NIOBIUM AND TANTALUM BENEFICIATION FROM TANTALITE ORE

by

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DECLARATION

I declare that the dissertation hereby submitted by me for the M.Sc degree at the University of the Orange Free State is my own independent work and has not previously been submitted by me at another university/faculty. I further more cede copyright of the dissertation in favour of the University of the Free State.

Fanie Koko

28/11/2013

Date

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Table of Contents

List of Figures

List of Tables

Keywords

Radioactive
Tantalite A
Digestion
Leaching
Beneficiation
Dissolution
Separation
Precipitation
Recovery
Regulations
Flux

List of abbreviations

Bq/g	Becquerel per gram
Bq/kg	Becquerel per kilogram
kBq	kiloBecquerel
Sv	Sievert
mSv/h	milliSievert per hour
mSv/yr	milliSievert per year
µSv/h	microSievert per hour
mg/kg	milligram per kilogram
Ci	Curie
nm	nanometer
K	Kelvin temperature scale
REE	Rare earth elements
CRM	Certified Reference Material
LOD	Limit of detection
LOQ	Limit of quantification
NORM	Naturally occurring radioactive material

Ligands and solvents

Me	Methyl
R	Alkyl group
Ph	Phenyl group
M	Nb and/or Ta

η^2-*t*Bupz	η^2-Tertiary Butyl pyrazolyl
X	Halogen (F, Cl, I, Br)
Thd	2,2,6,6-Tetramethyl-3,5-heptanedionate
Dmpe	1,2-*Bis* (dimethylphosphino) ethane
Py	Pyridine
Pr	Propyl
Diphos	1,2-*Bis*(diphenylphosphino)ethane
THF	Tetrahydrofuran
EDTA	Ethylenediaminetetraacetic acid
MIBK	Methyl isobutyl ketone
TBP	Tetrabutyl phosphate

Instrumentation

ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometer
ICP-MS	Inductively Coupled Plasma Mass Spectrometer
AA	Atomic Absorption
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
FAAS	Flame Atomic Absorption Spectroscopy
EDXRF	Energy Dispersive X-ray Fluorescence
SEM	Scanning Electron Microscope
EDXS	Energy Dispersive X-ray Spectroscopy
UV-vis	Ultra Violet - visible range
IR	Infrared

1 Background and motivation of the study

1.1 Study Motivation

The demand for niobium and tantalum and their compounds is increasing as new applications are found for the two metals. The inertness and corrosion resistance of the metals make them suitable for high temperature reactors and the refractory nature of niobium also finds use as a component in alloys. The major use of tantalum is in the capacitor manufacturing whereby purity of tantalum plays a major role as high purity tantalum powder is a requirement while niobium is largely consumed in the steel industry. The combination of high mechanical strength, high melting point and high index of refraction renders them ideal in the making of heat exchangers and games consoles and the electrical resistance of niobium alloys necessitates its use in particle physics experiments. The production of high quality niobium and tantalum compounds depends on the quality control of the starting material. HF is the only acid that readily dissolves both tantalum and tantalum pentoxides. This method works well, but has two main disadvantages, namely its extreme toxicity towards humans and the issue of disposing of HF-containing waste in an environmentally friendly manner. Despite this, HF dissolution is still a part of every industrial tantalum/niobium refining process.

South Africa does not have substantial reserves of niobium/tantalum minerals, but its neighbours such as Mozambique, Zimbabwe and Namibia and Uganda do have substantial reserves. These countries do not possess the necessary technological know-how of processing these minerals which necessitates the exportation of the mineral overseas for its beneficiation. The Department of Science and Technology (DST) in South Africa has identified the need to form a centre of excellence which will include the study of materials such as hard metals, metal alloys, metal oxides, ceramics, diamond and diamond-like materials and composites including carbon nanotubes.[1] This will be done as part of the development of these industries to add

[1] http://www.dst.gov.za/index.php/services/centres-of-excellence/strong-materials 20-03-2012

value not only to the country`s own mineral resource, but also to that of neighbouring countries. Niobium and tantalum fall into DST`s category for the development of skills and knowledge with the aim of the establishment of relevant industries in the country.

This project will build on studies done by Nete *et al.*[2] and Theron *et al.*[3] In these studies, the quantification and dissolution of niobium and tantalum in various materials were undertaken. Nete was successful in dissolving and accurately analyzing niobium in pure compounds and niobium containing minerals. Theron was successful in dissolving and analyzing tantalum compounds and magnetically removing iron and titanium from one of the tantalite minerals obtained from Mozambique. Analysis of the mineral samples in both studies was done using the inductively coupled plasma optical emission spectroscopy (ICP-OES), with X-ray fluorescence (XRF) that was used only by Nete.

Table 1.1: Chemical analyses of tantalite samples[2]

Metal oxide	Minerals		
	Tantalite A	Tantalite B	Sample 1
	%	%	%
Ta_2O_5	30.08	32.63	33.00
Nb_2O_5	27.01	15.72	8.74
ThO_2	0.54	0.41	0.29
U_3O_8	2.81	1.20	0.14
Al_2O_3	2.04	2.55	1.47
SiO_2	3.52	10.99	2.51
WO_3	1.18	0.61	0.16
TiO_2	2.77	6.50	8.19
Mn_3O_4	8.91	7.62	3.13
Fe_2O_3	8.34	7.01	18.71
SnO_2	1.64	2.91	0.15
Y_2O_3	...	...	0.24
CaO	...	...	0.52

... = below detection limit

[2] Nete, M. (2009). *Dissolution and analytical characterization of tantalite ore, niobium metal and other niobium compounds.* (M.Sc thesis), University of the Free State

[3] Theron, T. A. (2010). *Quantification of tantalum in series of tantalum-containing compounds.* (M.Sc thesis). University of the Free State

The chemical analyses (see **Table 1.1**) of the three different tantalite samples obtained from Mozambique clearly indicate the presence of two radioactive elements, thorium and uranium, in the samples. The presence of these naturally occurring radioactive materials (NORMs) poses difficult problems with the handling and processing of large quantities of these minerals as well as its transportation across international borders and within the country. The storage of the possible radioactive waste also poses another challenge for the beneficiators of niobium and tantalum using these types of minerals. The mineral sample under study, as characterised by Nete, was found to be composed of manganotantalite, microlite ($(Na,Ca)_2Ta_2O_6(O,OH,F)$), euxenite ($(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$), quartz ($SiO_2$), mica ($KAl_2(Si_3Al)O_{10}(OH,F)_2$), garnet ($(Mg,Fe,Ca)_3$-$(Al,Fe^{3+},Cr)_2(SiO_4)_3$) and tourmaline ($(Na,Ca)(Mg,Li,Al,Fe^{2+})_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$). Comparison with other minerals with similar composition indicated that the mineral's radioactivity is due to the presence of euxenite.

The transportation and handling of such minerals is subject to strict national and international regulatory laws such as the National Nuclear Regulator Act, 1999 (Act No. 47 of 1999), which regulates the handling which includes the removal of the radioactive material from the mineral before further processing which will be discussed in more detail in Chapter 3.[4] This sample is classified as a Class 7 material. According to this legislation, when the specific activity of each radioactive nuclide in radioactive material is 0,2 Bq/g and below, the provisions of the act do not apply and when the total radioactivity exceeds 0.5 Bq/g, a license has to be obtained from the National Nuclear Regulator to handle such material in large quantities. One of the clauses within the legislation also prescribe that the maximum radiation level permitted at 1 meter from the material source or container to be 0.4 mSv/h when it is being transported.

The presence of uranium and thorium doesn't affect the administration part of processing them only, but also the operational part as well. The processing plant must for example, not be constructed in such a way that the workers and the surroundings are exposed to amounts of radiation that exceed the limitations. The

[4] http://www.energy.gov.za/files/policies/act_nuclear_47_1999.pdf 20-03-2012

waste generated and its disposal is also a major concern. Waste with a specific activity less than 100 Bq/g and total activity less than 4 kBq may be disposed as normal waste or non-radioactive waste. Waste that has a higher specific activity must be incinerated or landfilled. All of these limitations and prescriptive measures in minerals containing NORMs can add a huge financial and operational burden on to a business that want to beneficiate tantalum and niobium from the mineral ore that contains U and Th.

Study objectives

The overall aim of this project is therefore the removal of the NORMs (thorium and uranium) from the mineral prior to its complete dissolution to increase the safety of its processing and/or transportation, as well as to decrease the quantities of these impurities before the complete dissolution of the mineral ore.

Specific aims:

- Perform an in depth literature survey of the existing methods of removal of U and Th from tantalite and columbite.
- Investigate the selective acid leaching of U and Th, before complete dissolution of the mineral.
- Investigate the separation effectiveness of column chromatography using zeolites.
- Perform spectrometric characterisation of the components of separation with ICP-OES.

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2 Tantalite mineral and compounds of contained elements

2.1 Introduction

Tantalite is a tantalum and niobium containing mineral with the general formula $[(Fe,Mn)(Ta,Nb)_2O_6]$ that is very similar to the mineral columbite. Tantalum and niobium are currently highly in demand due to their uses in the production of modern industrial materials and electronic equipment. The two minerals are often grouped together as a semi-singular mineral called columbite-tantalite or coltan. This can be partly explained by the fact that tantalum and niobium have similar chemistry and occur in nature mainly as the metal oxides which are derived from orthoniobic (orthotantalic), metaniobic (metatantalic) and pyroniobic (pyrotantalic) acids.[5] The elemental composition of the mineral varies greatly from location to location and the mineral is called tantalite when the tantalum content is more than the niobium content and columbite *vice versa*. However, tantalite has a much greater specific gravity than columbite, 8.0+ compared to columbite's 5.2.[6] The specific gravity increases with an increase in tantalum content and is a useful measurement in estimating the Ta content within the mineral. In another slight variation, iron-rich tantalite is called ferrotantalite and manganese-rich tantalite is called manganotantalite.

2.2 The occurrence of Ta and Nb

Tantalite occurs in granite pegmatites or in alluvial deposits resulting from the disintegration and deposition of these rocks.[7] It is associated with minerals such as beryl, tourmaline, spodumene, microlite, sumarskite, cryolite and tapiolite to name a few. This mineral could also be found associated with radioactive minerals of uranium and thorium depending on the location. Deposits of tantalite ores are found world-

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[5] Angulyansky, A., *the Chemistry of Tantalum and Niobium Fluoride compounds*, 2004, Pp. 4, 5,11,13, 19-21

[6] http://www.mindat.org/min-3882.html 5-09-2011

[7] Kraus, E.D., Hunt, F.W., Ramsdell, L.S. *Mineralogy: an introduction to the study of minerals and crystals*, 5th ed. 1959, p312

wide in countries such as Australia, Brazil, Canada, China, Congo, Malaysia, Mozambique, Namibia, Nigeria, Russia, Rwanda, Spain, Thailand, Zaire, Zimbabwe, Uganda and United States of America (**Figure 2.1**).

Figure 2.1: Worldwide Tantalite deposits[8]

The most important known tantalum/niobium resources are found in Brazil and Australia. Statistics indicate that in 2008 the main mining operations of tantalum/niobium ores were found in Australia, Brazil, Canada, Mozambique and Ethiopia. The worldwide economic recession in 2009 led to the shift in mining operations with mines being closed in countries such as Australia, Canada and Mozambique. As a result Brazil, Ethiopia and China were the major producers in the same year with smaller quantities coming from central Africa, Russia and South East Asia.[9] Mining was resumed in Mozambique in 2010 followed by Australia in 2011. Australia and Brazil are currently the major producers of tantalum raw materials. It was reported in 2003 that Africa has 16% of the world`s tantalum/niobium mineral deposits and Nigeria being the dominant niobium containing mineral producer in Africa, possesses tantalite deposits rich in tantalum oxide (40+%).[10] Since 2008 to 2010 the world supply of tantalum materials from Africa is estimated to have

[8] http://www.mindat.org/min-3882.html 5-09-2011

[9] http://www.tanb.org/tantalum 25-10-2011

[10] Adentunji, A. R., Siyanbola, W. O., Funtua, I. I., Olusunle, S. O. O., Afonja, A. A. and Adewoye, O. O., *J. Minerals & Materials Characterisation & Engineering*, 2005, 4, 2, pp.67-73

increased to 37% (**Figure 2.2**). [11,12] The world-wide supply of tantalum also includes those quantities which are produced as by-products in the mining and smelting of cassiterite ore for tin production in Malaysia and Thailand. Scrap recycling also accounts for about 20% of the total tantalum metal input each year.

Another very important mineral is pyrochlore $(Ce,Ca,Y)_2(Nb)_2O_6(OH,F)$ which is mainly a niobium containing mineral. The largest pyrochlore deposit is located in Brazil and is owned by Companhia Brasileira de Metalurgia e Mineração (CBMM). It is estimated that the mineral reserves from this deposit are enough to supply current world demand for about 500 years which accumulates to 438 million tons and interestingly is mined by open pit mining.[13,14] The second largest deposit, located in Brazil is owned by Mineração Catalão de Goias and contains 18 million tons while the third largest deposit is mined at Niobec mine owned by Camet Metallurgy in Quebec, Canada with 180 000 tons in reserves and these three companies account for approximately 85% of the world's niobium supply as indicated in **Table 2.1**.[15,16] Niobium is mainly used in the production of ferro-niobium alloys for making high-strength, low-alloy steel and accounts for apparently 90% of annual niobium consumption. Niobium is also produced as a side-product in small quantities from the smelting of some tin ores.[13] Niobium is further obtained as a by-product from the mining of tantalum-rich ores which contributes for 10 to 15% of the total niobium production.

[11] Roskill the economics of Tantalum, 9th ed. Roskill information services Ltd. 2005

[12] http://agmetalminer.com/2011/10/04/new-tantalum-supply-sources-to-ease-some-of-the-shortages 25-10-2011

[13] http://tanb.org/niobium 01-11-2011

[14] http://www.cbmm.com.br/english/index.html 01-11-2011

[15] http://www.angloamerican.com/business/other_mining/products/products_06 15-11-2011

[16] http://www.iamgold.com/English/Operations/Operating-Mines/Niobec-Niobium-Mine/Exploration-New-Developments/default.aspx 15-11-2011

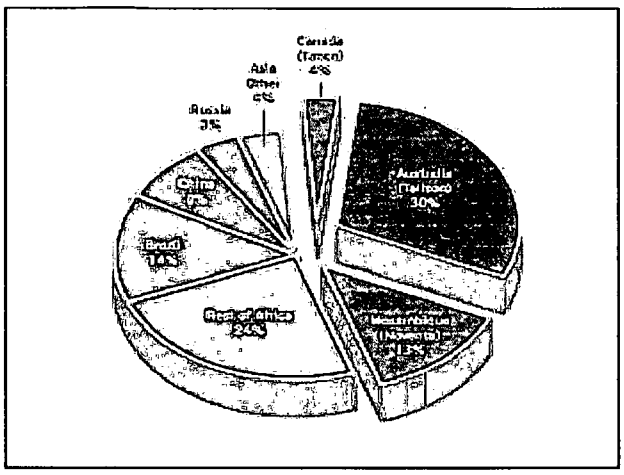

Figure 2.2: Major tantalum producers in 2009 and 2010[17]

Table 2.1 World production of niobium (tons)[18]

Country	2009	2010
Brazil	58 000	58 000
Canada	4 330	4 400
Other countries	530	600
Total	**62 860**	**63 000**

In South Africa, tantalite-columbite-bearing pegmatites are found in the Northern Cape pegmatite belt, north of Steinkopf, on the farms Steinkopf and Vioolsdrift. These minerals occur in beryl and spodumene bearing pegmatites. Random occurrences of lower grade deposits of tantalite can still be found in the Namaqualand area, however the lack of extensive geological information on its occurrence in the region is of concern.[19] Another source of tantalite used to be in Limpopo province, Palakop near the Klein Letaba River, but it is now depleted due to mining operations. There are no significant economic deposits in South Africa. However, in neighbouring states such as Mozambique, Zimbabwe, Malawi and Botswana there are.

Tantalum chemicals that are of industrial importance are tantalum carbide, tantalum chloride, lithium tantalate, and tantalum oxide and potassium tantalum fluoride.

[17] http://www.reeinternational.com/investors/ 08-02-2012

[18] http://minerals.usgs.gov/minerals/pubs/commodity/niobium/mcs-2011-niobi.pdf 08-02-2012

[19] http://www.northern-cape.gov.za/oldsite/ncpgds/mining/sec6.pdf 28-11-2011

Tantalum carbide is an extremely hard refractory material (Mohs hardness 9-10) and its hardness is only exceeded by that of diamond. It is used in making high strength cutting tools and is often added to tungsten carbide-cobalt powder alloys to enhance the hardness and inhibit the formation of large grains.[20] Tantalum chloride is used as ferro-electric films to make capacitors and in tantalum chloride coating which is mainly used as a starting material for the production of tantalum powder. Lithium tantalate exhibits unique electro-optical, pyroelectric and piezoelectric properties and combined with its good mechanical and chemical stability makes it well-suited to be used in electro-optical modulators, pyroelectric detectors and Surface Acoustic Wave (SAW) filters in mobile phones, hi-fi stereos and televisions which give exceptionally clear audio and video output.[21]

Tantalum oxide is used in the manufacturing of digital camera lenses, mobile phones and spectacles because of its high refractive index allowing for the manufacturing of smaller and thinner lenses for these consumable products. Yttrium tantalate phosphor is employed in X-ray film technology which has the ability to enhance the image quality for X-ray scans and is also used in ink jet printers due to its resistance properties. The metal powder is mainly used for the manufacturing of capacitors used in electronic circuits of medical equipments, automotive components and portable electronics such as video cameras, mobile phones and laptop computers for their faster reaction times and light weight.[22] It is also used in production of chemical process equipment, fasteners such as bolts, nuts and screws. Another important use of tantalum is in the manufacturing of cathodic protection systems for bridges and water tanks due to its corrosion resistance properties. The metal also has important applications in the medical field. It is used in the production of human prosthetic devices to repair damaged bones due to its high bio-compatibility with body fluids.

Niobium chemicals have almost the same functions as their tantalum counterparts in industry and can in some cases be direct substitutes of each other. The niobium metal is however the exception. Niobium metal is used mostly as an alloy with metals

[20] Lonnberg, B., Lundstrom, T. and Tellgren, R., *J. Less Common Metal,* 120, 2, 1986, pp.239–245

[21] Zheng, F., Liu, H., Liu, D., Yao, S., Yan, T. and Wang, J., *J. Alloys and Compounds,* 477, 2009, pp.688–691

[22] http://tanb.org/tantalum 28-11-2011

like iron, zirconium, titanium, tin and nickel. One of these alloys, namely ferro-niobium is utilised in the production of high strength steel and stainless steel and it accounted for 88.7% of the global niobium consumption in 2010.[23] The benefits of using ferro-niobium are its high strength, toughness and relatively low weight compared to other alloys and is employed in the manufacturing of oil and gas pipelines, car and truck bodies, architectural requirements, ship hulls and railroad tracks. The niobium-zirconium alloy Nb-1Zr is used in high temperature chemical processing equipment and in sodium vapour lamps for its corrosion resistance and oxygen fixation properties while Zr-2.5Nb is used as a cladding material in nuclear reactors for its low thermal neutron absorption. Niobium-titanium and niobium-tin alloys are used as wires in superconducting magnets found in instruments such as magnetic resonance imaging, nuclear magnetic resonance and particle accelerators. A niobium-titanium alloy also found its use in the construction of the Apollo 15 CSM nozzle, as shown in **Figure 2.3**. It is estimated that up to 600 tons of Nb_3Sn and 250 tons of NbTi strands were used in the construction of the International Thermonuclear Experimental Reactor. Other niobium containing alloys, namely a niobium-nickel as well as the vacuum-grade ferro-niobium alloy is used in the construction of turbine blades used in gas turbine engines.

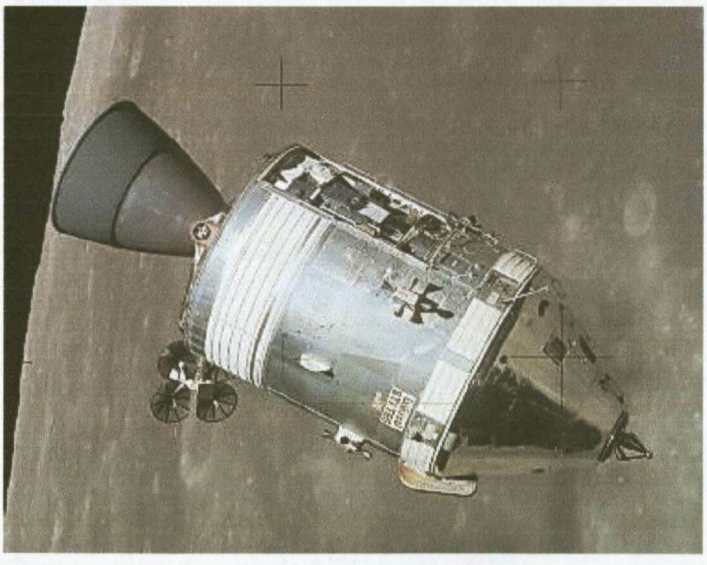

Figure 2.3: Apollo 15 CSM with dark grey Nb-Ti alloy nozzle[24]

[23] http://www.pacificwildcat.com/_content/documents/409.pdf 10-04-2012

[24] http://en.wikipedia.org/wiki/File:Apollo_CSM_lunar_orbit.jpg 08-02-2012

The two metals are also used in the making of jewellery by anodizing them in the presence of metals such as gold, titanium and aluminium to create hard and colourful surfaces (**Figure 2.4**).

Figure 2.4: Rings manufactured from a tantalum-gold alloy[25]

A large number of tantalum and niobium compounds are manufactured in similar processes involving similar chemistry. The industrial manufacturing of useful tantalum products such as TaC, $TaCl_5$ and $LiTaO_3$ is discussed. Tantalum carbide is manufactured by the heating of a powdered mixture of tantalum metal and graphite in vacuum or in an inert gas atmosphere at temperatures of approximately 2000 °C. Tantalum chloride, on the other hand is prepared by the chlorination of tantalum metal and tantalum oxychlorides. The production of lithium tantalate entails the heating of a mixture of lithium carbonate and tantalum pentoxide powder at 1050 °C for 2 hours. The reduction of potassium tantalum fluoride by sodium metal at elevated temperatures produces the tantalum metal powder. Tantalum metal however is also manufactured by a carbon or aluminium reduction process of the metal oxide. Another process involves the hydrogen and alkaline earth reduction of tantalum chloride. The very important ferro-niobium alloy is manufactured by the aluminothermic reduction process or the metal oxide reduction in an electric arc furnace (**Figure 2.5**). The remaining alloys such as Nb-Ti, Nb-Sn and Nb-Zr are

[25] http://en.mimi.hu/jewelry/tantalum.html 01-12-2011

generally produced by an electron beam or vacuum arc melting step of the pure metal in the presence of the alloying metal.

Figure 2.5: Production of ferro-niobium alloy in an electric arc furnace

2.3 Chemistry of Tantalum and Niobium

Niobium is a soft, malleable and ductile gray-white metal while tantalum on the other hand is a very hard and ductile blue-grayish metal (**Figure 2.6**). Both elements have a body-centered cubic crystalline structure (**Figure 2.7**). Niobium and tantalum have estimated crustal abundance of 200 mg/kg and 2.0 mg/kg respectively.

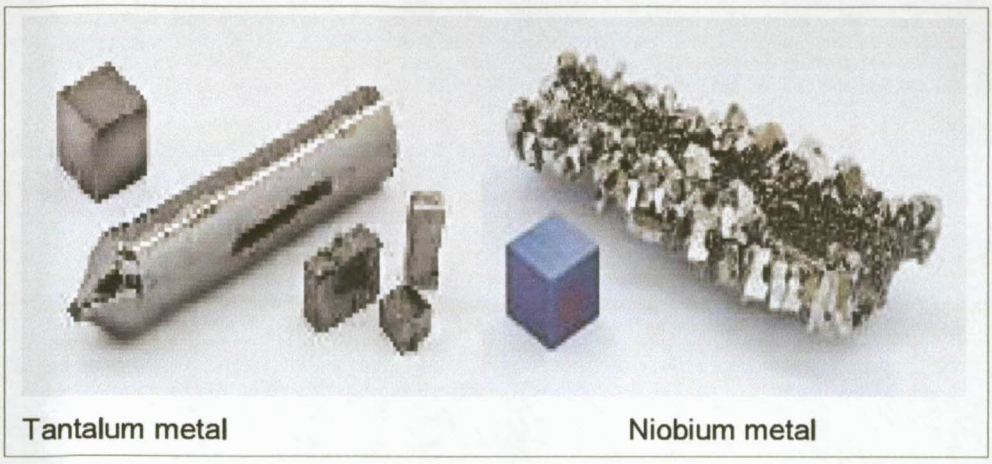

Figure 2.6: Examples of tantalum and niobium metals[26]

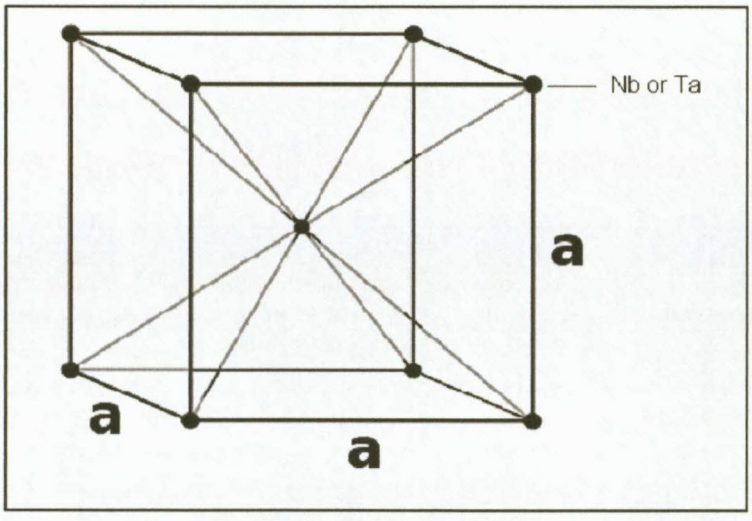

Figure 2.7: Body centered cubic structure of niobium and tantalum[27]

The two elements are part of the group 5 metals in the periodic table. Tantalum and niobium's electron configurations are $[Xe]4f^{14}5d^{3}6s^{2}$ and $[Kr]4d^{4}5s^{1}$ respectively. The metals have very little cationic chemistry, in contrast to its extensive anionic chemistry and the two metals form many complexes in oxidation states +2 to +5.[28] The +5 oxidation state is the most stable oxidation state mainly due to the loss of the

[26] http://en.wikipedia.org/wiki/File:Niobium_crystals_and_1cm3_cube.jpg 17-01-2012

[27] http://en.wikipedia.org/wiki/Body-centered_cubic_structure 5/09/2011

[28] Cotton, A.F., Wilkinson, W., *Advanced Inorganic Chemistry*, 5th *ed.* 1988, p787

five outer electrons to obtain a completely valence electron shell. Niobium looses the $5s^1$ and $4d^4$ electrons to reach the octet electron configuration of krypton ($[Ar]3d^{10}\ 4s^2\ 4p^6$) while tantalum looses the $5d^3$ and $6s^2$ electrons to achieve the configuration of erbium ($[Xe]4f^{14}$). Both elements can form complexes with metal-metal bonds in the lower oxidation states and also form clusters with all types of neutral and anionic donor groups (**Equations 2.1 - 2.4**).[29]

$$TaCl_5 + 4NaS_2CNR_2 \longrightarrow [Ta(S_2CNR_2)_4]Cl + 4NaCl \qquad \textbf{2.1}$$

$$NbCl_5 + 3Me_2SO \longrightarrow NbOCl_3 \cdot 2Me_2SO + Me_2SCl_2 \qquad \textbf{2.2}$$

$$2Ta + 5SiO_2 + 8TaCl_5 \xrightarrow{450/550\ ^\circ C} 10TaOCl_2 + 5SiCl_4 \qquad \textbf{2.3}$$

$$20KCl + 14NbCl_5 + 16Nb \longrightarrow 5K_4[(Nb_6Cl_{12})Cl_6] \qquad \textbf{2.4}$$

Another important property of the metals is that they do not react with water and air under normal conditions due to the protection by a metal oxide layer on the surfaces of the metals. The metals are also not easily attacked by acids, including *aqua regia* at room temperature. However they react with hydrofluoric acid, hot concentrated acids, molten alkali and halogens (**Equations 2.5** and **2.6**) at elevated temperatures. **Table 2.2** lists the physiochemical properties of niobium and tantalum.

$$2Ta_{(s)} + 5Cl_{2(g)} \xrightarrow{\Delta} 2TaCl_{5(s)} \qquad \textbf{2.5}$$

$$2Nb_{(s)} + 5Cl_{2(g)} \xrightarrow{\Delta} 2NbCl_{5(s)} \qquad \textbf{2.6}$$

[29] Koknat, F. W., Parsons, J. A. and Vongvusharintra, A., *Inorg. Chem.*, 13, 7, 1974, pp.1699-1702

Table 2.2: Physiochemical properties of niobium and tantalum

Property		Niobium	Tantalum
Atomic number		41	73
No. of naturally occurring isotopes		1	2
Electron configuration		[Kr] $4d^4\ 5s^1$	[Xe] $4f^{14}\ 5d^3\ 6s^2$
Electronegativity (Pauling)		1.6	1.5
Atomic radius (pm)		146	146
Ionic radius(pm) (6 coordinate)	V	64	64
	IV	68	68
	III	72	72
Density (20°C)/ g cm^{-3}		8.57	16.65
Melting point (°C)		2477	2980
Boiling point (°C)		4744	5534
ΔH_{fus} (kJ mol^{-1})		26.8	24.7
ΔH_{vap} (kJ mol^{-1})		680.2	758.2
ΔH_f (monoatomic gas) (kJ mol^{-1})		680.2	758.2
Ionization energy (kJ mol^{-1})		1: 652.1	1: 761
		2: 1380	2: 1500
		3: 2416	-
Thermal expansion [µm/(m·K)]		7.3	6.3
Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)		53.7	57.2
Young's modulus (GPa)		105	186
Mohs hardness		6	6.5
Thermal neutron absorption cross section (Barns/atom)		1.1	21.3

It is clear from the properties listed in **Table 2.2** that the two metals are similar in almost all respects except for the density, boiling point and the neutron absorption cross-section. The differences can be utilized in separation of the two metals by distillation and density separation for example. The neutron cross-section allows niobium metal to be used in the production of the cladding material for fuels in nuclear reactors. The large neutron cross-section of tantalum on the other hand makes it extremely suitable to be used as control rods in the same reactors. The major oxidation states and examples of the stereochemistry of niobium and tantalum are reported in **Table 2.3**. The two metals form a wider variety of complexes in the +2 to +5 oxidation states compared to that in the lower oxidation states, and complexes with coordination numbers as high as 8 have been isolated.

Table 2.3: Oxidation states and stereochemistry of Nb and Ta complexes

Oxidation state	Coordination number	Geometry	Examples
M^{+5}	4	Tetrahedron	NbE_4^{3-} (E = O, S), $NbO[N(SiMe_3)_2]_3$, $Ta(NR)(NMe_2)_3$
	5	Square-based pyramid	$Nb(NMe_2)_5$, $NbS(SPh)_4^-$, $NbOCl_4^-$, $NbSCl_3(Ph_3PS)$
	6	Trigonal prism	$[M(S_2C_6H_4)_3]^-$, $M(CH_3)_6^-$
	7	Pentagonal bipyramid	$[NbO(C_2O_4)_3]^{3-}$, $Ta(NMe_2)_3(\eta^2$-*t*Bupz$)_2$
	8	Bicapped trigonal prism	TaF_8^{3-}, $Ta(PS_4)S_2$
M^{+4}	4	Tetrahedron	$M(NR_2)_4$, $M(NR_2)_2Cl_2$
	6	Octahedron	NbX_4L_2, MCl_6^{2-}
	7	Pentagonal bipyramid	NbF_7^{3-}, $Ta(PhNCHNPh)_3(NPh)$
	8	Square antiprism	$Nb(thd)_4$, $TaCl_4(dmpe)_2$
M^{+3}	6	Octahedron	$MCl_3(py)_3$, $Nb_2X_9^{3-}$, $[M_3X_{10}L_3]^-$, $M_2(\mu$-Cl$)_2Cl_4L_4$, Nb_2Cl_5(O-*i*-Pr)(*i*-PrOH)$_4$
M^{+2}	6	Octahedron	$MCl_2(PMe_3)_4$,*t*-$NbCl_2(py)_4$
M^{+1}	7	Capped trigonal prism	$TaX(CO_2)(dmpe)_2$, $MCl(CO)_3(PMe_3)_3$
M^0	6	Sandwich	$M(\eta^6$-arene$)_2$
M^{-1}	6	Octahedron	$M(CO)_6^-$, $M(CO)_2(NO)(PPP)$
M^{-3}	5	-	$M(CO)_5^{3-}$

M = Ta or Nb

2.3.1 Chemistry of niobium and tantalum halides

Tantalum and niobium have extensive halogen chemistry, as illustrated by the large number of fluoride and other halogen complexes that have been isolated and successfully characterized.[5] The main reason for this is the reactivity of the metals towards HF and Cl_2 and the subsequent product formation when hydrofluoric acid or chlorine gas is used as the dissolution agent. The chemical composition of the products depends heavily on the reaction conditions. The addition of CsF to niobium metal in the presence of 50% HF, the $[CsNbF_6]$ complex is isolated (**Equation 2.7**), but when the acid concentration is decreased to 35% and lower, the $[NbOF_5]^{-2}$

complex is produced. [$CsTaF_6$] on the other hand can be precipitated from more dilute solutions than [$CsNbF_6$].

$$M + (50\%)\ 5HF + CsF \longrightarrow CsMF_6 + 2.5H_2 \qquad \textbf{2.7}$$

(M = Nb or Ta)

The pentafluorides of both the elements are synthesized by the direct fluorination of the metals or the pentachlorides with F_2 gas (**Equation 2.8**). These complexes are white volatile solids (NbF_5: m.p. 80 °C, b.p. 235 °C; TaF_5: m.p. 95 °C, b.p. 229 °C) and form colourless liquids and vapours.

$$2M_{(s)} + 5F_2 \longrightarrow 2MF_5 \qquad \textbf{2.8}$$

The rest of the halides of niobium and tantalum are best synthesized by the direct reaction of the metals with excess of the appropriate halogen gas and the colours of the products formed vary from colourless (NbF_5, TaF_5, $TaCl_5$) to yellow ($NbCl_5$, $TaBr_5$), red ($NbBr_5$, TaI_5) and brown-black (NbI_5). These products quickly hydrolyze to the pentoxides (**Equation 2.9**) and are soluble in a variety of organic solvents such as ethers and tetrachloromethane.

$$2MCl_5 + 5H_2O \longrightarrow M_2O_5 + 10HCl \qquad \textbf{2.9}$$

The pentahalides with melting and boiling points between 200 °C and 300 °C can be sublimed in an atmosphere containing the appropriate halogen gas, as part of a separation and purification process. In the vapour form they are mononuclear and trigonal bipyramidal, but are tetranuclear in solid form. Crystallography indicates, with the exception of the metal fluoride, that all pentahalides are isostructural. Research also indicates that niobium and tantalum pentachlorides are dinuclear in CCl_4 and $MeNO_2$, but form adducts with coordinating solvents such as CH_2Cl_2 and THF. The separation and purification of these elements are therefore based on the properties or differences thereof, of the halogen complexes. A variety of metal halide compounds that have been synthesized and successfully characterised are all related to their high electronegativity, strong oxidizing ability and low dissociation energy.[5] The reactivity order increases in the sequence (I<Br<Cl<F). The

pentahalides also have a tendency to react with an additional halide ion to form MX_6^- compounds (X = halide ion). They also react with neutral Lewis bases (N, O, P and S) donor groups to form MX_5L compounds (L = Lewis base). The pentahalides, especially the fluorides and chlorides, can act as catalysts in cyclotrimerizing reactions or linearly polymerization of acetylenes as well as in Friedel-Crafts and related alkylation reactions (**Equation 2.10**).

$$MCl_5 + K_{(s)} + H_2 + \text{diphos} \longrightarrow MH_5(\text{diphos})_2 \qquad \textbf{2.10}$$

The Lewis acid behaviour of the MX_5 affords extensive chemistry to produce compounds in which one of the halogens is replaced by an alkoxide (OR), a dialkylamine (NR_2) or an alkyl (CR_3) group. These compounds form neutral adducts or anionic complexes and may be coordinately unsaturated which makes them highly reactive towards addition reactions. The metal halides can react for example with amines to form $[M(NR_2)_xX_{5-x}]$ compounds. The $[M(NR_2)_xX_{5-x}]$ compounds have been intensely studied and have been used for the synthesis of other compounds such as $TaCl_2(NMe_2)_3$ and $Ta(S_2CNR_2)_5$.[30] The geometry of $[Ta(NMe_2)_5]$ and $[Nb(NMe_2)_5]$ is trigonal bipyramidal and square planar respectively, but at elevated temperatures these compounds are mononuclear with a square pyramidal geometry.[31] The pentahalides also react with a wide spectrum of other ligands including nitrides, silicides, selenides and phosphides. These products however do not form simple salts such as sulphates and nitrates. In HNO_3, H_2SO_4 and HCl solutions, Nb^{+5} can exist as cationic, neutral and anionic species. The products of these acid reactions can be hydrolyzed and polymerized at equilibrium depending on the reaction conditions.

2.3.2 Chemistry of niobium and tantalum oxides

Niobium and tantalum oxides are acidic in nature and very difficult to dissolve in mineral acids except hydrofluoric acid. Both oxides are relatively inert white solids which can also be dissolved by fusion with an alkali hydrogen sulphate, carbonate or

[30] Chisholm. M. H., Kirkpatrick. C.C. and Huffman. J.C., *Inorg. Chem.*, 20, 1981, pp.871-876

[31] Kolbjørn. H., Holwill, C.J., Runnacles, J.D. and Rice, A.D., *Inorg Chem.*, 31, 1992, pp .4733-4736

hydroxide. The metal oxides are obtained by heating the hydrous oxides (niobic and tantalic acids) in an excess of oxygen (**Equation 2.11**). The hydrous oxides have uncertain molar masses due to the inconsistency of the water content which varies, depending namely on the synthetic procedure and the drying procedure. The hydrolysis of the pentahalides (**Equation 2.12**) on the other hand produces only one product.

$$M_2O_5 \cdot xH_2O \xrightarrow{\Delta} M_2O_5 + xH_2O \qquad \textbf{2.11}$$

$$2MCl_5 + 5H_2O \longrightarrow M_2O_5 + 10HCl \qquad \textbf{2.12}$$

The pentoxides of both metals have complex structural relationships, especially Nb_2O_5. They are built up of MO_6 octahedra with shared edges and corners and which can be constructed in a number of ways (**Figure 2.8**).

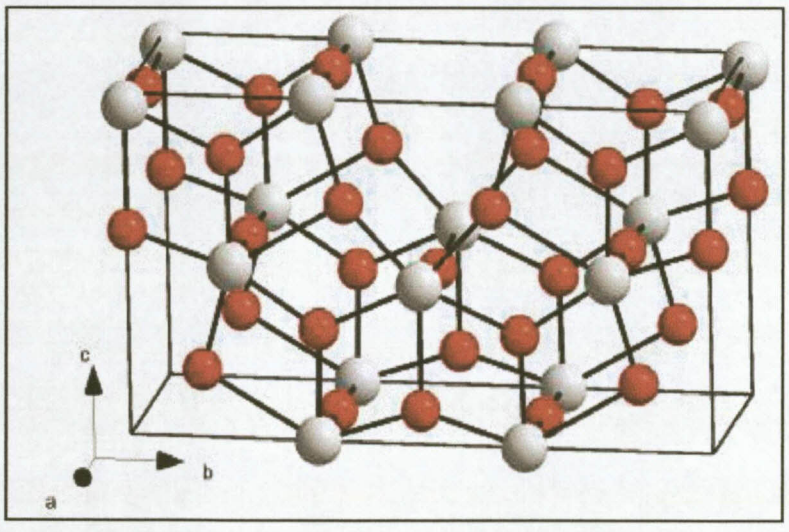

Figure 2.8: Crystal structure of M (V) oxide

The pentoxides can be reduced to M(IV) oxides (**Equation 2.13**) at elevated temperatures in hydrogen atmosphere which can further be reduced to the M(III) and M(II) oxides.

$$M_2O_5 + H_{2(g)} \xrightarrow{1000\ ^\circ C} 2MO_{2(S)} + H_2O \qquad \textbf{2.13}$$

The resulting tantalum (IV) oxide, obtained from the reaction with hydrogen has a rutile structure. Niobium (IV) oxide forms the same rutile structure as the tantalum (IV) oxide, but only at elevated temperatures. The metal oxides can also be fused in the presence of an alkali hydroxide or carbonate to produce the water soluble niobate and tantalate isopolyanions. These isopolyanions complexes are only stable at high pH with the precipitate of the tantalate at pH 10 and that of niobate at pH 7. This is one way of separating the two elements. The pentoxides can be converted to the pentahalides, especially the pentafluoride which form the starting material for the synthesis of a large variety of complexes. These complexes dissolve very slowly in hydrofluoric acid solutions (**Equation 2.14**), but the use of high HF concentrations and a mixture of HF and H_2SO_4 at high temperatures is recommended to enhance the formation of the pentafluorides.[5] The best precursors for the synthesis of the fluorides are however the hydroxides. Both metal hydroxides dissolve easily in concentrated or dilute HF solutions (Equation **2.15**).

$$M_2O_5 + 12HF \longrightarrow 2HMF_6 + 10H_2O \qquad \textbf{2.14}$$

$$2M(OH)_5 + 12HF \longrightarrow 2HMF_6 + 10H_2O \qquad \textbf{2.15}$$

Other reactions of the pentoxides include the reduction with aluminium and carbon (**Equations 2.16** and **2.17**) and the synthesis of the oxychlorides and lithiated oxides respectively (**Equations 2.18** and **2.19**).

$$3M_2O_5 + 10Al \longrightarrow 6M + 5Al_2O_3 \qquad \textbf{2.16}$$

$$M_2O_5 + 7C \xrightarrow{1800°C} 2MC + 5CO \qquad \textbf{2.17}$$

$$2M_2O_5 + 3CCl_4 \longrightarrow 4MOCl_3 + 3CO_2 \qquad \textbf{2.18}$$

$$M_2O_5 + Li_2CO_3 \longrightarrow 2LiMO_3 + CO_2 \qquad \textbf{2.19}$$

2.4 Chemistry of Tantalite

The natural colour of tantalite (**Figure 2.9**) differs from black to brown in colour and streak (the colour left by a mineral when dragged across a surface). It is mostly found mixed with columbite in the ore called coltan and consists of a mixture of the salts $Fe(NbO_3)_2$, $Mn(NbO_3)_2$, $Fe(TaO_3)_2$ and $Mn(TaO_3)_2$ with traces of tin, tungsten, titanium, aluminium and other elements such as uranium, thorium and silica as impurities. Iron-rich tantalite can be black to brown-black in colour while manganese-rich can be reddish brown to black. The geological properties of tantalite are shown in **Table 2.4**.

Figure 2.9: Tantalite $(Fe,Mn)(Ta,Nb)_2O_6$[32]

[32] http://www.alibaba.com/product/br101527135-215662275-0/Tantalite.html 09-02-2012

Table 2.4: Properties of Tantalite

Property	Value
Crystal system and class	Orthorhombic; 2 / m 2 / m 2 / m
Axial elements: *a* : *b* : *c*	0.402 : 1 : 0.357
Cell dimensions (Å)	a = 5.74, b = 14.27, c = 5.09, Z = 4 (17 % Ta_2O_5)
Twinning	Common on {201}, as contact twins
Cleavage	{010} distinct, {100} less distinct
Fracture and tenacity	Subconchoidal; brittle
Hardness (mohs scale)	6 (Columbite) to 6-6½ (Tantalite)
Density (gcm^{-3})	5.2 (Columbite) to 8.0 (Tantalite)
Colour	Iron black to brownish black; often tarnished iridescent
Streak	Dark red to black
Luster	Submetallic, often brilliant, subresinous
Opacity	Transparent in thin splinters, increasing in high manganese varieties
Fusibility	5-5½, with difficulty

2.4.1 Production procedures; extraction processes

Niobium and tantalum are mainly produced from minerals such as columbite - tantalite, pyrochlore, as well as from tin slag with high tantalum content by the fluorination of the mineral as a dissolution step followed by solvent extraction as element separation step. Another method used is the chlorination of the raw material to produce pentachlorides (bp: 236 °C Nb, bp: 248 °C Ta) followed by separation and distillation thereof.[5] Alternative methods are also used when they are better suited to particular conditions.[9] In one of these alternative processes the raw material is grinded and mixed with coke and passed through a chlorinating stage which separates all the other elements from niobium and tantalum. The temperature of the resulting niobium-tantalum oxychlorides gas is decreased resulting in the precipitation of additional impurities. The "cleaned" niobium-tantalum oxychloride gas is then further cooled to a liquid and distilled.

The method believed to be industrially the first to separate niobium and tantalum successfully is the so-called Marignac process (**Figure 2.10**).[5] The method is based on the solubility differences of the potassium fluoride salts of tantalum and niobium.

The potassium niobium oxyfluoride, K_2NbOF_5 is much more soluble in lower hydrofluoric acid concentrations compared to the potassium tantalum fluoride, K_2TaF_7. K_2NbF_7 is not formed in this process as is the case for tantalum as it is stable only in high hydrofluoric acid concentrations. The Marignac process involves the mixing of the raw material with concentrated hydrofluoric acid followed by the addition of potassium hydroxide or carbonate. Potassium niobium oxyfluoride and potassium tantalum fluoride are both formed in solution. The solution is cooled which allows for the fractional crystallization of the slightly soluble K_2TaF_7 while K_2NbOF_5 remains in solution (see **Equations 2.20** and **2.21**). The solubility of K_2TaF_7 is 12 times less than that of K_2NbOF_5.[5] Niobium is subsequently recovered by the addition of ammonia to a filtered solution to precipitate the niobium oxide. The purity of tantalum produced by this route of crystallization is very satisfactory. However, the niobium which is produced this way is not as successful as the tantalum due to the presence of titanium (~100 ppm), silica (~3000 ppm) and iron (~2000 ppm). The processes that are currently used for the separation of these metals are very similar to the original Marignac process (**Figure 2.11**).

$$H_2[TaF_7] + 2KF \longrightarrow K_2[TaF_7]_{(s)} + 2HF \qquad \textbf{2.20}$$

$$H_2[NbOF_5] + 2KF \longrightarrow K_2[NbOF_5]_{(aq)} + 2HF \qquad \textbf{2.21}$$

These modern processes involve the addition of the grounded minerals to mixtures of hydrofluoric acid and H_2SO_4. In this step the niobium and tantalum as well as other elements such as iron, manganese and titanium are dissolved, while silica, calcium, rare earths and aluminum remain insoluble and are removed by filtration. The solution containing tantalum and niobium along with some impurities is then subjected to solvent extraction, which is based on the dissolution of the different species into the organic phase and controlled by the acidity of the aqueous phase. Both niobium and tantalum are extracted into the organic layer at high acidity leaving the impurities in the aqueous phase. The organic phase containing niobium and tantalum is then brought into contact with an aqueous phase with different acidity conditions. Under conditions of lower acidity only the niobium is stripped into the aqueous phase since it requires higher acidity levels to be extracted into the organic

phase. This process can be repeated to achieve the required purity of the metals. The metals are then purified by precipitating them with ammonia from the aqueous solutions as niobium and tantalum hydroxides. The hydroxides are then separated by filtration, washed, dried and calcined to produce the respective metal oxides.

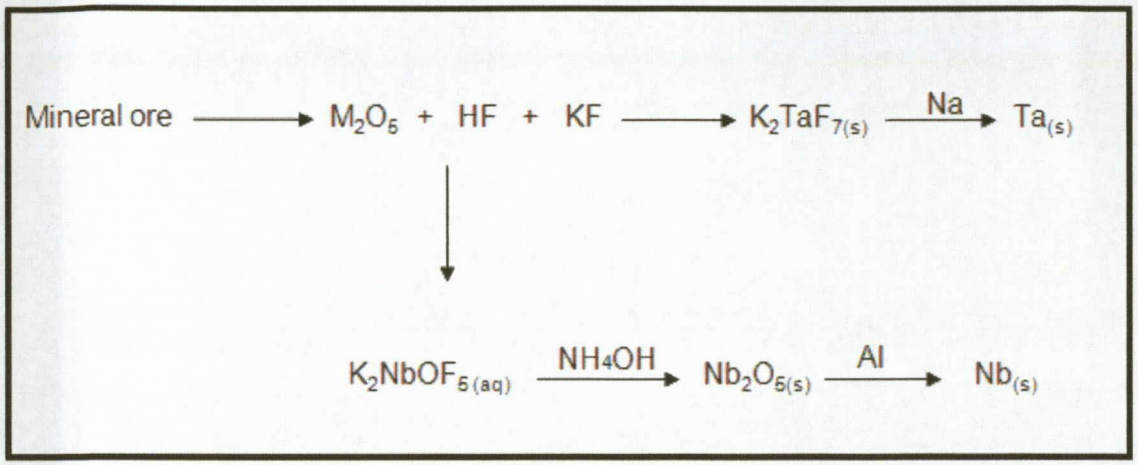

Figure 2.10: Separation of tantalum and niobium fluorides by the Marignac process

A large number of solvents have the potential to be used in the solvent extraction process, but the most useful solvents in industry are methyl isobutyl ketone (MIBK), cyclohexanone, tributyl phosphate (TBP) and 2-octanol. These solvents are readily available and can be recycled from the process to be used again and MIBK and cyclohexanone are cheaper extractants compared to TBP. The solubility of these extractants in water is however, a factor of importance in this extraction process. The solubility of TBP in water is 0.5 vol % compared to the 2 vol % of MIBK and 16 vol % of cyclohexanone. Similarly the boiling point of TBP (178 °C) is higher than cyclohexanone (155 °C) and MIBK (116 °C) which is important for distilling the extractant from the aqueous solution. These favorable physical properties of TBP such as low solubility and high boiling point outweigh the cost associated with its use as an extractant, which makes it the most attractive extractant for the separation of the two elements. The most important and vital factor in terms of the selection of organic extractants is the purity of niobium and tantalum that is finally obtained, which is far greater using MIBK as extractant compared to TBP and cyclohexanone. For this reason, MIBK is currently preferred to TBP and cyclohexanone as extractants of niobium and tantalum in industry. It is important to note that in all these systems (MIBK, TBP, and cyclohexanone) the required concentrations for the extraction of

niobium and tantalum are very high. The recovery of these extractants is also limited since they are amenable to degradation due to the high acid concentrations, especially HF used in these processes.

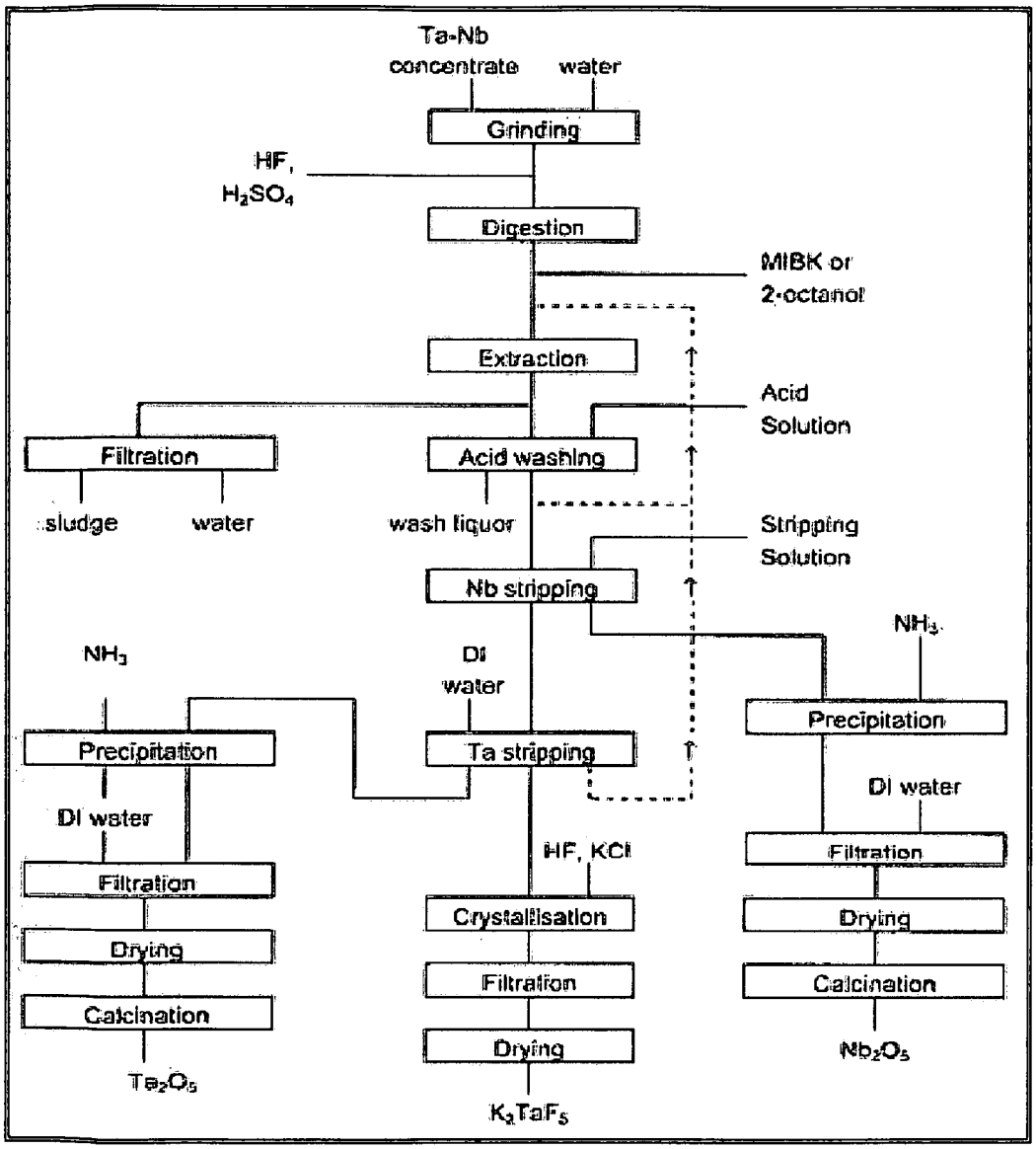

Figure 2.11: Flow chart of the modern Nb and Ta beneficiation process[33]

[33] Roskill Information Services Ltd. (2005). *The Economics of Tantalum.* 9th Ed.

2.5 Conclusion

Tantalum and niobium have a diverse and vast amount of chemistry that has been reported as indicated in the previous sections. Interestingly, the industrial processing of these elements is dominated by the halogen chemistry, in particular fluorine chemistry. The stability, the number of different complexes as well as the subtle chemical difference between the Nb and Ta fluoride complexes allow for the separation and purification. The problems associated with the use of HF, such as increased operation costs due to the toxicity of HF and the need for HF-resistant equipment necessitates the development of less dangerous and cost effective technologies for the processing of these elements.

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3 Naturally occurring radioactive materials

3.1 Introduction

The presence of radioactive elements in minerals such as tantalite complicates its beneficiation significantly. Constraints such as the maximum amount of sample that can be studied in laboratories as well as strict waste disposal requirements are introduced if samples contain elements such as uranium and thorium in their natural state. The removal of the radioactive material at an early stage of the beneficiation process of the minerals will ultimately reduce the cost as well as legal requirements for downstream processes.

The mineral used in this study is a tantalum/niobium mineral called tantalite from the Maquissupa region in Mozambique as mentioned in **Chapter 1**. This mineral contains approximately 2.8% and 0.5% of uranium and thorium respectively. The processing of this mineral to produce pure tantalum and niobium will generate waste with increased concentrations of both uranium and thorium. The construction of the processing plant will not only have to account for the processing of tantalum and niobium, but also to waste with an increase in radioactivity levels as well as the protection of the employees and the public against excessive radiation during the complete production process. The waste generated will also need specialized handling and disposing methods. The presence of these NORMs will also require drastic changes to the plant design, increasing the running expenses which may lead to additional construction costs including the beneficiation of the mineral which will require licenses to transport from Mozambique and to construct a processing plant. This chapter will investigate the occurrence of radioactive materials, its legal requirements as well as the chemistry of thorium and uranium oxides which are both present in the tantalite samples that were studied.

3.2 NORM

Naturally occurring radioactive materials (NORMs) are all radioactive elements or materials that are naturally found in the environment and were incorporated into the earth`s crust in various concentrations when it was formed. All living things, including humans are exposed to natural radiation called background radiation. Background radiation is that which is unavoidably present in our environment at levels that vary greatly from place to place. This background radiation arises from sources such as cosmic, terrestrial and internal radiation. Cosmic radiation comes from sources outside the earth`s atmosphere such as the interaction of charged particles from the sun and stars with the earth's atmosphere and magnetic field. This radiation increases with altitude which exposes flight crews and frequent flyers that normally work at elevated heights to increased levels of this type of radiation. Terrestrial radioactive compounds are normally found in the air, in the soil, in water sources and in vegetation which are released from mining and oil exploration activities. Low levels of the radioactive materials and their decay products are ingested in different food products such as Brazil nuts, cereal, bananas and peanut butter, while radon gas and its daughter radionuclides are inhaled with air into the body. On the other hand, internal radiation originates from inside the human body as radioactive ^{40}K, ^{14}C, ^{210}Pb and other isotopes from birth.[34] In addition, radiation can artificially be produced by man-made sources such as medical X-rays, nuclear medicine and microwaves for cooking purposes.

The important factor when measuring radiation is the amount of radiation and the degree of hazard it represents. Radioactivity is a measurement of the rate at which radiation is released from the source and is expressed in number of Becquerels (Bq). One Becquerel denotes one radioactive decay process in one second. An unit that is also used is Curie (Ci) where one Bq is equal to $2.703x10^{-11}$ Ci. It is important that the radioactivity is not confused with the radiation dose which measures the danger of radiation to a human being. The dose or the equivalent dose as sometimes used, which is measured in Sievert (Sv) or in Roentgens equivalent man (rem) with one Sievert being equivalent to 100 rems. **Table 3.1** shows the amount of radiation dose and the effects thereof.

[34] http://www.rrc.state.tx.us/environmental/publications/norm.php 29-03-2012

Table 3.1: Effects of radiation exposure[35]

Danger level	Radiation dose	Effect
	2 (mSv/yr)	Typical background radiation experienced by everyone (average 1.5 mSv in Australia, 3 mSv in North America)
	9 mSv/yr	Exposure by airline crew flying New York-Tokyo polar route
	20 mSv/yr	Current limit (averaged) for nuclear industry employees
	50 mSv/yr	Former routine limit for nuclear industry employees. It is also the dose rate which arises from natural background levels in several places in Iran, India and Europe
	100 mSv/yr	Lowest level at which any long-term increase in cancer risk is clearly evident.
	350 mSv/lifetime	Criterion for relocating people after Chernobyl accident
	400 mSv/hr	The level recorded at the Japanese Fukushima nuclear site, 15 March 2011
	1,000 mSv single dose	Causes (temporary) radiation sickness such as nausea and decreased white blood cell count, but not death. Above this, severity of illness increases with dose
	5,000 mSv single dose	Would kill about half those receiving it within a month

The acronym TENORM (technologically-enhanced naturally occurring radioactive material) is used when the concentrations of the NORMs are increased by human intervention or industrial processing. The NORM decay spontaneously in nature to release radiation in the form of alpha, beta and gamma rays. The most important or significant NORMs are ^{238}U and ^{232}Th, but other important naturally occurring elements include ^{224}Ra, ^{228}Ra, ^{210}Pb, ^{210}Po and ^{40}K. The released radiation is potentially harmful to the human body. **Figure 3.1** illustrates the penetration power of radiation.

[35] http://www.world-nuclear.org/info/inf05.html 23-04-2012

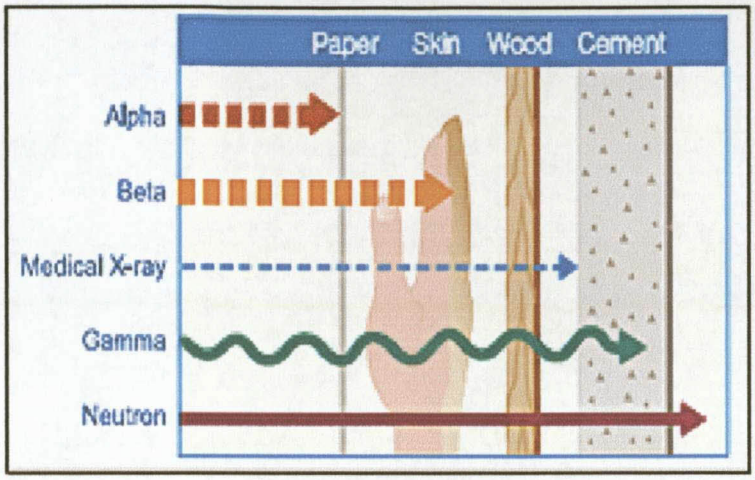

Figure 3.1: Penetrating power of radiation[36]

The presence of these NORMs in natural resources of industrial importance even at low concentrations, places additional burdens on the handling or processing of these materials in large volumes. This can leave large quantities of more concentrated NORM as waste material or in the waste stream. With the hazards in mind, the processing of NORM containing sources is subject to constant monitoring and regulation. Current legislation in South Africa determines that the radioactive waste remains the property of a business until someone else takes ownership of it. In practice it means that a mine cannot be closed or business terminated until it has legally sold its NORM, and this places large financial and legal hurdles on the owners. These regulations not only differ from country to country, but also change depending on the purpose of processing the source. This means that the material which is considered radioactive waste in one country may not be considered as such in another. Material which may contain low-level waste in the nuclear industry might also go entirely unregulated in another industry. Industries that are known to have NORM-related regulations are:[37]

- Nuclear fuel cycles
- Uranium mining
- The coal industry (mining and combustion)
- The oil and gas industry (production)

[36] http://www.nrc.gov/about-nrc/radiation/related-info/faq.html 29-03-2012

- Metal mining and smelting
- Mineral sands (rare earth minerals, titanium and zirconium).
- Fertilizer (phosphate) industry
- Building industry
- Recycling

The presence of NORMs in mineral sands and ores complicate the beneficiation process considerably. Mineral sands which include minerals such as zircon, rutile, tantalite, pyrochlore, ilmenite and monazite are mined and processed in many countries with production amounting to millions of tones. The processing and beneficiation of these minerals is important due to the numerous applications and use of the elements contained in them. Although the presence of uranium and thorium is usually at minor to trace levels in some of these minerals, their concentration can be increased by the extraction of the major constituents from the mineral, leaving behind waste streams with increased radioactivity levels. **Table 3.2** shows the radioactivity in different mineral sands and products. The table shows relative low levels of radioactivity are present in the majority of minerals, but that a mineral such as monazite which is the primary source of rare earth elements, is heavily contaminated with thorium and sometimes uranium.

[37] http://www.world-nuclear.org/info/inf30.html 29-03-2012

Table 3.2: Radioactivity in mineral sands and products[38]

Sample	Thorium		Uranium	
	ppm	Bq/kg	ppm	Bq/kg
Ore	5-70	40-600	3-10	70-250
Heavy mineral concentrate	80-800	600-6600	<10-70	<250-1700
Ilmenite	50-500	400-4100	<10-30	<250-750
Rutile	<50-350	<400-2900	<10-20	<250-500
Zircon	150-300	1200-2500	150-300	3700-7400
Monazite concentrate	10,000-55,000	80,000-450,000	500-2500	12,000-60,000
Processing tailings (including monazite)	200-6000	1500-50,000	10-1000	250-25,000

3.3 NORM regulations

The presence of uranium and thorium in any mineral sand or ore necessitates that these materials to be classified under NORM or TENORM regulations if the concentrations of the elements were enhanced by human intervention. Handling of NORM-containing samples is subject to strict regulations ranging from acquiring the sample to disposing the unwanted material as waste. These regulations can differ from country to country. The International Atomic Energy Agency (IAEA) is the regulating body that gives guidelines how to regulate the NORMs and countries can alter them when implementing these regulations as they see fit. The classification of materials as NORMs depends on the radioactive element present and the concentration of that particular element in the material. The concentration of radioactive material present is generally measured in terms of activity rather than mass, and is measured in the units Becquerel (Bq) and the Curie (Ci) as previously discussed. According to the National Nuclear Regulator Act of South Africa, no person may position, construct, operate, decontaminate or decommission a nuclear installation, except under the authority of a nuclear installation license. This legislation also prevents any vessel which has any radioactive material on board

[38] International Atomic Energy Agency, 2003, *Extent of Environmental Contamination by Naturally Occurring Radioactive Material (NORM) and Technological Options for Mitigation,* Technical Reports Series No. 419, STI/DOC/010/419 (ISBN: 9201125038)

which is capable of causing any nuclear damage to enter any port or cross any border of the Republic of South Africa without a nuclear vessel license.[39] According to the IAEA, any material with activity exceeding 1 Bq/g for each radionuclide in the ^{238}U and ^{232}Th series and 10 Bq/g for ^{40}K are regarded as NORMs and a license is required to handle such material.[40] Provisions of the National Nuclear Regulator Act of South Africa (Act no.47 of 1999), states that the act applies when the activity of natural uranium and thorium in any material exceeds 0.5 Bq/g and 10 Bq/g for ^{40}K.[41] Materials with lower activity concentrations than the values stated are exempted from the act.

3.3.1 Transportation of NORM

South Africa has accepted the recommendations made by the United Nations for the transport of Dangerous Goods as expressed in the International Maritime Organisation's Dangerous Goods Code (IMDG). These recommendations on the handling, temporary storage and transportation of hazardous materials have been implemented as legislation through the Department of Transport's Merchant Shipping Act (Act 57 of 1951), the Aviation Act (Act 72 of 1962) and the Nuclear Energy Act, (Act 46 of 1999).[42] The legislation dictates that the maximum radiation level at any point 1 meter from the external surface of the load should be less than 0.4 mSv/h for mineral ores. The radiation level at any point on the external surface of an excepted waste package shall also not exceed 5 μSv/h. The legislation also prescribe specific protocols for handling and transporting radioactive materials such as placing placards and labels on the truck as indicated in **Figure 3.2**. The tantalite mineral used in this study is classified as a Class 7 material under this legislation and as a Low Specific Activity (LSA 1) material under transport regulations.

[39] http://www.energy.gov.za/files/policies/act_nuclear_47_1999.pdf 05-04-2012

[40] International Atomic Energy Agency, *Naturally Occurring Radioactive Material (NORM VI)*. Proceedings of an International Symposium. Morocco, Marrakesh, 22–26 March 2010. STI/PUB/1497 (ISBN:978–92–0–113910–8)

[41] http://www.nnr.co.za/Portals/17/Regulation%20R388%2028%20April%202006.pdf 05-04-2012

[42] http://www.dwaf.gov.za/Documents/Other/WQM/RequirementsHazardousWasteSep05Part4.pdf 06-04-2012

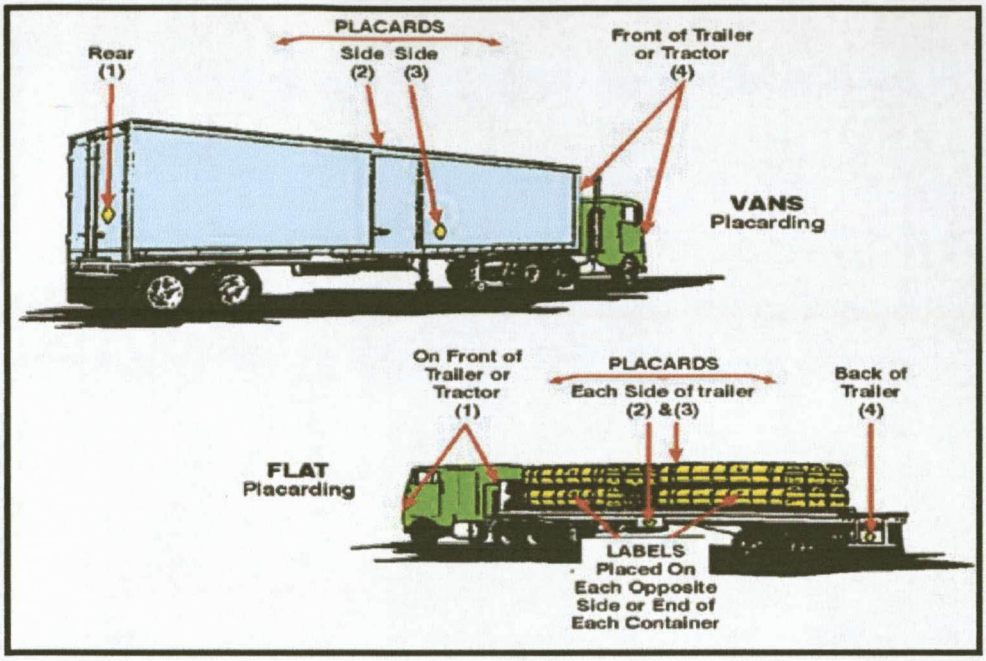

Figure 3.2: Protocols of transportation of radioactive material[43]

3.3.2 NORM waste

Radioactive waste could arise from all stages of mining and NORM processing and include waste rock and process water, including leaching solutions. Rainfall and runoff from stockpiles and areas of processing plants are also potential sources for the radioactive pollution. Radioactive waste is classified as high level waste (HLW), intermediate level waste (ILW) and low level waste (LLW). This depends on the source of the waste and radioactivity. The waste generated from tantalite processing may fall under intermediate and low level waste, depending on the activity it contains. Intermediate waste is one that dissipates less than 2 kW/m^3 of thermal power when packaged and transported for radionuclides with half lives less than 31 years. The activity in this waste should also be less than 400 Bq/g for alpha emitters and 4000 Bq/g for beta and gamma emitters with half lives greater than 31 years. The waste should be transported and stored in solid form for a period of 10 years and be disposed off to a maximum of 10 meters in the ground. This waste is also classified as NORM-E (enhanced activity) waste. Low level waste is one with activity less than 100 Bq/g for long lived radionuclides and dissipates no heat when packaged and transported. The waste can however, be disposed unpackaged. It is recommended

[43] http://www.nrc.gov/reading-rm/basic-ref/teachers/placarding.html 06-04-2012

that this waste be used as a backfill material for underground areas and also to be reprocessed for economical recovery of contained elements or minerals. Low level waste is also classified as NORM-L (low activity) waste.

The radiological hazards of waste are not the only issue operators should be concerned with also the presence of non-radiological substances in the waste can pose hazards to the public and to the environment. The presence of other species such as aluminium, manganese, tungsten and fluorinated compounds in the waste can also cause danger to the environment since HF is used to digest the mineral. Extraction processes and plant design should be carried out to minimise the exposure of these non-radiological hazards to the environment even though the activity may be of such a low level that is exempted from NORM classification. **Figure 3.3** shows the low level radioactive waste disposal site at Vaalputs.

Figure 3.3: Low level radioactive waste disposal site at Vaalputs[44]

3.3.3 Health hazards of NORMs

Workers at mines or NORM processing plants may receive radiation doses from ores, concentrates, the produced products, associated airborne dust, process fluids, industrial and analytical equipment (X-ray fluorescence), radon and radioactive

[44] http://financialresults.co.za/2010/eskom_ar2010/gb_nuc_env.htm 05-04-2012

waste. The protection of employees from the radiological hazards should not be considered in isolation without considering these sources of radiation exposure. The operators of these facilities should have a radiological protection programme in place which addresses all sources of radiation exposure associated with the functioning of the facilities, including the radioactive waste. The IAEA requires that the dose due to occupational exposure to radiation of workers should not exceed an effective dose of 20 mSv per year averaged over five consecutive years and 50 mSv in any one year. Furthermore, an effective dose to the lens of the eye of less than 150 mSv and a dose to the hands and feet or the skin of less than 500 mSv in a year are prescribed. It is also recommended that radiological protection be optimized so that doses received by the workforce are as low as reasonably achievable, social and economic factors being taken into account.[40] In addition, members of the public should receive doses that are attributed to these industrial practices should not exceed an effective dose of 1 mSv in a year or under special circumstances, an effective dose less of 5 mSv in a single year provided that the average dose over five consecutive years does not exceed 1 mSv per year. The National Nuclear Regulator Act, 1999 (Act No. 47 of 1999) regards any occurrence or succession of occurrences from the same origin and resulting in an unintended exposure to radiation or release of radioactive material capable of giving rise to an effective dose in excess of 1 mSv to the public or 50 mSv to a worker in a year on site received at the time of the event, as a nuclear accident.

The exposure to radiation can cause serious health effects such as cancer or even death if received in large doses. The lowest dose rate known not to cause cancer is 50 mSv/a and above this dose the chances of cancer occurrence increases with the increase in dose. If a total of 1000 mSv is accumulated over some time, there is a 5% probability of fatal cancer occurring in later years. On the other hand, if this dose is received in a short term, symptoms such as nausea and decreased white blood cells count would be experienced. Doses between 2000 and 10 000 mSv would cause severe sicknesses that can be fatal and above this dose sickness is immediate followed by death within few weeks.[45]

[45] http://www.dwaf.gov.za/iwqs/radioact/DWAFGuideline/section1.htm 05-04-2014

3.3.4 Determination of the activity concentration - application of the regulations[46]

The determination of the activity concentration of any radioactive material to be transported is necessary and should be compared with appropriate limits if it's established that compliance with the NORM regulations is obligatory. The activity concentration should be less than 10 Bq/g for it to be exempted from the regulations. For mineral ores and natural material containing NORMs that are in their natural state and that are not intended for the use of the radionuclides, this cut-off value is calculated using the sum of concentration of both ^{232}Th and ^{238}U, but it is not applicable to mining and milling operations.

Equation 3.1 is used to calculate the activity concentration only on the condition that the mineral ore had not been chemically and thermally processed previously. This equation estimates the total activity concentration assuming that Th and U are in their natural state (100% ^{232}Th and ^{238}U) and that their concentrations, in parts per million (ppm), are known.

$$[\text{Th (ppm)} \times (4.09\times10^{-3}\ \text{Bq/ µg}\ ^{232}\text{Th})] + [\text{U (ppm)} \times (1.25\times10^{-2}\ \text{Bq/µg}\ ^{238}\text{U})] \qquad \textbf{3.1}$$

The equation becomes more complicated (**Equation 3.2**) when the material has chemically and thermally been treated since the activity concentrations of the radionuclides in the Th and U decay series has to be determined and accounted for when calculating the total activity concentration. However, the analysis could take a long time to complete and could be costly.

$$\sum_j \left(\frac{C_i}{X_i}\right) \qquad \textbf{3.2}$$

In **Equation 3.2** is C_j the concentration of the radionuclide, X_j the exemption limit for each radionuclide present and j the total number of radionuclides present. The

[46] Department of Mines and Petroleum, 2010. *Managing naturally occurring radioactive material (NORM) in mining and mineral processing guideline. NORM - 4.3 Controlling NORM - Transport of NORM*, Department of Mines and Petroleum, Western Australia, 30pp. <http://www.dmp.wa.gov.au/>

material is exempt from the regulations when the sum of the activity concentration of the radionuclides is less than 1. The contributing factor to the complexity of the equation is the realization that the secular equilibrium of the radionuclides in the decay series is disrupted by chemical and thermal processing. Chemical processing of the material refers for example to processes such as leaching or addition of flotation agents to the material while thermal processing refers to heat treatment of the material. The latter has a suggested value of 250 to 300 °C as a general guide indicating that the secular equilibrium is been disrupted and that additional analyses is required for the radionuclides. The exemption values for these radionuclides are as follows:

^{232}Th = 100Bq/g, ^{228}Ra = 100Bq/g, ^{228}Th = 10Bq/g, ^{212}Pb = 100Bq/g
^{238}U = 100Bq/g, ^{230}Th = 10Bq/g, ^{226}Ra = 100Bq/g, ^{210}Pb = 100Bq/g

If it's established that the mineral is radioactive, then there is a need for the classification of the mineral to ensure that the proper display placards are used during transportation. To achieve this, the transport index and the category have to be determined first. The transport index is determined by measuring the maximum radiation level in mSv/h at a distance of 1 meter away from the surface of the package and multiplying that value by a factor of 100. On the other hand, the category is determined by measuring radiation on the surface and the classification will be as follows:-

- The categorization is "I-WHITE" if the transport index is 0 and the category is less than 5 μSv/h
- The categorization is "II-YELLOW" if the transport index is between 0 and 1 and the category is more than 5 μSv/h, but less than 500 μSv/h
- The categorization is "III-YELLOW" if the transport index is between 1 and 10 and the category is more than 500 μSv/h, but less than 2000 μSv/h

The marking "LSA-I" is put on the placard if the activity concentration is less than 300 Bq/g, but if the value exceeds 300 Bq/g the marking "LSA-II" is used instead.

3.4 Uranium and thorium

Uranium and thorium, which are present in the tantalite ore that was studied, are radioactive elements which are part of the actinide metals group with an abundance in the earth`s crust of 2.8 mg/kg and 9.6 mg/kg respectively. **Figure 3.4** shows the decay series of these two elements. Natural uranium consists of three major isotopes namely: ^{238}U (99.28%), ^{235}U (0.71%), and ^{234}U (0.0054%) and all three are radioactive, alpha emitting particles. ^{238}U is the most stable isotope of uranium with a half-life of 4.468×10^{9} years, followed by ^{235}U and ^{234}U with half-lives of 7.13×10^{8} years and 2.48×10^{5} years respectively. Thorium exists mainly as ^{232}Th in nature with a half-life of 14.05×10^{9} years and it also decays by emitting an alpha particle. Uranium is found in a variety of minerals such as pitchblende, uraninite, carnotite, autunite, uranophane, monazite and tobernite. Thorium, on the other hand occurs in several minerals including thorite, thorianite and monazite.

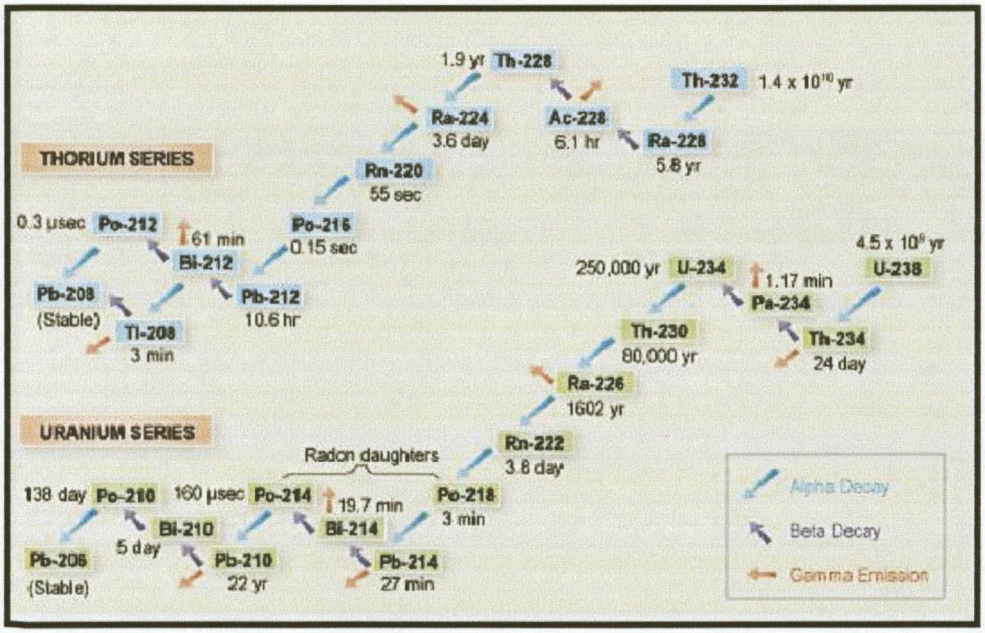

Figure 3.4: Uranium and thorium decay series[47]

Both metals have a wide variety of applications in industry, but their use in nuclear fuels attracts the greatest deal of attention. Thorium, as well as uranium can be used as nuclear fuels, even though the latter is not fissile. Uranium is enriched before

[47] http://www.world-nuclear.org/info/inf30.html 29-03-2012

being used in nuclear power reactors by increasing the percentage of ^{235}U to between 3% and 5% as it is only 0.71% in natural uranium. Uranium which is enriched to these levels is used to produce electricity. Current estimation indicate that at current prices and proven reserves, uranium will be depleted as energy source within the next 100 years while thorium as energy source will only be depleted in 15 000 years.[48] Thorium, as previously mentioned is not fissile, but it can be irradiated with neutrons to produce the ^{233}U isotope which is fissile and have a long half-live. ^{233}U is said to be better fuel than ^{235}U and ^{239}Pu because of its higher neutron yield per neutron absorbed when used as a breeder, which allows for a more efficient nuclear reaction. The major disadvantage of using thorium as a nuclear reaction breeder is the production of ^{233}Pa a neutron absorber, which diminishes the ^{233}U yield.[49] Recently there has been increasing interest in using thorium as a nuclear fuel since it is much more abundant than uranium and all the thorium is useable in a reactor compared to the 0.71% of natural uranium. Thorium therefore does not require enrichment as in the case of uranium.

South Africa has reasonable deposits of both uranium and thorium. Thorium is mainly found in the rare earth mineral monazite and zircon sand while uranium is mostly associated with gold and copper ores. However, monazite has never been commercially processed. Uranium is been processed as a by-product in gold and copper mining. New developments in the markets of thorium and uranium and other elements such as rare earths have sparked interest in processing the minerals containing these elements. These two elements however, are present in many minerals ores in trace quantities for example in zircon, pyrochlore, tantalum, gypsum and phosphate rocks. Mining and processing of these mineral ores for reasons other than for thorium and uranium mining becomes complicated by the presence of these radioactive elements. South Africa, having the mineral resources, has adopted a strategy to mine and process these minerals locally.[50] In the policy the need is also expressed to find additional sources of energy to replace the country's dependence on coal as a major source which accounts for approximately 90% of electricity

[48] Serfontein, D.E. and Mulder E.J., "Techno-economic overview of different thorium-based nuclear reactor design options". *Proceedings of the thorium and rare earth conference*. 2012, Cape town, pp 83-95

[49] http://www.world-nuclear.org/info/inf62.html 29-03-2012

[50] http://www.info.gov.za/view/DownloadFileAction?id=147564 05-04-2012

production in the country. Concerns over coal generated electricity include increases in the price of coal, reserve exhaustion and pollution as a result of greenhouse gas emissions and other atmospheric pollutants. These challenges present new opportunities to research and invest in the use of new nuclear energy sources in producing electricity due to its low carbon emission compared to fossil fuels.

3.4.1 Chemistry of uranium and thorium oxides

Thorium and uranium occur as the oxides in natural mineral ores. Thorium exists mainly as Th^{+4} in the minerals while uranium exists in two different stable oxidation states, namely as U^{+4} and U^{+6}. Thorium (IV) oxide is a white, crystalline powder while uranium oxides are black (UO_2), yellow-orange (UO_3) and greenish-black (U_3O_8) powders. Thorium and uranium oxides dissolve in nitric acid, sulphuric acid and hydrofluoric acid. Thorium oxide is formed by heating thorium nitrate or thorium hydroxide at 300 °C while uranium trioxide is also prepared by heating uranium nitrate.[51] UO_2 and U_3O_8 can be prepared by heating the trioxide, sometimes in the presence of a reducing agent (**Equation 3.3** and **3.4**).

$$3UO_3 \xrightarrow{700\ °C} U_3O_8 + \tfrac{1}{2}O_2 \qquad \textbf{3.3}$$

$$UO_3 + CO \xrightarrow{350\ °C} UO_2 + CO_2 \qquad \textbf{3.4}$$

The halides of uranium and thorium can be prepared by the halogenation of the metals or the oxides to form white polymeric solids. Industrially the most important uranium halide is the hexafluoride which is used for uranium enrichment. UF_6 can be synthesised by the ClF_3 fluorination method, but this method is not used at all on industrial scale because ClF_3 is explosive. UF_6 is synthesised by a method according to **Equation 3.5**. The hexachloride, on the other hand is manufactured by chlorination of U_3O_8 or UCl_4 at 400 °C. Uranium tetrahalides, except the fluoride compound are obtained by refluxing UO_3 with hexachloropropene, but the iodide decomposes to UI_3

[51] Hussein. G.A.M. and Ismail. H.M., Colloids Surfaces A: Physicochem. Eng. Aspects 99 (1995) 129-139

at room temperature. Thorium halides are best prepared by the reaction of the metal with a halide gas in THF at 0 °C (**Equation 3.6**).

$$UO_2 \xrightarrow{4HF} UF_4 \xrightarrow{F_2} UF_6 \qquad \textbf{3.5}$$

$$Th_{(s)} + 2X_2 \xrightarrow{THF\ 0°C} ThX_4(THF)_4 \qquad \textbf{3.6}$$

These thorium complexes, as well as uranium halogen compounds, are useful starting materials for the synthesis of a large range of compounds such as alkoxides, aryloxides, amido and phosphorus compounds (**Equation 3.7**).[52] Thorium oxide also reacts with thorium halides to form the oxohalides at elevated temperatures (**Equation 3.8**). The oxohalides can be precipitated from solutions of HF as the hydrated compounds. The addition of anions such as F^-, $C_2O_4^{2-}$, PO_4^{3-} and IO_4^- to strongly acidic solutions of thorium precipitates the thorium as insoluble salts and this allows the separation of thorium from other elements that form soluble complexes in strong acid medium.[53]

$$ThBr_4(THF) + 4KNPh_2 \longrightarrow Th(NPh_2)_4(THF) + 4KBr \qquad \textbf{3.7}$$

$$ThO_2 + ThX_4 \xrightarrow{\Delta} 2ThOX_2 \qquad \textbf{3.8}$$

The water soluble uranium oxohalides are produced by the heating of the oxide in a halogen acid (**Equation 3.9**).

$$UO_3 + 2HF \xrightarrow{400°C} UO_2F_2 + H_2O \qquad \textbf{3.9}$$

The uranium oxides can also be fused with a range of metal oxides, carbonates and acetates to form colourful compounds known as urinates (**Equation 3.10**).

[52] Clark, D. L., Frankcom, T. M., Miller, M. M. and Watkin, J. G., *Inorg. Chem.* 1992 31, pp.1628-1633.

[53] Cotton, A. F., Wilkinson, G., Murillo, A. C. and Bochmann, M., *Advanced Inorganic Chemistry.* 6th *ed.* 1999 p.1143

$$2UO_3 + Li_2CO_3 \longrightarrow Li_2U_2O_7 + CO_2 \qquad 3.10$$

3.4.2 Ore processing

The complexity of many uranium containing ores and the low concentrations of uranium in these ores, pose a difficult problem to the economic recovery of uranium. Uranium ores differ in chemical composition from the relatively simple pitchblende, which is accompanied by other minerals such as hiarneite, becquerelite and calciouranoite to exceedingly complex and refractory uranium-bearing titanites, niobates, and tantalates containing rare earths and many other metals. Thorium is mainly obtained from monazite which is the most important commercial source of thorium and the lanthanides and uranium is also sometimes extracted as a by-product. The processing for both elements includes acid or base leaching, recovery by ion exchange and solvent extraction (alkyl phosphoric acids and tertiary alkylamines in kerosene) and purification. The processing of uranium ores normally includes sulphuric acid or sodium carbonate as leachants while other acids such as hydrochloric acid and nitric acid can also be used to extract uranium from the ore. Sulphuric acid is however the most preferred due to its lower price and high boiling point. Carbonate leaching is preferred when the acid leaching of the ore is uneconomical and the process is based on the high stability of the uranyl (VI) tricarbonate ion, $UO_2(CO_3)_3^{4-}$ in aqueous solution at low hydroxide-ion concentrations. Carbonate leaching is also more selective than sulphuric acid leaching since it forms insoluble carbonates with a vast majority of elements except for U^{+6}. However, uranium in lower oxidation states does not dissolve in sodium carbonate requiring oxidants to complete the dissolution process. The advantages of carbonate leaching are the low reagent consumption and non-corrosiveness of the carbonate solution. The disadvantage however is lower uranium extraction compared to acid leaching and that the method is not suitable for ores having high gypsum or sulfide content.

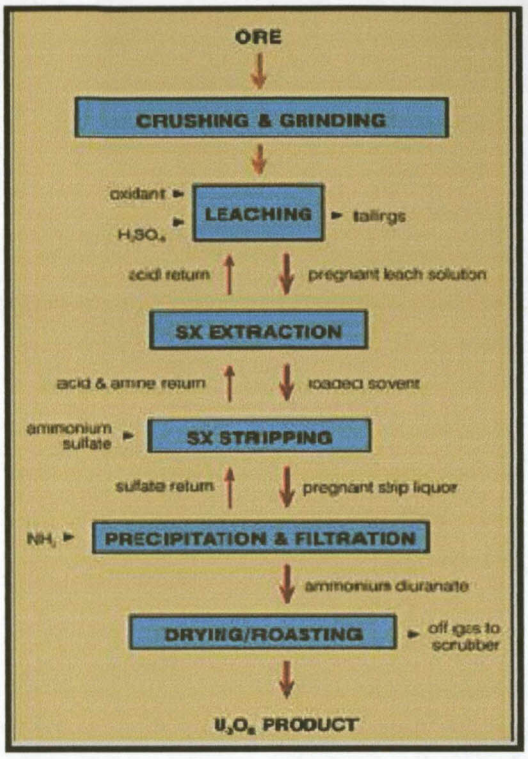

Figure 3.5: Processing of uranium ore[54]

The processing of uranium by sulphuric acid leaching is shown in **Figure 3.5**. In this process, an oxidant, usually Fe^{3+} is required to convert U(IV) to U(VI) which renders the uranium more soluble in sulphuric acid (**Equation 3.11** and **3.12**). Uranium is then separated by solvent exchange and precipitated by ammonia (**Equation 3.13**).

$$UO_2 + 2Fe^{3+} \longrightarrow UO_2^{2+} + 2Fe^{2+} \qquad \textbf{3.11}$$

$$UO_2^{2+} + 3SO_4^{2-} \longrightarrow UO_2(SO_4)_3^{4-} \qquad \textbf{3.12}$$

$$2UO_2(SO_4)_3^{4-} + 2NH_4OH \longrightarrow (NH_4)_2U_2O_7 \qquad \textbf{3.13}$$

Monazite is leached by either sulphuric acid or sodium hydroxide. In hydroxide leaching, an extra leaching step is necessary since insoluble hydroxides of uranium and thorium are formed. The advantage of alkaline over acid leaching is the production of sodium phosphate as a side-product which can be used in the fertilizer

[54] http://www.world-nuclear.org/education/chem.htm 07-05-2012

industry. **Figure 3.6** shows the processing of monazite using the alkaline leaching method. In this process the mineral ore is digested with sodium hydroxide at 140 °C to form a sodium phosphate solution and an insoluble cake of U, Th and rare earths (**Equation 3.14**). The insoluble cake is then dissolved in hydrochloric acid (**Equation 3.15**) and U and Th are precipitated by sodium hydroxide leaving the rare earths (RE) in solution.

$$(RE,Th,U)PO_4 + NaOH \longrightarrow (RE,Th,U)OH + Na_3PO_4 \qquad \textbf{3.14}$$

$$(RE,Th,U)OH + HCl \longrightarrow (RE,Th,U)Cl + H_2O \qquad \textbf{3.15}$$

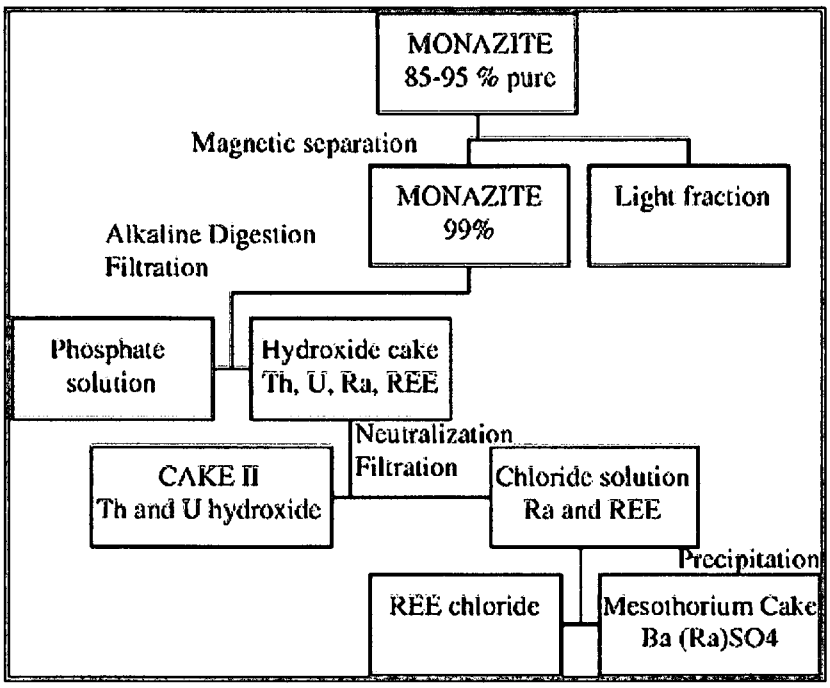

Figure 3.6: Alkaline processing of monazite[55]

[55] Da Costa Lauria. D. and Rochedo. E. R. R., Radiation Protection Dosimetry (2005) Vol. 114, No. 4, pp. 546–550

3.5 Conclusion

The exposure of people to radiation is unavoidable even if mining and processing activities are not taking place in their vicinity. The exposure arises from sources other than mining and processing and levels of it vary from place to place. Naturally occurring radioactive elements as sources of radiation, are present in a large variety of natural resources and can pose a great deal of danger if people are exposed to high concentrations of these materials. The presence of these NORMs in sources of industrial importance necessitates legislation to regulate the use of these sources and protect the workers and the public from excessive exposure to the NORMs. The legislation, however increase financial and operational hurdles to an organisation that intent to mine or process these sources.

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4 Analytical techniques for digestion and spectrometric analysis of niobium and tantalum containing minerals: Literature study

4.1 Introduction

Initially, the discovery of tantalum and niobium led to a lot of confusion and debate due to the similarity of the chemical properties of the two elements. At first it was believed that the two elements were different isotopes of the same element due to these similar chemical and physical properties. Niobium was, however, discovered in 1801 by English chemist Charles Hatchett (**Figure 4.1**) who analyzed the chemical composition of a "black rock" that was just sitting in the British museum for nearly 70 years. Tantalum on the other hand, was discovered a year later in Sweden by Anders Ekeberg (**Figure 4.1**). An English chemist William Hyde Wollaston compared the densities of the oxides derived from both columbite (5.918 g/cm^3) and tantalite (8 g/cm^3) and concluded that the two oxides were identical despite the significant difference in density. This conclusion was opposed in 1846 by the German chemist Heinrich Rose who proved that the two elements were indeed different from one another and not only isotopes of one element.[48,49] Further scientific evidence confirming the differences between the two elements came from Christian Wilhelm Iomstrand, Henri Etienne Sainte-Claire Deville, Louis J. Troost as well as Jean Charles Galissard de Marignac.[50,51]

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[48] Rose, H., *Annalen der Physik,* 139, 10, 1844, pp.317-341

[49] Rose, H., *Annalen der Physik*, 146, 4, 1847, pp.572-577

[50] Marignac, C.G.J., Blomstrand, C.W., Deville, E.H.S., Troost, J.L. and Hermann, R., *Fresenius' J. of Anal. Chem.,* 5, 1, 1866, pp.384-389

Figure 4.1: Anders Gustav Ekeberg (left) and Charles Hatchett (right)[52,53]

The discovery and the recent development of new and exciting commercial applications (**Chapter 2**) of both tantalum and niobium stimulated more interest and research into the processing and production of these elements from their respective minerals. Currently the main processing procedure of these elements entails the digesting of the mineral ores in HF at elevated temperatures and separating them from other impurities by solvent extraction.[9] However, HF is extremely toxic and the need for environmentally friendly digestion procedures is imperative. This chapter will deal with the reported studies on the dissolution and quantification of niobium and tantalum from their respective ores or minerals.

4.2 Digestion techniques and analysis

4.2.1 Acid digestion

Mineral ores containing niobium and tantalum are mainly digested by concentrated hydrofluoric acid and sulphuric acid. However, this method is most suited for high content niobium-tantalum ore.[54] Other digesting methods which include mineral acids,

[51] Marignac, M.C., *Annales de chimie et de physique,* 4, 8, 1866, pp.7-75

[52] http://www.nad.riksarkivet.se/sbl/Presentation.aspx?id=16798 13-06-2012

[53] http://www.liveinternet.ru/journalshowcomments.php?jpostid=199364035 13-06-2012

[54] Zhou, H., Yi, D., Zhang, Y. and Zheng, S., *Hydrometallurgy,* 80, 2005, pp.126-131

alkalis, flux fusion and microwave dissolution have being used to digest the mineral ores as well.

In 2001 El-Hussaini[55] reported the successful digestion of columbite by using combinations of HF-HNO_3 and HF-H_2SO_4 acids. Tantalum and niobium were then extracted from the acid solutions by solvent extraction using methyl isobutyl ketone (MIBK) and subsequently stripped from the organic layer using water or dilute hydrofluoric acid. In the HF/HNO_3/MIBK method 97.9% of tantalum was extracted into the organic layer while niobium remained in the aqueous later thus separating the two elements. The conditions for the extraction were i) HF (6.2 M)/HNO_3 (4.8 M), ii) 50% MIBK and iii) organic:aqueous (1:1). Tantalum was then stripped with successive amounts of HF (0.1 M) and then precipitated with ammonia. In the HF/H_2SO_4/MIBK method however, 96.3% Nb and 3% Ta were extracted into the organic layer and the optimal extraction conditions were found to be i) HF (4.3 M)/H_2SO_4 (11.4 M), ii) 100% MIBK and iii) organic:aqueous (10:1). Tantalum was then stripped with HF (1 M) from the organic layer while niobium along with trace amounts of tantalum was also stripped with water in this step. The concentrations of niobium and tantalum were quantified by UV-VIS spectroscopy using pyragallol as a complexing agent.

A year later the same group[56] reported the digestion of a tantalum and niobium ore from the Kab Amiri region in Egypt using a mixture of sulphuric acid (10.8 M) and nitric acid (5.3 M). Results obtained from this study indicated that the optimum dissolution conditions were i) the ore grounded to 74 μm, ii) digested with a mixture of 10.8 M sulfuric acid and 5.3 M nitric acid in a ratio of 1:3 and iii) 2 h reaction time at 200 °C. Tantalum and niobium were recovered at 93.38% and 99.5% respectively as indicated by UV-VIS spectroscopy. The results also indicate that 70% of REE oxides, 76.32% of ThO_2, 48.44% of TiO_2 and 44.98% of U_3O_8 along with tantalum and niobium were dissolved using this method.

[55] El-Hussaini, O. M. and EL-Hakam Mahdy, M. A., *Min. Pro. Ex. Rev.* 22, 2001, pp.633-650

[56] El-Hussaini, O. M. and Mahdy, M. A., *Hydrometallurgy* 64, 3, 2002, pp.219-229

In another study, El- Hussaini[57] digested the same tantalum-niobium ore from the Kab Amiri region which contained 16.16% Nb_2O_5 and 12.08% Ta_2O_5 with only sulphuric acid. The reaction conditions were the slightly different from the previously mentioned study, namely i) the digestion time of 3 hours, ii) a temperature of 80 °C and iii) the use of only sulphuric acid (10.8 M). The leach solutions were found to contain 11.49 g/L Nb, 10.05 g/L Ta and trace amounts of thorium, the rare-earth elements as well as U and Ti. This time the extraction ability of Alamine 336 was investigated by using kerosene or xylene as diluents. This method also employed the use of H_2O_2 and HF as oxidizing agents and the elements were stripped from the organic layer using potassium hydroxide and ammonium carbonate solutions. The optimum conditions for extraction and separation of niobium from tantalum were found to be 10% Alamine 336 diluted in kerosene which was mixed with a reaction solution containing HF (0.2 M), H_2SO_4 (0.5 M) and H_2O_2 (0.2%). Stripping of the loaded solvent was finally achieved with ammonium carbonate (25 g/L). The proposed processing of the ore is shown in the flowsheet **Figure 4.2**.

[57] El Hussaini, O.M. and Rice, N.M., *Hydrometallurgy*, 72, 2004, pp.259-267

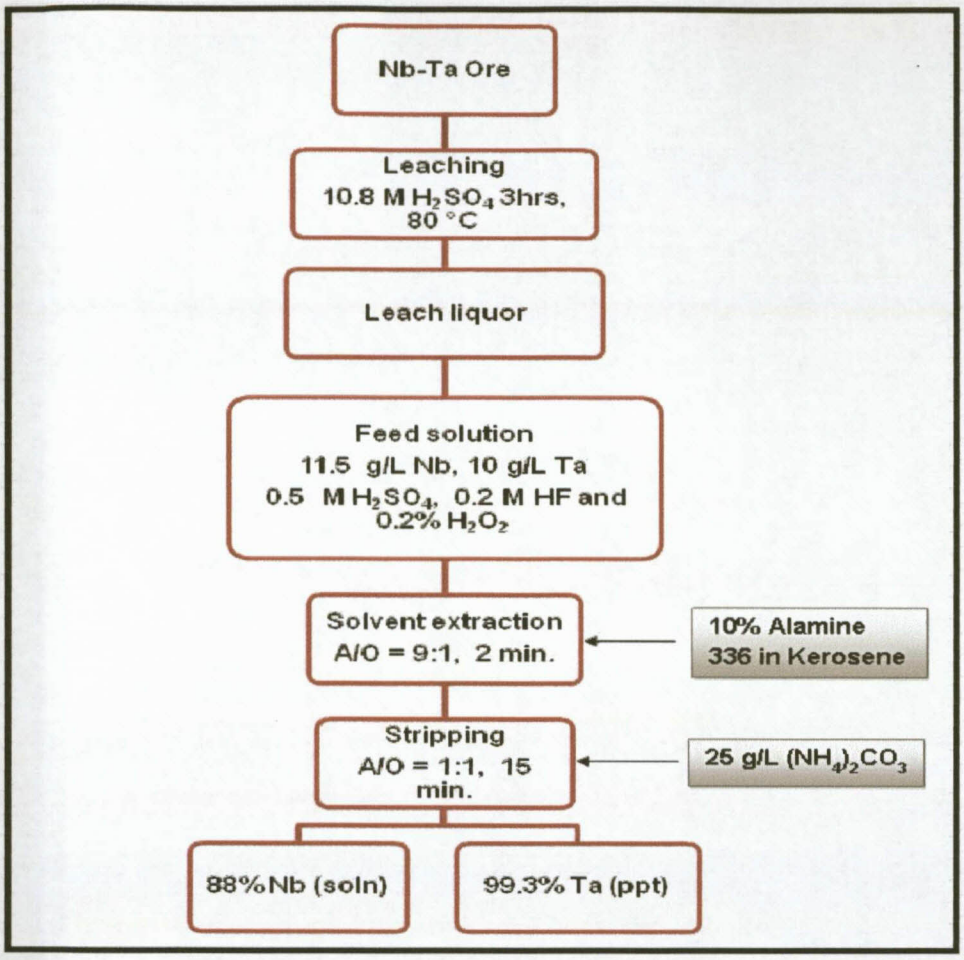

Figure 4.2: Proposed flowsheet for the extraction and separation of Nb and Ta[57]

In another study[58] niobium was successfully leached from a tantalite-columbite mineral from the Thayet Kon area in Pyinmana Township in the Republic of the Union of Myanmar, with a HF/H_2SO_4 mixture (6 M/2 M) at 100 °C. H_2SO_4 (4 M) was used to re-extract niobium from the MIBK layer back into the aqueous layer and the subsequent layer was treated with ammonia to precipitate niobium hydroxide. The precipitate was fluxed with sodium hydroxide, then extracted with hydrochloric acid and calcined to obtain niobium pentoxide with purity of 74%. The filtrate and the residue were dried and analyzed by X-ray fluorescence (XRF) and X-ray diffraction (XRD).

[58] Htwe, H. H. and Lwin, K. T., *World Academy of Science, Engineering and Technology*, 46, 2008, pp.133-135

Rodriguez[59] reported the digestion of ferrocolumbite with a mixture of tartaric acid and HF and succeeded to dissolve 95% of Nb and 91% of Ta in the sample. The digestion was done in a pressure reactor while the temperature, hydrofluoric acid concentration, solid/liquid ratio and carboxylic acid type (oxalic acid, tartaric acid and citric acid) as well as the concentration were varied to optimize the dissolution efficiency. It was found that the use of a mixture of tartaric acid 15% (w/v) and HF 15% (v/v) and digestion conditions of 220 °C for 80 minutes was the optimal conditions for this digestion method. The recoveries were determined on the residues by XRF analyses.

4.2.2 Alkali digestion

The alkali digestion of tantalum and niobium minerals has mostly been applied to low-grade ores due to the difficulty in digesting it with HF.[60] The use of this method attempted to eliminate volatilization, the consequent loss of analytes and fluorine pollution that is encountered as a result of HF digestion. Zhou *et al.*[61] reported the digestion of a niobium-tantalum ore with a concentrated KOH solution and recovered niobium and tantalum of 98.7% and 95.6% respectively after digestion at 300 °C for 1 hour. Various parameters such as temperature, KOH concentration, digestion time, ore:alkali mass ratio and particle size were examined to determine the most effective reaction conditions for the element recovery. The most efficient conditions for the digestion were found to be ore particle size with an average of 61 μm, 84 % (w/w) KOH solution and mass ratio of ore:alkali of 1:7. Analyses were accomplished using inductively coupled plasma optical emission spectrometry (ICP-OES).

Wang[62] modified Zhou's KOH digestion process by first adjusting the Nb:Ta ratio in the ore by the addition of Nb_2O_5 to the ore before digestion. Solid KOH was then heated in a reactor to the desired temperature and the adjusted ore was added. The hot mixture was stirred for some time, cooled to room temperature and dissolved in water. The optimal conditions were found to be a Nb:Ta mass ratio of 2.33:1;

[59] Rodriguez, M., Rivarola, J. and Ruizet, M. C., *Hydrometallurgy,* 74, 2004, pp.39-46

[60] Li, S., Zhou, Y., Du, H. and Qian, G., "*Development and Applying Technology of Niobium Resource*" Metallurgical Industry Press, 1992, Beijing, p.120.

[61] Zhou, H., Zheng, S. and Zhang. Y., *Hydrometallurgy,* 2005, 80, pp.83-89.

[62] Wang, X., Zheng, S., Xu, H. and Zhang, Y., *Hydrometallurgy,* 2009, 98, pp.219-223

KOH:ore mass ratio 2:1 and a reaction time of 60 minutes at 400 °C. Quantification indicates a 95% Nb and 94% Ta recovery of the extraction with water. The advantage of this method is that the amount of KOH used per ore quantity is much smaller in this modified method compared to that in Zhou`s original method and offers almost the same recoveries. It is suggested that the entire process favours the formation of water soluble $K_3(Nb,Ta)O_4$ and minimizes the formation of insoluble $KTaO_3$ and $K(Ta,Nb)O_3$ that is always encountered when digesting with KOH solutions.[61,62] All the quantitative analyses were carried out with ICP-OES.

4.2.3 Flux fusion

The flux fusion method has extensively being applied since 1856 to dissolve tantalum and niobium minerals. Different fluxes have been used by scientists to completely dissolve the minerals. One of the first recorded methods for the dissolution of a Nb/Ta containing mineral is the potassium hydrogen sulphate flux fusion by Berzelius in 1802.[63] The subsequent melt was dissolved in water producing hydrated species of niobium and tantalum oxides.

Sears[64] flux fused both tantalite and columbite with sodium pyrosulphate in a 1:7 ore:flux ratio at temperature which ranged between 800 to 900°C and 770 to 900°C respectively. Results indicated that the tantalum did not dissolve at any of the temperatures used, but that most of the niobium was dissolved from the tantalite. It was also found that the niobium dissolved completely at 770°C and 810°C from the columbite and only a relative small amount of tantalum was dissolved in the same process, indicating to some degree of separation and purification in this process. The subsequent melt was dissolved in water and filtered to remove the unreacted ore. The residue was dissolved in hydrofluoric acid and small amount of tantalum was crystallized as K_2TaF_7 by adding a potassium fluoride solution, leaving only the niobium in solution.

[63] Berzelius, J. J., *Afhand. Nya Handl.*, 1802, 23, p180

[64] Sears, G.W., *J. Amer. Chem. Soc.*, 1926, 48, pp.343-348

Greenland *et al.*[65] fused niobium containing minerals with sodium peroxide in the presence of a ^{95}Nb isotope. The obtained melt was washed with water and the insoluble part of the melt was then dissolved in a HF/H_2SO_4 acid mixture. The niobium in this solution was extracted with MIBK and further purified by ion exchange. Niobium was analyzed spectrophotometrically with 4-(2-pyridylazo)-resorcinol.

In another study Padmasubashini[66] fused a mineral sample with potassium hydrogen sulphate in a flux to sample ratio of 16:1. The clear melt was dissolved in 3% (w/v) ammonium oxalate followed by the precipitation of niobium and tantalum with NH_4OH. The filtrate was further digested on a hot water bath for 15 min, filtered and analysed separately for tungsten because of its spectral interference with niobium.

Premadas *et al.*[67] reported a simple and efficient method for the complete characterization of columbite-tantalite mineral. The method involved firstly the complete digestion of 0.6 g mineral sample by fusion with a flux made of KHF_2 and NaF in a 3:1 mass ratio. The melt was then dissolved in oxalic acid (0.2 M, 120 mL) and boiled with H_2O_2 (0.5 mL) for 2-5 minutes. Characterization of the mineral was carried out using ICP and flame atomic absorption spectrometry (FAAS).

In a recent study Mahanta *et al.*[68] performed a new flux dissolution method on a tantalum-containing mineral. The method entails the digesting of a mineral sample with a flux consisting of a 1:1 mixture of Na_2HPO_4 and $NaH_2PO_4 \cdot H_2O$ and a sample:flux ratio of 1:16. The obtained melt was dissolved in water and a quantitative analysis was performed with ICP-OES. The method was tested on 5 different mineral samples (see **Table 4-1**) and the validity of the dissolution method was confirmed with 2 CRMs and 3 synthetically prepared samples (see **Table 4-2**). The results of the proposed method are in good agreement with those of the compared methods

[65] Greenland, P. L. and Campbell, E. Y., *Analytica Chimica Acta*, 49, 1, 1970, pp.109-114

[66] Padmasubashini, V., Ganguly, M. K., Satyanarayana, k. and Malhotra, R. K., *Talanta,* 1999, 50, pp.669-676

[67] Premadas, A., Hanuman, V.V. and Dwivedi, V.N., *Atomic Spectroscopy.* 2004, 25, 2, pp.70-78.

[68] Mahanta, P.L., Hanuman, V.V., Radhamani, R. and Srivastava, P.K., *Atomic Spectroscopy.* 2008, 29, 5, pp.172-179.

used to dissolve Ta/Nb containing minerals from the 5 different mineral ores. The method also gives excellent dissolution and recovery of niobium and tantalum from the CRM and the synthetic materials.

Table 4.1: Comparison of results obtained by three different methods[68]

Samples	Ta_2O_5 (%)			Nb_2O_5 (%)		
	Proposed method	$KHSO_4$ method	$NaF+KHF_2$ method	Proposed method	$KHSO_4$ method	$NaF+KHF_2$ method
Cb-1	12.20	11.90	11.80	65.50	65.00	64.60
Cb-2	16.70	16.50	16.00	61.20	61.70	60.50
Cb-3	25.70	25.50	26.00	52.30	52.00	53.00
Ta-1	47.60	48.00	47.40	21.80	21.50	21.60
Ta-2	51.20	50.90	50.50	19.50	19.08	19.00

Table 4.2: Nb and Ta recovery from $Na_2HPO_4/NaH_2PO_4{\cdot}H_2O$ digestion[68]

Samples	Nb_2O_5 (%)		Ta_2O_5 (%)	
	Certified	Obtained	Certified	Obtained
IGS-33	68.71	69.00	5.52	5.10
IGS-34	27.45	26.90	49.80	49.70
SYN-1	9.80	10.0	5.1	5.0
SYN-2	4.1	4.0	9.90	10.0
SYN-3	1.9	2.0	2.9	3.0

In a study carried out by Nete[69] pure niobium and tantalum oxides were completely dissolved with the aid of a lithium tetraborate flux at 1100°C. The resultant melts were dissolved with sulphuric acid with simultaneous addition of ethanol to remove the excess of boric acid in solution as the $B(OEt)_3$ ester. In the case of Ta_2O_5[70] the combination of phosphoric acid and methanol was used for the melt dissolution and boron removal.

[69] Nete, M., Purcell, W., Snyders, E. and Nel, J.T., *S. Afr. J. Chem.*, 2010, 63, pp.130-134

4.2.4 Microwave digestion

In recent years, microwave digestion has gained increasing interest as dissolution technique for solid samples.[71] Its popularity is due to the fact that it is faster, cleaner, more reproducible, and more effective than traditional dissolution methods. Sen Gupta[71] developed a new microwave digestion method for the rapid determination of traces of niobium, tantalum and various elements in silicate rocks and lake, stream and river sediments. The method involved the dissolution of samples with a mixture of 2.5 mL of HF (27 M), 3 mL of HNO_3 (16 M) and 3 mL of HCl (12 M), in a microwave oven for a period of 16 minutes. The solutions were then cooled to room temperature, a mixture of 30 mL boric acid and EDTA were added to the solutions and heated for a further 8 minutes in the microwave. The translucent solutions were transferred into polypropylene tubes by rinsing with 2% HNO_3 and filled to the mark with water for analysis. The accuracy and recovery of the method were confirmed by 4 reference materials (**Table 4.3**). The recoveries were analyzed by ICP-MS using ruthenium and rhenium as internal standards.

Table 4.3 Recoveries of Ta and Nb from 4 reference materials[71]

Samples	Nb_2O_5 %		Ta_2O_5 %	
	Certified	Obtained	Certified	Obtained
SY-2	29 ± 6	32 ± 1	2.0 ± 0.2	2.0 ± 0.1
MRG-1	20 ± 4	21 ± 1	0.80 ± 0.05	0.84 ± 0.04
BCR-1	14 ± 3	13 ± 1	0.79 ± 0.03	0.64 ± 0.04
MAG-1	12[a]	18 ± 1	1.0 ± 0.2	1.2 ± 0.2

a = working value quoted from another source by author

In another study by Conte *et al.*[72] a tantalite ore was completely dissolved with a HBF_4 (10 mL), H_2SO_4 (2 mL) and $HClO_4$ (1 mL) mixture in the microwave by several sequential heating steps with varying pressure. The solution was quantitatively transferred into polyethylene flasks and filled to the mark with water. The mineral was

[70] Theron, T.A., Nete, M., Venter, J.A., Purcell, W. and Nel, J.T., *S. Afr. J. Chem.*, 2011, 64, pp.173-178

[71] Sen Gupta, J.G. and Bertrand, N.B., *Talanta,* 1995, 42, pp.1947-1957

[72] Conte, A.R., Mermet, J.M., Rodriues, D.J. and Di Martino, J.L., *J. Anal. Atom. Spectrom*etry, 12, 1997, pp.1215-1220

found to consist of Ta (37.9%) and Nb (11.8%) as the oxides and a synthetic sample was used to evaluate the accuracy of the method. It was found that tantalum and niobium were recovered at 96% and 97.5% respectively from the synthetic sample. Analyses were carried out by ICP-OES.

Nete[2] found an alternative method for the dissolution of niobium containing samples. Niobium metal, NbF_5, Nb_2O_5 and two different tantalite ore samples were dissolved by microwave assisted digestion using concentrated sulphuric acid. The method was successful in dissolving high purity niobium samples with recoveries up to 100%. The mineral ore samples however, were not completely dissolved and required longer digestion times to attain a maximum dissolution of 93.98%. However, the flux fusion method that was also investigated in this study as an alternative dissolution method afforded improved dissolution of the mineral ore samples compared to the microwave digestion method (**Table 4.4**).

Table 4.4: Nb recoveries from different dissolution methods

Sample	Nb recovery %	
	Microwave digestion	Flux fusion
NbF_5	100.95	...
Nb_2O_5	99.50	102.76
Nb metal	99.93	...
Tantalite A	90.00	98.56
Tantalite B	93.98	109.59

...= Not conducted

4.3 Comparison and selection of analytical techniques used in this study

4.3.1 Introduction

Elemental analysis of minerals is one of the most important steps in earth sciences since it allows for the identification and classification of these minerals. A large number of minerals are of economic and technological importance and hence elemental analysis becomes an indispensable requirement for quality assurance and

control. The selection of an analytical technique is therefore also an important decision since the sample type and analytical requirements have to be well thought-out before doing the analysis to ensure the correct qualification of the elements contained in these minerals.

In this study a tantalite mineral was used as the sample and the techniques that are mostly used for this type of samples will be briefly discussed while those that were selected are discussed in detail.

4.3.2 X-ray spectrometry

X-ray spectrometry[73] includes the measurement of absorption, scattering, diffraction and fluorescence of electromagnetic radiation of which are characteristic of different materials or elements. X-ray diffraction (XRD) and X-ray fluorescence (XRF) are the most universally applied techniques for the study of minerals and ores and are said to complement each other. For example, a sample can be found to contain 40% Si and 35% Al by XRF, however, XRD can distinguish between the different phases of samples and identify if the sample is Mullite ($Al_6Si_2O_{13}$) or Kaolinite ($Al_2Si_2O_5(OH)_4$) or any combination of these. The advantage of the use of these techniques for the identification and quantification of the different elements in the minerals is that no sample dissolution is needed prior to analysis

4.3.2.1 X-ray diffraction

X-ray diffraction is based on the interaction of X-rays with electrons of the atoms of a crystalline material, resulting in scattering of the X- rays. Constructive and destructive interference occurs if the spacing between the atoms is of the same magnitude as the wavelength of the X-rays. This result in X-rays that are diffracted at characteristic angles based on the spaces between the atoms. The technique operates on the important equation of Bragg`s law[74] (**Equation 4.1**) which relates the scattering angle (θ), the wavelength of radiation (λ) and the spacing of the scattering centres in the material.

[73] Skoog, D.A., Holler, F.J. and Crouch, R.S., *"Principles of instrumental analysis"* 6th *ed.* Thomson Brooks/Cole, 2007. pp. 291-292, 303, 309

[74] http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/bragg.htmL 14-07-2012

$$n\lambda = 2d \sin \theta \qquad 4.1$$

In this technique, X-ray beams of fixed wavelengths strike the surface of a crystal and the crystal planes at an incident angle (θ), intense reflected X-rays are produced when the wavelengths of the scattered X-rays interfere constructively. For the waves to interfere constructively, the differences in the distances travelled through the crystal planes must be equal to integer multiples of the wavelength then the diffracted beam of X-rays will leave the crystal at an angle equal to that of the incident beam. **Figure 4.3** illustrates the phenomena of X-ray diffraction.

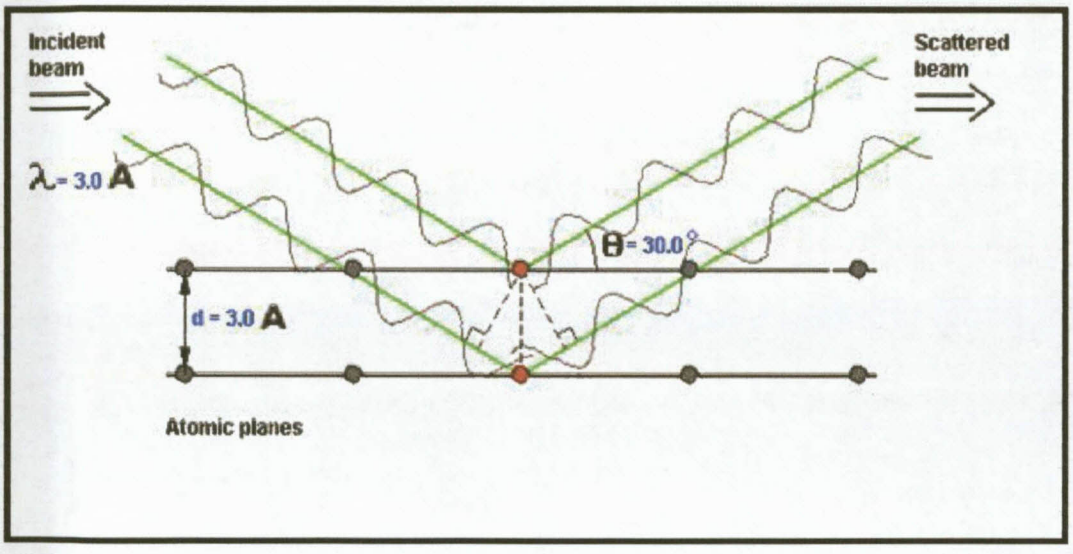

Figure 4.3: X-ray diffraction[75]

4.3.2.1 X-ray fluorescence

XRF is based on the analysis of the emitted characteristic secondary or fluorescent X-rays from a material that has been bombarded with high-energy X-rays. During this process, electrons are ejected from the inner shells, creating an unstable condition for the atom. Atoms return to their stable condition with electrons cascading from the outer shells to the inner shells and emit characteristic X-rays with energy equal to the difference between the two binding energies of the corresponding shells is given off

[75] http://www.asdlib.org/onlineArticles/ecourseware/Bullen_XRD/XRDModule_Theory_Diffraction_4.htm 13-08-2012

as indicated in **Figure 4.4.**[76] Each element has a unique set of energy levels; and therefore produces X-rays at a unique set of energies which is characteristic of the different elements, allowing for the non-destructive measurement of the elemental composition of a sample.

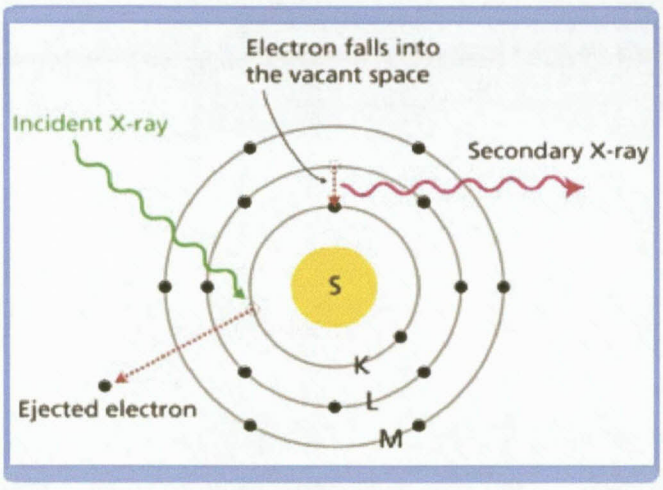

Figure 4.4: X-ray fluorescence

The major advantage of XRD and XRF as analytical techniques is the ease of sample preparation. Additionally, the techniques are non-destructive and require no sample dissolution when they are compared to other spectrometric techniques such as AA and ICP. Disadvantages include a large sample size compared to other methods and the accuracy is highly dependent on the homogeneity of the sample. The positive identification of the sample containing mixtures of crystalline complexes can be difficult with XRD. Although XRF generally has detection limits in the ppm[77] range, it is not as sensitive as for example ICP-OES and ICP-MS (ppm to ppb). The techniques were however not used in this study due to the availability of a dissolution method and that a smaller sample size was used throughout the study.

4.3.3 UV-VIS spectroscopy

The application of UV-VIS as a quantitative analytical technique is firmly based on the principle that coloured complexes can be formed between an analyte and a

[76] http://www.oxford-instruments.com/applications-markets/environment/environmental-monitoring/rohs/Pages/X-ray-fluorescence-xrf.aspx 03-09-2012

[77] http://serc.carleton.edu/research_education/geochemsheets/techniques/XRF.htmL 14-07-2012

particular ligand or complexing agent. For this technique to be successful, the analyte must completely react with the complexing agent resulting in a colourful solution, be sensitive (have lower limit of quantification) and obey Beer`s law over the working range of the calibration curve. **Figure 4.5** shows the principle of the technique and the equations involved in this technique including Beer`s law. The advantages of this technique are that it is simple, fast, versatile, accurate in the ppm range and cost effective. The disadvantages on the other hand are that non-coloured complexes cannot be analyzed and a suitable complexing agent must be found before doing the analysis. Furthermore, the interference of absorbing molecules in the sample and the non-linear behaviour of the absorbance due to the presence of other elements in the sample limits the use of this method.

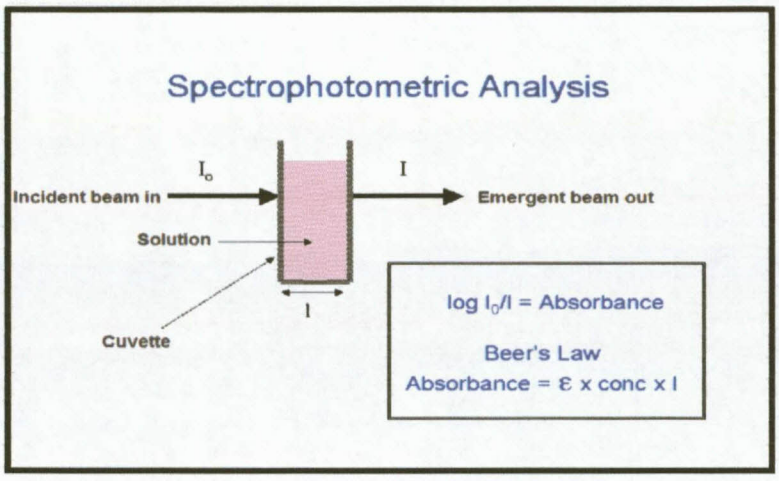

Figure 4.5: UV-VIS Beer`s law[78]

The sample used in this study is a tantalite mineral sample and it is anticipated that its successful analysis will be highly limited due to the large number of elements present in the sample which may interfere with the respective quantification of the different elements. Unless additional steps are introduced to separate the elements of the mineral ore which may increase the processing time and complexity, the use of this technique is considered not to be ideal for this study. In this instance, techniques such as AA, ICP-OES and ICP-MS are considered to be more appropriate due to

[78] http://www.paduiblog.com/pa-dui/wellspan-is-to-be-commended-but-why-people-who-have-been-convicted-for-decades-of-a-dui-should-be-upset 03-09-2012

their multi-elemental analysis capabilities and their independence to complex formation prior to analyses.

4.3.4 Atomic absorption

In atomic absorption (AA) spectroscopy, the absorption of light is used to measure the concentration of the analyte. The light source is usually a hollow cathode lamp which is made of the analyte metal to be analyzed and which produces wavelengths characteristic of the analyte. The lamp consists of a metal cathode (element of interest) and an anode and is filled with low pressure argon or neon gas. The application of a voltage across the electrodes causes ionization of gas particles and a series of reactions takes place. The ionized gas particles (**Equation 4.2**) strike the cathode with sufficient energy to dislodge some of the metal atoms producing an atomic cloud (**Equation 4.3**). Some of the dislodged atoms are in excited state (**Equation 4.4**) and emit characteristic wavelengths as they return to ground state (**Equation 4.5**) for example, Nb (334.91 nm), Ta (271.5 nm), Th (371.9 nm) and U (358.5 nm).

$$Ar + e^- \longrightarrow Ar^+ + 2e^- \qquad \textbf{4.2}$$

$$M_{(s)} + Ar^+ \longrightarrow M_{(g)} + Ar \qquad \textbf{4.3}$$

$$M_{(g)} + Ar^+ \longrightarrow M^*_{(g)} + Ar \qquad \textbf{4.4}$$

$$M^*_{(g)} \longrightarrow M_{(g)} + hv \qquad \textbf{4.5}$$

The samples must be in the gaseous state for them to be analyzed and vaporization of the sample is therefore a crucial step in this method of analysis. Vaporization is achieved by using a flame or a graphite furnace by the aspirating of the sample with a gas mixture to form small droplets which are then introduced into the flame or the furnace. Monochromators and detectors are used to isolate the absorption line from the background light and measure the absorbance by applying the Beer-Lambert law (**Figure 4.6**).

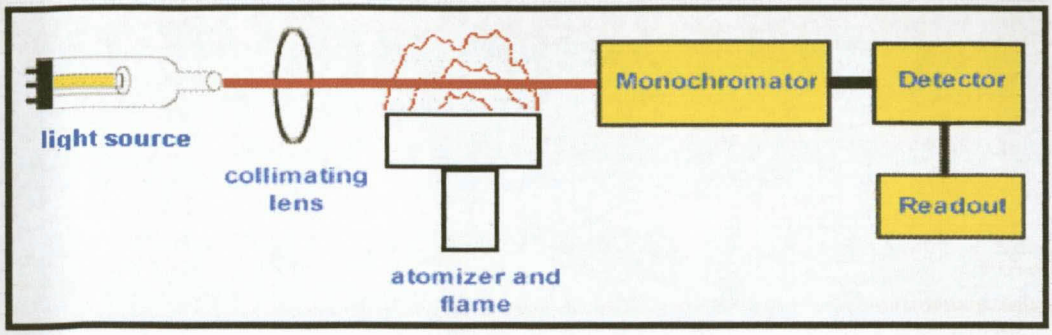

Figure 4.6: Operation principle of AA spectroscopy[79]

Advantages of this technique include the analysis of different elements, relatively low detection limits (even lower with graphite furnace) and ease of instrument operation. Major disadvantage however include not all elements of the periodic table can be analyzed, such as sulphur, phosphorous and other non-metals. A sequential analysis is also needed for the quantification of more than one element which leads to an increase in time for sample analysis and sample consumption.

4.3.5 Inductively Coupled Plasma - Optical Emission Spectroscopy

Inductively coupled plasma - optical emission spectrometry (ICP-OES), is an analytical technique that uses a high temperature flame to produce excited atoms, elemental ions and molecules in the analyte sample. Like AA spectroscopy, ICP measurements rely on the emission of electromagnetic radiation from excited atoms and/or ions at wavelengths characteristic and unique to a particular element. The intensity of this emission is directly proportional to the concentration of the element within the sample.

The basic components of an ICP instrument include the peristaltic pump to introduce the sample into the nebulizer. The nebulizer turns the sample into fine droplets by a stream of argon gas that also carries the droplets into the torch. The plasma flame is formed at the top of the torch and the sample droplets move through the torch into the plasma to get vaporised and excited. The excited ions emit light which is then detected by the optics of the equipment and is sent through a series of diffraction

[79] http://chemtech.org/cn/ctec2431/2431-7.htm 26-06-2012

gratings to take readings at each of the element's characteristic emission wavelengths. **Figure 4.7** shows the basic layout of an ICP instrument.

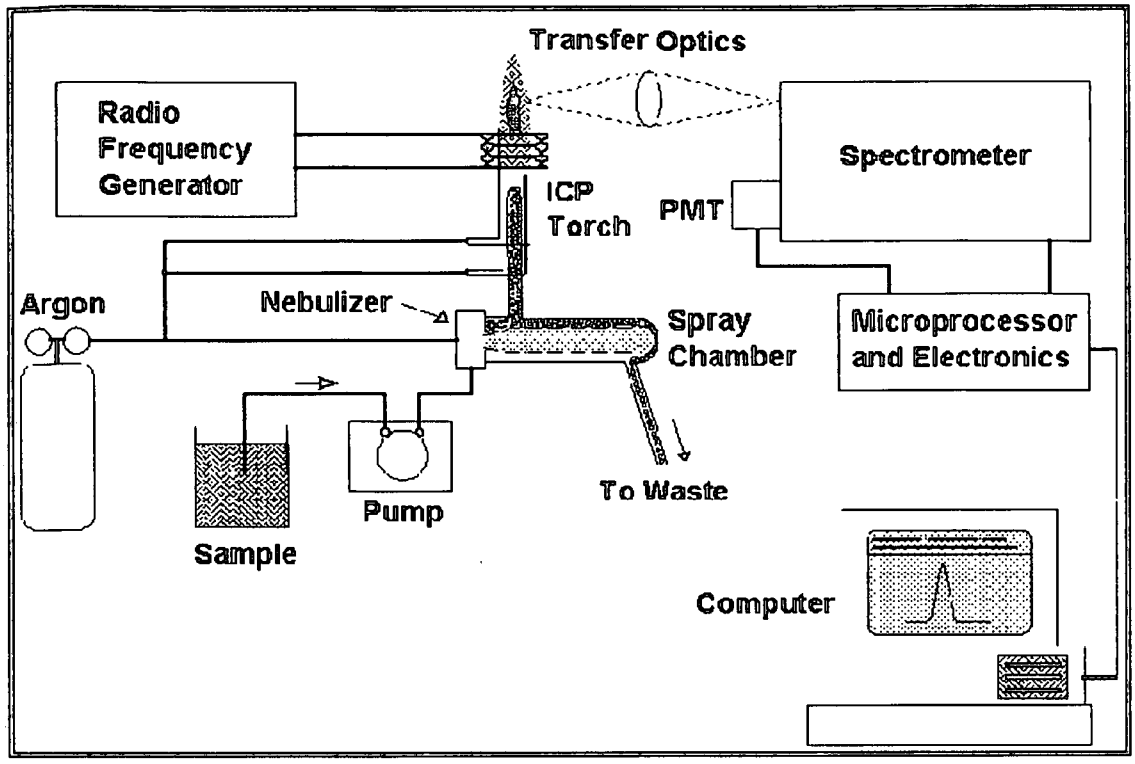

Figure 4.7: Schematic layout of an ICP instrument[80]

4.3.5.1 Sample preparation and introduction

The most important part in ICP analyses is sample preparation which has a direct impact on accurate and complete analysis of any element. The sample has to be in liquid form for ICP analysis which is mostly viewed as a drawback of the technique, but this avoids the homogeneity issues encountered in XRD and XRF. However, dissolution of minerals as samples is very difficult and problematic to achieve and another problem is that of matrix-matching when preparing samples, even if dissolution is achieved. The use of standards is required for any specific analysis to match the matrix as close as possible to that of the sample. Some ICP instruments are capable of analyzing samples in a slurry form and for this technique complete dissolution is not required. This procedure however involve a different sample introduction setup, especially regarding the nebulizer, spray chamber and the torch.

[80] Boss. B.C. and Fredeen. J.K., *Concepts, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectroscopy.* 2nd *ed.*, 1997. Pp.25, 31

Sample introduction is achieved by the use of a peristaltic pump (**Figure 4.8**) where a series of rollers is utilized to push the sample solution through the tubing using a process known as peristalsis. The pump itself does not come in contact with the solution and it is only the tubing that carries the solution from the sample vessel to the nebulizer that gets into contact with the solution. The tubing that is utilized must therefore be compatible with the sample that is passing through it. Weakly acidified aqueous solutions are in most cases used in ICP analyses, while strongly acidic solutions or organic solvents requires the use of tubing made of compatible materials and pumping. An advantage of using a peristaltic pump is that a solution with a fixed flow rate is allowed into the nebulizer and is independent of solution parameters such as viscosity and surface tension. On the other hand, the tubing must be inspected and replaced every so often to avoid wearing of the tubing which may lead to poor instrument performance.

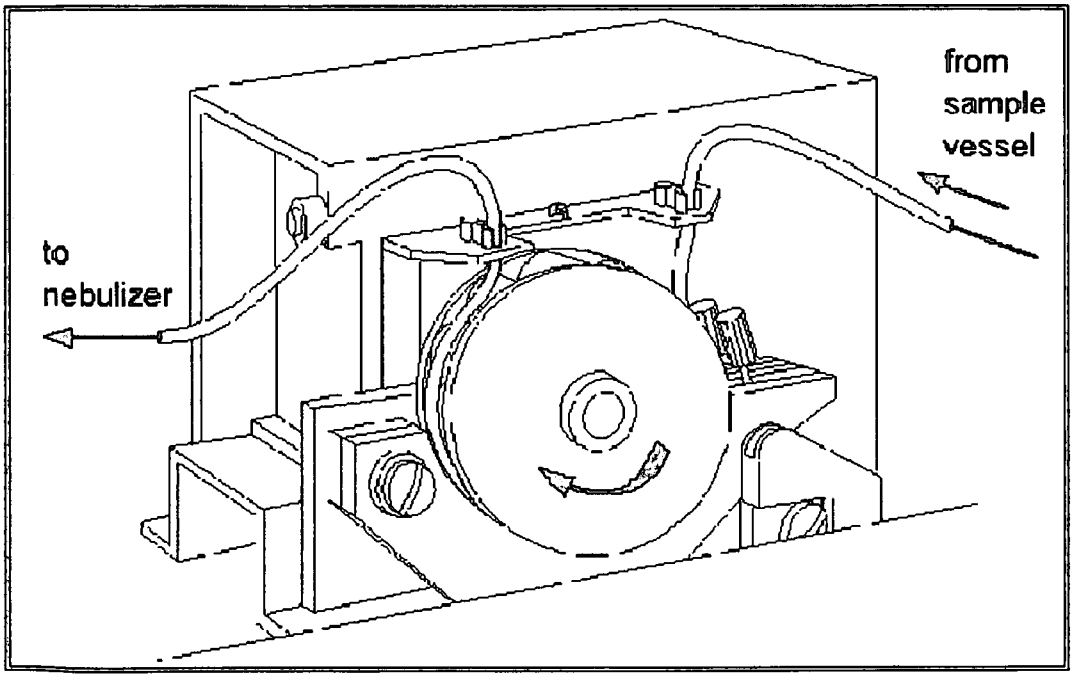

Figure 4.8: Peristaltic pump[80]

4.3.5.2 Nebulizer and spray chamber

The nebulisation process is one of the most important processes in ICP spectroscopy because only small droplets are required for analyses. There are two types of nebulizers that have been successfully used in ICP, pneumatic and ultrasonic

nebulizers. The pneumatic kinds are, however, the most commercially used ICP nebulizers. The pneumatic nebulizer also comes in different types, concentric tube, cross-flow, Babington and fritted disk, depending on how the solution is transferred into the plasma. The concentric pneumatic nebulizer (**Figure 4.9**), which was used in this study, introduces the solution through a capillary tube by a gas flowing rapidly past the end of the capillary. The high speed breaks the sample into an aerosol and carries it to the plasma.

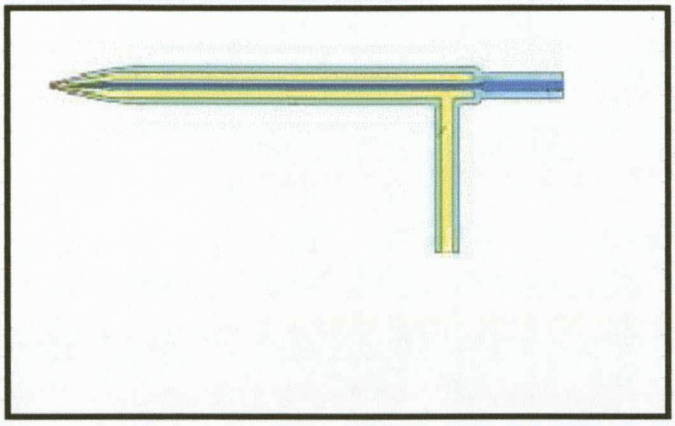

Figure 4.9: Concentric pneumatic nebulizer[81]

Once the sample aerosol is produced by the nebulizer, it is transported to the torch to be injected into the plasma. Since only very small droplets in the aerosol are appropriate for injection into the plasma, the aerosol is carried into the spray chamber while larger droplets are separated by gravity. This is done by the swirling of the droplets by the pressure of the argon gas flow from the nebuliser. The circular motion forces the larger droplets to collide within the side of the chamber and exit at the bottom and allow all the droplets of appropriate size to be blown into the torch.

4.3.5.3 Torch

The torch (**Figure 4.10**) consists of three concentric tubes through which argon gas flows. The outer loop or the tangential gas inlet main purpose is to cool the centre tube of the torch. The intermediate or auxiliary gas inlet together with the outer loop

[81] http://www.free-photos.biz/photographs/science/photos_of_chemistry/page 3/17-07-2012

gas flow forms the plasma source in the equipment. Lastly is the inner loop or nebulizer gas flow mainly carries the sample into the plasma. The torch is surrounded at the top by an induction coil, called the RF coil or the load coil and is powered by a radio frequency (RF) generator. The application of RF power to the load coil produces an alternating current which oscillates within the coil and this causes the magnetic field to be generated on top of the torch. The flowing argon is ionised by a spark from a Tesla coil and the resulting ions and electrons interact with the magnetic field which is produced by the RF coil. This interaction causes the ions and electrons to flow in a closed annular path and the friction produced by the movement of the electrons and the argon ions thus produces the high temperature plasma (6000 – 10000K). The plasma is sustained and stabilized by the argon ions that are formed in the plasma itself (**Equation 4.6**).

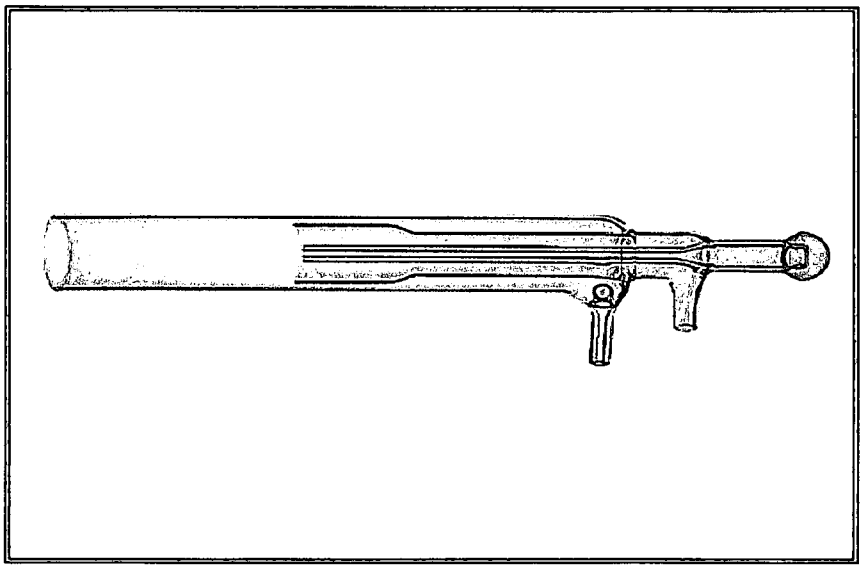

Figure 4.10: ICP quartz torch[82]

$$Ar + Energy \longrightarrow Ar^{+} + e^{-} \qquad \textbf{4.6}$$

4.3.5.4 Optics

The moment the sample aerosol is introduced in the plasma by the carrier gas, it gets desolvated, atomized, excited and ionized. The light emitted from the excited ions

[82] http://www.precisionglassblowing.com/catalog/icp-consumables-other-icp-torches-acc-c-1_78_107.htmL 26-07-2012

which is directly proportional to the amount of analyte present in the sample, is measured by the spectrometer. The light is resolved into a spectrum of its constituents' wavelengths by a grating system as it passes through within the spectrometer. The resolved light is then put through a monochromator which amplifies the light and obtains an intensity measurement that correlates with the concentration of the analyte. There are several types of optics being used in ICP, but the most used is Echelle type grating system. In this system light emitted from the plasma is splitted into a two-dimensional array which is then collected by a charge injection device (CID).

The operation of the instruments is controlled by a user interface which is a device consisting of programmes to convert wavelength and intensity readings to digital format and then sends it to a computer for the user to manipulate and use the data

4.3.5.5 Advantages and disadvantages

The ICP-OES technique has several advantages which include low detection limits (ppm to ppb), linear dynamic range, high sensitivity, multi-element detection capability and low chemical interference. Additionally, the technique is very rapid and stable, thus offering good precision. As long as the conditions of the plasma do not change significantly, due to the presence by easily ionized elements for instance, the calibration curve of an element can remain linear through several orders of magnitude, making this technique idea and convenient for the analysis of major, minor and trace and ultra-trace elements.

A major disadvantage of this technique compared to XRD/XRF, is that the sample must be in solution, preferably in aqueous solution. Among all other analytical atomic spectrometry techniques, ICP-OES is probably the one with the least number of types of interferences. The temperature of the plasma is high enough to atomise and excite any element, which reduces most of the chemical interference encountered by AA. The most important form of chemical interference is that produced by easily ionized elements (EIE). The EIE are those elements that have low ionization potentials such as alkaline elements that can suppress or enhance emission signals, depending on the analyte when present in high concentrations. This effect is illustrated in **Figure 4.11** where the sample was dissolved by flux fusion with a

mixture of Na_2HPO_4 and $NaH_2PO_4 \cdot H_2O$ (high Na content). **Figure 4.12** on the other hand shows the appearance of the plasma of a solution in acid matrix without the presence of Na. The EIE effect can be reduced by diluting the sample or by increasing the RF power and/or reducing the inner argon flow rate however remains a source of concern in the accurate determination of different elements.

Figure 4.11: Plasma appearance in the presence of a sodium salts flux fusion solution.

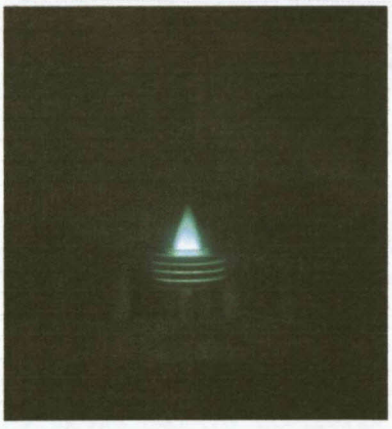

Figure 4.12: Plasma appearance in the presence of an acid digested solution.

Granting that ICP does not suffer that much from chemical interference compared to that of other spectrometric methods, it is also affected by matrix effects and spectral interferences as much as AA does. Matrix effects have to do with sample and standard solution preparation methods used for analysis. This interference can be eliminated by matching the matrix of the sample solution with that of the blank and the standards solutions or by using the standard addition method. Spectral

interferences are the most encountered interferences in ICP methodology and can be grouped in few categories. First is the simple background shift where a shift in the entire background intensity is observed in the region where emission of the analyte occurs. This interference can be caused by the presence in high concentration of another element in solution and can be corrected by selecting background correction points near the emission line of the analyte. Alternatively a different emission line that is not affected by the shift can be selected.

Secondly is the sloping background shift where another element in the same sample has a prominent peak near that of the analyte peak. This affects the background more on one side of the peak than the other and can be corrected in the same fashion as the simple background shift. A type of interference that is difficult to correct for is the direct spectral overlap whereby the emission of another element present in the solution overlaps with that of the analyte at a particular wavelength. The interference can be corrected by using the inter-element correction method or simply by choosing another wavelength for the analyte.

4.3.6 Inductively Coupled Plasma – Mass Spectroscopy

Inductively coupled plasma mass spectrometry (ICP-MS) is also an analytical technique utilized for elemental composition determinations. It follows the same principles as ICP-OES, but utilizes a mass spectrometer as a detector. In this technique, the constituent elements in the sample are converted to positively charged ions. The resulting ions and their isotopes are counted and then the ion count is converted to concentration for each element present in solution.

The instrumental setup of an ICP-MS (**Figure 4.13**) is almost the same as that of an ICP-OES with the exception of the detector. The sample introduction pathway is the same as in ICP-OES to as far as the peristaltic pump, nebulizer and torch are concerned. The sample is introduced into the ICP plasma as an aerosol by a nebulizer. Once the sample aerosol is introduced into the ICP torch, it is completely desolvated and the elements in the aerosol are converted first into gaseous atoms and then ionized in the plasma. The converted ions are then taken into the mass spectrometer by the interface cones. The quadrupole mass filter separates the ions according to their mass-to-charge ratio and then the ions get counted by a detector.

The main difference between IPC-OES and ICP-MS is how the sample is detected. It can be disputed that the role of the torch is different in both techniques, but the plasma excites the sample in the same way and the only difference is the sampling interface. In ICP-OES, the radiation emitted by excited atoms and ions is measured, and a lens is needed as a sampling interface. However, in ICP-MS, ions are physically extracted from the plasma into a mass spectrometer, so the sampling interface must be in direct contact with the plasma.[83]

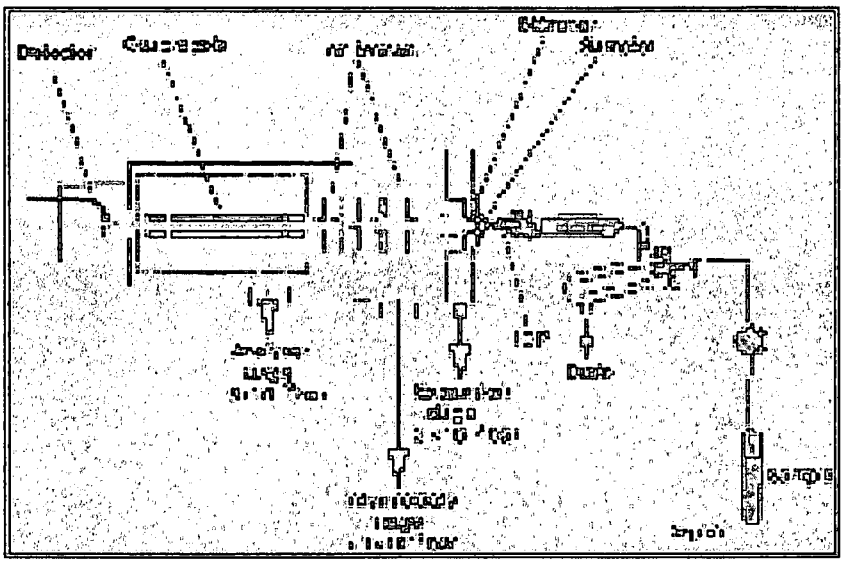

Figure 4.13: Instrumental setup of an ICP-MS[83]

4.3.6.1 Sampling interface[73]

The sample emerges as a mixture of ions, atoms and undissociated fragments from the flame into the interface[84] (**Figure 4.14**). The interface consist of a sampling cone with a small orifice (<1.0 mm) and a second cone (skimmer) with a smaller orifice than the sampling cone. The sample is transported through the orifice of the sampling cone by means of a pump at atmospheric pressure. The sample then passes through the skimmer into a chamber of high vacuum in the mass spectrometer. In this chamber the positively charged ions are separated from other sample constituents, focused and accelerated by a magnetic ion lens into the mass analyzer.

[83] Ebdon. L., Evans. E. H., Fisher. A. And Hill. J. S., *An introduction to analytical atomic spectrometry*, John Wiley and sons Ltd., Chichester, 1998, pp. 116, 118

[84] http://www.lhsc.on.ca/lab/metals/icpms.htm 27-09-2012

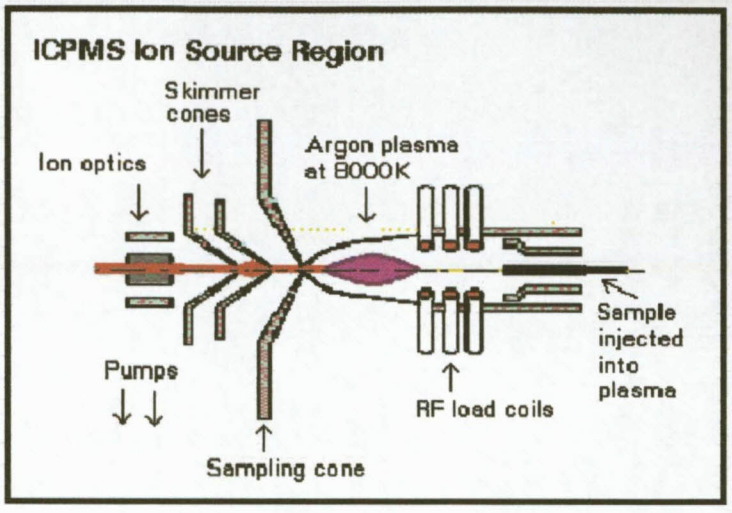

Figure 4.14: Schematic diagram of an ICP-MS sampling interface

4.3.6.2 Mass analyzer

In ICP-MS three different types of mass analyzers have been used and these are quadrupole, magnetic sector, and time-of-flight analyzers. The quadrupole is by far the most common mass analyzer used in ICP-MS. The quadrupole consist of 4 rods (1 cm in diameter and 15-20 cm long) as shown in **Figure 4.15**. In this mass filter, alternating AC and DC voltages are applied to opposite pairs of the rods. These voltages are then rapidly switched along with a RF-field resulting in an established electrostatic filter that only permits ions of a single mass-to-charge ratio (m/e) pass through the rods to the detector at a given moment in time.[85] However, the voltages on the rods can be switched at a very rapid rate, consequently allowing the quadrupole mass filter to separate up to 2400 amu (atomic mass units) per second. This allows for the selection of an ion with a specific m/e or permits the operator to scan for a range of m/z-values by continuously varying the applied voltage. The basic purpose of the mass analyzer is to allow analyte ions of a particular m/e through to the detector and to filter out all the non-analyte, interfering, and matrix ions as much as possible.

[85] Wolf. E. R., *"What is ICP-MS? And most importantly, what can it do?"* [Internet]. Available from http://minerals.cr.usgs.gov/icpms/intro.htmL 27-09-2012

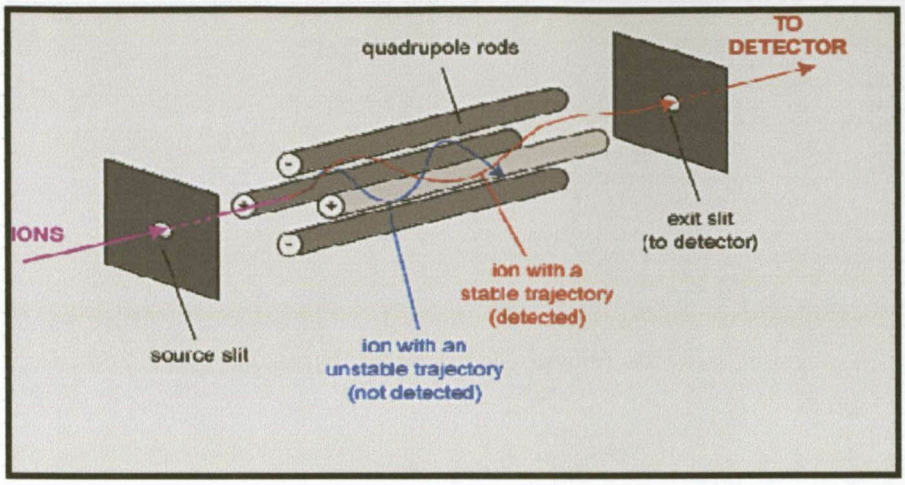

Figure 4.15: Quadrupole mass analyzer[86]

4.3.6.3 Detector

The ions leaving the mass analyzer strike the surface of the detector and generate a measurable electronic signal. The most common type of ion detector used in an ICP-MS system is the electron multiplier. The electron multiplier detects each ion as it exits the quadrupole by releasing an electron each time an ion strikes the surface of the detector. The detector electronics count and store the total signal for each m/e, creating a mass spectrum (**Figure 4.16**). The size of each peak is directly proportional to the concentration of an element in a sample and quantitative results are produced by relating signal intensities to those produced by calibration standards.

[86] http://www.chm.bris.ac.uk/ms/theory/quad-massspec.html 27-09-2012

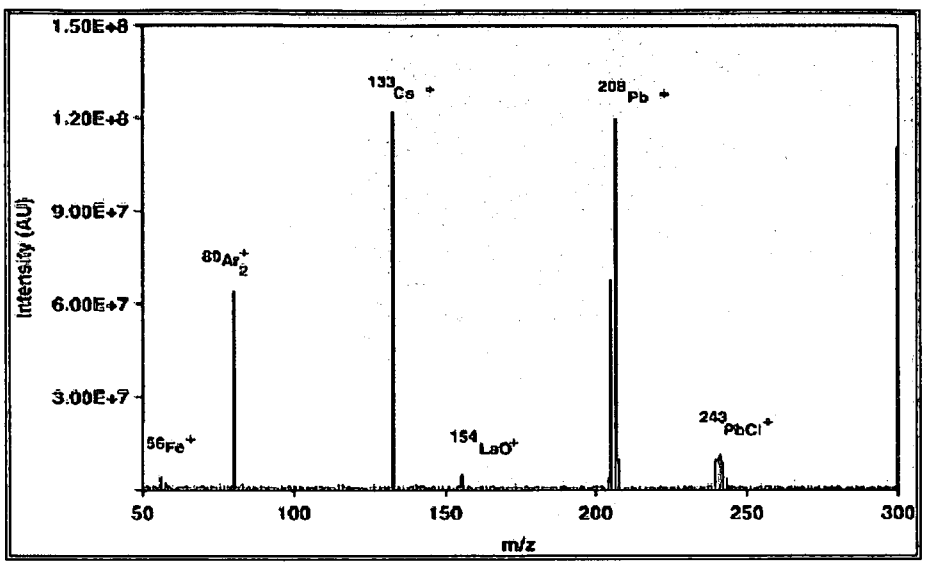

Figure 4.16: ICP-MS spectrum of a multi-element standard[87]

4.3.6.4 Advantages and disadvantages

A comparison of ICP-MS to other analytical techniques is shown in **Figure 4.17**. ICP-MS has several advantages over other techniques including detection limits that are comparable or even lower than those of graphite furnace AA. The linear dynamic range, high sensitivity and speed of analysis are better than those of ICP-OES rendering it suitable for quickly multi-element analysis. In addition, ICP-MS can do isotope counting that neither of the other mentioned techniques can do.

However, the disadvantage of ICP-MS is that it is very expensive compared to other techniques and also not easy to operate. It is also recommended that samples should not have more than 0.2% total dissolved solids (TDS) for best instrument performance and stability. If this is the case, the orifices in the cones will eventually become blocked, causing reduced sensitivity and detection capability and as a result requiring the system to be shut down for maintenance.

[87] http://www.sciencedirect.com/science/article/pii/S0584854708001018 27-09-2012

	ICP-MS	ICP-OES	Flame AAS	GF AAS
Detection limits	Excellent for most elements	Very good for most elements	Very good for some elements	Excellent for some elements
Sample throughput	all elements 2-6 min	5-30 elements /min	15 seconds/ element	4 min/element
Linear dynamic range	10^8 (10^9 with range extension)	10^6 to 10^8	10^3	10^2
Precision:				
Short term (n=run)	1-3%	0.3-1 %	0.1-1%	1-5%
Long term (4hrs)	<1%*	<3%*		
Isotopes	yes	no	no	no
Detection limit range, concentration	0.1-0.4	1-30	0.5-3	>30
No. of elements	>75	>75	>68	>50
Sample usage	low	low	very high	very low
Semi-quant analysis	yes	yes	no	no
Isotope analysis	yes	no	no	no
Routine operation	easy	easy	easy	easy
Method development	skill required	skill required	easy	skill required
Unattended operation	yes	yes	no	yes
Combustible gases	no	no	yes	no
Operating cost	high	high	low	medium
Capital cost	very high	high	low	medium-high

Figure 4.17: Comparison of atomic techniques[88]

4.3.6.5 Interferences

Although interferences do occur in ICP-MS, they are relatively few when compared to some other analytical techniques such as for example ICP-OES. These interferences are generally predictable and can often be corrected for and may be minimised by optimising instrument operating conditions. Three types of interferences that are encountered in ICP-MS are isobaric, molecular (or polyatomic) and doubly-charged ion interferences.

Isobaric interferences are found where a species has a similar m/e to that of the analyte. On the other hand, molecular interference is caused by ions consisting of more than one atom with the same m/e as the analyte while doubly-charged ions interferences are due to doubly-charged matrix or sample ions with twice the mass of the analyte and hence the same mass/charge ratio. These interferences are best

[88] Tyler. G., *"ICP-OES, ICP-MS and AAS Techniques Compared"* [Internet]. Available from http://www.jobinyvon.com/usadivisions/Emission/applications/TN05.pdf 27-09-2012

minimised by choosing alternative, non-interfered analyte isotopes or by optimising instrument operating conditions.

4.3.7 Conclusion

The ICP-OES technique was selected for the analysis of all the samples in this study. This was found to be preferable since the nature of all the samples was multi-element in nature and the total dissolved solids in the samples were higher than the recommended value for ICP-MS.

Different digestion methods were discussed and it was decided to investigate acid digestion (except hydrofluoric acid) and the flux fusion as suggested by Mahanta *et al*[68]. The magnetic separation and the microwave-assisted acid digestion methods from Theron and Nete respectively were also re-instated and incorporated in this study.

...

5 Uranium and thorium removal from tantalite

5.1 Introduction

The type of chemical beneficiation process which is usually selected for minerals such as tantalite depends on many factors which include cost of chemicals, the type of mineral, the complexity of the element matrix and waste composition. The presence of radioactive elements such as uranium and thorium in this type of minerals do not only increase the complexity of the chemical process, but also add legal and economic dimensions such as laboratory or plant design, worker safety, transport and/or shipping constraints and finally waste control to the mineral processing architecture. Current legislation determines that waste emanating from the processing of NORM`s and TENORM`s remain the property of the processing company until the ownership is officially taken over (bought) by another legal entity (contracts *etc.*). By implication it means that a company can never be officially closed at the end of its productive lifespan as long as it is still in the possession of large quantities of radioactive waste, NORM or TENORM`s. This increase the financial risk of owners or shareholders of mineral beneficiation plants who normally try to reduce their own risk by adding a premium on their own products, demand large discounts for the raw material or plainly refuse to process these kind of minerals.

The total or partial removal of uranium and/or thorium at an early stage of the mineral beneficiation process can therefore reduce the risk of expensive shipment refusals (sea and across international borders) or been classified as a Class 7 material (see **Chapter 3**). Added benefits also include less stringent working conditions and less financial risks for buyers or processors of the minerals. One of the main objectives of this study was therefore to try and develop a leaching process to remove all or the majority of uranium and thorium from tantalite at an early stage of the beneficiation process without the removal of the target elements Ta and Nb. Research into the possible mineral acid leaching and the selective precipitation of

uranium and thorium from the tantalite mineral ore will be described and discussed in this chapter.

The research process followed during this study is indicated in **Figure 5.1**. The first step was to perform a complete characterization of the mineral (Tantalite A) for comparisons (Step A). The next part of the study involved the leaching of the radio-active elements from the mineral ore (Step B) and finally the selective precipitation (possible removal) of U and Th with different mineral acids (precipitation as phosphates, sulphates *etc.*) after the mineral`s complete phosphate dissolution (Step C).

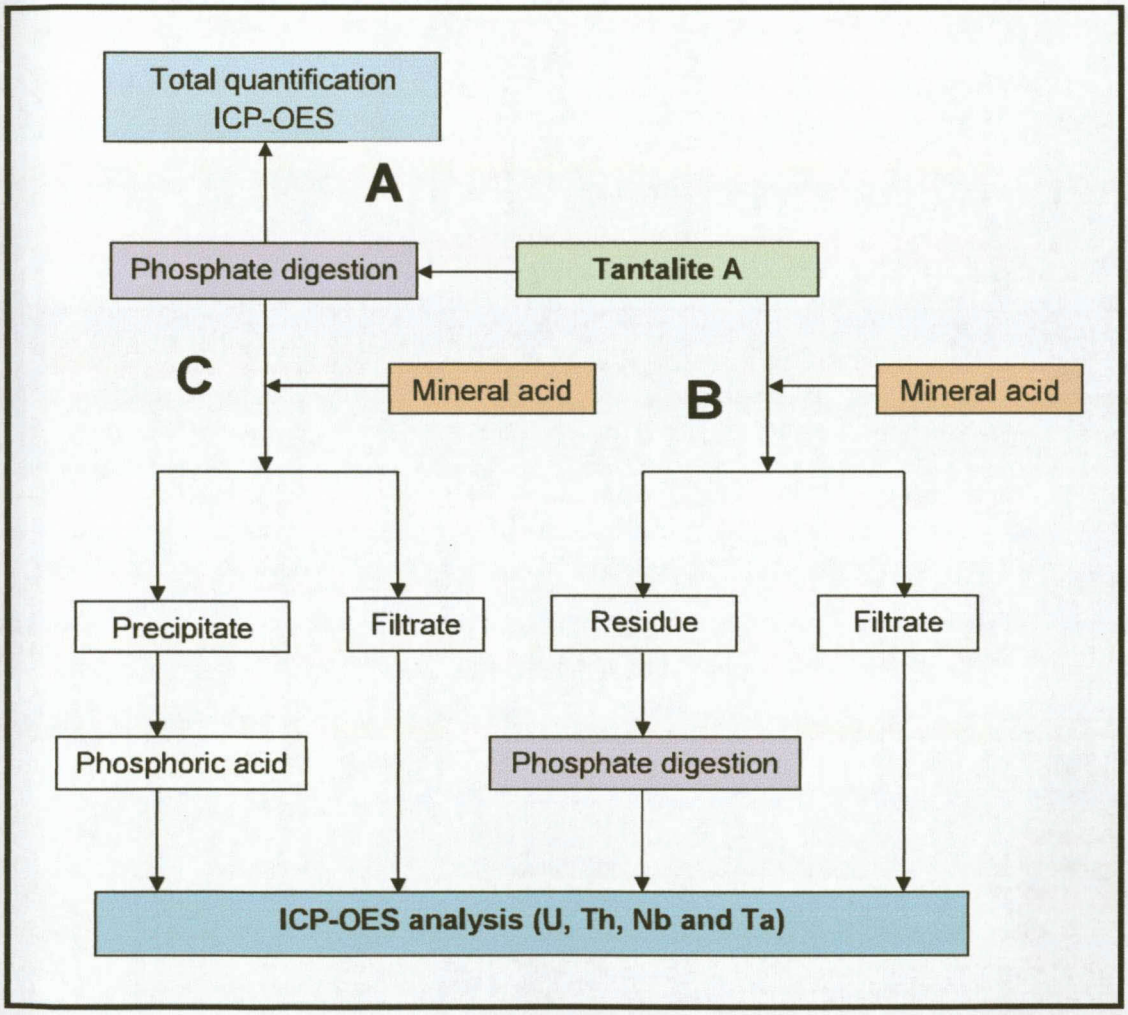

Figure 5.1: Flow chart indicating the research process during this study

5.2 Sample preparation, equipment and reagents

5.2.1 Equipment

A Shimadzu ICPS-7510 ICP-OES sequential plasma spectrometer was utilized for the quantification of the elements of interest after the dissolution step. The operating conditions for the ICP-OES are given in **Table 5.1** and were kept the same throughout the study.

Table 5.1: Operating conditions of the Shimadzu ICPS spectrometer

Condition	Setting
RF Power (kW)	1.2
Coolant gas (L/min)	14.0
Plasma gas (L/min)	1.20
Carrier gas (L/min)	1.10

A Thermolyne 1300 high temperature furnace which can reach a maximum temperature of 1100 °C in one hour was used for all fusions. An Anton Paar multi-wave 3000 microwave reaction system equipped with an 8SXF100 rotor with eight of both quartz and polytetrafluoroethylene (PTFE) reaction vessels was used for acid digestion of the samples. The microwave conditions which proved to be effective in the dissolution of tantalite used in this study are given in **Table 5.2**. Type 3.3 Duran volumetric flasks bought from Associated Chemical Enterprises (ACE) and grade B glassware bought from Merck was used in this project.

Table 5.2: Microwave operating conditions used in the study

Condition	Setting
Power (W)	600
Temperature (°C)	240
Pressure (Bar)	60
Reaction time (min)	45
No. of vessels	4

A Shimadzu ICPM 8500 inductively coupled mass spectrometer was utilized for the quantification of the isotope ratios of the elements of interest. A self-calibrating Shimadzu AW320 mass balance capable of weighing up to 320 grams with the accuracy of 0.1 mg was used in this study. The mass was recorded to four decimals of each and every sample that was used.

For small and accurate volume measurements a Brand Transferpette® micropipette with a volume capacity of 1.0 - 10.0 mL as well as a kartell Pluripet (II) micropipette with a capacity of 0.10 - 1.0 mL was used in this study. A silicone oil bath was used for heating the leach mixtures at the desired temperatures.

5.2.2 Reagents

General

The Zeolite (Clinobrite 814) cationic exchanger which was used as a resin was bought from Pratley Perlite mining Co. (Pty) Ltd. All the chemicals used during the study were of known concentration and the most commonly used chemicals in this study as well as their respective concentrations are listed in **Table 5.3**. ICP standard solutions containing 1000 ppm Sn, 1000 ppm Ta, 1000 ppm Nb, 1000 ppm Ti, 1000 ppm W, 1000 ppm Si as well as the multi-element standard (No.IV) (for Al, Fe and Mg analysis) were bought from Merck. The 1000 ppm U and Th standard solutions were bought from De Bruyn Spectroscopic Solutions. Double-distilled water was used throughout the study. The values are reported in two decimal places except for the average values that are reported according to their standard deviations. The raw data accumulated and used in this study (actual masses, calibration curves, *etc.*) are reported in the different appendixes on a CD which accompany the thesis.

Table 5.3: Chemical and physical properties of the most frequently used chemicals in the study.

Chemical	Formula	Grade	b.p/ m.p (°C)	Suppliers
Acids				
Nitric acid	HNO_3	65% AR	121	ACE
Hydrochloric acid	HCl	32% AR	85	ACE
Phosphoric acid	H_3PO_4	85% AR	158	ACE
Sulphuric acid	H_2SO_4	98% AR	340	ACE
Perchloric acid	$HClO_4$	60% AR	203	Merck
Reagents				
Sodium phosphate monobasic	$NaH_2PO_4.H_2O$	99.0%	100	PAL Chemicals
Sodium phosphate dibasic	Na_2HPO_4	99.0%	240	Holpro Analytics
Silicone oil	$[-Si(CH_3)_2O-]_n$	60 000 cSt	>140	Sigma Aldrich
Sample				
Tantalite mineral	$(Fe,Mn)(Ta,Nb)_2O_6$		N/A	Necsa

Tantalite mineral

The Tantalite A mineral which originated from Mozambique was supplied by the South African Nuclear Energy Corporation Limited (Necsa). This mineral was analysed by Alfred H Knight as well as by Nete[2] and Theron.[3] The chemical composition as found by Knight as well as in the two studies is given in **Table 5.4**. The results in the table clearly indicate the presence of two radioactive elements, thorium (0.57%) and uranium (2.87%) in the mineral.

Table 5.4: Chemical composition of the Tantalite A mineral

Metal oxides	Tantalite A (%)			
	A. H. Knight	Nete*	Theron**	Average
Ta_2O_5	27.71	30.08	27.69	28(1)
Nb_2O_5	27.41	27.01	30.51	28(1)
ThO_2	**0.65**	**0.54**	**0.52**	**0.57(7)**
U_3O_8	**2.83**	**2.81**	**2.97**	**2.87(8)**
Al_2O_3	1.85	2.04	0.25	1.9(3)
SiO_2	5.73	3.52	2.85	4(1)
WO_3	1.61	1.18	0.09	1.4(3)
TiO_2	2.68	2.77	2.85	2.77(8)
Mn_3O_4	8.03	8.91	7.08	8.0(9)
Fe_2O_3	8.29	8.34	7.35	8.0(5)
SnO_2	1.41	1.64	<0.01	1.5(2)

*= $Li_2B_4O_7$ fusion, dissolution in H_2SO_4/methanol. **= $Li_2B_4O_7$ fusion, dissolution in H_3PO_4/methanol

The mineral was found to be associated with other minerals such as microlite, quartz and tourmaline and also possessed magnetic properties. The physical properties of the tantalite mineral are shown in **Table 5.5**. The maximum particle diameter by volume frequency was determined as approximately 10 µm and the median value for the particle size (d_{50} value) was determined as 9.8 µm.

Table 5.5: Physical properties of Tantalite A mineral[89]

Analytical method	Identified property
XRD	Manganotantalite, microlite, quartz, muscovite
Microscopy	Manganotantalite, microlite, euxenite, quartz, muscovite, garnet, tourmaline
Scintillometry	Radioactive - 2.81% U_3O_8 and 0.54% ThO_2 (by ICP-OES)
Magnetic	Little magnetism (~ 8% Fe_2O_3), mass susceptibility (χ_g = 7.5(6) × 10^{-5} cgs or 2.8(2) × 106 cm^3/g)

[89] Nete, M., Purcell, W., Snyders, E., Nel, J.T. and Beukes G., *Journal of the Southern African Institute of Mining and Metallurgy*. 2012. 112. pp.1079-1086

This radioactive mineral sample, as well as the U and Th calibration standards was wrapped in lead foil stored in closed containers and kept locked in cabinets in a separate room to decrease the possible radiation dose in the working area and to put prevent any unauthorised access. The maximum time for analyses was set at a month to avoid long radiation exposure times. The experiments and measurements were done in the fume hood to avoid inhalation of dust and fumes from the mineral samples and chemicals. Proper disposable gloves were used when handling the samples and chemicals. All the waste solutions generated were kept in labelled polyethylene bottles and stored in the same room as the mineral sample before it was disposed off in the appropriate way.

5.3 Experimental work

The combination of steps taken to remove the radioactive materials and the quantification of each step is shown in **Figure 5.1**. These include the quantification of the mineral, acid leaching and acid precipitation of the digested mineral. On the other hand ion exchange chromatography was also investigated for its effectiveness in separating the elements in the mineral.

5.3.1.1 Preparation of standard solutions for tantalite characterization for ICP-OES

All standard solutions were prepared by adding 0.05, 0.1, 0.2, 0.25 and 0.5 mL of the different 1000 ppm ICP standard solutions (Nb, Ta, U, Th, Si, Sn, W, Ti, Al, Fe and Mn) into five 50.0 mL volumetric flasks using a micropipette. To these solutions 5 mL of mineral acid was added and were then filled to the mark with water. The prepared solutions contained 1.0, 2.0, 4.0, 5.0 and 10.0 ppm concentrations of each of the respective elements. The blank solution was prepared by adding 5 mL of mineral acid into a 50.0 mL volumetric flask and filling it up to the mark with water.

5.3.1.2 Standard solutions for phosphate fluxed solutions (matrix matching)

The standard solutions for fusion digested samples were prepared in the same way as the acids, but with an additional step. Sodium dihydrogen phosphate (12.5 g) and disodium hydrogen phosphate (12.5 g) were thoroughly mixed and fused in a

platinum crucible at 900 °C for 30 minutes. The resulting melt was dissolved in 25.0 mL phosphoric acid and qualitatively transferred into a 250.0 mL volumetric flask and diluted to the mark with water. Aliquots (2.0 mL) of the fused solution were transferred into five 50.0 mL volumetric flasks containing 5.0 mL of phosphoric acid and water. To these, 0.05, 0.1, 0.2, 0.25 and 0.5 mL of the different 1000 ppm ICP standard solutions were added respectively. The solutions were then diluted to the mark with water. The blank solution was prepared by adding a 2.0 mL aliquot of the fused solution and 5.0 mL of phosphoric acid into a 50.0 mL volumetric flask and diluting to the mark with water.

5.3.2 Determination of LOD and LOQ

An important step in the quantification step using ICP-OES is the selection of the appropriate emission lines for the elements in question. The composition of the sample plays a vital role in determining the sensitivity of the emission lines and to avoid possible interferences from elements that are not part of the analytes, but present in the sample. Nete *et al.*[69] investigated the determination of the detection limits of some of the elements under investigation in this study and the results are reported in **Table 5.6**. Five 50 mL standard solutions containing 1, 2, 4, 5 and 10 ppm of each of the elements respectively, were prepared along with the blank containing 5.0 mL of H_2SO_4. The calibration curve was drawn and the detection limits, calculated using **Equation 5.1**, are shown in **Table 5.7**.

$$LOD = \frac{Ks_{bl}}{m} \qquad \textbf{5.1}$$

Where K is a value that corresponds to the confidence level (a value of 3 corresponds to a 99.7% confidence interval), m is the gradient of the graph and s_{bl} is the standard deviation of the blank intensities. The limit of quantification (LOQ) is calculated as ten times the limit of detection and is also tabulated in **Table 5.7**.

Table 5.6: Detection and quantification limits at the three most sensitive lines[69]

Element	Limits of detection (ppm) at three sensitive wavelengths			Quantification limits (ppm)		
	Line order 1	Line order 2	Line order 3	Line order 1	Line order 2	Line order 3
Nb	0.0094	0.0093	0.01	0.094	0.093	0.1
Ta	0.024	0.0047	0.024	0.24	0.047	0.24
Li	0.0002	0.01	0.0043	0.002	0.1	0.043
Na	0.0034	0.0066	0.031	0.034	0.066	0.31
Mg	0.0004	0.0002	0.02	0.004	0.002	0.2
Al	0.0055	0.0074	0.013	0.055	0.074	0.13
Ca	0.0004	0.0011	0.0025	0.004	0.011	0.025
Ti	0.0015	0.0015	0.0015	0.015	0.015	0.015
Mn	0.0003	0.0004	0.0007	0.003	0.004	0.007
Fe	0.0035	0.008	0.0024	0.035	0.08	0.024
Ni	0.0029	0.0083	0.0029	0.029	0.083	0.029
Cu	0.002	0.0017	0.0058	0.02	0.017	0.058

Table 5.7: LOD and LOQ at selected wavelengths for the elements studied

Element	Wavelength (nm)	LOD (ppm)	LOQ (ppm)
Al	309.271	0.0536	0.5361
Si	212.415	0.0333	0.3328
Ti	337.28	0.0016	0.0156
Mn	259.373	0.0011	0.0109
Fe	238.204	0.0049	0.0489
Nb	313.079	0.0141	0.1415
Sn	198.898	0.0349	0.3489
Ta	240.063	0.0280	0.2803
W	218.952	0.0759	0.7592
Th	318.02	0.0275	0.2750
U	385.958	0.0130	0.1300

5.3.3 Mineral digestion for quantification

Tantalite A mineral (0.1 g) was accurately weighted to 0.1 mg in a platinum crucible. To this sodium dihydrogen phosphate (5.0 g) and disodium hydrogen phosphate (5.0 g) were added and thoroughly mixed and then fused in a furnace at 900 °C for 30 minutes. The melt was cracked by placing the hot crucible in cold water. The melt was then dissolved with the addition of 10.0 mL phosphoric acid and quantitatively transferred to a 100.0 mL volumetric flask and filled to the mark with water. A 10.0 mL aliquot was transferred into another 100.0 mL volumetric flask containing 9.0 mL phosphoric acid and diluted to the mark with water for ICP-OES analysis. This was done in five replicates and the results are summarised in **Table 5.8**.

Table 5.8: Quantification of the Tantalite A mineral

Metal oxide	Tantalite A (%)					
	1st run	2nd run	3rd run	4th run	5th run	Average
Ta_2O_5	27.82	27.77	27.93	27.34	27.57	**27.7(2)**
Nb_2O_5	27.62	28.24	28.11	28.45	28.07	**28.1(3)**
ThO_2	0.20#	0.56	0.50	0.49	0.47	**0.50(4)**
U_3O_8	2.68#	3.06	3.10	3.08	3.05	**3.07(2)**
Al_2O_3	1.70	1.93	1.95	1.97	1.86	**1.9(1)**
SiO_2	2.62	2.97	2.74	2.79	2.59	**2.7(2)**
WO_3	1.39	1.05	1.05	0.99	0.99	**1.1(3)**
TiO_2	2.26	1.97	2.07	2.07	2.04	**2.1(1)**
Mn_3O_4	7.35	8.09	7.65	7.69	7.44	**7.6(3)**
Fe_2O_3	8.19	7.96	8.15	8.05	8.03	**8.07(9)**
SnO_2	0.51#	1.12	1.14	1.08	1.12	**1.11(3)**

omitted during quantification

5.3.4 Mineral acid leaching of tantalite mineral

5.3.4.1 Sulphuric acid leaching

5.3.4.1.1 Effect of leaching time (at constant temperature) on Th and U removal

Tantalite A (2 g) samples were accurately weighed (to 0.1 mg) in 100 mL round-bottom flasks and digested with sulphuric acid using a silicone oil bath at 50 °C for 60 minutes. The filtrates were collected in different 100.0 mL volumetric flasks and filled to the mark with water. Aliquots (2.0 mL) of these samples were transferred into other 100.0 mL volumetric flasks containing 10.0 mL of H_2SO_4 and filled to the mark with water for ICP-OES analysis. The experimental procedure was repeated at time intervals of 90, 120, 150 and 180 minutes and done in triplicate and the quantitative results are reported in **Table 5.9** while the analytical results for Th, U and the two main elements leached at 50 °C and a maximum time of 3 hours, are graphically presented in **Figure 5.2**.

In order to obtain the mass balance for the whole mineral sample (0.05 g), the undigested mineral was dried and accurately weighed to 0.1 mg in a platinum crucible. To this sample, 0.25 g of sodium dihydrogen phosphate and 0.25 g of disodium hydrogen phosphate[68] were added and thoroughly mixed with the obtained residue and heated in a furnace at 900 °C for 30 minutes. The melt was subsequently cracked to facilitate the quick dissolution of the melt by placing the hot crucible in cold water. The melt was then dissolved in water and quantitatively transferred to a 100.0 mL volumetric flask containing 10.0 mL phosphoric acid and filled to the mark with water for ICP-OES analysis. The quantitative results are reported in **Table 5.10**

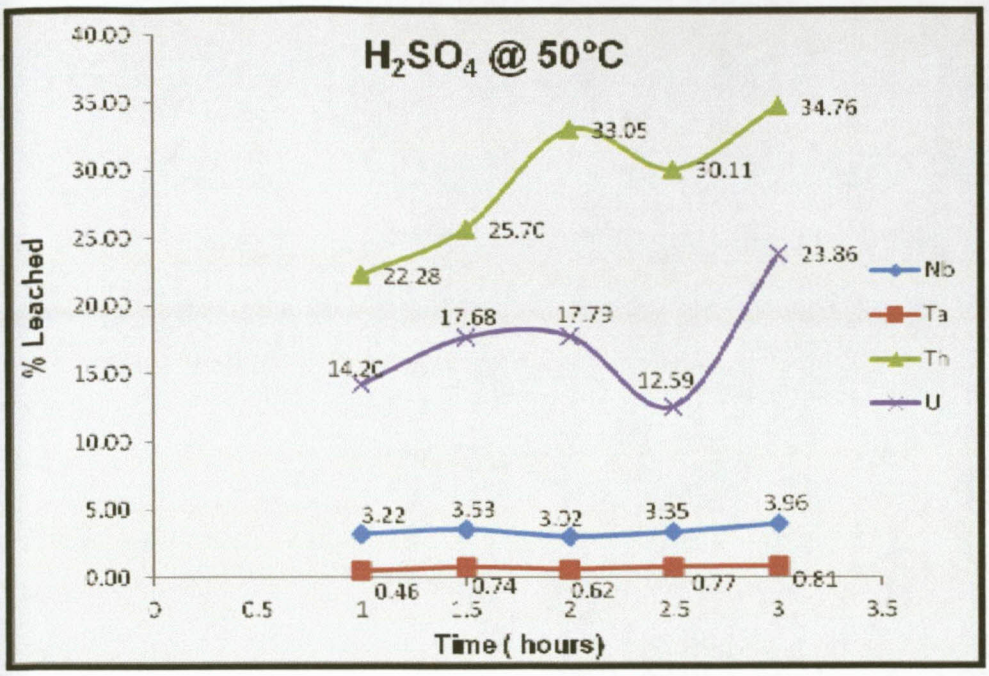

Figure 5.2: Quantification of Th, U, Nb and Ta after sulphuric acid leaching at 50 °C

Table 5.9: ICP-OES results of sulphuric acid leaching at 50 °C

Time (Hour)		Metal oxide (%)			
		Nb	Ta	Th	U
1					
		2.87	0.24	21.32	12.25
		3.25	0.55	21.46	13.64
		3.53	0.59	24.06	16.72
	Average	**3.2(3)**	**0.5(2)**	**22(2)**	**14(2)**
1.5					
		4.46	0.93	28.32	15.83
		4.50	1.08	26.99	23.22
		1.63	0.22	21.80	13.99
	Average	**4(2)**	**0.7(5)**	**26(3)**	**18(5)**
2					
		2.24	0.39	34.58	10.96
		3.69	0.76	32.12	21.79
		3.12	0.71	32.45	20.63
	Average	**3.0(7)**	**0.6(2)**	**33(1)**	**18(6)**
2.5					
		2.91	0.55	28.98	10.95
		3.54	0.93	29.96	5.42
		3.61	0.82	31.39	21.39
	Average	**3.3(4)**	**0.8(4)**	**30(1)**	**13(8)**
3					
		3.04	0.61	34.17	18.14
		4.43	0.94	35.97	27.81
		4.41	0.89	34.14	25.64
	Average	**4.0(8)**	**0.8(2)**	**35(1)**	**24(5)**

Table 5.10: The mass balance after sulphuric acid leaching at 50 °C

Time (hours)	Sample no.	Product	Metal oxide (%)			
			Nb	Ta	Th	U
1						
	1	Filtrate	2.87	0.24	21.32	12.25
		Residue	91.85	94.02	78.68	84.55
		Total	**94.72**	**94.26**	**100.00**	**96.80**
	2	Filtrate	3.25	0.55	21.46	13.64
		Residue	95.73	98.33	78.54	86.84
		Total	**98.98**	**98.88**	**100.00**	**100.48**
	3	Filtrate	3.53	0.59	24.06	16.72
		Residue	101.90	99.96	75.94	80.07
		Total	**105.43**	**100.55**	**100.00**	**96.79**
1.5						
	1	Filtrate	4.46	0.93	28.32	15.83
		Residue	96.03	95.35	71.68	85.66
		Total	**100.49**	**96.27**	**100.00**	**101.49**
	2	Filtrate	4.50	1.08	26.99	23.22
		Residue	97.12	99.39	73.01	86.83
		Total	**101.63**	**100.46**	**100.00**	**110.05**
	3	Filtrate	1.63	0.22	21.80	13.99
		residue	91.41	90.83	78.20	84.47
		Total	**93.04**	**91.05**	**100.00**	**98.46**
2						
	1	Filtrate	2.24	0.39	34.58	10.96
		Residue	90.26	88.79	65.42	82.01
		Total	**92.50**	**89.17**	**100.00**	**92.97**
	2	Filtrate	3.69	0.76	32.12	21.79
		Residue	90.28	92.05	67.88	78.43
		Total	**93.97**	**92.81**	**100.00**	**100.22**
	3	Filtrate	3.12	0.71	32.45	20.63
		Residue	99.07	99.07	67.55	85.83
		Total	**102.19**	**99.78**	**100.00**	**106.46**
2.5						
	1	Filtrate	2.91	0.55		10.95
		Residue	97.81	95.68	28.98	88.56
		Total	**100.72**	**96.23**	71.02	**99.51**
	2	Filtrate	3.54	0.93	**100.00**	5.42
		Residue	96.54	97.08	29.96	87.63
		Total	**100.08**	**98.01**	70.04	**93.05**
	3	Filtrate	3.61	0.82	**100.00**	21.39
		Residue	95.53	96.39	31.39	84.74
		Total	**99.14**	**97.21**	68.61	**106.13**
3					**100.00**	
	1	Filtrate	3.04	0.61		18.14
		Residue	92.52	92.80	34.17	83.29
		Total	**95.55**	**93.41**	65.83	**101.43**
	2	Filtrate	4.43	0.94	**100.00**	27.81
		Residue	91.91	88.77	35.97	78.33
		Total	**96.35**	**89.71**	64.03	**106.14**
	3	Filtrate	4.41	0.89	**100.00**	25.64
		Residue	92.71	93.66	34.14	79.82
		Total	**97.12**	**94.55**	65.86	**105.45**

5.3.4.1.2 Effect of temperature on Th and U removal

Tantalite A samples (2 g) were accurately weighed (to 0.1 mg) in 100 mL round-bottom flasks and digested with sulphuric acid using a silicone oil bath at a temperature range of 100 °C to 230 °C for 60 minutes. The filtrates were collected in different 100.0 mL volumetric flasks and filled to the mark with water. 2.0 mL aliquots of the samples were transferred into other 100.0 mL volumetric flasks containing 10.0 mL of H_2SO_4 and filled to the mark with water for ICP-OES analysis. The experimental procedure was repeated at time intervals of 90, 120, 150 and 180 minutes and done in triplicate except at 230 °C which was done only once. The quantification of the four main elements present in the acid leach is given in **Tables 5.11**, **5.13** and **5.15** while the results are graphically presented in **Figures 5.3**, **5.4**, **5.5** and **5.6** for Th, U and the two main elements that were leached at the different temperatures, 100 °C to 230 °C, and a maximum time of 3 hours obtained by ICP-OES.

In order to obtain the mass balance for the whole mineral sample (0.05 g), the undigested mineral was dried and accurately weighed to 0.1 mg in a platinum crucible. To this sample, 0.25 g of sodium dihydrogen phosphate and 0.25 g of disodium hydrogen phosphate were added and thoroughly mixed with the obtained residue and heated in a furnace at 900 °C for 30 minutes. The melt was subsequently cracked to facilitate the quick dissolution of the melt by placing the hot crucible in cold water. The melt was then dissolved in water and quantitatively transferred to a 100.0 mL volumetric flask containing 10.0 mL phosphoric acid and filled to the mark with water for ICP-OES analysis. The quantitative results are reported in **Tables 5.12**, **5.14**, **5.16** and **5.18**.

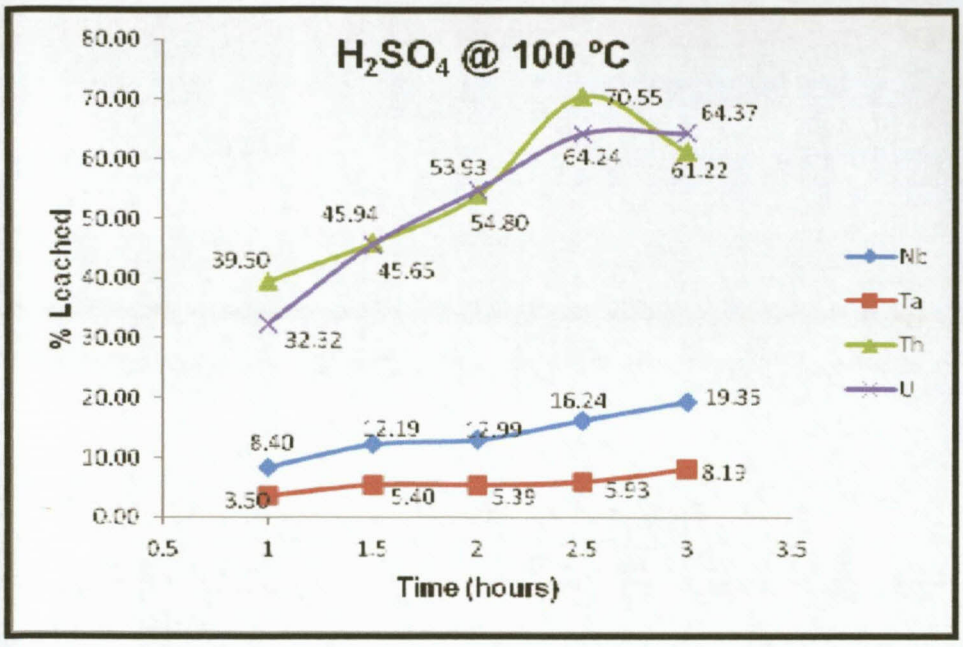

Figure 5.3: Quantification of Th, U, Nb and Ta after sulphuric acid leaching at 100 °C

Table 5.11: ICP-OES results of sulphuric acid leaching at 100 °C

Time (Hour)		Metal oxide (%)			
		Nb	Ta	Th	U
1					
		7.86	4.05	45.19	37.16
		9.56	3.52	37.18	30.88
		7.76	2.93	36.14	28.94
	Average	**8(1)**	**3.5(6)**	**40(5)**	**32(4)**
1.5					
		11.29	4.51	49.45	44.15
		11.71	5.66	40.84	42.54
		13.56	6.04	47.54	50.25
	Average	**12(1)**	**5.4(8)**	**46(5)**	**46(4)**
2					
		10.73	4.02	61.41	58.95
		15.46	6.70	50.77	53.48
		12.77	5.47	49.63	51.98
	Average	**13(2)**	**5(1)**	**54(6)**	**55(4)**
2.5					
		17.70	6.69	84.83	74.51
		13.73	5.49	53.12	45.94
		17.30	5.60	73.72	72.25
	Average	**16(2)**	**5.9(7)**	**71(16)**	**64.(16)**
3					
		18.84	6.98	64.48	70.33
		16.41	6.62	56.59	53.57
		22.79	10.96	62.60	69.20
	Average	**19(3)**	**8(2)**	**61(4)**	**64(9)**

Table 5.12: The mass balance after sulphuric acid leaching at 100 °C

Time (hour)	Sample no.	Product	Metal oxide (%)			
			Nb	Ta	Th	U
1						
	1	Filtrate	7.86	4.05	45.19	37.16
		Residue	85.48	99.53	54.81	55.48
		Total	**93.34**	**103.57**	**100.00**	**92.64**
	2	Filtrate	9.56	3.52	37.18	30.88
		Residue	83.61	96.97	62.82	70.98
		Total	**93.17**	**100.49**	**100.00**	**101.86**
	3	Filtrate	8.62	2.73	36.14	16.58
		Residue	88.68	93.68	63.86	81.12
		Total	**97.30**	**96.41**	**100.00**	**97.69**
1.5						
	1	Filtrate	11.29	4.51	49.45	44.15
		Residue	90.29	106.25	50.55	51.89
		Total	**101.58**	**110.76**	**100.00**	**96.04**
	2	Filtrate	11.71	5.66	40.84	42.54
		Residue	80.44	103.65	59.16	106.67
		Total	**92.15**	**109.31**	**100.00**	**149.21**
	3	Filtrate	13.56	6.04	47.54	50.25
		Residue	82.41	101.44	52.46	55.39
		Total	**95.97**	**107.48**	**100.00**	**105.64**
2						
	1	Filtrate	10.73	4.02	61.41	58.95
		Residue	79.03	93.99	38.59	37.79
		Total	**89.76**	**98.01**	**100.00**	**96.74**
	2	Filtrate	15.46	6.70	50.77	53.48
		Residue	83.12	95.97	49.23	52.86
		Total	**98.58**	**102.67**	**100.00**	**106.34**
	3	Filtrate	12.77	5.47	49.63	51.98
		Residue	80.98	86.17	50.37	57.30
		Total	**93.75**	**91.64**	**100.00**	**109.28**
2.5						
	1	Filtrate	17.70	6.69	84.83	74.51
		Residue	62.59	79.87	15.17	20.07
		Total	**80.29**	**86.56**	**100.00**	**94.58**
	2	Filtrate	13.73	5.49	53.12	45.94
		Residue	77.46	93.92	46.88	48.73
		Total	**91.19**	**99.41**	**100.00**	**94.67**
	3	Filtrate	17.30	5.60	73.72	72.25
		Residue	71.62	93.13	26.28	19.05
		Total	**88.92**	**98.73**	**100.00**	**91.30**
3						
	1	Filtrate	18.84	6.98	64.48	70.33
		Residue	63.75	94.20	35.52	20.21
		Total	**82.59**	**101.18**	**100.00**	**90.54**
	2	Filtrate	16.41	6.62	56.59	53.57
		Residue	73.85	64.20	43.41	34.86
		Total	**90.26**	**70.82**	**100.00**	**88.43**
	3	Filtrate	22.79	10.96	62.60	69.20
		Residue	72.14	95.11	37.40	23.49
		Total	**94.93**	**106.07**	**100.00**	**92.69**

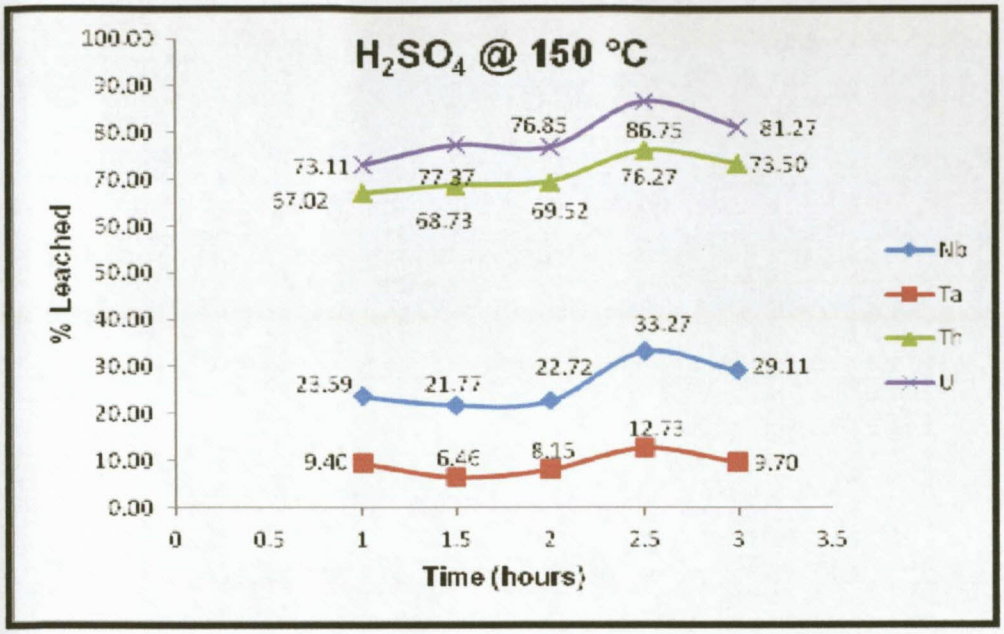

Figure 5.4: Quantification of Th, U, Nb and Ta after sulphuric acid leaching at 150 °C

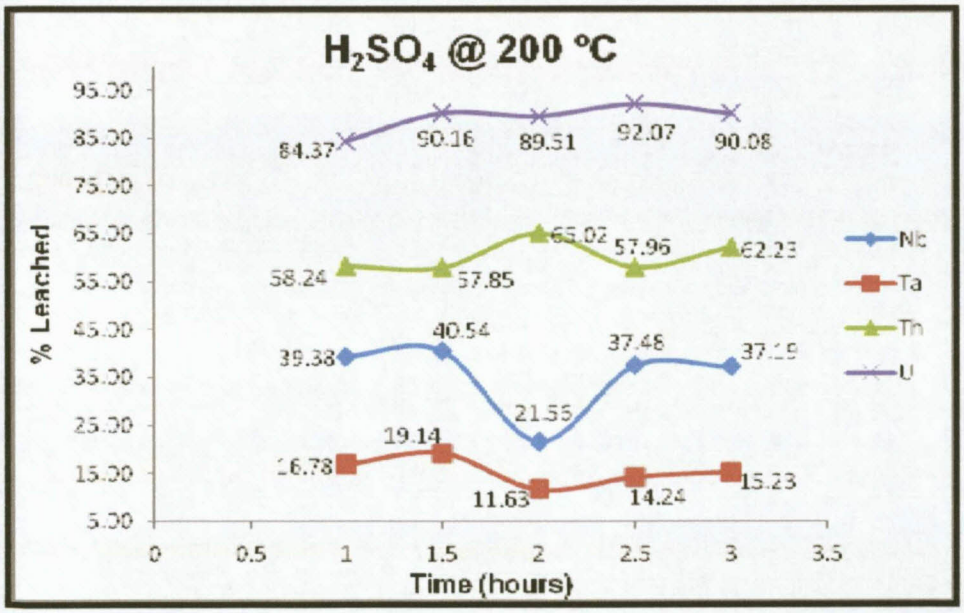

Figure 5.5: Quantification of Th, U, Nb and Ta after sulphuric acid leaching at 200 °C

Table 5.13: ICP-OES results of sulphuric acid leaching at 150 °C

Time (Hour)		Metal oxide (%)			
		Nb	Ta	Th	U
1					
		17.85	5.26	54.41	62.20
		23.45	9.11	71.67	74.47
		29.51	13.84	74.98	82.66
	Average	**24(6)**	**9(4)**	**67(11)**	**73(10)**
1.5					
		17.82	2.87	60.00	69.75
		22.67	5.23	71.34	79.94
		24.83	11.28	74.84	82.43
	Average	**22(4)**	**7(4)**	**69(8)**	**77(7)**
2					
		22.69	8.36	49.59	60.23
		26.35	10.33	74.66	84.03
		19.12	5.75	84.31	86.30
	Average	**23(4)**	**8(3)**	**70(18)**	**77(14)**
2.5					
		28.47	11.97	69.22	89.16
		40.79	16.38	77.97	82.10
		30.56	9.85	81.62	88.99
	Average	**33(7)**	**13(3)**	**76(6)**	**87(4)**
3					
		28.04	10.90	62.38	72.20
		29.07	11.59	77.97	85.11
		30.23	6.61	80.17	86.50
	Average	**29(1)**	**10(3)**	**74(10)**	**81(8)**

Table 5.14: The mass balance after sulphuric acid leaching at 150 °C

Time (hour)	Sample no.	Product	Metal oxide (%)			
			Nb	Ta	Th	U
1						
	1	Filtrate	17.82	5.26	54.41	62.20
		Residue	76.79	87.73	45.59	40.25
		Total	**94.62**	**92.99**	**100.00**	**102.45**
	2	Filtrate	23.45	9.11	71.67	74.47
		Residue	71.25	82.20	28.33	21.29
		Total	**94.70**	**91.31**	**100.00**	**95.76**
	3	Filtrate	29.51	13.84	74.98	82.66
		Residue	67.43	91.76	25.02	19.21
		Total	**96.94**	**105.60**	**100.00**	**101.87**
1.5						
	1	Filtrate	17.82	2.87	60.00	69.75
		Residue	73.09	87.84	40.00	32.19
		Total	**90.91**	**90.71**	**100.00**	**101.94**
	2	Filtrate	22.67	5.23	71.34	79.94
		Residue	69.26	94.44	28.66	27.70
		Total	**91.93**	**99.67**	**100.00**	**107.64**
	3	Filtrate	24.83	11.28	74.84	82.43
		Residue	79.33	90.26	25.16	25.38
		Total	**104.16**	**101.54**	**100.00**	**107.81**
2						
	1	Filtrate	22.69	8.36	49.59	60.23
		Residue	81.86	97.96	50.41	41.81
		Total	**104.55**	**106.32**	**100.00**	**102.04**
	2	Filtrate	26.35	10.33	74.66	84.03
		Residue	63.35	74.96	25.34	16.81
		Total	**89.70**	**85.29**	**100.00**	**100.84**
	3	Filtrate	19.12	5.75	84.31	86.30
		Residue	66.53	74.66	15.69	14.93
		Total	**85.65**	**80.41**	**100.00**	**101.23**
2.5						
	1	Filtrate	28.47	11.97	69.22	89.16
		Residue	66.74	87.31	30.78	30.33
		Total	**95.21**	**99.28**	**100.00**	**119.49**
	2	Filtrate	40.79	16.38	77.97	82.10
		Residue	59.58	85.38	22.03	17.98
		Total	**100.37**	**101.76**	**100.00**	**100.08**
	3	Filtrate	30.56	9.85	81.62	88.99
		Residue	71.05	91.63	18.38	15.18
		Total	**101.61**	**101.48**	**100.00**	**104.17**
3						
	1	Filtrate	28.04	10.90	62.38	72.20
		Residue	80.00	101.27	37.62	27.38
		Total	**108.04**	**112.17**	**100.00**	**99.58**
	2	Filtrate	29.07	11.59	77.97	85.11
		Residue	65.55	79.46	22.03	16.68
		Total	**94.62**	**91.05**	**100.00**	**101.79**
	3	Filtrate	30.23	6.61	80.17	86.50
		Residue	64.13	82.71	19.83	15.71
		Total	**94.36**	**89.32**	**100.00**	**102.21**

Table 5.15: ICP-OES results of sulphuric acid leaching at 200 °C

Time (Hour)		Metal oxide (%)			
		Nb	Ta	Th	U
1					
		36.92	3.69	59.67	85.16
		39.82	22.25	54.44	84.99
		41.40	24.41	60.60	82.96
	Average	**39(2)**	**17(11)**	**58(3)**	**84(1)**
1.5					
		34.24	5.91	58.13	88.53
		41.24	24.60	55.85	91.08
		46.12	26.91	59.58	90.86
	Average	**41(6)**	**19(12)**	**58(2)**	**90(1)**
2					
		20.95	1.48	59.24	87.02
		22.62	16.37	68.03	89.64
		21.12	17.03	67.79	91.89
	Average	**21.6(9)**	**12(9)**	**65(5)**	**90(2)**
2.5					
		51.35	4.60	63.04	97.74
		22.91	17.41	52.08	94.33
		38.18	20.70	58.77	84.14
	Average	**37(14)**	**14(9)**	**58(6)**	**92(7)**
3					
		39.10	2.92	67.51	85.48
		31.57	20.39	62.70	93.63
		40.92	22.37	56.47	91.11
	Average	**37(5)**	**15(11)**	**62(6)**	**90(4)**

Table 5.16: The mass balance after sulphuric acid leaching at 200 °C

Time (hour)	Sample no.	Product	Metal oxide (%)			
			Nb	Ta	Th	U
1						
	1	Filtrate	36.92	3.69	59.67	85.16
		Residue	69.63	95.26	40.33	44.61
		Total	**106.55**	**98.94**	**100.00**	**129.77**
	2	Filtrate	39.82	22.25	54.44	84.99
		Residue	59.02	80.85	45.56	16.31
		Total	**98.84**	**103.10**	**100.00**	**101.29**
	3	Filtrate	41.40	2.73	60.60	82.96
		Residue	67.10	102.21	39.40	12.15
		Total	**108.50**	**104.93**	**100.00**	**95.12**
1.5						
	1	Filtrate	34.24	5.91	58.13	88.53
		Residue	76.09	111.87	41.87	41.84
		Total	**110.34**	**117.79**	**100.00**	**130.37**
	2	Filtrate	41.24	24.60	55.85	91.08
		Residue	66.78	102.89	44.15	15.27
		Total	**108.02**	**127.49**	**100.00**	**106.35**
	3	Filtrate	46.12	26.91	59.58	90.86
		Residue	64.42	95.89	40.42	11.43
		Total	**110.54**	**122.80**	**100.00**	**102.29**
2						
	1	Filtrate	20.95	1.48	59.24	87.02
		Residue	78.34	89.09	40.76	41.09
		Total	**99.29**	**90.57**	**100.00**	**128.11**
	2	Filtrate	22.62	16.37	68.03	89.64
		Residue	48.80	55.73	31.97	11.38
		Total	**71.42**	**72.09**	**100.00**	**101.02**
	3	Filtrate	21.12	17.03	67.79	91.89
		Residue	46.93	53.38	32.21	12.09
		Total	**68.04**	**70.40**	**100.00**	**103.97**
2.5						
	1	Filtrate	51.35	4.60	63.04	97.74
		Residue	65.38	95.98	36.96	39.73
		Total	**116.73**	**100.58**	**100.00**	**137.47**
	2	Filtrate	22.91	17.41	52.08	94.33
		Residue	59.05	86.02	47.92	10.19
		Total	**81.95**	**103.43**	**100.00**	**104.52**
	3	Filtrate	59.89	20.70	58.77	84.14
		Residue	71.62	90.67	41.23	16.36
		Total	**131.51**	**111.37**	**100.00**	**100.50**
3						
	1	Filtrate	39.10	2.92	67.51	85.48
		Residue	51.81	98.87	32.49	29.93
		Total	**90.91**	**101.80**	**100.00**	**115.41**
	2	Filtrate	31.57	20.39	62.70	93.63
		Residue	53.23	80.08	37.30	15.90
		Total	**84.80**	**100.47**	**100.00**	**109.53**
	3	Filtrate	40.92	22.37	56.47	91.11
		Residue	59.09	77.40	43.53	9.50
		Total	**100.00**	**99.77**	**100.00**	**100.61**

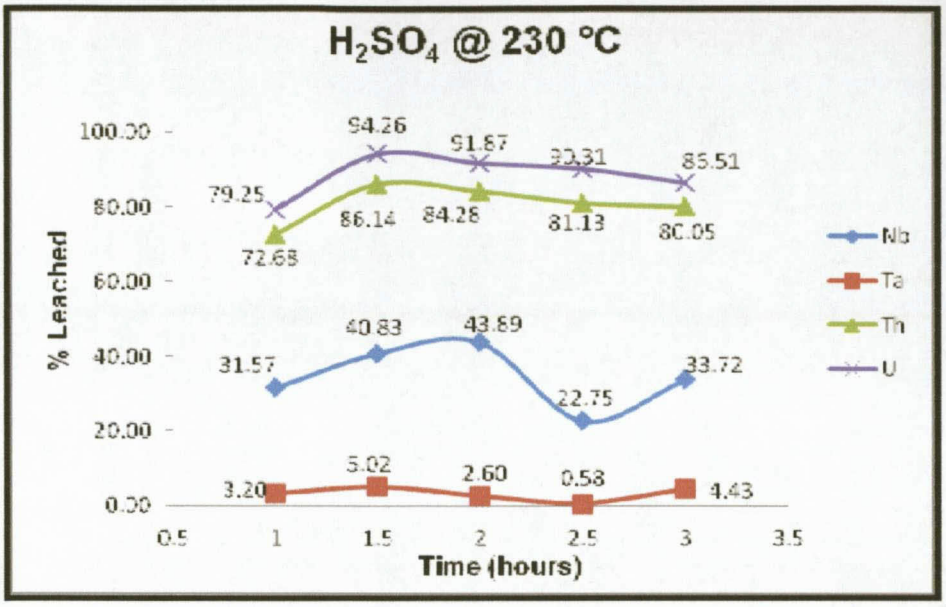

Figure 5.6: Quantification of Th, U, Nb and Ta after sulphuric acid leaching at 230 °C

Table 5.17: ICP-OES results of sulphuric acid leaching at 230 °C

Time (hour)	Metal oxide (%)			
	Nb	Ta	Th	U
1	31.57	3.20	72.68	79.25
1.5	40.83	5.02	86.14	94.26
2	43.89	2.60	84.28	91.87
2.5	22.75	0.58	81.13	90.31
3	33.72	4.43	80.05	86.51

Table 5.18: The mass balance after sulphuric acid leaching at 230 °C

Time (hour)	Product	Metal oxide (%)			
		Nb	Ta	Th	U
1					
	Filtrate	31.57	3.20	72.68	79.25
	Residue	58.29	83.12	27.32	22.51
	Total	**89.87**	**86.32**	**100.00**	**101.75**
1.5					
	Filtrate	40.83	5.02	86.14	94.26
	Residue	59.97	107.44	13.86	11.96
	Total	**100.79**	**112.47**	**100.00**	**106.22**
2					
	Filtrate	43.89	2.60	84.28	91.87
	Residue	54.49	110.34	15.72	11.72
	Total	**98.38**	**112.93**	**100.00**	**103.59**
2.5					
	Filtrate	22.75	0.58	81.13	90.31
	Residue	76.26	107.78	18.87	14.94
	Total	**99.02**	**108.36**	**100.00**	**105.25**
3					
	Filtrate	33.72	4.43	80.05	86.51
	Residue	57.80	92.48	19.95	17.64
	Total	**91.52**	**96.91**	**100.00**	**104.15**

5.3.4.2 Phosphoric acid digestion

5.3.4.2.1 Effect of leaching time on Th and U removal

Tantalite A samples (2 g) accurately weighed to 0.1 mg were quantitatively transferred into 100 mL round-bottom flasks and digested with phosphoric acid using a silicone oil bath at 50 °C for 60 minutes. The filtrates were collected in 100.0 mL volumetric flasks and filled to the mark with water. Aliquots of the samples (10.0 mL) were transferred into other 100.0 mL volumetric flasks containing 10.0 mL of H_3PO_4 and filled to the mark with water for ICP-OES analysis. The studies were repeated at time intervals of 90, 120, 150 and 180 minutes and done in triplicate and the

quantitative results are reported in **Table 5.19**. The results are graphically presented in **Figure 5.7** for Th, U and the two main elements leached at 50 °C and a maximum time of 3 hours.

In order to obtain the mass balance for the whole mineral sample (0.05 g), the undigested mineral was dried and accurately weighed to 0.1 mg and quantitatively transferred a platinum crucible. To this sample, 0.25 g of sodium dihydrogen phosphate and 0.25 g of disodium hydrogen phosphate were added and thoroughly mixed with the obtained residue and heated in a furnace at 900 °C for 30 minutes. The melt was subsequently cracked to facilitate the quick dissolution of the melt by placing the hot crucible in cold water. The melt was then dissolved in water and quantitatively transferred to a 100.0 mL volumetric flask containing 10.0 mL phosphoric acid and filled to the mark with water for ICP-OES analysis. The quantitative results are reported in **Table 5.20**.

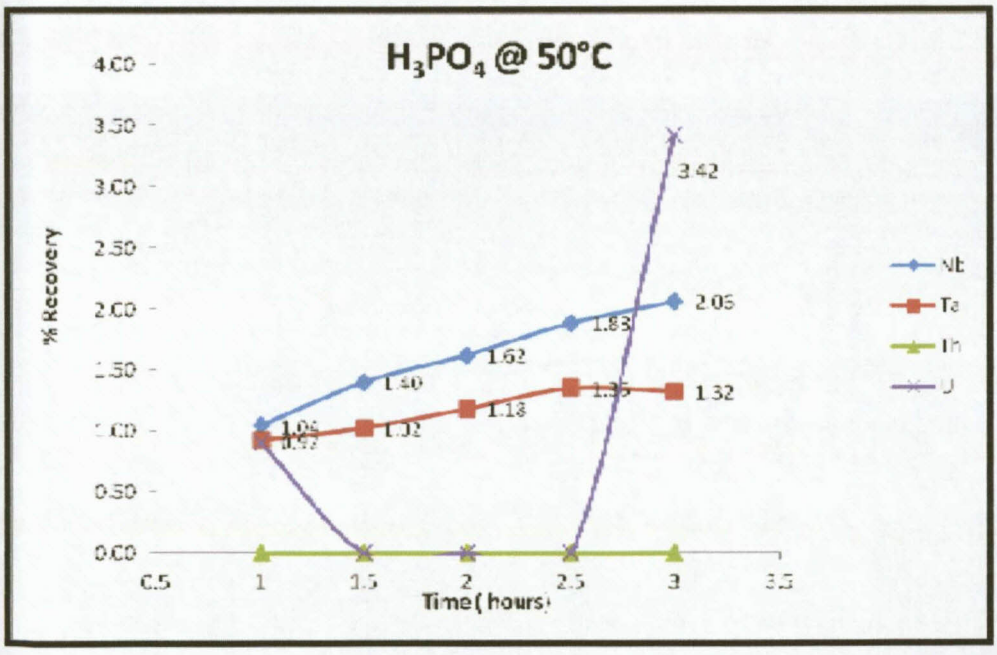

Figure 5.7: Quantification of Th, U, Nb and Ta after phosphoric acid leaching at 50 °C

Table 5.19: ICP-OES results of phosphoric acid leaching at 50 °C

Time (hour)		Metal oxide (%)			
		Nb	Ta	Th	U
1					
		1.15	0.86	...	0.49
		0.83	0.84	...	...
		1.15	1.05	...	1.31
	Average	**1.0(2)**	**0.9(1)**	**0**	**0.9(6)**
1.5					
		1.40	1.08	...	...
		1.25	1.02	...	...
		1.55	0.96	...	...
	Average	**1.4(2)**	**1.02(6)**	**0**	**0**
2					
		1.57	1.18	...	...
		1.80	1.19	...	...
		1.48	1.17	...	...
	Average	**1.6(2)**	**1.18(1)**	**0**	**0**
2.5					
		1.70	1.23	...	...
		2.20	1.53	...	...
		1.74	1.29	...	...
	Average	**1.9(3)**	**1.4(2)**	**0**	**0**
3					
		1.12	0.96	...	...
		1.76	1.28	...	...
		3.28	1.72	...	3.42
	Average	**2(1)**	**1.3(4)**	**0**	**3.42**

... = not detected

Table 5.20: The mass balance after phosphoric acid leaching at 50 °C

Time (hour)	Sample no.	Product	Metal oxide (%)			
			Nb	Ta	Th	U
1						
	1	Filtrate	1.15	0.86	0.00	0.49
		Residue	92.74	94.62	100	88.11
		Total	**93.89**	**95.49**	**100.00**	**88.60**
	2	Filtrate	0.83	0.84	0.00	0.00
		Residue	98.72	102.04	100	92.59
		Total	**99.55**	**102.88**	**100.00**	**92.59**
	3	Filtrate	1.15	1.05	0.00	1.31
		Residue	97.44	101.19	100	89.45
		Total	**98.58**	**102.24**	**100.00**	**90.75**
1.5						
	1	Filtrate	1.40	1.08	0.00	0.00
		Residue	96.60	99.62	100	91.26
		Total	**97.99**	**100.70**	**100.00**	**91.26**
	2	Filtrate	1.25	1.02	0.00	0.00
		Residue	96.90	99.66	100	92.88
		Total	**98.14**	**100.68**	**100.00**	**92.88**
	3	Filtrate	1.55	0.96	0.00	0.00
		Residue	94.51	103.38	100	87.99
		Total	**96.06**	**104.35**	**100.00**	**87.99**
2						
	1	Filtrate	1.57	1.18	0.00	0.00
		Residue	93.11	94.81	100	90.11
		Total	**94.68**	**95.99**	**100.00**	**90.11**
	2	Filtrate	1.80	1.19	0.00	0.00
		Residue	92.54	96.78	100	86.51
		Total	**94.34**	**97.97**	**100.00**	**86.51**
	3	Filtrate	1.48	1.17	0.00	0.00
		Residue	88.74	90.19	100	85.36
		Total	**90.22**	**91.36**	**100.00**	**85.36**
2.5						
	1	Filtrate	1.70	1.23	0.00	0.00
		Residue	90.44	93.96	100	86.40
		Total	**92.14**	**95.19**	**100.00**	**86.40**
	2	Filtrate	2.20	1.53	0.00	0.00
		Residue	90.16	98.76	100	84.32
		Total	**92.36**	**100.29**	**100.00**	**84.32**
	3	Filtrate	1.74	1.29	0.00	0.00
		Residue	86.98	90.06	100	84.08
		Total	**88.72**	**91.35**	**100.00**	**84.08**
3						
	1	Filtrate	1.12	0.96	0.00	0.00
		Residue	88.25	92.81	100	80.18
		Total	**89.37**	**93.77**	**100.00**	**80.18**
	2	Filtrate	1.76	1.28	0.00	0.00
		Residue	85.54	86.93	100	80.86
		Total	**87.30**	**88.21**	**100.00**	**80.86**
	3	Filtrate	3.28	1.72	0.00	3.42
		Residue	87.27	90.11	100	80.33
		Total	**90.55**	**91.83**	**100.00**	**83.75**

5.3.4.2.2 Effect of temperature on Th and U removal

Tantalite A samples (2 g) were accurately weighed to 0.1 mg and quantitatively transferred to 100 mL round-bottom flasks and subsequently digested with phosphoric acid in a silicone oil bath at temperature of 100 °C and 150 °C for 60 minutes. The filtrates were collected in 100.0 mL volumetric flasks and filled to the mark with water. Aliquots of the samples (2.0 mL) were then transferred into other 100.0 mL volumetric flasks containing 10.0 mL of H_3PO_4 and filled to the mark with water for ICP-OES analysis. The experimental procedure was repeated at time intervals of 90, 120, 150 and 180 minutes. **Tables 5.21** and **5.23** show the results of the acid leaching while **Figures 5.8** and **5.9** graphically present the amount of Th, U and the two main elements that were leached at 100 °C to 150 °C and a maximum time of 3 hours obtained by ICP-OES analysis.

In order to obtain the mass balance for the whole mineral sample (0.05 g), the undigested mineral was dried and accurately weighed to 0.1 mg and quantitatively transferred a platinum crucible. To this sample, 0.25 g of sodium dihydrogen phosphate and 0.25 g of disodium hydrogen phosphate were added and thoroughly mixed with the obtained residue and heated in a furnace at 900 °C for 30 minutes. The melt was subsequently cracked to facilitate the quick dissolution of the melt by placing the hot crucible in cold water. The melt was then dissolved in water and quantitatively transferred to a 100.0 mL volumetric flask containing 10.0 mL phosphoric acid and filled to the mark with water for ICP-OES analysis. The quantitative results are reported in **Tables 5.22** and **5.24**.

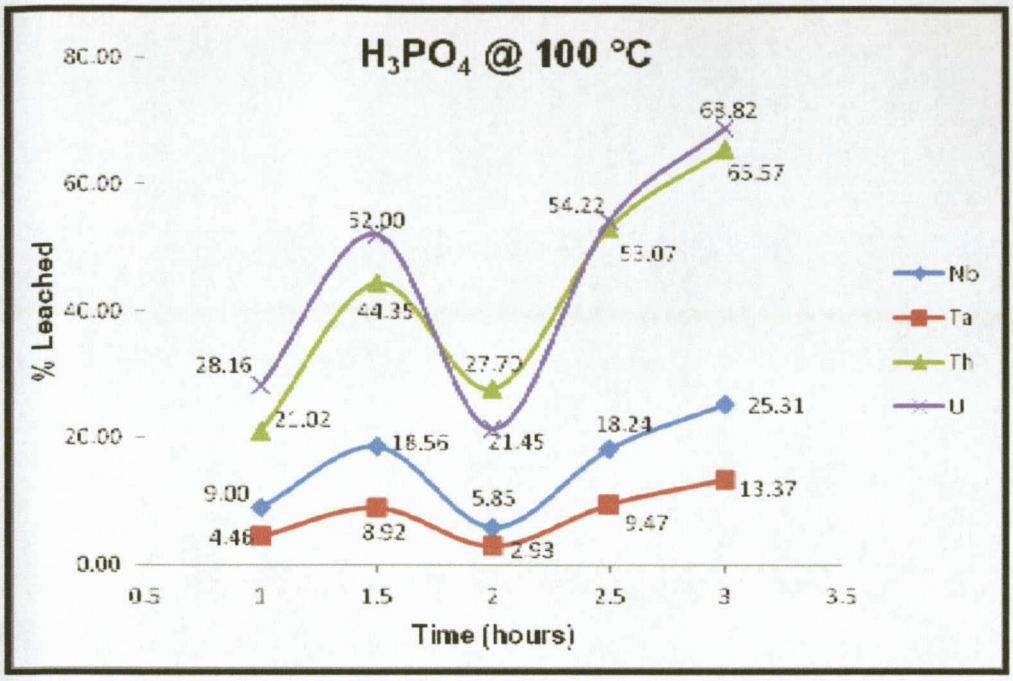

Figure 5.8: Quantification of Th, U, Nb and Ta after phosphoric acid leaching at 100 °C

Table 5.21: ICP-OES results after phosphoric acid leaching at 100 °C

Time (hour)	Metal oxide (%)			
	Nb	Ta	Th	U
1	9.00	4.46	21.02	28.16
1.5	18.56	8.92	44.35	52.00
2	5.85	2.93	27.70	21.45
2.5	18.24	9.47	53.07	54.22
3	25.31	13.37	65.57	68.82

Table 5.22: The mass balance of phosphoric acid leaching at 100 °C

Time (hour)	Product	Metal oxide (%)			
		Nb	Ta	Th	U
1					
	Filtrate	9.00	4.46	21.02	28.16
	Residue	85.73	98.15	78.98	78.04
	Total	**94.73**	**102.61**	**100.00**	**106.20**
1.5					
	Filtrate	18.56	8.92	44.35	52.00
	Residue	90.91	111.87	55.65	62.33
	Total	**109.47**	**120.79**	**100.00**	**114.33**
2					
	Filtrate	5.85	2.93	27.70	21.45
	Residue	90.37	95.66	72.30	88.99
	Total	**96.22**	**98.59**	**100.00**	**110.44**
2.5					
	Filtrate	18.24	9.47	53.07	54.22
	Residue	67.41	83.50	46.93	43.24
	Total	**85.65**	**92.97**	**100.00**	**97.46**
3					
	Filtrate	25.31	13.37	65.57	68.82
	Residue	56.84	74.30	34.43	26.58
	Total	**82.15**	**87.67**	**100.00**	**95.40**

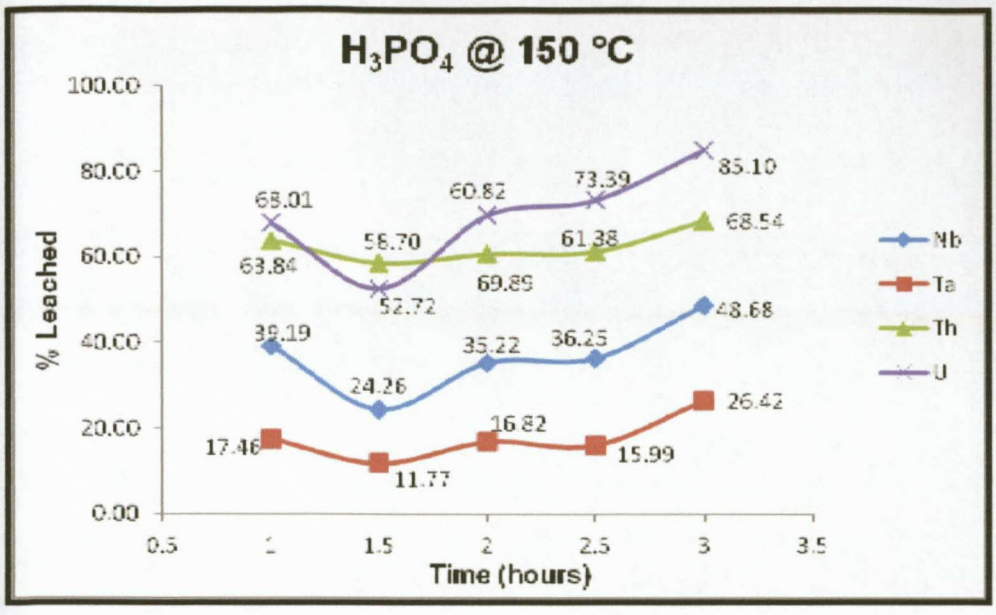

Figure 5.9: Quantification of Th, U, Nb and Ta after phosphoric acid leaching at 150 °C

Table 5.23: ICP-OES results after phosphoric acid leaching at 150 °C

Time (hour)	Metal oxide (%)			
	Nb	Ta	Th	U
1	39.19	17.46	63.84	68.01
1.5	24.26	11.77	58.70	52.72
2	35.22	16.82	60.82	69.89
2.5	36.25	15.99	61.38	73.39
3	48.68	26.42	68.54	85.10

Table 5.24: The mass balance of phosphoric acid leaching at 150 °C

Time (hour)	Product	Metal oxide (%)			
		Nb	Ta	Th	U
1					
	Filtrate	39.19	17.46	63.84	68.01
	Residue	82.05	110.85	36.16	36.06
	Total	**121.24**	**128.31**	**100.00**	**104.07**
1.5					
	Filtrate	24.26	11.77	58.70	52.72
	Residue	79.82	107.83	41.30	35.08
	Total	**104.08**	**119.60**	**100.00**	**87.80**
2					
	Filtrate	35.22	16.82	60.82	69.89
	Residue	78.50	99.36	39.18	42.07
	Total	**113.72**	**116.18**	**100.00**	**111.96**
2.5					
	Filtrate	36.25	15.99	61.38	73.39
	Residue	74.78	97.07	38.62	35.04
	Total	**111.03**	**113.06**	**100.00**	**108.43**
3					
	Filtrate	48.68	26.42	68.54	85.10
	Residue	68.76	109.23	31.46	23.98
	Total	**117.44**	**135.65**	**100.00**	**109.08**

5.3.4.3 Hydrochloric acid digestion

5.3.4.3.1 Effect of leaching time on Th and U removal

Tantalite A samples (2 g) were accurately weighed to 0.1 mg and quantitatively transferred to 100 mL round-bottom flasks and digested with hydrochloric acid in a silicone oil bath at 50 °C for 90 minutes. The filtrates were collected in 100.0 mL volumetric flasks and filled to the mark with water. Aliquots of the samples (2.0 mL) were transferred into other 100.0 mL volumetric flasks containing 10.0 mL of the hydrochloric acid and filled to the mark with water for ICP-OES analysis. The experimental procedure was repeated at time intervals of 120, 150, 180 and 240

minutes and the leaching results of the four main elements are shown in **Table 5.25** while **Figure 5.10** graphically presents the same results.

In order to obtain the mass balance for the whole mineral sample, the undigested mineral was dried and weighed (0.05 g) in a platinum crucible. To this sample, 0.25 g of sodium dihydrogen phosphate and 0.25 g of disodium hydrogen phosphate were added and thoroughly mixed with the obtained residue and heated in a furnace at 900 °C for 30 minutes. The melt was subsequently cracked to facilitate the quick dissolution of the melt by placing the hot crucible in cold water. The melt was then dissolved in water and quantitatively transferred to a 100.0 mL volumetric flask containing 10.0 mL phosphoric acid and filled to the mark with water for ICP-OES analysis. The quantitative results are reported in **Table 5.26**.

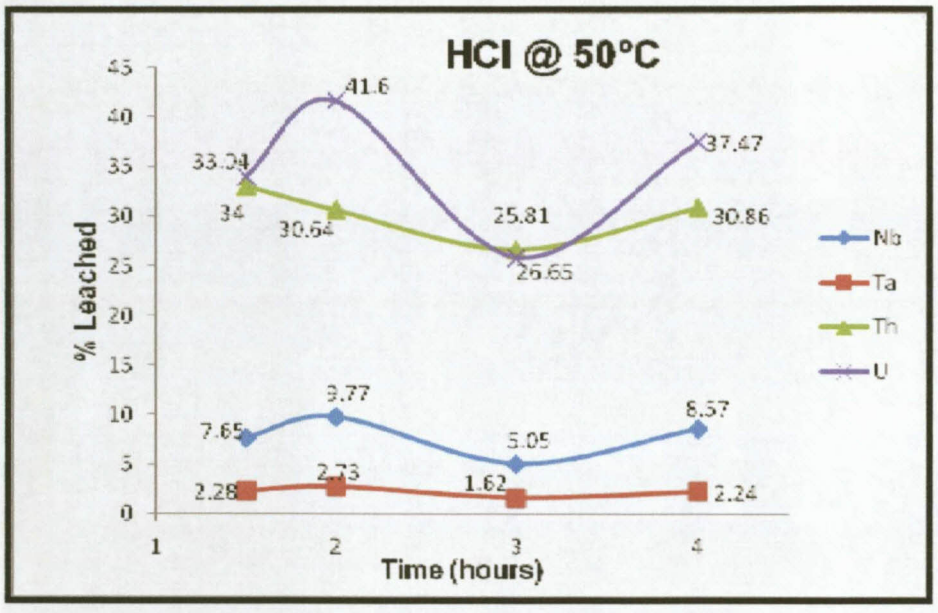

Figure 5.10: Quantification of Th, U, Nb and Ta after hydrochloric acid leaching at 50 °C

Figure 5.25: ICP-OES results after hydrochloric acid leaching at 50 °C

Time (hour)	Metal oxide (%)			
	Nb	Ta	Th	U
1.5	7.65	2.28	33.04	34.00
2	9.77	2.73	30.64	41.60
3	5.05	1.62	26.65	25.81
4	8.57	2.24	30.86	37.47

Figure 5.26: The mass balance of hydrochloric acid leaching at 50 °C

Time (hour)	Product	Metal oxide (%)			
		Nb	Ta	Th	U
1.5					
	Filtrate	7.65	2.28	33.04	34.00
	Residue	99.05	107.51	66.96	77.74
	Total	**106.7**	**109.79**	**100.00**	**111.74**
2					
	Filtrate	9.77	2.73	30.64	41.60
	Residue	96.48	110.32	69.36	66.71
	Total	**106.25**	**113.05**	**100.00**	**108.31**
3					
	Filtrate	5.05	1.62	26.65	25.81
	Residue	100.27	110.53	73.35	84.17
	Total	**105.32**	**112.15**	**100.00**	**109.98**
4					
	Filtrate	8.57	2.24	30.86	37.47
	Residue	99.40	110.99	69.14	72.94
	Total	**107.97**	**113.23**	**100.00**	**110.41**

5.3.4.3.2 Effect of temperature on Th and U removal

Tantalite A samples (0.1 g) were accurately weighed (to 0.1 mg) and quantitatively transferred to a glass vial and then digested with 10.0 mL hydrochloric acid in a silicone oil bath at approximately 20 °C and at 90 °C from 30 minutes up to 24 hours.

The filtrates were transferred into 100.0 mL volumetric flasks and filled to the mark with water for ICP-OES analysis. The quantitative results are given in **Tables 5.27** and **5.28** while **Figures 5.11** and **5.12** graphically illustrates the leaching of the four main elements at ≈ 20 °C and 90 °C.

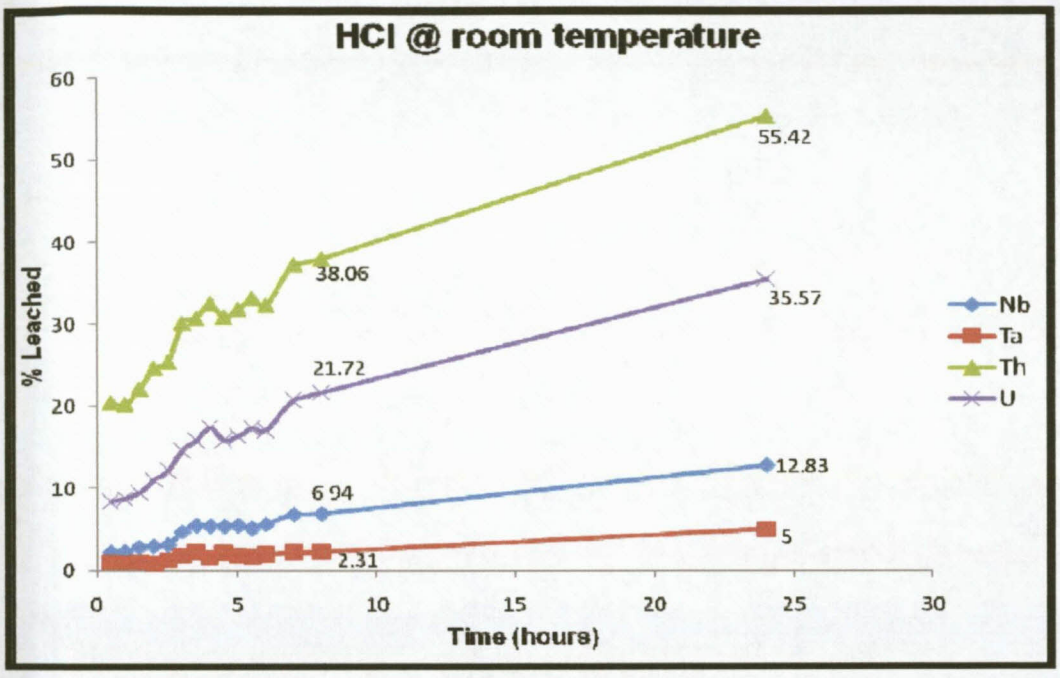

Figure 5.11: Quantification of Th, U, Nb and Ta after hydrochloric acid leaching at room temperature

Table 5.27: ICP-OES results after hydrochloric acid leached at approximately 20 °C

Time	Metal oxide (%)			
	Nb	Ta	Th	U
0.5	2.26	0.98	20.46	8.36
1	2.32	0.94	20.26	8.72
1.5	2.88	1.05	22.11	9.46
2	3.01	0.84	24.67	11.01
2.5	3.19	1.18	25.42	12.17
3	4.74	1.78	30.24	14.66
3.5	5.52	2.24	30.76	15.86
4	5.45	1.57	32.55	17.40
4.5	5.41	2.13	30.91	15.85
5	5.51	1.81	31.86	16.39
5.5	5.18	1.68	33.19	17.36
6	5.66	1.99	32.36	17.1
7	6.85	2.25	37.37	20.81
8	6.94	2.31	38.06	21.72
24	12.83	5.0	55.42	35.57

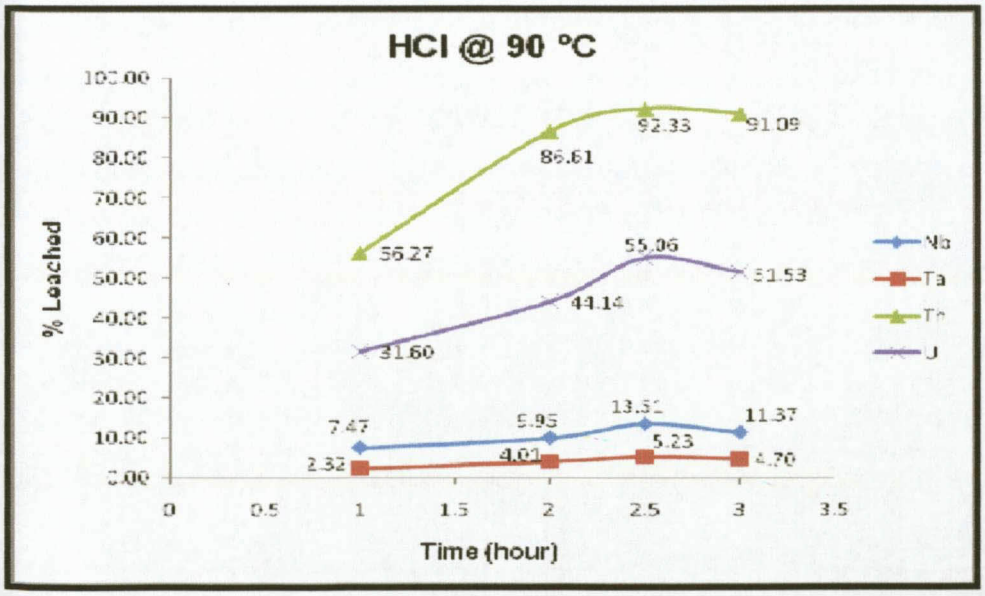

Figure 5.12: Quantification of Th, U, Nb and Ta after hydrochloric acid leaching at 90 °C

Table 5.28: ICP-OES results after hydrochloric acid leaching at 90 °C

Time (hour)		Metal oxide (%)			
		Nb	Ta	Th	U
1					
		6.95	2.40	51.93	25.59
		7.82	2.87	45.78	35.04
		7.65	1.70	71.11	34.19
	Average	**7.5(5)**	**2.3(6)**	**56(13)**	**32(5)**
2					
		8.47	3.41	74.75	37.52
		10.99	4.34	95.36	48.97
		10.41	4.28	89.73	45.94
	Average	**10(1)**	**4.0(5)**	**87(10)**	**44(6)**
2.5		11.23	4.50	81.32	52.08
		12.17	4.68	103.34	53.64
		17.14	6.51	717.61#	59.45
	Average	**14(3)**	**5(1)**	**92(16)**	**55(4)**
3					
		11.96	5.02	103.16	53.37
		11.09	4.68	77.69	49.74
		11.06	4.41	92.41	51.48
	Average	**11.4(5)**	**4.7(3)**	**91(13)**	**52(2)**

= omitted during calculations

5.3.4.4 Influence of other mineral acids on Th and U removal

5.3.4.4.1 Effect of nitric acid on Th and U removal

Tantalite A sample (0.1 g) was accurately weighed to 0.1 mg in a 50 mL beaker and 10.0 mL of nitric acid was added. The mixture was heated in an oil bath at 90 °C for 1.5 hours. The filtrate was then collected in a 100.0 mL volumetric flask, cooled to room temperature and filled to the mark with water. A 10.0 mL aliquot of the solution was transferred to another 100.0 mL volumetric flask containing 10.0 mL of nitric acid and filled to the mark with water for ICP-OES analysis. The solution was allowed to stand for a day or longer before ICP-OES determinations were made to allow

complete homogenization of the solutions. The experiment was conducted only once and the leaching results for the four main elements quantified by ICP-OES are reported in **Table 5.29**.

Table 5.29: Quantification of U, Th, Ta and Nb using different acids leaching at 90°C

Acid	Extraction (%)			
	Nb_2O_5	Ta_2O_5	ThO_2	U_3O_8
Nitric acid	0.45	0.49	28.48	3.07
Aqua regia	1.59	0.95	36.70	10.40
Perchloric acid	1.89	0.0	22.68	n.d

n.d= not done

5.3.4.4.2 Effect of aqua regia on Th and U removal

Tantalite A sample (0.1 g) was accurately weighed (to 0.1 mg) in a 50 mL beaker and 10.0 mL of *aqua regia* was added. The mixture was heated in an oil bath at 90 °C for 1.5 hours. The filtrate was then collected in a 100.0 mL volumetric flask, cooled to room temperature and filled to the mark with water. A 10.0 mL aliquot of the solution was transferred to another 100.0 mL volumetric flask containing 10.0 mL of *aqua regia* and filled to the mark with water for ICP-OES analysis. The solution was allowed to stand for a day or longer before ICP-OES determinations were made to allow complete homogenization of the solutions. The experiment was conducted only once and the leaching results for the four main elements quantified using ICP-OES are reported in **Table 5.29**.

5.3.4.4.3 Effect of perchloric acid on Th and U removal

Tantalite A sample (0.1 g) was accurately weighted (to 0.1 mg) in a 50 mL beaker and 10.0 mL of perchloric acid was added. The mixture was heated in an oil bath at 90 °C for 1.5 hours. The filtrate was then collected in 100.0 mL volumetric flask, cooled to room temperature and then filled to the mark with water. A 10.0 mL aliquot of the solution was transferred to another 100.0 mL volumetric flask containing 10.0 mL of perchloric acid and filled to the mark with water for ICP-OES analysis. The solution was allowed to stand for a day or longer before ICP-OES determinations

were made to allow complete homogenization of the solutions. The experiment was conducted only once and the leaching results for the four main elements obtained by ICP-OES are reported in **Table 5.29**.

5.3.5 Anion precipitation of metals after flux dissolution

The possible removal of Th and U from the rest of the elements with selective precipitation was investigated in this part of the study. 2.5 g of sodium dihydrogen phosphate, 2.5 g of disodium hydrogen phosphate and 0.5 g of the Tantalite A mineral ore were accurately weighed (to 0.1 mg) and thoroughly mixed in a platinum crucible and then heated to 900°C for 30 minutes in the high temperature furnace. The melt was subsequently cracked by placing the hot crucible in cold water. The melt was dissolved with 20 mL water and quantitatively transferred to a 100.0 mL volumetric flask and filled to the mark with distilled water. 10.0 mL Aliquots of this solution were transferred into five beakers and to these 10.0 mL of the different acids (H_2SO_4, HCl, HNO_3, $HClO_4$ and *aqua regia*) were added. Precipitation formation was observed in all cases upon the addition of the different acids.

The observed precipitates were separated from the filtrates by centrifuging and the filtrates were transferred to 100.0 mL volumetric flasks and filled to the mark with water. In the next step the precipitates were dissolved using 10.0 mL H_3PO_4 and quantitatively transferred into 100.0 mL volumetric flasks and filled to the mark with water for ICP-OES analysis. The quantitative ICP-OES results are reported in **Table 5.30**.

Table 5.30: Anion precipitation of the fluxed mineral solution

Product	Metal recovery (%)			
	Nb	**Ta**	**Th**	**U**
$HClO_4$ filtrate	0.16	0.61	9.30	31.75
$HClO_4$ precipitate	99.84	99.39	90.70	68.25
HCl filtrate	0.91	1.63	21.97	87.38
HCl precipitate	99.09	98.37	78.03	12.62
HNO_3 filtrate	0.17	0.62	16.16	64.40
HNO_3 precipitate	99.83	99.38	83.84	35.60
H_2SO_4 filtrate	19.87	0.79	17.42	94.89
H_2SO_4 precipitate	80.13	99.21	82.58	5.11
Aqua regia filtrate	0.40	0.62	17.27	81.83
Aqua regia precipitate	99.60	99.38	82.73	18.17

5.3.6 Selective removal of Th and U using ion exchange chromatography

5.3.6.1 Effect of different volumes of water on metal recovery

The selective removal of Th and U from the rest of the elements present in the tantalite mineral was investigated using the zeolite called clinobrite as the stationery phase. The column (2 cm diameter) was prepared by loading the resin to a height of 15 cm and washed it with water (clear eluent indicated prepared column). Approximately 1 g Tantalite A was accurately weighed (to 0.1 mg) into a platinum crucible containing 5.0 g sodium dihydrogen phosphate and 5.0 g of disodium hydrogen phosphate. The content was thoroughly mixed and fluxed at 900 °C for 30 minutes. The melt was subsequently cracked by placing the hot crucible in cold water, dissolved in water and transferred into a 200.0 mL volumetric flask and filled to the mark with water. The Ta, Nb, Th and U content was firstly quantified using ICP-OES analysis. 10.0 mL Aliquots were loaded on the column and eluted with 3 portions of water (10 mL and 15 mL respectively). The eluted solutions were collected in 100.0 mL volumetric flasks containing 10.0 mL hydrochloric acid and filled to the mark with distilled water. The ICP-OES results are shown in **Table 5.31**.

Table 5.31: Metal recovery from the zeolites using water as eluent

Products	Metal recovery (%)			
	Nb	Ta	Th	U
Initial concentration (ppm)	96.98	112.58	3.25	14.45
Strip 1 (10 mL)	0.71	0.98	14.46	17.99
Strip 2 (10 mL)	10.48	5.39	30.46	33.98
Strip 3 (10 mL)	10.96	6.23	23.69	27.40
Total stripped %	**22.15**	**12.60**	**68.62**	**79.38**
Total retained %	**77.85**	**87.40**	**31.38**	**20.62**
Strip 1 (15 mL)	5.00	3.84	18.15	26.64
Strip 2 (15 mL)	26.35	20.18	51.69	48.03
Strip 3 (15 mL)	4.29	3.82	6.46	4.98
Total stripped %	**35.64**	**27.84**	**76.31**	**79.65**
Total retained %	**64.36**	**72.16**	**23.69**	**20.35**

5.3.6.2 Effect of dilute hydrochloric acid elution and metal recovery

The column (2 cm diameter) was prepared by loading the resin to a height of 15 cm and washed it with water (clear eluent indicated prepared column). Approximately 1 g Tantalite A was accurately weighed (to 0.1 mg) into a platinum crucible containing 5.0 g sodium dihydrogen phosphate and 5.0 g of disodium hydrogen phosphate. The content was thoroughly mixed and fluxed at 900 °C for 30 minutes. The melt was subsequently cracked by placing the hot crucible in cold water, dissolved in water and transferred into 200.0 mL volumetric flask and filled to the mark with water. 10.0 mL aliquots were loaded on the column and stripped with 3 × 20 mL solutions of 0.01 M, 0.05 M and 0.1 M HCl respectively. The eluted solutions were collected in 100.0 mL volumetric flasks containing 10.0 mL hydrochloric acid and filled to the mark with distilled water. The ICP-OES results are shown in **Table 5.32**.

Table 5.32: Effect of dilute hydrochloric acid elution on metal removal

Products	Metal recovery (%)			
	Nb	Ta	Th	U
Initial concentration (ppm)	95.65	109.54	3.30	11.95
20 mL 0.01 M HCl (1)	46.91	39.47	50.30	63.60
20 mL 0.01 M HCl (2)	15.45	14.32	25.45	27.11
20 mL 0.01 M HCl (3)	3.00	3.58	11.21	14.48
Total stripped %	**65.36**	**57.38**	**86.97**	**105.19**
Total retained %	**34.64**	**42.62**	**13.03**	**0.00**
20 mL 0.05 M HCl (1)	42.43	41.75	51.52	57.49
20 mL 0.05 M HCl (2)	19.62	16.18	34.55	37.07
20 mL 0.05 M HCl (3)	0.81	0.60	16.97	19.00
Total stripped %	**62.85**	**58.53**	**103.03**	**113.56**
Total retained %	**37.15**	**41.47**	**0.00**	**0.00**
20 mL 0.1 M HCl (1)	55.74	52.58	82.12	91.46
20 mL 0.1 M HCl (2)	4.07	2.64	21.82	20.08
20 mL 0.1 M HCl (3)	0.50	0.46	17.88	20.75
Total stripped %	**60.31**	**55.68**	**121.82**	**132.30**
Total retained %	**39.69**	**44.32**	**0.00**	**0.00**

5.4 Discussion

5.4.1 LOD and LOQ

The detection and quantification limits are used to ensure the validity of the results that are obtained from the instrumental analysis. The experimentally obtained detection limits (LOD) for Ta, Nb, Th and U were determined as 0.0280, 0.0141, 0.0275 and 0.0130 ppm respectively (see **Table 5.7**). These low detection limits, together with the low quantification limits (LOQ) clearly indicate that the ICP-OES is capable of determining small quantities of the main elements in the tantalite minerals. Low LOD and LOQ values were also obtained for the rest of the elements that may be present in the mineral samples (see **Table.5.4**). The experimental LOD and LOQ values obtained for Nb in this study is slightly higher than those obtained in the study by Nete[89], but the LOD and LOQ for Ta was approximately the same. Matrix complexity of the mineral sample used in this study made wavelength selection a daunting task to ensure interference free analysis.

5.4.2 Mineral quantification

The fusion of the mineral ore with the sodium phosphate flux proved to be a reliable method for the complete dissolution of the mineral sample and it proves to be a very useful method for the dissolution and quantifying samples of this nature. The quantification of the mineral (**Table 5.8**) indicates that the major elements are indeed tantalum (27.7(2)%) and niobium (28.1(3)%) and this is in good agreement with the results obtained by K. H. Nights Laboratories (**Table 5.4**), with tantalum and niobium values of 27.71 and 27.41% respectively. Uranium and thorium were found to be 3.07(2) and 0.50(4)% respectively which are close to the quantities obtained by K. H. Nights Laboratories and by Theron[78] (2.97 and 0.52% respectively). These results indicate that fusion with the sodium phosphate flux is as good a method as the LTB method for the dissolution and quantification of the mineral sample. These values were used throughout the study as the reference values for the quantification of the elements of interest.

5.4.3 Mineral acid leaching of tantalite mineral

The initial idea behind the removal of Th and U from the mineral mix was to try and leach it selectively from the mineral mixture with a minimum loss of Ta and Nb prior to the complete dissolution and beneficiation processes to reduce the total reactivity the mineral mixture to simplify transport, shipping and handling. The first part of this NORM leaching involved the use of H_2SO_4 at different leaching times and temperatures.

5.4.3.1 Sulphuric acid leaching – time and temperature influence

The quantification of the elements present in the filtrate at 50 °C clearly indicate the presence of relatively high U and Th content, but low Nb, and even lower Ta content (see **Figure 5.2** and **Table 5.9**). The results in **Figure 5.2** clearly indicate an increase in Th content from 22.28 to 34.76% with an increase in leaching time from 1 to 3 hours. The same tendency was observed for U with an increase from 14.20 to 23.86% after 3 hours of leaching. Interestingly, the Nb and Ta content remained low within the filtrate during the duration of the leaching process. The Nb content increased from 3.22 to 3.96% while Ta increased only from 0.46 to 0.81% after 3 hours of leaching time.

An increase in temperature from 50 to 230 °C (see **Figures 5.3 – 5.6** and **Tables 5.11 – 5.17**) clearly indicates an increase in Th and U removal. The Th content increased from 34.76% at 50 °C (3 hour leaching) to 61.22% at 100 °C, to 73.50% at 150 °C and finally to 80.05% at 230 °C. The U content on the other hand increased from 23.86 to 64.37% at 100 °C, to 81.27% at 150 °C and finally to 90.08% at 200 °C and above. The same tendency of an increase in element content in the filtrate with an increase in temperature was observed for Ta, but more so for Nb. The Ta content increased from 0.46% at 50 °C to 15.23% at 200 °C while the Nb content increased from 3.96% at 50 °C to 33.72% at 230 °C.

The observation of the increasing solubility of Nb in H_2SO_4 compared to that of Ta corresponds with the results obtained in two previous studies. The results obtained in the study by Nete[89] indicated that 98.8% of Nb_2O_5 was dissolved by microwave-

assisted sulphuric acid digestion while only 4.19% of Ta_2O_5 was dissolved in the same reaction mixture by Theron[3] using microwave-assisted sulphuric acid digestion. Using microwave-assisted sulphuric acid digestion on the tantalite mineral On the other hand, resulted in the dissolution of more Nb (19.45% of a total of 27.01%) than Ta (6.99% of a total of 30.08%). It is clear from these results that it is possible to remove the majority of Th and U using H_2SO_4 as a leaching agent at temperatures of 150 °C and above at a leaching time span of 3 hours. The downside to these conditions is that a substantial amount of Nb (~30%) will be lost under these conditions and about 15% Ta. It appears that 3 hours leaching time at 50 °C appears to the best experimental conditions to remove a substantial amount of Th and U prior to complete dissolution with the maximum amount of Nb and Ta remaining undissolved.

The combined effect of time and temperature on the percentage of element leaching with H_2SO_4 is presented in **Figures 5.13 to 5.16**. These results clearly indicate that temperature has a greater influence on the amount of elements that are removed from the solid mineral sample (slope of the graphs) compared to time as a variable. It is also evident that the amount of Ta and Nb that are leached increases with temperature up to 200 °C, but then increases at 230 °C. The results for U and Th on the other hand increased as temperature is increased, but to a lesser extent (smaller slope) at the highest temperatures.

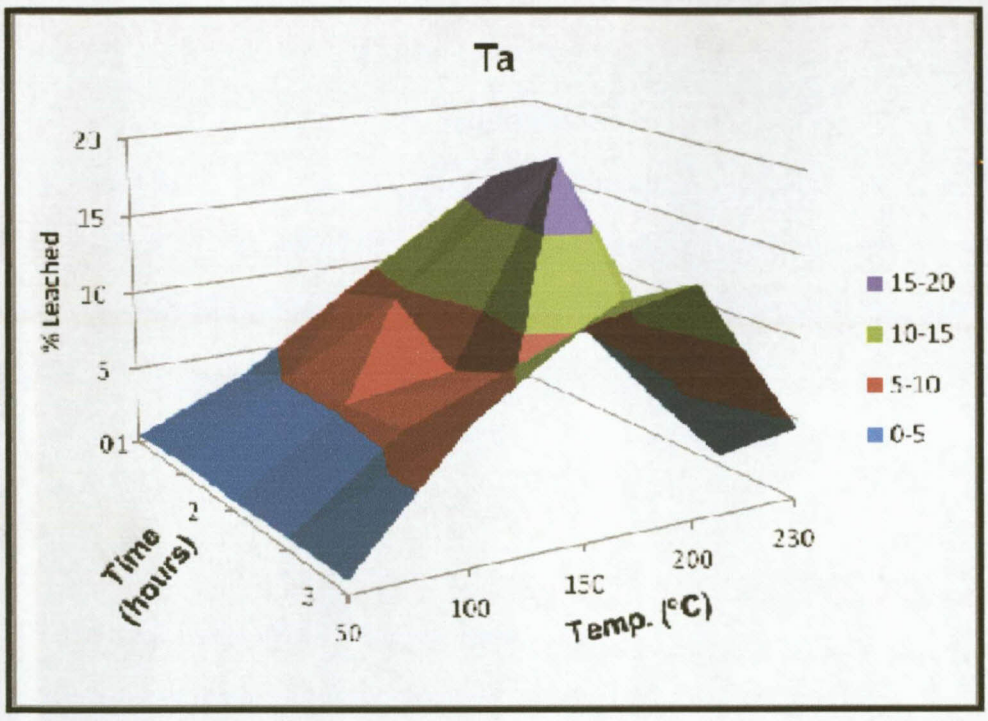

Figure 5.13: The combined influence of time and temperature on the % Ta leached with concentrated H_2SO_4

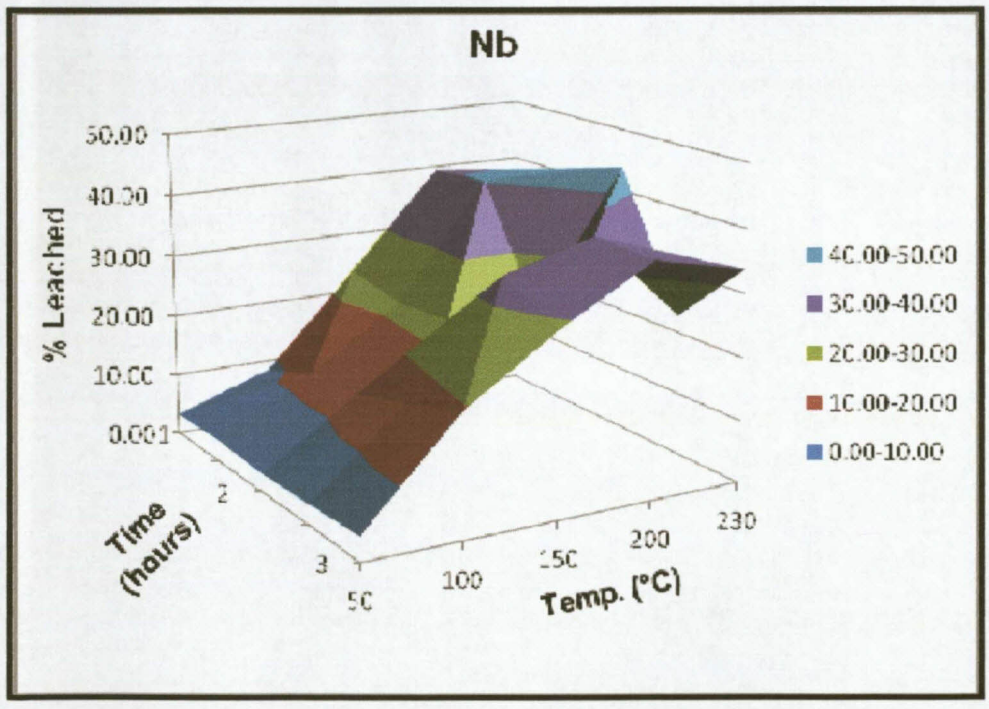

Figure 5.14: The combined influence of time and temperature on the % Nb leached with concentrated H_2SO_4

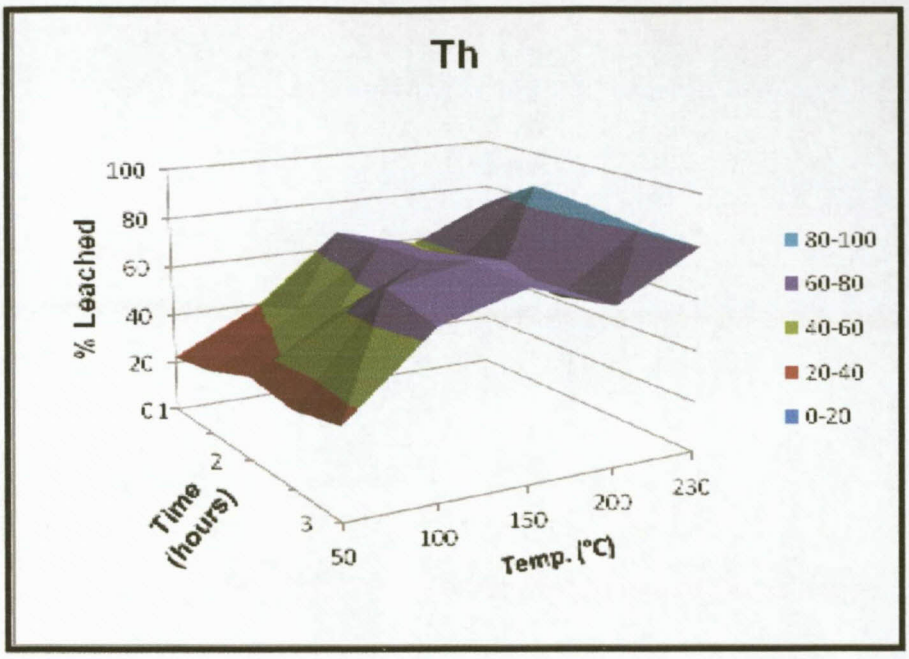

Figure 5.15: The combined influence of time and temperature on the % Th leached with concentrated H_2SO_4

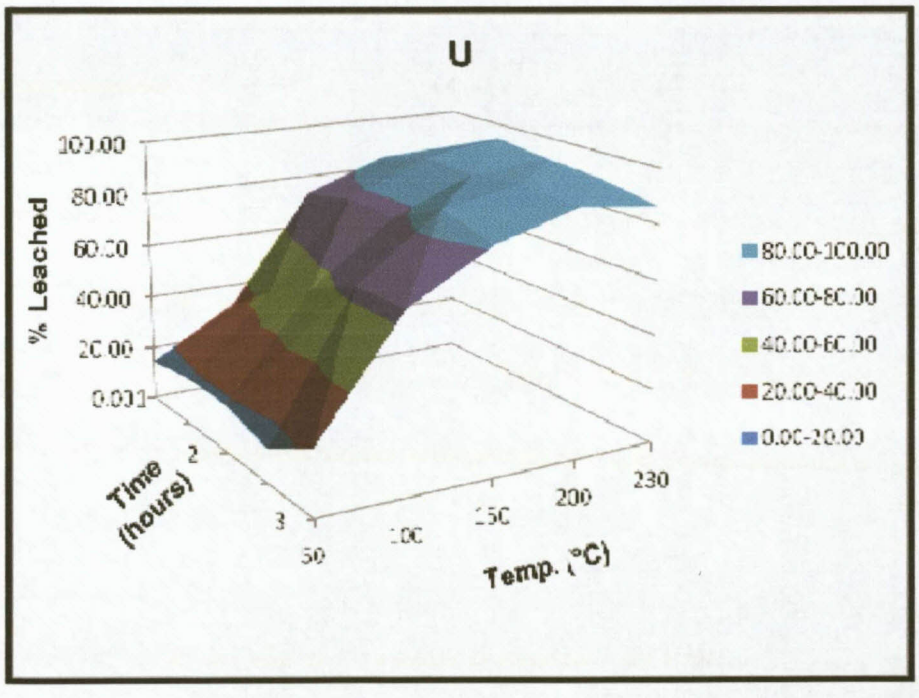

Figure 5.16: The combined influence of time and temperature on the % U leached with concentrated H_2SO_4

5.4.3.2 Phosphoric acid leaching – effect of temperature and leaching time

The use of phosphoric acid to remove U and Th from the mineral was the next step in the investigation. The leaching of the mineral ore with phosphoric acid at 50 °C removed 0.90 and 0 % of U and Th after 1 hour respectively (see **Figure 5.7** and **Table 5.19**). Furthermore, 0.92% of Ta was also leached under the same experimental conditions while phosphoric acid had little effect on removing Nb (1.04%). Increasing the leaching time to 2 hours had little or no effect in the additional removal of U and Th as almost none of them were removed from the mineral sample. However, the increase in time resulted in 1.18 and 1.62% of Ta and Nb being leached from the mineral respectively. A further increase to 3 hours of leaching time succeeded to remove only 3.42% of U while Th remained inert towards the acid. At this temperature, 1.32 and 2.05% of Ta and Nb were also removed from the mineral respectively. It is clear from these results that phosphoric acid is unable to remove U and Th from the mineral at 50 °C and also succeeded to remove very small quantities of tantalum and niobium. At this stage it was decided to expand the investigation to include the effect of temperature while the influence of time was also investigated concurrently.

An increase of reaction/leaching temperature from 50 to 100 °C increased the Th and U content to 21.02 and 28.16% while the Ta and Nb content increased to 4.46 and 9.0% respectively after 1 hour leaching time (**Figure 5.8** and **Table 5.21**). Increasing the leaching time to 2 hours decreased the U content from 28.16 to 21.45% while the Th content increased from 21.02 to 27.70%. This increase in leaching time to 2 hours also had a profound effect on Nb and Ta content with an increase from 9 to 25.31% for Nb and from 4.4 to 13.37% for Ta. At 150 °C and 3 hours of leaching, (**Figure 5.9** and **Table 5.23**) the Th removal was determined as 68.54%, that of U as 85.10% and Ta and Nb as 26.42 and 48.68% respectively.

These results clearly indicate that phosphoric acid is more effective than sulphuric acid at removing U and Th at 150 °C from the mineral. The only setback from using phosphoric acid as a leaching agent is that the elements that are supposed to be remaining in the mineral were also leached into the U and Th filtrate in even larger quantities than sulphuric acid. Phosphoric acid is therefore less selective in leaching only U and Th from the mineral as is also removing the major elements, Ta and Nb,

which have to be separated from U and Th. The increase in leaching time increases the overall leaching of the respective elements as was observed for the H_2SO_4 leaching process. However, the trend that was observed in the previous temperature investigation of an increase in leaching quantities with an increase in temperature was not the same as the trend observed in this study. The leaching of the elements still increased after 2 hours of leaching, but a further increase to 3 hours of leaching time had little or no effect on the mineral quantities. The combination of time and temperature clearly plays a crucial role in removing U and Th from the mineral.

5.4.3.3 Hydrochloric acid leaching – effect of temperature and leaching time

Hydrochloric acid was the next acid which was used to investigate the removal of U and Th from the tantalite mineral. At 50 °C 34.0 and 33.04% of the U and Th were removed while 2.28 and 7.65% of the Ta and Nb were leached from the mineral respectively during the same time (see **Figure 5.10** and **Table 5.25**). After 2 hours of leaching the U and Th content was determined as 41.60 and 30.64% of respectively. At this leaching time the Ta and Nb content increased to 2.73 and 9.77% respectively. A further increase in leaching time to 4 hours resulted in the removal of 37.47% of U, 30.86% of Th and 2.24 and 8.57% of Ta and Nb respectively. It is clear from these results that the hydrochloric acid removes more of U and Th than sulphuric acid at 50 °C. The disadvantage is that hydrochloric acid removed more of tantalum and niobium which should ideally remain in the mineral ore. An increase in time only had a small effect on the leaching of all the elements of interest. At this stage it was decided to investigate the effect of different temperatures on the removal of U and Th.

The mineral leaching was now performed without heating the mixture and the reaction was performed at room temperature (~ 20 °C). The leaching of the mineral ore at this temperature for 2 hours resulted in the removal of 11.01 and 24.67% of U and Th respectively (see **Figure 5.11** and **Table 5.27**) and 0.84 and 3.01% of Ta and Nb respectively. An increase in leaching time from 2 to 8 hours resulted in an increase from 11.01 to 21.72% for U content and from 24.67 to 38.06% for Th content, while the Ta and Nb content increased from 0.84 to 2.31% and from 3.01 to 6.94% respectively. Increasing the leaching time further to 24 hours succeeded in removing 35.57 and 55.42% of U and Th while 5.0 and 12.83% of the Ta and Nb

respectively were removed from the mineral ore. These results clearly indicate that time has a significant influence on the extent of leaching of all the elements mentioned. Leaching at this temperature favourably removed small amounts of tantalum and niobium, but unfortunately smaller amounts of U and Th were also removed from the mineral ore compared to H_2SO_4 and H_3PO_4 leaching.

The leaching temperature was then increased to 90 °C and this resulted in the leaching of 31.60 and 56.27% of U and Th respectively after 1 hour of leaching (**Figure 5.12** and **Table 5.28**). Furthermore, 2.32 and 7.47% of Ta and Nb respectively were also leached from the mineral. An increase in leaching time succeeded in removing 44.14% of U, 86.61% of Th, 4.10% of Ta and 9.95% of Nb respectively after 2 hours. The U and Th content in the acid increased to 51.53 and 91.09% while the Ta and Nb content increased to 4.70 and 11.37% respectively after a further increase in leaching time to 3 hours. At this temperature the removal of U and Th increases significantly with time. The results indicate that U and Th were satisfactorily being removed with leaching time in excess of 2 hours. These conditions however, are not only selective towards the removal of U and Th since considerable amounts of the major elements are also being removed along with U and Th. These results are consistent with the results reported by Theron[70] on the microwave assisted hydrochloric acid digestion of the niobium oxide. Dissolution of only 2.3% of Nb was achieved using HCl at 240 °C and 1200 W while the dissolution of tantalum was not investigated under these conditions.

5.4.3.4 Other mineral acids

The final step in the evaluation of different acids as leaching reagents for the removal of U and Th involved nitric acid, perchloric acid and *aqua regia*. The leaching of the mineral ore with nitric acid at 90 °C for 1.5 hours resulted in the removal of 3.07 and 28.48% of U and Th respectively (**Table 5.29**). On the other hand, 0.49 and 0.45% of Ta and Nb respectively were also leached from the mineral using nitric acid. Perchloric acid leached 0 and 22.68% of U and Th while the Ta and Nb content was determined as 0 and 1.89% respectively. Lastly *aqua regia*, under the same experimental conditions, leached 10.40 and 36.70% of U and Th respectively and 0.95 and 1.59% of Ta and Nb respectively from the mineral ore as well.

It is clear from these results that nitric acid has little effect in removing the major elements, Ta and Nb from the mineral. Although the nitric acid removed some of the U and Th from the mineral, it did not succeed in the removal of these elements to the same satisfactory levels as compared to the previously discussed mineral acids. Perchloric acid on the other hand, had no effect on removing Ta as indicated by the absence of any Ta in the acid and only small amounts of Nb present in the leaching solution. It succeeded in removing some of the Th from the mineral, but not to acceptable percentages when compared to the other acids such as H_2SO_4 and H_3PO_4. The perchloric acid succeeded in removing some of the Th within the mineral sample (22.68%), but had no effect on the U as indicated by the absence of any U in the leaching solution. The results (**Table 5.29**) indicated that the *aqua regia* was more effective in removing U and Th than the two previous mineral acids, but it was also not able to remove them in high quantities. Fortunately, Ta and Nb were only removed in low quantities leaving the majority in the mineral and these results are very similar to those obtained for the HCl leaching under the same conditions.

The quantitative results obtained from the exposure of the mineral sample to these three mineral acids namely, HNO_3, $HClO_4$ and *aqua regia*, clearly indicated that they are not able to remove U and Th in significant quantities from the mineral when they are compared to H_2SO_4, H_3PO_4 and HCl, making then less suitable for the purpose of this study.

5.4.3.5 Comparison of all the mineral acids as leaching reagents of U and Th

The investigation of the removal of U and Th from the mineral using different minerals acids showed interesting results. The leaching at 150 °C for 3 hours with H_2SO_4 and H_3PO_4 resulted in almost equal quantities of U (~80%) and Th (~70%) being removed from the mineral. However, H_3PO_4 removed more Ta and Nb from the mineral compared to H_2SO_4. H_3PO_4 Succeeded in removing 26 and 49% of Ta and Nb while H_2SO_4 removed only 10 and 29% of Ta and Nb respectively. On the other hand, HCl was effective enough to leach around 50 and 90% of U and Th respectively after 3 hours of leaching at 90 °C. Simultaneously only 5 and 11% of Ta and Nb were removed under the same experimental conditions.

The effect of other acids namely, HNO_3, $HClO_4$ and *aqua regia* on the removal of U and Th was evaluated at leaching conditions of 90 °C and 1.5 hours reaction time. From all of these acids that were evaluated, *aqua regia* proved to be the better of the three acids on U and Th removal with 10 and 37% of U and Th removed respectively. This was followed by HNO_3 which removed 3 and 28% of U and Th while, $HClO_4$ only removed 0 and 23% of U and Th respectively from the mineral. Alternatively these acids had little or no effect on Ta and Nb removal with only a maximum of 1 and 2% for Ta and Nb being removed from the mineral. A summary of all the evaluated acids at elevated temperatures is given in **Table 5.33**.

Table 5.33: Comparison of the leaching ability of the acids at elevated temperatures

Acid	Temp. (°C)	Time (hour)	Leached (%)			
			Ta	Nb	U	Th
H_2SO_4	150	3	√	√	√√√	√√+
H_3PO_4	150	3	√	√√	√√√	√√+
HCl	90	3	x	√	√√	√√√
HNO_3	90	1.5	x	x	x	√
$HClO_4$	90	1.5	x	x	x	√
Aqua regia	90	1.5	x	x	√	√√

x = (0 < 10), √ = (10 - 30), √√ = (30 - 60), √√+ = (60 – 70) and √√√ = (80 - 100)

The results in **Table 5.33** clearly indicate that H_2SO_4 and H_3PO_4 are the most suitable mineral acids for the removal of U and Th at elevated temperatures, but their disadvantage is that they remove significant quantities of Ta and Nb under the conditions specified. This study also demonstrates the ability of the acids to remove large amounts of Th and U with an increase in time and temperature. However, this increase is not to the same extent for all the acids. Leaching at high temperatures removes satisfactory quantities of U and Th, but unfavourably large amounts of Ta and Nb are also removed. A summary of all the acids evaluated at low temperatures is given in **Table 5.34**.

Table 5.34: Comparison of the leaching ability of the acids at low temperatures

Acid	Temp. (°C)	Time (hour)	Leached (%)			
			Ta	Nb	U	Th
H_2SO_4	50	3	x	x	√√	√√
H_3PO_4	50	3	x	x	x	x
HCl	50	3	x	x	√	√√

x = (0 < 10), √ = (10 - 30) and √√ = (30 - 60)

Table 5.34 clearly indicate that H_2SO_4 is more suitable for U and Th removal at 50 °C and 3 hours of leaching than the rest of the acids investigated. H_3PO_4 at low temperature shows little or no effect on removal of U and Th or the major elements (Ta and Nb). On the other hand, HCl removed little amounts of Ta and Nb, but the U and Th amounts that were leached were not as significant as compared to those of H_2SO_4 leaching. The estimated activity concentrations of the U and Th leached by the respective acids after 3 hours are shown in **Table 5.35.**

Table 5.35: Activity concentration after 3 hours leaching time

Temp (°C)	Acid	Theoretical (ppm)		Initial Activity conc. (Bq/g)	Removed (ppm)		Remaining (ppm)		Final Activity conc. (Bq/g)
50									
		U	Th		U	Th	U	Th	
	H_2SO_4	26034#	4394#	343	6248	3076	19786	1318	253
	H_3PO_4	26034	4394	343	890	0	25144	4394	332
	HCl	26034	4394	343	6719	2380	19315	2014	250
100									
	H_2SO_4	26034	4394	343	16662	4086	9372	308	118
	H_3PO_4	26034	4394	343	17917	4394	8117	0	101
	HCl*	26034	4394	343	13538	3999	12496	395	158
150									
	H_2SO_4	26034	4394	343	21088	4394	4946	0	62
	H_3PO_4	26034	4394	343	22155	4340	3879	54	49
200									
	H_2SO_4	26034	4394	343	23431	4394	2603	0	32
230									
	H_2SO_4	26034	4394	343	22522	4394	3512	0	44

* = 90 °C, # = see calculation at the end of the chapter

The results in **Table 5.35** indicate the resultant activity concentration in the mineral after the acid leaching and was calculated using **Equation 3.1** (see end of **Chapter**). The use of **Equation 3.1** for the calculation of the radioactivity concentration is technically incorrect since the mineral has been exposed to elevated temperatures and a leaching step (see **Chapter 3 paragraph 3.3.4**) and the use of **Equation 3.2** is more appropriate in this situation. However, since a complete analysis of all the radionuclides is extremely expensive and time consuming it was decided to use the more simplified equation to get an indication of the activity concentration after the leaching step. The activity concentration substantially decreases with an increase in leaching temperature. The final activity concentration reported in **Table 5.35** however still indicate that the activity concentration is still greater than the cut-off value of 10 Bq/g that determines if the material is exempted from being classified as radioactive (**Chapter 3, Section 3.3.4**). This implies that the acid leaching was not effective enough in removing U and Th from the mineral to such extent that its classification can be changed to not radioactive or a different level. It is also clear from the results in **Table 5.35** that the presence of even small amounts of U pushed the activity concentration above the cut-off limit. At 200 and 230 °C all the Th has been removed and only U is left behind in the sample. The presence of these small amounts of U account for 32 and 44 Bq/g radioactivity concentration respectively. It is however not surprising since the activity of U is a factor 3 times larger than that of Th (see **Equation 3.1**). These results suggest that a leaching process which is more selective towards the removal of U would be more appropriate to decrease the activity levels to adhere to the cut-off limit. Furthermore, this implies that the radioactivity in the mineral is still too high to allow for its transportation anywhere without a license from the National Nuclear Regulator in the Republic of South Africa.

5.4.3.6 Anion precipitation

The next step in the investigation of the selective removal of U and Th involved the possible selective precipitation of the elements after the mineral's complete dissolution. This possibility was recognized during the study when different acids were added to the dissolved mineral to affect matrix matching when precipitation unexpectedly occurred within the reaction mixture. It was then decided to investigate this precipitation phenomenon of the mineral acids on the fused mineral ore solution and identify the elements within the precipitates (see **Table 5.30**). Firstly, the addition

of perchloric acid precipitated 68.25 and 90.70% of U and Th while Ta and Nb were precipitated to almost completion at 99.39 and 99.84% respectively. Perchloric acid furthermore precipitated almost all of the elements (**Equation 5.2**) within the fused solution and thus shows no selectivity in separating U and Th from the major elements.

$$M^{n+} + nClO_4^- \rightleftharpoons M(ClO_4)_n \qquad \textbf{5.2}$$

(for M = Th, U, Ta and Nb)

Secondly, the addition of hydrochloric acid resulted in the precipitated amount of U being determined as 12.62% while that of Th as 78.03% and 98.37 and 99.09% for Ta and Nb respectively. Hydrochloric acid had the same effect as perchloric acid of precipitating Ta, Nb and Th in large amounts, but a significant amount of U stayed in solution. These results indicated that Cl^- is not an effective counter ion for the precipitation of U, but it does allow for the separation of U. The precipitation reactions are presented in **Equations 5.3** and **5.4**.

$$M^{n+} + nCl^- \rightleftharpoons MCl_n \qquad \textbf{5.3}$$

(where M = Th, Nb and Ta)

$$U^{n+} + nCl^- \rightleftharpoons UCl_n \qquad \textbf{5.4}$$

Thirdly, nitric acid exhibits the same trend as the previously discussed acids for the removal of U and Th. The precipitated content for U was determined as 35.60%, that of Th as 83.84% and those for Ta and Nb as 99.38 and 99.83% respectively. These results indicate some separation of U from the major elements in the filtrate rather than the precipitate with virtually all the Ta and Nb present in the precipitate (**Equations 5.5** and **5.6**). However, the precipitate still contains large quantities of thorium and uranium (as indicated in **Equation 5.5**) which render nitric acid to be not a very effective separating agent of U and Th from the rest of the elements.

$$M^{n+} + nNO_3^- \rightleftharpoons M(NO_3)_n \qquad \textbf{5.5}$$

(where M = Th, Nb and Ta)

$$U^{n+} + nNO_3^- \rightleftharpoons U(NO_3)_n \quad \textbf{5.6}$$

Fourthly, sulphuric acid addition to the mineral solution succeeded in precipitating only 5.11 % of U while the precipitated amount of Th was determined as 82.58% and that of Ta and Nb as 99.21 and 80.13% respectively. As observed from all the discussed acids, large amounts of Th are precipitated along with the major elements (Ta and Nb) and this is the case with sulphuric acid. However, a significant amount of Nb remained in the filtrate which was unexpected, but understandable. All the results up to this point clearly indicate (**Tables 5.10 – 5.15**, Nete[89]) the preference of Nb towards H_2SO_4 as a dissolution agent which agree with the large amount of Nb present in the filtrate. Sulphuric acid is also more selective in keeping U in solution compared to any of the acids mentioned so far. However, the only disadvantage is that a measurable amount of Nb and Th is also left unprecipitated in the filtrate. **Equations 5.7** to **5.10** demonstrate the chemical representation of the precipitation during the addition of H_2SO_4 to the reaction mixture.

$$Th^{4+} + 2SO_4^{2-} \rightleftharpoons Th(SO_4)_2 \quad \textbf{5.7}$$

$$2Ta^{5+} + 5SO_4^{2-} \rightleftharpoons Ta_2(SO_4)_5 \quad \textbf{5.8}$$

$$2Nb^{5+} + 5SO_4^{2-} \rightleftharpoons Nb_2(SO_4)_5 \quad \textbf{5.9}$$

$$2U^{6+} + U^{4+} + 8SO_4^{2-} \rightleftharpoons U(SO_4)_2 + 2U(SO_4)_3 \quad \textbf{5.10}$$

Lastly, the addition of *aqua regia* resulted in the precipitation of 18.17 and 82.73% of U and Th respectively while almost all of Ta (99.38%) and Nb (99.60%) were precipitated within this addition. These results clearly demonstrate that *aqua regia* exhibits the same precipitation abilities as the rest of the acids except for sulphuric acid. However, it is not that effective in separating U and Th from the major elements as the precipitate contains large amounts of the Th as observed from other acids (**Equations 5.11** and **5.12**).

$$M^{n+} + nL^- \rightleftharpoons ML_n \quad \textbf{5.11}$$

(where M = Th, Nb and Ta, L = Cl, NO_3)

$$U^{n+} + nL^{-} \rightleftharpoons UL_n \qquad 5.12$$

(where L = Cl, NO_3)

It is clear from these results that sulphuric acid is more successful in selectively removing the radioactive material from the mineral solution compared to all the acids investigated. Although a significant amount of Nb is remaining in the filtrate, the precipitate has a lower U content compared to the other acid precipitates.

5.4.3.7 Ion exchange chromatography

The selective removal of U and Th from the mineral is the overarching aim of this study. The use of mineral acids to remove U and Th was investigated and discussed in this chapter. The results clearly showed that there is no ideal method for the complete removal of all the U and Th without removing significant amounts of the major elements. In this part of the study it was decided to completely dissolve the mineral and try and separate U and Th from the rest of the elements using a zeolite as resin (**Table 5.31**). The results of the ion exchange show that 17.99 and 14.46% of U and Th were respectively eluted from the column by using water (10 mL) as an eluent. Additionally, 0.98 and 0.71% of Ta and Nb were also eluted from the same stripping solution. However, the use of an additional 10 mL of water as an eluent resulted in the elution of 33.98 and 30.46% of U and Th while 5.39 and 10.48% of Ta and Nb were also eluted by the second stripping solution. The additional eluted U and Th content from the third portion of 10 mL water was determined as 27.40 and 23.69% while that of Ta and Nb was determined as 6.23 and 10.96% respectively. Collectively, the combined eluent solutions resulted in 79.38 and 68.62% of U and Th being removed from the column. Additionally 12.60 and 22.15% of Ta and Nb respectively were also removed from the column. These results indicated that eluting with water was effective in removing the U and Th from the column, but also significant amounts of the major elements (Ta and Nb) were removed.

Increasing the volume of the eluent to 15 mL portions resulted in the overall elution of 79.59 and 76.27% of U and Th respectively with 3 15 mL portions collectively. Furthermore, an increase from 12.60 to 27.84% and from 22.15 to 35.64% for Ta and Nb respectively was observed by increasing the volume of the stripping solutions. Increasing the volume of the stripping solution did not have a significant increase in the overall elution of U and Th, but a significant increase was observed in the total elution of Ta and Nb. This increase in volume consequently resulted in the unfavourable enrichment of the major elements (Ta and Nb) in the eluent and thus decreased the efficiency of separating Th and U from the major elements.

The next step in this part of the study involved the investigation of the effect of dilute hydrochloric acid as an eluent on separating U and Th from the major elements. Eluting with hydrochloric acid (20 mL, 0.01 M) resulted in the stripping of 63.60 and 50.30% of U and Th while 39.47 and 46.91% of Ta and Nb were respectively also eluted (see **Table 5.32**) from the same stripping solution. The two additional stripping solutions succeeded in eluting a total of 100 and 86.97% of U and Th content respectively. Additionally, a total of 57.38 and 65.36% for Ta and Nb content were eluted from the column under the same experimental conditions. Elution with 0.01 M HCl turned out to be more effective in removing U and Th from the rest of the elements, but a major disadvantage was that large amounts of the major elements (Ta and Nb) are also eluted along with U and Th. Consequently, 0.01 M HCl had little effect in separating Th and U from the major elements compared to the water elution.

Increasing the concentration of the acid (HCl) to 0.05 M resulted in the total elution of 100% of both the U and Th content while the Ta and Nb content was determined as 58.53 and 62.85% respectively. A further increase in concentration to 0.1 M HCl resulted again in the total elution of 100% of both U and Th as well as 55.68 and 60.31% of Ta and Nb respectively. It is clear from the results that HCl is able to remove U and Th to satisfactory levels at all the concentrations investigated, but it also removes large quantities of Ta and Nb from the column. Therefore, HCl turned out to be not able to separate U and Th from the major elements (Ta and Nb) at all concentrations evaluated. It was also observed during the study that the HCl destroys the resin and this was confirmed by the unusually high amounts of Al and Si in the

eluent. The resin proved therefore is not to be selective in separating U and Th from the major elements.

5.5 Conclusion

The selective removal of the radioactive materials from the mineral prior to the subsequent complete dissolution thereof for the successful beneficiation of the mineral and quantification is of cardinal importance and has been emphasized in the introduction of this chapter. Various methods were evaluated for the removal of the radioactive materials from the mineral. These included acid leaching, anion precipitation and ion exchange chromatography. It's evident from the results obtained in this study that not one of the methods evaluated in this study provide clear-cut or ideal results and that a compromise between maximum U and Th leaching and minimum Ta/Nb removal had to be reached to identify the most suitable reaction conditions.

The $NaH_2PO_4.H_2O$/ Na_2HPO_4 flux fusion proved to be a very effective method for the dissolution of the tantalite mineral and analysis of all the mineral samples. The ICP-OES results indicated that HCl, H_2SO_4 and H_3PO_4 are more effective in removing U and Th from the tantalite mineral compared to $HClO_4$, *aqua regia* and HNO_3. H_2SO_4 and H_3PO_4 proved to be highly effective in the removal of significant amounts of the radioactive materials, but they also removed undesirably high amounts of the main elements such as Ta and Nb at elevated temperatures.

Visual inspection showed that all of the mineral acids used, precipitated some of the elements from the dissolved melt of the flux fused mineral. ICP-OES quantitative results also indicate that H_2SO_4 does not precipitate U to the same extent as the other acids. Ta and Nb are precipitated to almost the same extent by all the acids while Th is kept in solution by HCl to a large extent compared to the rest of the acids. In conclusion, it can be mentioned that the study succeeded in removing the radioactive materials from the mineral to an extent that the mineral itself may not be classified as a **class 7** materials.

Activity concentration calculations

For U:

3.07% U_3O_8 = 0.00307 g of U_3O_8 in 0.1 g of mineral (Quantified – see **Table 5.8**)

Therefore

0.0307 g of U_3O_8 in 1.0 g of mineral

$[U_3O_8]$ in ppm = 0.0307×10^6 = 30700 ppm (µg/g or mg/kg)

$[U]_{Total}$ = 30700 × (Mr U/Mr U_3O_8) = 30700 × (3×238.03/ 842.09) = 26 034 ppm (% of U in U_3O_8)

For the concentrations of U removed after leaching

$[U]_{removed} = [U]_{Total} \times$ % leached (for any temperature and time)

$[U]_{remaining} = [U]_{Total} - [U]_{removed}$

Example for $[H_2SO_4]$ leaching at 50 °C for 3 h:

$[U]_{removed}$ =26 034 × 24 % (average % in filtrate) = 6 248 ppm, see **Table 5.9**

$[U]_{remaining}$ = 26 034 – 6 248 = 19 786 ppm

For Th:

0.50% ThO_2 = 0.0005 g of ThO_2 in 0.1 g of mineral (Quantified – see **Table 5.8**)

Therefore

0.005 g of ThO_2 in 1.0 g of mineral

$[ThO_2]$ in ppm = 0.005×10^6 = 5000 ppm (µg/g or mg/kg)

$[Th]_{Total}$ = 5000 × (Mr Th/Mr ThO_2] = 5000 × (232.04/264.04) = 4 394 ppm (% of Th in ThO_2)

For the concentrations of Th removed after leaching

$[Th]_{removed} = [Th]_{Total} \times$ % leached (for any temperature and time)

$[Th]_{remaining} = [Th]_{Total} - [Th]_{removed}$

Example for $[H_2SO_4]$ leaching at 50 °C for 3 h:

$[Th]_{removed}$ =4 394 × 70 % (average % in filtrate) = 3 076 ppm, see **Table 5.9**

$[Th]_{remaining}$ = 4 394 – 3 076 = 1 318 ppm

...

6 Beneficiation of tantalite

6.1 Introduction

Nete *et al.*[89] reported in detail the geological analysis and qualitative characterization of three variations of a tantalite ore originating from Mozambique. In this study it was reported that the three different mineral ore samples exhibit different physical properties in terms of magnetism and radioactivity. Sample A was reported to have high radioactivity with low magnetic properties (amount of material separated using a permanent magnet), Sample B exhibited lower radioactivity, but very little to no magnetic properties while Sample C exhibited very low radioactivity and strong or high magnetic properties. These physical properties were correlated with the presence of U and Th which contributed to the radioactivity of the samples while the magnetic properties (para- or ferro-) were attributed to the presence of iron (Fe^{2+}) in these samples. Sample A was found to consist of a number of other minerals such as quartz, mica, manganotantalite, ferrocolumbite, microlite, euxenite and microlite as observed under the microscope and by XRD analysis.

Different studies (Nete, Theron)[3,69] on these mineral samples revealed interesting results. The study by Theron clearly indicated the removal of the majority of the Fe (as well as Ti) using magnetic separation (see **Table 6.1**) while the dissolution study by Nete indicated the "unsuccessful" dissolution of all the mineral material in the samples using H_2SO_4 in the microwave dissolution process with a recovery of 98.8% of Nb_2O_5 in the filtrate and only 4.19% of Ta_2O_5 in the same H_2SO_4 solution. The current study (**Chapter 5**) clearly demonstrates the possible removal of the radio-active material from the mineral sample prior to complete dissolution. It was therefore decided to combine all these steps, namely magnetic separation, radioactive material leaching and finally microwave dissolution in order to accomplish the possible beneficiation and separation of the Nb and Ta in these minerals samples. This process is illustrated in **Figure 6.1** which will involve i) the magnetic separation of Fe and/or Ti as an initial step, then ii) the leaching of Th and U from the mineral mix at the experimental conditions indicated in **Chapter 5** using H_2SO_4 and finally the separation of Nb and Ta using similar, but not identical microwave

dissolution applying the conditions that were used and reported by Nete. Sample A[69] was selected for this study due to the presence of high radioactivity and low magnetism compared to the two other mineral samples.

Table 6.1: Comparison of quantities after magnetic separation of Sample C[3]

Metal oxides	Quantity %						
	Non-separated	Separated					
		Non-magnetic			Magnetic		
		1	2	Average	1	2	Average
Ta_2O_5	29.98	30.63	27.17	28.90	2.14	2.13	2.14
Nb_2O_5	7.26	8.40	7.34	7.87	1.23	1.21	1.22
Al_2O_3	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
SiO_2	6.56	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
WO_3	1.18	<0.01	0.03	0.02	0.01	<0.01	0.01
TiO_2	10.68	1.21	0.45	0.83	11.7	9.14	10.42
Mn_3O_4	0.93	1.34	1.11	1.23	<0.01	<0.01	<0.01
Fe_2O_3	18.48	2.51	0.31	1.41	21.55	17.87	19.71
SnO_2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

6.2 Sample preparation, equipment and reagents

6.2.1 Equipment

A Shimadzu ICPS-7510 ICP-OES sequential plasma spectrometer was utilized for the quantification of the elements of interest after the dissolution step. The operating conditions for the ICP-OES are given in the previous chapter (**Chapter 5, Table 5.1**) and were kept the same throughout this study.

A Thermolyne 1300 high temperature furnace which can reach a maximum temperature of 1100 °C in one hour was used for all fusions. An Anton Paar Perkin-Elmer 3000 microwave reaction system equipped with an 8SXF100 rotor with eight of both quartz and polytetrafluoroethylene (PTFE) reaction vessels was used for acid digestion of the samples. The microwave conditions which proved to be effective in the dissolution of tantalite used in this study are given in (**Chapter 5, Table 5.2**).

Type 3.3 Duran volumetric flasks bought from Associated Chemical Enterprises (ACE) and grade B glassware bought from Merck was used in this project.

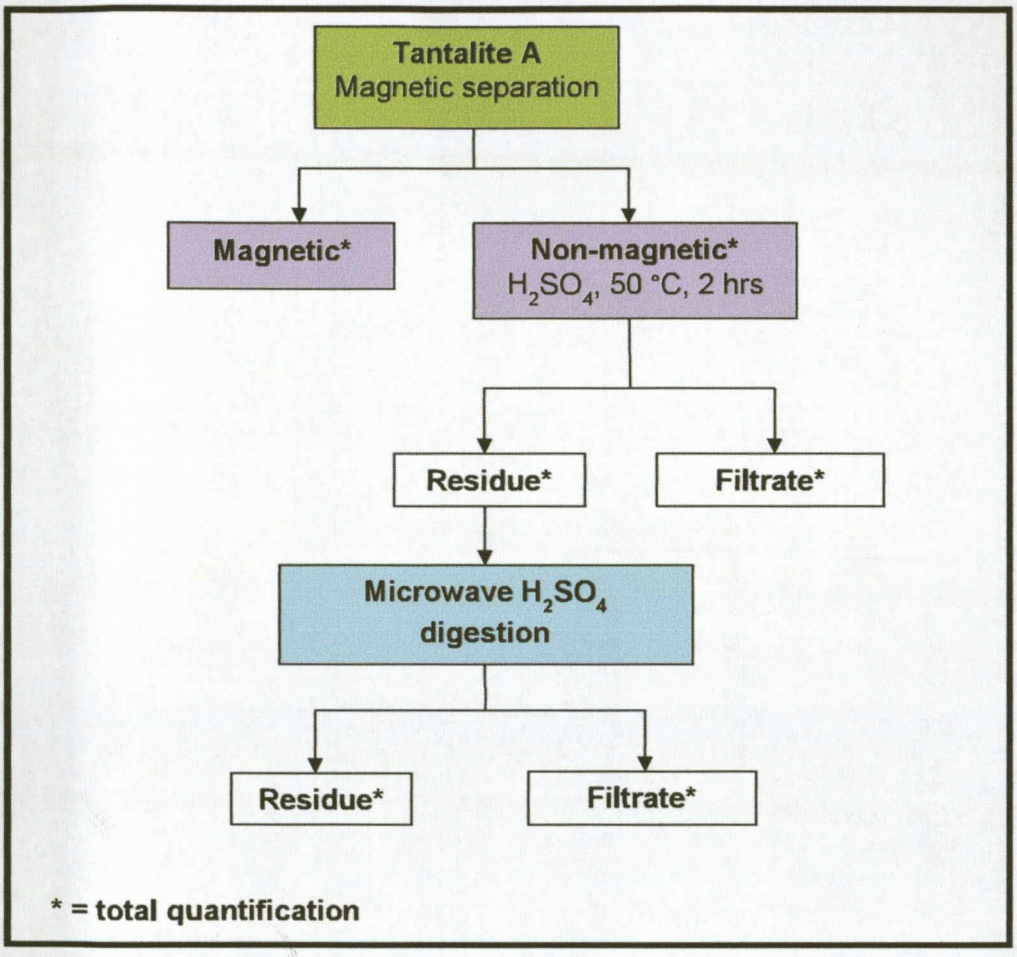

Figure 6.1: Steps taken to beneficiate the tantalite mineral in this study

A Shimadzu ICPM 8500 inductively coupled mass spectrometer was utilized for the quantification of the radio-isotope ratios of the elements of interest. A self-calibrating Shimadzu AW320 mass balance capable of weighing up to 320 grams with the accuracy of 0.1 mg was used in this study. The mass was recorded to four decimals of each and every sample that was used.

For small and accurate volume measurements a Brand Transferpette® micropipette with a volume capacity of 1.0 - 10.0 mL as well as a Kartell Pluripet (II) micropipette with a capacity of 0.10 - 1.0 mL was used in this study. A silicone oil bath was used

for heating the mixtures at the desired temperature when the NORM leaching was performed.

6.2.2 Reagents

General

The chemicals used during the study were of known concentration and the most commonly used chemicals in this study as well as their respective concentrations are listed in **Table 6.2**. ICP standard solutions containing 1000 ppm Sn, 1000 ppm Ta, 1000 ppm Nb, 1000 ppm Ti, 1000 ppm W, 1000 ppm Si as well as the multi-element standard (No.IV) (for Al, Fe and Mg analysis) were bought from Merck. The 1000 ppm U and Th standard solutions were bought from De Bruyn Spectroscopic Solutions. Double-distilled water was used throughout the study. The values are reported in two decimal places except for the average values that are reported according to their standard deviations. The raw data accumulated and used in this study (actual masses, calibration curves *etc.*) are reported in the different appendixes on a CD which accompany the thesis.

Table 6.2: Chemical and physical properties of the used chemicals in the study.

Chemical	Formula	Grade	b.p/ m.p (°C)	Suppliers
Acids				
Sulphuric acid	H_2SO_4	98% AR	340	ACE
Reagents				
Sodium phosphate monobasic	$NaH_2PO_4.H_2O$	99.0%	100	PAL Chemicals
Sodium phosphate dibasic	Na_2HPO_4	99.0%	240	Holpro Analytics
Sample				
Tantalite mineral	$(Fe,Mn)(Ta,Nb)_2O_6$		N/A	Necsa

Tantalite mineral

The Sample A mineral which was sampled in Naquissupa, Mozambique, was supplied by the South African Nuclear Energy Corporation Limited (Necsa). This mineral was analysed by Alfred H Knight as well as by Nete[2] and Theron.[3] The chemical composition as found by Knight as well as in the two studies is given in **Table 6.3**. The results in the table clearly indicate the presence of two radioactive

elements, thorium (0.57%) and uranium (2.87%), in the mineral as found by all the respective researchers.

Table 6.3: Chemical composition of the Sample A mineral mixture

Metal oxides	Sample A (%)			
	A. H. Knight	Nete*	Theron**	This study***
Ta_2O_5	27.71	30.08	27.69	**27.7(2)**
Nb_2O_5	27.41	27.01	30.51	**28.1(3)**
ThO_2	**0.65**	**0.54**	**0.52**	**0.50(4)**
U_3O_8	**2.83**	**2.81**	**2.97**	**3.07(2)**
Al_2O_3	1.85	2.04	0.25	**1.9(1)**
SiO_2	5.73	3.52	2.85	**2.7(2)**
WO_3	1.61	1.18	0.09	**1.1(3)**
TiO_2	2.68	2.77	2.85	**2.1(1)**
Mn_3O_4	8.03	8.91	7.08	**7.6(3)**
Fe_2O_3	8.29	8.34	7.35	**8.07(9)**
SnO_2	1.41	1.64	<0.01	**1.11(3)**

*= $Li_2B_4O_7$ fusion, dissolution in H_2SO_4/methanol. **= $Li_2B_4O_7$ fusion, dissolution in H_3PO_4/methanol

***= $NaH_2PO_4.H_2O$ +Na_2HPO_4 fusion

6.3 Experimental work

The combination of steps taken to beneficiate the tantalite mineral in this study is given in **Figure 6.1**. The first step was to separate the magnetic particles in the mineral. The second step was to leach the non-magnetic portion with sulphuric acid followed by microwave-assisted acid digestion.

6.3.1.1 Preparation of standard solutions for tantalite quantification for ICP-OES

All standard solutions were prepared by adding 0.05, 0.1, 0.2, 0.25 and 0.5 mL of the different 1000 ppm ICP standard solutions (Nb, Ta, U, Th, Si, Sn, W, Ti, Al, Fe and Mn) into five 50.0 mL volumetric flasks using a micropipette. To these solutions 5 mL of H_2SO_4 was added and were then filled to the mark with water. The prepared solutions contained 1.0, 2.0, 4.0, 5.0 and 10.0 ppm concentrations of each of the

respective elements. The blank solution was prepared by adding 5 mL of H_2SO_4 into a 50.0 mL volumetric flask and filling it up to the mark with water. These solutions were used to prepare calibration curves for the acid filtrates.

6.3.1.2 Standard solutions for phosphate fluxed solutions (matrix matching)

The standard solutions for fusion digested samples were prepared in the same fashion as the acids, but with an additional step. Sodium dihydrogen phosphate (12.5 g) and disodium hydrogen phosphate (12.5 g) were thoroughly mixed fused in a platinum crucible at 900 °C for 30 minutes. The resulting melt was dissolved in 25.0 mL phosphoric acid and qualitatively transferred into a 250.0 mL volumetric flask and diluted to the mark with water. 2.0 mL aliquots of these solutions were transferred into five 50.0 mL volumetric flasks containing 5.0 mL of phosphoric acid and water. To these, 0.05, 0.1, 0.2, 0.25 and 0.5 mL of the different 1000 ppm ICP standard solutions were added respectively. The solutions were then diluted to the mark with water. The blank solution was prepared by adding a 2.0 mL aliquot of the fused solution and 5.0 mL of phosphoric acid into a 50.0 mL volumetric flask and diluting to the mark with water. These solutions were used to prepare calibration curves for the fluxed mineral samples.

6.3.2 Magnetic separation

Portions of about 1 g Samples A were accurately weighed (to 0.1 mg) and the magnetic and non-magnetic particles were manually removed (using a permanent magnet and an in-house electromagnetic device). The collected magnetic and non-magnetic portions were then re-weighed to determine the amount of mass lost due to the adherence of small amounts of the finely ground mineral sample to the glass surfaces used during the separation process. The results obtained from the magnetic separation and the magnetic properties of the sample are discussed in the following sections.

Different portions, of approximately 0.05 g of the separated materials were accurately weighted (to 0.1 mg), quantitatively transferred into a platinum crucible and fused with the $Na_2HPO_4{\cdot}H_2O/Na_2HPO_4$ flux mixture at 900 °C for 30 minutes in a furnace. The melts were cracked by placing the hot crucibles in cold water. Each melt was

then dissolved in water and quantitatively transferred to a 100.0 mL volumetric flask containing 10.0 mL phosphoric acid and filled to the mark with water for ICP-OES analysis. The ICP-OES results are tabulated in **Table 6.4**.

Table 6.4: Quantification of the elements from the magnetic separation process using Sample A

Metal oxides	Metal oxide (%)						
	Non-magnetic			Magnetic			Theoretical content
	1	2	Average	1	2	Average	
Ta_2O_5	25.72	26.11	**25.91**	1.98	1.59	**1.79**	**27.7(2)**
Nb_2O_5	26.36	26.46	**26.41**	1.74	1.64	**1.69**	**28.1(3)**
ThO_2	0.47	0.47	**0.47**	0.03	0.03	**0.03**	**0.50(4)**
U_3O_8	2.89	2.88	**2.88**	0.18	0.19	**0.19**	**3.07(2)**
Fe_2O_3	7.44	7.43	**7.44**	0.63	0.64	**0.63**	**8.07(9)**
TiO_2	1.97	1.97	**1.97**	0.13	0.13	**0.13**	**2.1(1)**
SnO_2	1.05	1.04	**1.05**	0.06	0.07	**0.06**	**1.11(3)**
Mn_3O_4	7.17	7.16	**7.17**	0.43	0.44	**0.43**	**7.6(3)**
WO_3	1.03	1.03	**1.03**	0.07	0.07	**0.07**	**1.1(3)**
Al_2O_3	1.77	1.77	**1.77**	0.13	0.13	**0.13**	**1.9(1)**
SiO_2	2.51	2.53	**2.52**	0.19	0.17	**0.18**	**2.7(2)**

6.3.3 H_2SO_4 leaching at 50 °C

Different portions (0.5 g) of the non-magnetic material were accurately weighed (to 0.1 mg) were reacted with 10.0 mL of H_2SO_4 at 50 °C for 2 hours using a silicone oil bath. The cooled mixtures were filtered into different 100.0 mL volumetric flasks and filled to the mark with water. 5.0 mL Aliquots were quantitatively transferred into other 100.0 mL volumetric flasks containing 10.0 mL of H_2SO_4 and filled to the mark with water for ICP-OES analysis. The ICP-OES results are shown in **Table 6.5**.

After the H_2SO_4 leaching step, 0.05 g portions (accurately to 0.1 mg) of the resultant precipitates were quantitatively transferred to a platinum crucible. To these samples, 0.25 g of sodium dihydrogen phosphate and 0.25 g of disodium hydrogen phosphate were added and thoroughly and heated in a furnace at 900 °C for 30 minutes. The resulting melts were subsequently cracked by placing the hot crucible in cold water.

The melts were then dissolved in water and quantitatively transferred to a 100.0 mL volumetric flask containing 10.0 mL phosphoric acid and filled to the mark with water for ICP-OES analysis.

Table 6.5: Quantification of the elements in Sample A non-magnetic portion after H_2SO_4 leaching at 50 °C for 2 hours

Metal oxides	Metal oxide (%)							
	Actual content	Filtrate			Precipitate			Theoretical content
		1	2	Average	1	2	Average	
Ta_2O_5	**25.92**	0.45	0.56	**0.51**	25.46	25.35	**25.41**	**27.7(2)**
Nb_2O_5	**26.41**	1.02	1.44	**1.23**	25.39	24.97	**25.18**	**28.1(3)**
ThO_2	**0.46**	0.18	0.20	**0.19**	0.28	0.26	**0.27**	**0.50(4)**
U_3O_8	**2.88**	0.45	0.71	**0.58**	2.43	2.17	**2.30**	**3.07(2)**
Fe_2O_3	**7.44**	0.84	1.66	**1.25**	6.60	5.78	**6.19**	**8.07(9)**
TiO_2	**1.97**	0.31	0.33	**0.32**	1.66	1.63	**1.65**	**2.1(1)**
SnO_2	**1.04**	0.77	0.76	**0.76**	0.28	0.29	**0.28**	**1.11(3)**
Mn_3O_4	**7.17**	0.56	0.68	**0.62**	6.61	6.48	**6.55**	**7.6(3)**
WO_3	**1.03**	0.40	0.79	**0.59**	0.64	0.24	**0.44**	**1.1(3)**
Al_2O_3	**1.77**	0.81	0.81	**0.81**	0.97	0.96	**0.96**	**1.9(1)**
SiO_2	**2.52**	...	...	...	**2.52**	**2.52**	**2.52**	**2.7(2)**

··· = not detected

6.3.4 Microwave-assisted acid digestion of the mineral

Two 0.1 g (accurately weighed to 0.1 mg) portions of the undigested non-magnetic residues (after acid leaching) were quantitatively transferred into the microwave quartz reaction vessels and 10.0 mL of H_2SO_4 were added to each vessel. The vessels were then sealed and transferred into the microwave digester. The digestion was done applying the conditions reported in **Table 5.4**. The resultant reaction mixtures were then filtered into 100.0 mL volumetric flasks and filled to the mark with water for ICP-OES analysis. The ICP-OES results are indicated in **Table 6.6**.

The remaining solids were dried and 0.05 g portions (accurately weighted to 0.1 mg) were quantitatively transferred into platinum crucibles. To these samples, 0.25 g of sodium dihydrogen phosphate and 0.25 g of disodium hydrogen phosphate were added and thoroughly mixed and heated in a furnace at 900 °C for 30 minutes. The melts were subsequently cracked by placing the hot crucible in cold water, dissolved in water, quantitatively transferred to 100.0 mL volumetric flasks containing 10.0 mL phosphoric acid and filled to the mark with water for ICP-OES analysis.

Table 6.6: Microwave assisted digestion recoveries of the non-magnetic portions of Sample A

Metal oxides	Metal oxide (%)							
	Actual content	Filtrate			Precipitate			Theoretical content
		1	2	Average	1	2	Average	
Ta_2O_5	**25.40**	3.67	4.31	**3.99**	21.73	21.09	**21.41**	**27.7(2)**
Nb_2O_5	**25.18**	13.68	12.33	**13.00**	11.50	12.85	**12.18**	**28.1(3)**
ThO_2	**0.27**	0.16	0.13	**0.14**	0.11	0.15	**0.13**	**0.50(4)**
U_3O_8	**2.31**	0.99	0.96	**0.98**	1.31	1.34	**1.33**	**3.07(2)**
Fe_2O_3	**6.19**	3.21	2.79	**3.00**	2.98	3.40	**3.19**	**8.07(9)**
TiO_2	**1.65**	1.43	0.46	**0.95**	0.21	1.18	**0.70**	**2.1(1)**
SnO_2	**0.28**	0.12	0.20	**0.16**	0.16	0.08	**0.12**	**1.11(3)**
Mn_3O_4	**6.55**	1.87	2.72	**2.30**	4.67	3.83	**4.25**	**7.6(3)**
WO_3	**0.44**	0.32	0.37	**0.34**	0.12	0.07	**0.10**	**1.1(3)**
Al_2O_3	**0.96**	0.04	0.17	**0.10**	0.93	0.79	**0.86**	**1.9(1)**
SiO_2	**2.52**	...	...	...	**2.52**	**2.52**	**2.52**	**2.7(2)**

... = not detected

6.4 Discussion

6.4.1 Magnetic separation

The results of the magnetic separation as shown in **Table 6.4** indicate that small amounts of Ta and Nb are being removed from the mineral ore by the magnetic separation. The presence of Ta and Nb in the magnetic portion is surprising, but it correlates well with the observations of Theron[3] that small amounts of Ta and Nb (1.79 and 1.69% from total of 27.7 and 28.1%) respectively are associated with the

magnetic portion of the mineral. A difference in oxidation state of Ta and Nb (maybe +3) was proposed as a reason for this observation. Fe and Mn are also removed from the rest of the sample, but at much smaller amounts than were the case for Sample C which was used by Theron. A possible reason for this is that the majority of the iron in this sample is in a different oxidation state, possibly Fe^{3+} which has much lower para- or ferromagnetic properties compared to Fe^{2+}, which renders magnetic separation of the impurities less efficient. The rest of the elements are not affected by the magnetic separation step with all the elements remaining in the non-magnetic portion of the mineral sample.

The intention of this step in the beneficiation process was to remove the magnetic particles and therefore a large portion of the impurities from the elements from the elements of interest, in this case Ta and Nb. It is clear from these results, compared to those obtained by Theron that this separation step could only be highly successful if the impurities have significant para- or ferromagnetic properties which will allow this separation from the rest of the mineral sample.

6.4.2 Sulphuric acid leaching

The quantification of the sulphuric acid leaching of the non-magnetic portion (**Table.6.5**) indicated that about 1.96% (0.51 of 25.91%) and 4.66% (1.23 of 26.41%) of Ta and Nb respectively were removed on average from the two non-magnetic portions. On the other hand 20.08% (0.58 of 2.88%) and 41.39% (0.19 of 0.47%) of U and Th on average were also removed from the two non-magnetic portions respectively. These results of the sulphuric acid leaching of the non-magnetic sample are consistent with the results obtained for the mineral leaching with sulphuric acid at the same experimental conditions. The exception however, is the percentage of Th removed from the sample is higher than the expected value of 33% which was obtained from the non-separated raw mineral (see **Chapter 5**, paragraph 5.4.3.1). The leaching of Sn, W and Al are the only elements which seem to be influenced by this process or step with the removal of 72.90% (0.76 of 1.05%), 57.49% (0.59 of 1.03%) and 45.56% (0.81 of 1.77%) respectively. The difference between the theoretical metal oxide content and the total recovered during this step of the beneficiation process is due to the removal of these oxides in the previous step, namely the magnetic separation.

The results of U isotope counting as shown in **Table 6.7** indicate that the leaching of the mineral with sulphuric acid changes the ratios of the uranium isotopes. The natural abundance of the isotopes ^{234}U and ^{235}U increased from 0.0054 and 0.71% to 0.013 and 0.85% respectively while that of ^{238}U decreased from 99.28 to 99.14%. This increase appears to be more profound for ^{234}U with a two-fold increase while that of ^{235}U was less significant compared to ^{234}U. These results suggest that the secular equilibrium of the radio-isotopes has been disrupted by the acid leaching and that the use of **Equation 3.2** is more appropriate to calculate the activity concentration of the mineral after leaching. The setback, however is that a complete analysis of all the radionuclides involved is very expensive and time consuming.

Table 6.7: U isotope ratios of the sulphuric acid leach solutions of Sample A

Isotope	Isotope ratio (%)	
	Theoretical	Experimental (ICP-MS)
U^{234}	0.0054	0.013
U^{235}	0.71	0.85
U^{238}	99.28	99.14

6.4.3 Microwave sulphuric acid-assisted digestion

The microwave digestion of the non-magnetic residue using sulphuric acid (**Table 6.6**) resulted in 15.72% (3.99 of 25.41%) and 51.64% (13.0 of 25.18%) of Ta and Nb being dissolved on average from the two replicate samples respectively. From the same residues, 42.47% (0.98 of 2.30%) and 52.50% (0.14 of 0.27%) of U and Th respectively were also dissolved in the microwave. These results correlate well with those obtained by Nete and Theron which clearly indicate that Nb_2O_5 is much more soluble in H_2SO_4 compared to Ta_2O_5. Furthermore, U and Th were dissolved to almost the same extent although these two elements were present in small quantities. The trend observed from these results is the same as the one observed in the study by Nete[3], but the difference is that 72% (19.45% of a total of 27.01%) and 23% (6.99% of a total of 30.08%) compared to the 51.64% (13.0 of 25.18%) and 15.72% (3.99 of 25.41%) of Nb and Ta respectively were dissolved using microwave sulphuric acid-assisted digestion. This difference may be attributed to the fact that the microwave reaction parameters were not entirely the

same in both studies. A power of 600W and four reaction vessels were employed in this study compared to 1200W used in the study by Nete. The end-result of this study is that the resultant microwave precipitate contained on average 45.78 and 26.03% while the filtrate contained 15.99 and 52.06% of Ta and Nb respectively. Consequently this study proved the concept of the method as a possible step to enrich the Ta in the precipitate and Nb in the filtrate as first step in the beneficiation process.

The starting material contained on average 1:1 ratio of Nb and Ta. After applying all the separation steps on the mineral sample the ratio was increased to 1:2 for Nb:Ta in the precipitate while the ratio of Nb/Ta in solution changed to 3:1 and this is evident from the microwave digestion precipitate as well as the filtrate. The difference between the theoretical metal oxide content and the total recovered during this step of the beneficiation process is due to the removal of these oxides in the previous steps, namely the magnetic separation and the H_2SO_4 leaching. It is also evident from the quantification of the radio-active material that the Th compound is more soluble compared to that of the U as indicated by the larger percentage of the Th in the filtrate as compared to the U in the final precipitate containing the Ta product.

6.5 Conclusion

The selective removal of the magnetic and radioactive materials and microwave digestion of the mineral prior to the subsequent complete dissolution does indeed indicate the enrichment of two main elements in both the filtrate and the precipitate, proving the concept of method. It's apparent from the results obtained in this study that the same degree of separation of the methods were not obtained as those in previous studies and further research is needed to improve the efficiency of the methods evaluated.

Although the results obtained for this whole set of separating steps are not satisfactorily enough, the resulting mineral portions indicate an enriched amount of Ta in the residue and an enriched Nb in the filtrate with a small amount of the radioactive materials in both fractions as well as the loss of these elements in the

previous steps may consequently reduce the risk that the mineral be classified as a **Class 7** material.

7 Evaluation of the study and future research

7.1 Success of the current study

The overarching aim of this study, as mentioned in **Chapter 1**, was the removal of the NORMs (thorium and uranium) from the mineral prior to its complete dissolution to increase the safety of its processing and/or transportation, as well as to decrease the quantities of these impurities before the complete dissolution of the mineral ore. The specific objectives of this study were as follows:

- Perform an in depth literature survey of the existing methods of removal of U and Th from tantalite and columbite.
- Investigate the selective acid leaching of U and Th, before complete dissolution of the mineral.
- Investigate the separation effectiveness of column chromatography using zeolites.
- Perform spectrometric characterisation of the components of separation with ICP-OES.

The specific objectives of this study were successfully accomplished. The literature survey indicates that little or no research results have been reported for the removal of the NORMs from the tantalum and niobium containing minerals, especially tantalite and columbite. However, reported literature indicates that the NORMs are treated as by-products when present in the processing of these minerals. On the other hand, the processing of U and Th from their mineral ores is well documented with both acidic and alkaline leaching being the most preferred methods for the extraction of these elements.

The removal of U and Th from the mineral ore was, to a large extend, successfully accomplished in this study. The acid leaching of these NORMs indicated that sulphuric acid is more effective in removing the NORMs than all of the acids

investigated. Satisfactory amounts of the NORMs were removed by sulphuric acid at high temperatures from the mineral, but the main setback is that significant amounts of Ta and Nb were also removed in the process. A compromise was reached between maximum NORM leaching and minimum Ta and Nb removal to select the most suitable reaction conditions.

This study was a follow up of other studies. The magnetic separation and microwave acid-assisted digestion reported by Nete[2] and Theron[3] were also applied in this study to evaluate the combination of these processes on the overall beneficiation of the minerals. The magnetic separation was not successful in removing the major impurities such as Fe from the mineral, but the elements that were separated by the magnetism was due to the presence of small amounts of ferromagnetic Fe and surprisingly to Ta and Nb. The microwave sulphuric acid-assisted digestion succeeded in the partial separation of Tan and Nb with the Ta:Nb ratio changing from 1:1 to 1:3 ratio in the filtrate while the Ta:Nb ratio changed from 1:1 to 2:1 in the precipitate suggesting that the method enriched the Ta in the undissolved mineral sample.

The separation of the main elements using a zeolite as an ion exchange resin proved to be unsuccessful. This zeolite Clinobrite did not indicate any selectivity in retaining and/or elution of any element and it decomposes in the presence of concentrated acid solutions.

ICP-OES as an analytical technique proved to be an excellent and dependable quantification tool due to its ability to perform multi-element analysis and low detection limits. The main disadvantage when using this technique is the possible spectral interferences from other elements and interfering species, but this was minimised to a great deal by the proper wavelength selections of all the elements present in these mineral ores. However, quantification of Th proved to be a problem with high percentage recoveries in some of the studies which was attributed to quantification of Th close to its LOD and this resulted in unsatisfactory recoveries.

7.2 Future research

From the mentioned aims of this study and the outcomes reported, it is evident that further refinements and new studies are needed to improve the beneficiation process as a whole. The possible future research studies from this study include the following:

- Influence of particle size of the mineral sample on NORM removal using acid leaching
- Alkaline leaching and pressure influence on acid leaching
- Refinement of magnetic separations with respect to magnetic strength
- In-depth investigation of the microwave acid–assisted digestion conditions to improve the separation of Ta and Nb
- Complete isotope ratio analysis in all future leaching steps
- Evaluation of the beneficiation process on the other tantalite samples
- Evaluation of the U isotope ratios during the beneficiation process

7.3 Conclusion

This study is regarded as mostly successful by achieving most of the aims which were initially identified. Limitations to this study also allowed for the identification of further research opportunities on this topic to add valuable knowledge into the tantalum/niobium containing minerals processing.

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Summary

Tantalum and niobium occur in nature in the form of minerals such as tantalite and columbite. Recent advances in technology have increased the demand for these elements and their chemical compounds. Tantalum is extensively used in the electronics industry, especially in cell phones and laptops while niobium is used mainly in the production of super metal alloys for the use in the construction industry. The presence of U and Th in these Nb/Ta containing minerals (NORMs) however complicates the beneficiation process of the minerals immensely. Regulatory constraints on the quantity of material that can be handled at one time, processing equipment, transportation and waste disposal of these materials put more strain on the processing of these minerals. This strain adds a financial burden on the total beneficiation value chain when U and Th are present.

The overall aim of this study was to investigate the selective removal of U and Th from these minerals prior to their complete dissolution in order to increase the safety of processing and/or transportation procedures. The methods included acid leaching (time and temperature variation), anion precipitation and ion exchange chromatography. The results obtained from these studies indicated varying degrees of success. The acid leaching study involved the use of sulphuric acid, phosphoric acid, hydrochloric acid, nitric acid, perchloric acid and *aqua regia*, of which the first three of these acids proved to be the most effective in the removal of the majority of U and Th from the mineral.

Analytical results obtained for while using concentrated sulphuric acid as reagent indicated that an increased amount of radioactive material was removed from the mineral. The Th content removed from the mineral ore increased from 68.82% at 50 °C to approximately 100% at 100 °C after 3 hours of leaching in both cases. Additionally, the U content in the filtrate increased from 64.37% at 100 °C to 81.27% at 150 °C and finally to 90.08% at 200 °C. Phosphoric acid was less effective in the removal of uranium and thorium at 50 °C while an increase in temperature to 150 °C resulted in 85.10 and 98.77 % of U and Th respectively being removed after 3 hours.

On the other hand, hydrochloric acid exhibited the same trend as sulphuric and phosphoric acid with an increasing amount of U and Th present in the filtrate as time and temperature were increased. At 90 °C and 3 hours of leaching, hydrochloric acid succeeded in removing 51.53 and 91.09% of U and Th respectively. The main disadvantage of the use of these concentrated acids as leaching reagents at elevated temperatures and extended times, is the simultaneous removal of Ta and Nb from the mineral. Analytical results indicated that 9.70 and 29.11% of Ta and Nb respectively were dissolved at 150 °C after 3 hours using sulphuric acid. The use of sulphuric acid as reagent, a temperature of 50 °C and 2 hours leaching time were selected as the most suitable conditions for the subsequent beneficiation process as a compromise between the maximum U and Th removal and the minimum amount of Ta and Nb removed from the NORMs.

The selective removal of the radioactive elements using anion precipitation and ion exchange was also investigated. The selective precipitation using several different anions indicated that sulphate (SO_4^{2-}) was the most successful anion in the selective removal of U and Th from the mineral solution compared with all of the acids investigated. The sulphate resulted in the precipitation of 5.11 % of the total U precipitated along with 82.58 % of the Th, 80.13 % of the Nb and 99.21 % of the Ta. The ion exchange chromatography method, however, was unsuccessful in the separation of uranium and thorium from the tantalum and niobium as there was no selectivity in retention and/or elution of these elements.

The final step in this study was to investigate the possible beneficiation of the tantalite ore by combining the acid leaching with the magnetic removal and microwave dissolution of the mineral. The mineral sample which was investigated possessed minute magnetic properties and small amounts of Ta and Nb (1.79 and 1.69 % respectively) together were removed together with Fe by magnetic separation. The acid leaching resulted in consistent but lower U and Th removal. Interestingly, the microwave digestion preferentially removed U, Th and Nb, as indicated by their presence in the filtrate, leaving the precipitate with significantly more Ta. The ratio of niobium to tantalum changed from 1:1 in the initial mineral sample to 3:1 and 1:2 in the filtrate and the precipitate respectively. The final

insoluble mineral contained 0.13 % Th (initially 0.50 %), 1.33 % U (initially 3.07 %), 12.18 % Nb (initially 28.1 %) and 21.41 % Ta (initially 27.71 %). The filtrate, on the other hand, contained 0.14 % and 0.98 % of thorium and uranium as well as 13.00 % niobium and 3.99 % tantalum.

Opsomming

In die natuur kom die elemente tantaal en niobium in minerale soos tantaliet en kolumbiet voor en het die vraag na hierdie twee elemente in die afgelope paar jaar skerp toegeneem as gevolg van die gebruik daarvan in verbeterde tegnologiese produkte. Tantaal word veral gebruik in die vervaardiging van selfone en skootrekenaars terwyl die vernaamste gebruik van niobium in die konstruksiebedryf is waar dit in die vervaardiging van super metaal allooie gebruik word. Die teenwoordigheid van U en Th in hierdie Nb/Ta bevattende minerale bemoeilik egter die veredeling van hierdie minerale geweldig. Wetgewing beperk byvoorbeeld die hoeveelheid materiaal wat op 'n gegewe moment hanteer mag word, tipe verwerkingstoerusting, die vervoer daarvan asook afvalverwydering. Bogenoemde maatreëls plaas geweldige finansiële druk op die waarde-ketting vir die verwerking en veredeling van hierdie minerale indien U en Th teenwoordig is.

Die oorhoofse doel van hierdie studie was die bestudering van die moontlike selektiewe verwydering van U en Th uit hierdie minerale voordat die volledige vertering uitgevoer word. Die metodes wat ondersoek is, het onder andere suur-loging (funksie van tyd en temperatuur), anioon-presipitasie en ioonuitruilingschromatografie ingesluit. Die resultate wat uit die suur-loging studie verkry is, het wisselende grade van sukses in die verwydering van die radioaktiewe elemente aangetoon. Tydens die studie is swaelsuur, fosforsuur, soutsuur, salpetersuur, perchloorsuur en *aqua regia* as logingsreagense ondersoek en die analitiese resultate het duidelik getoon dat die eerste drie sure in bogenoemde reeks die suksesvolste was in die verwydering van die meeste van die U en Th uit die mineraal.

Resultate wat verkry is met die gebruik van gekonsentreerde swaelsuur as logingsreagens het 'n duidelik 'n toename in die verwydering van radio-aktiewe elemente met 'n toename in tyd en temperatuur aangetoon. Die Th-inhoud in die filtraat het vanaf 68.82% by 50 °C tot sowat 100% by 100 °C toegeneem. Daarbenewens het die U-inhoud in die filtraat vanaf 64.37% by 100 °C tot 81.27% by 150 °C verhoog en

uiteindelik tot 90.08% by 200 °C. Fosforsuur was duidelik ondoeltreffend in die verwydering van U en Th by 50 °C, maar met 'n temperatuur toename na 150 °C is 85.10 en 98.77% van U en Th na 3 ure uit die mineraal verwyder. Die kwantitatiewe analises het ook duidelik getoon dat soutsuur dieselfde tendens as swaelsuur en fosforsuur volg met 51.53 en 91.09% van U en Th wat by 90 °C en 3 uur verwyder is. Die nadeel van die gebruik van hierdie gekonsentreerde sure as logingsreagense by verhoogde hoë temperature en verlengde tye is die ongewenste verwydering van Ta en Nb van uit die mineraal. So byvoorbeeld loog swawelsuur 9.70 en 29.11% Ta en Nb by 150 °C na 3 ure uit die erts. As kompromie, met doel die maksimum verwydering van die radio-aktiewe elemente en die minimum Nb en Ta verwydering, is swaelsuur as logingsreagens by 50 °C en 2 ure vir die verdere mineraalveredelingstudie gebruik.

Die selektiewe verwydering van die radio-aktiewe elemente met behulp van die anioon-neerslag en ioonuitruiling is ook ondersoek. Die selektiewe presipitering met die verskillende anione het aangetoon dat SO_4^{2-} die mees suksesvolle anioon in die selektiewe verwydering van U en Th is. Eksperimentele resultate het verder aangetoon dat 5.11% van die U saam met Th (82.58%), Nb (80.13%) en Ta (99.21%) deur die byvoeging van swawelsuur gepresipiteer word. Ioonuitruiling was egter onsuksesvol in die skeiding van die U en Th van Ta en Nb of enige ander onsuiwerhede wat in die mineraal-oplossing voorgekom het.

Die finale stap in hierdie studie was 'n ondersoek na die moontlike stapsgewyse veredeling van die tantaliet-erts deur van deur eerstens van magnetiese verwydering van onsuiwerhede, daarna die suurlogingstap en laastens van mikrogolf-vertering gebruik te maak. Klein hoeveelhede Ta en Nb (1.79 en 1.69% onderskeidelik) is saam met die yster in die magnetiese skeidingsproses verwyder. Die daaropvolgende suurloging het tot konstante, maar effens laer hoeveelhede U en Th verwydering gelei, terwyl die mikrogolfvertering bykomende hoeveelhede van U, Th asook groot hoeveelhede Nb uit die mineraal opgelos het. Die finale van Nb:Ta verhouding het na 'n 3:1 en 1:2 in die filtraat en die neerslag vanaf die 1:1 verhouding na hierdie stap verander. Die oorblywende, onopgeloste mineraal bevat 0.13% Th (aanvanklik 0.50%)

en 1.33% U (aanvanklik 3.07), 12.18% Nb (aanvanklik 28,1%) en 21.41% Ta (aanvanklik 27.71%) Ta. Daarenteen bevat die filtraat 0.14% Th, 0.98% U, 13.00% Nb asook 3.99% Ta.