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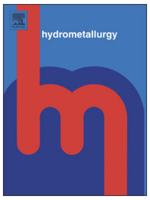

Direct precipitation of niobium and tantalum from alkaline solutions using calcium-bearing reagents

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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).

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

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 ($R > 18.2 * 10^6\ \Omega$). $Ca(CH_3COO)_2 \cdot H_2O$ (≥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

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