UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

EXTRACTION AND SEPARATION OF TANTALUM AND NIOBIUM FROM MOZAMBICAN TANTALITE BY SOLVENT EXTRACTION IN THE AMMONIUM BIFLUORIDE-OCTANOL SYSTEM

by

KABANGU MPINGA JOHN

Dissertation submitted in partial fulfillment of the requirements for the degree of

MSc (Applied Science): Chemical Technology

Department of Chemical Engineering

Faculty of Engineering, the Built Environment and Information Technology

Supervisor: Prof. Philip Crouse

University of Pretoria

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

DECLARATION

I, **Kabangu Mpinga John, student No. 28140045**, hereby declare that all the work provided in this dissertation is to the best of my knowledge original (excepted where cited) and that neither the whole work nor any part of it has been, or is to be, submitted for another degree at University of Pretoria or any other University or tertiary education institution or examining body.

SIGNATURE……………………………………………………………………………………

DATE……………………………………………………………………………………….

KABANGU MPINGA JOHN

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

SYNOPSIS

EXTRACTION AND SEPARATION OF TANTALUM AND NIOBIUM FROM MOZAMBICAN TANTALITE BY SOLVENT EXTRACTION IN THE AMMONIUM BIFLUORIDE-OCTANOL SYSTEM

Autor: **Kabangu Mpinga John**

Supervisor: **Prof. Philip Crouse**

Department: **Chemical Engineering**

Degree: **MSc (Applied Science): Chemical Technology**

The principal aim of this research was to determine the optimum conditions of extraction and separation of niobium and tantalum with octanol as solvent, from Mozambican tantalite using ammonium bifluoride as an alternative to hydrofluoric acid. The extraction of niobium and tantalum from tantalite can be divided into three activities, viz., acid treatment of the ore to bring the niobium and tantalum values into solution, separation of niobium and tantalum by solvent extraction and preparation of pure niobium pentoxide and tantalum pentoxide by precipitation followed by calcination.

An initial solution was prepared by melting a mixture of tantalite and ammonium bifluoride followed by leaching of the soluble component with water and separation of the solution by filtration. The solution filtered was successfully used after adjustment of the acidity for the extraction and separation of niobium and tantalum. After liquid-liquid extraction highly pure niobium pentoxide and tantalum pentoxide were obtained through precipitation with ammonium hydroxide and calcination.

Comparative experiments were performed modifying the following variables: decomposition temperature; decomposition time of the digestion of niobium and tantalum; acid concentration of feed solution; solvent agent; and stripping agent.

From the experimental results it was determined that the decomposition temperature, decomposition time of the digestion of niobium and tantalum, the acidity of the feed solution, the solvent agent, and stripping agent, all have an important effect on the extraction and separation of tantalum and niobium.

The optimal conditions were determined to be: tantalite-to-ammonium bifluoride 1:30; decomposition temperature 250°C; decomposition time 3 hours; and a water leach period of 10 minutes. Under these conditions the leach recovery of niobium and tantalum was about 95.07% and 98.52%, respectively.

For nearly complete extraction of tantalum and niobium with 2-octanol, two and three equilibrium stages, respectively, are required. The equilibrium data were obtained at an aqueous-to-organic ratio (A/O) of 1:1 using: 100% 2 octanol; 6 M H_2SO_4; 10 minutes contact time at room temperature for tantalum; and 100% 2 octanol, 9 M H_2SO_4, 10 minutes contact time at room temperature for niobium.

Different stripping agents were used and water seems to give good result for both. For the nearly complete stripping process four equilibrium stages are required. From the results obtained an optimum stripping efficiency is achieved after 15 minutes for a 1:1 ratio.

Niobium and tantalum were then neutralized using 28% ammonium hydroxide. The precipitate obtained was dried and placed in a muffle furnace for 4 hours at 900°C. After calcinations, pure tantalum pentoxide and niobium pentoxide were obtained and characterized using XRD and SEM. Tantalum pentoxide and niobium pentoxide synthesized contain trace impurities such as iron and titanium which can be removed by incorporating an appropriate intermediate treatment.

Keywords – Digestion, ammonium hydrofluoride, solvent extraction, octanol, niobium, tantalum, recovery.

ACKNOWLEDGEMENTS

Firstly, I would like to thank my Heavenly Father for endowing me with the required persistence and every necessary provision needed for the accomplishment of this work.

My very special thanks go to my supervisor, Prof. Philip Crouse, for his academic guidance and support.

I would like to express my profound gratitude to the University of Pretoria and National Research Fund for their financial assistance.

My sincere thanks also go to my colleague Onias Sitando for his encouragement.

Last, but certainly not least, I am grateful to my family for their endless love and unconditional support while I was working on this project. Special thanks to my wife Nathalie Kabangu and my children Chris, Jonathan and Glodice Kabangu for their loyal support and patience during those times when I was busy working on this dissertation.

TABLE OF CONTENTS

LIST OF SYMBOLS

α	Distribution coefficient.
K_{ex}	Extraction coefficient.
HA	Concentration of the acidic extractant in organic phase.
E	Extraction factor in percentage
B	Separation factor
α_{Ta}	Distribution coefficient for tantalum.
α_{Nb}	Distribution coefficient for niobium.
ρ_{HA}	Partition coefficient.
k_A	Acidity coefficient of the extractant.
k_f	Formation coefficient of the metal complex with the extractant.
ρ_{Man}	Partition coefficient of metal complex.
n	Charge of metal ion.
V_o	Volume of organic phase
V_{aq}	Volume of aqueous phase
A/O	Aqueous-to-organic mass ratio

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1 INTRODUCTION

1.1. Introduction

The scope of this dissertation is captured in its title, viz. “Extraction and separation of tantalum and niobium from Mozambican tantalite by solvent extraction in the ammonium bifluoride system”. The study focused on conditions that affect the digestion of the ore, separation and recovery of tantalum and niobium using 1−octanol and 2−octanol as extractants and their precipitation as oxides and characterization of the final products.

The principal minerals of niobium (Nb) and tantalum (Ta) are columbite and tantalite. This, depending on whether the concentration of niobium or tantalum is greater corresponds to the general formula $(Fe,Mn)(Nb,Ta)_2O_6$ (Damodaran et al.,1969).

Tantalite ore is found primarily in Australia, Canada, Brazil, Southern Africa, Nigeria and Central African countries such as the Democratic Republic of Congo-Kinshasa, Rwanda, Uganda, Gabon and Burundi. Pegmatites continue to be the largest source of tantalum. The Greenbushes pegmatite near Perth in Western Australia is one of the world’s largest resources, and is mined by the Australian company Sons of Gwalia. The firm alone accounts for over 75% of world production capacity and it is the world’s largest producer of tantalum (Baba et al., 2005; Amuda et al., 2007).

Deposits of tantalite ore are also found in Zimbabwe, Mozambique, India and the U.S.A. Australia has an output of about 17.3% and Canada 6.9% of tantalite. Developing countries like Thailand, the Democratic Republic of Congo, and Nigeria, produce 3.6% of the worldwide concentrates (Baba et al., 2005).

The particular properties of niobium and tantalum have resulted in increasing their usage in electronic, optic, mechanical, aerospace, nuclear and other modern applications. Tantalum and niobium are used widely, in the form of metals and alloys, in the process industry, vacuum techniques, chemical machinery, surgical devices, and the automotive industry (Agulyansky, 2004).

Niobium-tantalum ore materials are generally decomposed with alkali or acidic fusion at elevated temperature, or leaching with mineral acids. At present, most minerals containing niobium and tantalum are decomposed by concentrated hydrofluoric acid (El-Hussaini and Mahdy 2002; Gupta and Suri, 1994). However, such an approach is only appropriate for high-grade niobium-tantalum ore (Zhou et al., 2005). For a low-grade niobium-tantalum ore, a new process for the decomposition has been proposed by Zhou et al., (2005) and Wang et al., (2009) using a highly concentrated caustic potash (KOH) solution under atmospheric pressure and a KOH roast-water leach solution, respectively. The decomposition was greatly improved compared to hydrofluoric acid leaching.

According to the analysis the tantalite from Mozambique is of high-grade and can only be decomposed by hydrofluoric acid, HF, or mixture of hydrofluoric and sulfuric acid, HF and H_2SO_4. Hydrofluoric acid is not ideal for the decomposition stage because the process is accompanied by the loss of about 6-7% HF due to volatilization (He et al., 1998), which is hazardous. Furthermore, a large amount of wastewater containing fluoride is generated that needs to be treated (Wang et al., 2009).

Using ammonium bifluoride as an alternative to hydrofluoric acid, the leaching process is performed with water and a large amount of impurities are precipitated in the form of insoluble compounds that can be separated from the solution by filtration (Agulyansky, 2004). Leach liquor prepared in this way shows consistent concentrations of Ta and Nb. The most important property of the solution is its low acidity. Such a solution can be treated by liquid-liquid extraction using both the collective and selective methods after appropriate acidity adjustment (Agulyansky, 2004). Ammonium bifluoride is also easy to handle. In addition, in the context of South Africa, large quantities of inexpensive ammonium bifluoride are becoming available as byproduct from local plants producing e.g. NF_3.

In previous work (He et al., 1998), the efficiency of extraction with octanol is shown to be comparable with MIBK, the latter being commonly used in the industrial technologies of Ta and Nb (Babkin et al., 1988). However, octanol is preferable since MIBK is fire and explosion-hazardous and soluble in aqueous solutions (Mayorov et al., 2002).

The main advantages of 2-octanol compared with MIBK as extractant are: very low solubility in water (< 0.1%); lower volatility; less dangerous; and a relatively high flash point of 71℃ (Zhu et al., 2011). It has been shown, particularly in Russia, that for the separation and purification, the extractions of Nb and Ta with 1–octanol are very similar to those with 2–octanol (Mayorov et al., 2002).

1.2. The objectives of the study

The specific objectives of the study were:

- To determine if ammonium bifluoride can be used as an alternative to hydrofluoric acid;
- To determine the time and temperature for efficient recovery of niobium and tantalum from tantalite;
- To investigate the effect of sulfuric acid concentration in the feed solution;
- To determine the mass ratio tantalite ore-to-ammonium bifluoride;
- To compare performance of extraction between 1–octanol and 2–octanol;
- To investigate the effect of different stripping agents;
- To characterize the niobium and tantalum pentoxides and compare with the purchased product.

1.3. Methodology

The methodology used in this research was firstly the collection of information related to the objective of this study. The information was collected from different books, patents, encyclopedia and scientific journals. Secondly, a method was devised to set up and run different experiments. Thirdly, the results obtained were evaluated, analyzed and also compared to previous research. Finally, conclusions were presented and recommendations were suggested.

1.4. Outline of dissertation

The outline of this research can be subdivided in four main parts:

1 Literature review: It contains the information about the extraction, separation and precipitation of tantalum and niobium from tantalite. The information is focused on the conditions that affect the decomposition step, separation, extraction using solvent as extractant and using ammonium hydroxide as a precipitation agent.

2 Experimental methods: It describes the methods and materials used.

3 Results and discussions: In this chapter the results of the decomposition process, extraction, stripping, precipitation and characterizations of the products are presented and discussed in terms of optimum extraction parameters of niobium and tantalum.

4 Conclusions and recommendations: The chapter contains concluding remarks regarding decomposition, extraction, separation and precipitation conditions of niobium oxide and tantalum oxide and recommendations with regards to further test work.

CHAPTER 2 LITERATURE SURVEY

The extraction of niobium and tantalum from tantalite of Mozambique is investigated in this dissertation. In order to plan the relevant laboratory experiments, information was gathered on the raw materials utilized and general conditions for digestions, extraction and separation of niobium and tantalum from the raw materials.

2.1. Niobium and tantalum raw materials

Niobium and tantalum naturally occur in combination with oxygen and one or more other metals as niobates and tantalite in various types of deposits. Of these, the important ones are niobites-tantalites as pegmatite, pyrochlores as carbonites, and niobium-tantalum-bearing cassiterite as placer deposits (Gupta and Mukerjee, 1990).

Table 2.1, shows that the most important source of tantalum and niobium is tantalite–columbite, $(Fe, Mn)(Nb, Ta)_2 O_6$ (Agulyansky, 2004). The most important niobium mineral is pyrochlore with the general formula $(Ca, Na)_{2-m}Nb_2O_6(O,OH, F)_{1-n} .xH_2O$. The lattice positions of Na and Ca can also be occupied by Ba, Sr, rare earths, Th and U. Thorium and uranium are responsible for the radioactivity of some of the pyrochlore concentrate. The most important tantalum–containing minerals are tantalite, wodginite, microlite (the tantalum–rich end member of the pyrochlore series), and columbite (Fathi, 1997).

.

Table 2. 1: Composition of main tantalum-niobium containing minerals (Gibalo, 1970, Sean et al., 2007)

Minerals	Composition	Ta_2O_5, Wt.%	Nb_2O_5, Wt.%
Columbite	$(Fe,Mn)(Nb,Ta)_2O_6$	5-30	55-78
Tantalite	$(Fe,Mn)(Ta,Nb)_2O_6$	42-84	2-40
Pyrochlore	$(Ce,Ca,Y)_2(Nb,Ta)_2O_6(OH,F)$	0-6	37-66
Microlite	$(Na,Ca)_2Ta_2O_6(O,OH,F)$	66-77	0-7
Loparite	$(Ce,Na,Ca)_2(Ti,Nb)_2O_6$	0.5-3	4-20
Euxenite	$(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$	0-47	4-47
Limenorutile	$(Ti,Nb,Fe)_3O_6$	0-36	20-43
Simpsonite	$Al_4(Nb,Ta)_3O_{13}(OH)$	60-80	0.3-6
Thoreaulite	$SnTa_2O_6$	73-77	-
Strueverite	$(Ti,Ta,Fe^{3+})_3O_6$	6-13	9-13
Fergusonite	$(Re^{3+},Nb,Ta)O_4$	4-43	14-46
Sumarskite	$(Fe,Ca,U,Y,Ce)_2(Nb,Ta)_2O_6$	15-30	40-45
Tapiolite	$(Fe,Mn)(Nb,Ta,Ti)_2O_6$	40-85	8-15

2.2. Recovery of niobium and tantalum

Tantalum and niobium normally are found together in various minerals. The most important of these minerals are columbite and tantalite.

The procedure for recovery of pure niobium and tantalum from their minerals requires a complex sequence of processing operations. This sequence involves digestion or decomposition of corresponding raw materials with hydrofluoric acid, sulfuric acid, mixtures of these, or ammonium hydrofluoride (bifluoride), to allow a complete dissolution of ore. The accompanying elements, such as iron, manganese, titanium, etc., are dissolved in hydrofluoric acid solution along with the tantalum and niobium. Two types of complex ions are formed TaF_7^{2-} / TaF_6^{-} and $NbOF_5^{2-}$ / NbF_6^{-}, respectively (Agulyansky, 2004). The equilibrium between the complexes depends on the acidity of the solution and can be schematically displayed as follows for tantalum and niobium, respectively:

$$TaF_7^{2-} + HF \rightleftharpoons TaF_6^{-} + HF_2^{-} \quad (1)$$

$$NbOF_5^{2-} + 3HF \rightleftharpoons NbF_6^{-} + HF_2^{-} + H_2O \quad (2)$$

The complexes can be regarded as Lewis acids in which acidity increases in going from TaF_7^{2-} or $NbOF_5^{2-}$ to TaF_6^{-} or NbF_6^{-}. It is obvious that high acidity ions are more stable in high acidity media. At higher acidity, the equilibria (1) and (2) move to the right, yielding complexes of lower charge, TaF_6^{-} or NbF_6^{-}, that are mostly extracted into the organic phase (Agulyansky et al., 2004). Under this condition of lower acidity, the complexes are stripped from the organic into the aqueous media in the form of TaF_7^{2-} or $NbOF_5^{2-}$. Owing to their lower molecular weights niobium complexes are stronger Lewis acids and need higher acidity of the solution to be converted to the NbF_6^{-} form. This particular difference in the behavior of complexes provides a possibility for effective separation of tantalum and niobium by liquid-liquid extraction (Agulyansky et al., 2004).

After filtration of the insoluble residues (Al, Si, Ca, rare earth metals, etc.), the aqueous hydrofluoric or hydrofluoric-sulfuric acid solution containing tantalum and niobium is contacted with organic extractant such as methyl isobutyl ketone (MIBK), tributyl phosphate (TBP) and cyclohexanone in a multistage mixer-settler plant(Joachim et al., sa).

There are two main schemes that exist for the separation and purification of niobium and tantalum using liquid-liquid extraction (Agulyansky, 2004). The first method is a collective liquid-liquid extraction that consists of extraction of tantalum and niobium together in the organic phase from an initial solution, and most of the impurities remain in aqueous phase. Figure 2.1 shows the flow chart of the process. The second is a selective method that consists of bringing the organic solution of tantalum and niobium into contact with an aqueous solution. The niobium is back extracted into the aqueous phase with tantalum remaining in the organic phase. The aqueous niobium solution is re-extracted with a fresh solvent to remove traces of tantalum (Agulyansky, 2004). The acidity must be adjusted before niobium extraction because it requires a high concentration of acid. Figure 2.2 shows the flow chart of the process based on the selective extraction scheme.

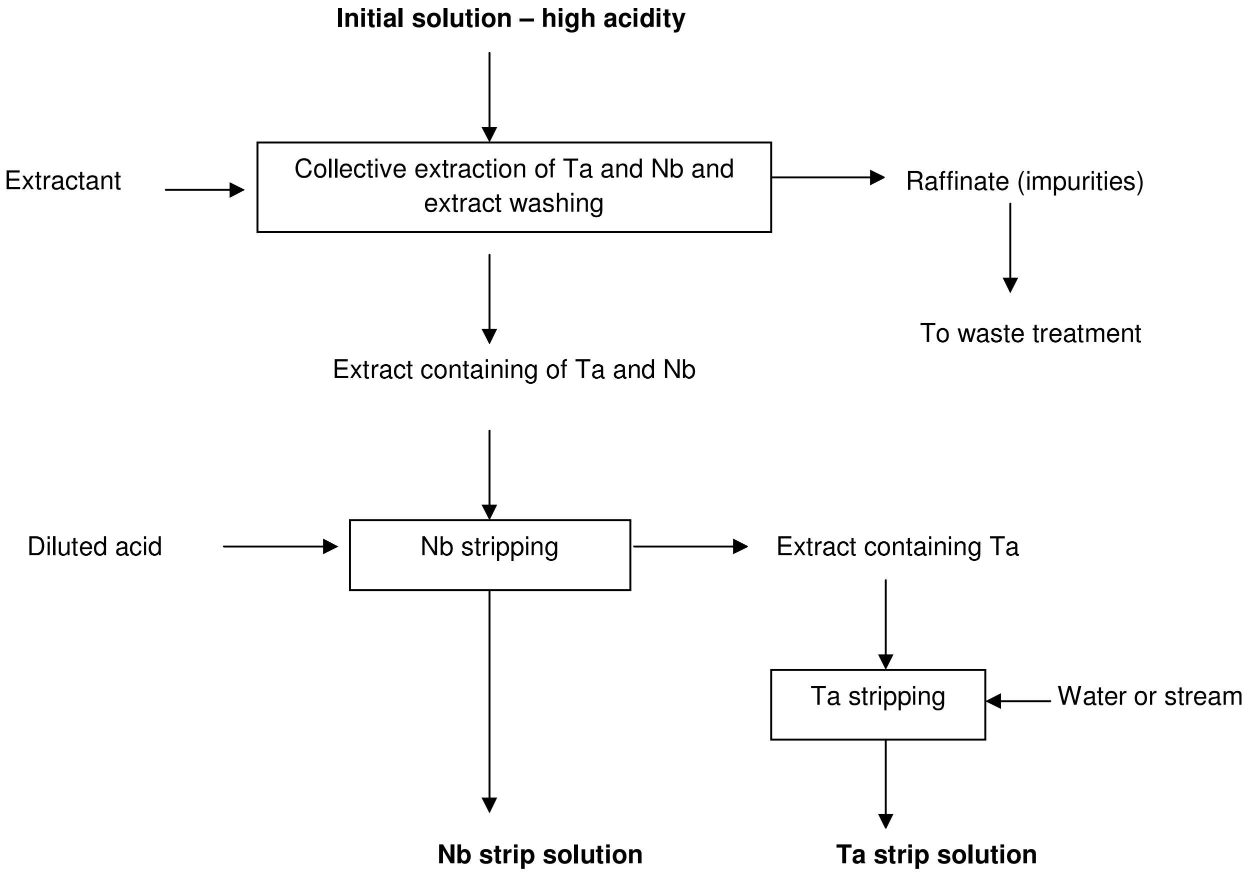


Figure 2.1: Collective extraction (Agulyansky, 2004)

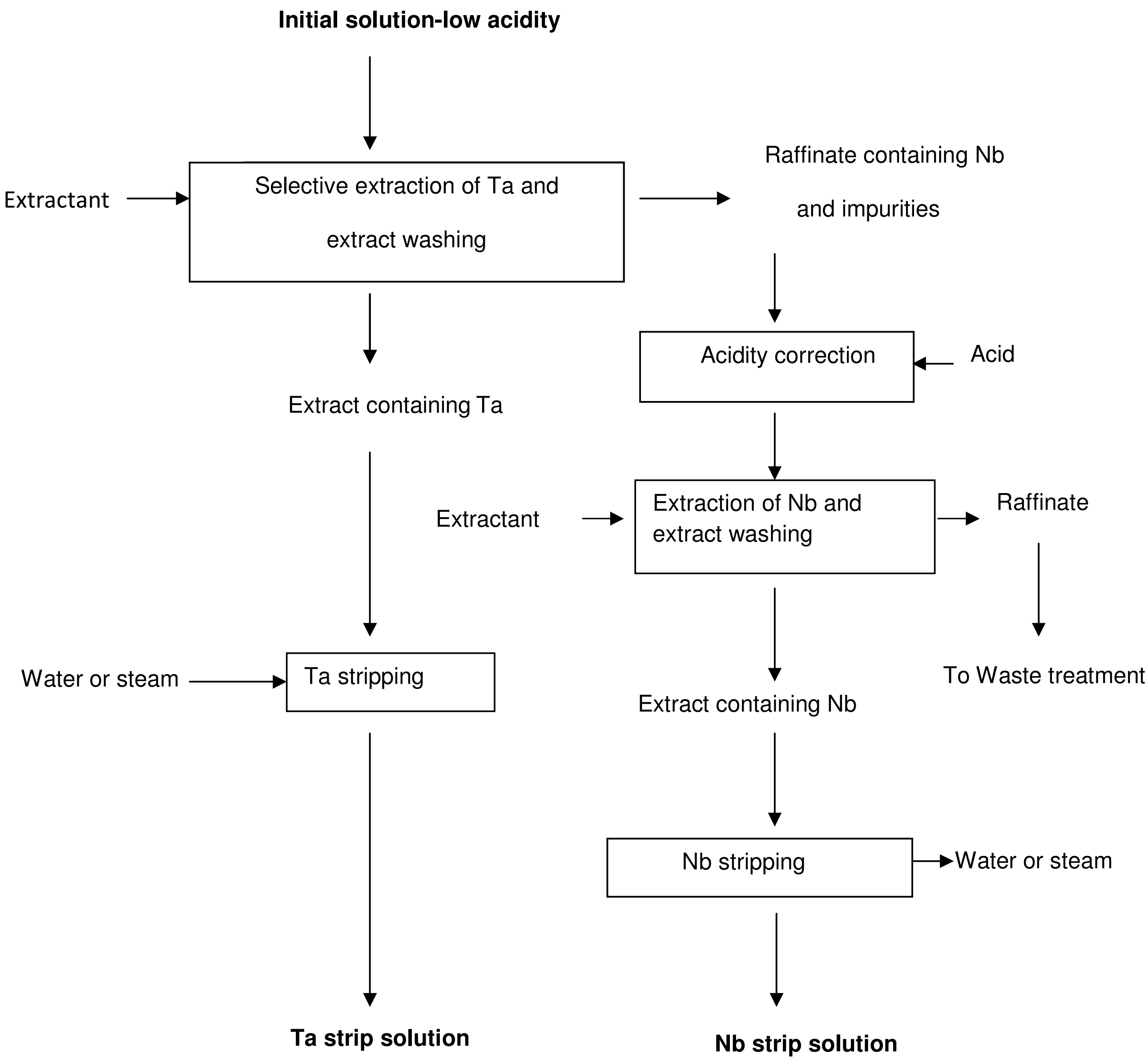


Figure 2.2: Selective extraction (Agulyansky, 2004)

The first approach is the more popular because currently existing technology is based on complete dissolution of the raw material in HF or HF-H_2SO_4 acids of high concentration (Agulyansky et al., 2004). The excessive acidity of the resulting solution allows one to perform only collective liquid–liquid extraction. The second method seems to be more effective and leads to a better separation of tantalum and niobium and to a more effective purification but needs an initial solution of sufficiently low acidity. Another known method (Eckert, 1995) is based on the collective extraction and subsequent collective stripping of tantalum and niobium. The strip solution is used for further selective extractive separation of tantalum followed by niobium. This way is more complex and expensive but it allows one to obtain tantalum and niobium products of higher purity (Agulyansky et al., 2004). Figure 2.3 shows the modified flow chart of the process.

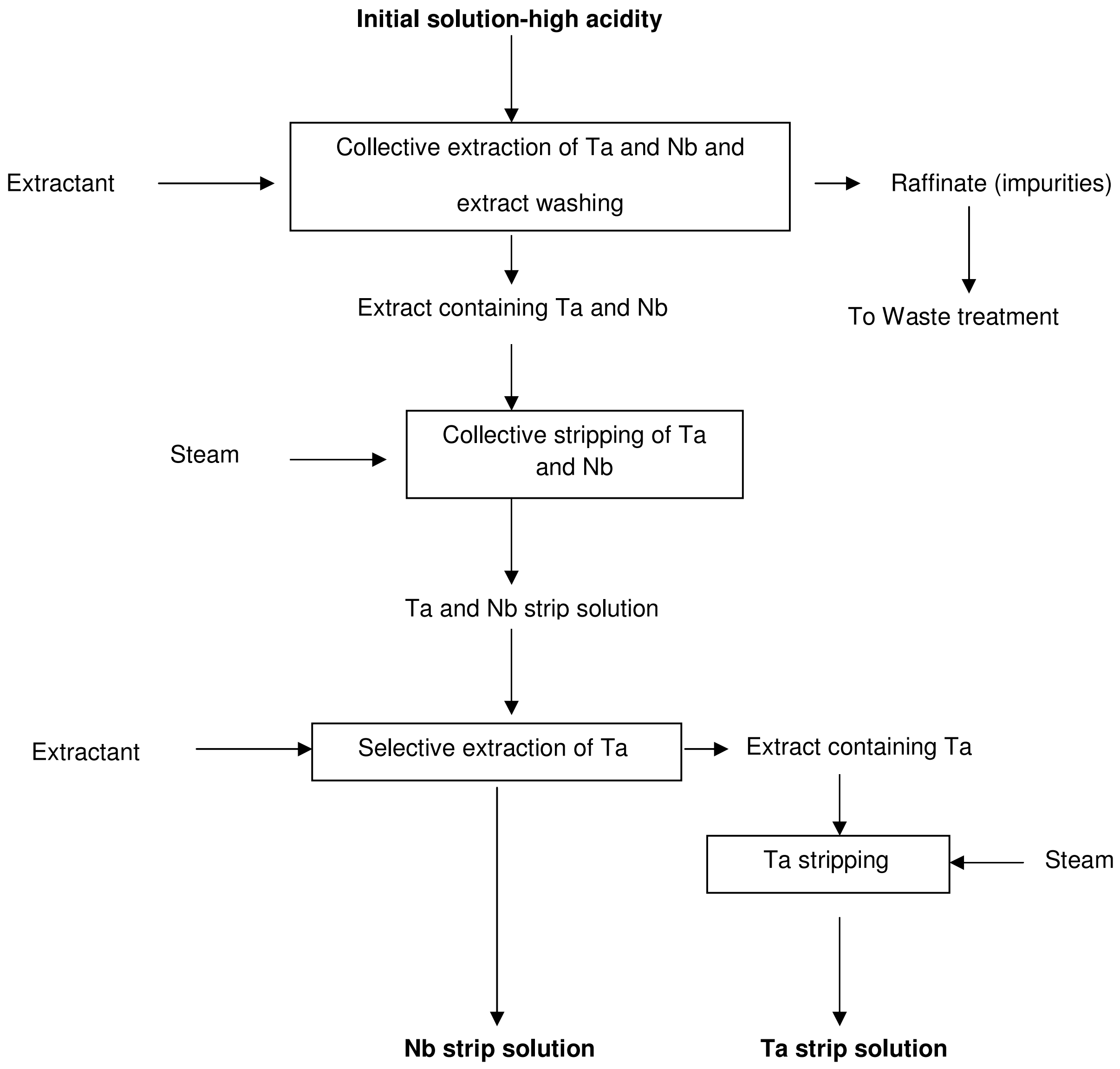


Figure 2.3: Modified scheme of collective extraction, including selective extraction of tantalum (Agulyansky, 2004)

The organic phase resulting is returned to the tantalum–niobium extraction stage. The niobium hydrate is precipitated by the addition of gaseous ammonia or ammonia dissolved in water. After re-extraction of the tantalum from the organic phase with water or a dilute ammonia solution, tantalum may be precipitated as the oxide hydrate with ammonia or, by addition of potassium salts, such as K_2TaF_7 (Joachim et al., sa). These compounds are used as starting materials for the production of tantalum metals for super alloys and tantalum powders for capacitor manufacture.

The precipitation of the oxides can be done in a batch process or in a continuously operated facility. The oxide hydrates are collected by filtration, dried and calcined at up to 1100℃ (Fathi, 1997). The conditions of precipitation, drying and calcinations are varied to produce different particle size distributions needed for oxides for various applications. Depending on the quality requirements, the calcinations are carried out in a directly or indirectly heated chamber or a rotary furnace. The nature of the furnace lining has a considerable influence on the purity of the oxide (Joachim et al., sa).

The primary tantalum and niobium chemicals of industrial significance in addition to K_2TaF_7, Ta_2O_5, K_2NbF_7 and Nb_2O_5, are tantalum chloride ($TaCl_5$), lithium tantalite ($LiTaO_3$), tantalum carbide (TaC), niobium chloride ($NbCl_5$), niobium carbide (NbC), or lithium niobate ($LiNbO_3$) (Giulio et al., 2009).

The various metallurgical products are generally produced from electron beam or vacuum arc melting of the metal feedstock. Tables 2.2 and 2.3 show the tantalum and niobium products, respectively, their applications and technical attributes (TIC, 2009).

Table 2.2: Applications of tantalum

Tantalum Product	Application	Technical Attributes/Benefits
Tantalum carbide	Cutting tools.	Increase high temperature deformation, control of grain growth.
Lithium tantalate	Surface Acoustic Wave (SAW) filters in mobile phones, hi-fi stereos and televisions.	Electronic signal wave dampening provides for clearer and crisper audio and video output.
Tantalum oxide	Lenses for spectacles, digital cameras and mobile phones. X-ray film. Ink jet printers.	Ta_2O_5 provides a high index of refraction so that lenses for a given focal strength can be thinner and smaller. Yttrium tantalite phosphor reduces X-ray exposure and enhances image quality. Wear resistance characteristics. Integrated capacitors in integrated circuits (ICs).
Tantalum powder	Tantalum capacitors for electronic circuits in: Medical appliances such as hearing aids and pacemakers; Automotive components such as ABS, airbag activation, engine management modules, GPS; Portable electronics e.g. laptop computers, cellular/mobile phones, video cameras, digital still cameras; Other equipment such as DVD players, flat screen TVs, games consoles, battery charges, power rectifiers, cellular/mobile phone signal masts, oil probes.	High reliability characteristics and low failure rates, operation over a wide temperature range from -55 to +200˚C, can withstand severe vibrational forces, small size per microfarad rating/electrical storage capacity.
Tantalum fabricated	Chemical process equipment including lining,	Superior corrosion

sheets and plates	cladding, tanks, valves, heat exchangers. Cathodic protection systems for steel structures such as bridges, water tanks. Corrosion resistance fasteners, screws, nuts, bolts. Spinnerettes in synthetic textile manufacture.	resistance equivalent in performance to glass.
Tantalum fabricated sheets, plates, rods, wires	Prosthetic devices for humans-hip joints, skull plates, mesh to repair bone removed after damage by cancer, suture clips, stents for blood vessels.	Prosthetic devices for humans-hip joints, skull plates, mesh to repair bone removed after damage by cancer, suture clips, stents for blood vessels.
Tantalum fabricated sheets, plates, rods, wires	High temperature furnace parts.	Melting point is 2996˚C although protective atmosphere or high vacuum required.
Tantalum ingot	High temperature alloys for: Air and land based turbine (e.g. jet engine discs, blades and vanes). Rocket nozzles.	Applications of tin coatings of tantalum, tantalum oxide or nitride coatings to semi-conductors to prevent copper migration.
Tantalum ingot	High temperature alloys for: Air and land based turbine (e.g. jet engine discs, blades and vanes). Rocket nozzles.	Alloys compositions containing 3-11% tantalum offer resistance to corrosion by hot gases, allow higher operating temperature and thus efficiency and fuel economy.
Tantalum ingot	Computer hard drive discs.	An alloy containing 6% tantalum has shape memory properties.
Tantalum ingot	Explosively formed projectile for TOW-2 missile.	Balance of density and formability allow for a lighter and more efficient system.

Table 2.3: Application of niobium

Niobium product	Application	Technical attributes/benefits
HSLA Ferro-Niobium (~60%Nb)	Niobium additive to high strength low alloy steel and stainless steel for oil and gas pipelines, car and truck bodies, architectural requirements, tools steel, ships, hulls, railroad tracks.	Impart a doubling of strength and toughness due to gain refining weight reduction.
Niobium oxide	Manufacturing lithium niobate for surface acoustic wave filters. Camera lenses. Coating on glass for computer screens. Ceramic capacitors.	High index of refraction. High dielectric constant. Increase light transmittance.
Niobium carbide	Cutting tool compositions.	High temperature deformation, control grain growth.
Niobium powder	Niobium capacitors for electronic circuits.	High dielectric constant, stability of oxide dielectric.
Niobium metals plates, sheets, wire, rod, tubing	Cathode protection system for large steel structures. Chemical processing equipment.	Corrosion resistance, formation of oxide and nitrite films. Increase in high temperature resistance and corrosion resistance, oxidation resistance, improved creep resistance, reduction erosion at high temperatures.
Niobium – titanium alloy Niobium – tin alloy	Superconducting magnetic coils in magnetic resonance imagery (MRI), magneto encephalography, magnetic levitation transport systems, particle physics experiments.	Electrical resistance of alloy wire drops to virtually zero at or below temperature of liquid helium (-268.8 ˚C).

Niobium-1% Zirconium alloy	Sodium vapor lamps. Chemical processing equipment.	Corrosion resistance, fixation of oxygen, resistance to embrittlement.
Vacuum-grade ferro-niobium and nickel-niobium	Superalloy additions for turbine blade application in jet engines and land-based turbines. Inconel family of alloys, superalloys.	Increasing in high temperature resistance and corrosion resistance, improved creep resistance, reduced erosion at high temperature.

Today niobium and tantalum compounds are processed in large tonnage by the fluoride process, including solvent extraction, as described by the flow chart given in Figure 2.4 (Joachim et al., sa)

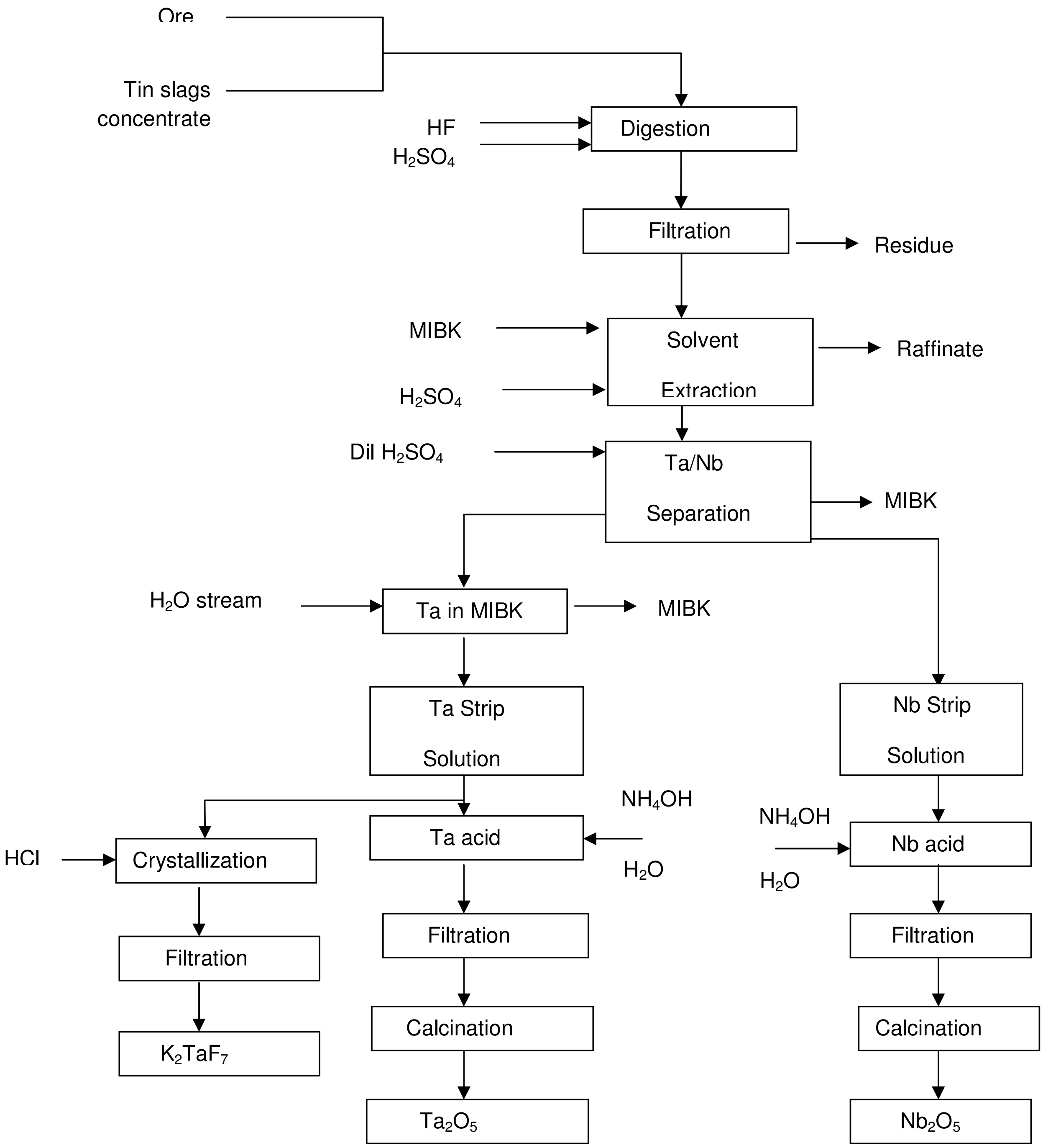


Figure 2.4: Hydrometallurgical processing of niobium and tantalum (Joachim et al., sa)

2.2.1. Decomposition (digestion) of niobium and tantalum

After preparation and separation of the ore according to chemical composition a number of processes follow. The next step after preparation and separation of ore in hydrometallurgical processes is to dissolve (digestion or decomposition) the constituents of the ore to form a solution.

The process of extraction of niobium and tantalum mainly depends on the decomposition and leaching of the tantalite ore. Obviously the better the leaching, the higher the quantity of tantalum and niobium to be extracted. The difficulty of tantalum and niobium extraction from the ore is due to the fact that only a few solvents can leach the ore and only in the presence of the fluorine ion (Maina et al., 2007).

Leaching is concerned with the extraction of a soluble constituent from a solid by means of a solvent (Coulson and Richardson, 2002); or it is the removal of a soluble fraction, in the form of solution, from an insoluble, permeable solid phase with which it is associated. The separation usually involves selective dissolution, with or without diffusion (Robert et al., 2007). The soluble constituent may be solid or liquid; and it may be incorporated within, chemically combined with, adsorbed upon, or held mechanically in the pore structure of the insoluble material. The process of leaching may be used either for the production of a concentrated solution of a valuable solid material, or in order to remove an insoluble solid. The method used for the extraction is determined by the proportion of soluble constituent present, its distribution throughout the solid, the nature of the solid and the particle size (Coulson and Richardson, 2002). The mechanism of leaching may involve simple physical solution or dissolution made possible by chemical reaction. The rate of transport of solvent into the mass to be leached, or of soluble fraction into the solvent, or of extract solution out of the insoluble material, or some combination of these rates may be significant. A membranous resistance may be involved. A chemical-reaction rate may also affect the rate of leaching (Coulson and Richardson, 2002; Robert et al., 2007). The process can be considered generally to comprise of three parts: firstly the change of phase of the solid as it dissolves in the solvent, secondly its diffusion through the solvent in the pores of the solid to the outside of the particle, and thirdly the transfer of the solute from the solution in contact with the particles to the main bulk of the solution.

The rate of leaching is affected by a large number of factors. These include particle size, the nature of solvent, temperature and agitation.

- Smaller particle sizes result in a greater interfacial area between the relevant solid and liquid. The diffusion path of solute through the porous structure of the residual solid is also shorter. Smaller particle may, however, impede circulation of the liquid and separation of the particle from the liquid, making subsequent drainage of the solid residues more difficult. Distribution of particle size is desired as this may lead to a uniform time of extraction and minimal obstruction to solvent flow (Coulson and Richardson, 1996).

- The solvent should be selective and its viscosity should be sufficiently low for it to circulate freely (Coulson and Richardson, 1996).

- The increase of temperature will also increase the solubility of the materials that are being extracted, to give a higher rate of extraction. The diffusion coefficient will be expected to increase as well. It has been shown that tantalum and niobium extraction seems to be unchanged at least within a temperature range of 25-50 °C (Agulyansky, 2004).

- Agitation of the fluid is important because it increases the eddy diffusion, prevents sedimentation and allows more effective use of the interfacial surface (Coulson and Richardson, 1996).

The chemical study of niobium and tantalum elements shows that the decomposition of their ore involves a large number of procedures. Among them, alkali fusion which is one of the first methods that was industrially adopted to achieve simultaneous breakdown of columbite-tantalite (Eckert, 1995). In this method, sodium hydroxide and sodium carbonate (or the potassium salts) were used as the main reactants. The shortcoming of this method is the high reaction temperature (typically 800 °C) required. To avoid this disadvantage, a hydrothermal method has been developed (Cardon, 1962; Zelikman and Orekhov, 1965) which requires high pressure and expensive autoclave equipment. Some types of minerals containing niobium and tantalum can also be processed by different approaches, such as chlorination (Gupta and Suri, 1994), alkali fusion followed by acid leaching (Foos, 1960), fusion with ammonium fluoride and bifluoride (Gupta and Suri, 1994), pressure dissolution with alkaline solution (Cardon, 1962; Zelikman and Orekhov, 1965), direct acid dissolution with H_2SO_4 (El-Hussaini and Mahdy, 2002) or combination of H_2SO_4 and HF (Krismer and Hoppe, 1984).

Currently, most of the niobium-tantalum ores are decomposed by concentrated hydrofluoric acid (El-Hussaini and Mahdy, 2002; Gupta and Suri, 1994). However, the decomposition process is accompanied by the loss of a considerable amount of HF due to volatilization (He et al., 1998), which brings great harm to human beings and equipment. A large amount of fluorspar sludge is generated and needs to be disposed off (Bludssus and Eckert, 1993).

In this investigation an initial solution was prepared by melting a mixture of ammonium hydrogen fluoride (bifluoride) (NH_4HF_2) and tantalite. The solution was then leached with water and the filtrate was successfully used for the precipitation of niobium hydroxide and tantalum hydroxide or further purification by liquid-liquid extraction after appropriate adjustment of the solution acidity. The possible interaction, based on equal concentrations of tantalum and niobium in the concentrate, can be represented by equation (3) (Agulyansky, 2004):

$$(M)(Ta, Nb)_2O_6 + 12NH_4HF_2 \leftrightharpoons NH_4MF_3 + (NH_4)_2TaF_7 + (NH_4)_3NbOF_6 + 5H_2O + 6NH_3 + 8HF \quad (3)$$

Here M = Fe or Mn. The efficiency of the fluorination process can be increased by milling and through mixing of the tantalum-niobium containing raw material with ammonium hydrofluoride. It is assumed that the process temperature can be set between 200–350℃. In general, the process flow chart of raw material decomposition by hydrofluoride method can be represented as shown in Figure 2.5 (Agulyansky, 2004).

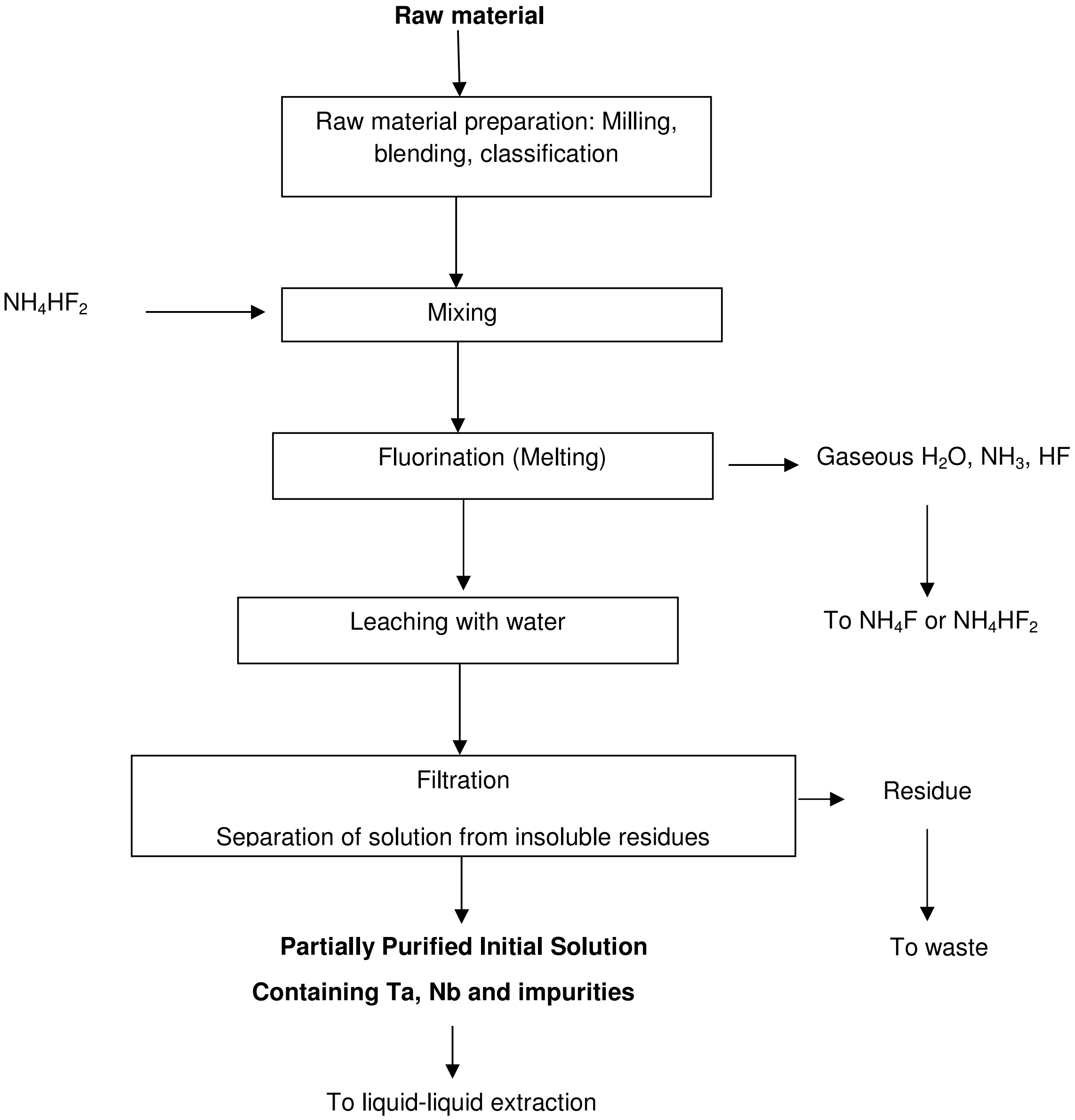


Figure 2.5: Possible flow chart of decomposition of tantalum- or niobium-containing raw material by the hydrofluoric acid method

The main advantages of this method compared to the decomposition with HF can be summarized as follows: The HF is not needed for decomposition of the raw materials; the amount of fluorine can be calculated or adjusted. Since the leaching is performed with water, a significant fraction of the impurities can be precipitated in the form of insoluble compounds which can be separated by filtration. A solution prepared in this way has high concentration of tantalum and niobium, independent of the initial raw material composition. The most important reason for this choice is that the solution has a low acidity level and such a solution can be treated by liquid-liquid extraction (solvent extraction) using both the collective and selective methods after an appropriate acidity adjustment (Agulyansky, 2004).

2.2.2. Solvent extraction theory

Liquid-liquid extraction (solvent extraction) is the only method available for the separation of the rare earth group elements to obtain individual metals (Agulyansky, 2004). This method is very effective for the separation of dissolved components and enables the production of high-purity products, in addition to its advantages of being a low-cost and simple method (Agulyansky, 2004).

During this process an organic solution is contacted with the filtrate produced from the leaching process. Intensive mixing is required to establish sufficient contact time between the organic and the aqueous phase. For a solvent reagent to perform satisfactorily in the recovery and purification of metals present in aqueous leach solutions the reagent must meet a number of criteria. Sudderth and Kordosky (1986) summarized the most important criteria as follows:

- Extraction of the desired metal selectively from the aqueous solution containing the dissolved metal.

- Be able to be stripped to produce a solution from which the desired metal can be recovered in an acceptable form.
- Be chemically and physically stable in the solvent extraction circuit so that it can be recycled through extraction and strip many times without experiencing undue physical loss or chemical breakdown.
- The reagents must meet today's stringent environmental and work-place regulations.
- The extract and strip kinetics must be sufficiently fast to allow these processes to take place in an industrially acceptable time frame.
- The extraction must be soluble, both in the loaded and stripped form, in relatively inexpensive diluents which also meets the environmental and workplace regulations. Alternatively the extractant may be capable of being used at a volume concentration of 100%, in which case the reagent forms its own diluents.
- The made-up circuit organic must phase separate from the aqueous solution at a reasonable rate and the separated phases must have acceptable levels of entrainment.
- The extractant must not transfer deleterious species back from the strip section to the extraction.
- The extractant should be tolerant of crud and should not promote crud formation.
- The extractant must have a reasonable cost, which will enable it to provide an economically attractive recovery route for the metal being treated.

It is interesting before using the currently available types of commercially accepted extractants and those factors which govern the selectivity of these reagents to consider the properties of the metals which are recovered by solvent extraction (Sudderth et al., 1986).

The simplest form of the extraction process with acidic extractant is expressed by the following reaction:

$$M^{n+} + \overline{nHA} \leftrightharpoons \overline{MA_n} + nH^{+} \qquad (4)$$

Here M^{n+} is the metal ion, HA is an extractant. H^{+} ions move from the organic to aqueous phase and M^{n+} from the organic to aqueous phase. Equation (4) indicates that the extraction of the metal described by this equation is heavily dependent on the equilibrium pH of the aqueous phase. Thus, as the pH is decreased (hydrogen ion concentration increased) the metal extraction will decrease since the equilibrium will be shifted towards the left. Conversely, as the pH is increased, metal extraction will increase (Ritcey and Ashbrook, 1984).

The effect of various parameters involved in the solvent extraction of metals can be quantified by the following equations:

$$\log \alpha = \log k_{ex} + \mathrm{n}\log[HA] + npH \qquad (5)$$

$$\alpha = \frac{\text{Concentration of the element in organic phase}}{\text{Concentration of the element in aqueous phase}} \qquad (6)$$

The distribution ratio is a function of temperature, the concentration of chemical species in the system, the phase (A/O) ratio, pH and a larger number of other parameters depending on the system. It is also quoted as a measure of how well-extracted a species is.

For practical purposes, as in industrial applications, it is often more popular to use the percentage extraction %E (sometimes named the extraction factor), which is given by Rydberg et al., (2004).

$$\%E = \frac{100\ \alpha}{(1+\alpha)} \qquad (7)$$

The technique of solvent extraction is employed to separate the solute of interest from substances that interfere in the ultimate quantitative determination of the material. In order to effect a simple separation, it is essential that the distribution ratios of the material of interest and interference be sufficiently different. The effectiveness of separation is usually expressed by means of the separation factor or separation coefficient (Morrison and Freiser 1957).

The separation coefficient, β, is calculated as the ratio between the two distribution coefficients. It is a measure of the ability of the system to separate two solutes. For instance, if the distribution ratio for tantalum is α_{Ta} and the distribution ratio for niobium is α_{Nb}, then the separation factor is equal to $\beta = \frac{\alpha_{Ta}}{\alpha_{Nb}}$ (8)

Separation factors of greater than one indicate that the two metals can be separated, but this gives no indication of the ease of separation or the number of stages which may be required (Ritcey and Ashbrook, 1984).

A plot of logα versus pH at constant concentration (HA), should give a straight line of slope n and an intercept equal to log K_{ex}. The extraction constant K_{ex} has the form (Ritcey and Ashbrook, 1984):

$$K_{ex} = \rho_{HA}{}^{-n} K^{n}{}_{A} K_{f} \rho_{Ma} \qquad (9)$$

The relative magnitude of K_f determines the amount of metal extracted at a defined reagent concentration and pH; therefore, metals with high K_f are extracted at lower pH than those with smaller K_f (Ullmann et al., 1988). A specific ion can be extracted by changing the pH of the feed to the contact step between the organic and the aqueous phase because different ions have different K_f values. Niobium is extracted at higher acidity level while tantalum is extracted at a lower acidity level. This shows that a good selectivity of extraction between niobium and tantalum can be obtained.

2.2.3. Separation of niobium and tantalum

Processing of various resources of tantalum and niobium as described above proceed to a number of separation processes. The main methods of separation are fractional crystallization, solvent extraction and chlorination.

Solvent extraction is the process generally adopted these days to separate tantalum and niobium to requisite purity levels. However, fractional crystallization was the first separation method adopted for the large-scale preparation of pure tantalum intermediate. This method that originated in the classic work of Marignac is based on the differences in the solubility of potassium fluotantalum K_2TaF_7 and potassium niobium oxyfluoride $K_2NbOF_5.H_2O$ (Bose and Gupta, 2001). Separation of tantalum and niobium with their mixed chloride as the starting point has not only attracted more interest but also has resulted in achieving good separation (Gupta, 1984). In this dissertation solvent extraction was the only method used for the extraction of niobium and tantalum.

This process was developed about 50 years ago and has found wide application in the hydrometallurgy of rare refractory and rare earth metals (Agulyansky, 2004). The process is based on the selective extraction of a compound of a given element from aqueous solution into an organic solvent which is immiscible with water. When the aqueous solution and the organic solvent are brought into contact, aqueous-phase species depending on their distribution coefficients are distributed between the two liquid phases (Gupta, 1994). The commercial technology for the separation of niobium and tantalum developed from the work carried out at the US Bureau of Mines and at the Ames Laboratory, Iowa, used two organic solvents, MIBK and TBP in contact with aqueous solution of Nb/Ta in HF-H_2SO_4. The separation process involved co-extraction of both niobium and tantalum fluoride complex from other metallic impurities in the first stage in the organic phase. Then the solvent is contacted with dilute HF-H_2SO_4 to remove niobium selectively. The resulting organic phase is rich in tantalum and the aqueous phase rich in niobium. Re-extraction of the aqueous phase with fresh organic solvent and the organic with dilute acid (HF-H_2SO_4) yield the organic phase loaded with tantalum and aqueous phase with niobium. The tantalum-bearing organic phase is stripped with water. The tantalum-product stream is fluotantalic acid solution from which tantalum can be precipitated either as potassium tantalum fluoride, by addition of potassium chloride or fluoride, or as Ta_2O_5, by addition of ammonia. The niobium-product stream goes forward to a similar chemical processing scheme to obtain either potassium niobium fluoride or Nb_2O_5 (Gupta 1994; Bose and Gupta, 2001).

2.3. Preparation of pure tantalum and niobium oxides

Tantalum and niobium oxides, Ta_2O_5 and Nb_2O_5, are among the final products obtained from tantalum and niobium strip solutions following the liquid-liquid extraction processes (Agulyansky, 2004). Pure Ta_2O_5 and Nb_2O_5 can be prepared from acidic solutions of H_2TaF_7 and H_2NbF_7 by ammonia precipitation, filtration, washing, drying and calcinations (Agulyansky, 2004).

The most frequently used method in the industry for the preparation of tantalum and niobium oxides is based on the precipitation of tantalum and niobium hydroxides from a strip solution by ammonium hydroxide and it consists of several steps (Agulyansky, 2004).

Figure 2.6 presents a flow chart of the process and the complete process can be represented as follows (Agulyansky, 2004):

In the case of the tantalum strip solution:

$$2\ H_2TaF_7 + 14NH_4OH \leftrightharpoons Ta_2O_5.nH_2O_{\ (solid)} + 14\ NH_4F + (9-n)H_2O \qquad (10)$$

In the case of the niobium strip solution:

$$2\ H_2NbOF_5 + 10NH_4OH \leftrightharpoons Nb_2O_5.nH_2O_{\ (solid)} + 10\ NH_4F + (7-n)\ H2O \qquad (11)$$

Equation (10) and (11) describe the equilibrium between the hydrolysis of complex fluoride acids and the fluorination of hydroxides. By applying an excessive amount of ammonia solution up to pH 8 to 9 a complete precipitation of hydroxides can be achieved (Agulyansky, 2004). It is recommended to perform the process at a pH no lower than 10, in order to achieve precipitation of tantalum and niobium hydroxides with minimal levels of fluorine contamination (Agulyansky, 2004).

The way in which ammonia hydroxide is added to tantalum or niobium strip solutions is also important for the quality of the precipitated hydroxides and final oxides. Pouring ammonium hydroxide into a container of strip solution and the mixture agitated is not optimal. This method slows the increase of pH and can cause contamination of the hydroxide with crystalline oxyfluoride compounds. The opposite process reduces the concentration of fluorine in the hydroxide formed significantly (Agulyansky, 2004). It was reported by Bludssus et al. (1993) that the introduction of tantalum or niobium containing acid solution to the ammonia solution until achieving a pH of 9 enabled the production of tantalum or niobium hydroxides with fluoride contents as low as 0.5% wt with a relatively low consumption of ammonia.

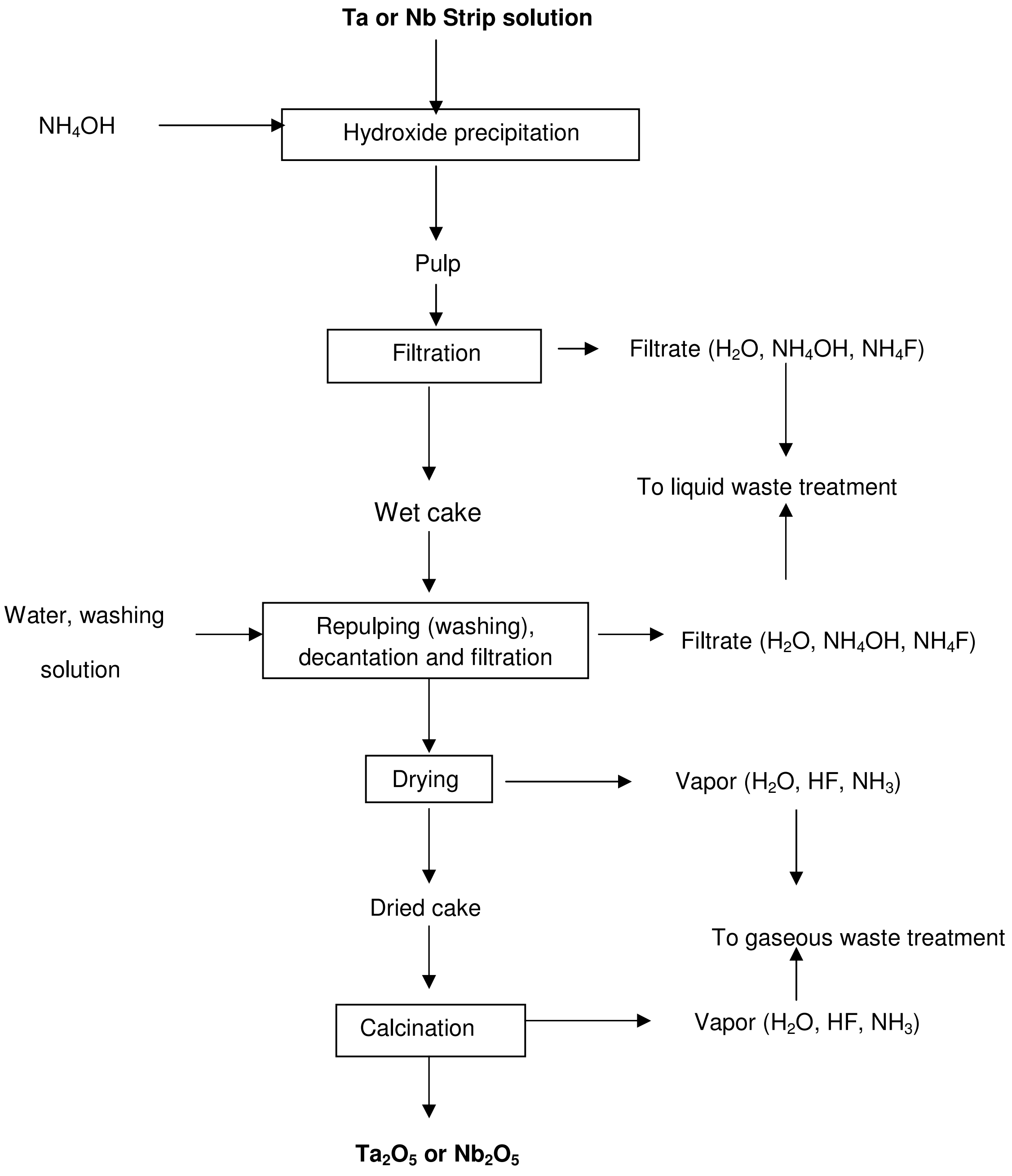


Figure 2.6: Flow chart of tantalum/niobium oxide preparation-precipitation of hydroxides by ammonia solution

CHAPTER 3 EXPERIMENTAL

Different experiments were performed in order to determine the optimal conditions for the extraction and separation of tantalum and niobium from the raw material. These optimal conditions of extraction and separation are determined by a number of factors. They include the decomposition temperature, decomposition time, the initial acidity of the feed solution, the nature of the solvent, and the nature of the stripping agents. Ammonium hydroxide was used as the precipitation agent. When changing certain of the variables, the effects on the percentage extraction of tantalum and niobium were determined. All experiments were batch experiments. The extraction and separation of tantalum and niobium from tantalite were performed with the apparatus, raw material and experimental set-up described below.

3.1. Apparatus and instruments

The apparatus and instruments used are bulleted below:

- Flasks and bottles made in polytetrafluroethylene (PTFE), perfluoroalkoxy (PTA), or polyethylene because glass apparatus cannot be used since HF dissolve silica.
- Beakers made of PTFE
- Separation funnel
- Furnace
- Stirring bar
- Magnetic stirrer
- Sampling pipette
- A measuring cylinder

- Thermometer
- Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES)
- X-Ray Diffractometry (XRD)
- X-Ray Fluorescence spectrometer (XRF)
- Scanning Electron Microscopy (SEM)

3.2. Raw materials

The following raw materials were used during the experimental procedures.

The tantalite ore was mined in Mozambique, and supplied by Thuthuka Group Ltd, South Africa. All chemical reagents employed were of analytical grade. Dionized water was used in all aqueous preparations. 1-octanol and 2-octanol, ammonium biflouride, ammonium hydroxide, sulfuric acids were obtained from Merck Chemicals (Pty) Ltd and used without further purification.

3.3. Planning

The extraction and separation of tantalum and niobium from tantalite was investigated using 1-octanol and 2-octanol as extracting agents. The extraction is influenced by the decomposition process, the initial solution acidity, decomposition temperature, time of decomposition, the extracting agent, the stripping agent and the effect of precipitation. These variables were changed to see the effectiveness of the extraction.

3.4. Experimental methods

The aim of this research was to find optimum conditions for extracting and separating tantalum and niobium from Mozambican tantalite and produce tantalum oxide and niobium oxide containing as few impurities as possible starting with a typical tantalite concentrate. The selected processes to accomplish this are as follows:

- Tantalite ore was first crushed; the particle size distribution and its corresponding particle surface area were determined by Mastersizer 3000 analyzer using water as dispersant.

- Digestion or decomposition of the tantalite with ammonium bifluoride. An initial solution was prepared by melting the mixture of ammonium bifluoride and tantalite at different temperatures and times followed by leaching of the soluble component with water and separation of the solution by filtration. The acidity of the original solution was adjusted by adding an equal volume of sulfuric acid to the feed solution. This solution is used to extract the metal values of interest, i.e. niobium and tantalum, along with iron, aluminum and titanium as the major interfering elements.

- An equal volume of the organic solvent either 1-octanol or 2-octanol, was contacted with the filtrate from the leaching process. The solution was then stirred at different times and then left to separate. The solutions were separated using a separation funnel. Extraction was performed using a polypropylene beaker and a magnetic stirrer.

- The aqueous phase was analyzed by ICP-OES (Appendix A.1) and the organic phase was stripped by different stripping agents, e.g. water and sulfuric acid. Tantalum and niobium stripping was carried out at room temperature by shaking equal volumes of the loaded solvent with a suitable stripping solution.

- By neutralizing the niobium and tantalum strip solution using an ammonia solution, niobium and tantalum were completely precipitated and after calcination, niobium oxide and tantalum oxide were identified and quantified by XRD (Appendix A.3) and SEM (Appendix A.4).

3.4.1. The effect of time and temperature on the recovery of Nb and Ta

The effect of duration of decomposition and temperature on the percentage recovery of Nb and Ta was studied for a temperature between 200°C and 250°C at a stirring speed of 500 rpm and reaction time from 1 to 3 hours. All other conditions were kept constant. They were:

- 50 g of tantalite
- 1 500 kg of ammonium bifluoride
- 500 ml of distilled water.

3.4.2. Concentration of sulfuric acid

This variable was investigated by first adding to the leach solution a predetermined concentration of sulfuric acid from 2 M to 9 M. Equal volume of organic solvent (1-octanol or 2-octanol) and aqueous solution obtained after adjusting the acidity of leach solution were contacted for 2 minutes at various sulfuric acid concentrations from 2 M to 9 M. Liquid-liquid extraction was performed using a polypropylene beaker and magnetic stirrer. The organic phase and aqueous phase were separated in a separating funnel after mixing for a certain time. The aqueous phase was analyzed using the ICP-OES while the concentration of the organic phase was inferred from a mass balance. The distribution coefficient (α), separation coefficient (β) was then determined along with the extraction factor (%E).

3.4.3. Selection of stripping agent

Different stripping agents such as distilled water and sulfuric acid were used to strip niobium and tantalum from the loaded solvent. The stripping experiments were conducted at different contact time from 5 to 20 minutes and at an A/O (i.e. aqueous to organic) ratio of 1/1. The organic phase from the extraction process was washed with distilled water and then extracted with dilute sulfuric acid to obtain niobium by selective extraction or stripping. The aqueous phase takes up the complex fluoroniobate while the complex fluorotantale remains dissolved in the organic phase. The acidity of the aqueous phase niobium solution was adjusted and then contacted with 2-octanol to extract niobium. Tantalum and niobium were stripped from the organic phase with water or sulfuric acid. Aqueous ammonia was then added to the solution to precipitate niobium and tantalum.

3.4.4. Precipitation

A 28% of ammonium hydroxide (NH_4OH) was added to the pregnant solution from the stripping process, to precipitate niobium and tantalum. The precipitate was allowed to settle for one day and then filtered. The precipitate were washed with boiling distilled water and dried in an oven at 100℃. The dried precipitate was put in a porcelain crucible and then placed in the muffle furnace. Calcinations were done at 900°C for four hours. Niobium and tantalum pentoxide were obtained. The products were then characterized by XRD and SEM analysis.

CHAPTER 4 RESULTS AND DISCUSSION

This chapter presents the results and discussion of the decomposition process, extraction, stripping, precipitation and characterizations of the products. It also discusses further treatment required in order to produce a pure tantalum and niobium oxide.

4.1. Particle size analysis

The influence of mineral particle size of the raw material plays a major role in hydrometallurgical treatment process which cannot be neglected. The typical particle size distribution of the tantalite ore determined by a Mastersizer 3000 analyzer is shown in Figure 4.1. The volume weighted particle size mean is 18μm and it corresponds to a surface area of 66,070 m^2/g. Particle size was not included as an experimental variable. The particle size was kept constant, or as constant as the technique allowed.

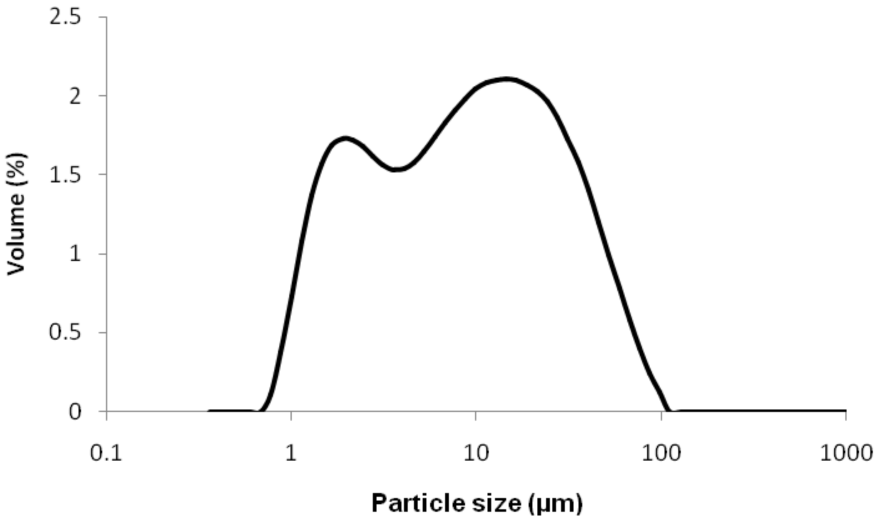


Figure 4.1. Particle size distribution of tantalite ore

4.2. Mineralogy of tantalite

For better understanding of the experiments presented in this dissertation, it is important to know the nature of the raw materials utilized, what compounds they consist of and what the characteristics and the values of these compounds are.

The mineralogical analysis of the ore sample was carried out by X-ray fluorescence (XRF) (Appendix A.2) and X-ray diffractometry (XRD) (Appendix A.3) analysis. The results of the XRF analysis are shown in Table 4.1 and it indicates that the sample is really a tantalite because it has more tantalum oxide (75.89%) than niobium oxide (4.72%) and also rich in iron oxide (15.09%). This mineral rich in tantalum and iron is called tantalite-(Fe) or ferrotantalite.

The mineral phase recorded by XRD analysis of the tantalite is provided in Figure 4.2. XRD analysis confirms that the main component in the ore sample is ferrotapiolite with small quantity of ferrocolumbite which have almost the same chemical composition as tantalite. Furthermore the XRF and XRD analysis showed the presence of associated minerals such as Fe_2O_3, TiO_2, MnO, etc.

Table 4. 1: Chemical composition of tantalite (XRF analysis)

Species	Percentage
SiO_2	0.37
TiO_2	1.26
Al_2O_3	0.1
Fe_2O_3	15.09
MnO	1.4
ZrO_2	0.12
SO_3	0.02
Cl	0.01
ZnO	0.03
Co_3O_4	0.02
HfO_2	0.11
Nb_2O_5	4.72
MoO_3	0.02
SnO_2	0.04
Ta_2O_5	75.89
OsO_4	0.04

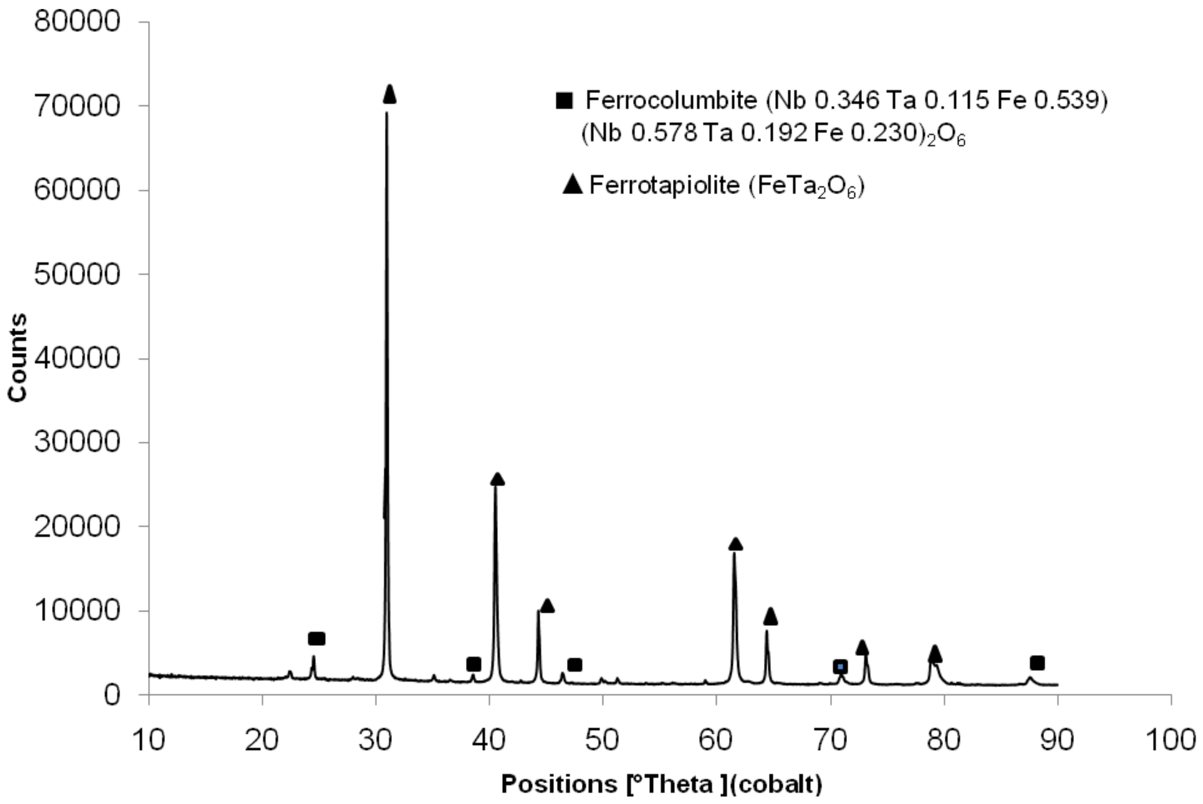


Figure 4.2: XRD pattern of tantalite

4.3. Preparation of the leach liquor

The decomposition process was performed by melting a mixture of ammonium bifluoride and tantalite ore.

For each experiment, ammonium bifluoride was first charged into the reactor and heated up to the dissolution temperature (230℃) and then the tantalite ore sample was added in the required amount. The mixture was then heated to the required temperature and kept there for the required time. After a given decomposition period the soluble components were leached with water and the insoluble component separated by filtration. The liquid sample was analyzed by ICP-OES to determine the content of niobium, tantalum, iron, titanium, etc. The produced pregnant solution has a pH of 3 and an assay of 32.82g/l of Ta_2O_5, 4.86g/l of Fe_2O_3, 2.51g/l of Nb_2O_5 and 2.43 g/l of TiO_2, after a leach period of 3 hours, at a ratio of tantalite ore-to-ammonium bifluoride of 1:30 and at decomposition temperature of 250℃.

4.4. Results of the decomposition experiments

The results are presented graphically in the paragraphs below. The variable ranges investigated were determined by values in the literature or by observations made during the preliminary experiments. The percentage of extraction was calculated from the concentration of niobium and tantalum present in the filtrate and the concentration reported in the feed solution.

The mass of niobium and tantalum present in the feed solution used during decomposition was calculated from Table 4.1. The mass of the metals present in the filtrate was also calculated from the concentration of niobium and tantalum present in the filtrate produced, analytically determined with the ICP-OES. The percentage extraction was then the mass of niobium or tantalum in the filtrate divided by the mass of the relevant metals present in the feed solution. All the experiments were repeated three times, the process error is below 4 percent and the percentage extraction reported are the average of three identical experiments in each case.

The following variables were investigated: time and temperature on the recovery of niobium and tantalum and the tantalite–to–ammonium bifluoride mass ratio.

4.4.1. Effect of time and temperature on the recovery of niobium and tantalum

The experimental conditions that were used to perform and evaluate time and temperature on the recovery of niobium and tantalum are described in section 3.4.1. The data are presented in Figures 4.3 and 4.4 for Nb and Ta, respectively. It can be seen that by increasing the temperature an increasing recovery of Nb and Ta was obtained, which was attributed to increase decomposition rate and diffusion of reactants and reaction products. The recovery of tantalum, niobium and other impurities such as titanium and iron did not change significantly when the decomposition temperature was increased from 250℃ to 300℃. It can also be seen that the recovery of Nb and Ta gradually improves with time. The highest extraction of 95.07% and 98.52% of Nb and Ta, respectively, was realized at 250℃ after 3 hours. A decomposition temperature of 250℃ and decomposition time of 3 hours are thus recommended. It was also reported in previous work, for all grade ore that increasing the decomposition time and temperature would increase the recovery of Nb and Ta significantly.

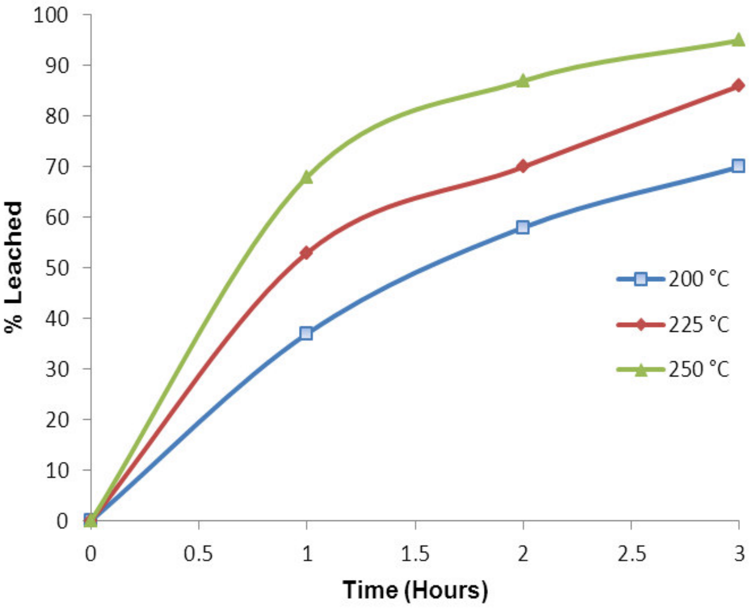


Figure 4.3: Effect of time and temperature on the recovery of niobium

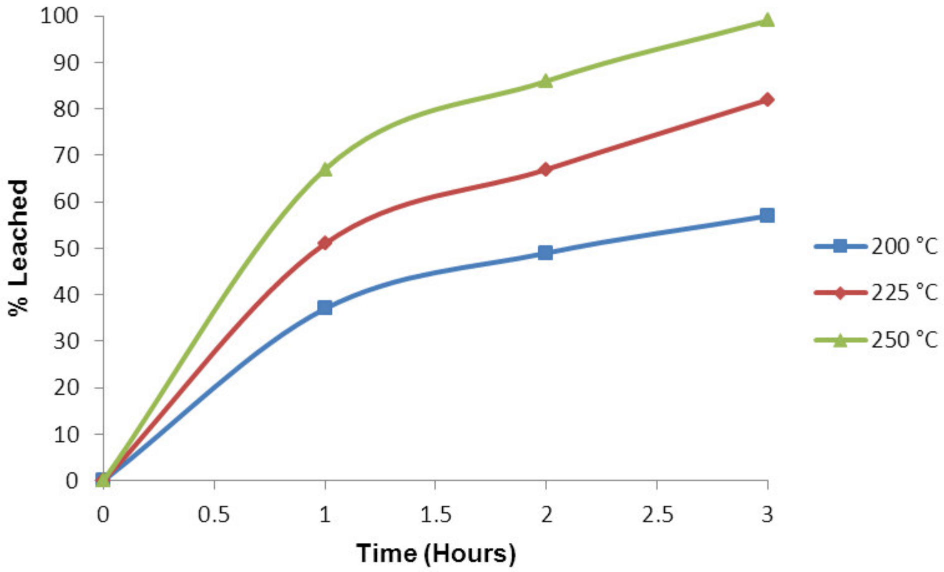


Figure 4.4: Effect of time and temperature on the recovery of tantalum

4.4.2. Effect of the mass ratio of tantalite-to-ammonium bifluoride

A set of experiments was carried out to examine the effect of the tantalite-to-ammonium bifluoride ratio. The experimental conditions were kept constant (500 ml of distilled water, 250℃, at a stirring speed of 500 rpm) as mentioned before while varying the tantalite-to-ammonium ratio from 1.0:20 to 1.0:50. The results are illustrated in Figure 4.5. From this result about 60% of titanium (IV) was leached. This foreign metal is one of the least separable from Ta and Nb but it can be removed by backwashing with 1.5-2 M H_2SO_4 at $V_o : V_{aq}$ of about (3.5-4.5):1 for Ta and with 5-10 M HF and 5-6 M H_2SO_4 at $V_o : V_{aq}$ = (3-4): 1 for Nb (Maiorov et al., 2001).

The percentage extraction of Ta, Nb, Fe and Ti increases up to a ratio of ~1:30, beyond which no further advantage is observed. This may be attributed to the fact that increasing the ammonium-to-tantalite mass ratio decreases the solid pulp density, and therefore decreases the mass transfer resistance in the liquid-solid interface. From this, an ammonium bifluoride-to-ore mass ratio of 1:30 was consequently regarded as the optimum value and considered as appropriate in this dissertation.

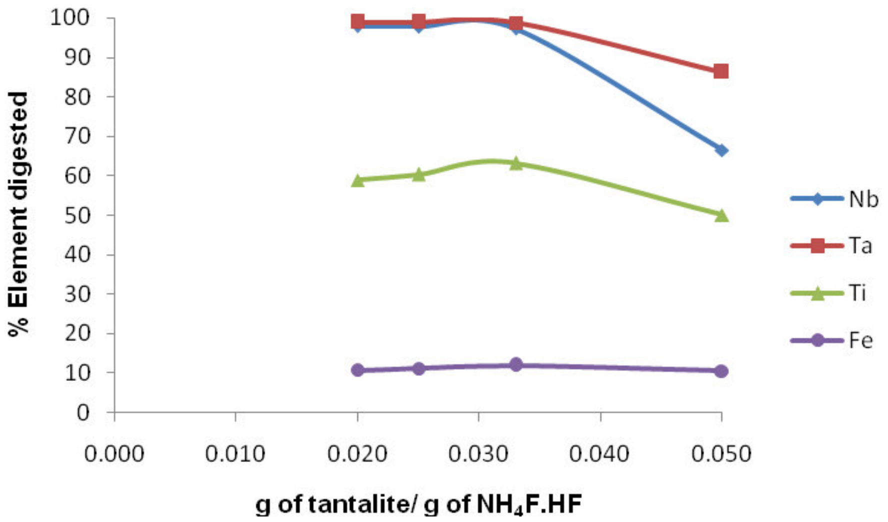


Figure 4.5: Effect of tantalite-to-ammonium bifluoride mass ratio (decomposition conditions: 3 hours, 250℃, 500 rpm)

As mentioned previously in section 3.4.2, different concentration of sulfuric acid was added to the leach solution. An equal volume of the mixture was then contacted with the organic solvent (1-octanol or 2-octanol). In this study the effect of contact time between the aqueous phase and organic solvent and the effect of sulfuric acid concentration were investigated. Consequently, the distribution and separation coefficients were determined along with the extraction efficiency.

4.4.3. Effect of contact time

The effect of contact time on the extraction efficiency of Nb and Ta by 2-octanol was studied over the time range of 2 to 15 minutes. A set of experiments was performed at different contact times at fixed conditions: an aqueous-to-organic (A/O) ratio of 1:1, 100% 2-octanol and with a feed solution concentration of 6 M for Ta extraction and 9 M for Nb extraction. As seen in Figure 4.6, optimum extraction efficiency is achieved after 5-10 minutes. Extending the time longer than 15 minutes did not significantly change the extraction efficiency. Therefore, a preferred contact time of 10 minutes is recommended.

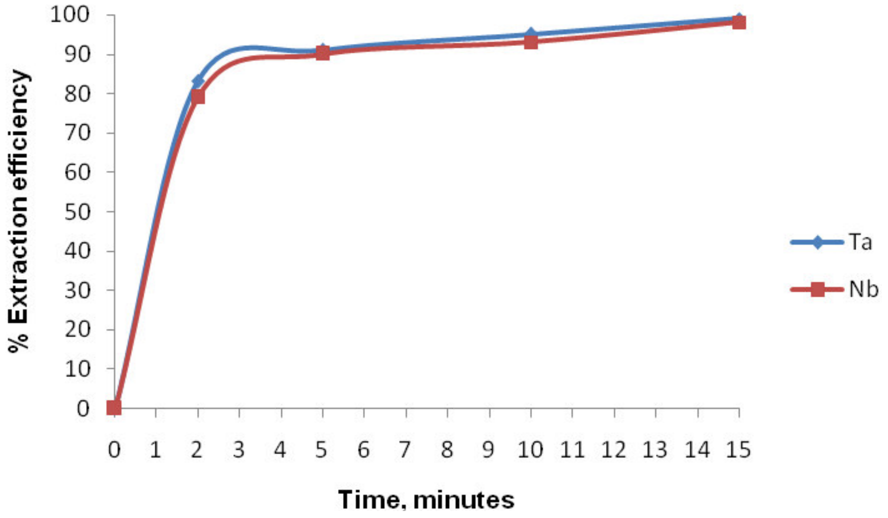


Figure 4.6: Effect of contact time on extraction efficiency of Nb and Ta

4.4.4. Concentration of sulfuric acid

As described in section 3.4.2, the effect of the concentration of sulfuric acid was evaluated by adding an equal volume of the aqueous phase to the organic phase. In Figure 4.7 and 4.8 the extraction efficiencies obtained by varying the amount of sulfuric acid concentration in the leach liquor solution which is contacted with the organic solvent are presented. The extraction efficiency of tantalum is higher than for niobium, and the extraction of both increases when the concentration of sulfuric acid increases. The extraction of tantalum increased from 93.1% to 99.6% with increasing H_2SO_4 concentration in the range of 2.0 to 5.0 M and from 55.2 % to 89.1% with increasing H_2SO_4 concentration in the range of 2.0 to 9.0 M H_2SO_4 for niobium with 1-octanol, (Figure 4.7). From 92.8% to 99.8% for tantalum with increasing H_2SO_4 concentration in the range of 2.0 to 6.0 M and from 55.5% to 89.2% for niobium with increasing H_2SO_4 concentration in the range of 2.0 to 9.0 M with 2-octanol, (Figure 4.8). Tantalum starts to move into solution at much lower acid concentration while niobium starts moving into solution only at higher concentration. As the extraction of both elements increased because of this reason, collective extraction can be done where both elements are in the organic phase at high concentration. However, a selective extraction was chosen in order to produce a product of higher purities.

Extraction of Nb and Ta with octanol has increased considerably on the introduction of sulfuric acid into the aqueous phase. It can also be seen that the extraction of tantalum and niobium with 2-octanol are almost similar to those with 1-octanol, as the literature also shows (Mayorov et al., 2002; Maiorov et al., 2001).The literature also show that the introduction of H_2SO_4 to the feed solution improve the extracting characteristics system with octanol considerably (Mayorov et al., 2002).

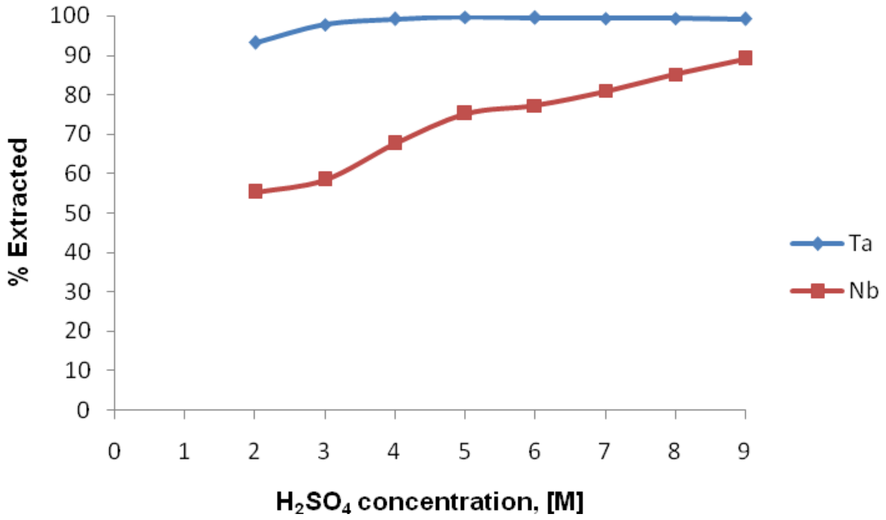


Figure 4.7: Effect of sulfuric acid concentration on Ta and Nb extraction by 1-octanol (error ± 0.04%) (A/O 1:1, 100% 1-octanol, 10 min).

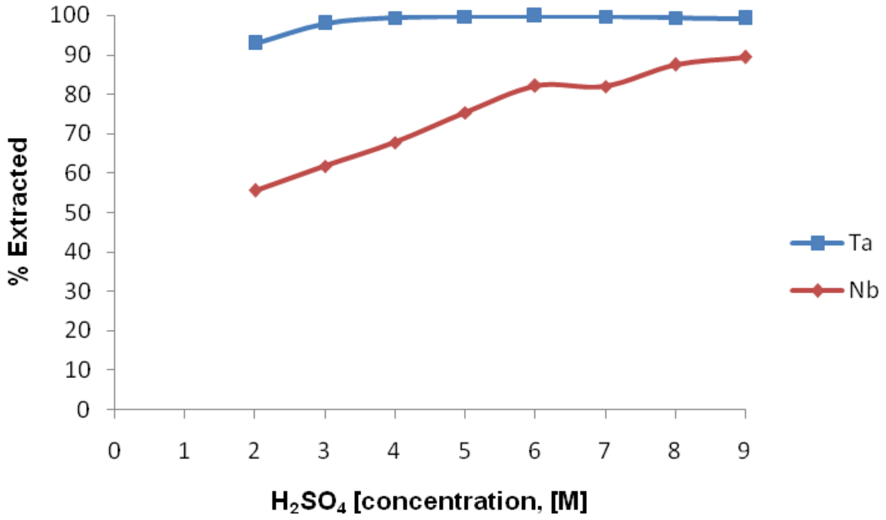


Figure 4.8: Effect of sulfuric acid concentration on Ta and Nb extraction by 2-octanol (error ± 0.04%) (A/O 1:1, 100% 2-octanol, 10 min).

4.4.5. Distribution and separation coefficient

The extraction of tantalum and niobium experiments were carried out by mixing 30 mL of the organic phase with an equal volume of aqueous phase, containing tantalum and niobium. Each mixture was shaken at room temperature (25°C) for about 10 minutes. The phases were then separated in a separating funnel.

Table 4.2 shows the 1-octanol results. The distribution coefficient of niobium increases with an increase of sulfuric acid concentration in the feed solution throughout the range investigated (from 2 M to 9 M). The distribution coefficient of tantalum on the other hand increases up to 5 M (sulfuric acid concentration), reaching a maximum, and then again decreases at higher acid concentrations. The separation factor also reaches a maximum at 5 M, indicating the optimal acid concentration for separation of niobium and tantalum.

The 2-octanol results in Table 4.3 show similar behavior, with the optimum shifted to a higher concentration of 6 M for Ta and 9 M for Nb. But in the work of Agulyansky et al., (2004) it was reported that a solution containing 2.5-3.5 M H_2SO_4 was optimal for Ta extraction while Nb begins to move into the organic phase at acidity level greater than that of 5 M. The difference could be attributed to the behavior of the ore in acid solution. The ore used in this study is different from the one used by Agulyansky and even the impurities attached to it which can react differently under acidic solution.

Table 4.2: Distribution-separation coefficient and extraction factor for 1-octanol with different H_2SO_4 concentrations

H_2SO_4(M)	α_{Ta}	α_{Nb}	β	E_{Ta} %	E_{Nb} %
2	16.952	1.460	11.614	94.429	59.343
3	52.711	1.794	29.378	98.138	64.212
4	167.753	2.421	69.378	99.407	70.765
5	250.183	2.995	83.533	99.602	74.969
6	246.944	3.612	68.349	99.577	78.322
7	216.477	4.288	50.483	99.540	81.090
8	157.333	5.722	27.498	99.368	85.123
9	126.478	7.368	17.166	99.216	88.050

Table 4. 3: Distribution-separation coefficient and extraction factor for 2-octanol with different H_2SO_4 concentrations

H_2SO_4	α_{Ta}	α_{Nb}	β	E_{Ta} %	E_{Nb} %
2	12.936	1.249	10.359	92.824	55.530
3	46.331	1.614	28.712	97.887	61.739
4	142.882	2.097	68.151	99.305	67.706
5	340.400	3.049	110.632	99.707	75.304
6	528.813	4.582	115.409	99.811	82.086
7	452.234	4.565	99.066	99.779	82.031
8	143.170	6.991	20.479	99.306	87.486
9	139.484	8.249	16.908	99.288	89.189

4.5. McCabe-Thiele analysis

4.5.1. McCabe-Thiele diagram for Ta extraction

Solvent extraction studies of niobium and tantalum with 2-octanol as a solvent from the NH_4.HF-H_2O system was carried out. After filtration of the insoluble residue, the aqueous solution of tantalum-niobium was extracted with the 2-octanol. The complex fluorides of niobium and tantalum were extracted with 2-octanol and the impurities like iron, manganese, titanium, etc., remained in the aqueous phase.

In order to determine the number of stages of extraction of Ta, a McCabe-Thiele diagram was constructed by plotting the equilibrium concentration data of Ta extraction in the organic and aqueous phases, followed by fitting a suitable operating line. The equilibrium data in Figure 4.9 was obtained at different A/O ratios using optimum extraction condition of 100% 2-octanol, 6M H_2SO_4, 10 minutes contact time at room temperature. From the McCabe-Thiele diagram for Ta, Figure 4.9, theoretically two stages are required for almost 99.7% Ta extraction from the feed solution. According to Agulyansky, (2004), for the collective extraction of Ta and Nb, 5 to 7 extraction stages are required. The difference could be attributed to the difference of concentration of niobium oxide and tantalum oxide in the sample ore. In the study by Agulyansky, (2004), the feed solution contain a concentration of 50-60g/l of Ta_2O_5 and 30 g/l of Nb_2O_5 while in this research the feed solution contain only 32.82 g/l of Ta_2O_5 and 2.51 g/l of of Nb_2O_5.

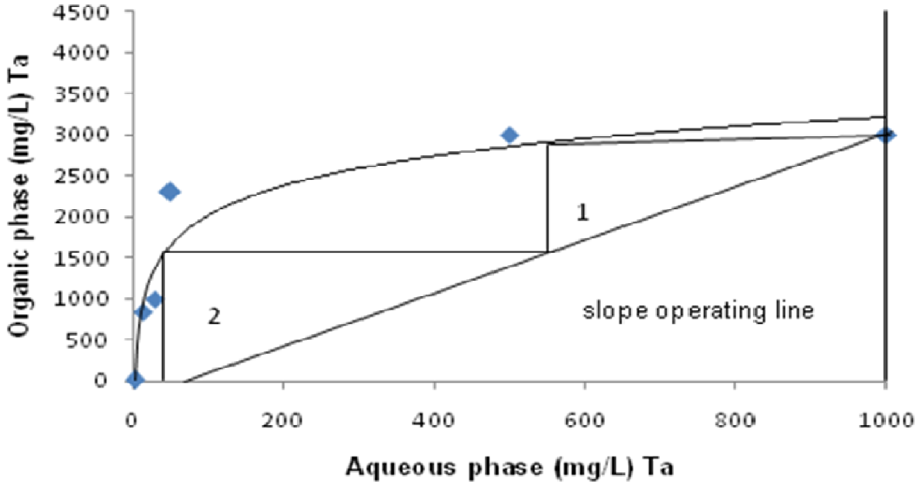


Figure 4.9: McCabe-Thiele diagram of Ta extraction (A/O 1:1, 100% 2-octanol, 10 min, 6 M).

In this thesis tantalum was extracted from the tantalite-$NH_4.HF$-H_2O solution at low sulfuric acid concentration. In order to remove traces of niobium from tantalum, distilled water and various concentrations of sulfuric acid were tested from 0.5 M to 2 M. According to this test, the concentration of 2 M sulfuric acid was chosen because this condition gave the maximum amount of niobium and tantalum, respectively, in the aqueous and organic phase. Then four stages of scrubbing of the tantalum-laden organic phase with 2-octanol can be used to reduce the amount of niobium contamination in tantalum. The aqueous phase takes up the complex fluoroniobate and free hydrofluoric acid, while the complex fluorotantalate remains dissolved in the organic phase. The pure tantalum in the form of H_2TaF_7 was then finally stripped.

4.5.2. Tantalum stripping

Different stripping agents were used to strip Ta from the tantalum-laden organic phase. These include distilled water and sulfuric acid. The experiments were carried out at room temperature by shaking equal volume of the tantalum-laden organic phase with a suitable stripping agent for the desired time. Different factors affecting the efficiency of stripping were studied. These include the stripping agent and its concentration and stripping time.

4.5.3. Effect of stripping agent

Different stripping agents such as distilled water and sulfuric acid with different concentrations (0, 5 and 1M) were used to strip Ta from the tantalum-laden organic phase. The tests were conducted at 15 minutes contact time and 1:1 A/O ratio. This test revealed that distilled water was the most efficient stripping agent of Ta from the tantalum-laden organic.

4.5.4. Effect of contact time

The effect of contact time on the stripping efficiency of Ta was studied over the time range of 2 to 15 minutes. A set of experiments were performed at different contact times at fixed conditions: A/O ratio of 1:1. From the results obtained in Figure 4.10 an optimum stripping efficiency is achieved after 15 minutes. A contact time of 15 minutes was then recommended.

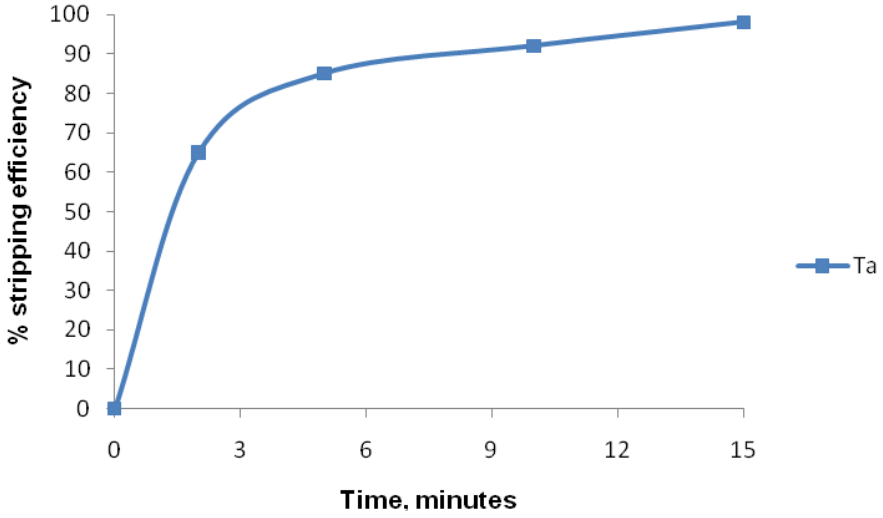


Figure 4.10: Effect of contact time on stripping efficiency of Ta

4.5.5. McCabe-Thiele diagram for Ta stripping

McCabe-Thiele diagrams were constructed in order to determine the number of steps needed to reach the desired separation. The data were obtained by shaking the tantalum-laden solvent with distilled water for 15 minutes using different A/O ratios. The diagram was constructed assuming these optimal operating conditions, as determined above. From the McCabe-Thiele diagram, theoretically four stripping stages are required for complete Ta stripping from the tantalum-laden solvent. Figure 4.11 shows the McCabe-Thiele diagram for Ta stripping. The stripping efficiency of our process is almost similar to that of Agulyansky (2004), who suggest that tantalum could be stripped from the loaded solution by 4 to 6 extractions stages.

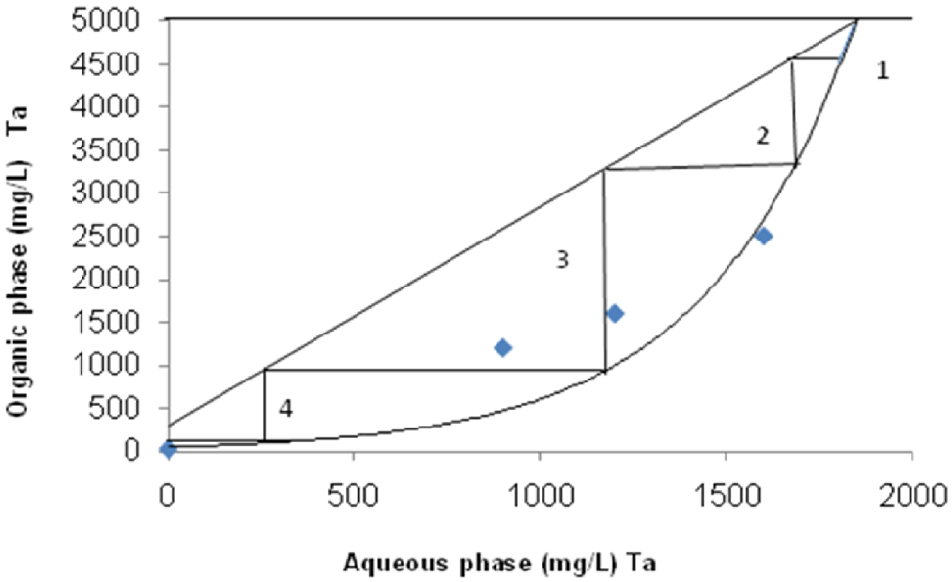
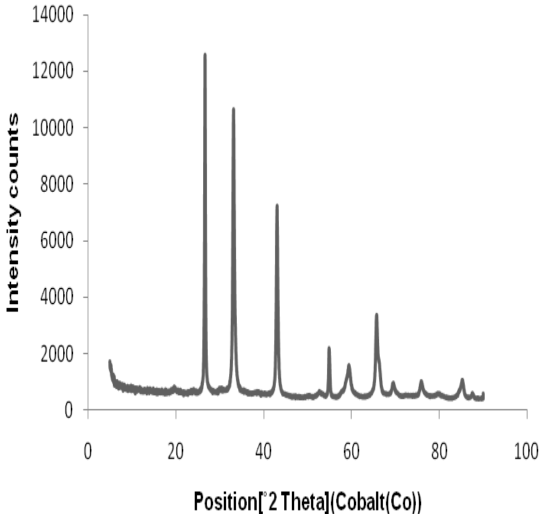


Figure 4.11: McCabe-Thiele diagram of Ta stripping

4.5.6. Ta precipitation

The precipitation of the tantalum oxide was done in a batch process. The tantalum strip solution was neutralized by adding 28% ammonium hydroxide (NH_4OH) solution to the strip solution. After filtration, the precipitates were washed with distilled water and dry in the oven at 100℃. The dried precipitates were then put in a porcelain crucible. The crucible was placed in the muffle furnace at 900℃ for 4 hours.

After calcinations, pure tantalum pentoxide was obtained and characterized using XRD and SEM analysis as shown in the following Figures 4.12, 4.13, 4.14 and 4.15.



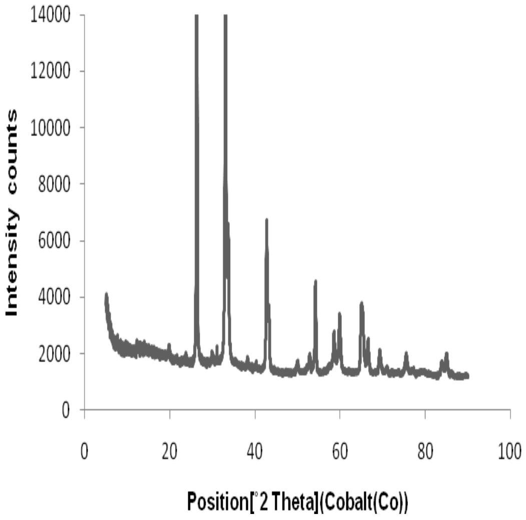
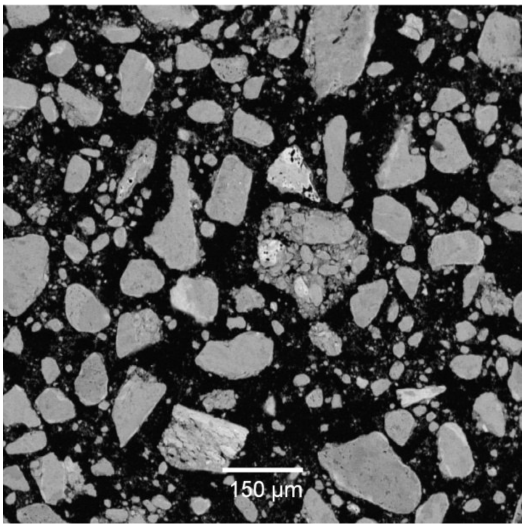


Figure 4.12: XRD pattern of synthesized Ta_2O_5

Figure 4.13: XRD pattern of purchased Ta_2O_5



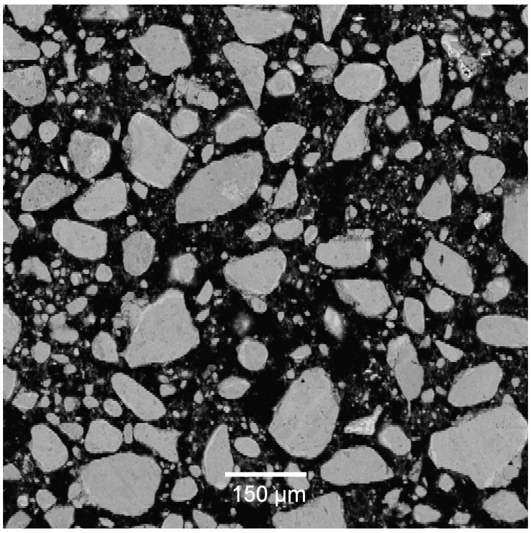


Figure 4.14: SEM result of synthesized Ta_2O_5

Figure 4.15: SEM result of purchased Ta_2O_5

The XRD patterns and SEM results of the synthesized and purchased products (Ta_2O_5) are shown in Figures 4.12, 4.13, 4.14 and 4.15, respectively. It can be seen that the XRD patterns of synthesized and purchased products (Ta_2O_5) are similar. An XRD pattern indicates that no other elements are presents except Ta_2O_5. The SEM results indicate the presence of traces of iron and titanium and this may be attributed to the excess of this oxide in the ore which was not removed completely during the extraction process. To obtain higher quality tantalum pentoxide, additional process may be needed.

For the removal of the last traces of iron and titanium, an intermediate treatment of the hydrated oxide precipitate with concentrated HCl can be incorporated (Damodaran et al., 1969).

4.6. McCabe-Thiele diagram for Nb extraction

After separation of tantalum and niobium by scrubbing the solution with 2 M H_2SO_4, the aqueous phase takes up the complex fluoroniobate. The pH of the niobium containing solution was adjusted by mixing the solution with 9 M H_2SO_4 for solvent extraction. The aqueous solution was then contacted with fresh octanol to extract niobium.

A McCabe-Thiele diagram was constructed by plotting the equilibrium concentration data of Nb extraction in the organic and aqueous phases. The equilibrium data in Figure 4.16 was obtained at different A/O ratios using optimum extraction condition of 100% 2-octanol, 10 minutes contact times, 9 M H_2SO_4 at room temperature. From the McCabe-Thiele diagram for Nb in Figure 4.16 it can be seen that three theoretical equilibrium stages are required for 93.6% Nb Extraction.

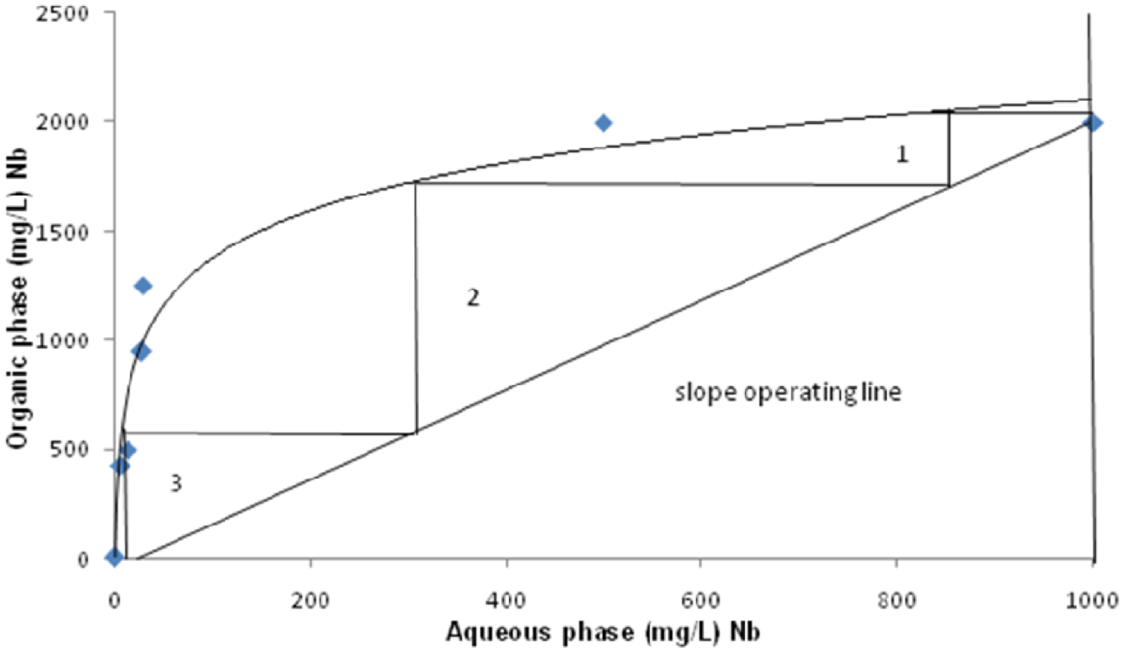


Figure 4.16: McCabe-Thiele diagram of Nb extraction(A/O 1:1, 100% 2-octanol, 10min, 9M)

The organic phase rich in niobium pregnant solution was obtained and stripped with different stripping agent.

4.6.1. Niobium stripping

Different stripping agents were used to strip Nb from the niobium-laden organic phase. These include distilled water and H_2SO_4. The stripping experiences were carried out at room temperature by shaking equal volumes of the niobium-laden organic phase with a suitable stripping agent for the desired time. Different factors affecting the efficiency of stripping were studied. These include stripping agent and its concentration, and stripping time.

4.6.2. Effect of stripping agent

Different stripping agents such as distilled water and sulfuric acid with different concentrations (1 M to 5 M) were used to strip the Nb from the niobium-laden organic phase. The tests were conducted at 10 minutes contact time and 1:1 A/O ratio. According to this test distilled water was the most efficient stripping agent of Nb from the niobium-laden organic.

4.6.3. Effect of contact time

The effect of contact time on the stripping efficiency of Nb was studied over the time range of 2 to 15 minutes. A set of experiments were performed at different contact time at fixed conditions: A/O ratio of 1:1 and H_2O. From the results obtained an optimum stripping efficiency is achieved after 15 minutes. A contact time of 15 minutes was then recommended.

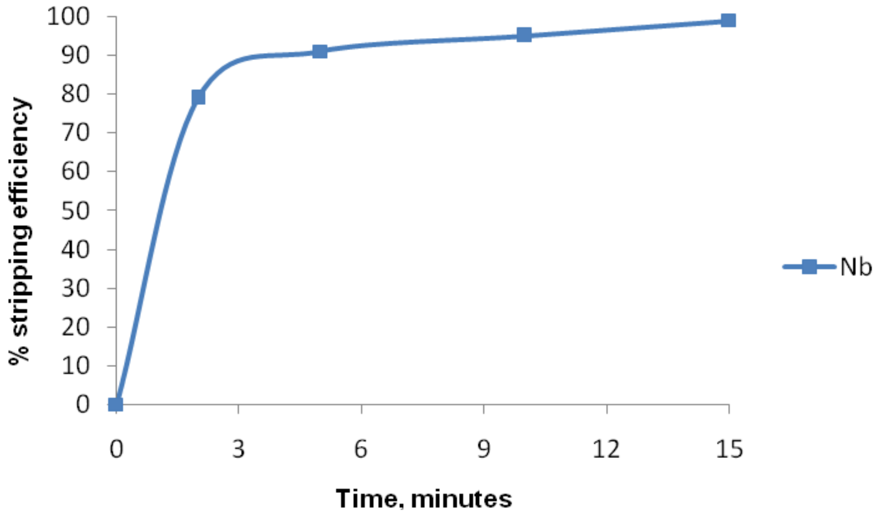


Figure 4.17: Effect of contact time on stripping efficiency of Nb

4.6.4. McCabe-Thiele diagram for Nb stripping

The data points were obtained by contacting metal-rich solvent with water for 15 min, using different A/O ratios.

From the McCabe-Thiele diagram in Figure 4.18, theoretically four stripping stages are required for almost complete Nb stripping from the loaded solvent.

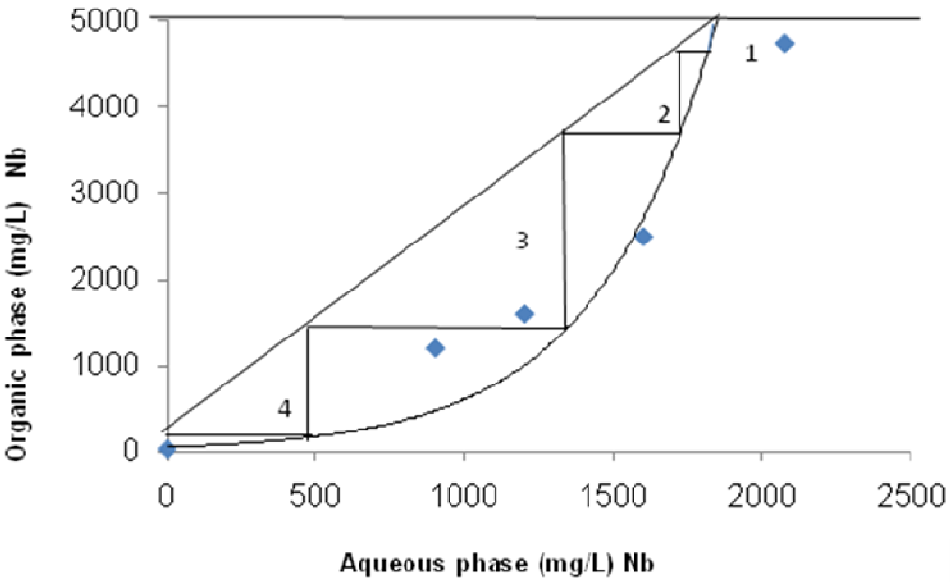


Figure 4.18: McCabe-Thiele diagram of Nb stripping

4.6.5. Nb precipitation

Precipitation of niobium pentoxide was done in a batch process. The niobium strip solution was neutralized by adding 28% ammonium hydroxide (NH_4OH) solution to the strip solution. After filtration, the precipitates were washed with distilled water and dry in the oven at 100℃. The dried precipitates were then put in a porcelain crucible. The crucible was placed in the muffle furnace at 900℃ for 4 hours. After calcinations, pure niobium pentoxide was obtained and characterized using XRD, and SEM as shown in different Figures 4.19, 4.20, 4.21, and 4.22. A general flow sheet for treating tantalite by the ammonium-octanol process is proposed and represented in Figure 4.23.

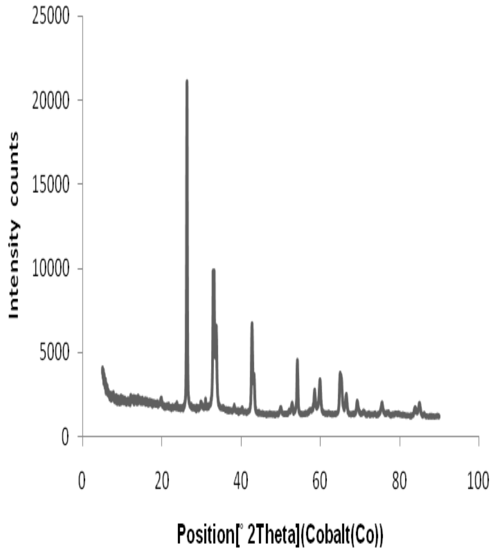


Figure 4.19: XRD pattern of synthesized Nb_2O_5

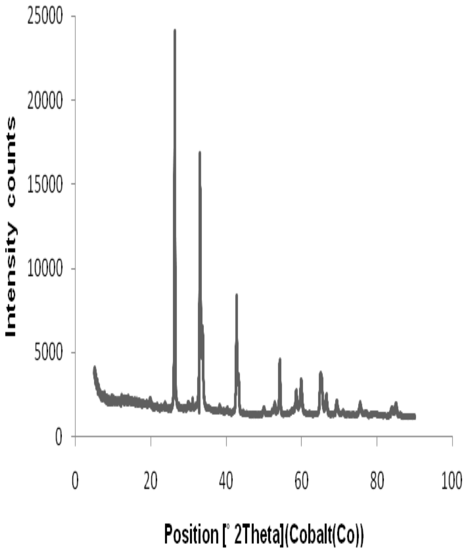


Figure 4.20: XRD pattern of purchased Nb_2O_5

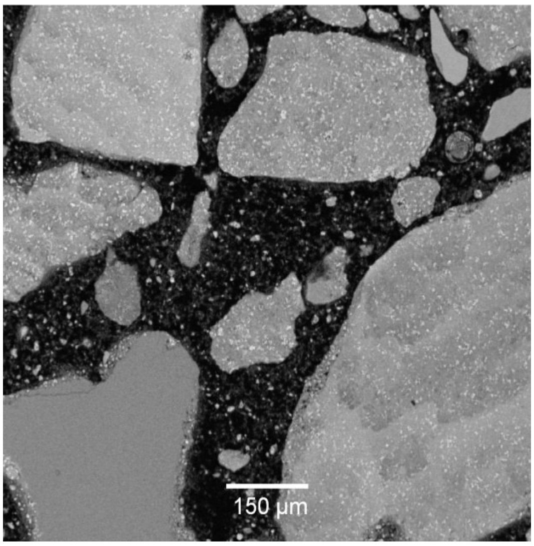


Figure 4.21: SEM result of synthesized Nb_2O_5

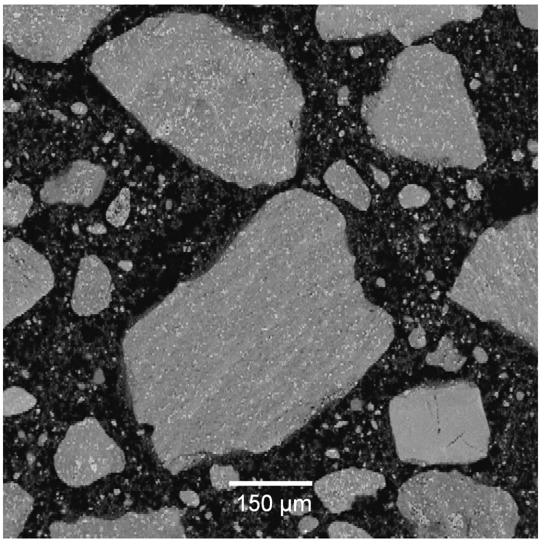


Figure 4.22: SEM result of purchased Nb_2O_5

The XRD patterns of the synthesized and purchased product (Nb_2O_5) are almost similar. An XRD pattern indicates traces of titanium and tantalum. According to Maiorov et al., (2001) titanium can be removed from niobium by backwashing. By stripping niobium with water it is possible to remove tantalum completely from niobium by increasing the number of steps. In order to remove the impurities completely, a HCl digestion could be necessary.

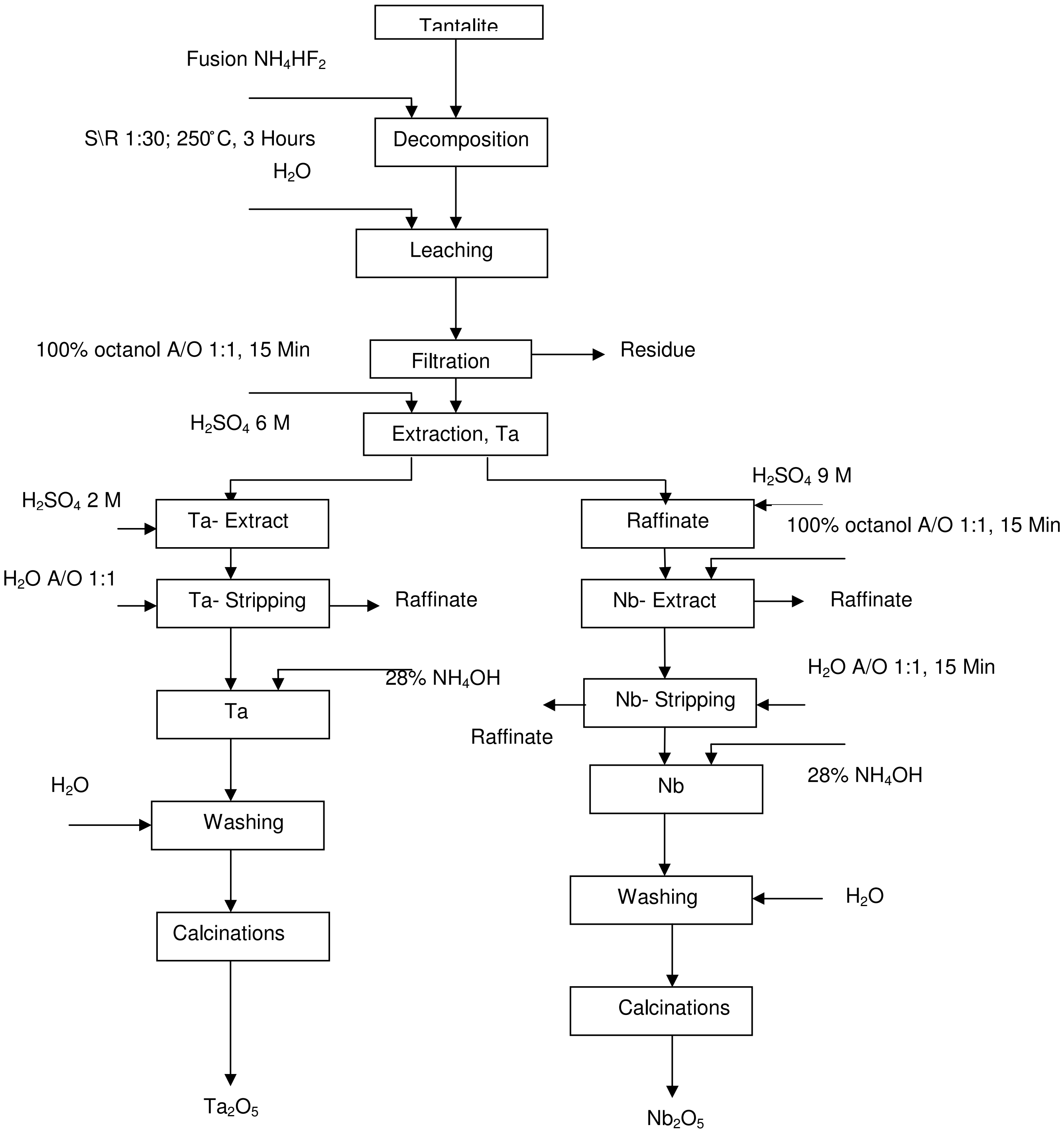


Figure 4.23: Proposed technical flow sheet for the extraction of Nb/Ta.

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The aim of this research was to extract and separate niobium and tantalum with octanol as solvent, from Mozambican tantalite using ammonium bifluoride as an alternative to hydrofluoric acid. The specific objectives were: 1) To determine if ammonium bifluoride can be used as an alternative to hydrofluoric acid in the decomposition process, determine the time and temperature for efficient recovery of niobium and tantalum and also the mass ratio between tantalite and ammonium bifluoride. 2) To investigate the effect of sulphuric acid concentration in the feed solution and the effect of different stripping agents. 3) To compare the performance of extraction between 1-octanol and 2-octanol. 4) To characterize the niobium and tantalum pentoxide and compare to the purchased product.

Ammonium bifluoride can be used successfully for the decomposition of Mozambican tantalite. The leach liquor prepared in this way is of consistent concentration and Ta and Nb can be extracted successfully using octanol as extractant. This process present some advantage compared to HF. Firstly the cost could be reduced because of the availability of ammonium bifluoride in South Africa and secondly could prove easier to handle compare to aqueous hydrofluoric acid.

From the experiment results it was observed that the increase of time and temperature was effective in increasing the leach recovery of Nb and Ta. The highest recovery was realized at 250℃ after 3 hours. By varying the tantalite-to-ammonium mass ratio, the percentage extraction increases for both Nb and Ta up to a ratio of 1:30, beyond this no further advantage was observed.

The introduction of sulfuric acid improved considerably the extraction efficiency of Nb and Ta with octanol. Tantalum starts to move into solution in the range of 2.0 to 6.0 M with highest percentage of extraction of 99.7% at 6.0 M with feed contacted with 2-octanol. Nb starts moving into solution at high sulfuric acid concentration. The highest value of extraction was 89.2% for 9.0 M sulfuric acid.

The performance of extraction of 1-octanol and 2-octanol was almost similar, as the literature also shows.

Mc-Cabe-Thiele diagrams of Nb and Ta extraction were constructed using optimum conditions: A/O of 1:1, 100% 2-Octanol, 10 minutes contact time and 6 M sulfuric acid concentration and A/O of 1:1, 100% 2-octanol, 10 minutes contact time and 9 M sulfuric acid concentration respectively for Ta and Nb extraction. The results show that two and three theoretically numbers of stages were observed respectively for Ta and Nb.

The Mc-Cabe-Thiele diagram of Nb and Ta stripping was also constructed using the following optimum parameters: A/O 1:1, H_2O as stripping agent and 15 minutes contact time. It can be concluded that four theoretically stripping stages are sufficient to strip Ta and Nb from the organic phase.

It was also observed that distilled water was the most efficient agent, compared to sulfuric acid, for stripping both Nb and Ta from the niobium and tantalum-laden organic phase.

After precipitation and calcination tantalum and niobium pentoxide with fewer impurities such as iron and titanium were obtained as characterized by XRD and SEM analysis. In order to obtain a pure product it is therefore necessary to incorporate an intermediate treatment.

5.2. Recommendations

The following recommendations are suggested for further investigations which could help the extraction and separation of niobium and tantalum from Mozambican tantalite by solvent extraction in the ammonium bifluoride-octanol system to be used efficiently.

- Further processing is necessary in order to produce a high purity tantalum and niobium pentoxide suitable for electronics industries for manufacturing capacitors, superconductivity and other specific applications.
- The economic aspects must be evaluated from the flow diagram.

REFERENCES

- Amuda, M.O.H, Esezobor, D.E, and Lawal, G.I (2007) “Adaptable technology for life-cycle processing of tantalum bearing minerals” Journal of Minerals & Materials Characterization & Engineering, vol.6, no.1, pp 69-77.

- Agulyansky, A (2004) *The chemistry of Tantalum and Niobium Fluoride compounds,* Elsevier, Amsterdam.

- Agulyansky, A, Ludmila, A and Viktor F. T (2004) “Liquid–liquid extraction of tantalum with 2-octanol” *Chemical Engineering and Processing*: *Process Intensification,* vol 43, no 10, pp. 1231-1237.

- Aprill, U and Richard L.D (2005) *Methods of Soil Analysis*, Madison, Wisconsin, U.S.A.

- Baba, A.A, Adekola, F.A, and Faseki, M(2005) “ A study of the kinetics of the dissolution of a Nigerian tantalite ore in hydrochloric acid” *Ife Journal of Science*, vol. 1, no 2, 221-227.

- Babkin, A.G, Mayorov, V.G, Nikolaev, A.I, (1988) “The Extraction of Niobium, Tantalum and other Elements from Fluoride Solutions” *Nauka,Leningrad* 204 pp.

- Bennett H and Graham J. O (1992) *XRF Analysis of Ceramics, Minerals and Allied,* John Wiley & sons, New York, U.S.A.

- Bludssus, W and Eckert, J (1993) “Process for the recovery and separation of tantalum and niobium”, *US Patent 5209910,* assigned to Hermann C. Starck Bertin, Berlin DE.

- Bose, D.K and Gupta, C.K (2001) “Extractive metallurgy of tantalum” *Mineral Processing and Extractive Metallurgy Review*, 22, pp 389-412.

- Cardon, P.B (1962)” Process for recovering niobium and tantalum from ores and ores concentrates containing same”, *U.S. Patent 3058825.*

- Charles B. B and Kenneth J. F (1997) *Concepts, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry*, Perkin Elmer second edition, U.S.A.

- Clive, W (1987) *X-ray Methods*, John Wiley and sons, New York, U.S.A.

- Coulson J.M and Richardson’s (1996) *Chemical Engineering,* Butterworth Heineman, vol 2, 287, Oxford.

- Coulson J.M and Richardson’s (2002) *Chemical Engineering*, Butterworth Heineman, Vol.2.5th Edition, oxford.

- Damodaran, A.D, Deshpande, S.G, Majmudar, A.A and Sastri, M.S (1969) “Extraction and utilization of pure niobium and tantalum from Indian ores” *Bhabha Atomic Research Center,* Trombay, Bombay, vol. 36, No.5, pp. 306-318.

- Eastell, J and Willis, J. P (1990) “A low dilution fusion technique for the analysis of geological samples” *X-RaySpectrometry*, 19, 1–14.

- Eckert, J, (1995)” Hydrometallurgical processing of Ta/Nb compounds”, Present state of the art. Proceeding of International Symposium on Tantalum and Niobium, Germany. *Tantalum-Niobium International Study Center, Belgium*, pp. 55 – 64.

- El-Hussaini, O.M. and Mahdy, M.A. 2002. Extraction of niobium and tantalum from nitrate and sulphate media by using MIBK. Minerals Processing and Extractive Metallurgy Review 22, (4-6) 633-650.

- El-Hussaini, M.O and Rice, M .N (2003) “liquid-liquid extraction of Niobium and tantalum from aqueous sulphate/fluoride solution by tertiary amine” *hydrometallurgy,* vol 72, no 3-4, pp 259-267.

- Fathi H (1997) *Handbook of Extractive Metallurgy*, volume III, Quebec, Canada.

- Foos, R.A (1960) “Recovery of columbium values”, *U.S. Patent 2953453*, assigned to Nat Distillers Chem Corp.

- Gibalo, I.M (1970) *Analytical Chemistry of Niobium and Tantalum*, Ann-arbor, London.

- Giulio, M, Pierfrancesco, R.I, Francesco, M, Luca, R, Paolo, F.M and Carlo, F (2009) " An overview about biomedical applications of micron and nano size" *Benthan science*, vol 3, No 3, 157-165.

- Gupta C.K, Mukherjee T.K (1990) *Hydrometallurgy in Extraction Processes*, CRC Press, Boca Raton, Florida, USA.

- Gupta, C.K (1994) *Extractive Metallurgy of Niobium, Tantalum and Vanadium,* CRC Press, Boca Raton, Florida, USA.

- Gupta, C.K and Suri, A.K (1994) in: *Extractive Metallurgy of Niobium*, CRC Press, Boca Raton, Florida, USA.

- Gupta, C.K (1984) "Extractive metallurgy of niobium, tantalum, and vanadium" *International Metals Reviews*, 29, pp 405-444(40).

- He, C, Liu, Z and Zhang, H (1998) "Treatment of fluorine-containing waste gas from hydrometallurgy of tantalum and niobium ore" *Nonferrous Metals* 50(4), 141-142.

- Hearle, J.W, Sparrow, J.T and Cross, P.M (1974).*The Use of the Scanning Electron Microscopy,* Pergamon Press, New York.

- Hutton, J, T. and Elliott, S. M (1980) "An accurate XRF method for the analysis of geochemical exploration samples for major and trace elements using one glass disc" *Chemical Geology*, 29, 1–11.

- James R.C (2007) “Introduction to X-ray Powder Diffraction”, available at http://epswww.unm.edu/xrd/xrdclass/01-XRD-Intro.pfd (accessed on 08 November, 2011).

- Joachim E, Karlheinz R, Christoph S and Hady S, sa, “Processing of columbite-tantalite ores and concentrates for niobium and niobium compounds in electronic applications” Germany, H.C. Starck GmbH and Co. KG. Available at www.cbmm.com.br (accessed 01.11.2011).

- Joseph, I.G, Dale. E.N, Patrick, E, David, C.J, Charles, F, Eric , L (1981) *Scanning Electron Microscopy and X-ray Microanalysis*, Plenum Press, New York.

- Krismer, B, Hoppe, A (1984)”Process for the recovering niobium and /or tantalum compounds from such ores further containing complexes of uranium, thorium, titanium and/or rare earth metals”, *U.S. Patent 4446116,* assigned to Hermann C. Starck Bertin, Berlin DE.

- Loubser, M and Verryn (2008) “Combining XRF and XRD analyses and sample preparation to solve mineralogical problems” *South African Journal of Geology*, vol.111, 2-3, pp.229-238.

- Maina, N.S., Ameh, A.O. and Orkuma, H.H (2007) “Leaching of Tantalum and Niobium from Tantalite ore in aqueous media” *Chemclass Journal* vol 4, 19-28.

- Mayorov, V.G. and Nikolaev, A.I (2002) "Tantalum (V) and niobium (V) extraction by octanol" *Hydrometallurgy,* vol. 66, no. 1-3, pp. 77-83.

- Maiorov V.G, Nikolaev A.I, and Kopkov V.K (2001) “Extraction Recovery of Tantalum (V) and Niobium (V) from hydrofluoric and hydrofluoric- sulfuric acid aqueous solutions with Octanol” *Russian Journal of Applied Chemistry* vol 74, no 4, pp 357-360.

- Moore, G.L (1989) *Introduction to Inductively Coupled Plasma Atomic Emission Spectrometry*, Elsevier, New York, U.S.A.

- Morrison, G.H and Freiser, H (1957) *Solvent Extraction in Analytical Chemistry*, New York, U.S.A.

- Ritcey.G.M and Ashbrook.A.W (1984*) Solvent Extraction Principles and Applications to Process Metallurgy*, Part 1; Elsevier, Amsterdam.

- Robert H. Perry and Don W. G (2007) *Perry’s Chemical Engineers’ Handbook*, seventh edition, McGrall-Hill, New York.

- Rydberg, J, Michael C, Claude M, Gregory R. C (2004) *Solvent Extraction Principles and Practice*, second edition, revised and expanded, New York, U.S.A.

- Sean,P, Arza, S, Michalina ,B, Kellsee C, Stephanie, A (2007) “Tantalum and tantalum compounds”, In Kirk-Othmer Encyclopedia of Chemical Technology, fourth edition, vol 24, John Wiley & Sons, New Jersey.

- Sudderth, R.B. and Kordosky, G.A (1986)"Some Practical Considerations in the Evaluation and Selection of Solvent Extraction Reagent" *Chemical Reagent in the Mineral Processing Industry*. Ed Malhotra and Riggs. S.M.E. Littleton Colorado. 181-196.

- TIC (2009) "Niobium and tantalum –raw materials and processing", Available at <http://www.tanb.org (accessed on 28, February, 2011).

- Thompson, M. J and Nicholas W (1989) *Handbook of inductively coupled plasma*, Chapman and Hall, New York, U.S.A.

- Ulman F, Gerhartz W and Elvers B (1988) *Ullmann's Encyclopedia of Industrial Chemistry*, 5th edition, B3: Unit Operations 2, 6-45.

- Wang, X., Shili, Z., Hongbin, X., Yi. Z., (2009). Leaching of niobium and tantalum from low-grade ore using a KOH roast-water leach system. *Hydrometallurgy* 98, 219-223.

- Zelikman, A.N, Orekhov, M.A (1965) "Decomposition of tantalum concentrates by sodium and potassium hydroxides at increased temperatures and pressures" *Izvestia Akademii Nauk SSSR*. Metally 6, 38 -45.

- Zhu, Z., Cheng, C.Y., 2011. Solvent extraction technology for the separation and purification of niobium and tantalum: A review. *Hydrometallurgy* 107 (1-2), 1-12.

- Zhou, H., Zheng, S., Zhang, Y., 2005. Leaching of a low-grade niobium–tantalum ore by highly concentrated caustic potash solution. *Hydrometallurgy* 80(1-2), 83-89.

APPENDICES A

A.1 INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY (ICP-OES)

THE THEORETICAL BACKGROUND

The inductively coupled plasma optical emission spectrometry is an effective source of atomic and ionic emission which can be used predominantly for quantitative multi-elements analysis of most types of samples except argon and helium. It is an ideal technique which allows the analysis of both major and trace element from single sample due to it high dynamic range. Certain elements cannot conveniently be determined using an ICP-OES without additional specific modifications to the instruments (Charles et al., 1997). .

In ICP-OES, the sample is usually transported into the instrument as a stream of liquid. Inside the instrument, the liquid is converted into an aerosol through a process known as nebulization. The sample aerosol is then transported to the plasma where it is desolvated, vaporized, atomized, and excited and/or ionized by the plasma. The excited atoms and ions emit their characteristic radiation which is collected by a device that sorts the radiation by wavelength. The radiation is detected and turned into electronic signals that are converted into concentration information for the analyst. A representation of the layout of a typical ICP-OES instrument is shown in Figure A.1 (Charles et al., 1997).

An ICP-OES system is comprised of the following components (Figure A.1):

- A sample introduction system, which houses a nebulizer, peristaltic pump, spray chamber and drains;
- A torch and radio frequency generator;

- The transfer optics;
- Spectrometer and detectors;
- Signal processing and instrument control system;
- Additional accessories, such as autosamplers, samples introduction accessories and hybrid generation unit.

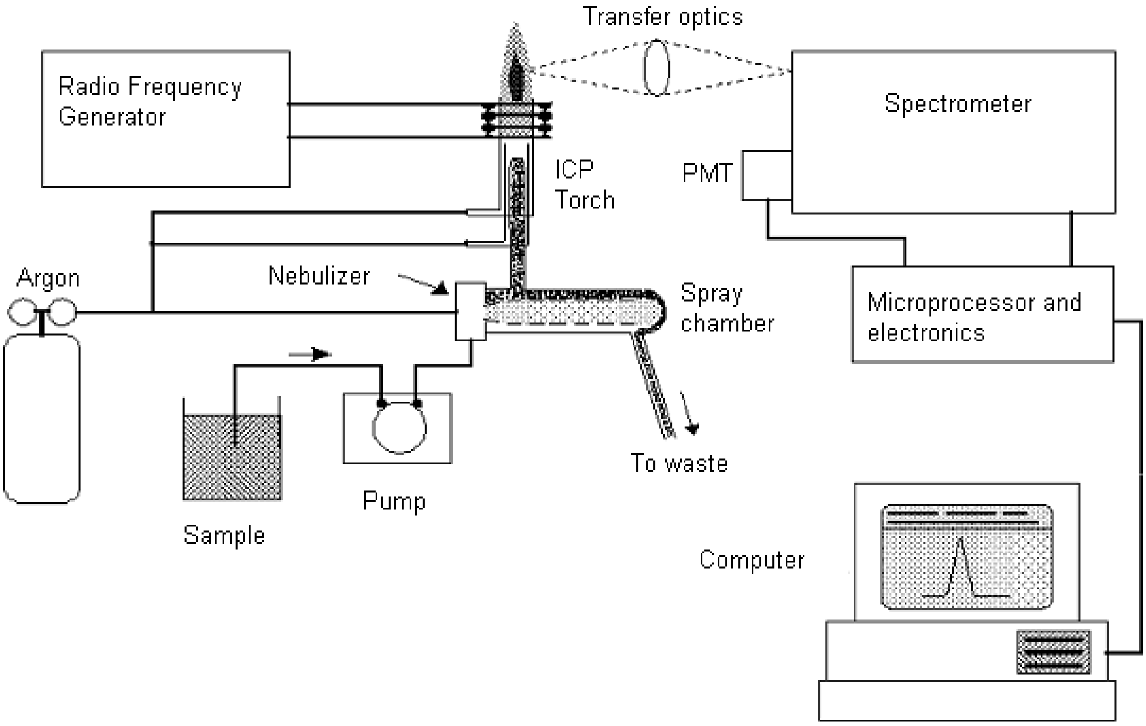


Figure A.1: Major components and layout of a typical ICP-OES instrument (adapted from Charles et al., 1997)

THE VARIOUS COMPONENT OF AN ICP-OES

Sample introduction

The sample introduction system consists of a nebulizer to aspirate sample that have been pumped through peristaltic pump, a spray chamber which removes large droplets from the aerosol and a drain which carries the excess of sample from the spray chamber to a waste container.

Peristaltic pump

The sample solution is transported by peristaltic pump through the tubing using a process known as peristalsis to the nebulizer' sample inlet connection. The pump used must be compatible with weakly acidified aqueous media. Proper tubing made of specific materials is usually required for strongly acidic solutions or organic solvents (Charles et al., 1997). By using a peristaltic pump it is possible to control and prevent a steady stream of sample which is being delivered to the nebulizer. Peristaltic pump must be frequently replaced to avoid permanent depressions in the tubing. This aspect can compromise the performance of the instrument. Figure A.2 shows the peristaltic pump used for ICP-OES.

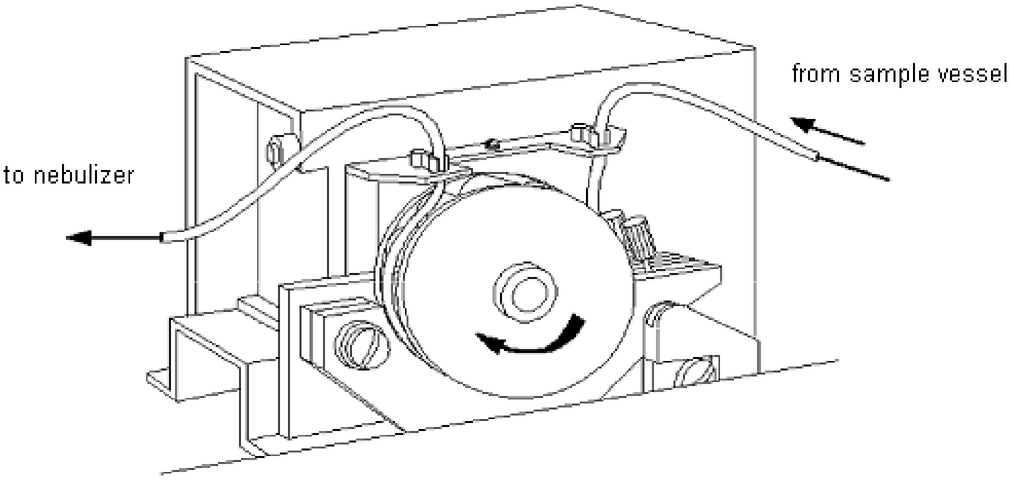


Figure A.2: Peristaltic pump used for ICP-OES (adapted from Charles et al., 1997**)**

Nebulizers

There is general agreement that sample introduction into the ICP is critical. Most samples pump into the ICP is in the liquid form which is converted to a fine aerosol. The smallest droplets (generally less than 10 μm in diameter) are transported to the plasma by the injector gas and the largest droplets are removed in the spray chamber (Moore et al., 1989; Thompson et al., 1989; Charles et al., 1997)

There are two main types of nebulizers: pneumatic and ultrasonic. Pneumatic nebulization is the most widely used method for introducing samples into the ICP. It uses a high speed gas flow to create an adequate aerosol from the introduced sample. Different types of pneumatic nebulizer are in use. The concentric, cross flow and Bablington types are most commonly used (Moore et al., 1989; Thompson et al., 1989; Charles et al., 1997).

In an ultrasonic nebulizer, the sample is pumped into a vibrating piezoelectric transducer (1 to 10 MHZ), which breaks the sample in a fine aerosol. The sensitivity of this nebulizer can be up to 4 times higher than the pneumatic type. Ultrasonic nebulizers suffer from poor long-term stability, and their performance is influenced by the change in the operational parameters. The advantage of this type is that the detection limits are in order of magnitude lower than those normally obtained by pneumatic nebulizers (Moore et al., 1989).

Spray chamber

The spray chamber classifies the aerosol droplets and determines the sizes of droplets that will pass into excitation source. Only small droplets in the aerosol are suitable for injection into the plasma. The main purpose of a spray chamber is to remove the larger droplets from the nebulizer, which are condensed and run to waste. An ideal spray chamber will have the best separation capabilities and the shortest memory effect for the particulars samples to be analyzed. The most widely used spray chamber is of the single pass or double passes (Moore et al., 1989; Thompson et al., 1989; Charles et al., 1997).

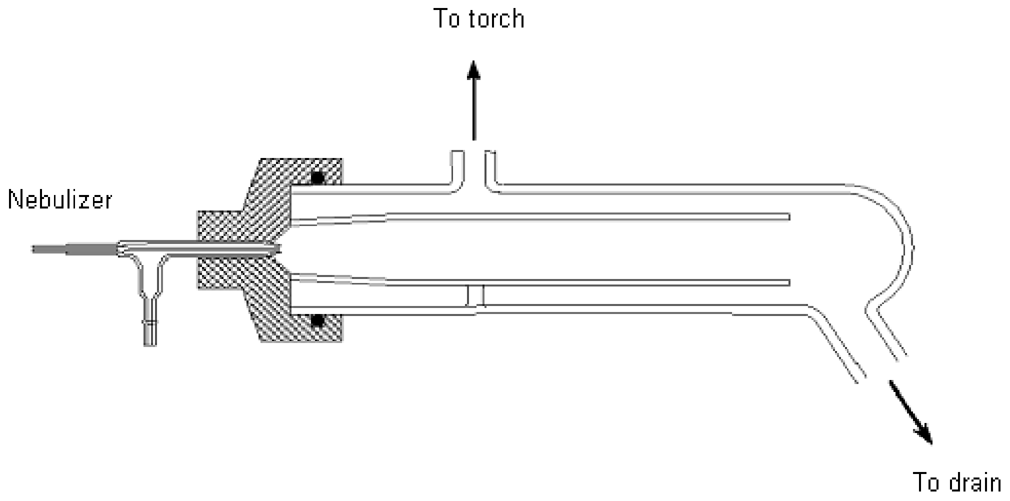


Figure A.3: A typical spray chambers used in ICP-OES (adapted from Charles et al., 1997)

Drains

The drain carries the excess sample from the spray chamber to a waste container. It can have an impact on the performance of the ICP instrument. It also provides the backpressure necessary to force the sample aerosol-carrying nebulizer gas flow through the torch's injection tube and into the plasma discharge. It is important to keep the liquid level within the drain system at a recommended position. Drains systems come in many forms loops, blocks, U–tubes, or even tubing connected to peristaltic pump (Charles et al., 1997).

PRODUCTION OF EMISSION

Torches

The torch consists of three concentric quartz tube for argon flow and aerosol injection. There are two types of torches. The first and the most popular torches are of the demountable type. This torch can be disassembled, modified or the parts replaced easily and inexpensively. The main advantage of this torch is the lower cost of replacement and the ability to use a variety of injector tubes (Charles et al., 1997).

The second torch is a fixed torch that has many designs, but the most commonly used is the Scott-Fassel type (Moore et al., 1989). This type of torch uses lower gas flow and requires a high degree of concentricity. The drawback of this torch is that it does not tolerate the injection of air and this may result in the plasma being extinguished (Thompson et al., 1989).

Radio frequency generators

The radiofrequency (RF) generator is used to provide a high frequency voltage to the ICP for the generation and sustainment of the plasma discharge. There are essentially two classes of generators. The first type is called crystal–controlled generator. It uses a piezoelectric quartz crystal to produce an output at constant frequency.

The second is a free-running generator, which operates at an oscillation frequency that is not only circuitry but also on the plasma discharge. Free-running generators are made from simpler parts and are smaller and less costly than crystal-controlled generators. The performance of the analytical instrument is not greatly dependent on which type of RF generator is used and there is no clear evidence which one is superior to the other.

COLLECTION AND DETECTION OF EMISSION

Transfer optics

The region, in which the emitted radiation from the plasma is collected, is known as the normal analytical zone (NAZ). There are two NAZ of the plasma that are employed. The first is a radical or side-on viewing of the plasma. The NAZ is observed from the side of the plasma operating in vertical orientation.

The second is referred as end-on viewing. In this type, the zone is observed axially from the end of the plasma.

Recently, a new type was introduced, which combines both radial and axial viewing, called dual viewing. The advantage of this is the ability to optimize the appropriate configuration for the types of the sample without the expense of two separate ICPs (Charles et al., 1997).

A combination radial (side-on) and axial (end-on) ICP is shown in Figure A.4.

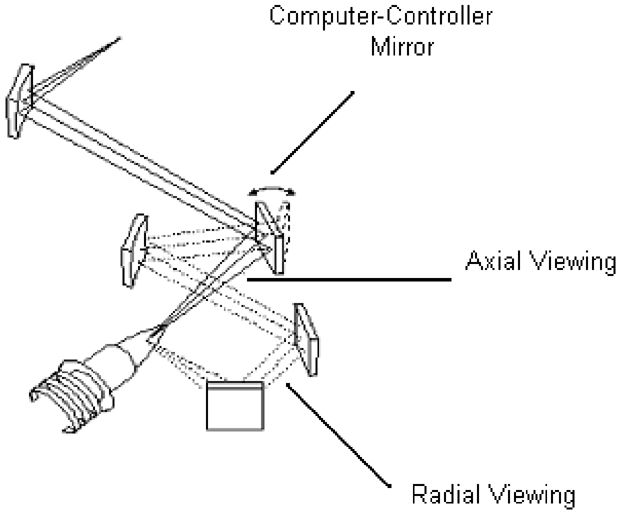


Figure A.4: A combination radial (side-on) and axial (end-on) ICP (adapted from Charles et al., 1997)

SPECTROMETER

The main functions of a spectrometer is to form the light into a well-defined beam and dispersed it according to wavelength with a grating and focus the dispersed light into an exit plane or circle (Charles et al., 1997). There are two types of spectrometers. The simultaneous spectrometer (or polychromotor), and the sequential spectrometer (or monochromotor).

Simultaneous systems have a higher sample throughput as more elements can be analyzed within a short period of time. The disadvantages of this are the higher cost and lack of flexibility. These can be improved by using an ICP-OES with more than one polychromotors systems. The most widely used mounting for polychromotor is the Pashen-Runge construction (Charles et al., 1997).

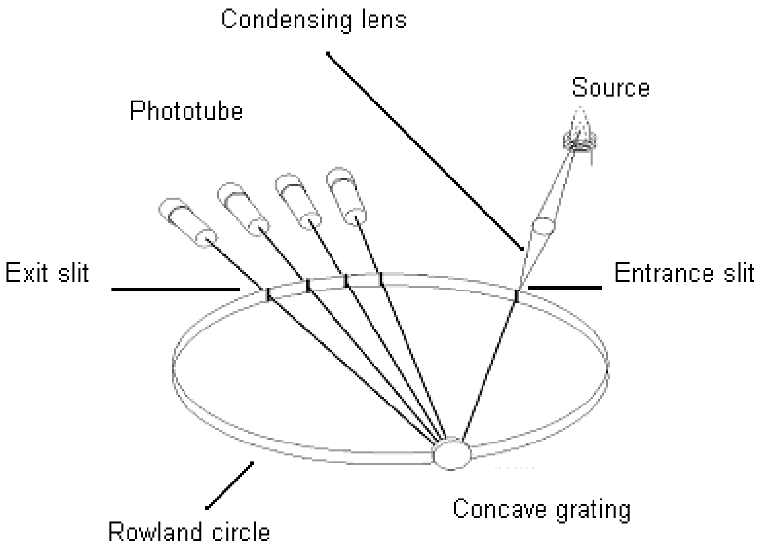


Figure A.5: The Pashen-Runge mount used in a Rowland circle polychromotor (adapted from Charles et al., 1997)

The sequential spectrometer is designed to move sequentially from one wavelength to the next during the measuring sequences. It therefore measures the elements in the sample in pre-defined order. Their main disadvantage is the speed. The most widely use sequential spectrometer is the Czerny-Turner spectrometers.

Detectors

Once the proper emission line has been isolated by the spectrometer, the detector is used to measure its intensity. The most used detector for the ICP-OES is the photomultiplier tube or PMT. The PMT is a vacuum tube that contains a photosensitive material called the photocathode. The photocathode ejects electrons when it is struck by light. These ejected electrons are accelerated towards a dynode which ejects two to five secondary electrons for every one electron which strikes its surface. The secondary electrons strike another dynode, and the multiplicative effect is caused along the way. Typical PMTs contain 9 to 16 dynode stages. The final step is the collection of the secondary electrons from the last dynode by the anode (Charles et al., 1997).

The main advantages of the PMT are that it can be used to measure light over a relatively wide wavelength range and it can amplify very weak emission levels and its range of response can be extended over nine orders of magnitude in light intensity (Charles et al., 1997).

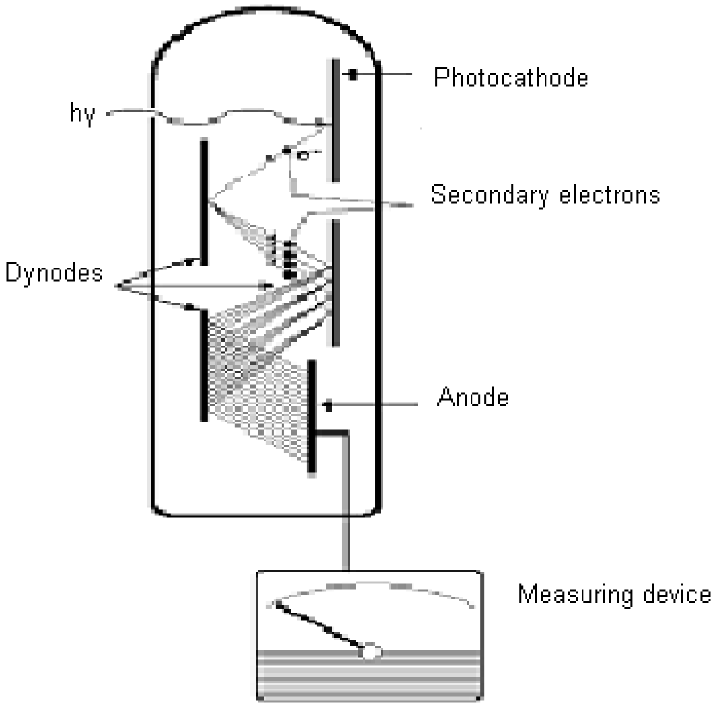


Figure A.6 : A typical PMT (adapted from Charles et al., 1997)

Signal processing and instrument control

Signal processing

Here, the electrical current measured at the anode of the PMT is converted into information that is used by a computer or analyst (Charles et al., 1997).

Computers and processors

The computer is an important part in any ICP-OES because it controls the function of the instrument. All parameter of the instrument such as argon flow, generator control and other parameters are controlled by computer.

A.2. X-RAY FLUORESCENCE (XRF)

An X-ray fluorescence (XRF) spectrometer instrument, model ARL9400 XP using UniQuant software was used for the analysis of the tantalite.

XRF (X-ray fluorescence spectrometry) is an analytical technique used to identify and determine chemical elements both quantitatively and qualitatively. It has the advantage of being non-destructive, multi-elemental, fast, cost effective and easy sample preparation. The major drawback is that analyses are restricted to elements from fluorine to uranium in the periodic table (Bennet and Oliver, 1992).

The main principle behind XRF spectrometry is that X-rays of characteristic wavelength (and energy) are emitted from a sample when the sample is ionized by a stream of X-rays; this process is known as X-ray fluorescence, and use of it is made in X-ray fluorescence analysis (Clive, 1987). The operating principle is illustrated in Figure A.7 below.

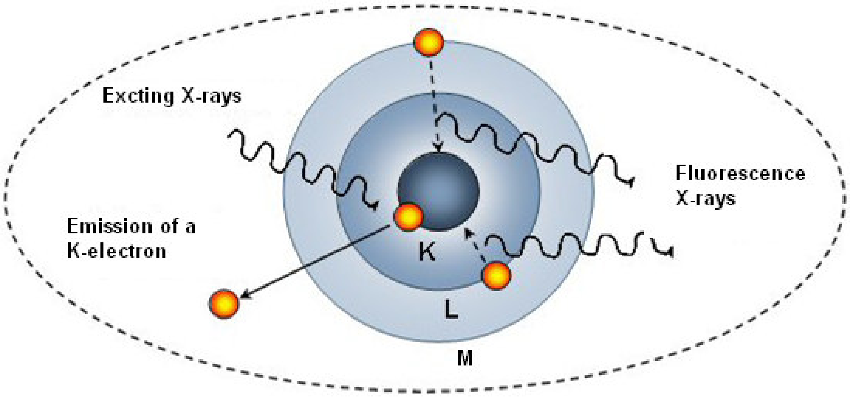


Figure A.7. X-ray fluorescence principle

In this method, an atom is excited by primary X-ray which originated either from a radioisotopic source or an X-ray tube. Subsequently detection of the X-rays emitted by the sample during the de-excitation process. The X-ray fluorescence spectrum of a sample reveals a number of characteristic peaks. The energy position of the peaks identifies the atoms present in the sample (qualitative analysis), whereas the peak intensity leads to the relative or absolute elemental composition of the sample (semi-quantitative or quantitative analysis)

Sample preparation is the most important step in any analytical technique. Therefore selections of the correct sample preparation technique play a major role and depend on the goals of accuracy and precision the analyst needs to attain. Sample preparation involves milling the sample in a tungsten carbide milling pot to particle size below 75 µm. The samples are dried at 110˚C (weight 1) and roasted at 1000 ˚C (weight 2), to determine the percentage loss on ignition (LOI) using the following equation (Laubser and Verryn, 2009):

$$\% LOI = \frac{weight_1 - weight_2}{weight_1 - weigth_{Crucible}} * 100 \qquad \text{(a.1)}$$

There are two main sample preparation methods: one is based on pressed powder and the other on the fusion of the sample mixed with a suitable flux, resulting in glass disc. In the pressed powder pellet method, the X-ray emission intensity can be affected by mineralogical structure and by the particle size. It is difficult to obtain a homogeneous sample with this technique and contamination of the surfaces of the pellet can frequently be observed. In the glass disc (bead) method, the powdered material is mixed in appropriate ratios with a boric flux, melted, poured into a mould and cooled. A great advantage of this technique is that reference materials of different natures can be used for calibration and synthetic standards can be prepared. Other advantages are due to the physical and chemical homogeneity of the vitreous disc (more reproducible results), and the possibility of widening the validity ranges of the regression curves and reducing the number of calibration (Hutton and Elliot, 1980; Eastell and Willis, 1990). Major elements analyses are done on fused beads methods.

A.3. X-RAY DIFFRACTION (XRD)

Tantalite, tantalum and niobium analysis was performed by an X-ray diffraction (XRD) analysis using a PANalytical X'Pert PRO powder X-ray diffractometer with Fe filtered CoK$_\alpha$ as a radiation source. The phases were identified using X'Pert Highscope plus software.

X-ray diffraction is a material characterization technique that provides detailed information about the atomic structure of crystalline substances. It is generally used in the identification of minerals. A simple way to intuitively understand the complex phenomenon of XRD is to consider a space plane of atoms in mineral structure Figure A.8. The d-spacing (distance between a given set of planes), on a scale of Amstroms, can be determined accurately using XRD. The principles underlying this determination are expressed by the Bragg equation (Aprill and Richard, 2005).

$$n\lambda = 2d \sin\theta \qquad \text{(a.2)}$$

Where n is an integer, λ is wavelength of the radiation, d is d-spacing, and θ is the angle between the planes and the incident X-rays beam.

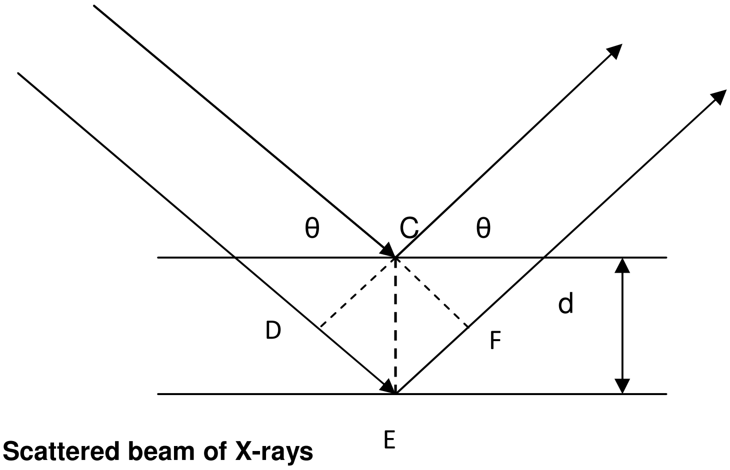
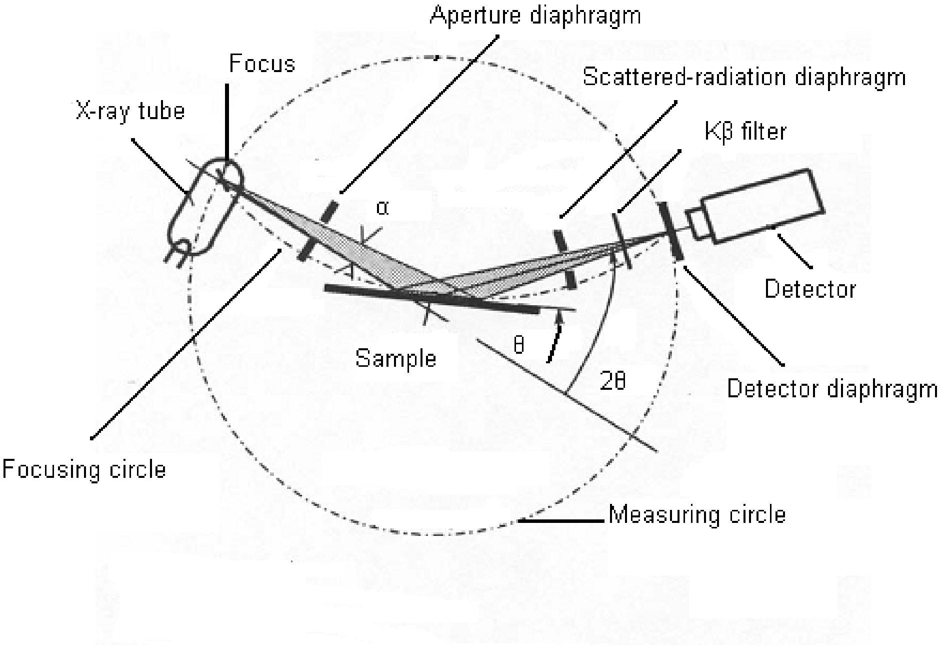


Figure A.8: Scattered beam of X-rays

A

The Bragg's equation is derived by setting the path difference between incoming beams, i.e. DE + EF, equal to an integral number of wavelengths.

Data are collected using X-rays of a known wavelength. The sample is rotated so that the angle of diffraction changes. When the angle at which the exiting rays will be in phase for diffraction a signal will be recorded by X-ray diffractrometers and then converted into peaks. Below is a schematic diagram of a diffractometer (James, 2007).



Θ Glacing angle, 2 θ Diffraction angle, α Aperture angle.

Figure A.9: Schematic diagram of a diffractometer

A.4. SCANNING ELECTRON MICROSCOPY

The scanning electron microscope (SEM) was used for the characterization of niobium and tantalum pentoxide.

The SEM is one of the most versatile instruments available for the examination and analysis of the microstructural characteristics of solids objects. The basic components of the SEM are the lens system, electron gun, electron collector, visual and recording cathode ray tubes (CRTs), and the electronics associated with them (Joseph et al., 1981).

The SEM machine works as follows: The heated element causes a beam of electron to be produced by electron gun from the top of the microscope. The electron beam travels down toward the sample through electromagnetic lenses which focus and direct them to the sample surface. When the beams collide with the sample, secondary electrons, backscattered electrons and X-rays are ejected from the sample. Detectors collects these electrons ejected and convert them to a signal in the display producing an image. A block diagram of a scanning electron microscopy is shown on Figure A.10 (Hearle et al., 1974)

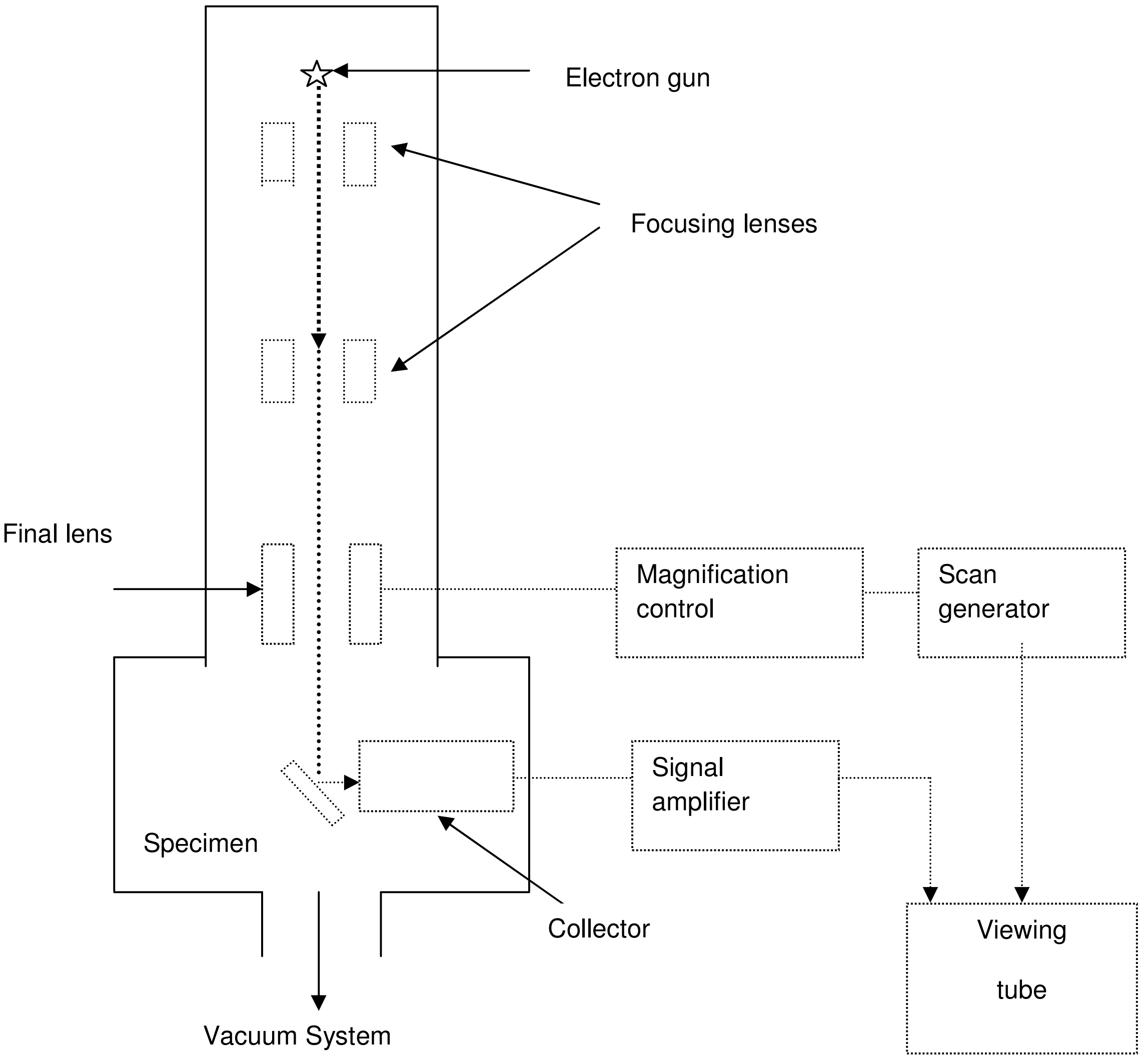


Figure A.10: Block diagram of scanning electron microscopy