after precipitation of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ as discussed above. Consequently, the obtained $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ cakes were washed two times with distilled water (150 mL) and the traces of $\text{Na}_2\text{C}_2\text{O}_4$ or $(\text{NH}_4)_2\text{C}_2\text{O}_4$ were successfully eliminated from the Nb product (8% during the first wash, 2% during the second wash) and were recirculated in the process so that the total oxalate recovery was > 99% (Figure S 6). The cake washes also eliminated about 15 % of the co-precipitated Fe while the Nb losses were lower than 0.2 %.

Interestingly, when the Nb precipitation step was performed with NaOH, a very Na content was detected in $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ even after multiple washes and total elimination of $\text{Na}_2\text{C}_2\text{O}_4$. Between 5 and 8 wt% Na (after drying at 110°C) were still detected in the $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ product, with a ratio Na/Nb of 0.09 to 0.15 g/g. This phenomena is due to the behavior of freshly precipitated $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ which can exchange certain alkaline ions with ions protonated sites. Inoue et al. [36,37] studied the uptake of alkali ion by $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ precipitate prepared by various methods and reported a loading capacity higher than 4 mmol of Na per g of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and the affinity increases as follows: $\text{K}^+ < \text{Na}^+ < \text{Li}^+$. The presence of sodium in the final Nb product represents a potential issue as it may result in the formation of refractory NaNbO_3 [38,39] during the final manufacturing of Nb products. The neutralization procedure was therefore switched to NH_4OH instead of NaOH for the second half of the pilot test. The utilization of ammonia instead of soda has multiple advantages since it is less expensive, doesn't introduced non-volatile elements, and it has been reported that $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ has a low affinity towards NH_4^+ which limits the potential contamination of the product [40]. As shown in Table 3, the neutralization of the purified Nb stripped solution by NH_4OH instead of NaOH clearly improves the purity of the final product with total elimination of the Na contamination and a Nb purity higher than 99.5 %. It is also worth noting that the use of NH_4OH also avoids the contamination of the Nb solid by Fe (Table 3).

This is most likely due to a higher solubility of the ammonium-iron-oxalate species compared to their sodium analogues. The sodium contamination of the final product (when using NaOH for neutralizing the stripped solution) was also observed in the case of $Ta_2O_5 \cdot nH_2O$ with up to 9 wt% Na detected in the dried solid. As in the case of Nb, this issue was solved by using NH_4OH for neutralization. Similarly the use of NH_4OH also decreases the co-precipitation of Fe and improves the quality of the final $Ta_2O_5 \cdot nH_2O$ concentrate. Overall, the precipitation method was found effective, simple to implement, and allows closing a strategy that aims at processing Nb and Ta raw materials without using any fluoride-based chemical. The general flowsheet of the process and its experimentally verified performances are given in Figure 9.

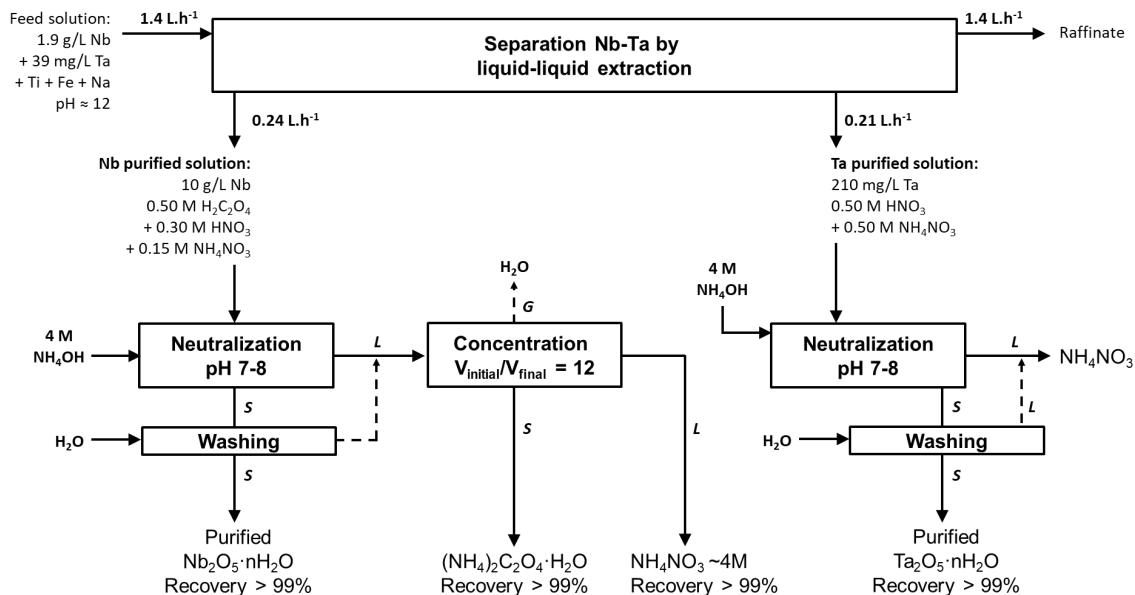


Figure 9. Simplified flowsheet of the process tested during the pilot campaign. The liquid-liquid extraction part has been detailed elsewhere [ref Sepa].

Conclusion

The recovery of Nb and Ta from oxalic-nitric acid solutions has been investigated for the first time. An innovative but simple process has been developed for simultaneous precipitation of Nb or Ta in the form hydrous oxides ($Nb_2O_5 \cdot nH_2O$ or $Ta_2O_5 \cdot nH_2O$) and separation Nb/oxalate or Ta/oxalate. The process consists of neutralizing at room temperature the acidic

metal-oxalate complexes with NaOH, KOH, or NH₄OH, preferentially NH₄OH, until pH 7-8 in order to decompose the metal-oxalate species and form i) an insoluble Nb or Ta hydrous oxide and ii) soluble sodium, potassium or ammonium oxalate and nitrate salts. The nitrate salts being about 50 times more soluble than their oxalate counterparts, the filtrates of the Nb or Ta precipitation step can be concentrated in order to selectively precipitate the oxalates while letting the nitrates in solution. This simple two-step process affords recovering the three components of the initial solution separately. The process has been validated on industrial solutions and the recovery yields were 99.9 % for Nb and Ta, 99 % for the oxalates, and 99 % for the nitrates.

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Supporting information

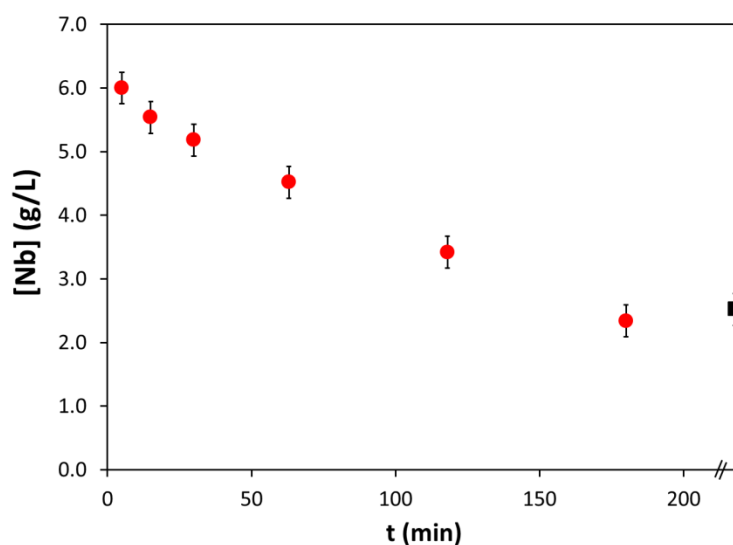


Figure S 1. Evolution of the Nb concentration in the filtrates as function of time after neutralization of an acidic Nb oxalate solution to pH 7.04 using a sodium bicarbonate solution (2 M). T = 20 °C. Initial solution: [Nb] = 15 g/L, $[C_2O_4]_{total} = 0.5$ M, $[HNO_3] = 0.5$ M. Black square point : Nb concentration measured after 24 h.

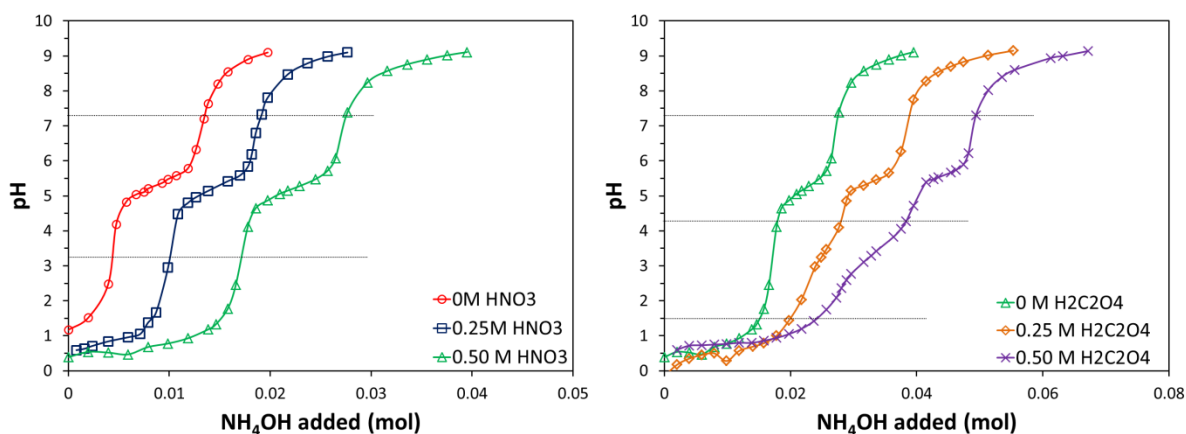


Figure S 2. Left: pH evolution observed during the neutralization of commercial Nb oxalate in HNO_3 . Right: pH evolution observed during the neutralization of commercial Nb oxalate in $H_2C_2O_4$ (+0.5 M HNO_3). Initial solution: [Nb] = 12.5 g/L. V = 25 mL. T = 20 °C. Neutralization performed with 4 M NH_4OH .

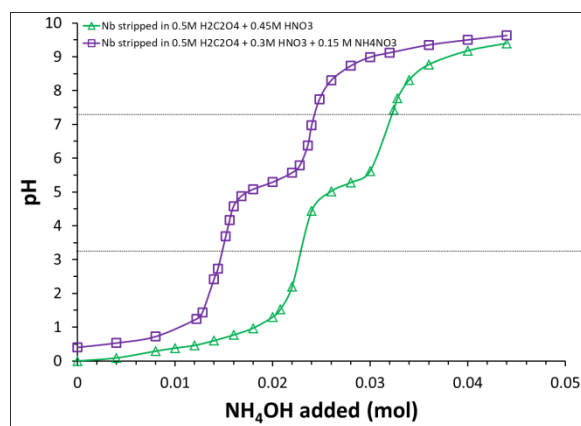


Figure S 3. pH evolution observed during the neutralization of industrial Nb stripped solution by 4 M NH_4OH . $[\text{HNO}_3]_{\text{ini}} = 0.455 \text{ M}$ (triangles) or 0.309 M (squares). $V = 25 \text{ mL}$. $T = 20 \text{ }^\circ\text{C}$.

Table S 1. Analysis of the filtrates after neutralization-precipitation of a Nb oxalate solution at pH 7.0 by 4 M NaOH. Initial solution: $[\text{Nb}] = 13 \text{ g/L}$ (0.140 M), $[\text{HNO}_3] = 0.50 \text{ M}$, $[\text{C}_2\text{O}_4]_{\text{total}} = 0.45 \text{ M}$.

Time after neutralization	Temperature ($^\circ\text{C}$)	%Oxalate in solution
0.5 h	21	100
2 h	18	100
4 h	18	100
5 h	18	100
24 h	18	83.5
49 h	18	71.6
96 h	18	68.5

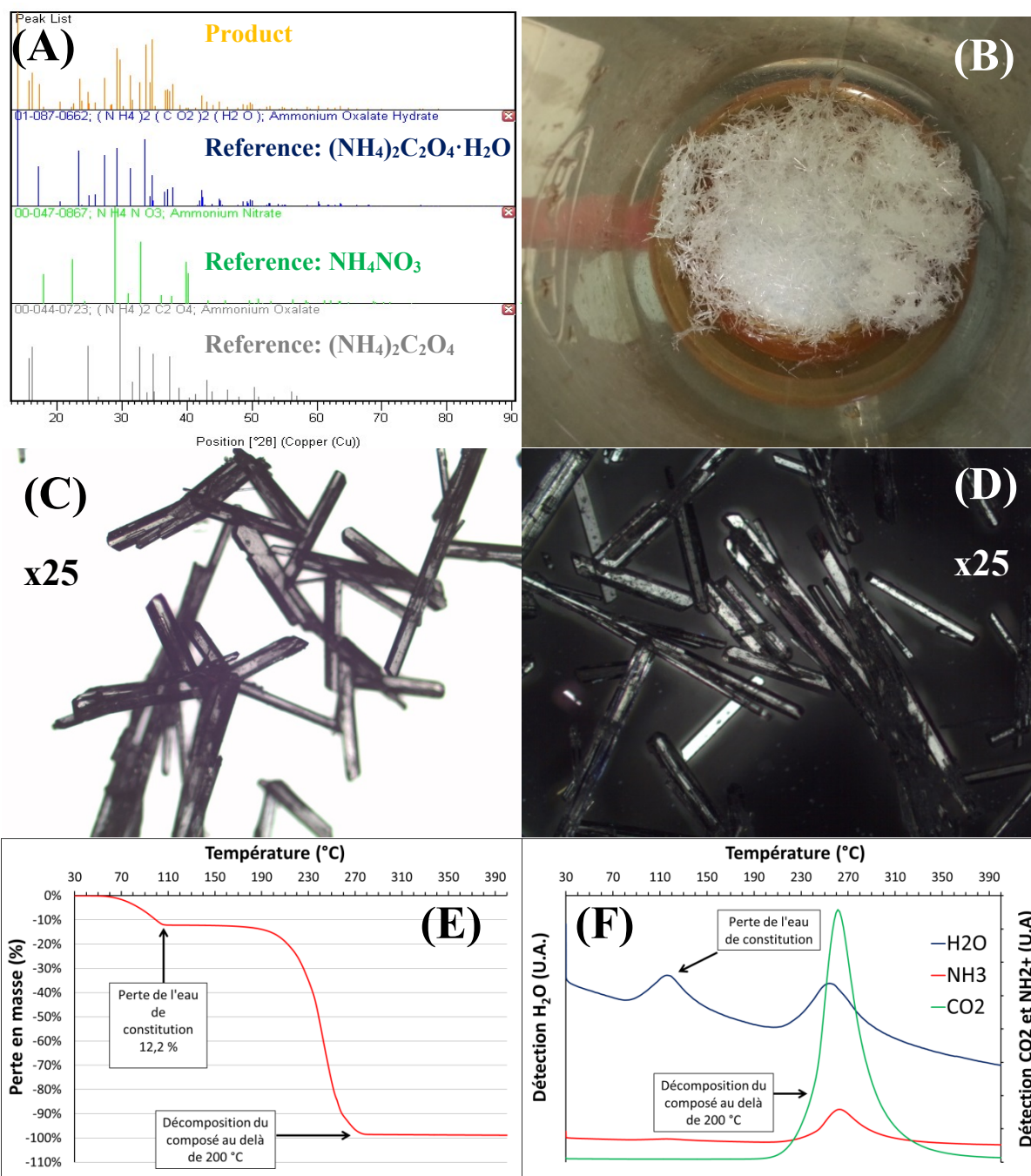


Figure S 4. Characterization of the ammonium oxalate precipitate obtained by neutralization of a Nb stripped solution by 4 M NH_4OH followed by filtration of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, followed by evaporation-concentration of the filtrates. Solid dried at 60°C . KMnO_4 titration yields $67.0 (\pm 3)$ wt% C_2O_4 (Calculated for $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$: 62.0 wt%). (A) XRD pattern of the obtained solid and comparison with some reference patterns. The product pattern matches that of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (B), (C), (D) Pictures of the obtained crystals. (E) and (F) TGA-MS analysis of the product. Measured loss of $\text{H}_2\text{O} = 12.2$ wt% (Calculated for $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$: 12.7 wt%).

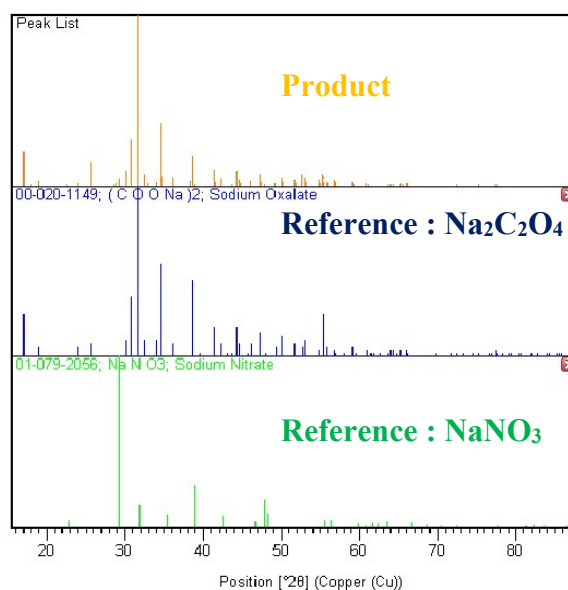


Figure S 5. Characterization of the ammonium oxalate precipitate obtained by neutralization of a Nb stripped solution by 4 M NaOH followed by filtration of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, followed by evaporation-concentration of the filtrates. Solid dried at 60°C . The XRD pattern of the obtained solid matches that of $\text{Na}_2\text{C}_2\text{O}_4$ with minor traces of NaNO_3 . KMnO_4 titration yields $61.0 (\pm 3)$ wt% C_2O_4 (Calculated for $\text{Na}_2\text{C}_2\text{O}_4$: 65.7 wt%). ICP-AES analysis: 32.4 % Na C_2O_4 (Calculated for $\text{Na}_2\text{C}_2\text{O}_4$: 34.3 wt%)

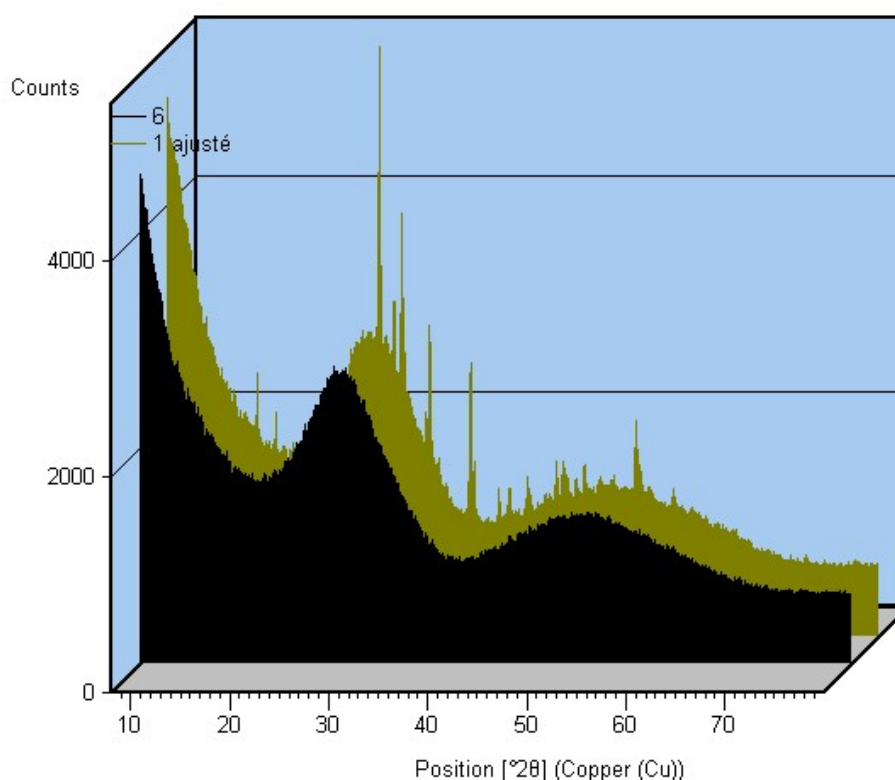


Figure S 6. XRD analyses of the amorphous $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ precipitate obtained for the industrial solution. The raw precipitate (Golden trace) contains traces of $\text{Na}_2\text{C}_2\text{O}_4$ that can be eliminated by washing with H_2O at room temperature (Black trace). The black trace is typical of amorphous $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ solids.