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Publication Date

2016-04-01

DOI

10.1016/j.seppur.2016.02.025

Peer reviewed



Selective recovery of niobium and tantalum from low-grade concentrates using a simple and fluoride-free process



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ARTICLE INFO

Article history:

Received 23 December 2015

Received in revised form 12 February 2016

Accepted 13 February 2016

Available online 13 February 2016

Keywords:

Niobium–tantalum ore

Hexaniobate

Alkaline process

NaOH

Purification

ABSTRACT

The current hydrometallurgical processes used for niobium and tantalum recovery are operated in strongly acidic and fluoride-containing solutions. To avoid the use of these highly toxic media, a fluoride-free process was developed to recover Nb and Ta from low-grade industrial concentrates. The process is based on the caustic conversion of the raw material with NaOH_(aq) at atmospheric pressure and at relatively low temperature which then allows the selective dissolution of sodium hexaniobates. Finally, Nb is recovered as purified hydrous oxide by acidification of the hexaniobate solution. The influence of many industry-relevant parameters (temperature, initial NaOH concentration, residence time, impurity content in the initial concentrate, pH of precipitation) was studied in order to optimize the recovery and purification of the valuable metals. Finally, the process was validated in continuous operation at a pilot scale. High recovery yields for Nb and Ta (65%) were obtained as well as high separation factors toward Ti, Fe, P, S, Th and U. The results demonstrate that it is possible to recover and purify Nb and Ta from industrial concentrates without using fluoride solutions.

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1. Introduction

Niobium (Nb; $Z = 41$) and tantalum (Ta; $Z = 73$) are two group V elements which remain largely unknown to the general public even if their unequalled properties make them essential for many key sectors. For example, Nb is a strategic ingredient in the manufacture of high-strength low-alloy (HSLA) steels [1]. The addition of Nb strengthens the steels without impairing their ductility. Moreover, the cost related to the Nb-alloying is generally insignificant compared to the final value of these steels. Hence even if the HSLA steels contain a low percentage of Nb, typically less than 1% (w/w), they account for nearly 90% of the niobium usage [2]. These low-grade Nb alloys are essential to the automotive market, the pipeline industry and the building and construction sectors. In a lesser extent (about 10% of the Nb market), Nb compounds are used as superconducting magnets, electronic components, nuclear fuel claddings, optical lenses, medical implants, catalysts, collection coils, etc. [3,4]. The most remarkable application of Nb is probably its use as NbTi superconducting magnets at the Large Hadron Collider (LHC) and as NbTi and Nb₃Sn superconducting magnets at the international nuclear fusion reactor project ITER [5–7]. The

tantalum market is smaller than the niobium one, with a production of 500–2000 t of Ta per year compared to about 100,000 t per year for Nb [8]. The main application of Ta is the manufacture of electronic components. Because of their high melting point and low thermal expansion, tantalum alloys are also used in cutting tools, military projectiles and in the aircraft industry.

1.1. Hydrometallurgical processes for Nb and Ta recovery

The numerous applications and the expanding market push the industrial and the academic researchers to develop new processes for the recovery of Nb and Ta from their ores and concentrates. Nb raw concentrates or colombo-tantalite concentrates (which typically contain 20–50% (w/w) Ta₂O₅ and 25–60% (w/w) Nb₂O₅ [8]), are usually treated by hydrometallurgical processes in highly acidic media due to the low solubility of Nb(V) and Ta(V) under mild aqueous conditions [9–11].

The fluoride media have been extensively studied for the extraction of the two metals. Actually, the first industrial process for the extraction and purification of Nb and Ta, called Marignac's process, required concentrated HF solutions [12]. This process allowed the production of high purity compounds and helped developing the Nb and Ta industries. In the current processes, the first step is generally the digestion of the Nb–Ta raw material

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in a concentrated solution of fluoride ions (HF or NH_4F) and in the presence of a mineral acid (most frequently H_2SO_4 and HCl). The main advantage of these processes is that Nb(V) and Ta(V) are highly soluble in the fluoride media. Solutions containing up to 5 mol/L of Nb can be obtained in HF 20 mol/L at 25 °C [13]. An extensive review of the chemistry of Nb and Ta in fluoride media has been done by Agulyanski [14]. Another advantage of the fluoride media is that Nb and Ta can form distinct complexes depending on the acidity and the metal concentration. Indeed, niobium forms NbOF_5^{2-} at low acidity and NbF_6^- at high acidity whereas tantalum forms TaF_7^{2-} at low acidity and TaF_6^- at high acidity. This difference in the speciation of the two metals allows their separation, so that, all the commercialized solvent extraction (SX) processes for the Nb–Ta separation are operated in fluoride media. An intensive effort is still being made to improve the Nb–Ta separation by SX in such media [15–20]. Nonetheless, the fluoride solutions are highly toxic and a large amount of effluents containing fluoride ions are generated by the processes mentioned above. Moreover, the fluoride processes are only appropriate for high-grade Nb–Ta concentrates [21].

1.2. The Maboumine process

The environmental footprint of the current hydrometallurgical processes used for the extraction and purification of Nb and Ta forces ones to devise cleaner methods. Especially, it appears essential to replace the fluoride compounds. In this regard, a fluoride-free hydrometallurgical process for the recovery of niobium from the Mabouinié mine has been developed since the early 2000s. The so-called Maboumine project aims at recovering niobium,

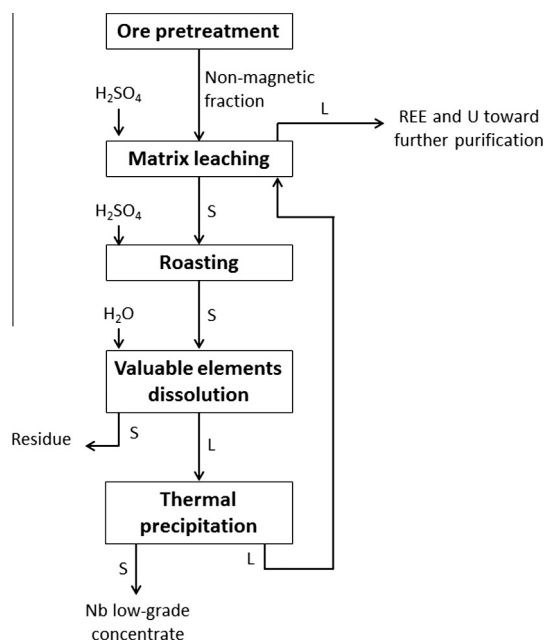


Fig. 1. Simplified flowsheet for the recovery of Nb from the Maboumine ore. Up-stream part of the process. Ore pretreatment consists in ore crushing, gravimetric and magnetic separation and sieving [25,26].

but also, tantalum, uranium and the REE from the Mabouinié ore deposit located in Gabon. The Mabouinié mine is a secondary Nb–Ta–REE–U deposit associated with carbonatite complexes [22] and contains pyrochlore minerals. The average composition of the ore is as follow (in % w/w): Fe 35%, Al 6.1%, P 2.7%, REE 1.4%, Nb 1.2%, Ti 1.2%, U 0.03% and Ta 0.02% [23]. The estimated resources are 360 MT at 1.02% Nb_2O_5 cut-off which makes the Mabouinié mine one of the most important Nb deposit worldwide [24]. The general flowsheet of the up-stream part of the Maboumine process is given in Fig. 1 and more details have been published elsewhere [25,26].

In the up-stream Maboumine process the non-magnetic fraction of the ore is first leached with concentrated H_2SO_4 in order to eliminate the goethite and crandalite minerals. The leaching residue, which contains the valuable elements, is mixed with H_2SO_4 and roasted at 250–300 °C which triggers the decomposition of the pyrochlore minerals. The roasted solid is then leached with water so that Nb, Ta, the REE and U are solubilized. Finally, Nb and Ta are precipitated selectively to the REE and U and the filtrates are recycled in the first leaching step to optimize the acid consumption. The filtrates containing the REE and U are processed in the down-stream part of the process. The method developed for the REE recovery is not discussed in the present paper but has been recently described [23]. Regarding the recovery of uranium, despite its low content in the Mabouinié ore, this element can be recovered as a by-product using classical processes [27,28]. The extraction yields for the process depicted in Fig. 1 are about 99% for U, 90% for the REE and 85% for Nb and Ta. The typical composition of the Nb raw concentrate obtained by the up-stream Maboumine process is given in Table 1.

Although the Nb recovery is high, the Nb concentrate obtained has a low Nb content and still contains lot of impurities, especially Ti and Fe, so that it has no commercial value. Consequently further purification is needed. In the continuity of the up-stream process (Fig. 1), a fluoride-free hydrometallurgical process was developed to selectively recover Nb and Ta from this low-grade concentrate.

Alkaline media have caught growing attention over the past few decades for the extraction of Nb and Ta. For example, Hongming Zhou et al. [29] studied the recovery of Nb from ores containing ~25% of Nb, ~25% of Ta, ~3% of Ti and ~7% of Fe. The method was based on the decomposition of the ore with KOH at 150–350 °C followed by a water leaching step. The extraction of Nb was higher than 70% and the extraction of Ta and Ti ranged between 40% and 90%. More recently, Wang et al. [21] also investigated the recovery of Nb from a natural ore using KOH. The initial ore contained ~19% of Nb, ~21% of Ta, ~3% of Ti and ~8% of Fe. The proposed method requires adjusting the Nb/Ta ratio by adding pure Nb_2O_5 before roasting the mixture with KOH at 300–500 °C. After roasting, the dissolution yields in water were 85–100% for Nb and Ta, 35–50% for Ti and 15–20% for Fe. Then Nb and Ta were selectively precipitated as $\text{K}_8(\text{Nb,Ta})_6\text{O}_{19} \cdot n\text{H}_2\text{O}$, namely hydrated potassium hexaniobate-tantalate. The salt was then dissolved in water and the solution was acidified with H_2SO_4 to produce a purified Nb–Ta hydrous oxide, $(\text{Nb,Ta})_2\text{O}_5 \cdot n\text{H}_2\text{O}$. Other studies, focused on the Nb recovery from synthetic concentrates by KOH roasting/leaching have also been published [30–32]. The main advantage of these processes is that Nb is highly soluble in KOH owing to the formation of hexaniobate ions $\text{Nb}_6\text{O}_{19}^{8-}$. Solubility data for

Table 1

Composition of the low-grade Nb concentrate obtained with the up-stream Maboumine process. Solid dried at 100 °C.

Element	Nb	Fe	Ti	P	S	Ta	REE	U	Th
% (w/w)	10–15	6–10	8–12	8–10	2–5	0.25	<0.2	<0.003	<0.21
Nb/impurity (w/w)	/	1–3	1–2	1–2	2–8	40	>50	>3300	>47

niobium in the Nb–KOH–H₂O system are scant but solutions containing up to 2.5 mol/L of Nb have been reported [33]. Nonetheless, the aforementioned methods work at high temperature which increases the environmental footprint and lower the cost-effectiveness of the process.

In the present paper, an innovative fluoride-free process has been developed for the recovery of Nb from low-grade concentrates like the one described in Table 1. The process is composed of three main steps and is based on a caustic conversion reaction with concentrated NaOH at atmospheric pressure (Fig. 2). The influence of many industry-relevant parameters is described like the conversion temperature, the initial NaOH concentration and the Nb/Ti and Nb/Fe ratio of the initial concentrate. Finally, a continuous running test at a pilot-scale was performed in order to validate the proposed process.

2. Experimental

2.1. Materials

NbCl_{5(s)} (99%; Alfa Aesar), TiOSO₄·nH₂O (Sigma–Aldrich), Fe₂(SO₄)₃ (97%; Sigma–Aldrich), concentrated NaOH solutions (50%; Sigma–Aldrich) and concentrated H₂SO₄ solutions (95.0–98.0%; Sigma Aldrich) were used without further purification. The industrial Nb low-grade concentrate used for the laboratory tests was provided by ERAMET Research (Trappes, France) and comes from the Maboumine hydrometallurgical process [25]. The solid phase was dried at 100 °C before the experiments and its elemental composition was as follow (in % w/w): Nb 13.5%, Ti 11.0%, Fe 6.7%, S 4.5%, P 6.8%, Si 0.50%, Al 0.30%, Ta 0.27% and Na 0.10%.

The concentrations of Al, Fe, P, S, T, Si, Ta and Nb were determined by ICP-OES using an ICP 720-ES spectrometer (Varian). Quantitative analysis were performed at 396.152 (Al) nm, 238.204 (Fe) nm, 177.434 (P) nm, 180.669 (S) nm, 334.188 (Ti) nm, 251.611 (Si) nm, 268.517 (Ta) nm and 313.078 nm (Nb) spectral emission lines. U, Th and REE were determined by ICP-MS using an ICP 820-MS spectrometer (Varian). Na concentrations

were determined by flame absorption spectroscopy using an AA 220 spectrometer (Varian) at 589.6 nm.

Powder XRD spectra were collected using Cu K_{α1} radiation ($\lambda = 1.54053 \text{ \AA}$). Diffraction patterns were obtained using a Panalytical X'Pert Pro diffractometer and identified with the software HighScore (Panalytical). UV–visible spectra were recorded on Cary 100-Scan spectrophotometer used in double beam mode. Each spectrum was acquired in Quartz Suprasil[®] cuvette (path length of 10.00 mm) and recorded against the corresponding blank sample. pH measurements were performed with a 827 pH-lab (Metrohm) pH-meter and a low alkaline error combined electrode (Unitrode, Metrohm). The pH-meter was calibrated with NIST standards at pH 4.00, 7.00 and 12.00.

2.2. Experimental procedures

Typically, about 40 g of dried raw concentrate were placed in a 500 mL reactor equipped with a controlled heating system, a mechanical stirrer and a condenser. All the experiments were performed at atmospheric pressure. The reactor was composed of Téflon[®] Perfluoroalkoxy (PFA) in order to sustain the alkaline conditions used during the caustic conversion step. Then 400 mL of NaOH solution at the desired concentrations (200 g L⁻¹, 250 g L⁻¹, 300 g L⁻¹, 350 g L⁻¹ and 400 g L⁻¹) were added to the reactor and the mixture was heated to the required temperature and stirred at 500 rpm. At the end of the caustic conversion step, the mixture was centrifuged for 20 min at 5000 rpm. The solid phase was recovered and the spent NaOH was discarded. The solid phase was washed 3 times with 100 mL of diluted NaOH (10 g L⁻¹). This step allows the selective removal of P, S and of the excess of NaOH without dissolving the valuable metals, especially sodium niobates. The Nb leaching step was performed as follow: 30 g of washed solid were placed in a 2000 mL beaker and 1500 mL of distilled water were added. The mixture was stirred at 500 rpm for 1 h and at 50 °C. Then, the mixture was centrifuged for 20 min at 5000 rpm. The mass and the density of the filtrates were measured and a sample was kept for elemental analysis. The leaching step was repeated until the Nb concentration in the leached solution was almost zero which ensured that all the water-soluble Nb phases were dissolved. Typically, the leaching step was repeated three times.

A series of tests were carried out on synthetic samples. The Nb–Ti and Nb–Fe concentrates were synthesized as follow: Typically 3–10 g of NbCl_{5(s)} and 0–20 g of TiOSO₄·nH₂O (or Fe₂(SO₄)₃) were placed in a 1 L beaker and 800 mL of distilled water were added. Then the mixture was stirred at 500 rpm and the pH was adjusted to 7 with concentrated NaOH. After stabilization of the pH value, the mixture was stirred for 30 min to ensure the complete hydrolysis of the metals. The mixture was then centrifuged for 20 min at 5000 rpm. The solid phase was recovered and washed three times with 200 mL of distilled water. After washing, the synthetic solid was immediately used for caustic conversion tests as described above.

Following the Nb leaching step, a series of precipitation tests was performed. Typically, 1000 mL of filtrates obtained were placed in a 2000 mL open beaker and stirred at 700 rpm. Then concentrated H₂SO₄ was added dropwise until the desired pH value was reached. The mixture was stirred for additional 30 min and then centrifuged for 20 min at 5000 rpm. The whole procedure was performed at room temperature. The filtrates were sampled and kept for elemental analysis. The solid phase was dried at 110 °C for 24 h before elemental analysis. The uncertainty of the results was estimated by repeating the entire procedure at least twice.

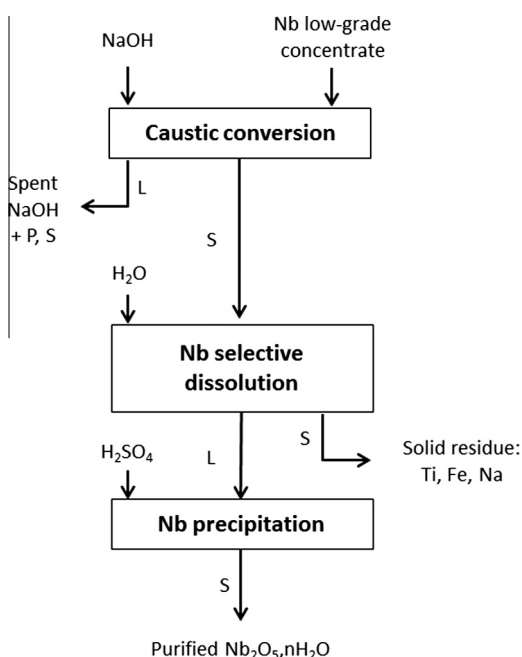


Fig. 2. Process developed for the recovery of Nb from low-grade concentrates. The spent NaOH can be purified and reused partially (not described in this study).

3. Results and discussion

3.1. Caustic conversion of the industrial concentrate

The primary goal of the process is to solubilize Nb in alkaline media while letting the impurities in the leaching residue. The first step of the process consists of a reaction between the raw concentrate and concentrated NaOH at atmospheric pressure. After reaction with NaOH, the solid is washed and then leached with water. Nb is solubilized during the water leaching step (Fig. 2). The dissolution yields were calculated as follow:

$$\text{Dissolution yield of } M = \frac{\sum_i C_i \times V_i}{\%M \times m_{\text{concentrate}}}$$

With:

$\%M$: Weight percent of element M in the initial concentrate;

$m_{\text{concentrate}}$: Mass of initial concentrate;

C_i : Mass concentration of M in the filtrates of the i -th water leaching step;

V_i : Volume of the filtrates of the i -th water leaching step.

3.1.1. Characterization of the caustic conversion reaction

The powder XRD analysis of the initial concentrate revealed that it is completely amorphous (Fig. 3) and the Nb-bearing phases could not be identified. Based on the conditions under which the initial concentrate is obtained [25,26] and due to the absence of crystalline Nb phases, the speciation of Nb in the initial concentrate was considered to be $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}_{(s)}$. Indeed, $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}_{(s)}$ is obtained in most of the niobium hydrometallurgical processes and it is known to be only amorphous [9,34]. After reaction with NaOH and washings, diffractions peaks corresponding to $\text{Na}_7\text{HfNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}_{(s)}$, namely hydrated sodium hexaniobate, appear (Fig. 3). $\text{Na}_7\text{HfNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}_{(s)}$ has been fully characterized in previous studies and is known to be soluble in water [35,36]. In fact, as discussed below, the diffraction peaks related to $\text{Na}_7\text{HfNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}_{(s)}$ disappear after the water leaching step (Fig. 9), confirming that $\text{Na}_7\text{HfNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}_{(s)}$ contributes to the Nb dissolution.

The presence of hexaniobate ions in solution after the water leaching step was also confirmed by UV–visible spectrophotometry (Fig. 4). The absorbance spectrum of the filtrates obtained after the water leaching step is in accordance with the one reported for an aqueous solution obtained after dissolving synthetic $\text{Na}_7\text{HfNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}$ [37].

Taking into account the XRD results, the UV absorbance spectrum of the leaching solution and previous works published on the alkaline processes for the treatment of Nb concentrates ([21,30,32]), Eqs. (1) and (2) are proposed to explain the

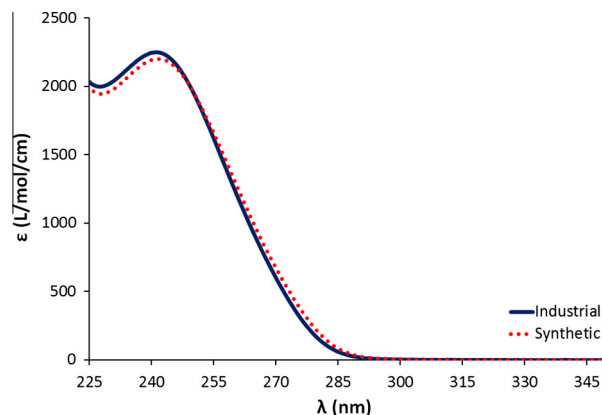
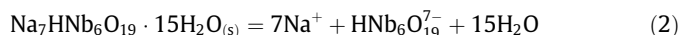
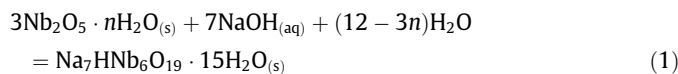


Fig. 4. Blue curve: Molar absorptivity (ϵ) of the filtrates obtained after (i) caustic conversion of the industrial Nb low-grade concentrate, (ii) washing with NaOH 10 g L^{-1} and (iii) leaching of the solid with water ($\text{pH} = 13$). The molar absorptivity reported [37] for a synthetic aqueous solution of $\text{Na}_7\text{HfNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}$ is also given for comparison. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

dissolution of Nb. Eq. (1) corresponds to the caustic conversion step and Eq. (2) corresponds to the dissolution equilibrium of $\text{Na}_7\text{HfNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}_{(s)}$.



3.1.2. Effect of NaOH

The effect of the initial concentration of NaOH used for the caustic conversion step on the recovery of Nb was studied. Fig. 5 shows the dissolution yields obtained for Nb, Ti and Fe obtained after reaction between the low-grade industrial concentrate and NaOH solutions at various concentrations. The behavior of the other impurities present in the initial concentrate (Table 1) will be discussed later on during the validation of the process in a continuous test. A high Nb recovery was observed, with a dissolution yield ranging between 69% and 76%. The recovery of Nb increases very slightly with the NaOH concentration. Higher NaOH concentrations could improve the recovery of Nb but this would increase the cost of the process and the solid–liquid separation would become arduous. Surprisingly, the dissolution of Ti and Fe were much lower than Nb with dissolutions yields below 15%. Thus,

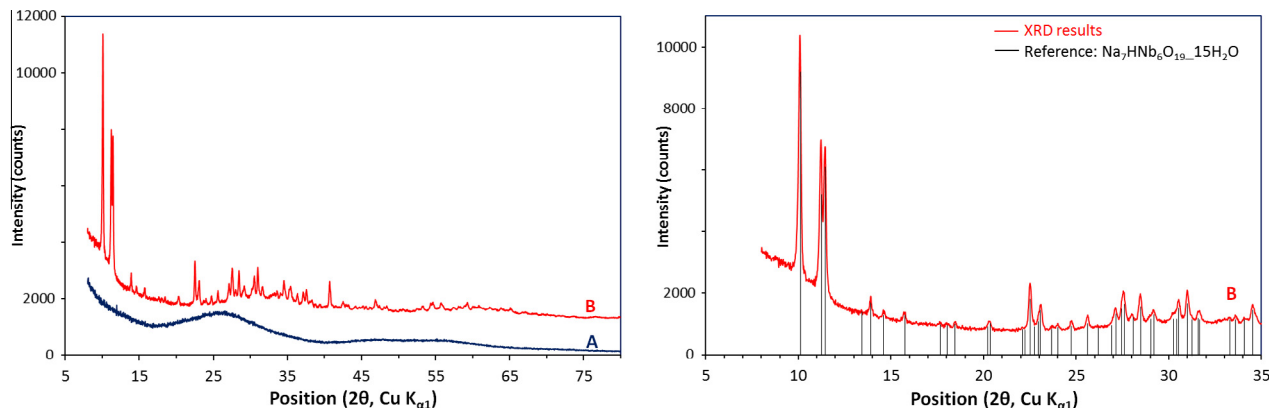


Fig. 3. Left: Powder XRD patterns of the initial industrial Nb concentrate (A) and the solid phase after reaction with an initial NaOH concentration of 400 g L^{-1} ($T = 110 \text{ }^\circ\text{C}$, $t = 5 \text{ h}$) and washing (B). Right: zoom between 5° and 35° (2θ) for the XRD pattern (B) and peak list of the reference $\text{Na}_7\text{HfNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}$ (ICDD PDF 01-077-4938).

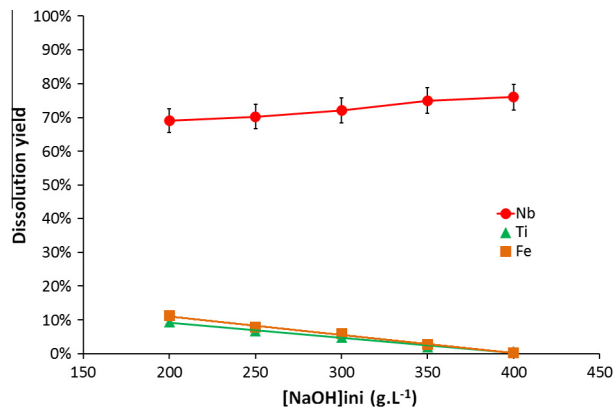


Fig. 5. Effect of the NaOH concentration used for the caustic conversion step on the dissolution yield of Nb (●), Ti (▲) and Fe (■). Caustic conversion conditions: solid to liquid ratio = 100 g of dried solid per liter, $T = 110\text{ }^{\circ}\text{C}$, $t = 18\text{ h}$. Error bars: $\pm 5\%$.

increasing the NaOH concentration used for the caustic conversion step from 200 to 400 g L⁻¹ decreases significantly the dissolution of Ti and Fe. At 400 g L⁻¹ of NaOH, the dissolution yields of Ti and Fe dropped to less than 1% whereas the dissolution yield of Nb reaches 76%. This means that the treatment of Nb–Ti–Fe industrial concentrates with NaOH_(aq) at atmospheric pressure, exhibits a high selectivity toward Nb and that highly purified solutions can be obtained by the process reported herein. Such a high selectivity was not expected given that previous studies showed that KOH conversions led to the dissolution of Nb but also Ti and Fe [21,29]. The difference observed between the KOH and NaOH-based processes might be due to the higher temperatures used in the previously reported KOH routes (up to 500 °C) which might have led to the formation of soluble Fe and Ti species.

3.1.3. Effect of the caustic conversion temperature and duration

Fig. 6 shows the dissolution yield of Nb obtained for different caustic conversion temperatures and at constant NaOH concentration. The procedure was performed between 50 and 110 °C which was the boiling point of the NaOH solution used during these optimization tests. It can be seen in Fig. 6 that the extraction of Nb from the low-grade concentrate is favored at high temperature. The Nb dissolution yield nearly doubles when increasing the temperature from 50 to 90 °C. Between 90 and 110 °C, the temperature of the caustic conversion step has no significant impact on the dissolution of Nb. Contrary to Nb, the dissolution yields of Ti and Fe were very low and almost independent of the temperature used during the caustic conversion step. With a

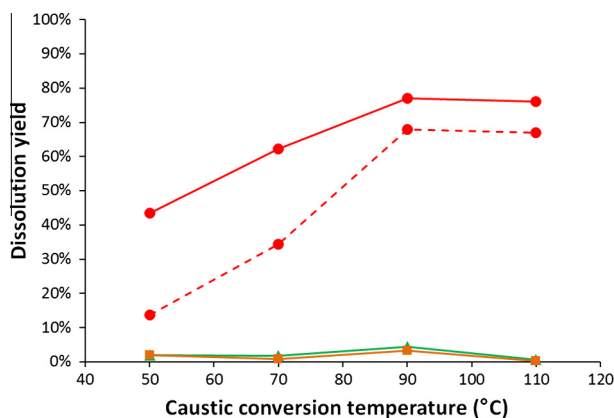


Fig. 6. Effect of the caustic conversion temperature on the dissolution yield of Nb (●), Ti (▲) and Fe (■). Caustic conversion conditions: [NaOH]_{initial} = 400 g L⁻¹, solid to liquid ratio = 100 g of dried solid per liter, reaction time of 5 h (solid lines) or 1 h (dashed line).

caustic conversion reaction performed at 110 °C, the Nb dissolution reaches about 75% whereas less than 2% of Ti and Fe are dissolved, which is in accordance with the results given in Fig. 5.

The results given in Fig. 6 also suggest that the recovery of Nb can be enhanced when using a prolonged time at the caustic conversion step. In our attempt to maximize the Nb recovery, the influence of the caustic conversion duration was investigated at 110 °C and at constant NaOH concentration. Fig. 7 shows the dissolution yields measured for Nb, Ti and Fe for various caustic conversion durations. The maximum Nb dissolution is reached after 5 h and further increase of the reaction duration does not improve significantly the Nb recovery.

Under the conditions given in Fig. 7, the dissolution of Nb plateaus at 76% but the dissolution of the impurities is very low with less than 2% for Ti and Fe. It is also important to underline that the recovery of niobium is not total (Figs. 5–7). Indeed, the maximum recovery seems to be about 75% even when using a high temperature and a very long NaOH conversion step. This clearly indicates that after the caustic conversion step, water-soluble Na₇HNb₆O₁₉·15H₂O_(s) is not the only Nb-bearing phase present in the solid.

3.2. Effect of the initial Ti/Nb and Fe/Nb ratio

Preliminary tests suggested that the maximum Nb dissolution yield might depend on the Ti and Fe content of the initial concentrate. In order to determine what was the factor limiting the Nb recovery, two series of caustic conversion tests were performed on synthetic Nb–Ti or Nb–Fe concentrates. Amorphous precipitates with different Ti/Nb and Fe/Nb ratio were synthesized and used as surrogates for our Nb–Ti–Fe industrial concentrate (see Section 2.2). The process described in Fig. 2 was applied to these synthetic concentrates and the dissolution yields were measured as a function of the initial Ti/Nb and Fe/Nb ratio.

It was found that increasing the Ti or Fe content of the initial concentrate has, in both cases, a detrimental effect on the Nb recovery (Fig. 8). The dissolution of Nb was quantitative when the initial concentrate did not contain Ti or Fe (*i.e.* the concentrate was totally transformed into soluble Na₇HNb₆O₁₉·15H₂O) whereas the dissolution of Nb fell to ~60% when (Ti/Nb)_{ini} was 6 mol/mol or ~80% when (Fe/Nb)_{ini} was 3 mol/mol. The Nb dissolution yield of 76% measured for the industrial Nb–Ti–Fe concentrate under similar conditions is also shown in Fig. 8. The dissolution yield of 76% can almost be explained by the cumulative effects of the presence of Ti and Fe in the industrial concentrate. The very low dissolution yields observed for Ti (<2%) with the synthetic Nb–Ti concentrates

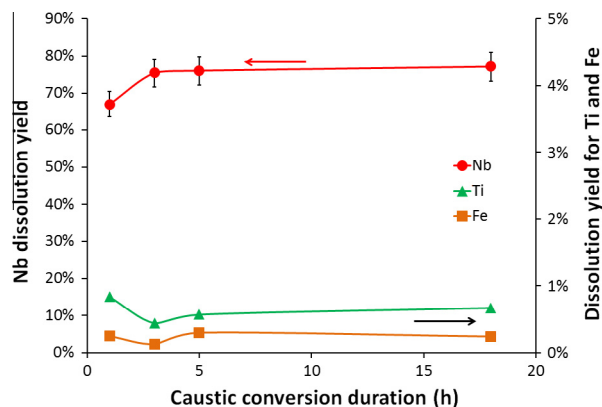


Fig. 7. Dissolution yield of Nb (●), Ti (▲) and Fe (■) measured as a function of the duration of the caustic conversion step. Caustic conversion conditions: [NaOH] = 340 g L⁻¹, solid to liquid ratio = 100 g of dried solid per liter, $T = 110\text{ }^{\circ}\text{C}$. Error bars: $\pm 5\%$.

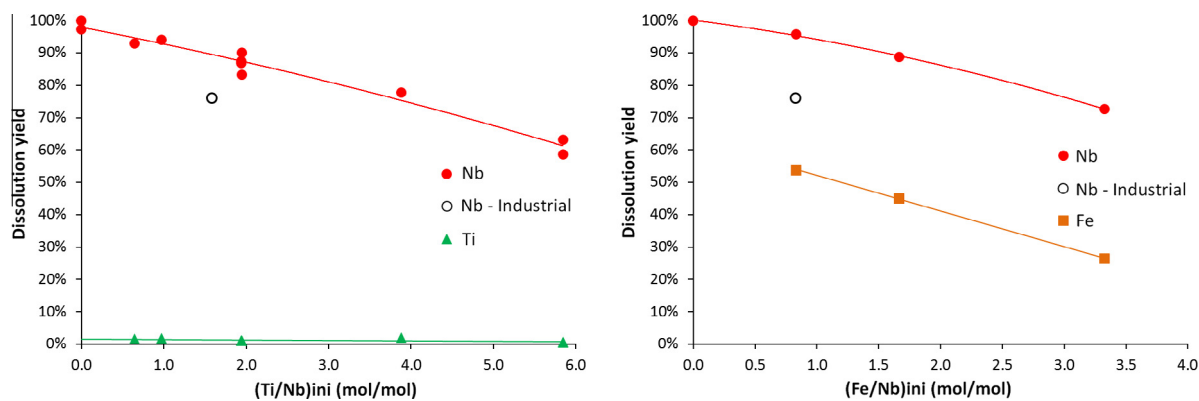


Fig. 8. Effect of the Ti/Nb (left) and Fe/Nb (right) ratio in the initial synthetic concentrate on the dissolution of Nb (●), Ti (▲) and Fe (■). Caustic conversion conditions: $[\text{NaOH}] = 400 \text{ g L}^{-1}$, caustic conversion duration = 18 h, $T = 110 \text{ }^\circ\text{C}$. (○) Nb dissolution yield measured for the Nb–Ti–Fe industrial concentrate under similar conditions.

are in accordance with the results obtained with the industrial Nb–Ti–Fe sample (Figs. 6 and 7). It should be noted that the dissolution yields of Fe, measured for the synthetic Nb–Fe concentrates, were much higher than the ones observed for the industrial sample. This suggests that the dissolution of Fe may also depend on the presence of Ti in the initial concentrate. Nonetheless, the results given in Fig. 8 corroborate the fact that, even if the process described in Fig. 2 exhibits a high selectivity toward Nb, the recovery of Nb is limited by the presence of Ti and Fe in the initial raw concentrate. When using the industrial concentrate, the residue obtained after the selective dissolution of Nb contains $\sim 24\%$ of the initial Nb and also $\sim 98\%$ of the initial Ti and Fe. This residue is therefore enriched in Ti and Fe and depleted in Nb. The residue typically exhibits Ti/Nb and Fe/Nb ratio of ~ 6.4 and $\sim 0.8 \text{ mol/mol}$, respectively. Hence, this residue cannot be treated a second time by the process described in Fig. 2 because the recovery of Nb would be very low (Fig. 8). However, an innovative process has been recently proposed [38] to extract Nb from such really depleted Nb concentrates. This option will be further studied in order to improve the total Nb recovery of the process.

The XRD powder analysis of the leaching residue obtained from synthetic or industrial concentrates indicates that it contains $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ (Fig. 9). The crystallinity of the residue was poor and attempts to improve it by calcination failed. The important peak widths observed on the XRD pattern also suggests that the crystalline phase might be partially substituted with Nb or Fe which would explain the decrease of the Nb dissolution when increasing the initial Ti/Nb ratio.

3.3. Precipitation of the purified $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$

During the water leaching step, Nb is solubilized whereas Fe and Ti remain in the residue so that a purified Nb solution is produced. The typical composition of the solution is given in Table 3. The Nb solution consists of aqueous sodium hexaniobate, $\text{Na}_7\text{HfNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}$, with traces of $\text{NaOH}_{(\text{aq})}$ and metal impurities as explained above. The Nb concentration reached 1.3 g L^{-1} at $25 \text{ }^\circ\text{C}$ which is in accordance with the solubility limit of $\text{Na}_7\text{HfNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}_{(\text{s})}$ reported in the literature [9]. One way to recover Nb from the leaching solution would be to concentrate the solution (by evaporation) in order to precipitate $\text{Na}_7\text{HfNb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}_{(\text{s})}$. Though, this would lead to a solid compound with only 43.1% (m/m) of Nb and also 12.5% (m/m) of Na. The high Na content could then be an issue for producing high purity Nb oxides or other niobium products like ferroriobium alloys.

The hexaniobate ions $\text{HfNb}_6\text{O}_{19}^{7-}(\text{aq})$ are known to be unstable at pH lower than ~ 9 because they protonate, polymerize and then

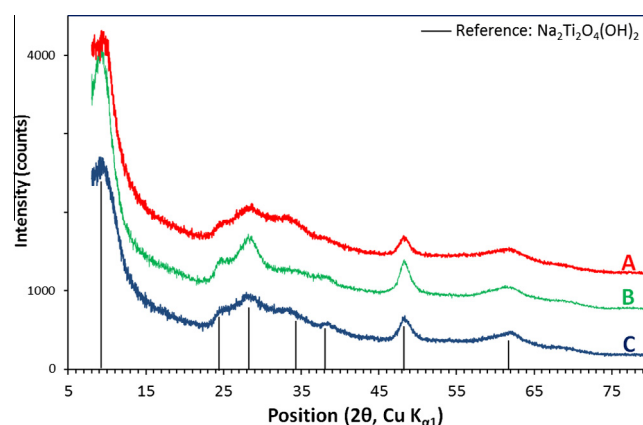


Fig. 9. Powder XRD pattern of the leaching residue obtained by the process given in Fig. 2 starting with the industrial Nb–Ti–Fe concentrate (A) or a synthetic Nb–Ti concentrate (B: dried at $110 \text{ }^\circ\text{C}$; C: calcined at $300 \text{ }^\circ\text{C}$ for 12 h). Vertical bars: reference peak list for $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ (ICDD PDF 00-057-0123).

Table 2

Precipitation yield of Nb, Ti and Fe as a function of pH after acidification with concentrated sulfuric acid. Initial solution: $[\text{Nb}] = 1310 \text{ mg L}^{-1}$, $[\text{Na}] = 1140 \text{ mg L}^{-1}$, $[\text{Fe}] = 0.8 \text{ mg L}^{-1}$, $[\text{Ti}] = 2.6 \text{ mg L}^{-1}$, pH = 12.0.

pH	Nb	Ti (%)	Fe	Na (%)
5.0	76.0	65.0	16.0	<1
4.0	>99.9	>96.0	>89.0	<1
3.0	>99.9	>96.0	>89.0	<1
2.0	>99.9	>96.0	>89.0	<1
1.0	>99.9	92.0	87.0	<1

decompose into amorphous $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}_{(\text{s})}$ [39–41]. Consequently, the purified Nb solution can simply be acidified in order to obtain $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}_{(\text{s})}$.

Table 2 gives the precipitation yield for Nb, Ti, Fe and Na measured when acidifying the leaching solution with H_2SO_4 . As expected, the Nb concentration dropped when the pH value decreased and a white and amorphous precipitate was recovered by centrifugation. The precipitation of Nb, but also Ti and Fe, is quantitative when the leaching solution is acidified to pH 2–4. The acidification step also exhibits an important separation factor between Nb and Na since Na^+ ions remain in solution. Furthermore, Ti and Fe seem to be partially re-solubilized when decreasing the pH down to 1. This feature could afford an additional leverage to improve the purity of the Nb precipitate but it also increases the acid consumption. Consequently, acidification to a pH value comprised between 3 and 4 was chosen for the precipitation of niobium.

Table 3

Composition of the initial concentrate, leaching residue, leaching solution and purified solid obtained during the pilot campaign.

	Nb	Fe	Ti	P	S	Si	Al	Ta	Na	Th	U
Initial concentrate (% m/m)	11.52	10.30	9.15	7.86	3.18	1.42	0.65	0.23	0.03	0.20	2.9×10^{-3}
Leaching residue (% m/m)	8.01	24.1	20.1	0.01	0.02	0.91	0.06	0.18	4.97	0.44	5.4×10^{-3}
Nb leaching solution (mg L ⁻¹)	2100	3.9	9.6	1.9	35	6.5	0.5	42.1	1340	<0.5	<0.5
Purified Nb concentrate (% m/m)	55.2	0.13	0.20	0.04	0.03	0.41	0.03	1.10	0.38	0.003	$<5.0 \times 10^{-4}$
Recovery (%)	64.9	0.17	0.30	0.07	0.13	3.91	0.63	64.8	/	0.20	/
Nb/impurity (g/g)	/	425	276	1380	1840	135	1840	50	145	1.8×10^4	$<1.1 \times 10^5$
Separator factor	/	380	219	942	508	17	104	1	/	319	>28

4. Validation of the recovery and purification of Nb in continuous running test

In order to validate the hydrometallurgical process developed at laboratory scale (Fig. 2), the recovery and purification of Nb contained in an industrial raw concentrate (Table 3) was performed in continuous operation at pilot scale. The process was operated for 7 days at steady-state conditions with an initial flow rate of 300 g h⁻¹ of Nb concentrate. For the reasons detailed above, the caustic conversion of the initial Nb concentrate was performed at atmospheric pressure and at boiling point (~110 °C), with a total residence time of 5 h, with an initial NaOH concentration of 400 g L⁻¹ and using an initial solid rate of 100 g of dried solid per liter. The solid was then washed three times with 10 g L⁻¹ NaOH solution and with a liquid to solid ratio of 4 mL g⁻¹ in order to remove impregnated NaOH. Concerning the niobium dissolution step, the chosen parameters were 50 °C, an initial solid rate of 20 g L⁻¹ and a residence time of 1 h. The purified Nb solution was then precipitated at room temperature by adjusting the pH to 4.0 with concentrated H₂SO₄. The final Nb precipitate was washed three times with de-ionized water (liquid to solid ratio of 20 mL g⁻¹) and then dried at 110 °C for 4 h.

The average dissolution yield of Nb measured during the pilot campaign varied from 59% to 69% with an average of 65% whereas less than 1% of Ti and Fe were dissolved. The dissolution of Nb was slightly lower than what was observed during the laboratory tests (65% versus 76%) which is mainly due to the higher Fe/Nb ratio of the raw concentrate used for the pilot test. As expected from the laboratory tests, the precipitation yield of Nb during the last acidification–precipitation step was higher than 99.9%. Hence, the total Nb recovery was nearly 65% and the main Nb loss was found in the leaching residue. About 6.8 kg of purified Nb₂O₅·nH₂O were produced during the pilot campaign. The average composition of the purified Nb solid is given in Table 3. Its Nb content was around 55% (w/w) after drying at 110 °C. This value could be increased to nearly 70% (w/w) since it is known that Nb₂O₅·nH₂O releases its water at around 500 °C [34]. Most of the impurities present in the initial raw concentrate were eliminated. The purified Nb₂O₅·nH₂O contained traces of P, S, Si and Al which is inherent to the process that we used as phosphate, sulfate, silicate and aluminate ions are formed in basic media. The presence of Fe and Ti in the final concentrate is more surprising taking into account the low solubility of these elements in alkaline media. The Fe and Ti pollution of the final Nb concentrate is thought to be due to the presence of fine particles at the Nb selective dissolution step or to the formation of Ti- or Fe-substituted niobates. It should be underlined that the Nb₂O₅·nH₂O concentrate also contained 0.4% (w/w) of Na. This may be related to the ion-exchange properties of the Nb concentrate. Indeed, it has been shown that freshly precipitated Nb₂O₅·nH₂O can act as a cationic exchanger toward alkaline ions [42–44]. Na⁺ ions could be removed from Nb₂O₅·nH₂O(s) by a specific chemical washing but this was not performed in the present study. The Nb/U and Nb/Th ratio were greatly improved, although the U and Th contents of the initial concentrate were already low. The

selectivity toward U and Th is thought to be due to the formation of insoluble sodium uranate and thorium hydroxide. Finally the content of Ta in the purified Nb₂O₅·nH₂O(s) concentrate was 1.10% (w/w). This value corresponds to a recovery yield of 65% for Ta. This means that Ta behaves like Nb throughout the process. This result was expected given the almost identical chemical properties that exhibit Nb(V) and Ta(V). Therefore, the process described in the present study allows the recovery of both Nb and Ta from low-grade concentrates.

Unlike the KOH-based processes previously reported [21,29], the process developed here yielded a Nb product of high purity which fulfils most of the commercial specifications (Table 3). Indeed, the majority of the purified Nb concentrates (about 90%) are used to produce Nb–Fe alloys [3], called ferroniobiums, and must comply with the 5453 ISO standard [45]. The Nb/impurity ratios, given by the ISO norm for a standard grade ferroniobium, are as follow: Nb/S ≥ 1200 g/g, Nb/P ≥ 600 g/g, Nb/Ti ≥ 150 g/g, Nb/Ta ≥ 120 g/g, Nb/Al ≥ 60 g/g and Nb/Si ≥ 24 g/g. The content of Ti, S, P, Al and Si in Nb₂O₅·nH₂O obtained in this study were low enough to respect the ISO specifications (Table 3). The only specification that is not fulfilled is the Nb/Ta ratio but this is generally accepted by the ferroniobium producers since Ta does not affect the quality of the Nb alloys. This could also be handled by mixing the purified Nb₂O₅·nH₂O with another Nb concentrate with a higher Nb/Ta ratio before the final production of ferroniobium. Furthermore, additional purification is expected during the pyrometallurgical step that is needed to produce the alloys from the Nb oxide. This means that standard grade ferroniobiums could be produced starting from low-grade Nb concentrates using the fluoride-free process described in this study.

5. Conclusion

The recovery and purification of niobium from low-grade concentrates was investigated. A novel hydrometallurgical process was developed to selectively extract Nb and Ta from Nb–Ti–Fe raw concentrates. The process is based on the formation of sodium hexaniobate by reaction between the initial concentrate and concentrated NaOH at atmospheric pressure. After caustic conversion, the sodium hexaniobate are selectively dissolved in water. The optimum conditions for the caustic conversion step were determined to be [NaOH]_{ini} = 400 g L⁻¹, T = 110 °C, t = 5 h. Under these conditions, the dissolution of Nb reaches nearly 70% whereas less than 1% of Fe and Ti are dissolved. It was found that the Ti and Fe content of the initial concentrate is the main factor limiting the Nb recovery. The sodium hexaniobate solution is then acidified in order to precipitate a purified Nb₂O₅·nH₂O concentrate. The best compromise between the acid consumption, the precipitation yield and the purification of Nb was to acidify the sodium hexaniobate solution to pH 4 at room temperature. Since Nb and Ta have similar chemical properties, Ta is also extracted by the proposed process. The global Nb and Ta recovery yields, measured in continuous operation at a pilot scale, were 65%. High purity Nb₂O₅·nH₂O was

obtained starting from low-grade industrial Nb–Ti–Fe concentrates. The present study demonstrates that fluoride-free process can be developed for the recovery and purification of niobium and tantalum.

Acknowledgements

Financial support for this work from ERAMET company (France) is gratefully acknowledged. The authors would like to thank Dr. Florent Chauveau, (ERAMET Research, France).

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