OPTIMIZATION OF NIOBIUM-TANTALUM RECOVERY FROM TYPICAL

RWANDAN AND NIGERIAN COLUMBITE-TANTALITE ORES

A thesis submitted to the Department of Material Science and Engineering

African University of Science and Technology,

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BY

Jean Baptiste HABINSHUTI

STUDENT ID: 70148

Abuja, Nigeria

September 2022

CERTIFICATION

This is to certify that the thesis titled "OPTIMIZATION OF NIOBIUM-TANTALUM RECOVERY FROM TYPICAL RWANDAN AND NIGERIAN COLUMBITE-TANTALITE ORES" submitted to the school of postgraduate studies, African University of Science and Technology (AUST), Abuja (Nigeria) for the award of the Doctor of Philosophy degree is a record of original research carried out by Jean Baptiste HABINSHUTI in the Department of Material Science and Engineering.

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A THESIS APPROVED BY THE MATERIAL SCIENCE AND ENGINEERING

DEPARTMENT

RECOMMENDED:　　　...…………………………………………

　　　　　　　　　　Supervisor, Dr. Adelana R. Adetunji

　　　　　　　　　　African University of Science and Technology, Abuja, Nigeria

　　　　　　　　　　…..………………………………………..

　　　　　　　　　　First **Co-Supervisor**, Prof. Brajendra Mishra

　　　　　　　　　　Worcester Polytechnic Institute, WPI, USA

　　　　　　　　　　………………………………………………

　　　　　　　　　　Second **Co-Supervisor**, Dr. Janvier Mukiza

　　　　　　　　　　University of Rwanda, Rwanda

　　　　　　　　　　………………………………………………

　　　　　　　　　　Prof. Grace Ofori-Sarpong, Committee member

　　　　　　　　　　University of Mines and Technology, Tarkwa, Ghana

　　　　　　　　　　…..………………………………………..…

　　　　　　　　　　Prof. Peter Azikiwe Onwualu, Committee member

　　　　　　　　　　African University of Science and Technology, Abuja, Nigeria

　　　　　　　　　　……………………………………………………

Dr. Abdullkhaleem Bello, Committee member

African University of Science and Technology, Abuja, Nigeria

APPROVED BY: …………………………………………………..

Head, Department of Material Science and Engineering

………………………………………….….…

Chief Academic Officer

………………………………………….….…

Date

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ABSTRACT

Niobium and tantalum are transition metals with a refractory character and unique properties that make them highly indispensable to the high-technologies and clean-energy. The metals are normally extracted from minerals of columbite-tantalite series, pyrochlore, and microlite of various deposits. The traditional method used for their extraction and recovery utilizes corrosive acidic media and highly volatile hydrofluoric acid or its mixture with sulfuric acid which blamed to be associated with cost and environmental challenges. To address these challenges, the present study aimed at optimization of Nb and Ta recovery from typical Rwanda and Nigerian columbite-tantalite ores reports mainly the results of characterization of the ore material-samples from Rwanda and their concentrates obtained after rough centrifugal gravity concentration. Further the columbite-tantalite concentrate materials from Rwanda and Nigeria were subjected to the alkali-assisted roasting to open-up and convert into soluble species the minerals of Nb and Ta followed by water-based leaching which solubilizes these refractory metals and then extract them via precipitation using guanidine carbonate. The alkali-assisted roasting at optimum conditions resulted in breaks-up and high dissolution of the (Nb, Ta)-bearing minerals, more than 93% and 90% of Nb and Ta were dissolved from the feed respectively. Guanidine carbonate precipitated effectively almost 100% of the total Nb and Ta contained in the pregnant leach solution. The (Nb, Ta)-guanidine precipitates obtained were calcined at 900°C for one hour which removed the guanidine and converted the metals into mixed oxides of Nb and Ta. This gives a total recovery between 96-98% and 92-94% for Nb and Ta respectively. The present work demonstrates the possibility of sustainable extraction in the metallurgy of Nb and Ta while the world is shifting toward the clean energy.

Key words: Niobium, tantalum, alkali-assisted roasting, columbite-tantalite, dissolution, guanidine, guanidine-induced precipitation, recovery, precipitate, calcination, (Nb-Ta)-oxides.

This thesis is dedicated to my parents, Pascal Muramira and late Melanie Mukakimanuka for their support, unconditional love not only during my PhD study but my whole academic journey.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATION AND SYMBOLS

AC   Alternative current

ASM   Artisanal and small-scale mining

AUST   African University of Science and Technology

BSEs   Backscattered electrons

C   Carr's compressibility index

CGM   Columbite group minerals

Coltan   Columbite-tantalite

COMIKA   Cooperative Miniere De Kagina in Kamonyi

DI: Deionized water

DEHPA   Bis (2-ethylhexyl) phosphoric acid

DC   Direct current

d   Inter-planar spacing distance of diffracting planes (m)

DRC: Democratic Republic of Congo

eV   Electron-volts

Gua   Guanidine carbonate

H   Hausner ratio

HF   Hydrofluoric acid

H_2SO_4 Sulfuric acid

HSLA   High strength low-alloy steel

ICP-OES   Inductively coupled-plasma optical emission spectroscopy

ICDD   International centre for diffraction data

KAB   Karagwe-Ankole Belt

KIB   Kibara Belt

KOH   Potassium hydroxide (caustic potash)

MIBK	Methyl isobutyl ketone
n	Diffraction order
Nb	Niobium
NTO	Niobium-Tantalum-Oxides
N-Nass Con	Nigeria-Nasarawa Concentrate
N-Jos Con	Nigeria-Jos Plateau Concentrate
PDF	Powder diffraction File
PLS	Pregnant leach solution
RF	Radio Frequency
R-KMY Con	Rwanda-Kamonyi Concentrate
R-KMY Raw	Rwanda-Kamonyi Raw
R-N1, R-N2, R-N3	Rwanda-Ntunga site 1, 2, 3
SEM	Scanning Electron Microscopy
SEM-EDS	Scanning electron microscopy with energy-dispersive spectroscopy
SEs	Secondary electrons.
Ta	Tantalum
TBP	Tributyl phosphate
3Ts	Tin, Tantalum, and Tungsten
WPI	Worcester Polytechnic Institute
XRD	X-ray diffractometer
λ	Wavelength of X-rays (m)
θ	Diffraction angle (degrees)

CHAPTER ONE

1. INTRODUCTION

1.1 Background

The element niobium (Nb) takes its name from Niobe, the daughter of the king Tantalus in Greek mythology from whom the element Tantalum (Ta) was named (*Niobium processing | History, Ores, Mining, & Extraction | Britannica*, n.d.). Due to their very similar physical and chemical properties, natural co-occurrence; the two metals are geochemically referred as 'twins' rather than father and daughter (Ahmed, 2016). Niobium was discovered in 1801 by Charles Hatchet, an English chemist whereas Tantalum was discovered one year later by Anders Ekeberg, a Swedish scientist (Agulyansky, 2004). However, there was difficulty to separate them due to the confusion between their separate identities, and they were thought to be the same element. Until in 1844, Heinrich Rose disputed this conclusion, and Jean Charles de Marignac in 1866 was able to separate niobium from tantalum and confirmed that they are two different elements (Linnen et al., 2013).

Niobium and tantalum are transition metals characterized by a refractory character with melting points of 2468°C and 2996°C respectively (Mirji et al., 2016). They have excellent electrical, mechanical, chemical, and physical properties which give them a wide space of applications (Mirji et al., 2016; Schulz et al., 2017). Nb has numerous applications; including the leading use (~75%) in production of steels where ferro-niobium material is used as an additive to the high-strength low-alloy steels. These structural alloys are widely used in manufacturing of oil-gas pipelines, modern automobiles sheet steels, and stainless steels for other various uses (Abo Khashaba, 2017; Agulyansky, 2004; Didier et al., 2020; Schulz & Papp, 2014). Niobium is also applied in the production of nickel, cobalt, and iron-based superalloys used in manufacturing of aircraft engine components, heat-resistant and combustion equipment (Schulz & Papp, 2014). Nb is mainly imported and exported in form of ferro-niobium materials (Didier et al., 2020). The refined tantalum finds its broad applications in manufacture of electronic components and other high-technological products; high-temperature applications; and surgical implants and chemical industries handling corrosive

materials. These include capacitors and resistors used in mobile phones, computers, digital cameras; and super-alloys used in aerospace and automotive applications (Espinoza, 2012); and bio-implants, superconducting magnets for biomedical applications (Arnould et al., 2010). The diversified field of applications led the growing demand for tantalum, mainly in electronics (Espinoza, 2012).

Niobium and tantalum are mainly extracted from Nb-Ta bearing concentrates through extraction and refining techniques. The rock-ores hosting Nb-Ta minerals are first mined and processed to increase the grade of valuable minerals as columbite-tantalite concentrates. The beneficiation of columbite-tantalite minerals is strongly decided by the nature of minerals contained in the ore (Bulatovic, 2010a). The principal method for beneficiation of (Nb,Ta)-ores is related to the higher densities of Nb, Ta and other (Nb,Ta)-carrier minerals that allow them to be concentrated by gravity separation (Bulatovic, 2010b). However, losses of the fine Nb/Ta particles are reported especially for -150 and -200 mesh fractions and cyclone overflow slimes. There is a possibility to float (Nb,Ta) gravity tailings which would increase overall metallurgical recovery, but only few plants have tested this (Bulatovic, 2010b).

Since niobium and tantalum are always found together and associated with other impurities, their concentrates should undergo the digestion process for separation and refining before they can be converted into a useful product. The current process involves treating the columbite and tantalum-bearing concentrates with a mixture of HF and H_2SO_4 at elevated temperatures which dissolve Nb and Ta into complex fluorides (Yang et al., 2016). The slurry is first filtered, and the filtrate is subjected to solvent extraction process which produce separately a highly purified solution of Nb and Ta which can be further converted into oxides or K-salts as needed (Yang et al., 2016). Ammonia solution is introduced to the purified solution of niobium to convert it into hydroxide which is then calcined into niobium oxide. However, in case of pyrochlore ore, it is first converted into high-strength low-alloy steels ferroniobium through aluminothermic reduction process or reduction in electric arc furnace (Admat, 2021).

1.2 Motivation

Niobium and tantalum are mentioned on the 2022 list of 50 strategic and critical minerals to the U.S for high performance technologies (Bruno Venditti, 2022; Soedarsono et al., 2018), and it is firstly due to their unique properties that make them of vital importance to the world's major and emerging economies particularly in aerospace, electronics, military, medical sector, and clean-energy technologies (Mackay & Simandl, 2014). Secondly, the potential risks associated to their production and supply due to geological scarcity, trade policy and geopolitical issues (Allain et al., 2019). The global production of niobium-tantalum is small and held by some key regions and producers including Central Africa (Rwanda, DRC, and Uganda) (Roskill, 2019). The world's transition to clean-energy is expected to raise the demand for the critical minerals by 2040 (Bruno Venditti, 2022). Thus, creation of knowledge and technologies supporting the transition toward more sustainable society is needed.

1.3 Problem statement

In addition to the refractoriness nature, resistance to chemical attack, and the need to separate Nb from the chemically similar Ta, the conventional methods used for their production in pure metallic form is complex and require highly concentrated and strong acid of HF or its mixture with H_2SO_4. The acidic media containing fluoride has economic viability and has environmental challenges due to its high volatility and corrosivity (Ungerer et al., 2014), volume of waste materials and their disposals (Schulz et al., 2017). Furthermore, hydrofluoric acid decomposition of the natural ores bearing niobium and tantalum is only effective for high-grade ores (Gebreyohannes et al., 2018). All these factors drove the attention of industrial and academic researchers to advance a cost-effective and eco-friendly alternative process that can help to overcome the supply risks and replace the fluoride media to bring the refractory metals into the solution for the recovery and purification of Nb and Ta from low-grade ores and concentrates (Deblonde et al., 2016; Ungerer et al., 2014).

1.4 Justification of the study

The use of alkaline or oxalate media in the treatment and digestion of Nb-Ta bearing materials as an alternative to fluoride media for extraction and separation of Ta and Nb has received much attention in the past few decades (Deblonde et al., 2019). Some authors reported promising results and potentiality for preference of using alkali-fusion to breakdown the poly-mineralized Nb-Ta containing ore-materials (Hazek et al., 2019), and (Zhou et al., 2005) reported that fusion using KOH as digestion-assisting reagent at 300°C, almost complete recovery of both niobium and tantalum was achieved in just one hour. (Deblonde et al., 2016) reported a fluoride-free process based on caustic conversion of niobium low-grade industrial concentrates in which selective dissolution of sodium hexaniobate was achieved at atmospheric pressure and low-temperature. (Wang et al., 2009) reported an approach in which the adjustment of Nb_2O_5-to-Ta_2O_5 ratio in the low-grade tantalum-niobium ores with addition of pure Nb_2O_5. The enriched concentrates obtained was roasted with KOH at 400°C for decomposition and then leached with water. The results of the water-leaching indicated extraction of 95% Nb and 94% Ta. The enrichment was found to facilitate formation of water soluble $K_3(Nb,Ta)O_4$ and minimize formation of the insoluble $KTaO_3$ and $K(Ta, Nb)O_3$.

Recently, (Berhe et al., 2018) reported similar rates of decomposition and comparable results for dissolution of tantalite ores with KOH-assisted fusion and those of acidic-assisted (HF/H_2SO_4) digestion. In addition, extensive research on the applicability of KOH on tantalum-niobium containing ores of various mineralogy is recommended to realize its applications on industrial scale and process for optimization (Berhe et al., 2018). Amines have been used as extractant in kerosene and produced a highly purified solution of niobium and tantalum (*Tantalum Processing | TIC*, n.d.). Guanidine is an amine, strong base which forms a highly stable cation (guanidinium $C(NH_2)_3^+$) in aqueous solution due to its efficient resonance stabilization and solvation by water molecules (Perrin & International Union of Pure and Applied Chemistry. Commission on Electroanalytical Chemistry., 1972). Guanidine has proven the potential to rapidly and selectively

precipitate Ta from a synthetic aqueous solution containing other metals such as Si and W (Ogi et al., 2018). In the same vein, alkaline-assisted fusion followed by water-based leaching might be a suitable alternative to the volatile, corrosive, and toxic hydrofluoric acid used to bring Nb and Ta into solution and application of guanidine carbonate salt-induced precipitation to selectively recover Nb and Ta from the leach-liquor solution.

1.5 Research objectives

The main objective of this study is to develop a simpler and eco-friendly alternative approach for optimum recovery of niobium and tantalum from its ores of different mineralogies. Specific objectives are to:

- Characterize tantalite ore-samples from different locations in Rwanda
- Investigate the response of analyte grade niobium and other metals contained in alkaline solution towards guanidine as precipitating agent.
- Evaluate different parameters for recovery of tantalum-niobium dissolved in alkaline pregnant leach liquor solution of the Nigeria and Rwandan columbite-tantalite samples.
- Precipitate selectively Nb and Ta from the pregnant leach liquor solution and convert them into their mixed oxides.

1.6 Scope of the study

Niobium and tantalum are mentioned on the 2022 list of 50 strategic and critical minerals to the U.S and European Union for high performance technologies (Bruno Venditti, 2022). The global production of niobium-tantalum is small and held by some key regions and producers including Central Africa (Rwanda, DRC, Uganda)(Roskill, 2019). The world's transition to clean-energy is expected to rise the demand for these critical minerals by 2040(Bruno Venditti, 2022). Therefore, creation of knowledge and technologies which support the transition toward more sustainable society is needed. For this purpose, the study presented in this thesis aimed to optimize recovery of niobium and tantalum from Rwandan and Nigerian columbite-tantalite ores using eco-friendly technology

highlight and address the above-mentioned issues. It investigates the update of the literature review and provides detailed information about occurrence and mineralogy of the niobium-tantalum containing minerals, their mining and production of raw materials, extraction and refining of Nb and Ta. The study assesses the mineralogical and physical characteristics of the tantalite ore-samples collected from different locations in Rwanda.

To achieve the ultimate goal of the study, dissolution induced by alkali-assisted roasting of the concentrates obtained from the centrifugal gravity separation of the ores were also investigated under different parameters.

This study is limited to the combined recovery of niobium and tantalum in form of oxides from their ores and not separation of the two metals individually. The separation of niobium from tantalum needs to be studied in a future work.

1.7 Thesis outline

The present thesis consists of eight chapters organized in the following structure:
Chapter one is the introduction that provides brief of the background of niobium and tantalum. It highlights the motivation, the problem statement, and the justification of the study, research objectives and methodology to achieve them, and present the scope of this study. Chapter two presents mainly the update of the literature review about the properties of niobium and tantalum, their occurrence and mineralogy are also discussed. It further discusses the chemistry of minerals containing niobium and tantalum, mining and production of raw materials, processing, and extraction methods. Chapter three highlights the general research methodology and experimental procedures. It also provides brief description of the sample-materials and chemical reagents, research methods, and materials characterization techniques used to perform this research. Chapter four is the already published article from the objectives of this study. It discusses the mineralogical and physico-chemicals characterization of the columbite-tantalite ores collected from different locations in Rwanda. It further gives details for a description of sample-materials and sampling sites, samples handling and preparation, relationship between materials before and after a rough centrifugal gravity concentration,

it presents the results of characterization and their discussions. Chapter five presents the results of investigation of the behavior of analytical grade niobium and other metals contained in alkaline solution toward guanidine. Chapter six discusses the results of alkali-assisted roasting of the Nigerian ferro-columbite, and the guanidine carbonate induced precipitation of Nb and Ta from the pregnant leach liquor solution. It also gives details on the effect of different parameters influencing the dissolution of Nb and Ta, test for the optimum conditions determined during the study. Chapter seven discusses the results of comparative study of alkali-assisted roasting of the Nigerian and Rwandan columbite-tantalite concentrate and guanidine carbonate-assisted extraction of Nb and Ta from their leach liquor solution. Chapters four and six have already been published as journal articles while a manuscript from chapter seven is ready for submission. Chapter eight highlights in summary the outcomes of this research, limitations, and recommendations for future work. List of cited references is provided at the end of each chapter.

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<center>**CHAPTER TWO**</center>

2. LITERATURE REVIEW

2.1 Introduction

This review discusses the characteristics of niobium and tantalum minerals and the rocks that host them using previous methods of processing route and extraction. Materials on the previous works were selected based on methods, parameters and techniques used to evaluate and analyze the minerals physical and chemical attributes, dissolution, separation and purification of niobium and tantalum.

2.2 Properties of Niobium and Tantalum

Niobium and tantalum are both transition metals located in the same group (VB) of the Periodic Table (Richard & Kathryn, 2011). They display very similar electrical, physical, and chemical properties and very strong geochemical coherence, thus their intimate occurring in nature. These comparable characteristic behaviors are results of their nearly identical atomic, and ionic sizes and similar electronic configuration as well as stable valences of Ta^{+5} and Nb^{+5} (Table 2.1) (Admat, 2021; Ayanda & Adekola, 2011; Parker L. Raymond, 1968; Shaw & Goodenough, 2011). Nb and Ta have excellent high-temperature and corrosion-resistance due to their strong metallic bonds (high melting points) and the impervious oxide layer formed on the metal surface when exposed to air and moisture. The layer acts as protective barrier which prevents occurrence of further reaction and chemical attacks (Rodriguez-Contreras et al., 2021). Nb and Ta are important refractory metals with high resistance to extreme heat and wear, and this makes them and their alloys ideal candidates for high-pressure and high-temperature applications. Ta is good conductor of heat and electricity. When a thin layer of Ta is coated on surface of other metals, a layer of stable Ta_2O_5 is formed to provide good rectifying and insulating (dielectric) properties, and therefore high-capacitance to store and release

<center>11</center>

electric charges can be achieved in a small volume. The high volumetric efficiency makes Ta capacitors more attractive for use in portable electronics and AC/DC rectifiers (Espinoza & Tercero Espinoza, 2012; International Study Center, 2016; Jeangrand, 2005).

At temperatures below 150°C, Ta is practically immune to chemical attack; it is only attacked by hydrofluoric acid and a mixture containing fluoride ion and free sulfur trioxide. Alkalis attack tantalum very slowly, but at high temperature tantalum is very reactive. Ta is immune to the body fluid and non-irritating, making it excellent bio-compatible material for medical applications (Konttinen et al., 2008, 2014). Nb has excellent alloying and superconducting properties which make it essential for steel production (HSLA), nickel-, cobalt- and iron-based superalloys for aerospace applications and superconducting magnets for MRI used in medical industry (Metal, n.d.). The properties of these metals are listed in Table 2.1.

Table **2.1**: Selected properties of niobium and tantalum properties (Ahmed, 2016).

Property	Niobium	Tantalum
Symbol	Nb	Ta
Atomic number	41	73
Electronic configuration	[Kr] $4d^3 5S^2$	[Xe] $4f^{14} 5d^3 6S^2$
Atomic weight	92.91	180.95
Atomic radius (pm)	145	145
Ionic radius +5 (pm)	64	64
Melting point (°C)	2468	2996
Boiling point (°C)	4930	5425
Density (g.cm^{-3})	8.58	16.67
Electrical resistivity (nΩm) at 25°C	144	134
Thermal conductivity W/[mK]	54	57
Crystal structure	Body-centered-cubic	Body-centered-cubic
Appearance	Shiny-gray metal	Heavy, shiny, silvery metal

Atomic and ionic radii as well as stable valence for both metals are the same, which induced their very similar physical and chemical properties (Ahmed, 2016).

2.3 Occurrence and mineralogy of Nb-Ta minerals

Relative to other metallic elements on our planet, tantalum and niobium are amongst the least abundant metals (Jeangrand, 2005), the overall estimated abundances of Ta and Nb being 0.9 and 12 ppm in the upper continental earth's crust and 0.7 and 8 ppm in the bulk continental crust respectively (Linnen et al., 2013). In nature, Nb and Ta co-occur exclusively as oxide in series of complex oxide minerals, often in solid-solution that contains also, iron, manganese, tin, titanium, thorium and uranium (Allain et al., 2019). Both Ta and Nb have a very strong geochemical coherence and they are always closely associated together in their minerals hosted in their hard rocks and delivered placer deposits. Nb and Ta have higher ionic radius-to-charge ratio, which results in formation of strong bonds with oxygen (Linnen et al., 2013). This is the reason why most of their compounds are oxides rather than being silicates and sulfides or phosphates in different geological settings (Linnen et al., 2013). Nb and Ta are frequently found in minerals of columbite-tantalite series in which columbite ($FeNb_2O_6$), and tantalite ($FeTa_2O_6$) occur in highly variable ratios. This is because of their similarities in size which enable the isomorphism between Nb and Ta in the chemical structure of their minerals (Ahmed, 2016; Inorganic Ventures, n.d.). In addition to columbite-tantalite series, the important minerals for production of Nb and Ta are pyrochlore-microlite series and wodginite (Mackay & Simandl, 2014). These minerals mainly occur as accessory minerals disseminated in rare-metal granites rocks and pegmatites associated with the granites as a result, of weathering and sedimentary processes of the hard-rock (A. A. Baba et al., 2008; Yang et al., 2016).

Despite variations in both quantity and quality of ores from one source to another, most of niobium-tantalum materials supplied to the global market are from primary and secondary sources. The contribution of secondary sources is relatively small, it includes scraps recycling and synthetic

concentrates from tin slags of cassiterite smelting and defense national stockpile (Allain et al., 2019; Jeangrand, 2005). There are two main types of deposits that host niobium and tantalum minerals: hard-rock mineral deposits that are associated with a specific type of igneous rock and secondary (placer) deposits delivered from primary deposits where heavy minerals including niobium and tantalum minerals have been concentrated through deep weathering, erosion, and sedimentary processes (Figure 2.1) (Richard & Kathryn, 2011; Yang et al., 2016).

Hard-rock deposits are primary and most common source of ore-concentrates supplied to the industries for niobium and tantalum production. All niobium and tantalum primary hard-rock deposits are associated with igneous rock and fall into three main types of deposits: pegmatites and granites of LCT family, carbonatites hosted and associated rocks, and alkaline-peralkaline-granites and syenites (Parker L. Raymond, 1968; Shaw & Goodenough, 2011).

Pegmatites hard-rock deposits and specialty granites are most common and predominant rocks that host tantalite ores for production of tantalum (Linnen et al., 2013). Carbonatites and alkaline complexes are igneous rocks with more than 50% primary carbonate minerals. They are typically enriched in most niobium-sourcing minerals, such as member of perovskite and pyrochlore groups but rarely to host profitable concentrations of tantalum and even neither as by-product (Richard & Kathryn, 2011; Yang et al., 2016). The pegmatite deposits as main primary sources of tantalum are widespread in the world (eg. Wadgina in Australia, Mibra in Brazil, Tanco in Canada). In some cases, due to magmatic crystallization processes, columbite-tantalite minerals can concentrate in specific areas and led to an enriched zone. For example, most mineralization of niobium-tantalum minerals hosted in granite-related pegmatites are reported in the Great Lakes region countries (Rwanda, DRC, Uganda, and Burundi) (Melcher et al., 2017; Schütte & Näher, 2020). Alkaline-, peralkaline-granites and syenites deposits are igneous rocks enriched in alkali-based minerals and can contain appreciable concentrations of rare earth elements, tin, zirconium, niobium, and tantalum minerals and the ore mineralogy is dominated by columbo-tantalite, wodginite, and microlite minerals.

Placer or alluvial deposits are soft rocks deposited as results of weathering and sedimentary of the metamorphic rocks having high concentrations of heavy minerals including columbite-tantalite and many other minerals. In the deposits leucogranites, pegmatites bodies and quartz veins bearing cassiterite and tantalite have been emplaced into sedimentary matrices. The minerals in these deposits are very friable, and rocks can be broken apart quite easily (Parker L. Raymond, 1968). The high specific gravity of tantalite and columbite minerals, allowed them to be deposited as stream channel sediments, thus gravity separation is the best method for their processing and beneficiation. They are rare but some can be found in many central African countries, particularly the DRC(Jeangrand, 2005).

2.4 Chemistry of niobium-tantalum bearing minerals

Niobium and tantalum mainly co-occur in nature exclusively as oxide in a series of complex oxide minerals, often the solid-solution also contains iron, manganese, tin, titanium, thorium and uranium (Allain et al., 2019). These oxide minerals mainly occur in variety of tectonic and metamorphic settings particularly in minerals of the columbite-tantalite series hosted in granitic pegmatites, peraluminous granites, and in their weathered placer deposits associated with carbonatite complexes and alkaline igneous rocks (Černý & Ercit, 1989; Mackay & Simandl, 2014). Columbite-tantalite, pyrochlore, wodginite, and microlite are economic minerals for production of niobium and tantalum (Mackay & Simandl, 2014). The most important minerals of niobium are columbite $[(Fe,Mn)Nb_2O_6]$ and pyrochlore $(Na,Ca)_2Nb_2O_6(OH,F)$ (*Niobium Minerals & Production | TIC*, n.d.; Shikika et al., 2020).

Columbite is the niobium-rich end member of the columbite-tantalite isomorphous series in which Nb and Ta can freely substitute each other. The common ratios range from 3:1 to 1:3, hence the mineral is referred to columbotantalite or tantalocolumbite with formula $[(Fe,Mn)(Ta,Nb)_2O_6]$ (Agulyansky, 2004). Columbite is an orthorhombic oxide of niobium containing iron and manganese, and shares the same mineral composition and crystal structure with tantalite $[(Fe,Mn)Ta_2O_6]$ (Ahmed, 2016; Inorganic Ventures, n.d.). The isomorphous substitution also exist between iron and manganese

with the end-members being Columbite-Fe, Columbite-Mn, Tantalite-Fe and Tantalite-Mn minerals (Linnen et al., 2013). Tantalum-rich mineral is called 'tantalite' and contains 42-84% of Ta_2O_5 and 2-40% of Nb_2O_5, whereas the niobium -rich end member is called 'columbite' and contains 55-78% of Nb_2O_5 and 5-30% of Ta_2O_5 (Agulyonsky, 2004; M. Nete, Purcell, et al., 2014b). Columbite-tantalite minerals have similar chemical composition with tapiolite series but different crystal structure, tetragonal for tapiolite. The tapiolite group includes tapiolite-Fe and tapiolite-Mn minerals (Linnen et al., 2013). Columbite and tantalite have very similar properties, although their specific densities are very different, (8+ for tantalite and 5.2 for columbite) (Amethyst Galleries, n.d.). The principal minerals of niobium and tantalum are listed in Table 2.2

Table **2.2**: Principal minerals of niobium and tantalum (Nzeh et al., 2022; Sanchez-Segado et al., 2015)

Mineral	Mineral group	Formula	Nb$_2$O$_5$ (%)	Ta$_2$O$_5$ (%)
Columbite	Columbite-Tantalite	(Mn, Fe) (Ta, Nb)$_2$O$_6$	78.72	30
Tantalite	Columbite-Tantalite	(Mn, Fe) (Ta, Nb)$_2$O$_6$	40	86.17
Pyrochlore	Pyrochlore	(Na, Ca)$_2$ Nb$_2$O$_6$(O, OH, F)	75.12	6
Microlite	Pyrochlore	(Na, Ca)$_2$Ta$_2$O$_6$(O, OH, F)	10	83.53
Tapiolite	Tapiolite	(Mn, Fe) (Ta, Nb)$_2$O$_6$	1.33	83.96
Ixiolite	Ixiolite	(Ta, Nb, Sn, Mn, Fe)$_4$O$_8$	8.3	68.96
Wodginite	Wodginite	(Ta, Nb, Sn, Mn, Fe) O$_2$	8.37	69.58
Struverite	Rutile	(Ti, Ta, Fe) O$_2$	11.32	37.65
Ilmenorutile	Rutile	Fe$_x$(Nb, Ta)$_{2x}$ 4Ti$_{1-x}$O$_2$	27.9	n.a

Pyrochlore is a complex oxide mineral [(Na,Ca)2Nb2O6(O,OH,F] with octahedral crystals disseminated in carbonatites and other deposits related to orogenic magmas. In the pyrochlore chemical structure, tantalum atoms can replace niobium and results in a solid-solution series with the mineral microlite [(Na,Ca)2Ta2O6(O,OH,F)] (*Niobium processing / History, Ores, Mining, & Extraction / Britannica*, n.d.).

The chemical specialty of these oxides is their reactivities with halogens (fluoride and chloride) which has significantly influenced to their separation and purification processes

(Agulyonsky, 2004; M. Nete, Purcell, et al., 2014a). In the presence of fluoride ion, Nb and Ta form highly soluble and distinct fluoride complexes depending on the acidity level and metals concentration. Fluorination of niobium-tantalum containing minerals enabled the development of the Marignac process in 1866, the first industrial process for separation of tantalum and niobium (Agulyonsky, 2004; Deblonde et al., 2016; EL HUSSAINI, 2009).

2.5 Production of raw materials, Processing and Extractions Methods

The general recovery of Nb-Ta is from the primary ore minerals. Tantalum-niobium concentrates are also produced from scraps recycling and tin slags of cassiterite smelting process. Generally, tin slags contain more tantalite than niobite, the content depends on nature of the ore and smelting practice (Soedarsono et al., 2018). The schematic procedures are presented in Figure 2.1.
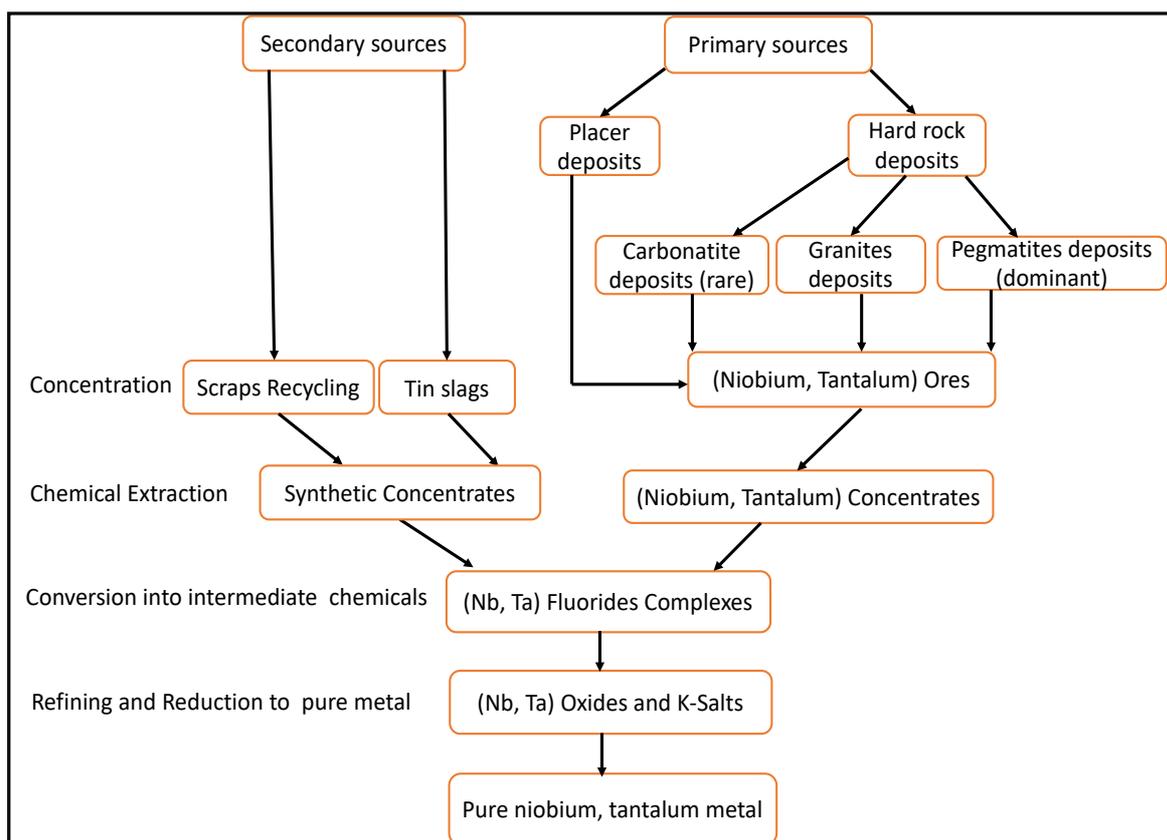
Figure **2.1**: Flowchart for production of niobium and tantalum (Jeangrand, 2005).

2.5.1 Mining of niobium and tantalum containing minerals

Mining is the process of extracting valuable materials (rocks) from the earth's crust simultaneously ensuring health and safety of miners and environment, and the economic viability of the process (National Research Council, 2002). The mining methods employed to mine niobium and tantalum containing materials are like those of other metals of comparable occurrence and requires thoroughly understanding of the ore-mineralogy (Černý & Ercit, 1989). Alluvial and open pit (surface) mining which deal with either weathered soft or hard-rocks and the sub-surface (underground) mining generally for the hard-rocks and sufficiently profitable ore-grade are the main methods (Yang et al., 2016). The pyrochlore is the primary mineral from which niobium is produced. Due to the altered and disintegrated nature of the overburden and ore-materials, the pyrochlore ore is simply mined and operated by open pit without the use of drilling and explosives; this is the case of the largest pyrochlore deposit in Araxa, Brazil (*Niobium mine production worldwide by country 2021 | Statista*, 2022). The production of tantalum raw material is through primary industrial mining and artisanal small-scale mining of weathered minerals or as by-product. Tantalum-ores and concentrates of this type are largely produced in DRC, Brazil, Rwanda, Nigeria, and China (*Tantalum: global production by country 2021 | Statista*, 2022). The mining method employed is selected based on number of factors such as physical and chemical properties of the ore, tonnage and grade, geometry, and depth of the ore-body.

Since the material bearing minerals of Nb and Ta fall into two main types of mineral deposits; hard-rock (primary) deposits and placer (weathered) deposits, niobium and tantalum ores are mostly mined either by open pit or underground mining or combination of both. Artisanal and small-scale mining (ASM) is also used for mining of weathered deposits (Richard & Kathryn, 2011). For example, open pit mining of weathered coltan practiced in most central African countries can be carried out with pick and shovel (*Where is Tantalum Mined | TIC*, n.d.) whereas TANCO mine in Manitoba and Niobec mine in Quebec, Canada, are examples of underground tantalum and niobium mines (CABOT, n.d.; Yang et al., 2016).

The miner's job is to extract the rocks from the ground and provide the mineral processing plant with only the rocks bearing niobium and tantalum at a manageable size and to dispose the barren rocks in separate piles. The mining of hard-rock involves drilling followed by blasting and then load and haul. The broken rock is delivered by trucks, conveyor belts or elevators to the surface, run-of-mine (ROM) stockpiles (R. Burt, 2004).

2.5.2 Processing of niobium and tantalum containing minerals

Generally, after mining and once the ore is delivered to the mineral processing plant, where the downstream operations should proceed to increase their niobium and tantalum contents. The purpose of mineral processing or ore dressing is to separate different constituents of the ore into two or more fractions through separation of valuable minerals from the gangue materials. Efficient minerals processing requires thorough understanding of the ore-mineralogy assembly and texture (Černý & Ercit, 1989). Mineral processing consists of two main operations: *comminution or liberation* (particle sizes reduction by crushing and grinding) of valuable minerals from their waste gangue minerals, and c*oncentration* which takes advantage of physical and surface chemical properties of the valuable minerals and those of the gangue materials to separate them and produce a concentrate and tailings (Wills & Napier-munn, 2006). The selection of concentration methods depends on the nature and quality of the ores, this means the type of target elements and impurities present have influence on the cost of the ore-processing. For example, presence of other valuable minerals such as tin, and lithium in spodumene, could be recovered as valuable by-products (Amuda et al., 2007). Sometimes, the association of tin and tantalum is so intimate that ordinary mineral dressing techniques cannot separate them. This requires expertise of the processor to separate niobium and tantalum from them. The presence of radioactive materials like thorium and uranium in the niobium-tantalum ores complicates its transport, handling, and processing (M. Nete, Koko, et al., 2014).

19

2.5.2.1 Ore beneficiation

In mining hard-rock hosting Nb and Ta minerals, whether from open pit or underground mine, the first stage is the liberation of niobium-tantalum mineral particles from the host rock. In soft-rock, the valuable minerals have been set free from the host rocks by nature during the weathering process leaving niobium-tantalum mineral particles, and other heavy minerals as discrete individual particles (R. Burt, 2004). The liberation of these mineral particles is usually carried out with either jaw or cone crushers to break down large rocks into manageable-size particles and by screening with the oversize being returned to the crusher. The undersize fraction proceeds for the grinding, the second liberation step carried out with rod or ball mills but avoiding overgrinding which produce unnecessary very fine particles which may lead to the loss of valuable minerals since the gravity separation become inefficient as the particle-size decreases (R. Burt, 2004).

Depending on the grain size, texture and accessory minerals present, physical, and chemical properties of the ore, the products of grinding proceed through various separation strategies for concentration of Nb and Ta minerals. These techniques include conventional and centrifugal gravity separation, advanced froth flotation, regular or high-intensity magnetic separation, and electrostatic separation, and acid leaching (Shaw & Goodenough, 2011). Concentration of the niobium-tantalum minerals consists of primary and secondary concentration or concentrate clean-up. In the primary concentration, niobium and tantalum and other heavy minerals such as cassiterite, ilmenite, rutile, zircon, monazite, iron minerals are separated from the light minerals (quartz, feldspar) by gravity separation. In the secondary concentration niobium-tantalum minerals are separated from other heavy minerals either wet, or dry or combination of both. Various techniques like gravity, floatation, leaching, magnetic and electrostatic separation may be employed depending on the physical and chemical characteristics of the ore (Richard & Kathryn, 2011).

Concentration produces concentrate and tailings. Some associated minerals in the concentrate are of economic value; therefore, the concentrate clean-up will not only increase the quality of Nb and Ta minerals but also revenue generated from by-products. The concentrate would contain as much of

the commercially valuable minerals of interest, as few of the other minerals (R. Burt, 2004). The final stage of concentration is the concentrate clean-up, If the concentrates indicate the presence of magnetically susceptible materials, its beneficiation proceeds with the removal of all magnetic compounds before the dissolution and leaching of the concentrate (Motlalepula Nete et al., 2014). Similarly, when radioactive elements are present in the concentrate, they should also be removed by acid leaching before the actual chemical leaching for separation of tantalum from niobium. The concentrate may contain up to 70% of mixed Nb_2O_5 and Ta_2O_5 (Gebreyohannes et al., 2017; M. Nete, Koko, et al., 2014; Motlalepula Nete et al., 2014)

Niobium-tantalum are also concentrated from scraps recycling and tin slags of cassiterite smelting process. Generally, tin slags contain more tantalite than niobite and the content depends on nature of the ore and smelting process (Soedarsono et al., 2018). It can be used directly as feedstock, or it may first be upgraded to the synthetic tantalum concentrates.

Gravity separation

Most commercial concentration of the niobium-tantalum ores is effectively carried out by gravity concentration because of the higher density of its minerals. In practical, columbite-tantalite ores contain minerals of low-specific-gravity (2.8-3.0) such as quartz, aluminosilicates, calcite, etc, as associated minerals and the heavy minerals including Nb-Ta minerals and their carriers have a specific gravity of (4-4.4). This condition is sufficiently enough for gravity concentration (Bulatovic, 2010). The gravity separation is performed using circuit of shaking tables, spirals, and jigs (Shaw & Goodenough, 2011). The practice is performed on fractions of different sizes after grinding and sizing the ore, but the losses of very fine Nb-Ta mineral particles are reported especially for -150 and -200 mesh fractions and cyclone overflow slimes and lead to the low recovery ranging from 55% to 65%. There is possibility to float (Nb,Ta) gravity tailings which would increase overall metallurgical recovery, but only few plants have tested this (Bulatovic, 2010).

Floatation

Froth floatation is a mineral concentration technique that utilizes the difference in surface physico-chemical properties (hydrophobic or hydrophilic) of the material to selectively separate valuable minerals of interest from worthless materials or other valuable minerals (Crawford & Quinn, 2017). In the process, very fine niobium-tantalum mineral particles with hydrophobic surfaces that would be reported in the tailings during the gravity separation, are attached on the air-bubbles and brought to the surface of liquid, forming a froth layer which can be removed and collected as a concentrate. The tailings along with hydrophilic materials remain in the liquid phase and collected through the bottom of floatation cell.

Froth floatation is also based on the ability of some chemicals (collectors) to alter the surface properties of the desired minerals. For instance, using sodium oleate as collector, zircon and niobium can be floated with good recoveries from complex-pegmatite-bearing niobium ores. The process is very important for the extraction of metal sulfides, non-sulfides, as well as native metals and depends upon the density and hydrophobicity of the floating material (Crawford & Quinn, 2017; Woods, 1981). However, sulfide compounds of niobium and tantalum are not known in nature, thus there is difficulty and high cost-associated with floatation of their minerals. There is very little literature about floatation properties of tantalum minerals (Bulatovic, 2010; Nheta & Ruwizhi, 2020). Floatation is effective in processing the material in the size range of 850 μm to 100 μm (Gökelma et al., 2016).

The main challenge with froth floatation is to find a selective chemical for valuable minerals that would leave behind their gangue minerals; particularly floatation of valuable mineral oxides which have similar floatation properties to those of the gangue materials. However, the advancement in materials processing technology have expanded the use of floatation to recover oxide minerals such as hematite, cassiterite, malachite, fluorite, and phosphates. Three types of surfactants are used in floatation: collectors (promoters), frothers (surface-active) to prevent air-bubbles from bursting by lowering surface-tension of the slurry, and modifiers (regulators) to change the slurry and mineral conditions that assist selection of mineral for floatation (Ish Grewal, 2006). Literature on floatation of rare-earth elements and various metal oxides is limited compared to floatation of sulfide-bearing ores. Sulfide minerals have higher floatability than that of pyrochlore or columbite (Bulatovic, 2010). Thus,

floatation may be used to float out associated sulfide minerals, leaving the Nb-Ta minerals for further processing.

2.5.2.2 Chemical extraction techniques

After the process of concentration, niobium and tantalum concentrates must undergo the chemical extraction, separation and refining processes depending on the desired end-user. Production of niobium and tantalum in their pure metallic form is a complex and challenging process. This is due to their refractory nature, resistance to chemical attack and the need to separate Nb from the chemically similar Ta. Production of niobium and tantalum metals and various metallurgical products from their concentrates involves three major stages:

(i)   Production of niobium and tantalum intermediate compounds from the concentrates

(ii)   Production of niobium and tantalum powder from their intermediate compounds

(iii)   Refining and further processing of the niobium and tantalum powder for various applications

Generally, production and purification of metals from their ore-concentrates involves three main steps: (i) conversion of the original ore-concentrate into a form that is suitable for subsequent separation technique, (ii) identification of a cost-effective separation process which promotes more sustainability and (iii) quantification or concentration of the final product and the levels of associated impurities. The success of a metallurgical process is based on the knowledge of characteristics and properties of target elements and type of impurities present in the feedstock material as well as the economy of the overall process.

2.5.2.2.1 Digestion/Dissolution of the Nb-Ta concentrate

In order to produce metals in their pure form, the ore-minerals containing the metals must be broken-down either by the action of heat (pyrometallurgy) or chemical solvents (hydrometallurgy) or electricity (electrometallurgy) alone or in combination (Wills & Napier-munn, 2006). Both hydro- and

pyro-metallurgical routes are used to recover Nb and Ta from their ores after appropriate pre-treatment step depending on the nature and type of ore-materials being handled (Shikika et al., 2020). The most common and frequently adopted processing routes used to treat the columbo-tantalite, columbite, and tantalite concentrates for production of niobium and tantalum is the hydrometallurgy related to the very famous Marignac's process. The process is based on digestion of the concentrate in a mixture of highly concentrated hydrofluoric acid HF and sulfuric acid H_2SO_4 at elevated temperatures (Gupta & Suri, 1994). It allows decomposition and conversion of the Nb-Ta minerals into water-soluble compounds in form of fluoride complexes H_2NbF_7 and H_2TaF_7 and co-dissolution of some associated impurities (El-Hussaini & El-Hakam Mahdy, 2008; Gupta & Suri, 1994; Kabangu & Crouse, 2012). After dissolution, KF or KOH, or KCl is added to the reaction mixture for formation of K-salts (K_2NbOF_5 and K_2TaF_7). The slurry mixture is filtered, and the resulting liquor solution is subjected to selective crystallization of the less soluble salt K_2TaF_7 followed by solvent decantation and filtration to recover Ta. Then the more soluble salt K_2NbOF_5 is recovered from the solution as niobium oxide by precipitation via addition of ammonia solution. The limitation of the process is co-precipitation of multiple impurities such as Ti, Si, and Fe which contaminate the Nb_2O_5 (El-Hazek et al., 2012) as well as the challenges related to the use of highly toxic and corrosive hydrofluoric acid HF (Shikika et al., 2020).

The alternative to the wet chemical process treating tantalum-bearing ores is pyrometallurgical upgrading tantalum-containing tin-slags and chlorination of ores and ferro-alloys. When the material is a concentrate of an ore-containing titanium-niobium-tantalum-rare earth minerals, it is first chlorinated under heating system, in presence of coke to remove most thorium, rare earths, and other elements in form of gases. The temperature of the resulting titanium-niobium-tantalum oxychloride gas is then dropped which causes precipitation of iron, thorium, and alkali metals, and separated from the mixture. The titanium-niobium-tantalum oxychloride gas is then liquefied and stilled to remove low-boiling titanium chloride gas, while the niobium-tantalum oxychloride gas is further chlorinated to produce $NbCl_5$ and $TaCl_5$. After fractional distillation, niobium chloride is reacted with steam and converted into hydroxide followed by calcination to the

oxide. Tantalum chloride is reacted with NH_4OH to produce Ta_2O_5 (Eckert, 1996; *Tantalum Processing / TIC*, n.d.-a).

When the feedstock material being handled is pyrochlore concentrate, it is first reduced to high strength low-alloy ferro-niobium either through aluminothermic reduction process or reduction in electric-arc furnace. From HSLA ferroniobium, a highly pure-oxide can be produced and used to make vacuum grade ferro- and nickel-niobium alloy as well as niobium ingot (*Tantalum Processing / TIC*, n.d.-b). The traditional Marignac's process was replaced by the modern process that uses liquid-liquid extraction or ion exchange to effect separation of Nb and Ta loaded into the acidic fluoride liquor solution followed by further purification and refining processes but the same challenges of acidic media still remain (Agulyansky et al., 2004; Shikika et al., 2020).

2.5.2.2.2 Solvent extraction

The acidic liquor solution-containing niobium-tantalum and other dissolved elements is contacted with organic phase such as methyl isobutyl ketone (MIBK), tributyl phosphate (TBP) and cyclohexanone to effect solvent extraction. At high acidic level (>8M H_2SO_4), niobium and tantalum values are selectively trapped into organic phase leaving most impurities in aqueous phase. The organic layer is commonly washed with 3-7.5M H_2SO_4 to selectively back-extract niobium fluoride complex into flesh aqueous phase leaving tantalum fluoride complex dissolved into the organic phase. The aqueous niobium solution is contacted with small amount of methyl isobutyl ketone MIBK to remove traces of co-extracted tantalum. Tantalum is extracted or stripped from the organic phase with steam or water or addition of diluted ammonium hydroxide. Tantalum is crystalized to K_2Ta_7 by addition of KF or KCl into the aqueous tantalum solution or converted to Ta_2O_5 via the addition of ammonia. The niobium-containing aqueous phase is converted to solid niobium hydroxide $Nb(OH)_5$ by addition of ammonia followed by filtration, drying and calcination to niobium oxide Nb_2O_5 (*Tantalum Processing / TIC*, n.d.-b). Ion-exchange using amine extract in kerosene is also used and produce a highly-purified solution containing niobium and tantalum.

2.5.3.3 Refining of niobium and tantalum

There are different processes for production of niobium and tantalum metal grades of various purity and structure from impure sources or intermediates. These include, electron-beam melting, vacuum-arc melting or sintering process. Halides and oxides of niobium and tantalum are preferred intermediates or starting chemicals for production of metal grades and other compounds of industrial significance as needed (K V Mirji, 2014; Mirji et al., 2016). Among halides, fluorides are commonly used since they are relatively easy to handle (non-hygroscopic) and easy to obtain them in pure form. Pure niobium metal can be produced via alumino-thermic reduction, or magnesium reduction of niobium oxide followed by electron-beam refining. The electron-beam melting reduces various impurities to an acceptable level for aerospace-grade applications. The impurities include alkali metals, trace elements and interstitial impurities from the input powder due to the combined effect of high vacuum and high melt-surface temperature which induces evaporation and degassing (Sankar et al., 2016). It can also be produced by reduction of K_2NbF_7 with sodium. Different metallurgical products of highest purity are mostly produced via electron-beam melted niobium or tantalum ingots (BUCKMAN, 1994).

Most tantalum metal powder (90%) is produced by sodium reduction of K_2TaF_7 in molten salt system at high temperature and the rest by electrowinning and other processes (Borchers & Korinek, 2008). Three process options for reduction of K_2TaF_7 are employed here: electrolytic reduction, reduction with sodium in static bed and reduction in liquid condition. The tantalum metal ingot can also be prepared by calcium or aluminium or carbon/carbon-nitrogen reduction of the tantalum oxide. The crude metal produced in this route of reduction is purified either by pyrovacuum treatment or electron-beam melt refining (Borchers & Korinek, 2008). Tantalum ingot serves for fabrication of various metallurgical products (tantalum powder, sheets, wires, rods, tubing etc). The choice depends on specific application (*Tantalum Processing | TIC*, n.d.-a).

2.6 Some Previous Related Studies

Nigeria is enriched with several natural resources of which the vast oil deposit has been driving the economy of the country. However, strategies for national development calls to focus also on the exploitation of solid minerals of which the high in demand, niobium and tantalum bearing minerals have been reported in the country. The country contribute largely to the world's production and supply of these commodities (Nzeh et al., 2022). Significant production of columbite concentrates from placer deposits of Nigeria was between 1950s and 1970s. Since the starting of 21st century, Brazil and Canada are the world's largest producers of niobium concentrates while, DRC, Rwanda, Nigeria, Australia, Mozambique are main suppliers of tantalum concentrates with columbite-tantalite deposits (G. Perrault and E. Manker, 1981; Nzeh et al., 2022). From 2015 to 2020, Central African countries were world's leading producers of tantalum concentrates where DRC Congo, Rwanda followed by Brazil produced tantalum concentrates amounted to 3000, 2000, 1000 total metric tons respectively (Oluwole Ojewale, 2022; United States Geological Survey, 2020). However, in Nigeria until recently, there was no official attention paid to the tantalite mineral like columbite and tin. The strong growth in demand for tantalum averaging over 10% per year since 1992 and expected to continue to boom over in the future as the new markets continue to emerge. The strong global interest for this mineral has also aroused the attention in many parts of Nigeria including those of Nasarawa, Kaduna, Osun, Kogi states and the Federal Capital Territory and large quantities of crude ore of tantalum are sipped from Nigeria for concentration and/or processing.

(Adetunji et al., 2005) reported results of mineralogical and compositional analysis of the Nigeria tantalite ore from different selected deposits. The results confirmed that the ore is of high quality with significant content of Ta_2O_5 associated with Nb_2O_5 and other constituents that would be of added economic benefits and concluded the requirement of direct clean-up operations to extract tantalum from most the Nigerian tantalite ores without complex and expensive pre-concentration treatments. Therefore, the clean-up operations favor direct digestion of the Nigerian tantalite ores in hydrofluoric acid or strongly acidic media.

(Amuda et al., 2007) reported the characteristics of the Nigerian tantalum reserves and assessment of the competent technologies for the beneficiation of the Nigerian tantalite deposits. Apart from Ta_2O_5 and Nb_2O_5, the Nigerian tantalite reported to contain also other minerals of economic significance in which a multi-ore beneficiation scheme has been developed and produces primary and secondary concentrated mineral products. The deposit can effectively be exploited for extraction and recovery of tantalum through hydrometallurgical route. However, the scheme needs to be evaluated for its optimum dissolution of main constituents and their chemical equilibria parameters.

The Nigerian tantalite and columbite ores characterized with single phase were evaluated for their kinetic dissolutions in nitric acid by (A. A. Baba et al., 2008) and (Ayanda et al., 2012), the results of the two studies demonstrated the effect of concentration of hydrogen ion $[H^+]$, reaction temperature, stirring speed and particle size on the dissolution rate. The ore dissolution rate increases with acid concentration, temperature and stirring speed but decreases with particle size. In all cases, the dissolution kinetic respected the shrinking core model and it is diffusion-controlled process via the action of hydrogen ion. Further, the kinetic dissolution of the Nigerian columbite mineral ore was also investigated in hydrochloric acid and sulfuric acid by (S. Ayanda & A. Adekola, 2012) and (Alafara Abdullahi Baba et al., 2018), the results showed similar trend to those of tantalite and columbite dissolution in nitric acid mentioned-above. The same trend results for kinetic dissolution was also observed by (A. Baba et al., 2006) when dissolved the Nigerian tantalite ore in hydrochloric acid. The only difference is the acid concentration, particle size and the resulting dissolution percentage. However, the value of activation energy for dissolution of columbite ore is 22.40 and 30.30 $Kj.mol^{-1}$ when digested with hydrochloric acid and sulfuric acid respectively whereas the activation energies of columbite and tantalite ores are 15.22 and 22.37 $Kj.mol^{-1}$ respectively when digested in nitric acid.

Rwanda as part of the Karagwe-Ankole Belt system, contains many mineral commodities of vital role for the current high-tech industry worldwide. Geology of Rwanda is mostly similar to that of

neighboring countries like Burundi, DRC, and southern Uganda. The most exploited minerals in Rwanda are the so called 3Ts: tin (cassiterite), tantalum (coltan), and tungsten (wolframite) (Kabatesi, J. C. and Sichone, 2018; Muchez, 2014). These minerals are exported to European nations, USA and China as concentrates after mineral processing and concentration operations. Rwanda is well-known among the top producers of tantalum and tin concentrates, and Rwandan coltan is well-known to be of high quality reflected by its high tantalite content. (Kabatesi et al., 2022) reported the results of improved efficiency recoveries and grades of cassiterite and columbite-tantalite minerals from Gatsibo, Eastern Province of Rwanda when mechanized processing techniques which combine shaking tables and magnetic separation are used relatively to the artisanal methods. However, recently (Shikika et al., 2021) reported an isothermal alkaline roasting of the coltan bearing ores from the region, Numbi deposit of South Kivu, DRC was investigated for its Nb and Ta dissolution. Roasting temperature, KOH-to-ore ratio, and particle size have strong effect on the degree of dissolution of Nb and Ta and optimum dissolution was obtained at 550°C, 3:1 and +75 to 45µm and one hour roasting.

2.7 Knowledge Gap

The Nigerian columbite and tantalite ores have been digested utilizing various acidic media and evaluated for their dissolutions aimed to extract Nb and Ta, however no alkaline media has been yet reported for assisted break-up and solubilization of minerals contained in either the Nigerian or Rwandan columbite and/or tantalite ores. Further the chemicals and reagents currently used for extraction, separation and purification of Nb and Ta are expensive, corrosive and not environmentally-friendly. The coltan of Rwanda has been reported on the market to be of high quality (high tenor in oxide of tantalum) (Ntungane, 2016). However, there is lack of enough scientific data for the geology of the exploited minerals, mining, minerals processing, and extraction of these commodities, specifically when it comes to different methods used for the chemical leaching and solubilizing the minerals from Rwanda. The very few available studies are only limited on characterization of the ores and the products of simple and traditional artisanal processing. And so far, the government of Rwanda has made some good advance to become a reginal hub for mineral services. It has revised its mining policy and laws, established legal and institutional framework to

improve geological knowledge, mining conditions and value addition, and created high institutions for training (Ntungane, 2016).

2.8 Conclusion

Niobium and tantalum are both transition metals with very similar physical and chemical properties. They are refractory metals characterized with very high melting points, excellent corrosion resistance and extreme temperatures resistance. They have a very strong geochemical coherence and always found together in the same mineral deposits. Their unique performances particularly in electronics, aerospace, military, and clean-energy technologies make them of vital importance in the world's major economy. In addition to this, their scarcity and trade policy make them to be classified as critical materials. Nb and Ta are extracted mainly from minerals of columbite-tantalite series, pyrochlore and microlite hosted in pegmatites, granites and other associated deposits originated from the igneous rocks. These minerals are reported in different parts of the world including Brazil, Canada, Central African countries (DRC, Rwanda, Burundi, and Uganda) and Nigeria.

Processing of the raw materials for extraction and production of Nb and Ta utilizes strong and highly concentrated hydrofluoric acid or its mixture with sulfuric acid to digest the feed material and convert Nb and Ta minerals into water-soluble fluoride complexes of $HNbF_7$ and $HTaF_7$. The resulting acidic leach solution containing the dissolved metals is subjected to solvent extraction process to effect separation of Nb from Ta followed by further purification and refining processes. The process produces Nb and Ta-intermediates (K-salts and oxides) which are the starting materials for production of these metals and other compounds of various applications. However, this route is blamed to be complex, expensive, and non-environmentally friendly as it uses highly toxic and corrosive acidic media. The use of alkaline media as alternative to the hydrofluoric acid have been investigated and it is still in its infancy and has not yet tested for the Nigerian and Rwandan Nb and Ta-bearing minerals samples.

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CHAPTER THREE

3. RESARCH METHODOLOGY AND EXPERIMENTAL TECHNIQUES

3.1 Introduction

In the present chapter, a brief description of sample materials and chemical reagents, research methods, and materials characterization techniques used to perform this research is provided. The general working principle of some of the characterization instruments used are also emphasized to capture the basic knowledge behind the operation. The characteristic details of the materials, experimental procedures and characterization techniques used for various experiments performed to achieve the objectives of this research are given in the materials and methods section in each of the ensuring chapters.

3.2 Materials

The sample-materials used in this research work were obtained from two different countries: Rwanda and Nigeria. The samples were of two types: ore-samples and concentrates. The six samples from Rwanda include four ore-samples named R-N1, R-N2, R-N3 collected from different points of the Ntunga mine located in Rwamagana, Eastern Province. The other two samples are R-KMY and its concentrate R-KMY Con obtained from COMIKA, a mining company located in Kamonyi District, South Province of Rwanda. The Nigerian samples were both concentrates N-Jos Con and N-Nass Con received from the mining company (S. Danboyi Rinn Nigeria Ltd) after gravity concentration of the ore-minerals mined from Jos Plateau and Nasarawa states of Nigeria. The chemical reagents used in the work were of analytical grade and were purchased from Sigma Aldrich and they were used without any further purification process. These include guanidine carbonate salt (99%w/w) and potassium hydroxide (ACS reagent) pellets for analysis, niobium (v) oxide (99.9%w/w), tantalum (v) oxide (99%w/w) and sodium tungstate dihydrate (ACS reagent).

3.3. Experimental methods

Figure 3.1 shows the general flowsheet used in this study. This research work comprises two main sections: the first section focused on ore-samples characterization, handling, and processing; the second section focused on alkali-assisted digestion, water-based leaching, and the guanidine induced extraction of mixed oxides of niobium and tantalum.
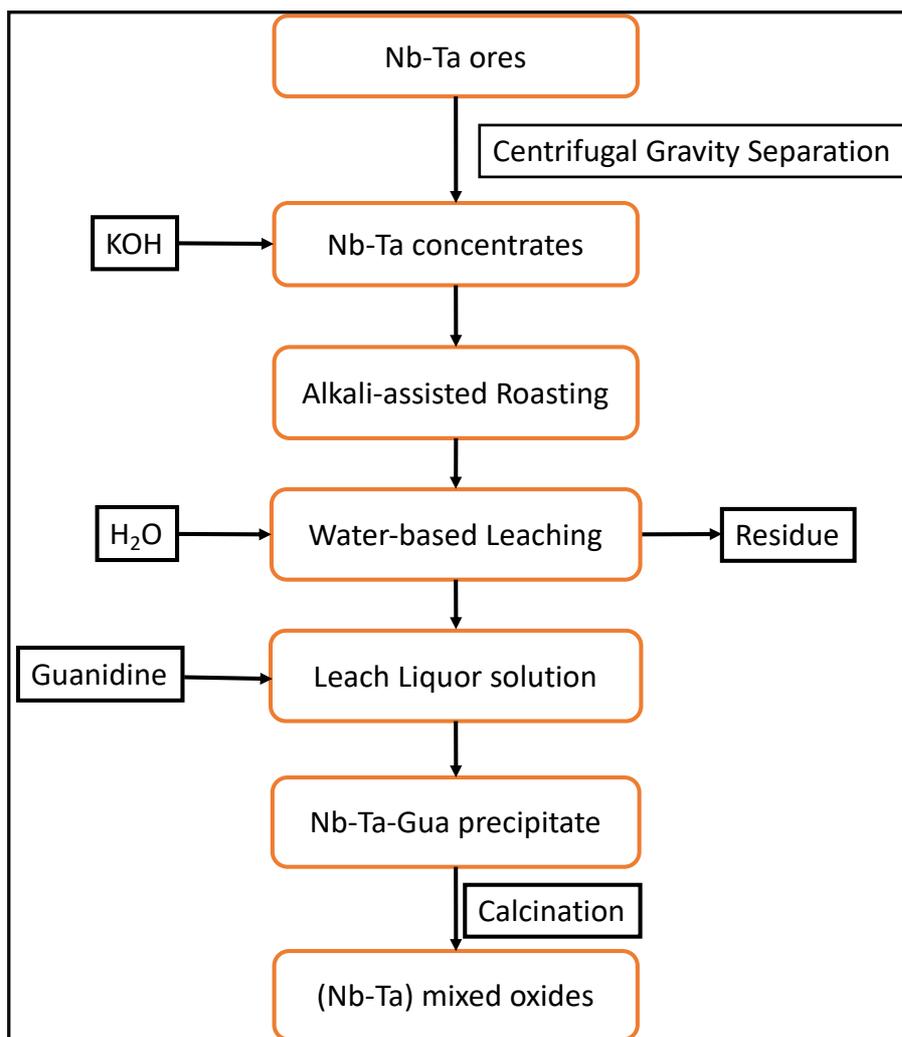
Figure **3.1**: Diagram for the methodology followed in this study

3.3.1 Sample preparation for centrifugal gravity separation

The sampled ores were crushed, and ground to finer size of 125 μm using a ball mill. After grinding, the ore-powder obtained were mixed thoroughly, sieved, and classified into different size fractions ranging from 355 through 250 to 125 μm to get more understanding on the mineral's particle size distribution. A representative sample from each size fraction was taken for physico-chemical and mineralogical characterization. The remaining low-grade ore-samples were subjected to a rough centrifugal gravity separation using a bowl concentrator for beneficiation to increase their niobium-tantalum contents and reduce the gangue materials, mostly the light alumino-silicates minerals.

3.3.2 Centrifugal gravity concentration

The centrifugal gravity concentrator used in the beneficiation stage of this study was custom-made Falcon Bowl concentrator (1V_BBPP B01). Gravity force used in the centrifugal concentrator was the centrifugal force. The use of centrifugal force and water-pressure increase the relative settling speed between particles of different size and density in the centrifugal field (Farajzadeh & Chehreh Chelgani, 2022). The system consists of a bowl, a water pump attached to the concentrator device and a control valve to regulate the flow of water inside bowl and achieve the desired centrifugal force for density separation. The feed slurry of ground sample is carefully dropped into the bowl from the top and afterwards, the water supply valve was closed before adding more sample. Water with low pressure is released as it rotates around the center cone within the bowl; this carries up the lighter materials to the water-surface while leaving the heavier particles of Nb and Ta minerals settled at the bottom of the bowl. The lighter materials continue with water and pass through the center discharge cone and collected as tailings mixed with waste-water which is pumped out to the sewage.

3.3.3 Sample preparation for alkali-assisted roasting and water-based leaching

The concentrated ore-sample as received from the mining company was dried, screened into two different size fractions, +250 and -250 µm with a sieve. For heat treatment, appropriate amount from each of the size fractions of the concentrate sample was accurately weighed and thoroughly mixed with an appropriate weight of ground pellets of KOH. The mixture was put in high quality alumina crucible for roasting.

3.3.4 Alkali-assisted roasting and water-based leaching

The roasting process was carried out in a muffle furnace (Mellen Microtherm). The furnace was pre-heated at specific desired temperature (100-500°C) and when the temperature reached the preset value, a well-prepared sample was carefully introduced into the furnace after which the furnace was completely closed. The furnace was allowed to regain the desired temperature before the timer was started. After a particular time of roasting, the crucible was taken out of the furnace and the melt was allowed to cool at room temperature.

After cooling, the melt was leached with deionized water and the resulting solid-liquid mixture was stirred at room temperature for 90 minutes. Then, slurry mixture was filtered on vacuum pump, and the liquor solution and residue obtained were both analyzed. For leaching experiments carried out at room temperature (no roasting required), appropriate quantity of concentrate was charged into a beaker containing concentrated KOH solution and stirred for 90 minutes followed by filtration and analysis of the liquor solution and residue obtained.

3.3.5 Guanidine carbonate induced precipitation

The amount of Nb and Ta contained in the pregnant leach solution (PLS) obtained was recovered by precipitation using guanidine carbonate salt as precipitating agent. Appropriate volume of the pregnant leach solution was measured and appropriate amount of guanidine salt in solid form were added to the solution on continuous stirring to precipitate Nb and Ta. The Nb/Ta-guanidine precipitate appeared in the solution immediately in less than a minute. The mixture was stirred for 30 minutes to ensure complete precipitation. After 30 minutes, the mixture was filtered on vacuum pump and the precipitate was dried at 100°C, both filtrate and precipitate were analyzed.

3.3.6 Calcination

The calcination of the Nb/Ta-precipitate was carried out in high quality alumina crucible at 900°C for 1 hour to convert metals into oxides and remove the guanidine through evaporation in form of carbon and nitrogen oxides (Ogi et al., 2018; Pierret & Wilhelm, 1956).

3.4 Materials characterization techniques

Scientifically, credibility and success of any separation and purification process is accompanied with its evaluation process; this means careful determination the percentage recovery and quality control of different target elements. It is therefore very imperative that every step of the whole process to be controlled and assessed for its success. To achieve this, measurement and

quantification of separated elements, determination of chemical compositions and mass balance of all main elements and present impurities are required. The choice of suitable analytical methods for accuracy determination of niobium and tantalum and other elements concerned in this study depends on its availability and the limit of detection. The characterization techniques used include x-ray diffraction analysis (XRD), inductively coupled-plasma optical emission spectroscopy (ICP-OES), scanning electron microscopy attached with energy-dispersive spectroscopy (SEM-EDS). A brief description of the basic concept behind each of these techniques is provided below:

3.4.1 X-Ray Diffraction

X-ray diffraction (XRD) is a non-destructive material characterization technique that uses scattered/reflected x-rays of single wavelength to provides detailed information about the crystallinity, physical properties and the phases present in a material. The basic operating principle of XRD involves production of monochromatic x-rays, diffraction of X-rays when they strike on the crystal surface of the sample and then measuring the intensities and scattering angles by detector. In XRD, an incident x-ray beam is irradiated on powder material sample and hits a crystal surface of the material at an angle θ of atomic planes of various d-spacing and get reflected in the same direction angle (Figure 3. 2). The intensity of the scattered x-rays is plotted as function of the scattering angle and then the crystallographic structure of the material is determined from analysis of the location in angle, and intensity of the peaks (*X-Ray Diffraction for Determining Atomic and Molecular Structure | Materials Engineering | JoVE*, n.d.). Depending on the crystalline nature of the sample, diffracted x-rays undergo either constructive or destructive interference which is recorded as diffraction patterns in the detector. A diffraction peak intensity is recorded when the x-rays striking the sample satisfy the Bragg's law (Equation 1) which relates the diffraction order (n), the wavelength (λ) of x-rays, the diffraction angle (θ) and the inter-planar spacing distance (d) between diffracting planes in the specimen (Mitchell Sharon, 1998).

$$n\lambda = 2d \sin \theta \qquad \text{Eq. } \mathbf{3.1}$$
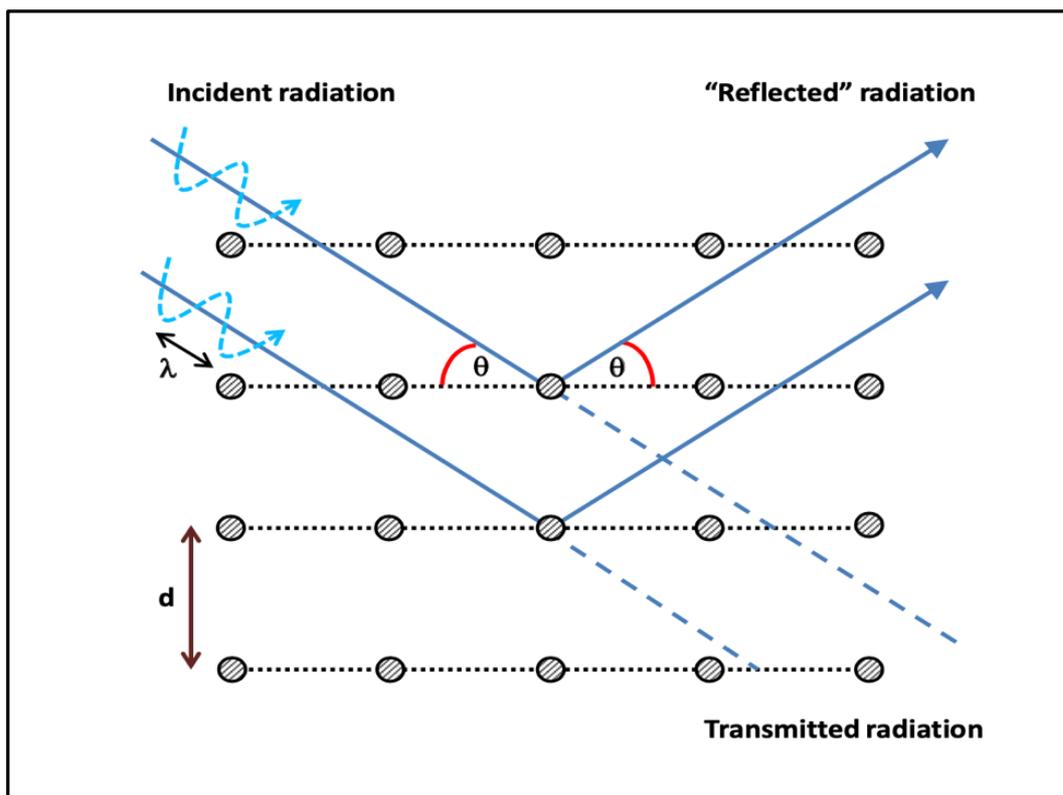
Figure **3.2**: Illustration of the basic principle of x-ray diffraction (Mitchell Sharon, 1998)

A plot of the XRD peak intensity as function of the peak position (2θ) gives a spectrum that provides details about the crystallinity of the sample and phases present. Materials with crystalline nature are characterized with sharp and well-defined diffraction peaks whereas those of non-crystalline like amorphous have broad humped peaks. An x-ray diffraction pattern is a unique characteristic for each material and identification of unknown material can be deduced by matching its diffraction with that of reference sample. The method provides rapid and non-destructive analysis of multi-component mixtures with simple sample preparation.

The International Centre for diffraction Data (ICDD) collects powder diffraction data from variety of sources, classifies the data via an editorial review process, and incorporates the data into the experimental patterns and calculate patterns databases, which comprise the Powder Diffraction File (PDF) as reference file. ICDD then publishes this data and selects portions of database to produces field-specific specialized databases (i.e., minerals, organics). The PDF is now a collection of 272,000

materials data sets that have been characterized by X-ray analysis and edited to include physical properties, experimental preparation, and literature citations.

3.4.2 Inductively coupled plasma-optical emission spectroscopy

Inductively coupled plasma optical-emission spectroscopy technique is based on the measurement of the spontaneous emissions of photons from atoms, ions, and molecules after they have been excited with RF signal. A high energy plasma (6000-10000K) is used to excite these particles (atoms, ions, and molecules) in the nebulized spray containing the analyte sample. The sample introduction system consists of peristatic pump connected to the nebulizer. The analytical advantages of ICP-OES include its multiple-elemental analysis capabilities in various sample matrices, high operating temperature which enable excitation of refractory elements. It also has low-detection limits which allows analysis of trace elements and target element with high levels of concentration (Saran et al., 2004). In the present study Nb, Ta, Fe, and Sn were detected at 309.418, 226.230, 238.204, and 189.927 nm wavelength respectively. The limitations of ICP-OES are spectral overlap and matrix effects due to the interferences in case of complex matrix like mineral sample. Presence of other elements that emit similar line to the analyte line. Acid digestion and hydride generation are used to prepared sample in solution (Elemental, 2002; Emilia Raszkiewicz, 2014).

3.4.3 Scanning electron microscopy

Scanning Electron Microscopy (SEM) is a non-destructive microanalytical technique that use a very fine and focused probe of electrons of ~ 40 keV to scan the sample surface for examination and analysis of its microscopic features. The SEM works on the principle of focusing a highly collimated beam of high-energy electrons on sample surface to provide information about its physical and chemical properties on microscopic scale. Under the impact of electrons on the sample, they undergo some reflection or scattering from various regions of the sample depending on their energies. The most important phenomena are the emission of secondary electrons (SEs) with energies of few tens of eV and re-emission of high-energy backscattered electrons (BSEs) from the primary beam. The scattered electrons are collected by different detectors and processed to give various information

about different features of the sample such as morphology, topography, crystallography, and element composition. Intensity of both secondary and backscattered electrons is very sensitive to the angle at which electron beam strikes the surface. The secondary electrons are usually responsible for image topographical contrast with visualization of surface texture and roughness, whereas BSEs carry compositional and topographical information about features that are deep below the surface. Another signal generated is characteristic x-rays which provide chemical information about the specimen. The magnification produced by scanning microscopy is the ratio between the dimensions of the final image displayed and the field scanned on the specimen. Normally, magnification of SEM ranges from 10-200,00X and the resolution is between 4 -10 nm (Zhou et al., 2007).

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CHAPTER FOUR

4. MINERALOGICAL AND PHYSICAL STUDIES OF LOW-GRADE TANTALUM-TIN ORES FROM THE SELECTED AREAS OF RWANDA

4.0 Brief background

Rwanda is located north-east of the traditional Kibara Belt which is recently subdivided by Tack et al. into two segments of the same age: the Karagwa-Ankole Belt (KAB) extended in Rwanda, Burundi, Maniema and Kivu in DRC and the Kibara Belt (KIB) in the Katanga region of DRC (Heizmann, J.; Liebetrau, 2017; Tack et al., 2010). The mentioned area is well-known to host a large metallogenic province of many mineral deposits such as Nb, Ta, Sn, W, Au, base metals, etc. The mineralization of these minerals exists in various styles of primary granitic pegmatites, quartz veins hosted in metasediments or related sediments as secondary deposits (Heizmann, J.; Liebetrau, 2017; Muchez, 2014). Rwanda as part of the system is endowed with lots of these mineral commodities and is among the world's largest producers of concentrates of the 3Ts minerals (tin, tantalum-niobium, and tungsten) that are of global economic significancy for the high-tech industry (Muchez, 2014; *Rwanda - Mining and Minerals*, n.d.). Central African countries are major contributors to the global supply of tantalum concentrates and have been under the international pressure resulting from niobium-tantalum's status as conflict minerals (LAUREN WOLFE, 2015; Oluwole Ojewale, 2022a, 2022b). However, Rwanda has recently shown good reputation for the conflict-free policies and assuring reasonable mining practices (REMBAR, 2019).

The mining is a key export sector in Rwanda and accounts for 55% of the revenue generated from export and has been facing a number of challenges. The most exported minerals from Rwanda include the so called 3Ts minerals: tantalum (coltan), tin (cassiterite), and tungsten (wolframite) ores. The mining practice in Rwanda is mainly dominated by artisanal and small-scale mining (ASM) with few industrial and semi-industrial activities (Ntungane, 2016). The ASM is characterized by low-technology and low-investment operations which dramatically harm the environment and disrupt the ecosystems around the mining sites. It also lacks knowledge about the geological and mineralogical features of the exploited deposits and operational data for production (Heizmann, J.; Liebetrau, 2017).

Monitoring of the ASM focuses only on the labor cost and quantity of concentrates produced, therefore improving mining practices, stability of the sector, additional monitoring and providing geological data can enhance the processing efficiency in ASM. In this regard, Rwanda is now exploring the opportunity to become a regional hub for mineral services such as processing and beneficiation, smelting and extraction (Crawford & Bliss, 2017). And so far, the government of Rwanda has revised its mining policy and laws, established legal and institutional framework to improve geological knowledge, mining conditions and value addition, and creation of future high institutions training (Ntungane, 2016). In this chapter, niobium-tantalum ore-samples collected from different locations of Rwanda were characterized and their mineralogical and physico-chemical results are reported to add some inputs to the available data.

4.1 Introduction

Tantalum (Ta) is a transition metal of high economic importance due to its rising demand for technological applications (Klaus J. Schulz, Nadine M. Piatak, 2017; Melcher et al., 2013). The unique properties of Ta such as high dielectric constant, the stability of its oxides and corrosion resistance (Bleiwas et al., 2015; Espinoza & Tercero Espinoza, 2012; Toure et al., 2018) make this metal attractive in the field of electronics, aerospace, nuclear and automobile industries, military and medicine (Amuda et al., 2007; Klaus J. Schulz, Nadine M. Piatak, 2017; Muchez, 2014). The metal, tantalum is always associated with niobium and both are recovered mainly from columbite-tantalite group minerals which are present as minor components in both primary granites, granitic pegmatites and greisen rocks (Melcher et al., 2013). Tantalum and niobium are also known to occur in tin-bearing ore-deposits and have been concentrated and successfully extracted from the tin slags disposed as an industrial waste from cassiterite smelting processes (Allain et al., 2019; Briant & Banerjee, 2016; Subramanian et al., 1998). The secondary deposits resulting from the strong weathering and erosion processes acting on the primary tantalum-tin bearing rocks, form a weathered rock that hosts an appreciable amount of tantalum and tin minerals (Richard & Kathryn, 2011; United States Geological Survey, 2020). Tantalum-tin containing mineral is one of the highly valuable and unexploited mineral resources in Africa, but lack of technology for exploration, beneficiation and

extraction to efficiently harness the potential of this resource, make it impossible for it to contribute to the wealth of Africa (Bleiwas et al., 2015; United States Geological Survey, 2020).

In nature, tantalum co-exists with niobium as oxides associated with oxides of iron and manganese. The association may include tin, titanium, lithium, cesium, and trace amounts of tungsten, uranium, and thorium in pegmatites rocks and other related lithologies (Jeangrand, 2005; Motlalepula, 2013). Tantalum and niobium have a strong coherence in geochemical behaviors, and are always closely associated and freely substitute each other in the same type of mineral deposits (Ahmed, 2016; Parker & Fleischer, 1968). The main reason for such coherence is the ionic potential associated with their identical ionic radii and valency states (Parker & Fleischer, 1968). This gives them a high ionic charge-to-ionic radius ratio, which makes them lithophilic elements with a strong affinity to oxygen and high concentration in silicates of the earth's crust (Ahmed, 2016; Parker & Fleischer, 1968). Columbite-tantalite group minerals [(Fe, Mn)O(Ta,Nb)$_2$O$_5$] are major sources for production of tantalum and niobium. The group include [tantalite-(Fe) or tantalite-(Mn)] and [columbite-(Fe) or columbite-(Mn)] (Klaus J. Schulz, Nadine M. Piatak, 2017; Shaw & Goodenough, 2011). Tantalum, tin and niobium also exist in other types of minerals such as pyrochlore, ixiolite, wodginite as complex oxides and hydroxides minerals (Motlalepula, 2013).

In Africa, the tantalum industry suffers from lack of smelting and processing plants to separate tantalum from niobium. These metals are thus sold together as concentrates of tantalum minerals but only the value of Ta$_2$O$_5$ contained is paid for. Tantalum and niobium are not traded on any metal exchange as there is no official price. The price is based on negotiations and contracts between the seller and the buyer (Bleiwas et al., 2015; TIC, n.d.). Central African countries are major contributors to the global supply of tantalum concentrates (Figure 4.1) and have been under international pressure resulting from tantalum's status as conflict mineral (LAUREN WOLFE, 2015). Rwanda has however shown good reputation for conflict-free policies and assuring reasonable mining practices (REMBAR, 2019).

Tantalite ores are mined and processed through several steps using different technologies for production of pure tantalum. Successful processing of minerals into various useful products is usually based on the understanding of the differences in the physical or chemical properties of various species present (Shergold, 1984). In this regard, a proper knowledge of the physico-chemical and mineralogical features of the tantalum-tin ores is required to come up with efficient and eco-friendly processing techniques. For instance, depending on the nature of the ore, the beneficiation process may include pre-concentration, primary concentration, and concentrate clean-up (Adetunji et al., 2005; M. Nete et al., 2014). If the ore-sample contains less than 0.1% Ta_2O_5 and Nb_2O_5, its beneficiation starts with an enrichment step, which may involve a gravity separation (Baba et al., 2008). If the concentrates indicate the presence of magnetically susceptible materials, its beneficiation proceeds with the removal of all magnetic compounds before the dissolution and leaching of the concentrate (Motlalepula Nete et al., 2014). Similarly, when radioactive elements are present in the concentrate, they should also be removed before chemical leaching for separation of tantalum from niobium (Gebreyohannes et al., 2017; M. Nete et al., 2014; Motlalepula Nete et al., 2014)

Musha-Ntunga and Kamonyi are well-known areas in Rwanda for production of cassiterite and tantalite concentrates. However, there is no significant work that has been done to characterize the low-grade tantalum-tin ores from these areas. In this study, physical studies of low-grade tantalum-tin ore-samples collected from two selected areas in Rwanda (Ntunga and Kamonyi) are reported. In addition, various characterization techniques such as scanning electron microscopy with energy-dispersive x-ray spectroscopy (SEM-EDS), inductively coupled plasma-optical emission spectroscopy (ICP-OES), X-ray diffraction (XRD), were used for deep understanding of their mineralogical and chemical characteristics. The nature and associated minerals of the ore are usually revealed through characterization studies. This in turn dictates the processing routes for the ore. This study is therefore intended to provide the baseline data for the selecting and designing the appropriate technique to effectively harness this mineral resource from the areas.
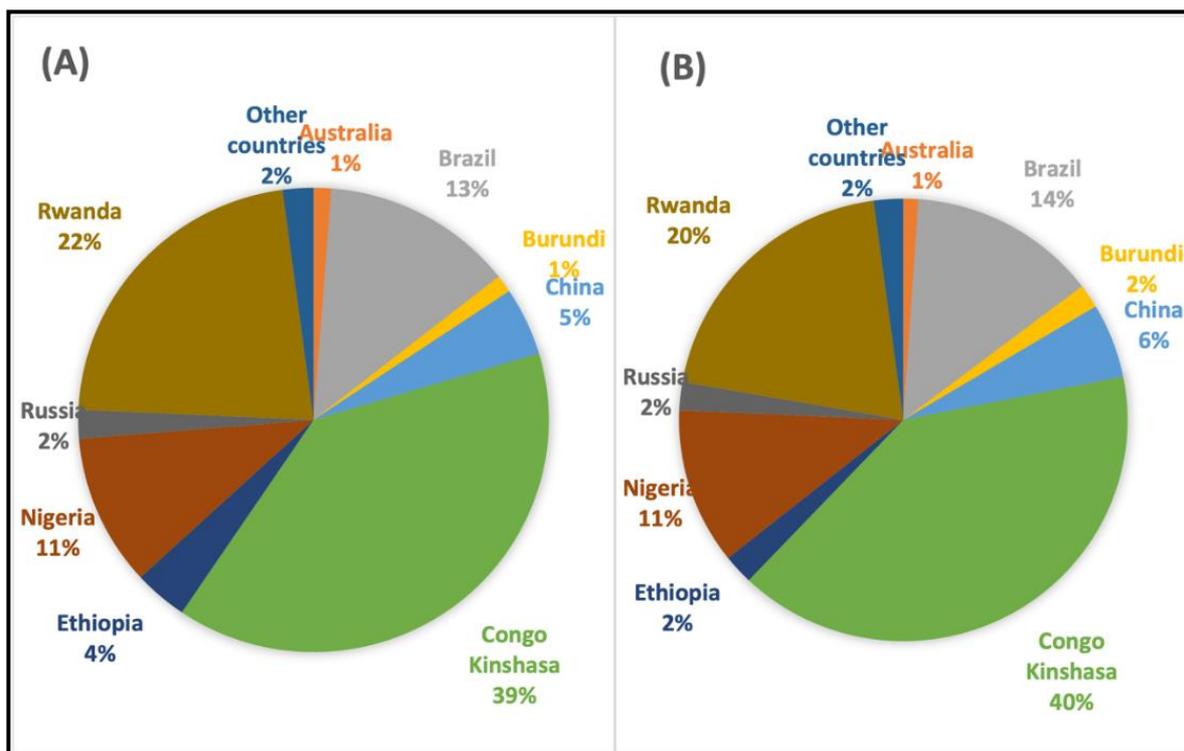
Figure **4.1**: Global Tantalum Mines Production (A) 2018 and (B) 2019 (United States Geological Survey (USGS), 2020)

4.2 Materials and Methods

4.2.1 Materials sampling and handling

Tantalum-tin ore samples used in this study were collected from two different active mines in Rwanda. The first three samples (**R-N1**, **R-N2**, **R-N3**) were collected in raw form from three different points (1°57′43″S 30°21′44″E, 1°57′45″S 30°21′45″E, 1°57′46″S 30°21′39″E) at Ntunga mine in the Eastern Province of Rwanda. Sample **R-KMY Raw** and its concentrate **R-KMNY-Con** were obtained from the Southern Province; Kamonyi District, COMIKA Ltd mine concession (1°55'11.0"S 29°56'33.4"E). These areas have been known for their productions of cassiterite and tantalite ores in Rwanda. The concentrate as received had earlier been pre-concentrated on site by gravity separation. The sampling points were chosen based on known locations of veins in the mining area and sometimes particles of tantalite ore were visible with necked eye. Samples were collected at the surface of the mining pit or inside the shaft and sometimes where landslide occurred due to erosion.

The sampled ores were crushed, and ground to finer size of 125 μm using a ball mill. After grinding, the ore powder obtained were mixed thoroughly, and a representative sample was taken for physico-chemical and mineralogical characterization. The ore-samples were sieved and classified into different size fractions ranging from 355 to 125 μm to further understand more the particle size distribution of the minerals of interest within the ore-samples.

4.2.3 Instrumentation and analytical sample preparation

The particle size analysis of the ore sample was performed by using particle size analyzer, the Microtrac flowSync that uses two blue lasers for laser diffraction analysis (approximately 14 nm resolution) combined with 2D image analysis to capture the particle size distribution data. The carrier fluid is deionized (DI) water with a refractive index of 1.33. The sample was prepared by adding the powder sample to a 1:100 dilution of Triton-X100, to allow particles integration into the DI water and micro-pipetted in until the loading factor was 0.950 - 0.956. The sample system (wet) operates at a flow rate of 55% and before introduction of the subsequent samples, the system is rinsed two times, and deaerated three times. The particles size with upper and lower edge is 2000 and 0.0107 μm, respectively.

The mineralogical characteristics and phases of the investigated ore-samples were determined using PANAnalytical Empyrean X-ray Diffractometer with a Cu-Kα (λ = 0.1540 nm) radiation source operated at 45 kV and 40 mA. The well-ground powder sample was filled in hole of sample holder and smoothened surface aligned with the upper edge of the sample holder before introduced into the x-ray machine at the sample stage and being scanned between 5° and 90° 2theta degrees range. The diffractograms obtained were interpreted using X'Pert HighScore Plus (version 4.6a (4.6.1.23823)).

The Scanning Electron Microscopy attached with energy-dispersive x-ray spectroscopy (A JSM 700F SEM/EDS) was also used for surface morphology and elemental analysis of the investigated samples. The SEM/EDS powder sample was carefully prepared first by fixing a carbon

double-sided sticker on sample holder and using a spoon to collect a small amount of sample and allow it to fall on the exposed side of the carbon sticker. Then, using air spray to remove the excess particles and mounting the sample into the specimen holder and now sample-specimen is ready to be inserted into SEM chamber.

The quantitative elemental compositions of the ore-samples were determined using the Perkin Elmer Optima 8000 ICP-OES. The elemental analysis was performed at different spectral emission lines using RF Power of 1500W with a Plasma and pump flow rate of 14.0 L/min, and 1.5ml/min, respectively. All the analytical instruments used for the analysis and characterization of the investigated ore-samples are located at Worcester Polytechnic Institute (WPI), USA.

The samples for ICP-OES characterization were prepared by fusing in furnace at 1000°C a mixture of the ore-sample (0.1g) with (1.0g) of fluxing material (lithium tetraborate) in graphite crucible. After one hour of heating, the melt was immediately dissolved in 25% nitric acid and stirred at room temperature for 90 minutes. To ensure a complete dissolution of all elements, a small amount (1.5 mL) of concentrated hydrofluoric acid was added. Then, 1.5 mL of the dissolved sample solution were taken and diluted 10 or 100 times depending on concentration of the analyte with 2% nitric acid to obtain 15 mL of analytical solution (Delijska et al., 1988). The standard solutions for calibrating ICP-OES were prepared by mixing appropriate volumes of all the relevant metals stock standard solutions and diluting the mixture with an appropriate volume of 2% nitric acid to make a total volume of 15 mL. From this solution, calibration solutions with concentrations of 10.0, 1.0, 0.1, and 0.01 ppm were prepared, and 2% nitric acid was used as blank solution.

4.2.4 Sample preparation and characterization

The sampled ores were crushed, and ground to finer size of 125 μm using a ball mill. After grinding, the ore powder obtained were mixed thoroughly, and a representative sample was taken for physico-chemical and mineralogical characterization. The bulk density, tapped density, Carr's compressibility index (C) and Hausner ratio (H) were determined to get some information about

powder properties and inter-particulate interactions in the studied samples. These interactions influence the bulk properties of the powder material and its flow due to the mechanical overlapping and interlocking of rock fragments (Clayton, 2018; Mukhopadhyay et al., 2018). The bulk and tap densities determination were carried out by filling the ore-sample into a graduated cylinder and weighing the mass of ore and its corresponding volume. The ratio of the mass to the volume obtained gives the value of the bulk density of the material. The tapped density was calculated after tapping mechanically the graduated cylinder containing the powdered ore-sample at least 125 taps and allowing it to fall under its own mass until the smallest final volume is obtained (Honarpour et al., 2012; USPC, 2014). The compressibility index (C) and Hausner ratio (H) of the different samples were determined using Equation (1) and (2):

$$C = 100(1 - \rho_B/\rho_T) \qquad \text{Eq. } \mathbf{4.1}$$

$$H = \rho_T/\rho_B \qquad \text{Eq. } \mathbf{4.2}$$

where ρ_B and ρ_T are the powder's bulk and tapped densities respectively (USPC, 2014).

A table of flowability characteristics based on values of C and H was used to compare and evaluate the flowability of the ore-samples studied (Usama M. Attia, Andrew Fones, Ross Trepleton, Hugh Hamilton, Susan Davies, 2014). The C and H values for the sample R-KMY Con are 9.98 and 1.11 which indicate that the sample has excellent flowability; the particles are mainly heavy, large size and of irregular shapes, thus increased volume. The values of bulk density, tapped density, C and H for the different samples are summarized in Table 1.

4.3 Results and Discussions

4.3.1 Physical Properties

Physical properties used to study and describe the ore mineral samples (powder) include particle size distribution, densities and interparticle voids interactions. The inter-particle interactions influence the bulk properties of the powder material and its flow due to the overlapping and

interlocking of rock fragments (Mukhopadhyay et al., 2018). Rock density is an important source of information required for mineral resource and ore reserve estimation such as the ore tonnage and mineralization grades (Abzalov, 2013; Haldar, 2018; Makhuvha et al., 2014). The bulk density of a rock is defined as the total mass of dried rock sample to its volume (Blistan et al., 2020). Since powders and granules are composed of particles and voids, bulk densities of free-flowing powders and granular substances depend on their texture, mineralogy, mass, particle shape and size distribution, and handling practices (Scogings, 2015). For a given mass, higher bulk densities indicate the powder compactness state, increased strength and lack of powder structure whereas lower bulk density indicates higher coarse-fragments content (Hossain et al., 2015; Mukhopadhyay et al., 2018).

In order to get some insights on the inter-particulate voids interactions and to assess the flow properties of the different ore samples, we determined their bulk and tapped densities. Figure 4.2 shows the comparison between bulk and tapped densities of the investigated ore samples. From the figure, sample R-KMY Con has the largest bulk and tap densities implying that the inter-particulate voids interactions are lesser than those in R-N1, R-N2 and R-N3. This increase in densities is attributed to the fact that the R-KMY Con has heavy particles with different sizes and shapes, thus higher volume and density when packed and compared to the rest of the samples. We also determined the Hausner ratio and Carr's compressibility index from the bulk and tapped densities to understand the flowability characteristics of the samples. The C and H values of all the raw samples; R-N1, R-N2 and R-N3; range from 32.00 to 36.00 and from 1.47 to 1.56 respectively, showing that the particles are likely to be fine and spherical, thus the samples have poor flowability or good cohesive character (Usama M. Attia, Andrew Fones, Ross Trepleton, Hugh Hamilton, Susan Davies, 2014). The C and H values for the sample R-KMY Con are 9.98 and 1.11 which indicate that the sample has excellent flowability; the particles are mainly heavy, large size and of irregular shapes, thus increased volume. The values of bulk density, tapped density, C and H for the different samples are summarized in Table 4.1.
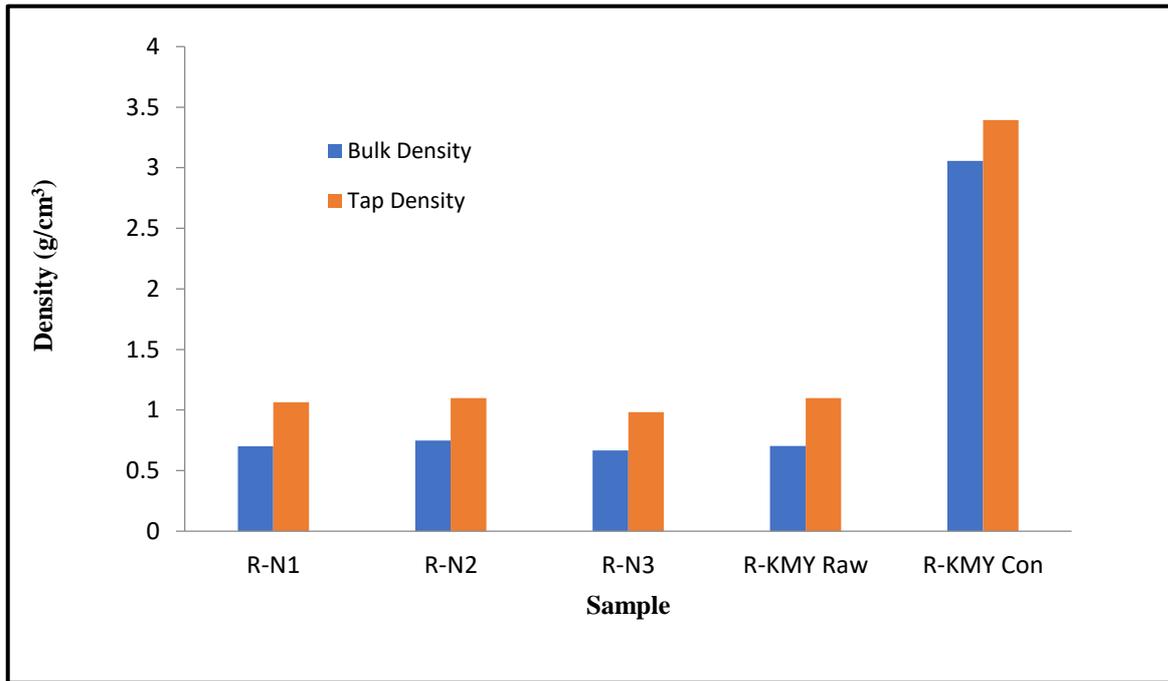
Figure **4.2**: Comparison between bulk and tap densities of investigated ore-samples

Table **4.1**: Bulk, Tap Densities, Carr's Index and Hausner Ratio for the different samples

Sample	Mass (g)	Bulk volume (cm^3)	Tapped volume (cm^3)	Bulk Density (g.cm^{-3})	Tapped Density (g.cm^{-3})	Carr's index (%)	Hausner ratio
R-N1	7.54	25	16.50	0.701	1.063	34.05	1.51
R-N2	8.69	25	17.00	0.747	1.099	32.02	1.47
R-N3	6.68	25	17.00	0.667	0.981	32.00	1.47
R-KMY Raw	7.56	25	16.00	0.702	1.097	36.00	1.56
R-KMY Con	6.40	25	22.50	3.056	3.395	9.98	1.11

The particle size distributions indicate the range size in which particles of minerals with commercial value are likely to be concentrated. The particle size distributions of the ore-samples were evaluated using the particle size analyzer, the Microtrac flowSync, and the results obtained are expressed as log-normal distributions as depicted in Figure 4.3. From the figure, the particle size distribution for sample R-N1 showed a multi-modal distribution where 10% of the total volume of

particles have diameters smaller than 4.05 µm, 50% have diameters smaller than 51.35 µm and 90% have diameters below 229.20 µm. Sample R-N2 displays a bimodal distribution where 10% of the particles have diameters less than 4.67 µm, 50% have diameters smaller than 39.83 µm and 90% of the particles have diameter lower than 230.10 µm. Samples R-N3 and R-KMY Raw showed normal particle distributions with 10%, 50 % and 90% of the particles having diameters which are respectively less than 4.20, 37.0, 202.0, and 4.60, 32.60, 189.70 µm. The sample R-KMY Con showed a negatively skewed particle size distribution with one peak. The particle sizes are distributed in such way that 10% have diameters below 7.60 µm, 50% below 83.20 and 90% less than 225.40 µm. From the analysis, we see that samples R-N1 and R-N2 have more coarse-grained particles.
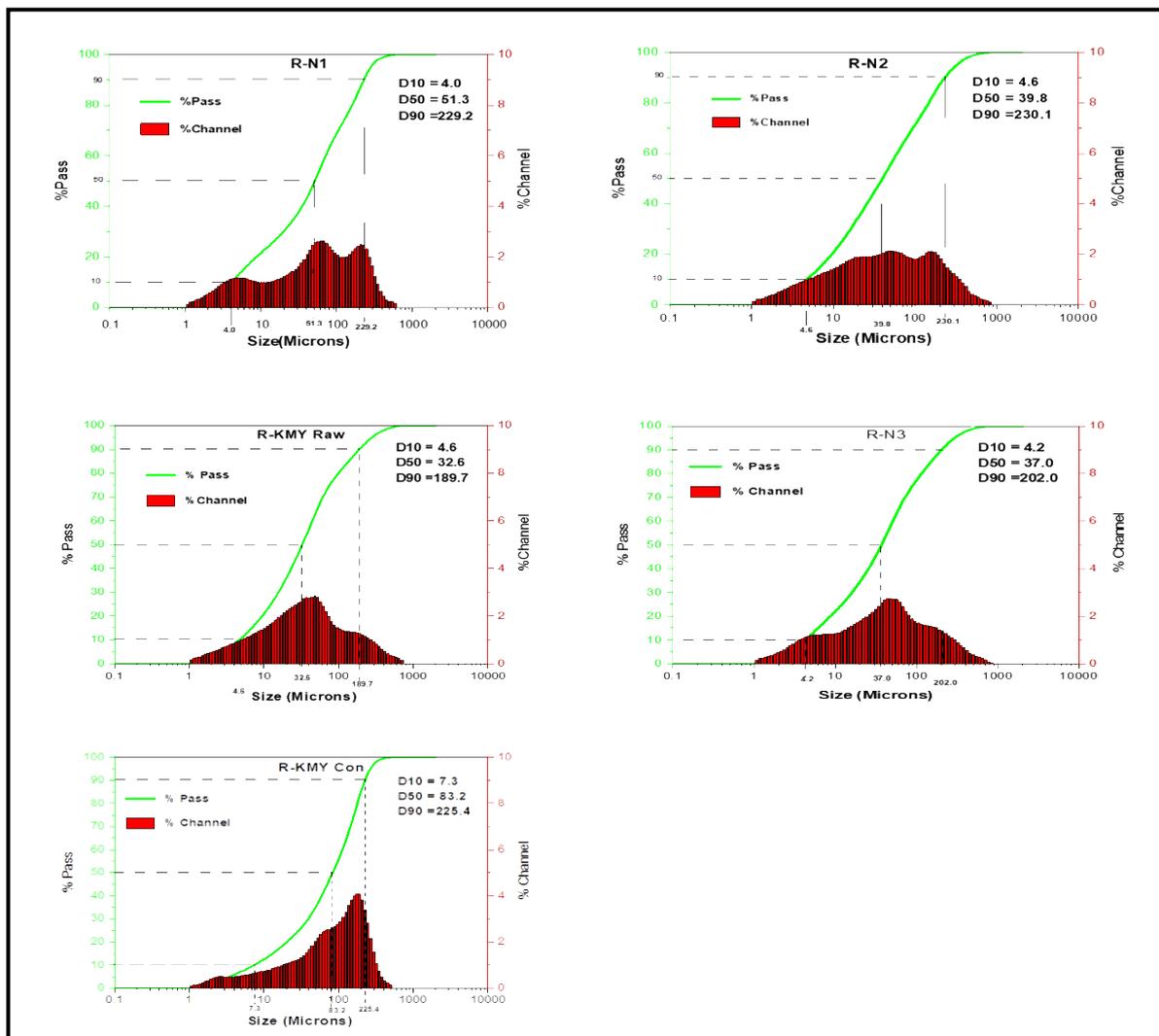
Figure **4.3**: Particle size distribution of samples R-N1, R-N2, R-N3, and R-KMY Con

To get more understanding on the particle size distribution of the ore-samples, the samples were sieved and classified into different size fractions from 355 to 125µm; as presented in Table 4.2; and each fraction obtained were beneficiated by gravity concentration to reduce the amount of gangue materials, mostly the light alumino-silicates minerals. The feed and concentrate obtained were taken for further characterization using ICP-OES. From Table 4.2, it is seen that the valuable minerals are likely to be located within the fraction with the highest percentage retained (wt%), 125 µm.

Table **4.2**: Size classification of investigated ore-samples

Sample	Total mass (g)	Sieve size (µm)	Mass retained (g)	Percentage retained (wt%)
R-N1	1062.59	355	210.79	19.83
		250	359.31	33.81
		125	492.49	46.34
R-N2	1199.71	355	110.43	9.20
		250	149.92	12.50
		125	939.39	78.30
R-N3	1514.52	355	124.25	8.20
		250	450.94	29.78
		125	939.33	62.02
R-KMY	1019.68	355	185.75	18.22
		250	639.07	62.67
		125	194.86	19.11

4.3.2 Chemical and Mineralogical Studies

The major elements associated with tantalum, which mostly contribute to the physical characteristics of the containing minerals, dictate the suitable method for its beneficiation (Adetunji et al., 2005). The ICP-OES analysis of the ore-samples revealed the presence of Ta, Nb, Mn, Fe, Sn,

Mg, Ti, U, Th, O among others. These elements are mainly dominated by Fe and Nb followed by Mn, Sn and Mg which are the main components of tantalite, columbite and cassiterite minerals. These elements were then expressed as oxides to reflect their natural occurrence in the investigated samples and the results are presented in Table 4.3.

Table **4.3**: ICP-OES Results of the studied ore-samples before size classification and beneficiation

Oxides (%)	R-TN1	R-TN2	R-TN3	R-KMY Raw	R-KMY Con
Ta_2O_5	0.063	0.039	0.042	0.057	4.594
Nb_2O_5	0.062	0.050	0.057	0.062	2.666
Fe_2O_3	0.242	0.440	0.194	0.769	1.357
MnO	0.178	0.080	0.160	0.1860	1.420
MgO	0.124	0.133	0.103	0.113	0.653
SnO_2	0.256	0.067	0.088	0.469	53.443
WO_3	0.055	0.052	0.046	0.046	0.372
TiO_2	0.093	0.139	0.073	0.109	0.666
CaO	0.118	0.092	0.085	0.104	0.381
SiO_2	22.858	22.474	21.304	30.370	10.130
Al_2O_3	31.620	20.421	22.909	18.046	3.139
Na_2O	0.361	0.310	0.296	0.434	1.295
ZrO	0.054	0.054	0.051	0.056	0.446
ThO_2	0.083	0.086	0.100	0.098	0.095
U_3O_8	0.160	0.116	0.148	0.121	0.076

From Table 4.3, compositions of tantalum and niobium oxides in the raw samples R-N1, R-N2, R-N3, and R-KMY Raw were almost the same. The highest levels of Ta_2O_5 and Nb_2O_5 were 0.063wt% and 0.062wt% respectively in sample R-N1, while the lowest concentrations were 0.039wt% and 0.050wt% in samples R-N2. The percentage weights of Ta_2O_5 and Nb_2O_5 increased

from 0.057 and 0.062 to 4.594 and 2.666 in samples R-KMY Raw and R-KMY Con respectively. The results further showed an appreciable concentration of tin oxide ranging from 0.067wt% to 0.469wt% in samples R-N2 and R-KMY Raw respectively. In all ore-samples, concentration of Sn is higher than that of Ta and Nb, and concentration of Nb and Fe is higher than that of Ta and Mn. This means that the main mineral with commercial value in the ore-samples is cassiterite associated with particles of columbite-(Fe). The highest concentration of tin oxide 53.44wt% associated with tantalite-(Mn) (4.59wt% Ta_2O_5 and 1.42 wt% MnO) was observed in the concentrate R-KMY Con.

Radioactive elements such as thorium and uranium were also detected in trace amount below the critical value of 0.5wt% in all ore-samples. All investigated ore-samples have almost similar mineralogical compositions, however sample R-KMY Raw showed higher concentrations of most elements analyzed except for aluminium. This may be due to the variations in mineralization of vein deposits hosting these minerals.

To further understand the mineralogy of the samples, we beneficiated the ore-samples by rough gravity concentration to reduce the gangue materials. The feed and concentrate obtained were characterized by ICP-OES to know their chemical compositions and the results are presented in Table 4.4 and Table 4.5. In the feed (Table 4.4), most of the minerals with commercial value are concentrated in the size of 125 and 250 μm. In the concentrate portion (Table 4.5), particles of valuable minerals such as those of Ta, Nb, Fe and Mn are concentrated in the size of 125 μm except for the samples R-N3 and R-KMY where they are more retained in the size of 250 μm and 355 μm respectively. Tin in form of cassiterite; which is the main mineral; is concentrated within the size of 355 μm except for sample R-N2 where it is concentrated within 125 μm along with Ta, Nb, and Fe.

Table **4.4**: Results of ICP-OES Characterization of the Feed (ore-samples) in different sizes

Sample	Size (µm)	Feed composition (%)						
		Ta	Nb	Fe	Mn	Sn	Si	Al
R-N1	355	0.026	0.043	0.402	0.058	0.014	24.48	19.49
	250	0.0064	0.010	0.367	0.0484	0.042	9.406	19.24
	125	0.0143	0.016	0.400	0.075	0.082	9.887	20.70
R-N2	355	0.008	0.008	0.630	0.0456	0.074	40.393	8.428
	250	0.027	0.030	0.795	0.060	0.183	36.87	11.41
	125	0.004	0.014	1.151	0.088	0.059	7.434	20.47
R-N3	355	0.010	0.016	0.267	0.051	0.048	7.317	13.73
	250	0.010	0.016	0.406	0.060	0.064	7.905	18.07
	125	0.013	0.020	0.367	0.082	0.064	7.684	17.50
R-KMY	355	0.033	0.015	1.068	0.053	0.152	33.55	9.93
	250	0.013	0.025	1.270	0.060	0.228	9.876	10.44
	125	0.007	0.017	1.468	0.093	0.276	6.276	10.32

However, in both the feed and the concentrate, concentration of Sn is higher than that of either Ta or Nb. In the feed, the percentage content of Nb and Fe is higher than that of Ta and Mn respectively for most of the fraction sizes. The highest amount of Fe and Nb in the concentrate is 5.90wt% and 5.38wt% respectively in samples R-N2 and R-N3 while for Ta the value is 6.27wt% in sample R-N1. With exception of sample R-N1, Mn content is always lower than that of Fe. These facts make samples R-N2 and R-N3 to be columbite-(Fe) while R-N1 is tantalite-(Mn) as later confirmed by XRD analysis. The percentage of silicon and aluminium in form of kaolinite and muscovite which are the main components of the gangue materials, they are significantly reduced in the concentrate.

Table **4.5**: Results of ICP-OES Characterization of the Concentrate in different sizes

Sample	Size(µm)	Concentrate composition (%)						
		Ta	Nb	Fe	Mn	Sn	Si	Al
R-N1	355	2.527	2.143	0.378	0.773	52.094	10.44	2.30
	250	4.178	3.226	1.544	1.215	41.486	10.639	3.14
	125	6.279	4.831	1.235	1.896	33.340	4.052	2.65
R-N2	355	2.717	2.839	5.299	1.201	19.939	26.601	5.01
	250	2.273	2.320	5.907	1.000	23.254	26.419	2.46
	125	3.932	3.571	5.044	1.576	40.128	3.152	0.876
R-N3	355	3.937	4.755	1.689	1.740	48.798	8.238	1.30
	250	4.960	5.388	2.273	2.001	23.531	11.937	1.47
	125	4.538	4.909	2.865	1.825	22.625	14.4	1.79
R-KMY	355	4.55	1.75	3.78	0.82	41.75	15.43	1.73
	250	3.94	1.45	2.84	0.71	35.34	10.55	1.53
	125	3.38	1.17	2.35	0.60	37.75	9.20	1.24

4.3.3 SEM-EDS Results

A representative portion was taken from the raw samples R-N1, R-N2 and R-KMY Raw and their concentrates for SEM-EDS analysis to know their surface characteristics and elemental compositions, the results are depicted in Figure 4.4. The SEM image of raw samples Figure 4.4(a, b, c) demonstrates surface morphology characterized by coarse particles of different shapes and sizes on which the very fine particles are stacked and create a rough surface with porous structures. The morphology of the concentrate Figure 4.4 (d, e, f) is described by granular structure of particles of larger sizes with compact and smooth surface. This means that most of the gangue minerals were removed from the particle surface leaving larger and heavier particles, thus the grade of valuable minerals increased as determined in the semi-quantitative EDS.
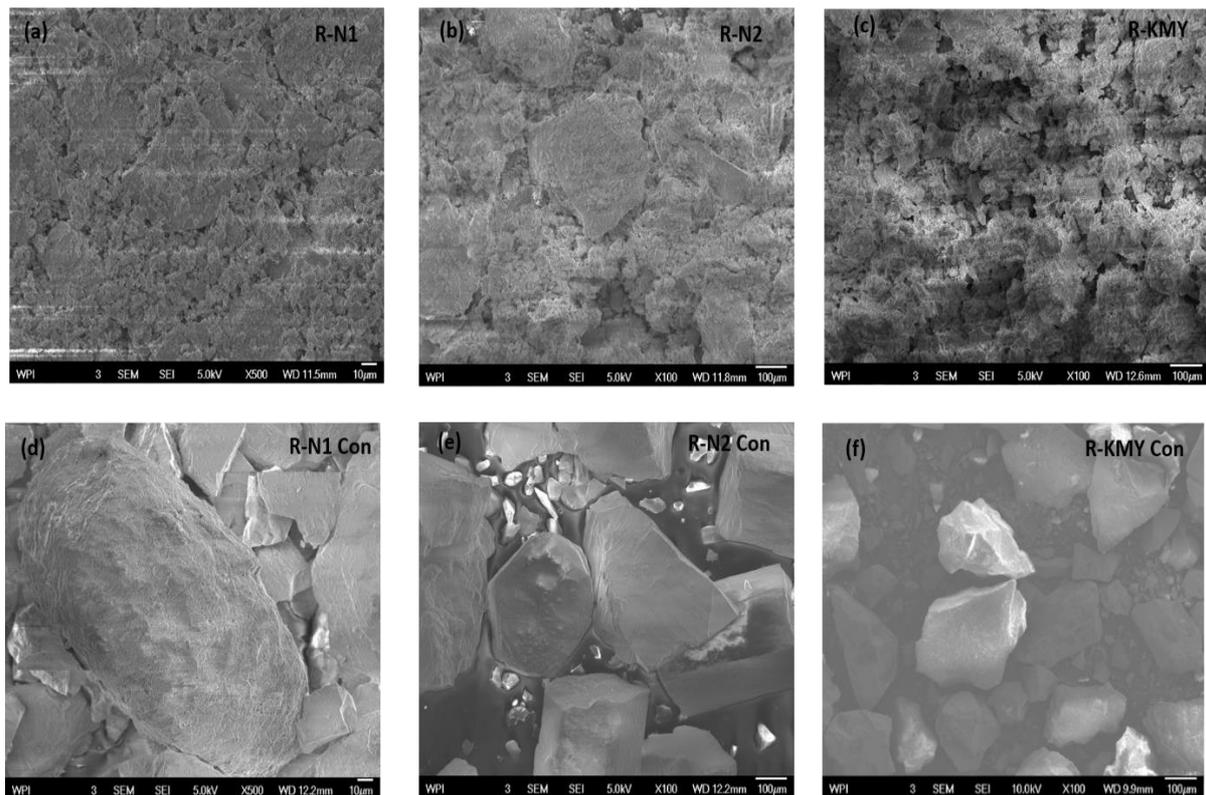
Figure **4.4**: SEM images of the raw (a, b, c,) and concentrated ore-samples (d, e, f)

The semi-quantitative EDS analysis of the ore-samples investigated in their raw forms, indicated that the surface composition is predominated with O, Si, and Al (Figure 4.5) which confirm the presence of quartz, kaolinite and muscovite phases as further indicated by the XRD analysis in the Figure 4.7. The percentages of elements with commercial value such as tantalum, niobium, tin, and iron were very low, and some were not even detected. However, after beneficiation which reduced the gangue minerals mainly silicon and aluminium, the percentage composition of these valuable elements was increased, and mostly dominated by tin, niobium and iron as presented in Figure 4.6. From the figure, it is evident that tin in form cassiterite is the main mineral of commercial value present in all samples, although samples R-N2 and R-KMY displayed in addition good signal columbite-(Fe).
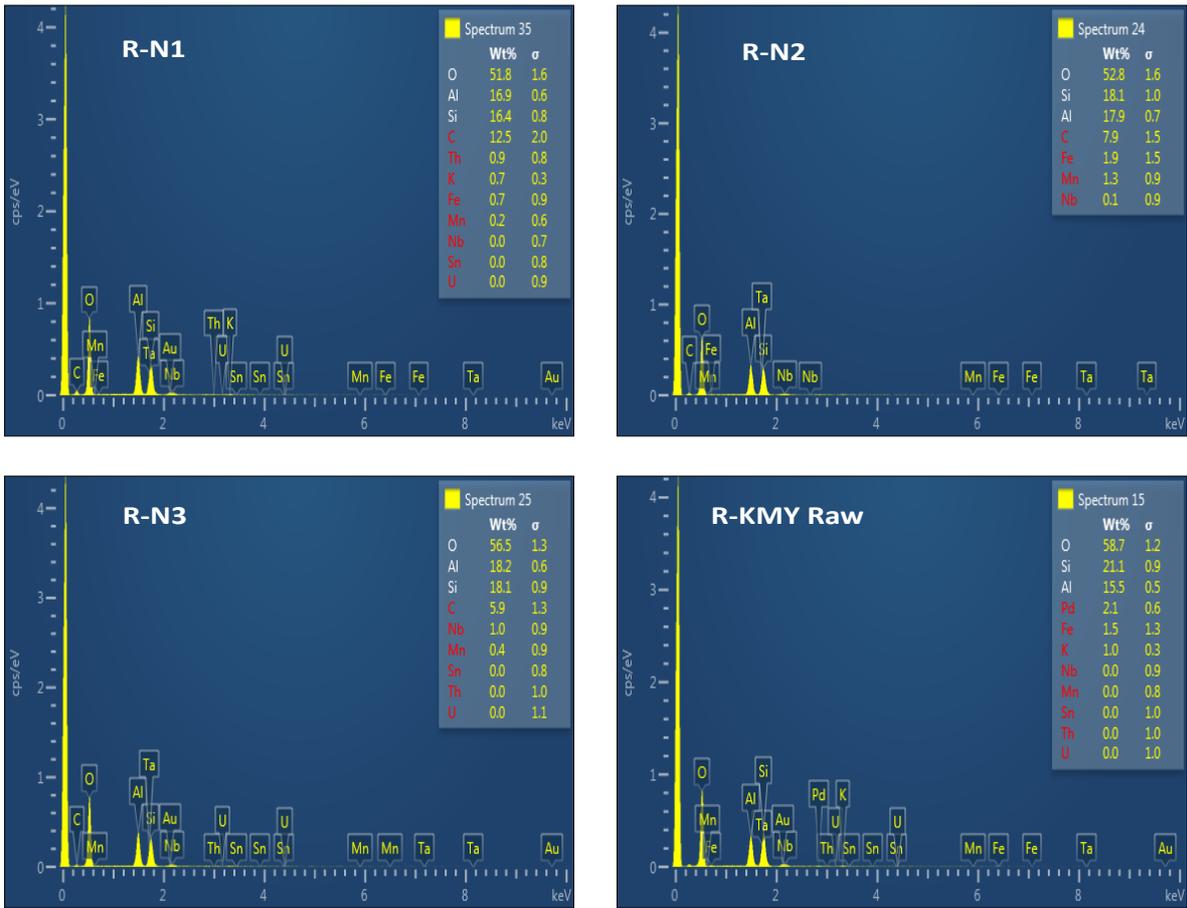
Figure **4.5**: EDS Spectra of the ore-samples before beneficiation
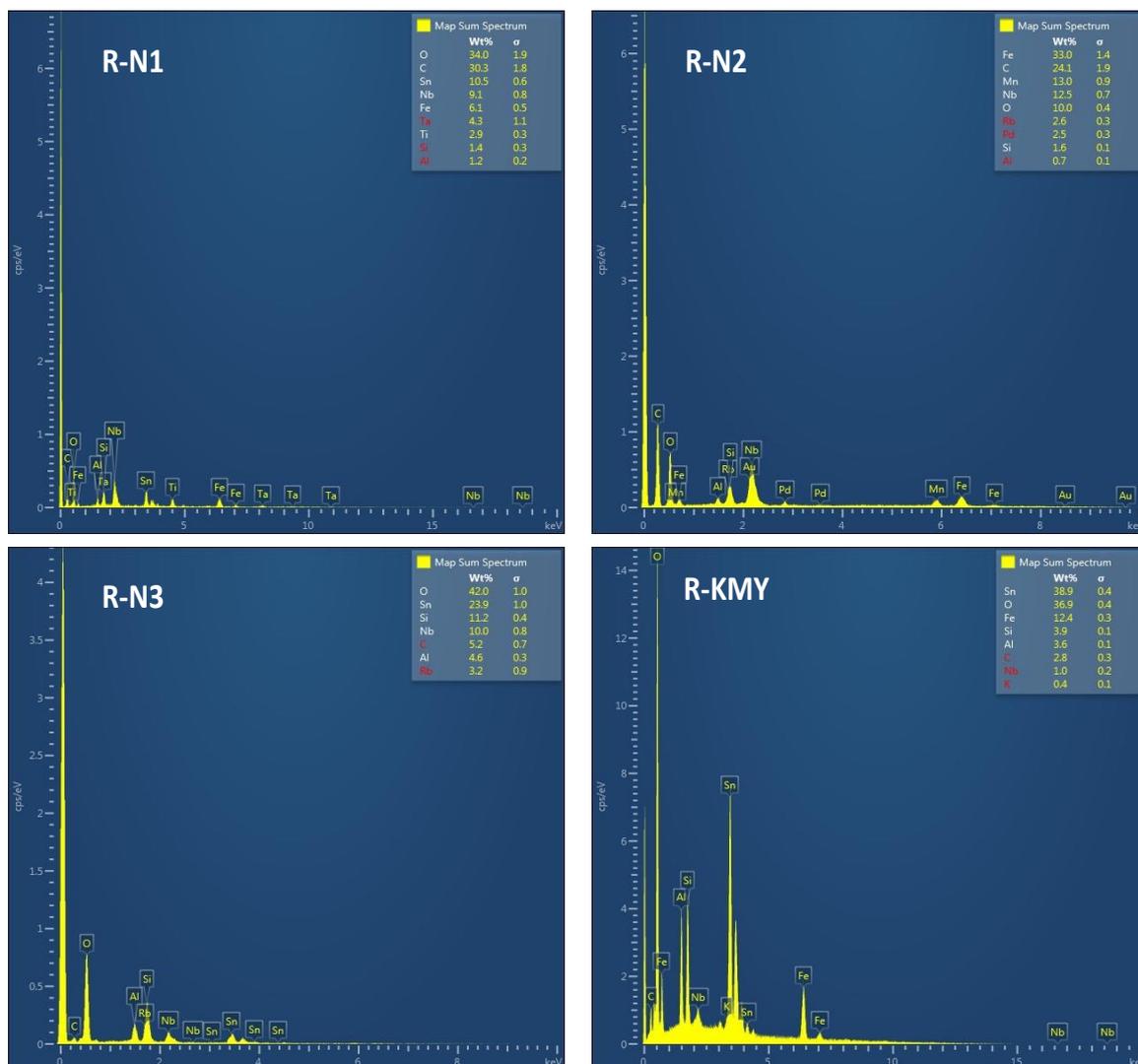
Figure **4.6**: EDS Spectra of the concentrates after beneficiation of the ore-samples

4.3.4 XRD Analysis

Figure 4.7 present a comparison of XRD patterns of the ore-samples studied in their raw forms. From the figure, the diffractograms of all the ore-samples were found to have similar characteristic peaks with minor differences in intensities. Relative to the rest of the samples, R-KMY showed diffraction patterns with smaller peak intensities. The analysis of the diffractograms of the samples revealed the presence of quartz, kaolinite, and muscovite minerals, though quartz was not detected in sample R-N2. These minerals are usually found in placer deposits of pegmatite rocks resulting from deep weathering of igneous rocks and are also known to harbor some valuable minerals such as tin, tantalum, iron, niobium and manganese (Goodship et al., 2019; Klosek-Wawrzyn et al., 2013; Szegediensis, 2003).
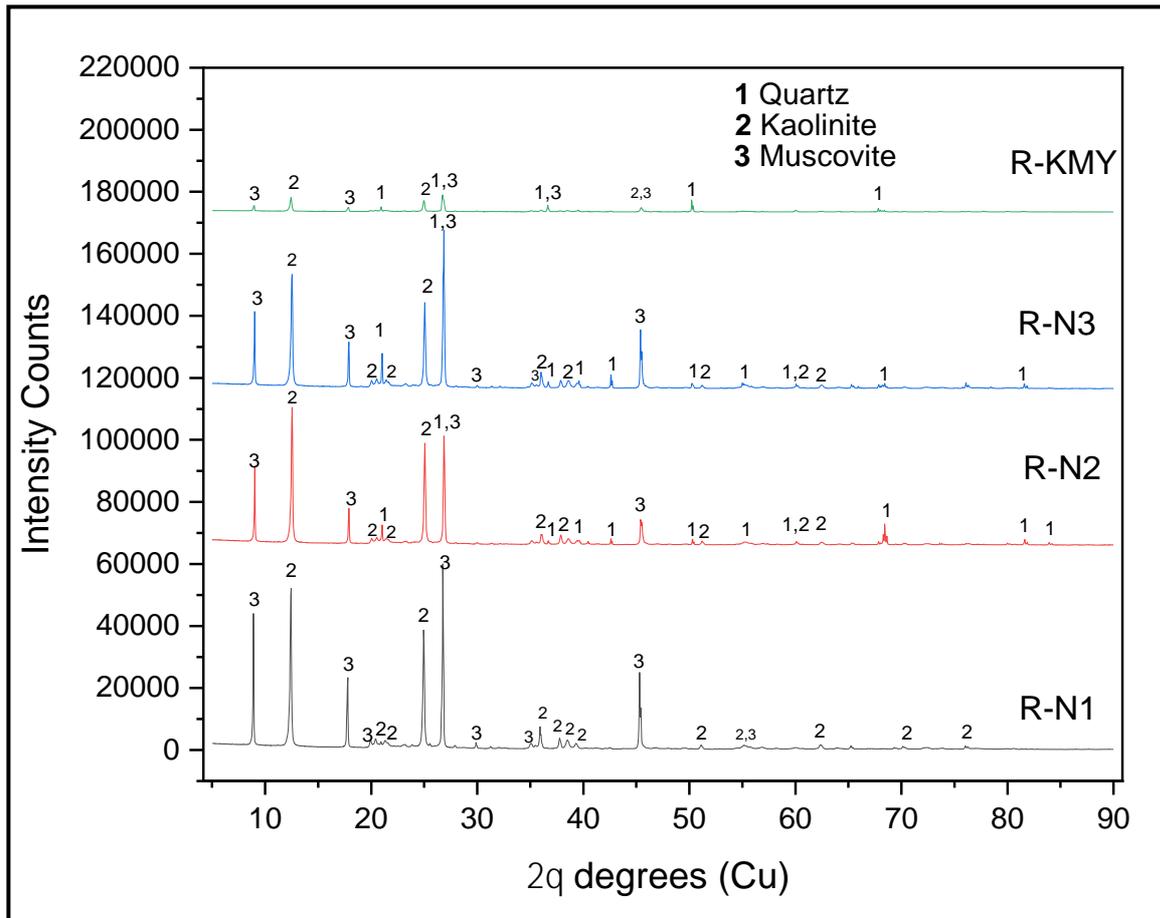
Figure **4.7**: XRD Pattern of ore-samples (Minerals in Raw Form)

The peaks corresponding to the valuable minerals such as cassiterite, columbite, and tantalite were not visible possibly because they were masked by other peaks from the gangue. To figure out the presence of these minerals, we carried out XRD analysis of the concentrated portion of the samples, and the results are presented in Figure 4. 8 and Figure 4. 9. The XRD pattern of samples R-N1 and R-N2 showed almost similar characteristic peaks with minor differences in peak intensities. The analysis of these peaks revealed that the main constituent phases are cassiterite associated with tantalite-(Mn) and columbite-(Fe) minerals with minor peaks of quartz. The diffractogram of samples R-N3 and R-KMY presented in Figure 4. 9 showed distinctive peaks with those of sample R-N3 corresponding mainly to columbite-(Fe) and alpha iron hosted in zeolite and quartz phases. The diffraction peaks in sample R-KMY mainly correspond to cassiterite and quartz minerals. This observation agrees with the results of ICP-OES characterization (Table 4. 4).
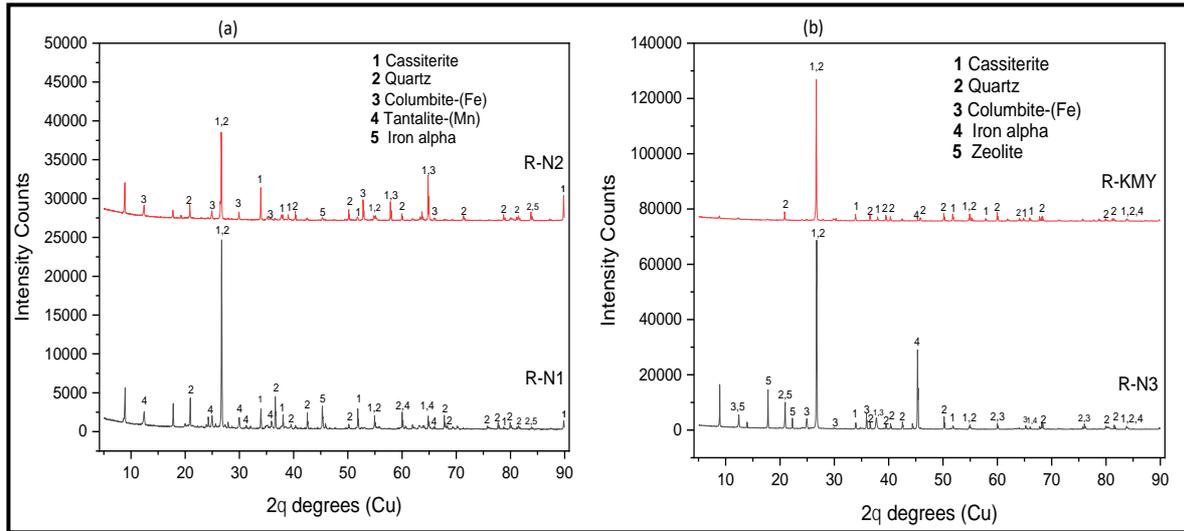
Figure **4.8**: XRD Pattern of concentrates of R-N1, R-N2, R-N3 and R-KMY after beneficiation of their ore-samples

The presence of high concentration of light minerals such as quartz and alumino-silicates (specific gravity ~2.8) and the heavy minerals such as cassiterite and columbite-(Fe) allows the ore-samples to be concentrated by gravity and magnetic separation as a possible beneficiation route. The observed differences in composition of valuable minerals of the studied ore-samples could be explained in terms of the diversity in mineralization of the ore deposits from site to site and from vein to vein (Adetunji et al., 2005), and mainly to the fact that niobium and tantalum can substitute each other freely in their minerals, the same situation also exists for iron and manganese (Inorganic Ventures, n.d.).

4.4 Conclusion

The present study investigated physico-chemical and mineralogical characteristics, and compositions of tantalum-tin minerals in the ore-samples collected from different locations in Rwanda (Ntunga and Kamonyi). The studies based on ICP-OES revealed that all the ore-samples investigated have nearly similar chemical and mineralogical compositions, except sample R-KMY Raw which showed higher concentrations of most elements analyzed. The XRD results confirmed the similarities with identical characteristic peaks of the main minerals of quartz, kaolinite, and muscovite, although minor variations in peak intensities were noticed. The elements such as iron, tin, tantalum, and

niobium were detected in low quantities, but their grades increased upon beneficiation of the ore-samples. The main ingredient present was cassiterite in association with columbite-(Fe) and tantalite-(Fe) minerals. The ore-sample was classified as low-grade ore as it contained less than 0.1% Ta_2O_5 and Nb_2O_5, and non-radioactive as the percentage of radioactive oxides were below the critical value of 0.5%. Thus, it requires to under-go concentration processes before dissolution and chemical leaching. The gravity concentration done on the ore-samples resulted in concentrate with compositions of 66.14% SnO_2, 7.66% Ta_2O_5 and 7.70% Nb_2O_5. This study therefore provides the baseline data for the selection and design the appropriate techniques to effectively harness the tantalum-tin minerals from the sampled areas.

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CHAPTER FIVE

5. INVESTIGATION OF THE BEHAVIOR OF ANALYTE GRADE NIOBIUM AND OTHER METALS CONTAINED IN THE ALKALINE SOLUTION TOWARD GUANIDINE CARBONATE

5.1 Introduction

Niobium is a transition metal with chemical properties that are very similar to those of tantalum. Their similarities allow them to be concentrated together and occur in the same geological settings, therefore their metallurgies require to separate them. Tantalum was first successfully separated from niobium in the 'Marignac process' discovered by Jean Charles Galissard de Marignac in 1866 (Linnen et al., 2013). The hydrometallurgical process uses hydrofluoric acid and since that time it has undergone several development where related techniques utilizing acidic media for digestion of the ores were developed to efficiently separate tantalum and niobium. However, in all cases the use of hydrofluoric acid or mixture of highly concentrated acidic solution containing fluoride ion and sulfur trioxide offered excellent results. The limitations of the process are related to the cost of the corrosive HF and environmental concerns (Deblonde et al., 2016; Ungerer et al., 2014).

Only few works have been reviewed on the success of separation of tantalum and niobium in non-fluoride media, for example due to the interesting solubilities of the (Nb, Ta)-containing minerals in alkaline media, it was reported as promising eco-friendly alternative route to be explored more. Thus, since guanidine carbonate was found to possess excellent ability to rapidly and selectively precipitate tantalum from a synthetic alkaline solution containing other metals (Ogi et al., 2018) and due to the similarities between tantalum and niobium, guanidine carbonate would be an excellent chemical reagent to be used in the non-fluoride metallurgy of niobium and tantalum which would eliminate completely the use of fluoride media. Therefore, this study reports an alkali-assisted roasting of the analytical grade niobium oxide aimed to investigate the response of guanidine carbonate towards niobium contained in a synthetic aqueous alkaline solution containing other metals. During roasting, caustic potash becomes fluid and reacts with the molecules of Nb_2O_5 and Ta_2O_5 converts them into K_3NbO_4 and K_3TaO_4 which further hydrolyze and polymerize into

polyoxometalate anionic species ($K_8Nb_6O_{19}$ and $K_8Ta_6O_{19}$) in the leaching step (Gupta & Suri, 1994; Saran et al., 2004; Wang et al., 2010). Guanidine is an amine, strong base which forms a highly stable cation (guanidinium $C(NH_2)_3^+$) in aqueous solution due to its efficient resonance stabilization and solvation by water molecules (Perrin & International Union of Pure and Applied Chemistry. Commission on Electroanalytical Chemistry., 1972). The information obtained from the results would be a baseline to design experiments for the study of the alkali-assisted dissolution of the Nigerian and Rwandan columbite-tantalite concentrates aimed to extract Nb and Ta from their pregnant leach solutions. The findings are ensured in the subsequent chapters of this work. Previous studies (Ogi et al., 2018) has already investigated the response of analytical tantalum oxide to guanidine-assisted precipitation.

5.2 Materials and Methods

5.2.1 Materials

All materials used in this study were chemical reagents of analytical grade. Niobium (v) oxide, -325Mesh, with purity of 99.9%, sodium tungstate dihydrate (ACS reagent), guanidine carbonate salt (99%w/w) and potassium hydroxide (ACS reagent) pellets for analysis were purchased from Sigma Aldrich Inc.

5.2.2 Experimental procedures

A stock solution of 9.50 mM of niobium was prepared by roasting a mixture of 1.26 g of niobium oxide and 2.52 g of ground potassium hydroxide at 300°C after one hour of roasting, the melt was allowed to cool at room temperature and dissolved in 500 mL of deionized water. 0.783 g of sodium tungstate dihydrate was dissolved in 500 mL of deionized water to prepare a solution of 9.50 mM of tungsten and then 1.130, 2.25 and 4.5 g of guanidine carbonate salt were dissolved in 250 mL of water to prepare a stock solution of 25, 50 and 100 mM of guanidine respectively. The study was carried out by mixing a solution containing dissolved niobium and tungsten and adding to it an appropriate volume of dissolved guanidine carbonate salt. In the first instance, the effect of guanidine

concentration on precipitation of niobium and tungsten were evaluated each independently by fixing the concentration of the metals at 9.5 mM and varying the guanidine concentration.

In the second case, 10 mL of each of the stock solution of niobium and tungsten were mixed in 250 mL beaker to which 20 mL of the guanidine solution were added on continuous stirring at room temperature. This was to evaluate if guanidine can selectively precipitate niobium or co-precipitate together. A precipitate appeared in the solution in lesser than 3 minutes. After a particular time of stirring the mixture was filtered on vacuum pump. The filtrates and stock solution were taken for analysis with ICP-OES to determine the amount of Nb and W remained in the solution after the guanidine precipitation.

5.3 Results and Discussions

The results obtained in both cases are presented in Figure 5. 1 and 5. 2. From Figure 5. 1, it is clear that at lower concentration of guanidine (15 mM), precipitation of Nb was significant but not much higher in 5 mins. However, the recovery of niobium gradually increased as time increased from 96.0% to 97.5% in 10 and 30 minutes. When the guanidine concentration was increased to 50 and 100 mM, the precipitation of niobium was almost the same within 30 minutes and a total recovery of approximately 100% was obtained in 10 minutes. From Figure 5.1 (b) and Figure 5. 2, it was observed that guanidine did not precipitate tungsten from the solution and most of the it remained in the solution and no precipitate was formed when a solution containing tungsten was tested with guanidine. A maximum of 0.65% of tungsten was recovered in 10 minutes with 50 mM of guanidine concentration and the recovery decreased considerably with increase of time. This means that the precipitate formed re-dissolved as time increased.

The general observation was that at 100, 50, and 15 mM guanidine, the niobium-guanidine precipitate appeared in the solution in 3 minutes and the recoveries were maximum at higher guanidine concentration, however no tungsten guanidine precipitate was observed. 50 mM of guanidine which is equivalent to 2.25 g in 250 mL or ~10 mg/mL was consider as the minimum guanidine carbonate concentration that would be sufficient to precipitate the total amount of niobium.

Therefore, an excess of guanidine carbonate would be required during the precipitation of Nb and Ta contained in the pregnant leach solution. For pregnant a leach solution and due to the presence of other dissolved impurities in the leach solution, we presume an excess of guanidine like 12.5 g of guanidine in 250 mL of water as minimum guanidine concentration to precipitate the total Nb and Ta dissolved in PLS.

When guanidine is added to an aqueous solution containing ions of Nb and Ta; the guanidinium ion $C(NH_2)_3^+$ interacts electrostatically with ions of these metals (polyoxometalate) and a white precipitate is formed instantaneously (Equation 5.1) (Ogi et al., 2018).

$$(Ta, Nb)_6O_{19}^{8-}{}_{(aq)} \quad + \quad 8C(NH_2)_3^+{}_{(aq)} \quad \rightarrow \quad (C(NH_2)_3)_8(Ta, Nb)_6O_{19\,(s)} \qquad \text{Eq. } \mathbf{5.1}$$
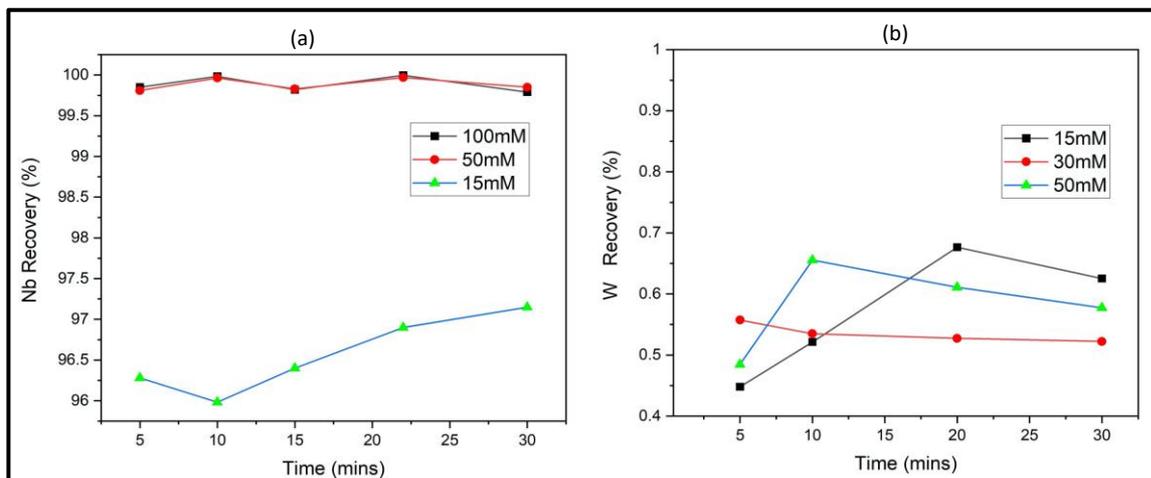
Figure **5.1**: Effect of guanidine concentration on precipitation of (a) niobium and (b) tungsten
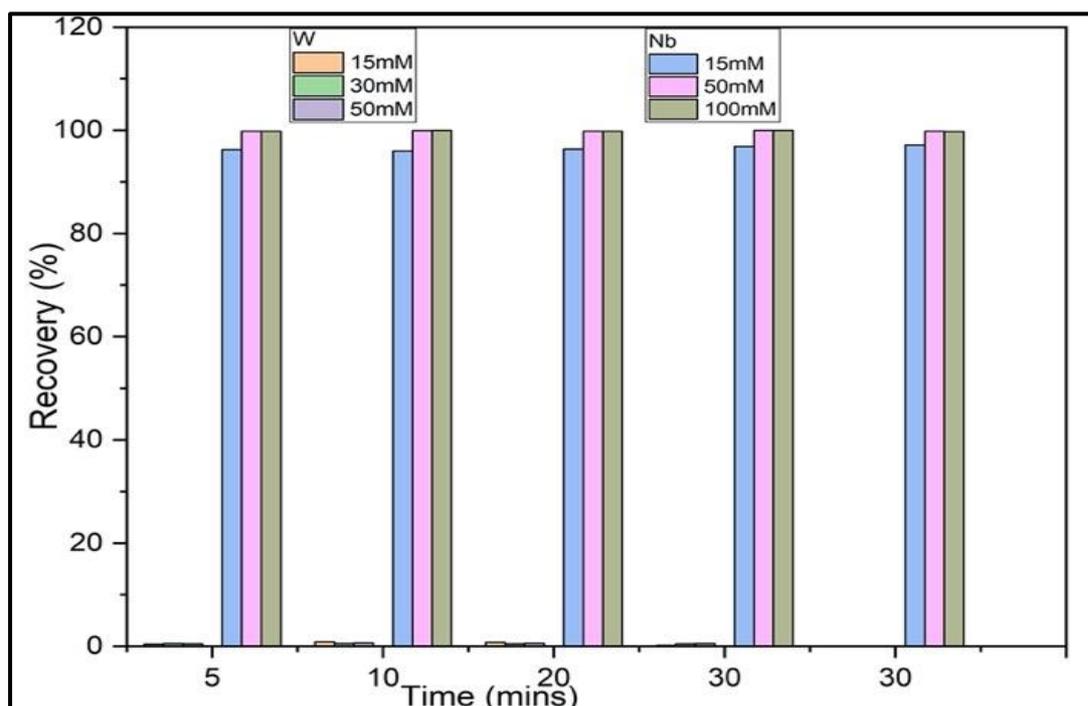
Figure **5.2:** Recovery of niobium and tungsten via induced guanidine precipitation at different time.

5.4 Conclusion

From these results, it is clear, that guanidine carbonate precipitated selectively Nb and Ta from a solution containing other metals, therefore it can be useful in the metallurgy of Nb and Ta. The precipitation of Nb and Ta depends on the concentration of guanidine in the solution. 50 mM of guanidine that is equivalent to approximately 10.0 mg/mL was found to be sufficient to precipitate the total amount of niobium dissolved in the solution while leaving almost the total amount of tungsten in the same solution. Therefore, we expect an excess of guanidine carbonate for a pregnant leach solution, for instance 50 mg/mL of guanidine which is almost equivalent to 277.5 mM to be sufficient to precipitate the total amount of niobium and tantalum dissolved in the pregnant leach solution.

5.5 References

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CHAPTER SIX

6. CAUSTIC POTASH ASSISTED ROASTING OF THE NIGERIAN FERRO-COLUMBITE CONCENTRATE AND GUANIDINE CARBONATE-INDUCED PRECIPITATION: A NOVEL TECHNIQUE FOR EXTRACTION OF NIOBIUM-TANTALUM MIXED-OXIDES

6.0 General background

Nigeria is one of the few countries endowed with mineral deposits of niobium and tantalum and contribute largely to the world's production and supply of these commodities (Nzeh et al., 2022). Significant production of columbite concentrates from placer deposits of Nigeria was between 1950s and 1970s. Since the starting of 21st century, Brazil and Canada are the world's largest producers of niobium concentrates while, DRC, Rwanda, Nigeria, Australia, Mozambique are main suppliers of tantalum concentrates with columbite-tantalite deposits (G. Perrault and E. Manker, 1981; Nzeh et al., 2022). From 2015 to 2020, Central African countries were world's leading producers of tantalum concentrates where DRC Congo, Rwanda followed by Brazil produced tantalum concentrates amounted to 3000, 2000, 1000 total metric tons respectively (Oluwole Ojewale, 2022; United States Geological Survey, 2020). In Nigeria, columbite ores and its associated minerals are mostly found in the northern part of the country specifically in Plateau, Nasarawa, Kogi, Kaduna and Bauchi states. Columbite in Jos, Plateau state usually occurs as accessory minerals disseminated in placer deposits of cassiterite in only few 10 km from the granitic parent rock. Since the installation of smelters for production of columbite, Jos Plateau became a very well-known host of mineral deposits including columbite concentrated by gravity separation from the specific rock source (*Columbite Ore Mineral Deposits in Nigeria with their Locations and Uses*, 2022).

In the second section of this research work, the alkali-assisted roasting of the columbite-tantalite concentrates from two different countries (Nigeria and Rwanda) and the guanidine carbonate-induced extraction of mixed (Nb, Ta)-oxides. Two different samples of concentrated ores from two mining sites in Nigeria were investigated separately for their sustainable dissolution and extraction of mixed oxides of Nb and Ta. One sample from Jos Plateau state named N-Jos Con was investigated independently and the findings are reported in the chapter five. The second sample was from

Nasarawa state, named N-Nass Con, was investigated together with another concentrated sample from Rwanda, named R-KMY Con for comparison purpose. Their results are reported in chapter six. The investigation focused on the alkali-assisted dissolution of main constituents of the concentrate and guanidine carbonate-induced precipitation of niobium and tantalum and then calcination of the resulting (Nb, Ta)-guanidine precipitate.

6.1 Introduction

Niobium (Nb) and tantalum (Ta) are refractory metals due to their unique properties such as extreme corrosion, shear, and high temperature-resistance. Nb has numerous applications; including production of ferro-niobium used as an additive to high-strength low-alloy steels. These structural alloys are widely used in manufacture of oil gas-pipelines, modern automobiles, and stainless steels for other various uses (Abo Khashaba, 2017; Agulyonsky, 2004; Didier et al., 2020; Schulz & Papp, 2014). Further application of niobium is in the production of nickel, cobalt, and iron-based super-alloys used in aircraft engines components, heat-resistant and combustion equipment (Schulz & Papp, 2014). Nb is mainly imported and exported in form of ferro-niobium materials (Didier et al., 2020). The global demand for ferro-niobium has risen and is expected to continue rising by over 8% per year, driven by the increasing global markets for steel in constructions, infrastructure and automotive applications as well as high-strength low-alloy steels (Christmann, 2017; Didier et al., 2020). The refined tantalum finds its broad applications in manufacturing of electronic components; and other high-technology products. These include capacitors and resistors used in mobile phones, computers, digital cameras; and super-alloys used in aerospace and automotive applications (Abo Khashaba, 2017; Espinoza, 2012); and bio-implants served for biomedical applications (Arnould et al., 2010).

Nb and Ta have a very strong geochemical coherence; they are always found together as oxides in the same mineral deposits (Alexander Sutulov and Chun Tsin Wang, 2017; Deblonde et al., 2015). The natural co-occurrence implies their co-extraction from primary resources (MSP-REFRAM, 2020). The common raw materials used for the production of Nb include Nb-Ta containing ores and secondary resources such as scraps, and slags from cassiterite (SnO_2) smelting

processes (Filella, 2017; Luidold, 2019). The economically important ores for sourcing Nb includes the Ta-free pyrochlore $[(Na,Ca)_2Nb_2O_6(OH,F)]$, and the Nb,Ta mixed-oxides of the general formula $[(Fe,Mn)(Nb,Ta)_2O_6]$ with various ratios of Nb-to-Ta (Agulyonsky, 2004). The mineral is called 'columbite' when Nb is the predominant constituent (40-78 % of Nb_2O_5) and 'tantalite' when Ta is the major component (38-86 % of Ta_2O_5) (Agulyonsky, 2004). In these materials, the isomorphism exists between Nb and Ta where they substitute each other freely, the same also exists for iron (Fe) and manganese (Mn) (Ahmed, 2016; Inorganic Ventures, n.d.). These minerals normally occur as accessory minerals disseminated in intrusive pegmatites, granitic pegmatites, and carbonatites of igneous rocks (Melcher et al., 2013). Rocks hosting Nb-Ta minerals are mined and processed to increase the grade of valuable minerals as columbite-tantalite concentrates. The principal method for beneficiation of (Nb,Ta)-ores is related to the higher densities of Nb, Ta and other (Nb,Ta)-carrier minerals that allow them to be concentrated by gravity separation (Bulatovic, 2010). However, losses of the fine Nb/Ta particles are reported especially for -150 and -200 mesh fractions and cyclone overflow slimes. This led to the very low recovery, ranging from 55% to ~65%. There is possibility to float (Nb,Ta) gravity tailings which would increase overall metallurgical recovery, but only few plants have tested this (Bulatovic, 2010).

Traditional and current processing of (Nb, Ta)-bearing minerals

From an industrial viewpoint, current production and purification of these metals and their compounds is a complex process due to their very similar physical and chemical properties (Morrison, 1958; Nete et al., 2014). It involves decomposition and conversion of the Nb-Ta concentrates or their ore deposits into water-soluble compounds. The Nb and Ta containing mineral ores can be decomposed or digested by concentrated hydrofluoric acid (HF) or its mixture with H_2SO_4 or alkali-assisted fusion at elevated temperature (El-Hussaini & El-Hakam Mahdy, 2008; Gupta & Suri, 1994; Kabangu & Crouse, 2012). After digestion of the Nb and Ta mineral ores, the next step is to separate dissolved Nb and Ta from other associated impurities and subsequent separation of Nb and Ta from each other (Gebreyohannes et al., 2018). The first commercially successful process for production and separation of Nb and Ta is called the Marignac process. The process requires complexation of the two

metal ions with fluoride ions (F⁻) during their dissolutions (Agulyonsky, 2004; Deblonde, Chagnes, et al., 2016; EL HUSSAINI, 2009). The dissolution and complexation are accomplished by using a highly concentrated solution of HF or any other sources of fluoride ions. Advantages of fluoride media is that Nb and Ta are highly soluble and can form distinct complexes depending on the acidity level and metals concentration, thus difference in formed Nb and Ta complexes enables their separation. After dissolution, KF or KOH, or KCl is added to the reaction mixture for formation of K-salts (K_2NbOF_5 and K_2TaF_7). The resulting liquor solution is subjected to selective crystallization of the less soluble K_2TaF_7 followed by solvent decantation and filtration to recover Ta. Then the more soluble K_2NbOF_5 is recovered from solution as niobium oxide by precipitation via addition of ammonia solution. The drawback of the process is co-precipitation of multiple impurities such as Ti, Si, and Fe which contaminate the Nb_2O_5 (El-Hazek et al., 2012).

The modern process uses liquid-liquid extraction to effect Nb and Ta loaded into the solution obtained after filtration of the slurry resulting from the digestion of the Nb/Ta minerals with a mixture of HF and H_2SO_4 at elevated temperatures (Agulyansky et al., 2004). At higher acidic level (> 8M H_2SO_4), Nb and Ta are selectively extracted into organic phase leaving other dissolved impurities in aqueous phase. Lowering the acidity level 3-7.5 M H_2SO_4, Nb fluoride complex is back-extracted into flesh aqueous layer leaving the Ta into the organic layer. The Ta fluoride complex is then extracted from organic phase into aqueous layer at low acidic level ~ pH 7 by simply using water (Agulyansky et al., 2004; Nete et al., 2014). However, the process uses corrosive reagents and generates large amount of highly toxic fluoride solution, and it is only appropriate for high-grade (Nb, Ta)-concentrates, thus recently use of alkaline media have caught growing attention for the extraction of Nb and Ta.

In the process of solvent extraction performed in the presence of fluoride, organic solvents such as methyl isobutyl ketone, Octanol, Cyclohexanone, Tributyl phosphate (TBP), Alamine 336, bis (2-ethylhexyl) phosphoric acid (DEHPA) have been investigated for separation of Nb from Ta (Ayanda & Adekola, 2011; Rodríguez et al., 2020; Zhu & Cheng, 2011). The hydrometallurgical

production of Nb and Ta has been historically relying on the use of highly acidic media mentioned above which have many challenges including high-energy demand, corrosivity, terrestrial acidification, and human toxicity (Deblonde et al., 2019; Gebreyohannes et al., 2018). Thus, development of cost-effective and eco-friendly method for the recovery of Nb and Ta from primary and secondary resources has attracted the attention of many researchers (Gebreyohannes et al., 2018; Zhou et al., 2005).

The insolubility nature of compounds, minerals, and ores of Nb and Ta in minerals acids with exception of highly acidic solution of HF or its mixture with sulfuric acid, has led to an alkali-based process for dissolution of these resources. Alkaline roasting or alkaline leaching of Nb-Ta bearing ores produces highly water-soluble Nb-Ta compounds (Shikika et al., 2021). The alkali roasting process has been investigated using various fluxing and complexing agents for decomposition and dissolution of geological samples containing Nb and Ta (Inorganic Ventures, n.d.; Pierret & Wilhelm, 1956). The alkali processing is carried out either by direct leaching of the ore at high pressure and temperature or alkaline roasting (molten salt) to decompose the ore (Ayanda & Adekola, 2011; Nguyen & Lee, 2019; X. Wang et al., 2009; Zhou et al., 2005). During roasting, caustic potash becomes fluid and reacts with the ore-particle where Nb_2O_5 and Ta_2O_5 convert into K_3NbO_4 and K_3TaO_4 which further hydrolyze easily and polymerize into polyoxometalate anionic species ($K_8Nb_6O_{19}$ and $K_8Ta_6O_{19}$) during the leaching (Gupta & Suri, 1994; Saran et al., 2004; X. H. Wang et al., 2010). These species can be leached out by water and recovered via precipitation or solvent extraction. After selective alkaline leaching, dissolved Nb and Ta must be precipitated out of the liquor solution to obtain commercial product or intermediate concentrate.

Calcium-bearing reagents such as ($CaCl_2$, calcium acetate, or calcium hydroxide) have been reported to efficiently precipitate Nb and Ta as calcium hexaniobate and hexatantalate from alkaline solution (Deblonde, Chagnes, et al., 2016). High purity of mixed oxides $(Nb,Ta)_2O_5$ (99.3%) have been recovered from the alkali leach solution through evaporation, then crystallization, and phase transformation with diluted acid and calcination (X. Wang et al., 2009). Nb and Ta have been

precipitated as mixed oxides from strip solution of oxyfluoroniobic and fluorotantalic acids from alkaline liquor by addition of ammonia solution (Agulyonsky, 2004). Acidification of the alkaline leach liquor solution containing polyoxometalate ions of Nb and Ta to pH 2-7 resulted in precipitation of these metals in form of hydrous pentoxides (Equation 6.1) but the process claimed not to be economic for recovering Nb and Ta (Babko & V V; Nabivanets, 1963; Deblonde et al., 2015; Deblonde, Weigel, et al., 2016; InoueYasushi et al., 1985).

$$H_x(Ta, Nb)_6O_{19}^{x-8}{}_{(aq)} + (x-8)H^+{}_{(aq)} \rightarrow 3(Ta, Nb)_2O_{5\ (s)}.nH_2O_{(s)} + (4-3n)H_2O \quad \text{Eq.}$$
6.1
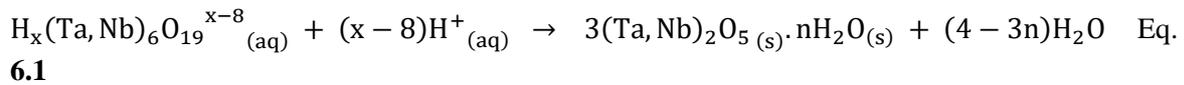
$$0 \leq X \leq 3$$

Amines have been used as extractant in kerosene and produced a highly purified solution of niobium and tantalum (*Tantalum Processing / TIC*, n.d.). Guanidine is an amine, strong base which forms a highly stable cation (guanidinium $C(NH_2)_3{}^+$) in aqueous solution due to its efficient resonance stabilization and solvation by water molecules (Perrin & International Union of Pure and Applied Chemistry. Commission on Electroanalytical Chemistry., 1972). Guanidine has proven the potential to rapidly and selectively precipitate Ta from a synthetic aqueous solution containing other metals such as Si and W (Ogi et al., 2018). Since Ta behaves similarly as Nb and always occur together in the same geological samples, therefore guanidine could be useful to extract these commodities.

The present study focuses on caustic potash assisted-roasting of columbite-Fe concentrate, water-based leaching and precipitation using guanidine carbonate salt to extract Nb and Ta from the liquor solution. Different roasting parameters such as temperature, mass flux-to-concentrate ratio and residence time were evaluated for high dissolution and elucidate the optimized conditions. Furthermore, recovery of mixed Nb and Ta from the optimized leach liquor solution is carried out with application of guanidine carbonate salt ($C_3H_{12}N_6O_3$). To the best of our knowledge, this would be the first-time guanidine amine salt was utilized in the extractive metallurgy of Nb and Ta. The new

processing flowsheet is environmentally friendly, does not require any toxic acid reagents (such as HF) and results in higher extraction yield than existing methods

6.2 Materials and Methods

6.2.1 Materials description and characterization

The material used in this study was a ferro-columbite concentrate (N-Jos Con) provided by S. Danboyi Rinn Nigeria Ltd, a mining company. The concentrate was obtained after gravity concentration of the ore-deposits mined at Kwang in Jos Plateau State of Nigeria, 9°49'52.0"N 8°54'50.0"E (Figure 6.1). 1.053 Kg of the concentrated material (N-Jos Con) as-received from the company was dried and ground to finer size, then screened into two different size fractions, +250 and -250 μm with a sieve. The concentrate-sample was analyzed with X-ray diffractometer for mineral phases identification. Scanning Electron Microscopy attached with Energy Dispersive Spectroscopy (SEM/EDS) was also used for surface morphology analysis and to determine elemental and semi-quantitative chemical compositions of the concentrate sample. However, for ICP-OES characterization, the sample was analyzed before and after sieving to see if further grinding was required to liberate Nb and Ta minerals. All other materials used were chemical reagents and were of analytical grade. Guanidine carbonate salt (99%w/w) and potassium hydroxide (ACS reagent) pellets for analysis were purchased from Sigma Aldrich Inc.

Figure **6.1**: Mining site at Kwang, Jos Plateau, Nigeria

6.2.2 Procedures for experimental alkali-assisted roasting and water-based leaching.

Different mass flux-to-concentrate ratios (50-200%) were tested and assessed for alkaline assisted roasting decomposition and transformation of the (Nb, Ta)-bearing phases into water-soluble compounds to determine optimum conditions for dissolution and extraction of these metals. Parameters investigated in the heat treatment and water based-leaching tests included temperature, flux-to-concentrate ratio, and roasting time. For sake of brevity, alkali roasting parameters were optimized without any size classification and furthermore optimized conditions were tested for different size class samples.

In the first stage of heat treatment, 1.0 g of the concentrate sample was accurately weighed and thoroughly mixed with an appropriate weight (0.5-2.0 g) of ground pellets of KOH. The mixture was put in high quality alumina crucible. The roasting process was carried out in a muffle furnace (Mellen Microtherm). The furnace was pre-heated at specific desired temperature (100-500°C) and when the temperature reached the preset value, a well-prepared sample was carefully introduced into the furnace after which the furnace was completely closed. The furnace was allowed to regain the desired temperature before the timer was started (0.5-2.0 hrs). After a particular time of roasting, the crucible was taken out of the furnace and the melt was allowed to cool at room temperature.

After cooling, the melt was leached with 100 mL of deionized water and the resulting solid-liquid ratio of ~ 0.015-0.03 g/mL was stirred at room temperature for 90 minutes. Then, slurry mixture was filtered on vacuum pump, and almost 100 mL of liquor solution was obtained. For leaching experiments carried out at room temperature (no roasting required), 2.0 g of concentrate were charged into 250 mL beaker containing 100 mL of 1M KOH and stirred for 90 minutes. For each set of experiment performed, the leach solution and residue obtained after filtration were both analyzed with ICP-OES to determine the percentage content of Nb, Ta, Sn, Fe, and other impurities. Conditions for optimum dissolution of metals of interest were also determined. In addition to ICP-OES, the residue was analyzed with X-ray diffractometer to know the crystalline phases remained in

the residue. The percentage of element leached in the solution was determined by using the following expression (Equation 6.2):

$$\% \text{ element leached } = \left(1 - \frac{\text{Mr}}{\text{Mo}}\right) \times 100 \qquad \text{Eq. } \mathbf{6}.2$$

Where $\boldsymbol{Mr}$ is the weight of element in the residue after leaching $\boldsymbol{Mo}$ is the weight of element in the in the feed.

6.2.3 Guanidine carbonate-assisted precipitation of Niobium and Tantalum

The optimized conditions were tested at large scale (15.0 g of sample and flux each) and 1L of deionized water was used for leaching these metals. The amount of Nb and Ta dissolved in the resulting pregnant leach solution (PLS) was recovered by precipitation using guanidine carbonate salt as precipitating agent. Appropriate volume of pregnant leach solution (200 mL) was measured from almost 1L of PLS and 5-15.0 g of guanidine salt in solid form were added to the solution on continuous stirring to precipitate Nb and Ta. The Nb/Ta-guanidine precipitate appeared in the solution immediately in less than a minute. The mixture was stirred for 30 minutes to ensure complete precipitation. After 30 minutes, the mixture was filtered on vacuum pump and the precipitate was dried at 100°C, both filtrate and precipitate were analyzed with ICP-OES for Nb, Ta, Sn, Fe, Mn, Si, and Al. The Nb/Ta-guanidine precipitate was then calcinated at 900°C for 1 hour to convert precipitate into oxides of Nb and Ta and remove the guanidine. The percentage recovery/extraction was calculated by using the following expression (Equation 6.3):

$$\% \text{ Recovery} = \frac{(\text{wt}\% \text{ of element in precipitate} * \text{total weight of precipitate})}{(\text{wt}\% \text{ of element in the feed} * \text{total weight of feed})} * 100 \qquad \text{Eq.}\mathbf{6.3}$$

6.2.4 Calcination of the (Nb-Ta)-guanidine precipitate

After precipitation of Nb and Ta dissolved in the pregnant leach solution of the Nigerian ferro-columbite samples, the (Nb-Ta)-guanidine precipitate recovered was dried in oven at 100°C and analyzed. The precipitate was further calcined at 900°C for one hour to convert the metals into their oxides and remove the guanidine moiety through evaporation as carbon and nitrogen oxides (Ogi et

al., 2018; Pierret & Wilhelm, 1956). The calcined precipitate was characterized with ICP-OES and XRD. The experimental flowsheet followed in this study is shown in Figure 6.2.
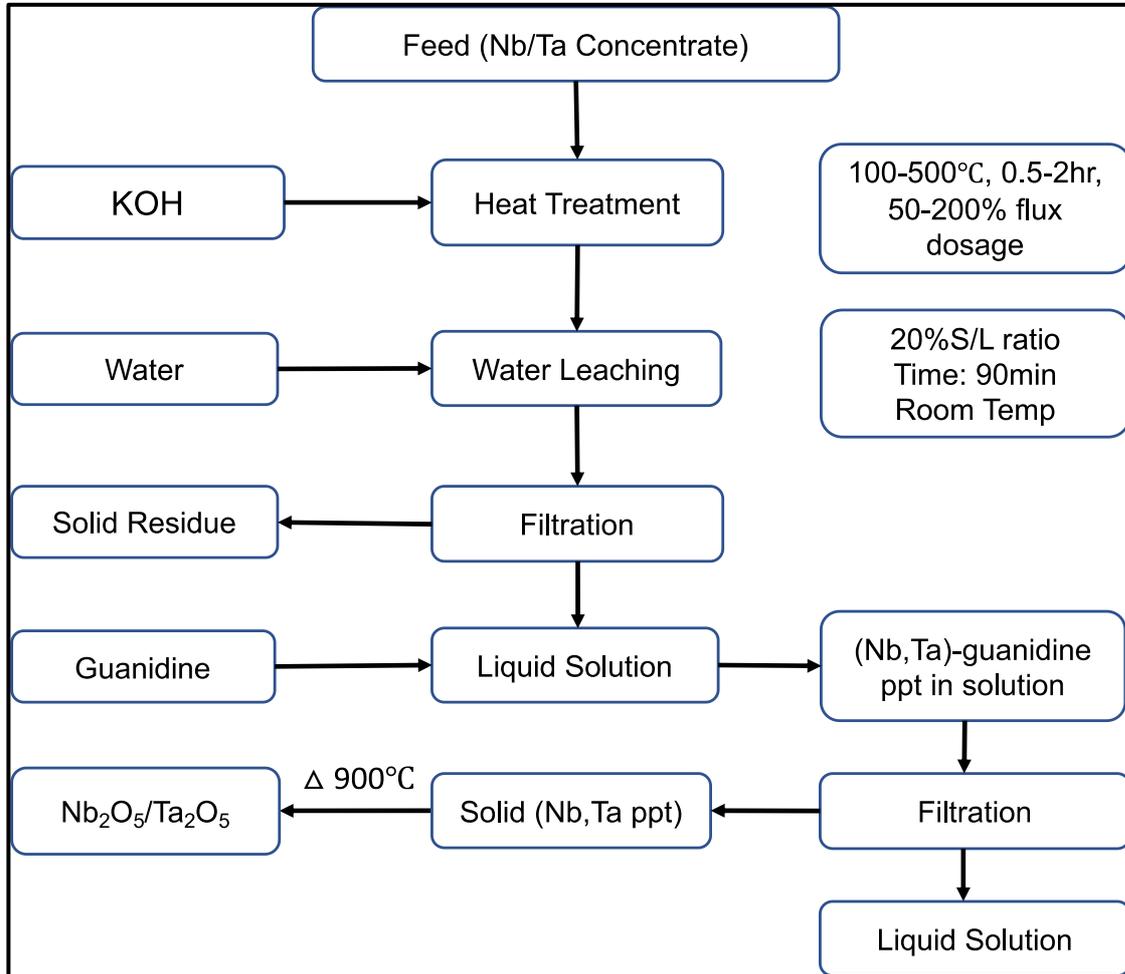
Figure **6.2**: Experimental flowsheet followed in this study

6.2.4 Analytical techniques and sample preparation

The starting material sample and products of each step of the process were analyzed and characterized. The mineralogical characteristics were determined using PANAnalytical Empyrean X-ray Diffractometer (XRD) with a Cu-Kα (λ = 0.1540 nm) radiation source operated at 45 kV and 40 mA at Worcester Polytechnic Institute (WPI), USA. The XRD samples were prepared by adding sufficient powder sample on a sample-holder and smoothen the surface to ensure a flat surface to the x-ray analyzer. The diffraction data were measured in 2-theta range of 5 to 90 degrees, with a scanning rate of 2 degree/min and a step size of 0.02 degree. The diffractograms obtained were

interpreted using X'Pert HighScore Plus software package (version 4.6a (4.6.1.23823)) matched with ICSD database. The Scanning Electron Microscopy attached with energy-dispersive x-ray spectroscopy (A JSM 700F SEM/EDS) was also used for surface morphology and elemental analysis of the investigated samples. The SEM/EDS powder sample was carefully prepared first by fixing a carbon double-sided sticker on sample holder and using a spoon to collect a small amount of sample and allow it to fall on the exposed side of the carbon sticker. Then, using air spray to remove the excess particles and mounting the sample into the specimen holder and now sample-specimen is ready to be inserted into SEM chamber.

The quantitative elemental compositions were determined using inductively coupled plasma-optical emission spectroscopy (Perkin Elmer Optima 8000 ICP-OES) at WPI. The elemental analysis was performed at different spectral emission lines using RF Power of 1500 W with a Plasma and Pump flow rate of 14.0 L/min, and 1.5 mL/min, respectively. The solid samples were prepared by fusing a mixture of 0.1 g powder sample and 1.0 g of fusion flux (lithium tetraborate) in a graphite crucible and put it in a preheated furnace at 1000°C. After one hour of heating, the melt was dissolved in 25% nitric acid. To ensure a complete dissolution of Nb and Ta, a small amount (1.5 mL) of concentrated hydrofluoric acid (40%) was added after 20 min of continuous stirring. After 90 min stirring was stopped and an appropriate volume of the solution was taken and diluted 10 or 100 times (depending on concentration of the analyte) with 2% nitric acid and then analyzed with ICP-OES (Delijska et al., 1988; Habinshuti et al., 2021).

6.3 Results and Discussions

6.3.1 Sample Characterization

Chemistry and mineralogy of the Nb-Ta concentrate from Jos Plateau of Nigeria were analyzed before the size classification and heat treatment process. The chemical compositions of the concentrate under investigation were analyzed with ICP-OES Table 6.1. The mineralogical evaluation indicated that the main constituents of the sample are columbite-Fe (25.5% Nb_2O_5, 3.6% Ta_2O_5 and 15.8% Fe_2O_3) associated with cassiterite 25.9% SnO_2. XRD results confirmed the presence of

Columbite and Cassiterite as the major mineral phases in the sample Figure 6. 3(a). The SEM micrograph of the Nb-Ta concentrate at 100 magnifications in Figure 6.3(b) depicts a smooth surface morphology characterized by particles of larges size of different shapes. The surface composition indicates presence of Nb (22.3%), Ta (3.2%), Fe (12.2%), and O (33.2%) as the major components of the columbite-Fe phase Figure 3(c). Some of Sn in form of cassiterite (SnO_2) was also detected with minor Al and Si oxides.

Table **6.1**: Chemical compositions of the ferro-columbite concentrate feed analyzed by ICP-OES

Sample	Compositions (wt%)							
	Nb_2O_5	**Ta_2O_5**	**SnO_2**	**Fe_2O_3**	**MnO**	**SiO_2**	**Al_2O_3**	**WO_3**
N-Jos Con	33.045	5.565	26.852	17.723	1.982	2.891	3.261	1.105
+250 microns	25.902	3.249	23.918	17.692	0.964	0.621	0.280	0.303
-250 microns	25.090	3.978	28.013	14.018	0.986	1.075	0.435	0.394
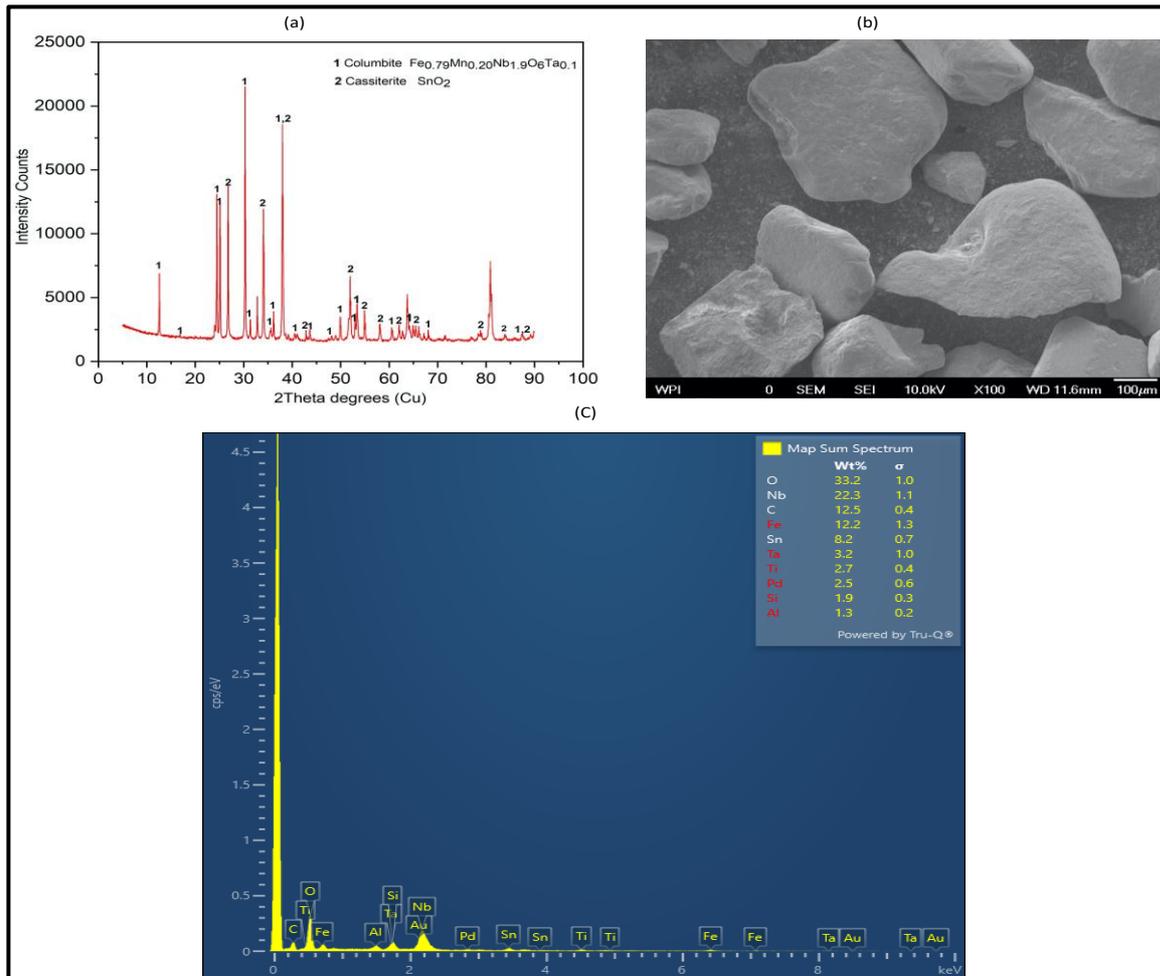
Figure **6.3**: Characterization of the concentrate feed sample (a) XRD spectrum, (b) SEM micrograph, (c) EDS spectrum

The Nb-Ta concentrate sample as received from the mining company was also screened with a sieve and classified into two different size fractions (+250 and -250 microns). Each fraction was analyzed to determine its compositions and crystalline phases present in the sample. The results of XRD analysis confirmed the presence of ferro-columbite phases associated with cassiterite and some iron and manganese oxides Figure 6.3(a). The chemical compositions information complemented with ICP-OES analysis, revealed no difference in chemical compositions between the two fractions. The main components present in each size fraction of the concentrate sample under investigation were columbite-Fe with average values of 25% Nb_2O_5, 3.5% Ta_2O_5 and 15.5% Fe_2O_3 accompanied with cassiterite, almost 25% SnO_2 Table 6.1.

6.3.2 Alkali-assisted roasting and water-leaching of the Nigerian ferro-columbite concentrate (N-Jos Con)

Minerals and ores of Nb and Ta in addition to their oxides are generally insoluble in mineral acids except in HF or in mixture of HF and H_2SO_4, which is not environmental benign. Thus, fusion of the geological samples containing Nb, and Ta is conducted to bring these metals of interest into the solution. A fusion process using KOH as flux was used to breakdown the components of the Nb-Ta concentrate into water-soluble compounds. In alkaline media ($8 \leq pH \leq 12$), Nb polymerizes into hydrated hexaniobate salts which are soluble, the solubility increases with decreasing concentration of alkaline solution and temperature, whereas Ta form similar salts at $pH \geq 12$ (Gupta & Suri, 1994). The hexaniobate and hexatantalate salts are well-known (Nb, Ta)-species which are predominant in the solution with pH higher than ~10 (Deblonde et al., 2015).

During the alkali-assisted roasting (100-500°C), the Nb-Ta and other elements contained in the concentrate-feed sample react with molten KOH according to the mechanism of chemical reactions presented in scheme 1. In the process, some of the Ta_2O_5 converts into soluble K_3TaO_4 and other part into insoluble $KTaO_3$ while Nb_2O_5 converts only into the soluble K_3NbO_4. However, depending on the alkali roasting conditions, the insoluble $KNbO_3$ can exist in the system via the isomorphism replacement between Nb^{5+} and Ta^{5+} where Nb can replace Ta and form a continuous solid solution of $KTaO_3$-$KNbO_3$. At low alkali concentration, the product is mainly the insoluble form of $KNbO_3$ ($KTaO_3$) and cannot be leached with water whereas at high alkali concentration, the product is mainly in the soluble form K_3NbO_4 (K_3TaO_4) equation (1) in Scheme 1. In addition to $K_3(Nb,Ta)O_4$ and $K(Nb,TaO_3)$, other salts resulting from equation (5) to (8) in scheme1 of the roasting process goes immediately for leaching process. In the leaching, (Nb,Ta)-salts undergo hydrolyze and polymerize into water-soluble polyoxometalates species $K_8Nb_6O_{19}$ ($K_8Ta_6O_{19}$) which can be easily recovered (X. H. Wang et al., 2010). On the other hand, FeO and MnO from equation (1) in Scheme 1 are oxidized by high temperature into Fe_2O_3 and MnO_2 with respect to the equations (3) and (4) in Scheme 1. The oxide products react with molten KOH to give salts $KFeO_2$ and K_2MnO_3

according to the equations (5) and (6) in Scheme 1 whereas SnO_2 and SiO_2 react to form salts K_2SnO_3 and K_2SiO_3 respectively as shown in equations (7) and (8) in Scheme1 (X. Wang et al., 2009).
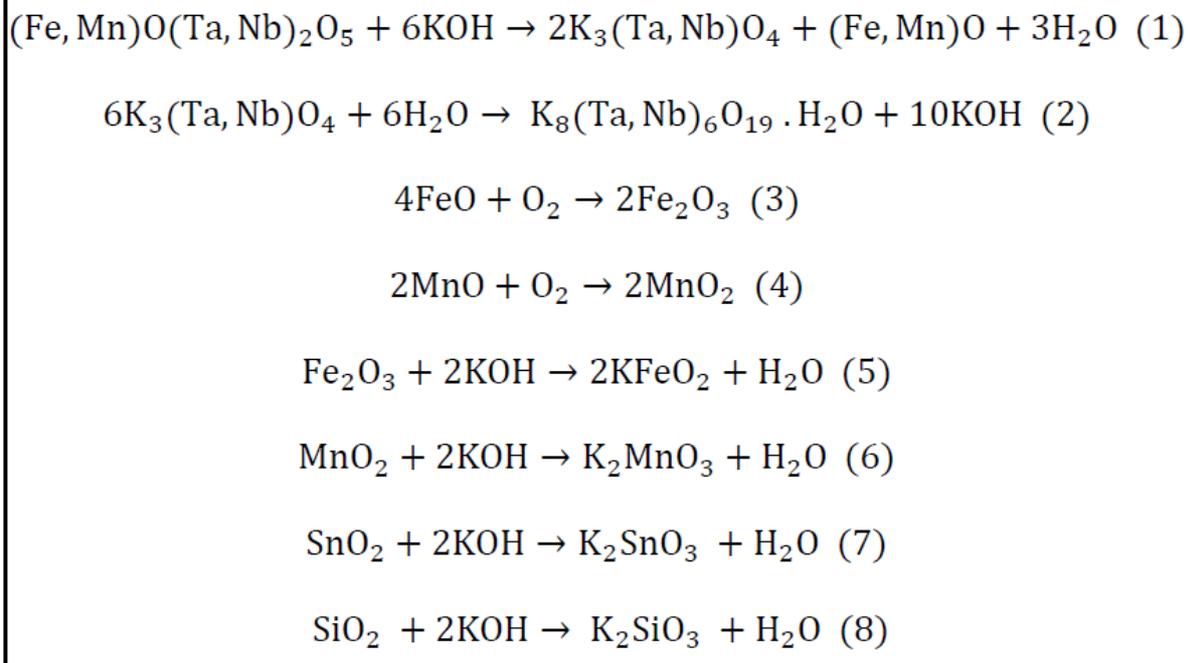
$$(Fe, Mn)O(Ta, Nb)_2O_5 + 6KOH \rightarrow 2K_3(Ta, Nb)O_4 + (Fe, Mn)O + 3H_2O \quad (1)$$

$$6K_3(Ta, Nb)O_4 + 6H_2O \rightarrow K_8(Ta, Nb)_6O_{19} . H_2O + 10KOH \quad (2)$$

$$4FeO + O_2 \rightarrow 2Fe_2O_3 \quad (3)$$

$$2MnO + O_2 \rightarrow 2MnO_2 \quad (4)$$

$$Fe_2O_3 + 2KOH \rightarrow 2KFeO_2 + H_2O \quad (5)$$

$$MnO_2 + 2KOH \rightarrow K_2MnO_3 + H_2O \quad (6)$$

$$SnO_2 + 2KOH \rightarrow K_2SnO_3 + H_2O \quad (7)$$

$$SiO_2 + 2KOH \rightarrow K_2SiO_3 + H_2O \quad (8)$$

Scheme 1: Main reactions that take place during the alkali-assisted roasting and water leaching of the columbite-tantalite materials (X. Wang et al., 2009)

6.3.2.1 Effect of temperature on decomposition and dissolution of the niobium-tantalum contained in the Nigerian ferro-columbite concentrate

The effect of temperature on dissolution of different elements at mass flux-to-concentrate ratio of 200% and 1hour heating time is shown in Figure 6. 4. From the figure, we can see that increasing of temperature has significant effect on dissolution of Nb and Ta. At the beginning, room temperature (25°C), dissolution of Ta was minimum (< 20%) while that of Nb was almost zero due to the insolubility nature of Nb/Ta minerals and compounds. Dissolution starts to increase at 100°C through 150°C, may be because of decrease in system's viscosity and mass transfer resistance at liquid-solid interface. At 250°C, maximum dissolution for Nb (93.79 %), Ta (85.23 %) and W (91.93 %) was achieved and no further change as temperature increases, reaction was completed at 250°C.

The dissolution of Mn, Fe, and Si start to decrease from their first maxima to minima at 400°C, then increase again to the maximum at 500°C. The dissolution of Fe (27.07 %) and Sn (1.08 %) was not significant at the beginning and start to increase at 150°C through 350°C, and decrease to 400°C before attaining the maximum at 500°C. This observed discrepancy in dissolution behavior between Nb, Ta and other elements is because the reaction of $(Nb, Ta)_2O_5$ with KOH occurs more readily than other reactions in the system. The behavior indicates efficient separation of Nb, Ta and W from Fe and Sn at 250°C. The concentration of Mn, Si, Al, and W is relatively less in the starting feed and is of least concern to contaminate the final product.
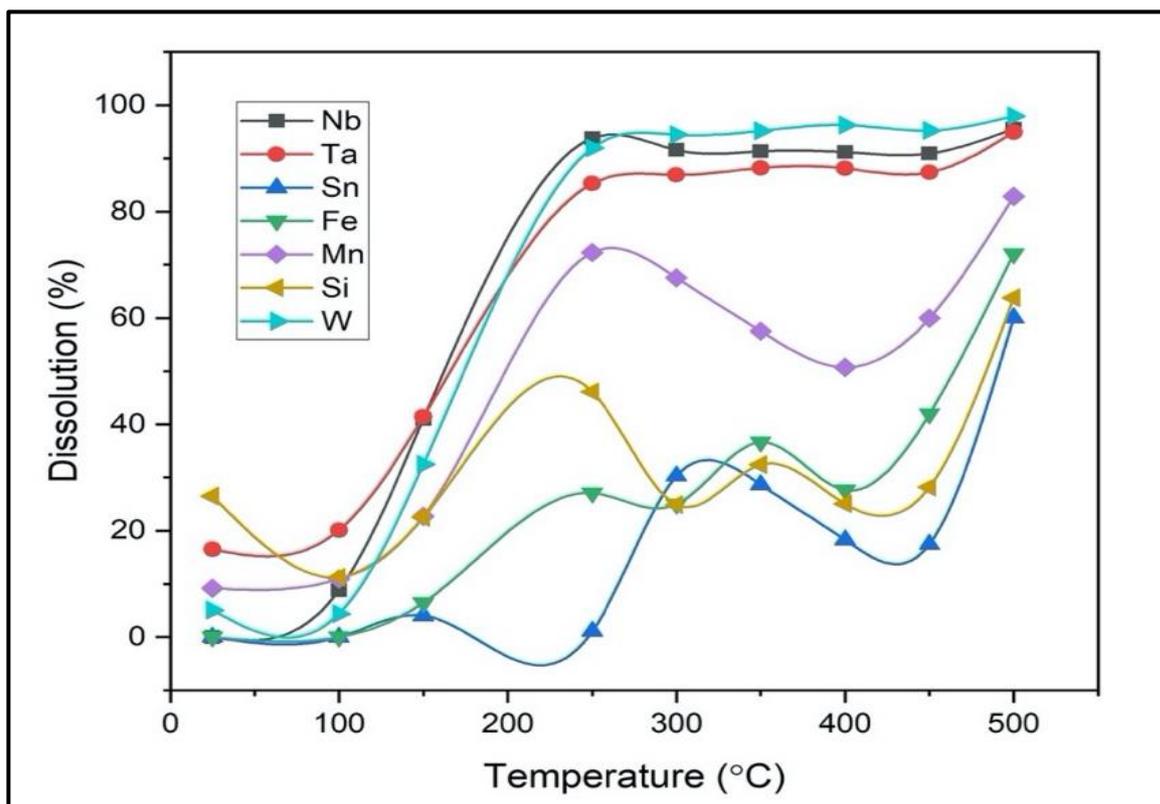
Figure **6.4**: Effect of temperature on dissolution of different elements at flux ratio 2:1 KOH: concentrate and 1h heating duration

6.3.2.2 Effect of flux-to-concentrate ratio on dissolution of niobium-tantalum in concentrate

Figure 6.5 illustrates the effect of mass flux-to-concentrate ratio on the dissolution of different elements at 250°C Figure 6.5 (a) and 500°C Figure 6. 5 (b). Stoichiometrically from equation 1, almost 337 g of KOH would be required to convert 755 g of the Nb/Ta phases present in the concentrate feed sample. This is 44.5 % flux-to concentrate ratio, thus the excess of KOH was beneficial to complete reaction and achieve optimum Nb/Ta dissolution since the concentrate is not 100% Nb and Ta compounds and other side reactions 5-8 will also occur. Therefore, at lower temperature 250°C and 50% flux ratio, the dissolution of Nb, Ta, and W was minimum and start to increase to its maximum at a flux-to-concentrate ratio of 100% and remained almost constant as the flux-to-concentrate increases through 150 % and 200 %. At a mass flux-to-concentrate ratio of 100 % approximately 94.88 % Nb, 91.36% Ta, 48.37% Fe and 30.82% Sn dissolution was achieved. The dissolution of Mn, Fe and Sn decreased slowly from the maximum when flux-to-concentrate ratio increased from 100 % through 150% to 200%. At higher temperature Figure 6.5(b) similar trend was

observed with 100% flux-to-concentrate ratio being sufficient for highest dissolution value. Only dissolution of Si, Mn and Fe were improved slowly whereas that of Nb, Ta and Sn dropped relatively to that of lower temperature, may be due to the formation of insoluble compounds. As the ratio of flux-to-concentrate increases, dissolution of Nb, Ta and W also increases to the maximum at 100 % flux ratio and approximately 88.54% Nb, 88.54% Ta, 49.47% Fe and 24.96% Sn were dissolved.
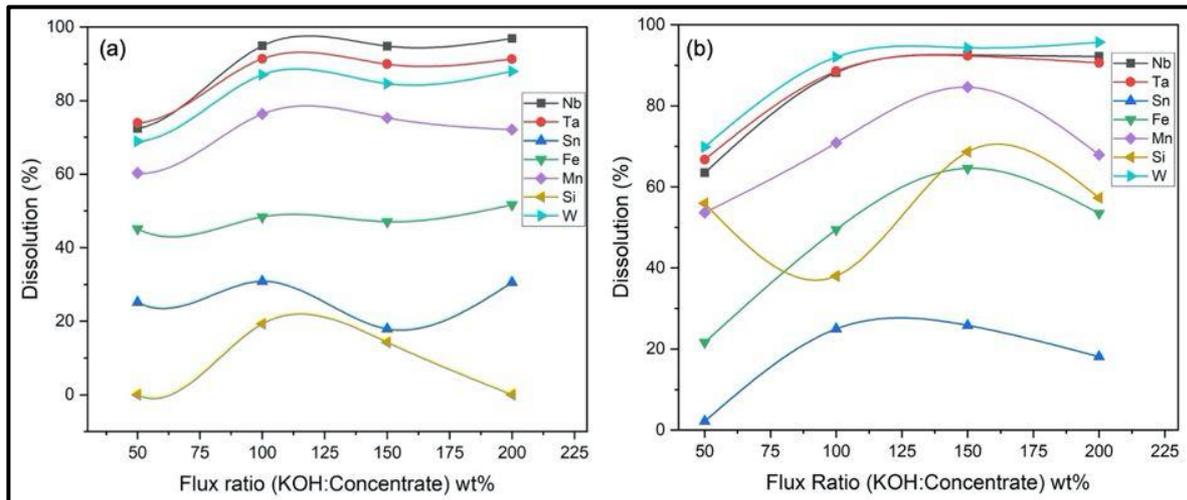
Figure **6.5**: Effect of flux-to-concentrate ratio on dissolution of elements in the concentrate at (a) 250°C and (b) 500°C.

6.3.2.3 Effect of roasting decomposition time on dissolution of elements contained in the concentrate.

The effect of roasting time on dissolution of different elements at 250°C using 100% mass flux-to-concentrate ratio is shown in Figure 6.6. The dissolution of Nb, Ta, W, and Mn increased with roasting time and reached equilibrium after 60 mins of roasting. Sn showed least dissolution and remained in the residue in form of cassiterite as it is confirmed by XRD analysis of the residue. Fe was also dissolved at some extend and mainly found in the residue as hematite. Under optimal conditions 94.91% Nb, 90.24% Ta, 51.39% Fe and 20.57% Sn dissolution was obtained.
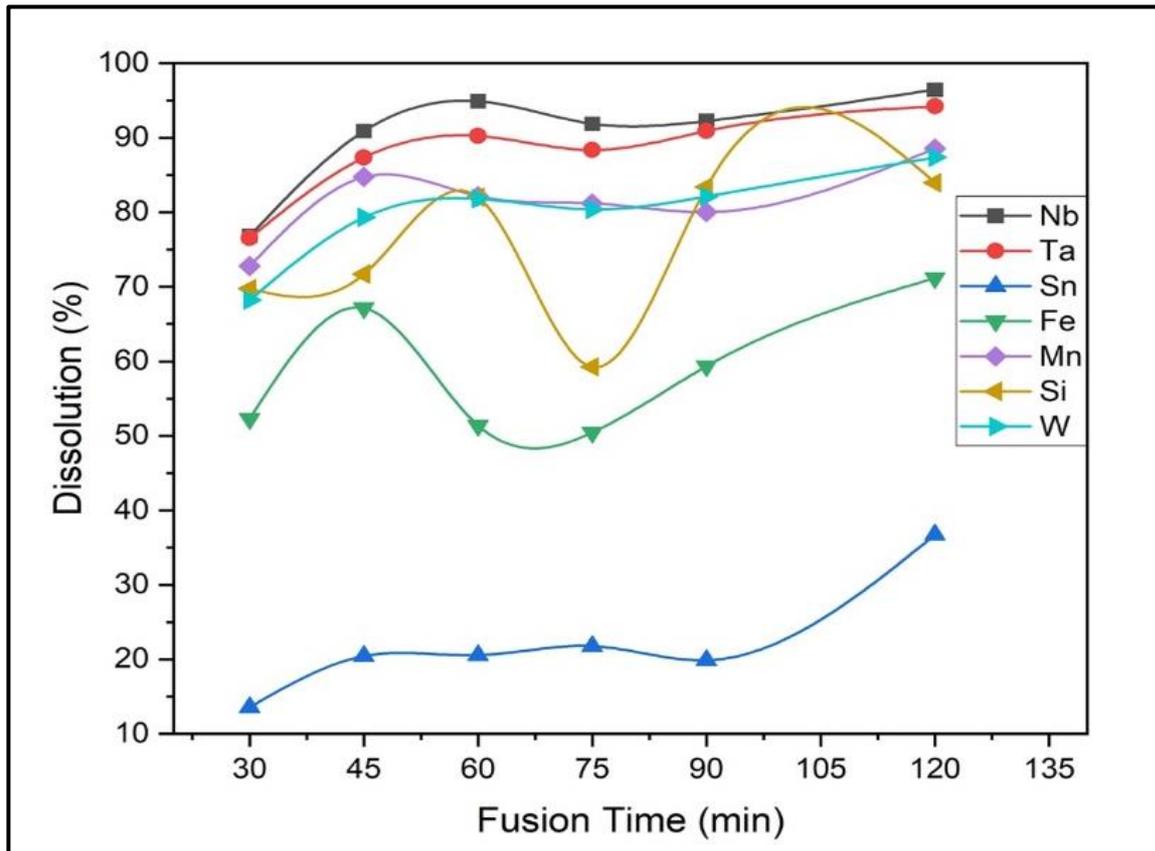
Figure **6.6**: Effect of fusion time on dissolution of different elements: flux-to-concentrate ratio 100%, and 250°C temperature

6.3.2.4 Effect of particle size on elements dissolution induced by alkali-assisted roasting

Alkaline assisted roasting was performed using samples of two different size classes at optimized conditions (250°C, flux-to-concentrate ratio 100%, and 1hour of roasting). The pregnant leach solution was subsequently collected for assessment and optimization of the Nb/Ta precipitation using guanidine. The roasting experiments were conducted using the oversize and undersize of the classified sample at a cutoff size of 250 microns. Different size fractions were tested to determine whether the material needs to be grounded to a finer particle size for minerals liberation.

The alkaline dissolution of the chemical elements contained in the Nb-Ta concentrate sample was found to be approximately the same within the two-size class as shown in Figure 6.7(a). Similar dissolution trend indicates that the fusion process can effectively dissolve even the larger particles in the molten flux without any diffusion-based limitations and eliminates energy intensive for fine

grinding requirements. The dissolution of Nb and Ta was found to be higher than 95% and 80% respectively, irrespective of the particle size. Dissolution of Mn and W was found to be approximately 65-64% and 91-92% respectively for +250 and -250-microns size fractions. Furthermore, dissolution of Fe, Sn, and Al was limited to a maximum of 17%, 19%, and 46% respectively. The particle size does not have a significant effect on the alkaline assisted dissolution of the main constituents of the concentrate sample under investigation.
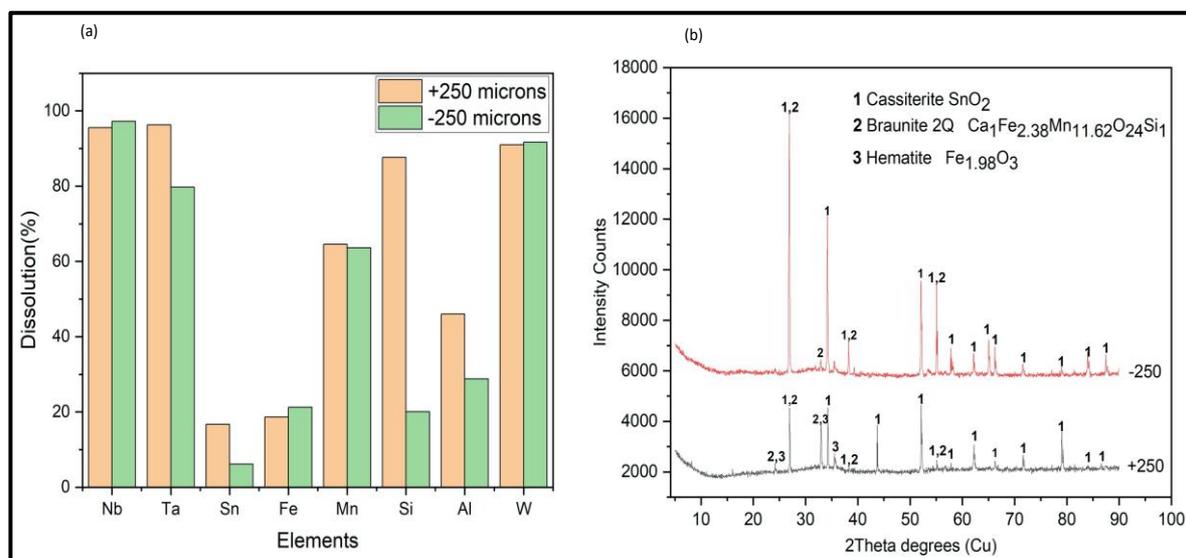
Figure **6.7**: (a) Alkaline dissolution of elements contained in the two size fractions +250 microns and -250 microns; (b) XRD spectrum of the residue obtained at different size fraction.

The XRD spectrum of the residue obtained after roasting and leaching of the Nb-Ta concentrate depicts the presence of cassiterite as the major mineral phase. Other minor phases such as hematite and braunite were also detected in the residue Figure 6.7(b). Because the reaction of (Nb, Ta)$_2$O$_5$ with KOH occurs more readily than other reactions involved and form highly soluble compounds while the insoluble remain in the residue. The hematite phase (α-Fe$_2$O$_3$) in residue may results from the oxidation of magnetite (Fe$_3$O$_4$) or the inversion of maghemite (γ-Fe$_2$O$_3$) when heated at temperature between 250-750°C (Michael W. McElhinny, 2000; Moskowitz et al., 2015). The braunite 2Q is a silicate mineral containing both iron and manganese. In presence of KOH, silicon in

the ore first form soluble silicate K_2SiO_3 in equation 8 which transform into insoluble silicate that remained in the residue as braunite 2Q (X. Wang et al., 2009). This agrees with the chemical composition information obtained from ICP-OES analysis, where the percentage content of Sn and Fe is high in the residue, whereas Nb and Ta get concentrated in the solution together with some dissolved Fe and Sn.

Furthermore, the elemental dissolution during leaching and corresponding materials balance are presented in Table 6.2. The PLS consist of approximately 2754-2811 ppm Nb, along with 405-394 ppm Ta, 204-497 ppm Sn, and 321-335 ppm Fe for +250 and -250-microns size fractions respectively. Whereas the concentration of other elements (Mn, Si, Al, W) was less than 100 ppm. The concentration of Nb in PLS is significantly higher compared to other elements reflecting effective roasting and separation from other elements. The collected PLS was further processed to precipitate Nb-Ta values with novel application of guanidine amine salt as precipitating agent. The reported dissolution was calculated based on composition of PLS by using the following formula (Equation 6.4):

$$\% \, Dissolution = \frac{(Conc \, of \, PLS \, in \, ppm * Volume \, (L)}{(wt\% \, of \, feed * total \, weight \, of \, feed)} * 100 \qquad \text{Eq.6.4}$$

Table **6.2**: Material balance for alkali roasting and water leaching of different size fractions at optimized conditions: 250°C, flux ratio 100%, and 1h roasting

	+250 microns size fraction				-250 microns size fraction			
	Feed	Residue	PLS	Dissolution	Feed	Residue	PLS	Dissoluti
Elts	(wt%)	(wt%)	(ppm)	(%)	(wt%)	(wt%)	(ppm)	on (%)
Nb	18.223	1.831	2754.120	95.536	19.030	3.164	2811.087	97.204
Ta	2.660	0.630	405.201	96.275	3.258	1.070	394.482	79.759
Sn	18.840	26.336	497.419	16.690	22.065	29.202	204.919	6.117
Fe	11.385	12.860	335.451	18.625	9.962	12.764	321.645	21.268
Mn	0.746	0.380	76.185	64.537	0.764	0.483	73.765	63.615
Si	0.290	0.461	40.240	87.620	0.503	0.583	15.328	20.091
Al	0.148	0.166	10.787	46.017	0.230	0.315	10.069	28.795

W	0.240	0.098	51.580	90.993	0.313	0.101	43.541	91.711
Wt (g)	**15.345**	**8.702**	**970** mL	-	**15.355**	**9.47**	**1012** mL	-

6.3.3 Precipitation of Nb-Ta from PLS using guanidine carbonate

The PLS collected after alkaline heat treatment and water leaching process was processed to recover the dissolved Nb-Ta via precipitation using guanidine carbonate salt. Guanidine has proven the potential to rapidly and selectively precipitate Ta from a synthetic aqueous solution containing other metals such as Si and W (Ogi et al., 2018). When guanidine is added to an aqueous solution containing Nb and Ta; the guanidinium ion $C(NH_2)_3^+$ interacts electrostatically with ions of these metals (polyoxometalate) and a white precipitate is formed instantaneously (Equation 6.5) (Ogi et al., 2018)

$$(Ta, Nb)_6O_{19}{}^{8-}{}_{(aq)} \quad + \quad 8C(NH_2)_3{}^+{}_{(aq)} \quad \rightarrow \quad (C(NH_2)_3)_8(Ta, Nb)_6O_{19\ (s)} \qquad \text{Eq. } \mathbf{6.5}$$
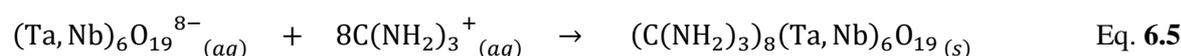
Precipitation of Nb and Ta using guanidine carbonate salt was carried out with PLS obtained from fusion and water leaching of +250 and -250-microns size samples. The Figure 6.8(a) and (b) shows the Nb/Ta precipitation efficiency at different dosage of guanidine using PLS obtained from the two different size fractions. The precipitation efficiency was almost constant through increase of guanidine concentration and had no effect on the quality of precipitate. 25 mg/mL of guanidine was found sufficient to precipitate total amount of Nb and Ta reported in the PLS, however, the overall recovery of (Nb, Ta) decreases as guanidine increases. More than 99% precipitation efficiency was observed for Nb, Ta, Fe and Mn whereas a minimal amount of less than 20% of Sn, Al and W was co-precipitated with them. The composition of precipitate obtained is shown in Figure 6.8(c) and (d). The precipitate composition was almost constant with variation of guanidine concentration. The precipitate obtained from liquor solution of -250 microns size fractions seems to have high percentage compositions relatively to that of +250 microns size fractions. The composition consists of approximately 79% Nb and 8.7% Ta along with 7.5% Fe and 1.4 % Mn as minor impurities. The percentage recovery/extraction was calculated by using the expression described in Equation 6.3.

Comparison of PLS and the solution obtained after precipitation is shown in Figure 6.8(e) and (f). Concentration of Nb and Ta remained in the solution after guanidine precipitation were 3.32 and 1.56 ppm and 2.1 and 0.97 ppm for size fractions +250 and -250 microns respectively. The concentration of Sn, Al, and W in the solution remained unchanged after precipitation, this reflects their inert behaviors toward guanidine in the alkaline media. Contrary, the dissolved Fe and Mn were co-precipitated along with Nb-Ta as the main impurities of the precipitate. The expression used for calculating guanidine precipitation efficiency is given below (Equation 6.6):

$$\% \text{ Precipitation Efficiency} = \left(1 - \frac{\text{Mr}}{\text{Mo}}\right) \times 100 \qquad \text{Eq. } \textbf{6.6}$$

Where **Mr** is the weight of element in solution obtained after guanidine precipitation and **Mo** is the weight of element in pregnant leach solution before precipitation.
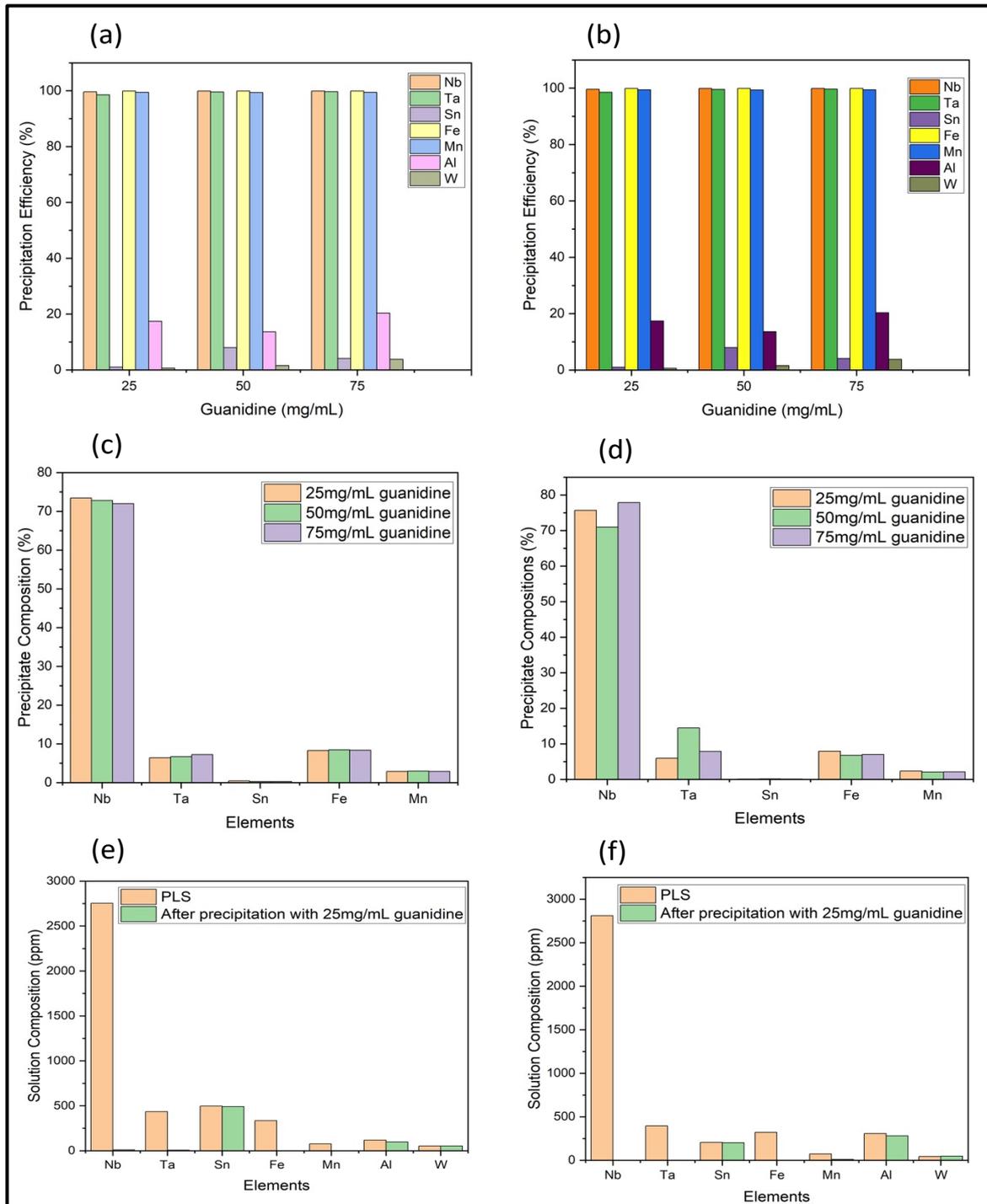
Figure **6.8**: Precipitation efficiency for (a) +250 microns size sample, (b) -250 microns size sample, Composition of precipitate at different guanidine dosage: (c) +250 microns size sample, (d) -250 microns size sample; Composition of PLS before and after precipitation (e) +250 microns size sample, (f) -250 microns size sample.

From Table 6.3, at an optimum guanidine of 50 mg/mL, it is possible to obtained 734.5 kg of precipitate in form of (Nb,Ta)-guanidine salt from one tonne of the feed concentrate. By converting Nb and Ta into oxides, 4.201 g of (Nb,Ta)-mixed oxides were obtained from 15.0 g of feed

concentrate, this gives 280.067 kg of mixed-oxides from one tonne of feed concentrate. Then, by comparing with $(Nb,Ta)_2O_5$ presented in Table 6.1, for concentrate feed of +250 microns size fraction, it contains 29.151% of mixed Nb_2O_5 and Ta_2O_5, this would give 291.51 kg of $(Nb,Ta)_2O_5$ from one tonne of the feed concentrate. Therefore, overall efficiency recovery of 96.06 % for $(Nb,Ta)_2O_5$ was obtained.

Table **6.3**: Total recovery of Nb/Ta after guanidine precipitation (Roasting: 250°C, flux ratio 100%, and 1h roasting), Precipitation: 25, 50, 75 mg/mL guanidine, 30 mins, 25°C.

Elements	Guanidine (mg/mL)	+250 microns size fraction			-250 microns size fraction		
		Feed (%)	Precipitate (%)	Extraction (%)	Feed (%)	Precipitate (%)	Extraction (%)
Nb	25	18.223	25.075	95.249	19.030	27.468	97.726
Ta		2.660	3.065	79.748	3.258	3.022	62.799
Sn		18.839	0.155	0.568	22.065	0.032	0.099
Fe		11.385	2.564	15.590	9.962	2.618	17.791
Mn		0.746	0.587	54.427	0.764	0.500	44.325
Al		0.148	0.083	38.940	0.230	0.097	28.623
W		0.240	0.018	5.312	0.313	0.011	2.342
Weight(g)		**15.000**	**10.380**	-	**15.000**	**10.160**	-
Nb	50	18.223	24.035	96.897	19.030	25.686	93.631
Ta		2.660	3.083	85.134	3.258	3.757	79.981
Sn		18.839	0.082	0.320	22.065	0.041	0.127
Fe		11.385	2.545	16.422	9.962	2.231	15.534
Mn		0.746	0.586	57.681	0.764	0.443	40.231
Al		0.148	0.073	36.025	0.230	0.100	30.177
W		0.240	0.016	4.877	0.313	0.012	2.646
Weight(g)		**15.000**	**11.02**	-	**15.000**	**10.4**	-
Nb	75	18.223	22.526	87.564	19.030	25.458	90.572
Ta		2.660	3.153	83.948	3.258	3.597	74.751
Sn		18.839	0.079	0.296	22.065	0.028	0.085
Fe		11.385	2.375	14.781	9.962	2.081	14.139
Mn		0.746	0.538	51.071	0.764	0.411	36.388
Al		0.148	0.069	33.035	0.230	0.097	28.458
W		0.240	0.015	4.382	0.313	0.014	3.018

Weight(g)		15.000	10.62	-	15.000	10.16		-

6.3.4 Calcination of the (Nb-Ta)-guanidine precipitate

The (Nb, Ta)-guanidine precipitate obtained was calcined at 900°C for one hour to convert the metals into oxides and remove the guanidine through evaporation in form of carbon and nitrogen oxides (Equation 6.7) (Ogi et al., 2018; Pierret & Wilhelm, 1956).

$$(C(NH_2)_3)_8(Ta,Nb)_6O_{19\,(s)} \xrightarrow{900°C} (Ta,Nb)_2O_{5\,(s)} + CO_{2\,(g)} + NO_{x(g)} + H_2O_{(g)} \qquad \text{Eq. } \mathbf{6.7}$$
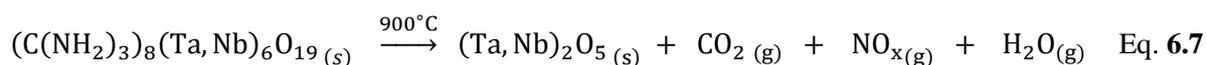
The calcination resulted in mass loss of almost 50% and mixed oxides (Nb, Ta)$_2$O$_5$ with purity of 97%. The XRD spectrum of Nb/Ta-guanidine precipitate and calcined precipitate presented in Figure 6.9 depicts that the guanidine precipitate was amorphous, and no crystalline peak were obtained (Ogi et al., 2018; Rodrigues & da Silva, 2010). The amorphous precipitate converted into crystalline Nb/Ta oxide phases upon calcination at 900°C for 1hour and is reflected in the XRD spectrum in Figure 6.9. The calcination process destroyed and removed the guanidine in form of carbon and nitrogen oxides (Ogi et al., 2018). The SEM/EDS micrograph of guanidine precipitate and calcined product is shown in Figure 6.10 (a) and (b) where particles of the precipitate are characterized by smooth and uneven sized morphology mainly composed of Nb and Ta which was confirmed from results of EDS analysis. Micrograph of the calcined precipitate had a powdery texture and broken surface morphology contrary to uncalcined precipitate.
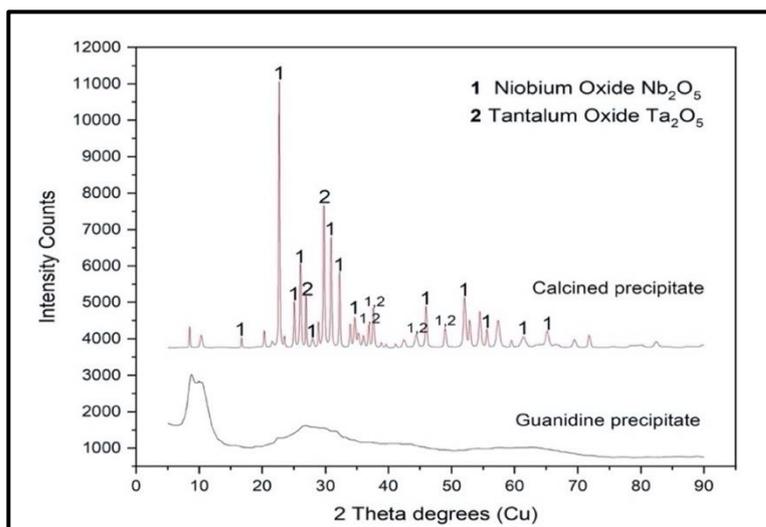
Figure **6.9**: XRD spectrum of Nb/Ta guanidine precipitate and calcined precipitate
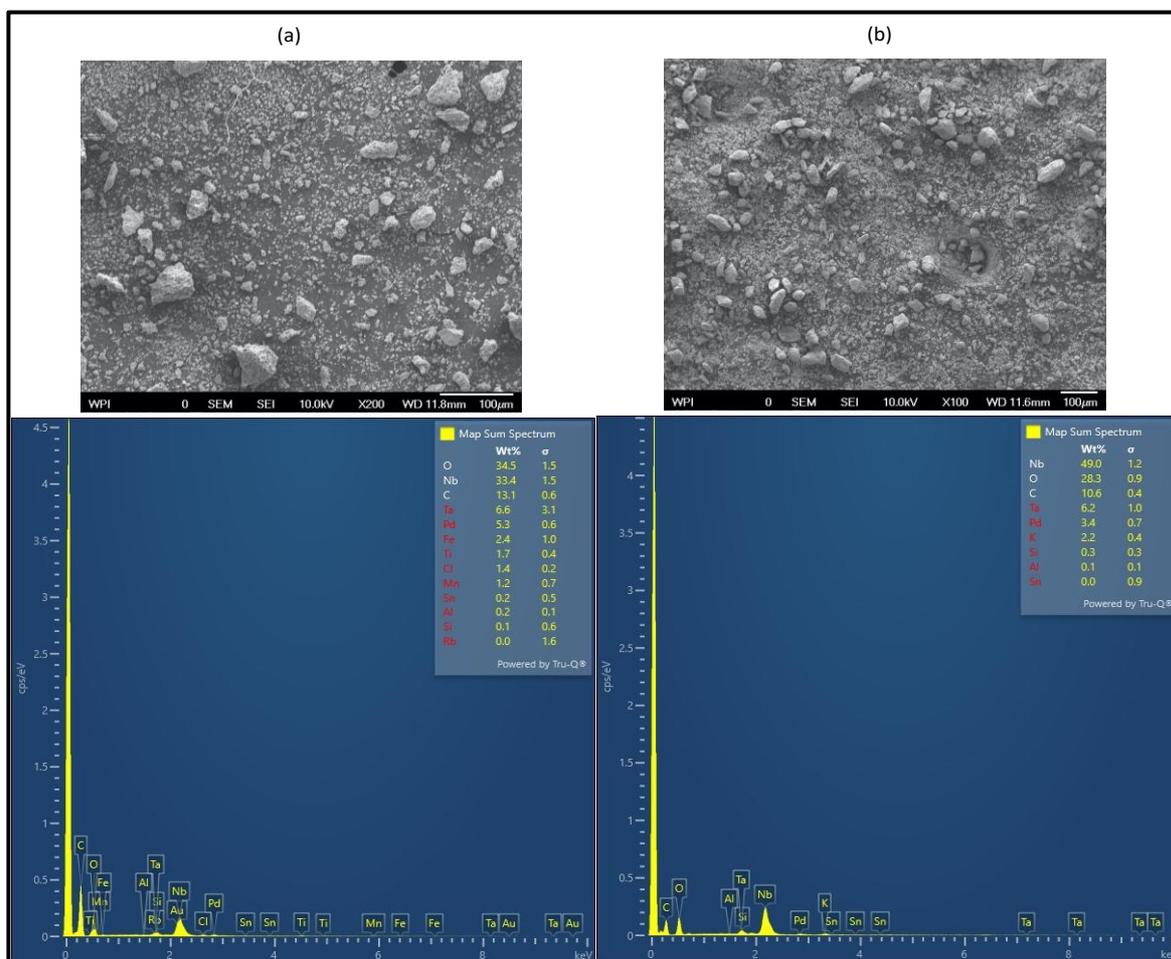
Figure **6.10**: (a) SEM /EDS of guanidine precipitate, (b) SEM/EDS of calcined Nb-Ta precipitate

Sample specimen photographs and composition at different stages of treatment are shown in Figure 6.11 and the corresponding material balance and overall recovery values are presented in Table 6.3. Under the optimized conditions, (Nb-Ta)-guanidine precipitate with purity more than 84% was obtained. The calcination of the precipitate produced a mixed oxides of Nb and Ta having purity of 97%. The percentage recovery/extraction was calculated by using the expression presented in Equation 6.3
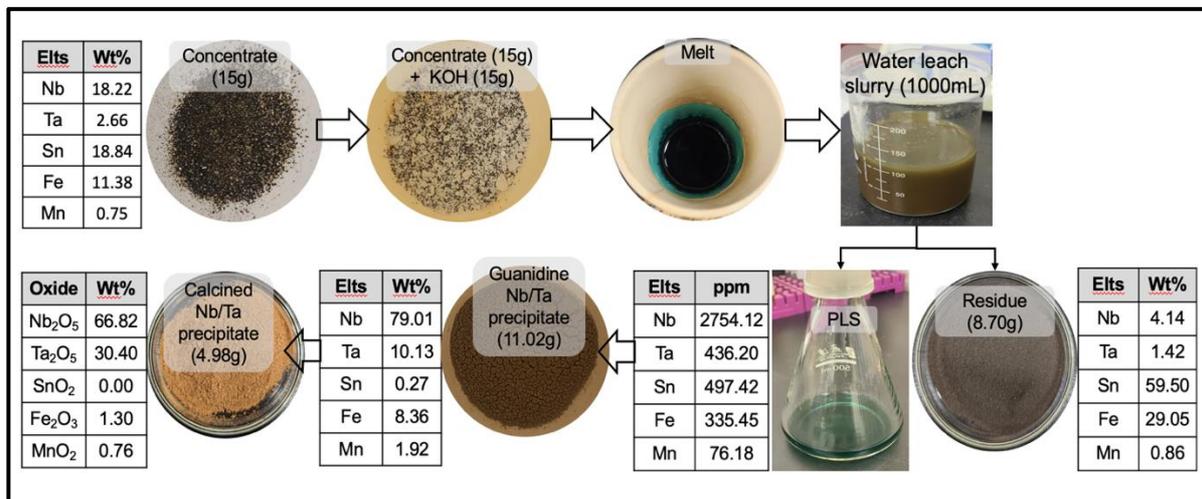
Figure **6.11**: Sample specimen photographs at different stages of treatment

However, for +250 microns size fractions, recovery of Nb and Ta increases from 95 to 97% and from 80 to 85% respectively then decreases to their minimum of 86 and 84% with 25, 50 and 75 mg/mL of guanidine concentration. Contrary to the fine materials (-250 microns), the recovery of Nb decreased from 98 through 94 to 91% while that of Ta increased from 63 to 80% then decrease to 75% at 25, 50 and 75 mg/mL guanidine. The observed decrease in % recoveries may be related to the kinetics of the precipitation process which would require more investigations in the future studies. For some cases, due to calculation errors, there is a slight increase in % recoveries relatively to their % dissolutions but still in the same range.

6.4 Conclusion

The extraction of Nb-Ta from Ferro-columbite concentrate of Jos plateau (Nigeria) using alkali roasting, water-based leaching and precipitation with guanidine amine salt was investigated. Characterization of the concentrate sample under investigation indicated presence of columbite-Fe and cassiterite as main constituents with Nb_2O_5 (33.3%wt), Ta_2O_5 (5.5%wt), Fe_2O_3 (18%wt), MnO (2%wt) and SnO_2 (27%wt). The concentrated ore-sample was screened into two different size fractions, +250 and -250 microns with a sieve. The alkali assisted roasting and water leaching of the two size fractions at optimum conditions (250°C, 100% flux-to-concentrate ratio and 1h roasting) resulted in dissolution of 97-96 %wt Nb, 80-96 %wt Ta, 92-91 %wt W and 64-65%wt Mn respectively. The process leaves behind in the residue most of the Sn (94-83%wt), Fe (79-81%wt) and other associated impurities. The amount of Nb and Ta reported in the resulting liquor solution were recovered by precipitation using guanidine carbonate salt as precipitating agent. Guanidine salt effectively precipitated out total amount of Nb and Ta contained in the PLS. This resulted in a high recovery of almost 97% and 85% of the total amount of Nb and Ta contained in the +250 microns concentrate sample (feed) with optimum of 50 mg/mL guanidine.

Irrespective of the size fractions, variation of guanidine does not show a significant effect on composition of the Nb-Ta precipitate. However, precipitate from -250-microns size fraction seems to have high percentage compositions for Nb and Ta. Regardless of the guanidine concentration, higher Ta recoveries were achieved for +250 microns size whereas that of Nb were obtained for -250 microns except at 50 mg/mL guanidine. Based on material balance, it was found that approximately 734.5 kg of (Nb, Ta)-guanidine precipitate with purity higher than 84% could be obtained from one tonne of ferro-columbite feed concentrate. Since the content of Mn in the feed sample and PLS is not high and the extent at which iron dissolve is not such high (35%wt). In addition, their reaction with KOH is too slowly compared to that of Nb and Ta, thus their presence in the precipitate does not affect much the purity of the final product. The Nb-Ta guanidine precipitate obtained was then calcined at 900°C for one hour to convert the precipitate into mixed oxides of Nb and Ta and remove the guanidine. The calcination resulted in mass loss of almost 50% and $(Nb,Ta)_2O_5$ product with 97%

purity containing Fe_2O_3 (1.3%) and MnO_2 (0.7%). The use of guanidine carbonate salt to recover Nb and Ta from aqueous solution is environmentally friendly process providing high yield (~100%) and high potential to replace the traditional approach which use hydrofluoric acid.

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CHAPTER SEVEN

7. INVESTIGATION OF THE ALKALI-ASSISTED ROASTING OF THE NIGERIAN AND RWANDAN COLUMBITE-TANTALITE SAMPLES AND THE GUANIDINE CARBONATE-ASSISTED EXTRACTION OF MIXED OXIDES OF NIOBIUM AND TANTALUM

7.0 Background

The concentrated materials used in the study as-received from the mining and minerals processing companies had been pre-concentrated by gravity separation method using shaking tables. In this chapter, two columbite-tantalite concentrates sample materials from two different countries, Nigeria and Rwanda were investigated for comparisons. The investigation started with materials characterization followed with materials digestion and minerals open-up through alkali-assisted roasting and then water-based leaching of the digestion products. Finally, the extraction and recovery of the dissolved Nb and Ta via precipitation using guanidine carbonate salt and then calcination of the resulting (Nb, Ta)-guanidine precipitate to remove guanidine and convert the metals into oxides.

7.1 Introduction

Niobium (Nb) and Tantalum (Ta) are both important refractory metals with high meting points and the ability to retain strength at elevated temperatures (Suri et al., 2008). Nb and Ta are excellent materials for electronic capacitors as they are highly good conductors of heat and electricity

and form an extremely thin oxide layer that acts as dielectric and protective layer (*Tantalum and Niobium Materials | Metal and Compound Powders | JX Nippon Mining & Metals*, 2022; *Tantalum Market - Growth, Trends | 2022 - 27 | Industry Forecast*, 2022). High-purity and high-quality tantalum and niobium metal powders are used as additives to improve corrosion-resistance of super-alloys and turbine blades used in aerospace and energy industries, and of high strength low-alloy steel used for construction (*Tantalum and Niobium Materials | Metal and Compound Powders | JX Nippon Mining & Metals*, 2022). As 5G technology grows, the tantalum market is being driven by the growth of the electrical and electronic industry and extensive applications of tantalum alloys in aviation and gas turbines, medical and chemical processing equipment(*Tantalum and Niobium Materials | Metal and Compound Powders | JX Nippon Mining & Metals*, 2022). The niobium market is largely dominated by the construction, automotive and transportation industries for production of stainless steels and high-strength low-alloy steels used in construction of oil and gas pipeline, car and truck bodies (*Niobium Market | 2022 - 27 | Industry Share, Size, Growth - Mordor Intelligence*, 2022; *Niobium Uses & Applications | TIC*, 2022). Other consumers of niobium include production of nickel-, cobalt, and iron-based super-alloys used in the manufacture of components of aircraft engines, rockets and high-temperature and corrosion resistant used in aerospace and defense (Heisterkamp & Carneiro, 2001; *Niobium Uses & Applications | TIC*, 2022). The application of these materials in high-quality products for high-tech and major economies has pushed the market further.

Nb and Ta are always found together as oxides in the group of minerals of columbite-tantalite series known as columbite-group minerals (CGM) hosted in pegmatites, granites, carbonatites, and alkaline related igneous rocks and their delivered placer deposits (Melcher et al., 2013). Apart from CGM, there is a range of other important minerals containing Nb-Ta oxides (NTO) such as pyrochlore, tapiolite, microlite, wodginite, and ixiolite hosted in aplite-pegmatites-greisen rocks where leucogranites, pegmatites bodies and quartz veins have been deposited in metasedimentary rocks (Melcher et al., 2013).

CGM and pyrochlore are the main sources for production of Nb and Ta metals. The current industrial production requires treatment of the CGM concentrates through digestion of the concentrate using highly concentrated hydrofluoric acid (HF) or its mixture with sulfuric acid (H_2SO_4) at moderate temperatures (Sanchez-Segado et al., 2017). The digestion using acidic media containing-fluoride leads to the formation of soluble (Nb, Ta)-fluoride complexes which are then separated via solvent extraction utilizing organic solvents. The commonly used organic solvents include methyl iso-butyl ketone (MIBK), cyclohexanone, octanol, Tributyl phosphate (TBP), Alamine 336, bis (2-ethylhexyl) phosphoric acid (DEHPA) (Ayanda & Adekola, 2011; Rodríguez et al., 2020; Zhu & Cheng, 2011). However, this leaching in acidic media is not selective and produces large amounts of co-dissolved impurities, solid and liquid wastes that are difficult to dispose. The use of corrosive HF and organic solvents have been blamed for cost and environmental challenges (Sanchez-Segado et al., 2017). Therefore, advancing a sustainable alternative approach that can reduce solid and liquid wastes and replace the use of HF for the treatment of the CGM and NTO concentrates to extract Nb and Ta is still needed. In this study, we reported the dissolution of the main elements of the Nigerian and Rwandan columbite-tantalite concentrates (N-Nass Con and R-KMY Con) in an alkali-assisted roasting followed by water-based leaching systems and the guanidine carbonate-induced selective precipitation of the dissolved Nb and Ta.

7.2 Materials and Methods

7.2.1 Sample information

The mineral samples used in this study consists of columbite-tantalite concentrate obtained from two different countries: Nigeria and Rwanda. The Nigerian sample was named N-Nass Con and it was obtained from a mine located in the Nasarawa state of Nigeria while the Rwandan sample named R-KMY Con was obtained from a mine located in Kamonyi District, South Province of Rwanda. Both materials as received from the mining companies were pre-concentrated by gravity separation method at the mine site. The materials were further ground with a ball mill to a finer size and classified into two different size fractions, +250 and -250 microns using a sieve. Before and after size classification, a representative sample for each size fraction was taken for material

characterization. All the chemical reagents used in the study were of analytical grade and were used without any further purification. Guanidine carbonate salt (99%w/w) and potassium hydroxide (ACS reagent) pellets were purchased from Sigma Aldrich Inc.

7.2.2 Materials characterization

The concentrate-material samples used in the study was characterized before and after size classification and prior to any processing with analytical techniques. Analytical techniques used include X-ray diffraction (XRD), inductively coupled plasma-optical emission spectroscopy (ICP-OES), and the scanning electron microscopy attached with an energy-dispersive spectroscopy (SEM-EDS). The characterization serves as to understand better the distribution of the minerals of interest, their chemistries, their mineralogies as well as morphologies and texture features. The chemical compositions determined with the help of ICP-OES analysis are expressed in oxides form to reflect their natural occurrences. The mineral phases present in the sample were identified with the help of an X-ray diffractometer (PANAnalytical Empyrean X-ray Diffractometer) operated with a radiation source Cu-Kα ($\lambda = 0.1540$ nm), at 45 kV and 40 mA.

7.2.3 Experimental Procedures

7.2.3.1 Alkali-assisted roasting and water-based leaching concentrate samples

Alkali-assisted roasting with KOH for decomposition and water-based dissolution of the niobium-tantalum bearing minerals was adopted to brake-up the mineral matrix and bring these metals of interest into the solution. The two concentrate samples namely N-Nass Con and R-KMY Con were first tested at different temperature (200, 250 and 300°C) and then at optimum conditions (250°C, 100% flux-to-concentrate ratio and 1h roasting) as determined in the previous chapter and earlier publications (Habinshuti et al., 2022).

In the first stage, 1.0 g of the concentrate sample was accurately weighed and thoroughly mixed with 1.0 g of well-ground pellets of potassium hydroxide (KOH). The

mixture was put in high quality alumina crucible for roasting. The roasting process was carried out in a muffle furnace (Mellen Microtherm) for one hour. The furnace was pre-heated at specific desired temperature and when the temperature reached the preset value, a well-prepared sample was carefully introduced into the furnace after which the furnace was completely closed. The furnace was allowed to regain the desired temperature before the timer was started. After one hour of roasting, the crucible was taken out of the furnace and allowed the melt to cool at room temperature before leaching it with water.

After cooling, the melt was leached with 100 mL of deionized water and the resulting solid-liquid mixture was stirred at room temperature for 90 minutes. Then, slurry mixture was filtered on vacuum pump, and almost 100 mL of liquor solution was obtained. For each set of experiment performed, the leach solution and residue obtained after filtration were both analyzed with ICP-OES to determine the percentage content of Nb, Ta, Sn, Fe, and other impurities present. In addition to ICP-OES, the residue was also analyzed with X-ray diffractometer and SEM-EDS to know which crystalline phases remained in the residue, their morphology, and elemental compositions after the roasting and leaching processes. The percentage of element leached in the solution was calculated by using the following expression:

$$\% \text{ element leached} = \left(1 - \frac{\text{Mr}}{\text{Mo}}\right) \times 100 \qquad \text{Eq 7.1}$$

Where Mr is the weight of element in the residue after leaching and Mo is the weight of element in the in the feed

Based on the results obtained in the first stage and the results we reported in previous chapter, the present material samples were further investigated at optimum conditions and large scale (15.0 g

of concentrate and 15.0 g of fluxing material (KOH)) and 1L of deionized water was used for leaching the metals and to obtain enough solution for precipitation. Almost 1L of pregnant leach solution (PLS) was obtained after filtration. The amount of Nb and Ta dissolved in the PLS were recovered by precipitation using guanidine carbonate salt as precipitating agent.

7.2.3.2 Guanidine carbonate-assisted extraction of Nb and Ta from PLS via precipitation

After alkali-assisted heat treatment with KOH and water-based leaching of the Nigerian and Rwandan columbite-tantalite concentrate samples at optimum conditions, the resulting pregnant leach liquor solution (PLS) was further processed for the recovery of dissolved Nb and Ta. The recovery of solubilized Nb and Ta was carried out via precipitation utilizing guanidine carbonate salt as precipitating agent. Guanidine carbonate is a salt with proven potential to rapidly and selectively precipitate out Ta from a synthetic aqueous solution containing other metals such as Si and W (Ogi et al., 2018). Guanidine is an amine and strong base which forms a highly stable cation, guanidinium $C(NH_2)_3^+$ in aqueous solution due to its efficient resonance stabilization and water molecules solvation (Perrin & International Union of Pure and Applied Chemistry. Commission on Electroanalytical Chemistry., 1972). Therefore, due to the strong similarities between Ta and Nb and their natural co-occurrences, guanidine could be a powerful tool for sustainable extraction of these critical commodities not only from ore-deposits but also from synthetic and recycling sources.

In this investigation, the guanidine-induced precipitation of dissolved Nb and Ta was carried out with leach liquor solution obtained after alkali-assisted roasting and water-based leaching of both +250 and -250-microns size fraction samples at optimum conditions. Appropriate volume of pregnant leach solution was measured from the almost 1L of PLS, since we reported in our previous studies that guanidine precipitation efficiency toward Nb and Ta is almost constant and 25 mg/mL of guanidine salt was found to be sufficiently enough to precipitate the total amount of Nb and Ta contained in the leach liquor (Habinshuti et al., 2022). Therefore, 20.0 g of guanidine carbonate salt in solid form were added to the pregnant leach solution (400 mL) on continuous stirring to extract Nb

and Ta from the pregnant solution. The (Nb, Ta)-guanidine precipitate was formed and appeared in the solution immediately in less than a minute. The mixture was stirred for 30 minutes to ensure complete precipitation. After 30 minutes, the mixture was filtered on vacuum pump and the precipitate was dried at 100°C, both filtrate and precipitate were analyzed with ICP-OES for Nb, Ta, Sn, Fe, Mn, Si, and Al. The (Nb-Ta)-guanidine precipitate must undergo the calcination process to remove the guanidine and convert metals into their oxides. The percentage recovery/extraction was calculated by using the following expression:

$$\%\text{Recovery} = \frac{(\text{wt}\% \text{ of element in precipitate} * \text{total weight of precipitate})}{(\text{wt}\% \text{ of element in the feed} * \text{total weight of feed})} * 100 \qquad Eq.\textbf{7}.2$$

7.2.3.3 Calcination of the (Nb-Ta)-guanidine precipitate

After precipitation of Nb and Ta dissolved in the pregnant leach solution of the Nigerian and Rwandan columbite-tantalite concentrate samples, the (Nb-Ta)-guanidine precipitate obtained was dried in oven at 100°C and analyzed. The precipitate was further calcined at 900°C for one hour to convert the metals into their oxides and remove the guanidine moiety through evaporation in form of carbon and nitrogen oxides (Ogi et al., 2018; Pierret & Wilhelm, 1956). The calcined precipitate was analyzed with ICP-OES and XRD

7.3 Results and Discussions

7.3.1 Materials Characterization

The materials sample used in this study were two concentrate-types N-Nass Con and R-KMY Con from Nasarawa State of Nigeria and Kamonyi District in the Southern part of Rwanda. The materials were ground with a ball mill to a finer size for high reaction efficiency. The materials were characterized before and after size classification and the results of ICP-OES analysis are presented as oxides in Table 7.1. From the table, the main constituents in the two samples are cassiterite minerals associated with some columbite-tantalite mineral phases hosted in the aluminosilicate matrix. Compositions of 64, 26.5% of SnO_2 and 5, 4.6% of Ta_2O_5 and 2.6, 4.8% of Nb_2O_5 were recorded for the N-Nass Con and R-KMY Con respectively. From mineralogical point of view, samples from the

two countries have almost similar mineralogical characteristics with major phases being cassiterite associated with minerals of iron and columbite-tantalite series. The Nigerian sample is of columbite type while the Rwandan is of columbite-tantalite (coltan) nature. However, the minerals of Nb_2O_5 and Ta_2O_5 were almost equally distributed before and after size classification for R-KMY Con and N-Nass Con respectively. Contrary to R-KMY Con, the finer size fraction of N-Nass Con seems to have higher percentage compositions of the main constituents relatively to coarser size fraction.

Table **7.1**: Chemical compositions expressed in oxide form of the (N-Nass Con and R-KMY Con) before and after size classification

Sample	Compositions (wt%)						
	Nb_2O_5	Ta_2O_5	SnO_2	Fe_2O_3	MnO	SiO_2	Al_2O_3
N-Nass Con	2.670	4.979	63.903	3.416	1.521	8.475	7.821
+250 microns	5.161	4.497	51.757	6.144	1.630	8.840	6.042
-250 microns	5.725	5.028	59.629	2.350	1.819	6.490	3.953
R-KMY Con	4.853	4.643	26.527	3.929	2.186	9.208	12.26
+250 microns	2.512	5.170	70.313	1.766	0.874	6.343	1.819
-250 microns	2.220	4.650	65.793	2.685	0.757	7.107	2.948

The above results of chemical compositions are supported by the mineralogical findings from the X-ray diffraction analysis presented in Figure 7.1 where most of the characteristic peaks are completely matched with cassiterite and ferro-columbite phases hosted in aluminosilicate and quartz matrixes. The ferro-tantalite phases were not detected in the XRD spectrum, they have similar crystal structure to the ferro-columbite crystals.
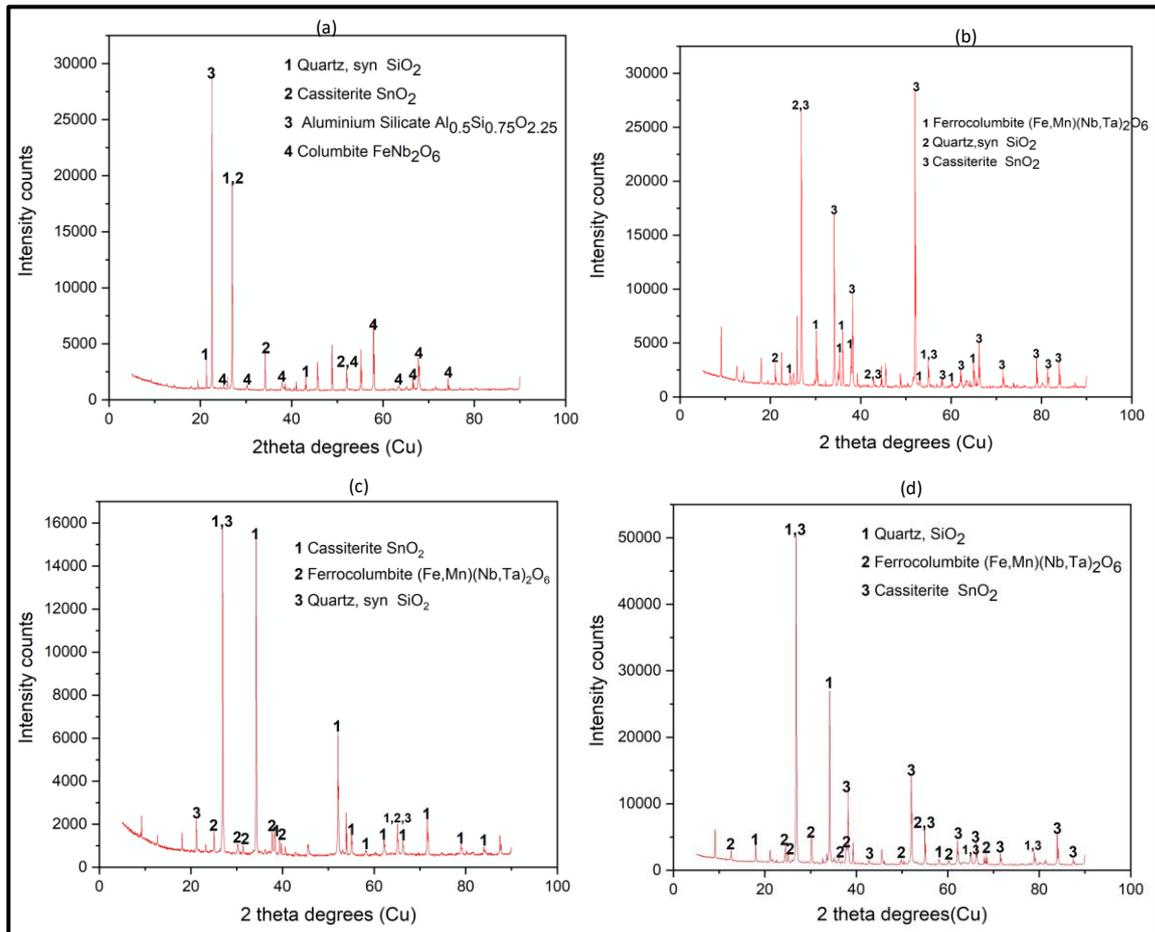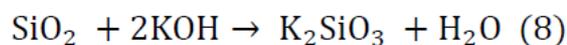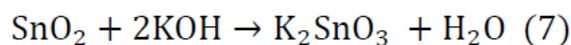
Figure **7.1**: XRD Spectra of the Nigerian and Rwandan concentrate feed after size classification: N-Nass Con (a) +250 and (b) -250 microns and R-KMY Con (c) +250 and (d) -250 microns)

7.3.2 Alkali-assisted roasting and water-based leaching of the concentrate samples.

The concentrate samples under investigation were characterized and classified into two size fractions. Each fraction was subjected to the alkali-assisted heat treatment with KOH followed by water-based leaching after cooling the melt for the recovery of both Nb and Ta as well as optimize their recoveries. Due to the critics of the currently used HF, the insolubility and refractory nature of the Nb and Ta minerals (Fairbrother et al., 1958), alkali-assisted roasting using KOH was adopted and the heat facilitated the open-up of the minerals which then reacted with the molten potassium hydroxide and get converted into water-soluble compounds according to reactions presented in scheme 1 (X. H. Wang et al., 2010; X. Wang et al., 2009) These species can be easily recovered from the leach liquor solution via precipitation or solvent extraction (Deblonde et al., 2015).
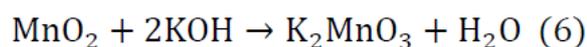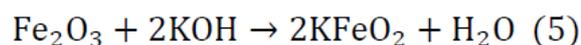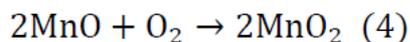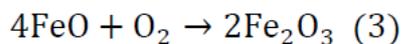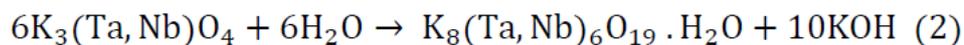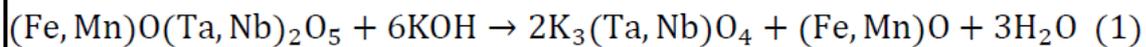
$$(Fe, Mn)O(Ta, Nb)_2O_5 + 6KOH \rightarrow 2K_3(Ta, Nb)O_4 + (Fe, Mn)O + 3H_2O \ (1)$$

$$6K_3(Ta, Nb)O_4 + 6H_2O \rightarrow K_8(Ta, Nb)_6O_{19} . H_2O + 10KOH \ (2)$$

$$4FeO + O_2 \rightarrow 2Fe_2O_3 \ (3)$$

$$2MnO + O_2 \rightarrow 2MnO_2 \ (4)$$

$$Fe_2O_3 + 2KOH \rightarrow 2KFeO_2 + H_2O \ (5)$$

$$MnO_2 + 2KOH \rightarrow K_2MnO_3 + H_2O \ (6)$$

$$SnO_2 + 2KOH \rightarrow K_2SnO_3 + H_2O \ (7)$$

$$SiO_2 + 2KOH \rightarrow K_2SiO_3 + H_2O \ (8)$$

Scheme 1: Main reactions that take place during the alkali-assisted roasting with KOH and water leaching of the columbite-tantalite materials (X. Wang et al., 2009)

Since from the literature and our previous studies, temperature proved to have profond effect on the dissolution of elements, thus by fixing flux-to-concentrate ratio at 100% and 1h roasting, each fraction of the sample was first tested at different temperatures (200, 250 and 300°C) for their element dissolution. Then based on the results obtained in Figure 7.2 and the previous results we reported (Habinshuti et al., 2022), it is clear that roasting the samples with a ratio of KOH-to-concentrate of 100% at 250°C, maximum dissolution of 93, 91.5% for Nb and 85.5, 82.5% for Ta were achieved for finer fraction of R-KMY Con and N-Nass Con respectively. Coarser fraction had lower dissolution relatively to the finer fraction where maximum dissolution of 86.7, 89% for Nb and 84, 82% for Ta were obtained for R-KMY Con and N-Nass Con respectively. Meanwhile, dissolution of other elements has a clear tendency to decrease as temperature increases. This was a good indication of the possibility to separate Nb and Ta from other associated impurities. Unfortunately, some Fe and Mn were also co-dissolved along at lesser extent of 30.5, 29 and 33, 19% respectively for finer size fractions of R-KMY Con and N-Nass Con as presented in Figure 2. The decrease in the dissolution of tin and iron as temperature increases, may be attributed to the formation of their insoluble compounds and this makes them to remain in the residue as their main constituents as indicated by the results of

XRD analysis depictured in Figure 7.3. The percentage of element leached in the solution was calculated by using the expression described in the equation 7.1:
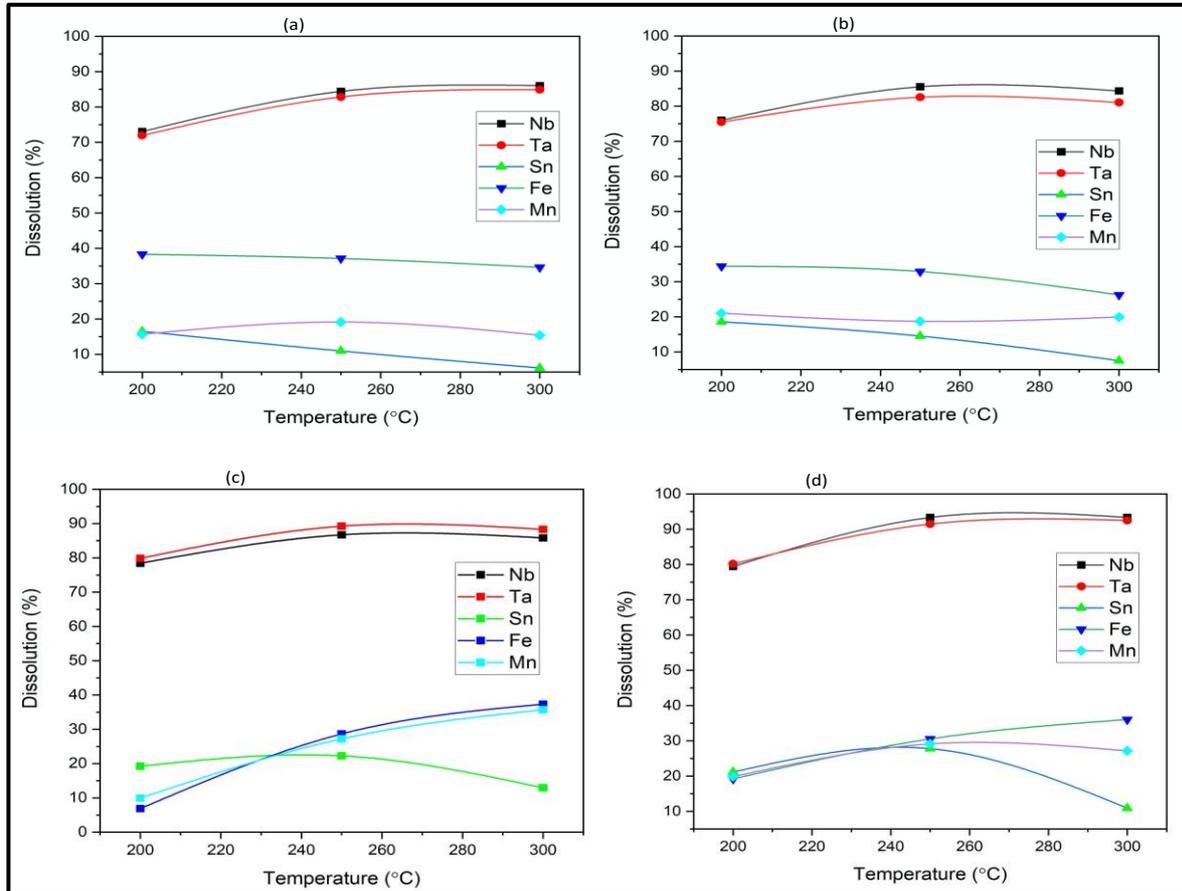
Figure **7.2**: Effect of temperature on dissolution of the main elements contained in the different size fractions of the Nigerian and Rwandan columbite-tantalite concentrate samples: N-Nass Con (a) +250 and (b) -250 microns and R-KMY Con (c) +250 and (d) -250 microns size fractions.

Comparison of the material balance and dissolution of main elements contained in the Nigerian and Rwandan columbite-tantalite concentrate samples treated at large scale (15 g) are presented in Table 2. From the table, it is clear, that more than 91.0 % of niobium and tantalum contained in the feed sample were dissolved leaving most of tin and iron as cassiterite and hematite as the main residue components. Although, some iron and manganese were also dissolved along but because of their less content in the feed and the extend they dissolve, they don't affect much the final product. However, the finer size fraction seems to have high percentages dissolution of main constituents relatively to coarser fraction, thus grinding to relevant fine size was necessary.

Table **7.2**:Material balance for alkali-assisted roasting and water-based leaching of different size fractions of the Nigerian and Rwandan concentrate samples at optimized conditions: 250°C, flux-to-concentrate ratio 100%, and 1h roasting.

N-Nass Con	+250 microns size fractions			-250 microns size fractions		
Elements	Feed (%)	Residue (%)	Dissolution (%)	Feed (%)	Residue (%)	Dissolution (%)
Nb	3.608	0.304	91.886	4.002	0.239	94.259
Ta	3.683	0.352	90.786	4.118	0.345	91.954
Sn	40.768	38.758	8.484	46.968	41.783	14.659
Fe	4.297	3.915	12.290	1.643	1.425	16.813
Mn	1.263	1.103	15.931	1.408	1.308	10.934
Si	4.132	3.099	27.812	3.034	2.660	15.892
Al	3.197	4.930	-48.445	2.092	3.585	-64.396
Weight(g)	**15.25**	**14.68**	**-**	**15.24**	**14.62**	**-**
R-KMY Con						
Nb	1.756	0.144	92.485	1.552	0.107	93.685
Ta	4.235	0.423	90.830	3.808	0.351	91.525
Sn	55.383	54.084	10.342	51.823	48.108	14.670
Fe	1.235	1.132	15.866	1.878	1.620	20.736
Mn	0.677	0.550	25.452	0.586	0.4667	26.780
Si	2.965	1.843	42.938	3.322	2.162	40.182
Al	0.963	2.395	-128.446	1.560	1.828	-7.709
Weight(g)	**15.39**	**14.13**	**-**	**15.47**	**14.22**	**-**

The residue obtained was also analyzed with X-ray diffractometer and the results supported the above-mentioned observation and confirmed the presence of cassiterite and hematite. The hematite phase (α-Fe_2O_3) observed in the residue might have resulted from the oxidation of magnetite (Fe_3O_4) or the inversion of maghemite (γ-Fe_2O_3) upon heating at temperature between 250-750°C (Michael W. McElhinny, 2000; Moskowitz et al., 2015). Natanite which is an iron-tin hydroxide mineral that normally crystalize in Sn-W-As veins located in Nb and Ta-bearing pegmatites environment was also identified within the residue of +250 microns of N-Nass Con Figure 7.3

(Betterton et al., 1998).
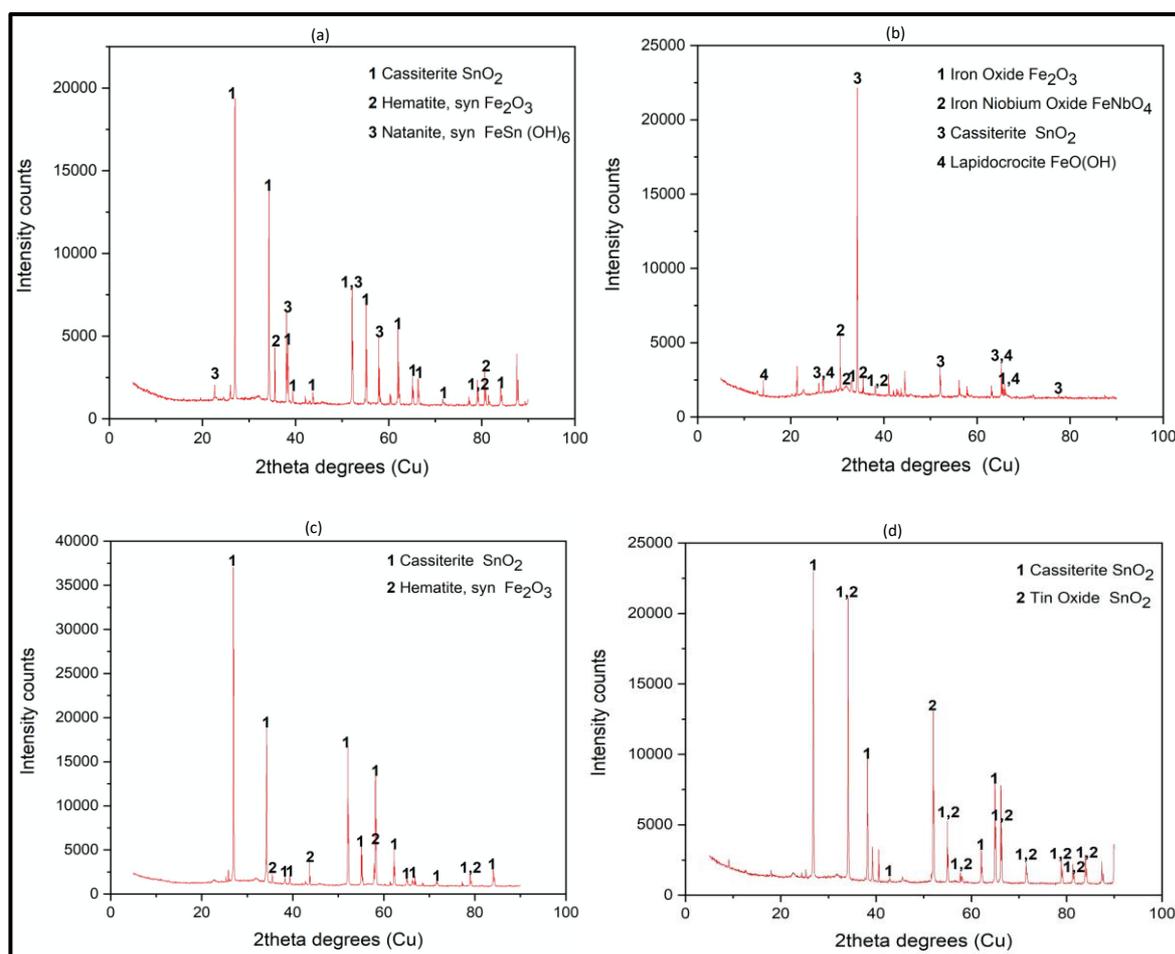
Figure **7.3**: XRD Spectra of the residues obtained after alkali-assisted roasting and water leaching of N-Nass Con (a) +250 and (b) -250 microns size and R-KMY Con (c) +250 and (d) -250-microns size fractions at optimum conditions (250°C, 100% flux-to-concentrate ratio, and 1h roasting).

The SEM image of the residue obtained after alkali-assisted roasting with KOH and water leaching presented in Figure 7. 4 shows morphology of particles of large size and different shapes but mostly spherical and oval with smoothen surface and sometime porous. This means that during the process the finer particles have reacted and get dissolved from the large particles.

The EDX spectrum depictured in Figure 7.4 shows the semi-quantitative chemical compositions mainly of 35.1%, 6.3% and 12.6%, 22.6% of tin and iron contained in the residues of alkali-assisted roasting and water leaching of the +250 and -250 microns size fractions of the N-Nass Con. All these results confirm the potentiality of the process to solubilize the insoluble and refractory

Nb and Ta into the aqueous solution. The palladium detected in the residue-sample is from the sputter coating used for coating to avoid sample charging during the SEM scanning.
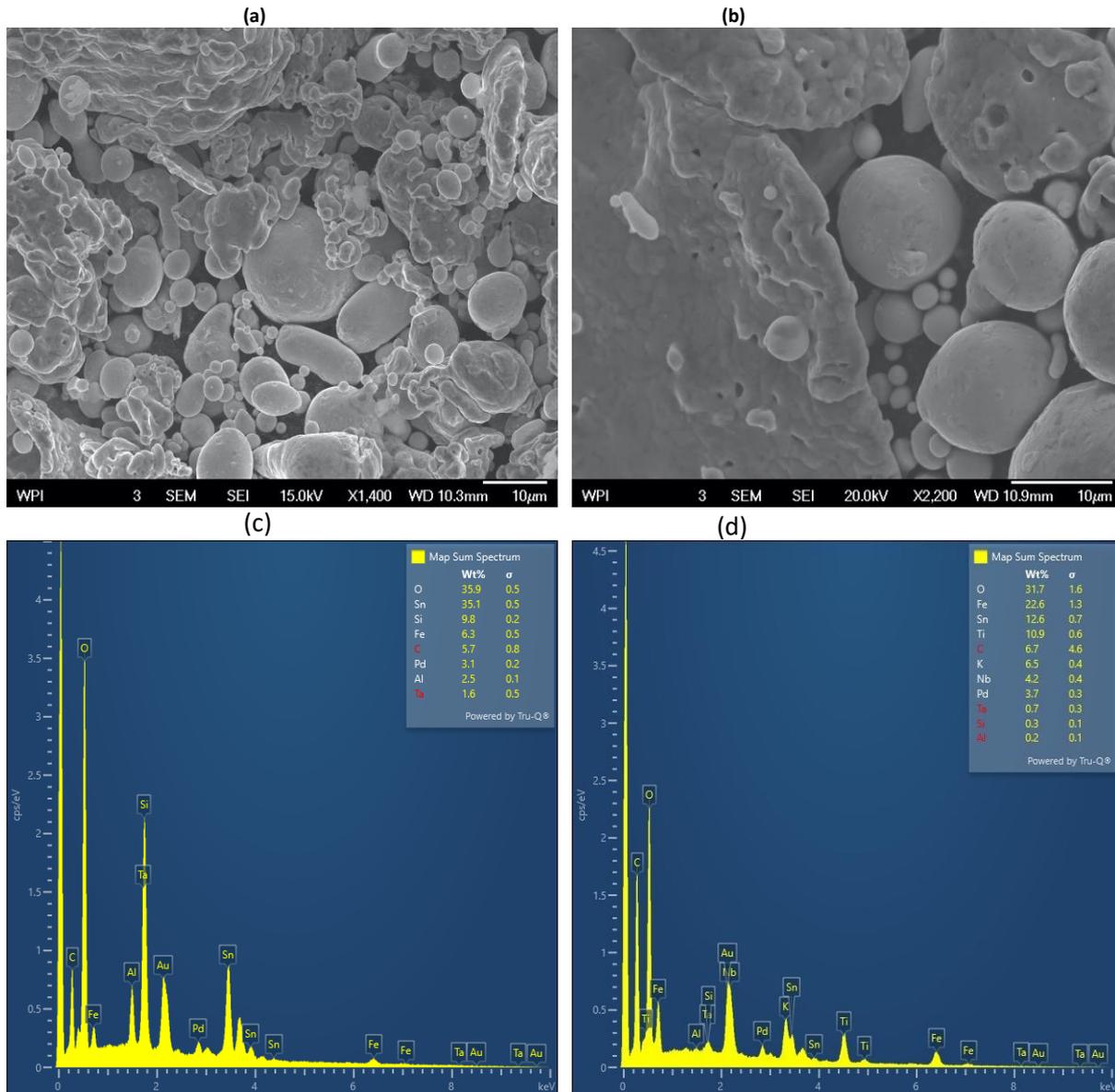

Figure **7.4**: SEM images and EDS Spectra of residue obtained after the alkali-assisted roasting and water-based leaching of R-KMY Con (a) +250 and (b) -250 microns size fractions

7.3.3 Guanidine carbonate-assisted extraction of Nb and Ta from PLS of the N-Nass Con and R-KMY Con

The pregnant leach liquor solution obtained after the alkali-assisted heat treatment of the N-Nass Con and R-KMY Con samples followed by water-based leaching was further processed for the recovery of the dissolved Nb-Ta *via* precipitation. The precipitation of (Nb-Ta) contained in the PLS

was performed using guanidine carbonate salt as precipitating agent. The Nb-Ta-guanidine precipitate obtained after filtration was dried in oven at 100°C and analyzed with ICP-OES prior to calcination for its chemical composition determination. The results are presented in Table 7.3 and from the table, the Nb-Ta-guanidine precipitate is only contaminated at lesser extent with some iron and small amount of manganese. For N-Nass Con sample, a Nb-Ta-precipitate with purity of more than 95.0% was recovered from the leach liquor of -250 microns size fraction and contains Nb (48.5%), Ta (47.5%), with Fe (2.6%) and Mn (0.1%) whereas the precipitate obtained from leach solution of +250 microns size fraction has a purity higher than 86.0% with Nb (43.64%), Ta (42.90) with Fe (8.06%) and Mn (1.7%).

Table **7.3**: Elemental compositions of uncalcined (Nb, Ta)-guanidine precipitate extracted from pregnant leach solution of N-Nass Con and R-KMY Con samples analyzed with ICP-OES

Sample	Precipitate compositions (wt%)							
N-Nass Con	Nb	Ta	Sn	Fe	Mn	Si	Al	W
+250 microns	43.340	43.188	0.935	8.084	1.743	1.854	0.634	0.205
-250 microns	74.522	19.317	1.073	4.057	0.150	0.322	0.279	0.279
R-KMY Con								
+250 microns	28.455	65.745	0.417	3.317	0.769	0.880	0.287	0.130
-250 microns	28.857	62.707	0.399	5.037	1.240	1.248	0.399	0.113

In the case of Rwandan sample, R-KMY Con, a precipitate with purity of more than 94.0% with chemical compositions of Nb (28.45%), Ta (65.75%) along with Fe (3.32%) and Mn (0.77%) was recovered from the leach liquor of +250 microns size fraction and for -250 microns size, a Nb-Ta-guanidine precipitate having purity of 91.5% containing Nb (28.09%), Ta (63.69%) with Fe (4.9%) and Mn (1.21%) was obtained.

The EDX spectrum of the uncalcined (Nb-Ta)-guanidine precipitates presented in Figure 7. 5 shows dominance in chemical compositions of Nb (13.8%), Ta (2.0%) and Nb (22.3%), Ta (3.2%) contained respectively in the precipitates of +250 and -250-microns size fractions of the N-Nass Con

sample. However, some amount of tin (8.3%) and iron (12.2%) was also detected in the -250 microns size fraction which reflect their high amount observed with ICP-OES analysis relatively to the +250 microns size fraction. The EDX analysis of the precipitate recovered from the pregnant leach solution of the Rwandan concentrate sample, R-KMY Con presents chemical compositions of Nb (43.4%), Ta (6.4%) and Nb (26.9%), Ta (15.1%) from +250 and -250 microns size fractions respectively. The observed percentage of carbon reflect the presence of the guanidine.
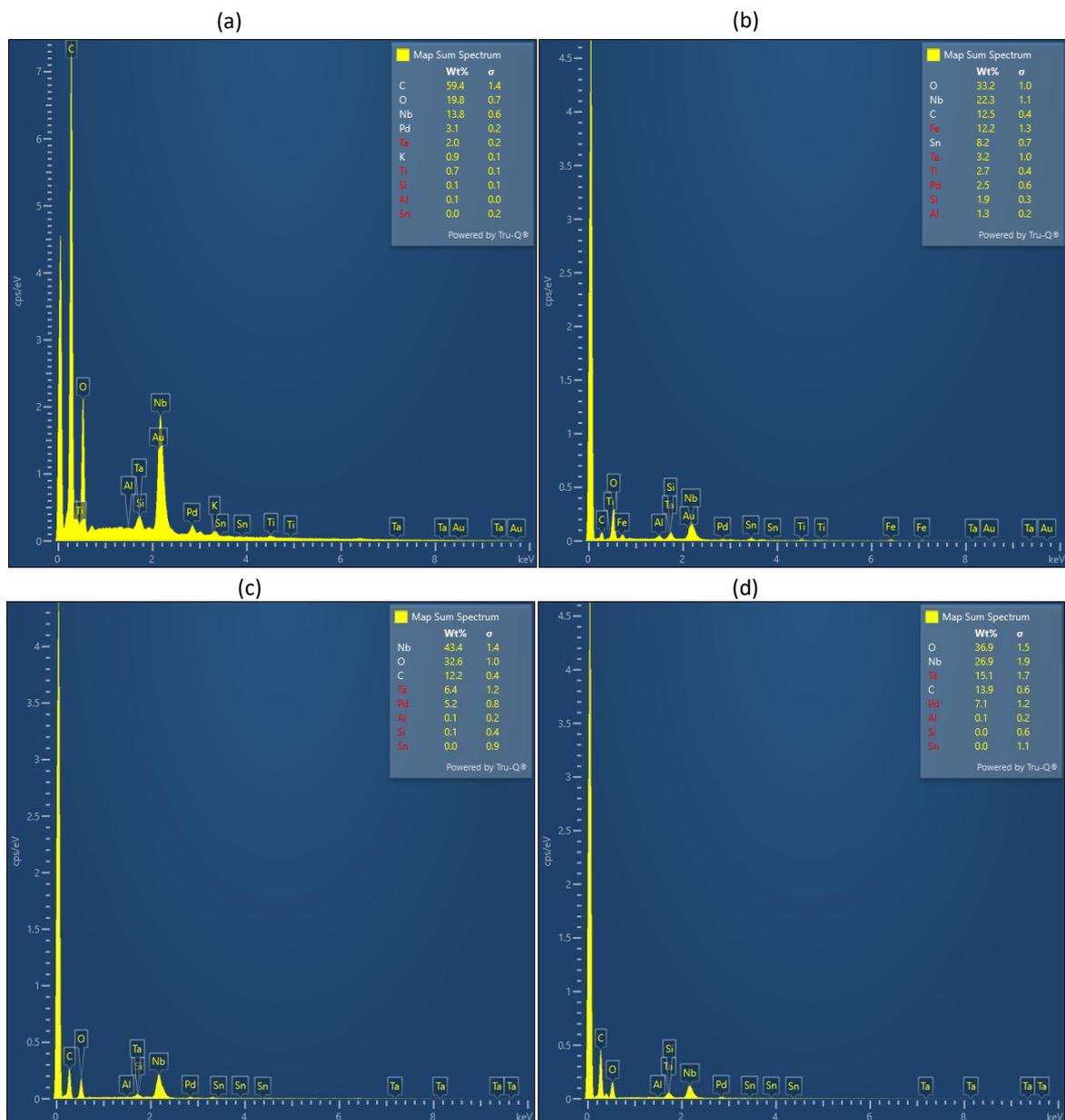

Figure **7.5**: EDS Spectra of the uncalcined (Nb, Ta)-guanidine precipitate obtained after precipitation of Nb and Ta from PLS of the N-Nass Con (a) +250 and (b) -250 μm and R-KMY Con (c) +250 and (d) -250 μm size fractions.

Under the optimized conditions, (Nb-Ta)-guanidine precipitates with purity more than 95%, 86% and 91%, 94% were recovered from the pregnant leach solution of -250 and +250-microns size fractions of the N-Nass Con and R-KMY Con samples respectively. High percentage recoveries were obtained for the finer fractions of the Nigerian sample relatively to coarser size and Rwandan sample. The percentage recovery/extraction was calculated by using the expression described in equation 7.2.

The percentage recovery of total Nb and Ta contained in the feed concentrate N-Nass Con was 98%, 94% and 99%, 94% for the coarser and finer fractions respectively as presented in Table 7.4. In case of R-KMY Con, the total recovery of Nb and Ta was 97%, 93% and 98%, 90% for +250 and -250 microns size fractions respectively. From these results, it is clear, that the recovery of niobium relatively to tantalum generally increases as the particles size decreases. This is probably due to the increased contact surface areas and high solubility of niobium complexes enhanced by presence of potassium ions compared to that of tantalum (Deblonde et al., 2015; Fairbrother et al., 1958). However, the recovery of some impurities such as iron decreases as particles size decrease while that of manganese increases.

Table **7.4**: Total recovery of Nb and Ta from pregnant the leach liquor solution obtained when the samples were treated at optimum conditions (Roasting: 250°C, flux ratio 100%, and 1h roasting), Precipitation: 50 mg/mL guanidine, 30 mins, 25°C.

N-Nass Con	+250 microns size fraction			-250 microns size fraction		
Elements	Feed (%)	Precipitate (%)	Recovery (%)	Feed (%)	Precipitate (%)	Recovery (%)
Nb	3.608	25.530	97.843	4.002	31.000	98.737
Ta	3.683	25.099	94.240	4.118	30.360	93.964
Sn	40.768	0.546	0.185	46.968	0.545	0.547
Fe	4.297	4.719	15.184	1.643	1.687	4.247
Mn	1.262	1.018	11.147	1.408	0.063	5.245
Si	4.132	1.082	3.622	3.034	0.134	6.089

Al	3.197	0.370	1.601	2.092	0.116	3.553
Weight (g)	**15.250**	**2.109**	**-**	**15.240**	**1.942**	**-**
R-KMY Con	+250 microns size fraction			-250 microns size fraction		
Nb	1.756	25.989	96.879	1.552	29.957	97.633
Ta	4.234	60.048	92.825	3.808	67.910	90.180
Sn	55.383	0.381	0.045	51.823	0.414	0.0403
Fe	1.235	3.029	16.050	1.878	5.229	14.078
Mn	0.677	0.702	6.788	0.586	1.287	11.107
Si	2.965	0.804	1.775	3.322	1.296	1.972
Al	0.963	0.262	1.783	1.560	0.414	1.342
Weight (g)	**15.390**	**1.0074**	**-**	**15.247**	**0.771**	**-**

From these data, it is possible to obtain 50.567 and 127.428 kg of the (Nb-Ta)-guanidine precipitate from one tone of the finer fraction of Rwandan and Nigerian concentrate samples respectively. Since 0.970 and 1.581 g of mixed Nb_2O_5 and Ta_2O_5 were obtained from 15.24 g of the concentrate materials, that is 63.603 and 103.751 kg from one tone of each of the samples. The chemical compositions of the concentrate feed materials revealed that they contain 6.870% and 10.753% of mixed Nb_2O_5 and Ta_2O_5, this is equivalent to 68.7 and 107.53 kg from one tone of each of the Rwandan and Nigerian concentrate samples, therefore overall efficiency recovery of 92.58% and 96.5% of mixed oxides of Nb and Ta were achieved respectively for the R-KMY Con and N-Nass Con samples.

7.3.4 Calcination of the (Nb, Ta)-guanidine precipitate

The (Nb-Ta)-precipitate recovered from the leach liquor solution was amorphous and its calcination at 900°C for one hour converted the metals into their corresponding oxides. The XRD spectrum of both uncalcined and calcined (Nb-Ta) precipitate is depicted in Figure 7.6. From the figure, the uncalcined (Nb-Ta)-guanidine precipitate showed a spectrum with broad peak, means that the precipitate was amorphous, and cannot be assigned to any clear crystalline peaks. Upon calcination, the amorphous precipitate was converted into clear and sharp crystalline peaks corresponding mainly to the oxides of niobium and tantalum as presented in the XRD spectrum in

Figure 5. The iron that co-precipitated along into the precipitate was also converted into magnetite after calcination.

$$(C(NH_2)_3)_8(Ta, Nb)_6O_{19\ (s)} \xrightarrow{900°C} (Ta, Nb)_2O_{5\ (s)} + CO_{2\ (g)} + NO_{x(g)} + H_2O_{(g)} \quad \text{Eq. \textbf{7.3}}$$
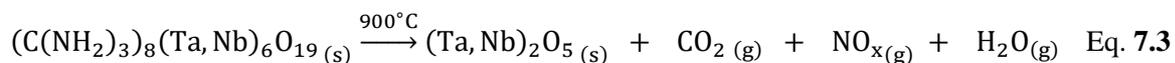
The calcination of the amorphous (Nb-Ta)-guanidine precipitate converted the metals into their oxides and removed guanidine in form of carbon and nitrogen oxides as evidenced with their crystallographic peaks presented in Figure 7.6. The calcination resulted in mass loss of 44.7% and 41.2% for the precipitate obtained from the guanidine-induced precipitation of Nb and Ta from leach solution of +250 and -250-microns size fractions of N-Nass Con. For R-KMY sample, mass loss of 42% and 41.1% were reported after calcination of the precipitate obtained from the pregnant leach solution of +250 and -250-microns size fractions respectively. The calcined precipitate recovered from the Nigerian sample has 64% Nb_2O_5 and 35% Ta_2O_5 whereas the precipitate from the Rwandan sample contained approximately 55% Ta_2O_5 and 45% Nb_2O_5 respectively, Table 7.5.

Table **7.5**: Compositions of calcined precipitate recovered from PLS of N-Nass Con and R-KMY Con

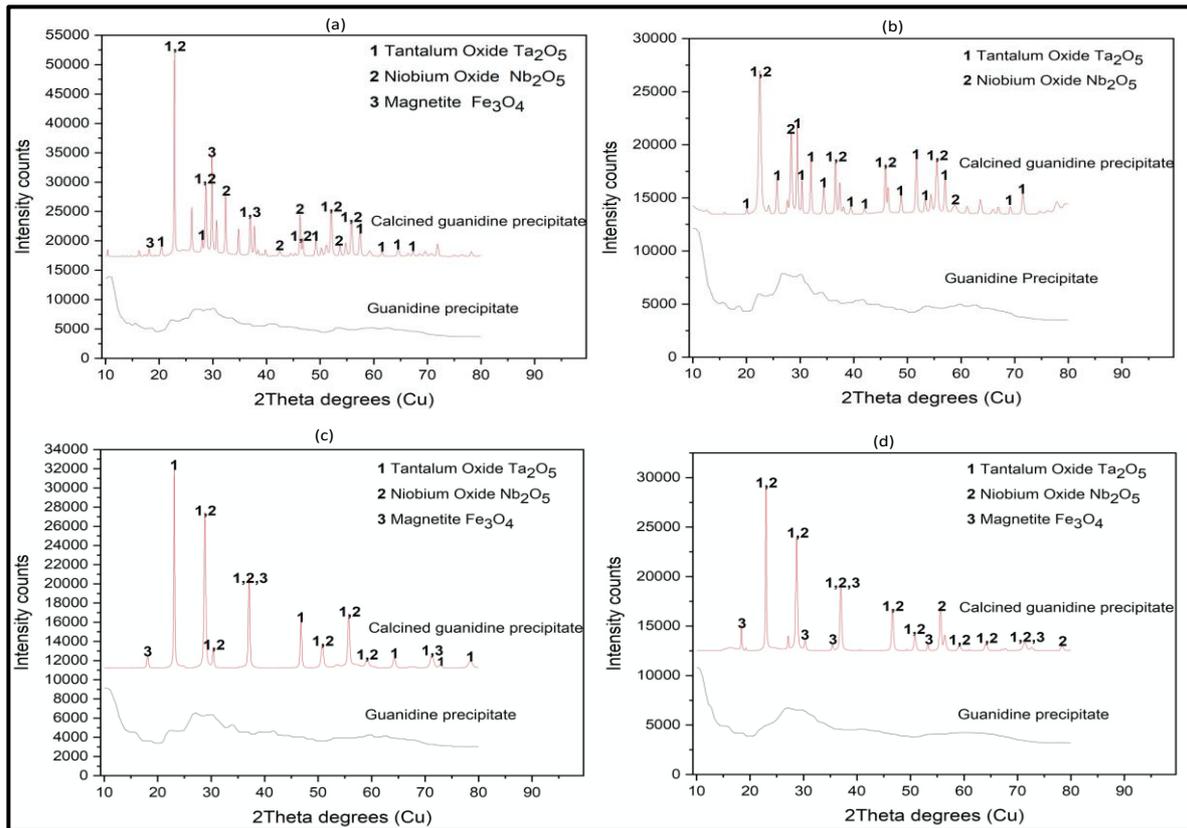| Feed Sample		Compositions of Calcined precipitate (wt %)				
Sample	Sample size	Mass loss (%)	Nb_2O_5	Ta_2O_5	SnO_2	Fe_3O_4
N-Nass Con	+250 microns	44.7	65.702	33.763	0.000	0.534
	-250 microns	41.2	62.321	36.980	0.000	0.698
R-KMY Con	+250 microns	42.0	43.010	56.217	0.000	0.771
	-250 microns	41.1	46.288	53.581	0.000	0.130

Figure **7.6**: XRD spectra of uncalcined and calcined (Nb-Ta)-guanidine precipitate recovered from pregnant leach solution of N-Nass Con (a) +250 and (b) -250 μm size fractions and R-KMY Con (a) +250 and (d) -250 μm size fractions.

7. 4 Conclusion

The Nigerian and Rwandan concentrate samples (N-Nass Con and R-KMY Con) used as feed in this study were first characterized before any processing. The results obtained confirm the presence of major minerals of cassiterite associated with columbite-tantalite minerals. Then, the samples were subjected to the alkali-assisted roasting followed by water-based leaching and the process enabled sufficient dissolution of Nb and Ta at relatively low-temperature. The dissolution of approximately 92%, 91% and 94%, 92% for Nb and Ta contained in the +250- and -250-microns size fractions of N-Nass Con was achieved respectively at optimum conditions (250°C, 100% flux ratio and 1h roasting). For R-KMY Con sample, dissolution of 92%, 91% and 94%, 92% were obtained for Nb and Ta contained in the +250- and -250-microns size fractions respectively. The subsequent extraction of both Nb and Ta from the leach liquor collected were performed *via* precipitation utilizing guanidine

carbonate salt. The (Nb, Ta)-guanidine precipitates of purity of 93.0%, 86.0% and 94.0%, 91.0% were recovered from leach liquors of +250 and -250 microns size fractions of N-Nass Con and R-KMY Con respectively. A total recovery of 97%, 95% and 99%, 95% of the total amount of Nb and Ta contained in the +250- and -250-microns size feed of N-Nass Con was obtained respectively.

For R-KMY Con sample, the recovery of 97%, 93% and 98%, 86% of Nb and Ta were realized from the fractions of +250 and -250-microns size. However, small amount of iron was co-dissolved and co-precipitated along with Nb and Ta but did not affect the final product due to their content and the extent to which they dissolve. The amorphous (Nb, Ta)-guanidine precipitate recovered were further calcined at 900°C for one hour and the process converted the metals into their corresponding oxides and removed the guanidine moiety in the form of carbon and nitrogen oxides. The calcination of the amorphous (Nb,Ta)-guanidine precipitate resulted in mass loss of 44.7%, 41.2% and 42%, 41.1% for the precipitate recovered from the leach liquor of +250 and -250-microns size of the N-Nass Con and R-KMY Con respectively. The amorphous structure was converted into clear and sharp crystalline phases of mainly mixed Nb_2O_5 and Ta_2O_5 as confirmed from XRD analysis. Mixed oxides of Nb and Ta with purity more than 99% were obtained after calcination of the precipitate.

Generally, the alkali-assisted roasting and water-based leaching of the Nigerian and Rwandan columbite-tantalite concentrates at temperatures ranging from 200 to 300°C displayed similar dissolutions trend for Nb, Ta and Sn, however the Rwandan sample showed higher dissolution percentage. The optimum dissolutions of approximately 85% and 90% of Nb and Ta being recorded at 250°C for Nigerian and Rwandan columbite-tantalite samples respectively. In all samples at optimum conditions, the finer fraction seemed to have higher dissolution percentage relatively to the coarser fraction and the dissolution of Ta remained lower and almost constant compared to Nb. Sn is the least dissolved and remained in the residue as cassiterite associated with iron as hematite. Application of guanidine carbonate resulted in a total recovery ranging between 97-99% and 86-95% for Nb and Ta

respectively, and higher recoveries were obtained for the finer fraction and Rwandan sample compared to the Nigerian. Finally, the calcined precipitate with higher percentage content of Nb_2O_5 was obtained from the Nigerian sample whereas the one with higher Ta_2O_5 content was from the Rwandan concentrate sample. The present study demonstrates the possibility of the sustainability in the extractive metallurgy of Nb and Ta while the world is shifting toward the clean energy.

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CHAPTER EIGHT

8. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

This chapter summarizes the important conclusions drawn based on the results of the experimental investigations conducted in this research work. It also emphasizes on the important challenges and opportunities in the extractive metallurgy of niobium and tantalum that need to be addressed in the future pursuit of this work.

8.1 Conclusions

From experimental studies of the present research aimed at optimizing the recovery of niobium and tantalum from the typical Nigerian and Rwandan columbite-tantalite concentrates using eco-friendly techniques, the following conclusions can be drawn:

i) The results of ICP-OES, SEM-EDS and XRD characterization of the columbite-tantalite ores collected from Ntunga and Kamonyi of Rwanda revealed that the ore-samples from the selected areas were classified as low-grade ores as it contained less than 0.1% Ta_2O_5 and Nb_2O_5, and non-radioactive materials as the percentage of radioactive oxides was below the critical value of 0.5%. However, the ores contained sufficient concentration of SnO_2, therefore, it was required to undergo a rough concentration process before the dissolution and chemical leaching to upgrade the content of Ta_2O_5 and Nb_2O_5 minerals.

ii) The rough beneficiation of the ore samples using a centrifugal gravity concentration technique resulted in a concentrate with upgraded concentration of minerals of interest such as Nb_2O_5, Ta_2O_5 and SnO_2 with compositions of 7.70%, 7.66%, and 66.14% respectively. This study therefore provides the baseline data for the selection and design of appropriate techniques to effectively harness tantalum-tin minerals from the sampled areas.

iii)   The results of characterization of the columbite-tantalite concentrates after beneficiation of the ores collected from Ntunga and Kamonyi of Rwanda revealed that all the samples analyzed had nearly similar chemical and mineralogical compositions, with the main mineral phases being cassiterite associated with minerals of columbite-(Fe) and tantalite-(Fe). In the next step, the concentrate samples were subjected to alkali-assisted heat treatment and water-based leaching to extract Nb and Ta.

iv)   The alkali-assisted roasting of the columbite-tantalite concentrates from Rwanda and Nigeria enabled the break-up and digestion that allowed the formation of (Nb, Ta) water-soluble species to be recovered from the pregnant leach liquor solution. The process leaves behind in the residue most of Sn and Fe undissolved and other associated impurities. Temperature, flux-to-concentrate ratio, roasting time, and particle size were investigated for their influences on dissolution of the main constituents of the concentrate samples.

v)   The alkali-assisted roasting and water-based leaching of the Rwandan and Nigerian columbite-tantalite concentrates at optimized conditions 250°C, 100% flux-to-concentrate ratio and 1h roasting resulted in dissolution of more than 91.0% and 90.0% of Nb and Ta contained in the concentrate and higher dissolutions were recorded from the Rwandan sample. However, higher dissolution of Nb and Ta between 96.0-97.0% and 80.0-96% Ta was achieved respectively for the concentrate sample (Jos Con) from Jos Plateau of Nigeria.

vi)   The amount of Nb and Ta reported in the pregnant leach liquor solution were recovered by precipitation utilizing guanidine carbonate salt as precipitating agent. Guanidine carbonate salt effectively precipitated out the total amount of Nb and Ta contained in the PLS in a very shorter time. This resulted in high recovery ranging between 97-99% and

86-95% respectively for the Nb and Ta contained in the concentrate samples (feed) with optimum of 50 mg/mL guanidine. However, higher recoveries were obtained for the finer fraction and the Rwandan sample compared to the Nigerian sample.

vii)   The co-precipitation of Fe and Mn along with Nb and Ta from the pregnant leach liquor solution was observed but were not so high as to affect the purity of the final product. For samples of N-Jos Con and R-KMY Con, dissolution of Fe and Mn were 35 - 15% and 15 - 25% respectively.

viii)   Irrespective of the size fractions, variation of guanidine did not show a significant effect on the composition of the Nb-Ta precipitate, therefore, 25 mg/mL guanidine was found and considered as sufficiently enough to precipitate Nb and Ta. However, high dissolution and recoveries of both Nb and Ta were achieved for the finer size fraction relatively to the coarser particle samples.

ix)   The guanidine carbonate was removed from the Nb-Ta precipitate via calcination process. The amorphous (Nb-Ta)-guanidine precipitate was calcined at 900°C for one hour which converted the precipitate into mixed oxides of Nb and Ta and removed the guanidine moiety. The calcination of the precipitate obtained from guanidine-induced precipitation of Nb and Ta contained in the leach liquor solution of +250 and -250-microns size of the N-Nass Con and R-KMY Con, resulted in mass loss of 44.7%, 41.2%, 42.0% and 41.1% respectively. Mixed oxides of Nb_2O_5 and Ta_2O_5 having purity more than 98% and 99% were obtained for N-Nass Con and R-KMY Con respectively after calcination. The calcined precipitate with higher percentage content of Nb_2O_5 was from the Nigerian sample whereas the one with higher Ta_2O_5 content was from the Rwandan concentrate sample.

x)   However, very low percentage of iron was also detected in the precipitate of N-Nass Con and R-KMY Con. Therefore, the use of guanidine carbonate salt for the recovery of Nb

and Ta from alkaline-aqueous solution present an environmentally friendly and sustainable approach providing high yield (~100%) and high potential to replace the traditional approach which uses the hydrofluoric acid to extract Nb and Ta from their ores.

8.2 Recommendations for future work

From the research carried out in this work, the following challenges need to be investigated in the future work in order to come up with a cost-effective and more sustainable strategies to harness fully the benefits of niobium and tantalum:

1) Based on the results obtained in this study and the works reported previously by other authors, the alkali-assisted roasting of the columbite-tantalite concentrates, and water-based leaching and the application of guanidine carbonate salt to extract Nb and Ta as mixed oxides is an eco-friendly and sustainable process which must be investigated at large and industrial scale (10-15 kg of concentrate).

2) Knowledge about the efficiency of a process and mechanism of chemical reactions play a critical role in the success of the process, therefore thermodynamic and kinetic control factors in the alkali-assisted roasting of the columbite-tantalite concentrates, water-based leaching and the application of guanidine carbonate to extract dissolved Nb and Ta, need to be explored more to understand the stability and rate of phenomena and changes that are taking place in each step of the whole process. It will involve investigation of properties, behavior, and equilibrium compositions of the system.

3) The guanidine-induced precipitation of Nb and Ta is accompanied with some impurities such as iron and manganese, therefore we recommend a follow-up study to develop a process that cleans up the (Nb, Ta)-guanidine precipitate before the calcination process. This will

specifically focus on the removal of iron and manganese as well as other possible impurities depending on the mineralogies of the concentrate.

4) This study is limited to the combined recovery of oxides of niobium and tantalum from their ores and not the separation of the two metals individually. The separation of niobium from tantalum needs to be studied in a future work.