



Non-fluoride dissolution of tantalum and niobium oxides and their separation using ion exchange



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ABSTRACT

The study involved the separation of Ta and Nb in a phosphate matrix using ion exchange chromatography. Experimental variations included different types of Ta/Nb containing samples, types of resin, phosphoric acid concentration as eluent, flow rate and column dimensions. Experimental conditions were developed and refined using a pure 1:1 (Ta/Nb)₂O₅ synthetic mixture and the optimum conditions were then applied to a real tantalite mineral sample. Experimental results indicated the successful separation of the Ta and Nb in the synthetic sample using the weak basic Dowex Mathon and Dowex 66 free base resins. Almost complete recovery of Nb was achieved with 200 mL of 8 M H₃PO₄. It was found that Ta was more strongly absorbed but by using a stronger acid concentration of 10 M H₃PO₄, almost complete recovery was also obtained for Ta. Excellent elemental separation ($\alpha = 11.5$) and recoveries were also obtained with tantalite mineral as sample under identical experimental conditions. Almost complete recoveries for both Nb and Ta were obtained after elution with 8.0 M and 10.0 M H₃PO₄ respectively. Apart from the complete separation of Ta and Nb, minor elements which are also present in tantalite like Fe, Mn and U could also be successfully separated and quantitatively recovered. However, the Nb fraction was contaminated with Ti because under these conditions these two elements are simultaneously eluted.

The successful separation and recovery of both Ta and Nb from a phosphate matrix suggest a possible alternative to the conventional fluoride beneficiation methods. This method also has the potential of industrial applications.

1. Introduction

Niobium and tantalum are conjugate in natural mineral deposits and are mainly present as metal oxides. The chemical similarities of the two oxides, such as their high resistance to chemical attack and their nearly identical atomic radii, complicate the separation of the two elements. The most important Ta/Nb minerals include columbite (Mn,Fe)(Nb,Ta)₂O₆ containing 40 to 78% Nb₂O₅ and tantalite (Mn,Fe)(Ta,Nb)₂O₆ containing 38 to 86% Ta₂O₅ (Angulyansky, 2004).

One of the most important chemistry features of the two metals is the dominance of their halogen chemistry (Angulyansky, 2004) and its application in the isolation, separation and purification of the two elements. The chlorination (Cl₂ and HCl) and fluorination (HF, NH₄F·HF, KF and KF·HF) (Angulyansky, 2004; Conte et al., 1997; Grebneva et al., 1997; Nete et al., 2014a; Uria et al., 1987) of the minerals introduce sufficient modifications in the chemistry of the two elements to allow for their separation. The chlorination of the two elements produces (Ta/Nb)Cl_{5(g)} which is separated by fractional

distillation while the fluorination produces heptafluorotantalato and oxypentafluoronioobato complexes which are separated with solvent extraction or selective crystallization. The fluorination of the ores led to the development of the first successful industrial separation process in 1866 (Marignac process) (Angulyansky, 2004), which included the fractional crystallization and the subsequent separation of the two elements as potassium heptafluorotantalate and potassium oxypentafluoronioobate (Angulyansky, 2004; Roskill Information, 2005). The process was troubled with low recoveries or product contamination. In 1957 this separation process was replaced by the liquid-liquid extraction process developed by Ames Laboratory and the US Bureau of Mines (Angulyansky, 2004), which utilized the solubility differences of TaF₇²⁻/NbOF₅²⁻ anions in different organic solvents to separate the two elements. Despite the huge success of the fluoride dissolution and subsequent separation of Ta and Nb, this technique has several disadvantages which include the generation of an environmentally harmful HF gas during dissolution and the difficult to handle hydrofluoric acid in aqueous solutions.

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Several research reports, however, describe the successful dissolution of the minerals or the pure metal oxides by non-halogen methods. Nete et al. (2010) reported the successful fusion dissolution of tantalite using $\text{Li}_2\text{B}_3\text{O}_7$ as flux while Radhamani et al. (2010) showed that a combination of mono and disodium hydrogen phosphate as fluxing agent was successful in dissolving Ta and Nb minerals. A study by Koko (2013) found that the dissolution of a tantalite/ $(\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O})$ melt in dilute HCl, HNO_3 and H_2SO_4 was accompanied with immediate precipitate formation. Hahn (1951) suggested the possible formation of linear polyphosphates (TaOPO_4 and NbOPO_4) when phosphoric and nitric acids were added to potassium niobate or tantalate solutions which was supported by Radhamani et al. (2010). Yaroslavtsev and Nikolaev (1995) dissolved Ta_2O_5 with fusion using KH_2PO_4 as flux and isolated $\text{KTa}(\text{PO}_4)_2$. The melt was dissolved in dilute HCl and H_3PO_4 , to produce $\text{HTa}(\text{PO}_4)_2\cdot 2\text{H}_2\text{O}$, which was later evaluated as a possible ion exchange resin for the separation of alkaline and alkaline earth elements (Na^+ , K^+ and Ba^{+2}) (Tarnopolskii et al., 2000; Yaroslavtsev and Nikolaev, 1995).

Only a few studies reported the possible successful separation of the two elements in non-halogen environments. Schoeller and Powell (1955) succeeded in precipitating Nb and Ta (with Ti and W) with tannic acid in a slightly acidic solution. Milner et al. (1955) successfully separated Nb and Ta using sulphosalicylic acid at a pH = 0.5, while Sankar Das et al. (1956) isolated the two elements (with Ti, Sn, Pb, and W) with a combination of tannin and EDTA. Research also indicated that a number of organic precipitants such as cupferron (Majumdar and Ray Chowdhury, 1958), *N*-benzoyl-*N*-phenyl-hydroxylamine (Moshier and Schwarberg, 1957) and *n*-propylarsonic acid (Majumdar and Ray Chowdhury, 1958) were utilized to isolate Nb and Ta with some affording good separation. A recent study (Nete et al., 2016) investigated the separation of Ta and Nb in phosphate matrix by elution using different cationic exchange but no separation was achieved with the investigated resins. The difficulty experienced with the non-halogen Ta/Nb separation of the two elements are attributed to their formation of complex metal ions and their hydrolyzation in water which does not introduce sufficient differences in their chemical and physical properties for separation.

The overall objective of this study was to develop an alternative, non-halogen separation process for Ta and Nb which is less corrosive and toxic and more environmentally friendly and may have industrial applications. A previous investigation (Nete et al., 2014b) confirmed the similarity of the chemistry of the pure oxides and that of the elements in the minerals, confirming the use of the pure metal oxides as model systems to investigate different aspects of the dissolution and separation of the two elements. The different aims of the current study include i) dissolution of a pure $(\text{Ta/Nb})_2\text{O}_5$ mixture using a phosphate flux fusion and refinement of the experimental conditions for ion exchange separation using different resins and ii) evaluation of the separation of the two elements in tantalite minerals using the optimal experimental conditions.

2. Experimental

2.1. Reagents and equipment

High purity Ta_2O_5 (99.99%), Nb_2O_5 (99.9%), as well a tantalite sample from the Naquissupa mine in Mozambique were supplied by the South African Nuclear Energy Corporation SOC Ltd. (Necsa). Na_2HPO_4 , $\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$, the weakly basic Dowex marathon resin (26–32 mesh), the Dowex 66 free base (50–125 mesh) resin, the strongly basic Amberlite IRA-900 (16–50 mesh) resin as well as the Amberlite IRA 402 (20–25 mesh) exchange resins were bought from Sigma Aldrich. Analytical grade H_3PO_4 (85%) was purchased from Associated Chemical Enterprises. All solutions were prepared using ultra-pure water produced by a Milli-Q integral water purification system (conductivity = 0.02 mS/cm). Properties of the anion exchange resins

Table 1
Types of anion exchange resins investigated and their properties.

Resin trade name	Type of resin	Functional group	Exchange capacity (eq/L)
Dowex marathon wba	Weakly basic anion exchanger	Tertiary amine	1.3
Dowex 66 free base	Weakly basic anion exchanger	Tertiary amine	1.60
Amberlite IRA-900	Strongly basic anion exchanger	Quaternary ammonium	≥ 1.00
Amberlite IRA-402	Strongly basic anion exchanger	Quaternary ammonium	≥ 1.20

investigated are given in Table 1.

Flux fusion digestions were performed in a Thermo Scientific Thermolyne Compact Bench top Muffle Furnace. A glass burette with a 1.2 cm internal diameter and 50 cm length was used as the column for the separation of Ta and Nb using the different ion exchange resins. Infrared spectra were obtained using a Scimitar Series Digilab spectrometer. Ta and Nb quantifications were performed using a Shimadzu ICPS-7510 ICP-OES sequential plasma spectrometer. The ICP operating parameters for quantification and recovery of the tantalum and niobium were as follows: RF power 1.2 kW, coolant gas flow 14.0 L/min, plasma gas flow 1.2 L/min, carrier gas flow 0.7 L/min. All determinations were performed at Ta and Nb wavelengths of 240.068 nm and 309.418 nm respectively.

2.2. Preparation of Ta/Nb phosphate solutions

A synthetic mixture of Ta_2O_5 and Nb_2O_5 was prepared by accurately weighing approximately equal amounts (~0.1 g) of each salt and homogeneously mixing it with $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$ mixture to yield a 1:16 sample:flux $(\text{Ta/Nb})_2\text{O}_5$:phosphate mixture mass ratio in a platinum crucible. The sample/flux mixture in this phosphate matrix was fused at 800 °C for 30 min and the clear melt was cooled to room temperature and dissolved with 30 mL water. The solution was quantitatively transferred to a 100.0 mL volumetric flask and filled to the mark with water. The tantalite sample obtained from the mine in Mozambique was prepared in a similar manner.

2.3. Separation of Ta and Nb by ion exchange

Different anionic exchange resins (~10 g) were separately added to a 0.5 M H_3PO_4 solution in a 250 mL beaker and stirred to form free flowing slurry. The slurry was transferred to the column of 1.2 cm internal diameter and was packed to a height of 20 cm. A 5.0 mL aliquot of the phosphate sample solution (from Section 2.2) was transferred to the column and sequentially eluted with 200 mL of 8.0 M H_3PO_4 followed by 250 mL 10.0 M H_3PO_4 at a rate of 0.7 mL/min. The effluent volumes were collected in 100.0 mL volumetric flask in 10 mL fractions. The acidity of the solution was adjusted using 85% H_3PO_4 , to match as closely as possible the standard solutions' matrix, before filling to the mark with water. Each of these fractions was analysed by ICP-OES. The separation of Ta and Nb in a complex tantalite mineral matrix was evaluated with phosphoric acid concentrations ranging from 0.5 M to 10.0 M. The ion exchange separation procedure was performed in triplicates and the recoveries (or in other words the extraction or elution efficiency), with their standard deviation values, are presented and the values reported are based on the average of three different measurements with the ICP-OES. The total recovery of Ta and Nb was calculated by adding up the amount of Ta and Nb in each of the 10 mL fractions that were eluted from the column and by expressing this total as a percentage of the amount of Ta or Nb in the original, starting solution.

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