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Direct precipitation of niobium and tantalum from alkaline solutions using calcium-bearing reagents

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ABSTRACT

The recovery of Nb(V) and Ta(V) from alkaline solutions was investigated using calcium-bearing reagents ($CaCl_{2(aq)}$, $Ca(CH_3COO)^+{}_{(aq)}$, $Ca(NTA)^-{}_{(aq)}$, $Ca(EDTA)^{2-}{}_{(aq)}$, $CaCO_{3(s)}$ and $Ca(OH)_{2(s)}$) at 25 °C. It was found that hexaniobate and hexatantalate ions ($H_xNb_6O_{19}^{x-8}$ and $H_xTa_6O_{19}^{x-8}$; $0 \leq x \leq 3$) can be quantitatively precipitated with calcium chloride, calcium acetate or calcium hydroxide when the ratio $(Ca/M)_{initial}$ is at least 0.4 mol/mol (M = Nb, Ta). Precipitation yields higher than 95% are obtained for solutions that contain, as low as, $3 * 10^{-4}$ mol/L of Nb and $1 * 10^{-4}$ mol/L of Ta. Moreover, the proposed precipitation method can be operated in a wide pH range and consumes two times less reactant than the classical way for recovering Nb and Ta which consists of neutralizing their alkaline solutions with a mineral acid. The amorphous calcium niobate concentrate was characterized by elemental analysis (ICP-OES), thermogravimetric analysis (TGA-MS) and Raman spectroscopy and the solid phase $K_3Ca_{2.2}(H_{0.6}Nb_6O_{19}) \cdot nH_2O$ was identified under specific conditions.

1. Introduction

Niobium (Z = 41) and tantalum (Z = 73) are two valuable metals that are useful for many applications. Niobium is mainly consumed for the production of ferroniobium alloys but it is also used to produce superconducting magnets, electronic components, catalysts, medical implants, commemorative coins etc. (Roskill Information Services, 2009; Nikishina et al., 2013). Tantalum is a critical element for catalyst, electronic and high temperature alloy industries. Tantalum compounds are generally more expensive than their niobium counterparts because of the low natural abundance of Ta compared to Nb: 2 ppm for Ta and 20 ppm for Nb in the continental crust (Taylor, 1964).

The conventional hydrometallurgical processes developed for the recovery and purification of Nb and Ta require strongly complexing agent, like fluoride ions (Agulyanski, 2004; El Hussaini, 2009; Zhu and Cheng, 2011; Nete et al., 2014). Nonetheless, alkaline processes have recently caught growing attention for the recovery of Nb and Ta owing to the high solubility of Nb(V) and Ta(V) in NaOH or KOH and thanks to the lower environmental impact of the alkaline reagents when compared to fluoride ones. For example, the KOH roasting of a natural ore bearing Nb and Ta has been investigated by Wang et al. (2009). The recovery of Nb and Ta from a low grade ore was also studied by Zhou et al. (2005a) using concentrated KOH under atmospheric pressure. More recently, a method for purifying niobium and tantalum concentrates using a caustic conversion step with concentrated NaOH, followed by a water leaching step, has been patented (ERAMET et al., 2015). In these examples, very high recovery yields were obtained along with separation from impurities such as manganese, titanium and iron.

The dissolution of Nb(V) and Ta(V) in alkaline media is due to the formation of the hexaniobate and hexatantalate ions, namely $Nb_6O_{19}^{8-}$ and $Ta_6O_{19}^{8-}$ and their solubility increases along the series Li < Na < K < Rb < Cs (Zhou et al., 2005b; Zhou and Tokuda, 2000; Nyman et al., 2006). The hexameric ions dominate the chemistry of Nb(V) and Ta(V) in basic solutions and can be triply, doubly, simply or non-protonated at pH higher than 10 (Nyman, 2011; Klemperer and Marek, 2013; Deblonde et al., 2015a). Consequently, hydrometallurgical processes that aim at recovering Nb and Ta by alkaline leaching or alkaline roasting have to deal with these polyoxometalate ions in solution. On the other hand, after the selective leaching step, Nb and Ta have to be precipitated in order to obtain an intermediate concentrate or the commercial product. The precipitation of Nb and Ta from alkaline leaching solutions can be done by acidification to pH 2–7, as described in Eq. (1) (Babko et al., 1963; Inoue et al., 1985; Deblonde et al., 2015b).

$$H_xM_6O_{19}{}^{x-8}{}_{(aq)} + (8-x)H^+{}_{(aq)} = 3M_2O_5 \cdot nH_2O_{(s)} + (4-3n)H_2O \; (M = Nb, Ta; 0 \leq x \leq 3). \quad (1)$$

In addition to consuming acid, due to Eq. (1), the acidification of Nb or Ta alkaline solutions also neutralizes the excess of NaOH or KOH required for the formation of $H_xM_6O_{19}{}^{x-8}{}_{(aq)}$ ions starting from the

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raw concentrates. Moreover, the utilization of sulfuric acid (one of the less expensive mineral acid typically used for such purpose) for neutralizing Nb alkaline solutions could be questioned because of the drastic sulfur specification (S ≤ 0.05 wt.% in the final product) regarding the production of ferroniobium, which is the main Nb commercial product (International Organization for Standardization, 1980). Furthermore, the recovery of Nb and Ta in the form of hydrous pentoxide is known to produce a precipitate that has a very high water content, typically 70–80% for $Nb_2O_5 \cdot nH_2O$ and 60–70% for $Ta_2O_5 \cdot nH_2O$ (Nikishina et al., 2012). Given the huge reagent consumption and the water content of the resulting hydrous pentoxide, acidification of hexaniobate or hexatantalate solutions is not the most economical way for recovering Nb and Ta from alkaline solutions. Therefore, even if there is a recent interest for the recovery of Nb and Ta in alkaline media, new methods for precipitating these valuable metals at basic pH have to be developed.

We here investigated the precipitation of hexaniobate and hexatantalate solutions by addition of calcium-containing reagents. Studies on the precipitation of $H_xNb_6O_{19}^{x-8}$ ions by divalent cations are handful. To our knowledge, the first report is a qualitative study performed by Süe (1937). The author performed several tests and claimed to precipitate "alkaline Nb solutions" with Ba^{2+}, Sr^{2+}, Ca^{2+}, Ag^{+}, Tl^{+}, Hg^{+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+} and Al^{3+} ions. Nonetheless, the experimental details are scarce and the speciation of Nb(V) in alkaline media was also not established at the time. Another study was performed by Dartiguenave et al. (1965) who used barium chloride as precipitating reagent. Based on pH and conductometric titrations, the authors claimed to precipitate $Ba_4Nb_6O_{19} \cdot nH_2O$, $Ba_7(HNb_6O_{19})_2 \cdot nH_2O$ and $Ba_4(H_2Nb_6O_{19})_2 \cdot nH_2O$ starting from solutions of $K_8Nb_6O_{19} \cdot 16H_2O$, $K_7HNb_6O_{19} \cdot 12.5H_2O$ and $K_6H_2Nb_6O_{19} \cdot 10H_2O$, respectively. Fifty years later, these results seem speculative, due to lack of characterization of the solids and because the pH decreased from ~12 to ~7 during their experiments, and it is nowadays well-known that $H_xNb_6O_{19}^{x-8}$ ions are not stable below pH ~9 and yield hydrous niobium oxide, $Nb_2O_5 \cdot nH_2O$ (Etxebarria et al., 1994; Klemperer and Marek, 2013). The authors also did not take into account the presence of potassium ions in the background electrolyte and this might have led them to wrong conclusions, as discussed in the present paper. To our knowledge, the precipitation of hexatantalate ions by divalent cations has never been investigated, so far.

In the present work, we investigated the precipitation of hexaniobate and hexatantalate solutions by addition of calcium ions or calcium complexes at constant temperature and ionic strength. The influence of the calcium excess, nature of the reactant, nature of the background electrolyte, initial metal concentration and pH are discussed. The Nb–Ca and Ta–Ca concentrates were characterized by elemental analysis, thermogravimetric analysis and Raman spectroscopy.

2. Experimental

2.1. Reagents

All stock solutions were prepared with deionized water ($R > 18.2 * 10^6$ Ω). $Ca(CH_3COO)_2 \cdot H_2O$ (≥99%) and $Sr(CH_3COO)_2$ (≥99%) were purchased from Sigma Aldrich. $CaCl_2 \cdot 2H_2O$ and $Ca(OH)_2$ (ACS grade) were purchased from Merck. NaCl, NaOH, Na_2EDTA, $2H_2O$, $NTA \cdot H_2O$, KCl and KOH were obtained from VWR. $Na_7HNb_6O_{19} \cdot 15H_2O$ and $K_8Nb_6O_{19} \cdot 16H_2O$ were synthesized as previously reported (Deblonde et al., 2015a). $Cs_8Nb_6O_{19} \cdot 14H_2O$ was synthesized from literature method Nyman et al. (2006).

The synthesis of $Na_8Ta_6O_{19} \cdot 24.5H_2O$ was inspired from Abramov et al. (2011) 5.9 g of NaOH pellets was finely ground and mixed with 3.3 g of Ta_2O_5. The mixture was placed in a Pt crucible and heated to 450 °C for 5 h. The purification of the calcinate was performed similarly to $Na_7HNb_6O_{19} \cdot 15H_2O$ synthesis. The yield was 44% based on Ta. Elemental analysis for $Na_8Ta_6O_{19} \cdot 24.5H_2O$, calculated (wt.%): 21.9 H_2O, 9.1 Na, 53.9 Ta. Found: 22.0 H_2O, 8.9 Na, 51.9 Ta. Raman (cm^{-1}): 861; 754; 511; 420; 346; 213; 187; 172. IR (cm^{-1}): 3226 (vs); 1657 (m); 831 (s); 767 (s); 692 (vs); 617 (s).

2.2. Materials

Concentrations in the samples were determined by ICP-OES using an iCAP 6000 series spectrometer (Thermo Scientific). Samples were diluted in 2% HNO_3 and 0.7% H_2O_2. Quantitative analyses were performed at 309.418 and 240.063 nm spectral emission lines for Nb and Ta, respectively. K concentrations were determined by flame atomic absorption spectrometry using an AA 220 spectrometer (Varian). Thermogravimetric analyses were performed with a SETSYS Evolution device (SETARAM Instrumentation) equipped with an MS detector for the gas analysis. The samples were purge for 30 min with synthetic air at 30 °C prior to analysis. The analyses were performed in a Pt crucible under synthetic air flow and the samples were heated from 30 °C to 700 °C with a ramp up of 3 °C/min. Raman spectra were recorded at the Institut de Chimie et des Matériaux Paris Est (UMR 7182 CNRS, Thiais, France) as described by Baddour-Hadjean et al. (2012, 2014). The spectra were obtained with a LaBRAM HR 800 (Jobin–Yvon–Horiba) Raman microspectrometer. An Ar ion laser (514.5 nm) was used as the excitation source. The Raman spectra were measured in backscattering geometry. pH measurements were performed with a 827 pH-lab (Metrohm) pH-meter and low alkaline error combined electrode (Unitrode, Metrohm). The pH-meter was calibrated with NIST standards at pH 4.00, 7.00 and 12.00.

2.3. Precipitation procedure

Series of batch precipitation were performed as a function of pH, of the quantity of reactant and of the initial Nb or Ta concentration. A typical procedure contains the following steps. Stock solutions of $Na_7HNb_6O_{19} \cdot 15H_2O$, $K_8Nb_6O_{19} \cdot 16H_2O$ or $Na_8Ta_6O_{19} \cdot 24.5H_2O$ were prepared and the pH was adjusted to the desired value with the corresponding base (NaOH or KOH). The pH of the stock solutions of calcium-bearing reagent was also adjusted before precipitation experiments. The series of batch precipitations were performed in 50 mL polypropylene tubes (BD Falcon™) containing 25 mL of samples. The samples were shaken for 30 min at constant temperature in a thermoshaker (VTO 500, Gerhardt). The samples were then centrifuged for 5 min at 4000 rpm. The liquid phase was filter at 0.25 μm with a syringe filter (Minisart® RC25, Sartorius). The pH of the samples was measured immediately after filtration and the concentrations at equilibrium were determined by ICP-OES. The precipitates were washed 3 times with deionized water and dried in air for 24 h before analysis.

3. Results and discussion

3.1. Precipitation of hexaniobate and hexatantalate ions with alkaline earth metals

The direct precipitation of niobium and tantalum from alkaline solutions was investigated. Fig. 1 gives the precipitation yield of niobium by addition of a calcium acetate solution to a sodium hexaniobate solution at pH ~11. The calcium acetate complex was chosen for its high solubility in water (3.1 mol/kg of H_2O at 25 °C) and its weak formation constant ($\log \beta\ (Ca(CH_3COO)^{+}) = 0.55$ at $I = 0.1$ M) (Saury et al., 1993; Smith et al., 2004). A quantitative recovery of niobium was observed at pH ~11 when the ratio Ca/Nb is higher than 0.372 ± 0.005 mol/mol. Similar results were obtained when using strontium acetate instead of calcium acetate (Fig. S1). At pH 10–13, the solution chemistry of Nb(V) is dominated by the mono-protonated species $HNb_6O_{19}^{7-}$ (Etxebarria et al., 1994; Deblonde et al., 2015a) meaning that the neutralization of this species by an acid would require a ratio H/Nb of 1.17 mol/mol to precipitate $Nb_2O_5 \cdot nH_2O$ (Eq. (1)). Therefore, the direct precipitation of Nb by a calcium-bearing reagent consumes less reactant that its precipitation

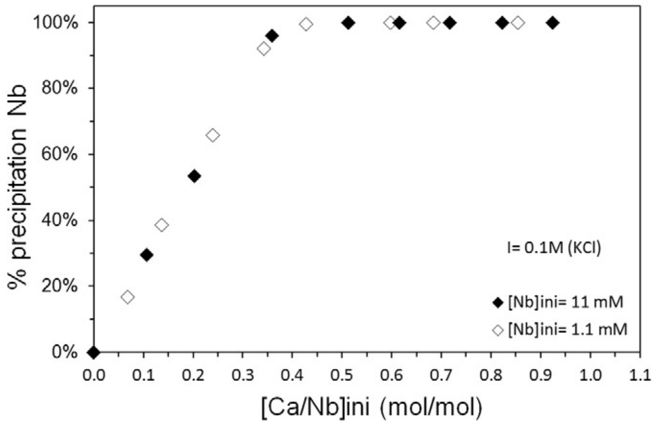

Fig. 1. Precipitation yield of Nb when adding a calcium acetate solution to a potassium hexaniobate solution. pH = 10.7 ± 0.1, T = 25 °C. $[Nb]_{ini} = 1.1 * 10^{-2}$ mol/L (filled symbols), $[Nb]_{ini} = 1.1 * 10^{-3}$ mol/L (open symbols). I = 0.1 mol/L (KCl).

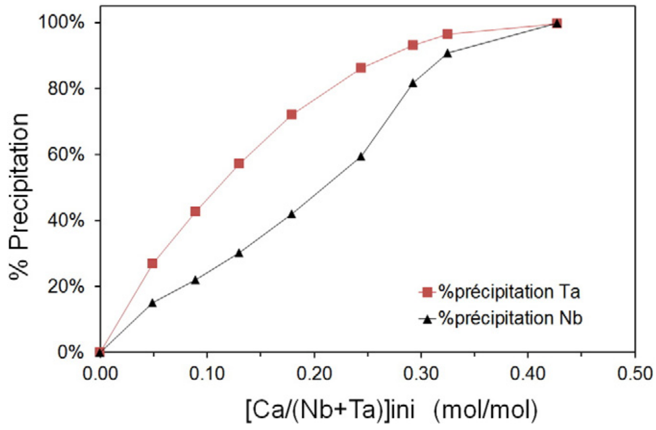

Fig. 3. Precipitation yield of Nb (triangles) and Ta (squares) when adding a calcium acetate solution to solution containing both $K_8Nb_6O_{19}\cdot16H_2O$ and $Na_8Ta_6O_{19}\cdot24.5H_2O$. $[Nb]_{ini} = 1.1 * 10^{-3}$ mol/L and $[Ta]_{ini} = 1.1 * 10^{-3}$ mol/L. pH = 10.7 ± 0.1, T = 25 °C. I = 0.1 mol/L (KCl).

by a mineral acid. Moreover the Nb precipitation by a calcium-bearing reagent does not neutralize the excess of NaOH or KOH present in solution which affords a possible recycling of the filtrates in the process.

Similar experiments were also performed with hexatantalate ions in KCl media. Fig. 2 gives the precipitation yield of tantalum at pH ~ 11 as a function of the quantity of calcium added. The precipitation yield of calcium was also measured in order to confirm the results. Like niobium, a quantitative recovery of tantalum is obtained when the ratio Ca/Ta is higher than 0.385 mol/mol. These results were expected as Nb(V) and Ta(V) generally exhibit a very similar chemistry. This means that the method proposed in the present paper could be used to recover both niobium and tantalum.

Precipitation tests performed with solutions containing both Nb and Ta at identical concentration revealed that calcium ions have a stronger affinity for tantalum (Fig. 3). Nonetheless, even if the precipitation yields were slightly higher for tantalum, the difference was too weak to consider any practical separation between tantalum and niobium by this method.

3.2. Influence of the initial Nb and Ta concentrations

The influence of the initial metal concentration on the precipitation yield of Nb and Ta was also investigated for solutions containing either hexaniobate ions or hexatantalate ions (Fig. 4). The recovery of the valuable metals decreases when the metal content of the initial solution decreases. Nonetheless, a quantitative precipitation was observed even for solutions containing as low as $3 * 10^{-4}$ mol/L of Nb and $1 * 10^{-4}$ mol/L of Ta when the ratio Ca/M was 0.75 mol/mol. Moreover it is expected that a higher excess of calcium would lead to higher precipitation yields even for the low concentrated solutions. Consequently, the precipitation of Nb and Ta using a calcium-bearing reagent could be helpful even for hydrometallurgical processes that operate at very low concentrations or for the treatment of effluents. It should be underlined that the precipitation of low concentrated hexaniobate solutions, by neutralization with an acid, is somewhat difficult because it can produce colloids (Fairbrother, 1967). No colloidal formation was observed when precipitating Nb or Ta with a calcium-bearing reagent at basic pH.

3.3. Effect of the nature of the calcium-bearing reactant

The Nb precipitation was then attempted with different calcium-containing reagents, namely, calcium chloride, calcium acetate, calcium 2-[bis(carboxymethyl)amino]acetate (NTA), calcium 2-({2-[bis(carboxymethyl)amino]ethyl}(carboxymethyl)amino)acetic (EDTA), calcium carbonate and calcium hydroxide. Very high precipitation yields were obtained with calcium chloride, calcium acetate and calcium hydroxide whereas no precipitation was observed with calcium carbonate, calcium NTA and calcium EDTA (Table 1).

These results are of importance in regard to the solubility model currently used for Nb(V) under mild alkaline conditions. Indeed, Nb(V) is

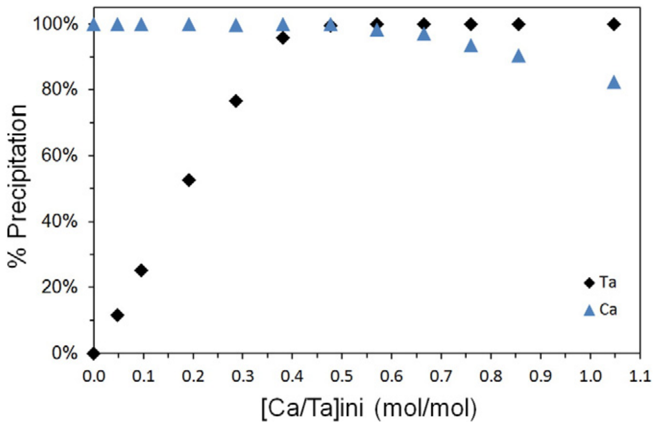

Fig. 2. Precipitation yield of Ta (lozenges) and calcium (triangles) when adding a calcium acetate solution to a sodium hexatantalate solution. pH = 10.9 ± 0.1, T = 25 °C. $[Ta]_{ini} = 1.1 * 10^{-2}$ mol/L. I = 0.1 mol/L (KCl).

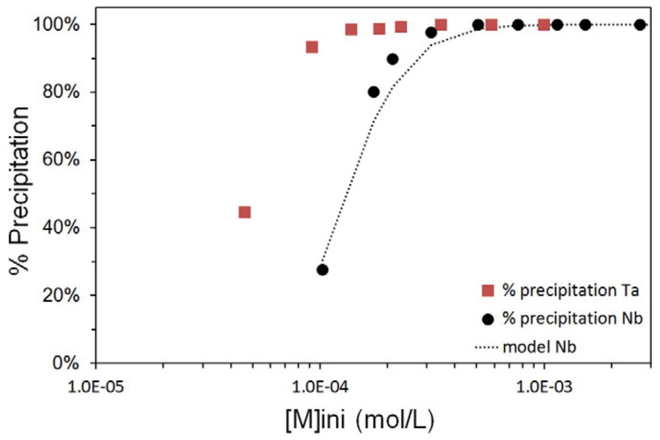

Fig. 4. Precipitation yield of Nb (triangles) and Ta (squares) as a function of the initial metal concentration. T = 25 °C. [Ca]ini/[M]ini = 0.75 mol/mol, (M = Nb, Ta). I = 0.1 mol/L (KCl). pH = 10.7 ± 0.1 for Ta. pH = 11.1 ± 0.1 for Nb. Dotted-line: model for Nb precipitation using Eq. (2) and log K(25 °C) = 12.7 (see text).

Table 1
Precipitation yield obtained with various calcium-bearing reagents. T = 25 °C, I = 0.1 mol/L (KCl). pH = 11 ± 0.1. $[Ca]_{ini}/[Nb]_{ini} = 0.75$ mol/mol. The stability constant of the complexes and solubility product of the solids are given for comparison.

Ca species	$\log \beta_{11}$ or $\log K_s$ (T = 298 K)	Nb precipitation yield
$CaCl_{2(aq)}$	/	≥99.8%
$[Ca(CH_3COO)]^{+}{}_{(aq)}$	0.55 (I = 0.1 M)[a]	≥99.8%
$[Ca(NTA)]^{-}{}_{(aq)}$	6.44 (I = 0.1 M)[a]	0%
$[Ca(EDTA)]^{2-}{}_{(aq)}$	10.65 (I = 0.1 M)[a]	0%
$Ca(OH)_{2(s)}$	−5.29 (I = 0)[a]	≥99.8%
$CaCO_{3(s,calcite)}$	−8.48 (I = 0)[a]	0%

[a] Stability constants taken from Smith et al. (2004) (NIST database).

found in the nuclear wastes as ^{94}Nb and ^{93m}Nb but its behavior under mild alkaline conditions, like those found in long term nuclear waste repository, is still poorly understood (Pilkington and Stone, 1990; Deblonde et al., 2015b). The results given in Table 1 highlight that the solubility of Nb(V) could be driven by the calcium content of the ground water. It is interesting to note that, Talerico et al. (2004) reported that the presence of calcium in the background electrolyte decreases the solubility of Nb(V) under cementitious conditions but the authors could not identify the solid phase formed between niobium and calcium. A recent sorption study (Ervanne et al., 2014), also showed that the sorption of Nb(V) on clay minerals, at basic pH, increases when calcium ions are added to the background electrolyte. We previously showed (Deblonde et al., 2015b), that the solubility of Nb(V) and Ta(V), in $NaCl_{(aq)}$ or $KCl_{(aq)}$ at pH ≥ 10, is driven by the formation of the polyoxoanions $H_xNb_6O_{19}^{x-8}$ and $H_xTa_6O_{19}^{x-8}$ ($0 \leq x \leq 3$); the present study now reveals that the presence of calcium in the media could limit the dispersion of Nb(V) and Ta(V) in the environment.

From a hydrometallurgical process point of view, it should be mentioned that the precipitation of Nb with calcium hydroxide was slow (about 30 min) contrary to calcium chloride and calcium acetate with which the precipitation of Nb occurs at the second time scale. Regarding calcium carbonate, calcium NTA and the calcium EDTA the lack of precipitation is thought to be due to the low solubility of $CaCO_{3(s)}$ at high pH and due to the high stability of the calcium NTA and calcium EDTA complexes, respectively (Table 1). Nonetheless, these results could be helpful for hydrometallurgical processes and waste treatment since calcium hydroxide is a very inexpensive reagent. Moreover the recovery of Nb and Ta from alkaline solutions using $Ca(OH)_2$ regenerates NaOH or KOH present in the initial solutions.

3.4. Effect of the pH

The hexaniobate and hexatantalate ions, $H_xM_6O_{19}^{x-8}$ (M = Nb, Ta; $0 \leq x \leq 3$), can be triply, doubly, simply and non-protonated in the pH range 10–14 (Etxebarria et al., 1994; Deblonde et al., 2015a). Nonetheless, as given in Table 2, very high precipitation yields for Nb and Ta were observed in the pH range 9–13 while using a calcium-bearing reagent. This suggests that the precipitation method proposed in this paper can be operated in wide pH range, highlighting its robustness.

Table 2
Precipitation yield measured for Nb and Ta as a function of pH. T = 25 °C, I = 0.1 mol/L (KCl). $[Nb]_{ini} = 5.0 * 10^{-4}$ mol/L. $[Ta]_{ini} = 5.0 * 10^{-4}$ mol/L. $[Ca]_{ini}/[M]_{ini} = 0.75$ mol/mol (M = Nb, Ta).

pH	9.1	9.8	10.3	11.0	11.2	12.0	13.0
% precipitation Nb	98.9	99.0	99.6	≥99.8	≥99.8	≥99.8	≥99.8
pH	9.1	9.8	10.4	10.8	11.0	12.1	13.0
% precipitation Ta	≥99.8	≥99.8	≥99.8	≥99.8	≥99.8	≥99.8	≥99.8

3.5. Characterization of the amorphous Nb–Ca and Ta–Ca concentrates

The concentrates formed by precipitation of potassium hexaniobate or hexatantalate solutions with $CaCl_{2(aq)}$ in the presence of 0.1 mol/L KCl were characterized. Firstly, it should be mentioned that all the precipitates obtained at ambient temperature by addition of a calcium-bearing reagent ($CaCl_2$, $Ca(OH)_2$ or $Ca(CH_3COO)^+$) to an hexaniobate ions solution or hexatantalate solution were amorphous. The elemental analyses of the Nb–Ca concentrate revealed that the concentrate contains 40.2 ± 0.1 wt.% of niobium. These results show that precipitate with high niobium content can be obtained from low concentrated solutions by the method developed in the present study.

The ICP-OES analyses also revealed the presence of potassium in the Nb–Ca concentrate with a ratio K/Nb of 0.50 ± 0.01 mol/mol. The presence of potassium in the Nb–Ca provides information regarding the behavior of Nb(V) in alkaline solutions. Indeed, since less than a decade, the ion-pairs formation in hexaniobate solutions was found to be of primary importance, strongly influencing the solubility and acid–base properties of the $H_xNb_6O_{19}^{x-8}$ ions (Antonio et al., 2009; Fullmer et al., 2014; Deblonde et al., 2015a, 2015c). The first study on this effect was reported by Antonio et al. (2009), and the authors observed by small-angle X-ray scattering experiments that the fully deprotonated ion $Nb_6O_{19}^{8-}$ forms predominantly ion-pairs ($[K_8Nb_6O_{19}]$ or $[K_{10}Nb_6O_{19}]^{2+}$) in concentrated $KOH_{(aq)}$. In the study reported herein, the precipitation of $H_xNb_6O_{19}^{x-8}$ ions was investigated at pH ~11 and the mono-protonated species $HNb_6O_{19}^{7-}$ predominates at this pH (Etxebarria et al., 1994; Deblonde et al., 2015a). Hence, the presence of potassium in the Nb–Ca concentrate suggests that (i) the mono-protonated species $HNb_6O_{19}^{7-}$ also forms ion-pairs with potassium ions and (ii) the affinity of $HNb_6O_{19}^{7-}$ for calcium ions is stronger that for potassium ions. The influence of ion-pairing on the precipitation of $HNb_6O_{19}^{7-}$ by calcium ions was also confirmed by performing similar experiments in NaCl media (Fig. S2). Indeed, it is known that the ion-pairing effect follows the order Cs > Rb > K > Na > Li for hexaniobate ions. Figs. 1 and S2 show that a higher ratio Ca/Nb is needed in Na^+ media than in K^+ media for precipitating Nb quantitatively. This is in accordance with the fact that the ion-pair effect is lower in Na^+ media, thus more calcium ions are required to neutralize the charges of $[Na_xHNb_6O_{19}]^{x-7}$ compared to $[K_yHNb_6O_{19}]^{y-7}$.

Thermogravimetric analyses coupled with an MS detector in the emitted gas were also performed and revealed that the Nb–Ca concentrate releases its water at a temperature lower than 250 °C (Fig. 5). These results have to be compared with those generally obtained with the hydrated niobium pentoxide, $Nb_2O_5 \cdot nH_2O_{(s)}$. Indeed, $Nb_2O_5 \cdot nH_2O_{(s)}$ is obtained when neutralizing a Nb(V) solution at pH 2–7 (Inoue et al., 1985; Jehng and Wachs, 1991a). $Nb_2O_5 \cdot nH_2O_{(s)}$ is therefore obtained

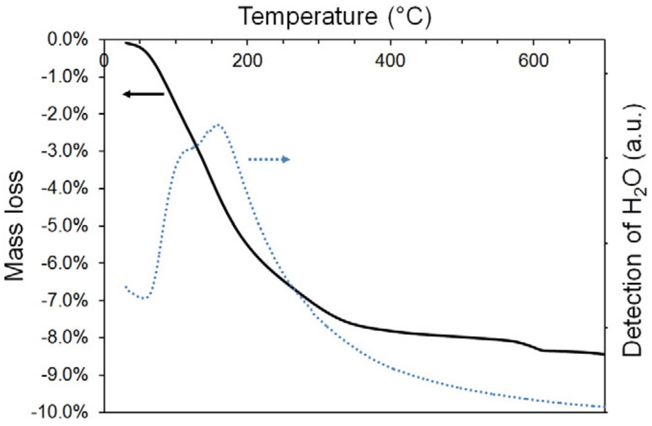

Fig. 5. TGA-MS analysis of the concentrate obtained by precipitation of a potassium hexaniobate solution with $CaCl_{2(aq)}$ at T = 25 °C, pH = 11 and I = 0.1 mol/L (KCl). Black curve: mass loss. Blue dotted curve: detection of H_2O in the emitted gas.

in several hydrometallurgical processes but this hydrated oxide exhibit a high water content and retains its water even at high temperature; up to 550 °C depending on the method of synthesis (Nikishina et al., 2012).

The Raman spectra of Nb–Ca and Ta–Ca concentrate were measured and compared with those of $Na_7HNb_6O_{19}\cdot 15H_2O_{(s)}$, $K_8Nb_6O_{19}\cdot 16H_2O_{(s)}$, $Cs_8Nb_6O_{19}\cdot 14H_2O_{(s)}$ and $Na_8Ta_6O_{19}\cdot 24.5H_2O_{(s)}$ (Figs. 6 and 7). The hexaniobate and hexatantalate compounds possess a strong and sharp Raman band in the high wavenumber range (800–950 cm^{-1}, depending on the counter-ion, see Fig. 6) due to the stretching modes of the NbO and TaO bonds, respectively. This sharp band is accompanied by another band of low intensity around 50 cm^{-1} lower owing to the MO antisymmetric stretching mode (MNb, Ta). In the intermediate wavenumber region, the Raman band at around 530 cm^{-1} is characteristic of the Nb–O–Nb (or Ta–O–Ta) symmetric stretching mode (Jehng and Wachs, 1991a). It is clear from Figs. 6 and 7 that the Nb–Ca and Ta–Ca concentrates contain bonds similar to those found in hexaniobate and hexatantalate alkali salts, suggesting that the hexametalate structure is retained when precipitating Nb and Ta with calcium.

It should be noted, that the Raman spectra of the Ca–Nb concentrate does not correspond to those of already known calcium niobates. For example, Jehng and Wachs (1991b) published the Raman spectra of a series of layered compounds, $KCa_2Na_{n-3}Nb_nO_{3n+1}$ ($3 \leq n \leq 5$). All of these potassium–calcium niobates exhibit a very sharp Raman band at 930 cm^{-1} compared to 908 cm^{-1} for the Ca–Nb concentrate described in the present study.

Based on several Nb compounds, Hardcastle and Wachs (1991) have developed an empirical correlation between the Nb–O bond length and the corresponding Raman frequency. We applied their correlation to the Nb–Ca concentrate obtained by precipitation of a potassium hexaniobate solution with calcium acetate, and we also compared it to the hexaniobate alkali salts (Na, K, Cs), whose crystallographic structures are known (Fig. 8) (Nyman et al., 2006; Anderson et al., 2007).

The NbO and Nb–O–Nb bond lengths calculated for Ca–Nb concentrate are 1.749 and 2.027 Å, respectively. These calculated values are close to those previously determined for $Na_7HNb_6O_{19}\cdot 15H_2O$, $K_8Nb_6O_{19}\cdot 16H_2O$ and $Cs_8Nb_6O_{19}\cdot 14H_2O$ by XRD. It is interesting to note that the terminal NbO bond length follows the series Ca < Na < K < Cs, i.e. that the NbO bonds shorten when the charge to ionic radius ratio of the counter-ion increases. A similar trend for the TaO bonds can be deduced when comparing the Raman spectra given in Figs. 6 and 7.

On the basis of the precipitation studies, the elemental analysis, the ATG analysis and Raman study of Nb–Ca precipitate, we propose the following reaction for the precipitation of hexaniobate solutions with a calcium-bearing reagent (at pH ~11):

$$HNb_6O_{19\ (aq)}^{7-} + y\,Ca^{2+} + z\,K^{+} = K_zCa_y(H_xNb_6O_{19})\cdot nH_2O_{(s)} + (1-x)H^{+}. \quad (2)$$

With: x = 0.6, y = 2.2, z = 3.0 and n = 5.2.

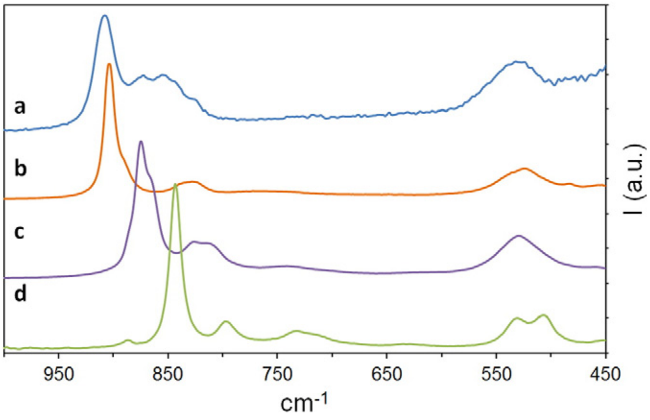

Fig. 6. (a) Raman spectrum of the Nb concentrate obtained by the precipitation of a potassium hexaniobate solution with a calcium acetate solution at pH = 11, T = 25 °C and I = 0.1 mol/L (KCl). (b) Raman spectrum of $Na_7HNb_6O_{19}\cdot 15H_2O_{(s)}$. (c) Raman spectrum of $K_8Nb_6O_{19}\cdot 16H_2O_{(s)}$. (d) Raman spectrum of $Cs_8Nb_6O_{19}\cdot 14H_2O_{(s)}$.

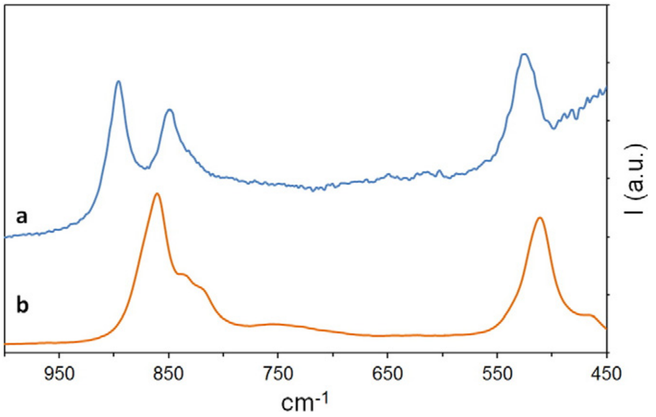

Fig. 7. (a) Raman spectrum of the Ta concentrate obtained by the precipitation of a sodium hexatantalate solution with a calcium acetate solution at pH = 11, T = 25 °C and I = 0.1 mol/L (KCl). (b) Raman spectrum of $Na_8Ta_6O_{19}\cdot 24.5H_2O_{(s)}$.

The fact that the sum of the charges brought by K^+ and Ca^{2+} equals 7.4 (±0.1) and not 7.0, as we might expect for the neutralization of $HNb_6O_{19}^{7-}$, is in accordance with the experimental observations where we noticed a small decrease of the pH when precipitating the $HNb_6O_{19}^{7-}$ solutions. It is also worth noting that the presence of proton, potassium and calcium in the Nb–Ca concentrate could lead to the formation of several isomers which might explain why we only obtained amorphous precipitates. Taking into account the precipitation of $K_3Ca_{2.2}(H_{0.6}Nb_6O_{19})\cdot nH_2O$, we calculated the apparent formation constant related to Eq. (2). Under the conditions given in Fig. 4, log K(25 °C) = 12.7 (±0.2). This value was used to model the precipitation curve obtained for niobium as depicted in Fig. 4.

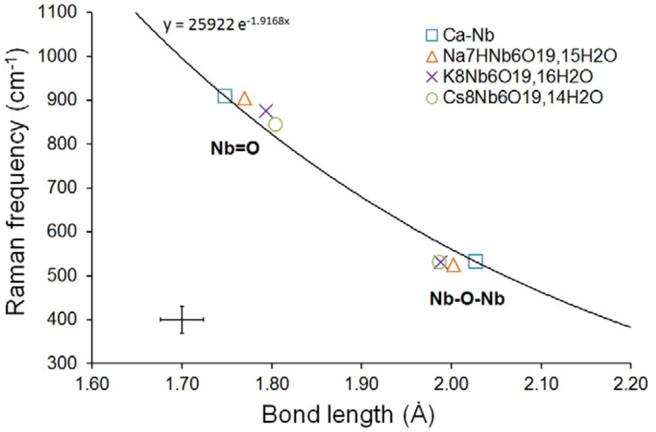

Fig. 8. Calculated Nb–O bond length for the Ca–Nb concentrate obtained by the precipitation of a potassium hexaniobate solution with a calcium acetate solution at pH = 11, T = 25 °C and I = 0.1 mol/L (KCl). The bond lengths were calculated using Hardcastle and Wachs' correlation ($y = 25{,}922 * \exp(-1.9168 * x)$) and the Raman bands given in Fig. 6. The experimental Raman frequencies (this work) and bond lengths (Nyman et al., 2006; Anderson et al., 2007) for $Na_7HNb_6O_{19}\cdot 15H_2O$ (triangles), $K_8Nb_6O_{19}\cdot 16H_2O$ (crosses) and $Cs_8Nb_6O_{19}\cdot 14H_2O$ (circles) are given for comparison. The errors bars on the bottom left of the graph represent the uncertainties of the correlation given by Hardcastle and Wachs (1991).

4. Conclusion

The recovery of niobium and tantalum from alkaline solutions has been investigated. We showed that, instead of neutralizing the Nb and Ta solutions by mineral acids, calcium-bearing reagents can be used to quantitatively precipitate Nb and Ta. Calcium chloride, calcium acetate and calcium hydroxide were found to be efficient at precipitating Nb and Ta. High precipitation yields were obtained in a wide pH range and even for low concentrated solutions highlighting its potential use in industrial processes. The ICP-OES, ATG-MS and Raman analyses of the Nb–Ca concentrate suggest that the precipitate is an hydrated potassium–calcium-hexaniobate, $K_3Ca_{2.3}(H_{0.6}Nb_6O_{19})\cdot 5H_2O$. Future works will aim at determining if the precipitate synthesized by the present method has any interesting photocatalytic properties as it is the case for other calcium-niobates.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.hydromet.2015.12.009.

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