



Separation and isolation of tantalum and niobium from tantalite using solvent extraction and ion exchange



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ABSTRACT

A step-wise separation process for niobium and tantalum from tantalite by extraction and ion exchange was developed. A tantalite mineral was dissolved by a fusion technique using ammonium bifluoride as flux. Tantalum and niobium form stable anionic fluoride complexes in fluoride solutions. This fact was used to develop an analytical method to separate tantalum and niobium from other metals within the tantalite mineral and from each other.

Tantalum was separated from the rest of the mineral matrix by solvent extraction using methyl isoamyl ketone. The analytical results indicated that 98.9(9)% Ta₂O₅ was recovered from the organic portion while 101.6(3)% Nb₂O₅ and the rest of the elements were recovered from the aqueous solution. Niobium was subsequently separated from the tantalite matrix by anion exchange technique using Dowex Marathon resin and HCl solution as a mobile solvent. The analytical results indicated Nb₂O₅ recovery of 101(2)%.
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1. Introduction

Tantalum and niobium are frequently found together in nature and are simultaneously extracted from a variety of minerals (Roskill Information 10th ed., 2005a). The most abundant Nb and Ta containing mineral is columbite–tantalite (Fe,Mn)(Nb,Ta)₂O₆. The Nb rich mineral columbite normally contains 5–30% Ta₂O₅ and 55–78% Nb₂O₅ while the most abundant Ta containing mineral tantalite contains 42–84% Ta₂O₅ and 2–40% Nb₂O₅. Another important source of Nb is pyrochlore (Ce,Ca,Y)₂(Nb,Ta)₂O₆(OH,F) with the Nb₂O₅ content between 37 and 66% and Ta₂O₅ content up to 6% (Agulyansky, 2004). The two elements are also present in a large number of other minerals (more than 150), either as main elements or as impurities, which include ilmenorutile Fe_x(Ta,Nb)_{2x}4Ti_{1-x}O₂ (Mineral Data Publishing, 2001–2005) tapiolite (Fe,Mn)(Ta,Nb)₂O₆ (Agulyansky, 2004; Kabangu and Crouse, 2012) and wodginite (Ta,Nb,Sn,Mn,Fe)O₂ (Kabangu and Crouse, 2012). The two elements naturally occur as the metal oxides (M₂O₅ (Roskill Information 9th ed., 2005b) or hydroxides in the majority of these minerals, with the exception of the borate mineral behierite (Ta,Nb)(BO₄) and the only known non-oxide mineral, tantalum carbide (TaC) (Ta–Tantalum, 2011).

The chemical separation or purification of Ta and Nb from their minerals is a complex and difficult process. This is mainly due to the chemical and physical similarities of the two elements such as their ionic radii, resistance to chemical attack and the ease with which their

compounds are hydrolyzed in aqueous solutions (Morrison and Freiser, 1962). The two elements are also present as the metal pentoxides, M₂O₅, in most of the natural minerals. These oxides are well-known for their chemical inertness and it is the formation of thin metal oxide layers on the metal surface of both Ta and Nb, which give these metals their extremely good anti-corrosive properties.

The commercially successful processes used to separate Nb and Ta from one another (Ta/Nb)₂O₅ are related to the Marignac process (Agulyansky, 2004; Roskill Information 10th ed., 2005a; Roskill Information 9th ed., 2005b; Singh, 2001) and the alternative process developed by the U.S. Bureau of Mines and Ames Laboratory of Iowa State University in the 1950s (Agulyansky, 2004; Roskill Information 9th ed., 2005b). The separation in both the processes ultimately involves the complexation of the two metal ions with the smaller fluoride anions (F⁻) during the dissolution from the mineral (Conte et al., 1997; Gaur and Mendenhall, 2007; Grebneva et al., 1997; Hall et al., 1990; Uria et al., 1987) (Eq. (1)).



The differences in the chemical and physical properties of newly formed fluoride complexes allow the separation of the two elements. In the Marignac process KF or KCl is added to the reaction mixture after the mineral's successful dissolution (Eq. (1)) (Singh, 2001) and a mixture of K-salts (K₂TaF₇ and K₂NbOF₅) is produced. Ta is initially separated from Nb by the selective crystallization of the less soluble

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K_2TaF_7 salt. Separation of the two metal compounds is achieved by solvent decantation and the subsequent crystallization of K_2NbOF_5 by further concentration, or its reaction with NH_3 to produce Nb_2O_5 . This method is excellent for the production of a relatively pure Ta compound (Gaur and Mendenhall, 2007). The Nb compounds obtained by the Marignac process are always contaminated with titanium (Okada, 2001).

The Ames Laboratory process (Agulyansky, 2004) achieves separation with solvent extraction. This process utilizes the selective extraction of the two metals at high acid concentrations (greater than 8 M H_2SO_4) using organic solvents such as methyl isobutyl ketone (MIBK), tributyl phosphate (TBP) cyclohexane and 2-octanol. In this process the Ta/Nb containing minerals is initially treated with HF/conc H_2SO_4 at elevated temperatures. The Nb/Ta fluoro complexes and some impurities are dissolved and separated from the remaining insoluble matter by filtration. The two metals are subsequently extracted via a continuous process into the organic solvent at these high acid levels, leaving the remaining impurities in the aqueous layer. Niobium is then separated from the Ta by reducing the acidic levels (3–7.5 M H_2SO_4) during which the Nb fluoro complex is back-extracted into the fresh aqueous layer, leaving the Ta in the organic layer. The Ta fluoro complex is finally extracted from the organic layer into the aqueous layer at low acid concentrations (~pH 7 using only water).

Another highly successful separation method, which has merit in producing high purity Nb, involves chlorination of the raw materials (Eq. (2)) followed by the distillation of the resultant Nb and Ta chloride complexes. The pentachloride compounds (Ta/Nb) Cl_5 are separated via distillation (b.p.'s for $TaCl_5 = 236^\circ C$ and $NbCl_5 = 248^\circ C$) (Agulyansky, 2004; Sadoway and Flengas, 1980).



The distillation process produces good separations with relatively pure products. Bayot and Devillers (2006) indicated that the resulting $NbCl_5$ obtained from a ferro-niobium alloy (or Nb scrap) contained less than 5 mg/L Ta and 1 to 2 mg/L other metallic impurities. This method of separation requires sophisticated equipment to avoid loss of volatile compounds of interest and is more suitable for synthetic concentrates (such as alloys) with high Nb content. Complex matrices containing a large number of elements normally complicate the purification process through contamination due to similar physical properties such as boiling points. A study (Gaballah et al., 1997) on the chlorination of Ta and Nb oxides in tin slag indicated that approximately 95% Ta and Nb compounds were extracted from the low grade concentrate (LGC = tin slag leached with HCl prior to chlorination) at $1000^\circ C$. The Ta and Nb products, however, contained significant concentrations of other metal chlorides such as Fe, Mn and Al. Chlorination of the high grade concentrate (tin slag leached with HCl followed by NaOH prior to chlorination) on the other hand produced ~84% Nb and 65% Ta compounds of a relatively high purity under similar experimental conditions ($1000^\circ C$). A combination of acid and base leaching (for production of high-grade concentrate) was found to be highly effective for the removal of the oxides of Fe, Mn, Al, and Ca leading to purer Ta and Nb distillation products.

Thus, complex formation is vital for the successful separation of Ta and Nb from their mineral ores. HF has extensively been used as both a dissolution and complexing agent, but properties such as toxicity to humans and the environment make it an unpopular and dangerous chemical to be used for the beneficiation of minerals such as tantalite. Recent research demonstrated the success of $NH_4F \cdot HF$ as dissolution agent for Ta/Nb containing minerals (Nete et al., 2014). The ICP-OES analysis of the major elements in two different tantalite minerals, using lithium tetraborate (LTB), Na_2HPO_4/NaH_2PO_4 and $NH_4F \cdot HF$ as dissolution methods, indicated the efficiency of $NH_4F \cdot HF$ as dissolution agent. The Nb recovery (Nb_2O_5) was 98.76% using $NH_4F \cdot HF$ as flux compared to the 101.16 and 103.14% for LTB and phosphate fluxes while Ta_2O_5 recoveries of 100.29, 102.16 and 99.89% were obtained for

$NH_4F \cdot HF$, LTB and phosphate as fluxes (Nete et al., 2012). The potential for Nb and Ta separation, using $NH_4F \cdot HF$ and MIBK as extractant, was reported by Gaur and Mendenhall (2007). The results obtained in that study indicated that 59% of Ta were extracted into the MIBK solution.

The aim of the current research is to evaluate the separation of Ta and Nb from a tantalite matrix using the less dangerous $NH_4F \cdot HF$ salt (flux) as dissolution and complexing agent. The extraction efficiency of both Ta and Nb as a factor of $[H_2SO_4]$ is evaluated. Different organic solvent extractants are tested and include methyl-isopropyl ketone (MIPK), methyl isoamyl ketone (MIAK), 4-heptanone (4-hept) and 1-octanol (1-oct), with the subsequent separation of Nb from other impurities using ion exchange chromatography.

2. Experimental

2.1. Reagents and equipment

A tantalite sample (Sample A) from Mozambique was supplied by the South African Nuclear Energy Corporation Limited (Necsa). Previous chemical analysis of Sample A (Nete et al., 2012) indicated the presence of 27.8(3)% Ta_2O_5 and 27.0(2)% Nb_2O_5 . Other impurities included 2.77(2), TiO_2 , 8.91(7), Mn_3O_4 , 8.3(2), Fe_2O_3 , 1.64(3), SnO_2 , 2.04(6) Al_2O_3 , 3.5(1) SiO_2 , 0.54(2) ThO_2 , 2.81(2) U_3O_8 and 1.18(2)% WO_3 . A strong basic anion exchanger, Amberlite IRA-900 (16–50 mesh), as well as a weak basic anion exchanger Dowex Marathon (350–450 μm), were purchased from Sigma Aldrich. High purity ammonium bifluoride ($NH_4F \cdot HF$) was sourced from Merck. ICP standard solutions containing 1000 mg/L Ta, Nb, Ti, Sn, W, and Si as well as multi-element standard No. XXVI containing 1000 mg/L each of Mn, Al, Fe and Ca were also bought from Merck. ICP standard solutions containing 1000 mg/L Th and U were bought from De Bruyn Spectroscopic. Methyl isobutyl ketone, methyl isopentyl ketone, 4-heptanone, 1-octanol and methyl isoamyl ketone were also procured from Merck and used as received. Analytical grade HCl (32%) and H_2SO_4 (97%) were bought from Associated Chemical Enterprises. Double distilled water was used in all investigations.

Samples were weighed using a Shimadzu AW220 analytical balance while the flux fusions were performed in a Thermo Scientific Thermolyne Compact Benchtop Muffle Furnace using a Pt crucible. Grade B glass and PTFE volumetric flasks bought from Merck and Boeco SP series adjustable volume pipettes were used for sample preparations. A Shimadzu ICPS-7510 ICP-OES sequential plasma spectrometer was used for the elemental analysis of the sample solutions. The distribution ratio (D) and the separation factor (α) were calculated from the actual concentration values (mg/L) of the elements as determined by ICP-OES analysis but only the average D and α values are reported due to the fact that different masses were weighed. All the results are reported as the percentage metal oxides of the most stable oxidation state of the elements for comparison purposes. The average values for the results are reported based on the standard deviations to indicate the uncertainty in the last digit of the value throughout this paper. The % metal oxide recovery as well as standard deviations is based on the triplicate analyses of different weighed mineral samples.

2.2. Analytical procedures

2.2.1. Preparation of ICP-OES calibration solutions and measurements

Standard solutions for ICP-OES analysis were prepared in 100.0 mL volumetric flasks. Appropriate volumes of the 1000 ppm metal stock, fused flux and acid solutions were added in 100.0 mL volumetric flasks and diluted to the mark with double distilled water to ensure matrix matching. Calibration standards with concentrations 1.0, 3.0, 5.0, 7.0, and 10.0 ppm were prepared. The blank solution was prepared by diluting 5.0 mL solution of fused flux and 10.0 mL 97% H_2SO_4 with double distilled water in a 100.0 mL volumetric flask. Quantitative analyses were performed at 309.418 and 240.063 nm spectral emission lines

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