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JIMMA INSTITUTE OF TECHNOLOGY:
SCHOOL GRADUATE STUDIES, JIMMA UNIVERSITY

BENEFICIATION, DECOMPOSITION AND SEPARATION OF NIOBIUM AND TANTALUM FROM ETHIOPIAN KENTICHA PEGMATITE ORE

A PHD DISSERTATION SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES OF JIMMA UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY (PH.D.) IN METALLURGICAL ENGINEERING

By: GOITOM GEBREYOHANNES BERHE
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SHOOL OF MATERIALS SCIENCE & ENGINEERING

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Cover illustration: The picture on the cover page represents the deposit area of this study is called Kenticha Pegmatite field, which is found on the Adola greenstone belt, Southern Ethiopia.

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TABLE OF CONTENTS

LIST OF ABBREVIATIONS

Analytical equipment

- ✓ Atomic Absorption Spectroscopy (AAS)
- ✓ Energy Dispersive X-Ray Fluorescence (EDXRF)
- ✓ Extended X-ray absorption fine structure (EXAFS)
- ✓ Fourier-transform Infrared Spectroscopy (FT-IR)
- ✓ Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES)
- ✓ Scanning Electron Microscopy (SEM)
- ✓ Thermal Gravimetric Analysis (TGA)
- ✓ X-ray Diffraction (XRD)
- ✓ X-ray Fluorescence (XRF)

Miscellaneous terms

- ✓ Polytetrafluoroethylene (PTFE)
- ✓ Ethiopian Mineral Petroleum and Biofuel Corporation (EMPBC)
- ✓ Lower critical solution temperature (LCST)
- ✓ Perfluoroalkoxy (PTA)
- ✓ Solvent extraction (SX)
- ✓ Upper critical solution temperature (UCST)

Ligands and solvents

- ✓ 1-Ethyl-3-methylimidazolium chloride (EMIC)
- ✓ 1-(2-pyridylazo)-2-naphtol (PAN)
- ✓ 2-thiazolyl)-2-naphtol (TAN-1)
- ✓ Aqueous bi-phase separation (ABS)
- ✓ Octyl (phenyl)-N,N-diisobutyl carbamoylmethyl phosphine oxide (CMPO)
- ✓ Cyclohexanone (CHO)
- ✓ Ionic liquids (ILs)
- ✓ Methyl iso butyl ketone (MIBK)
- ✓ N,N,N’,N’-tetra (octyl)diglycolamide (TODGA)
- ✓ Octanol (OCL) and
- ✓ Tri-butyl phosphate (TBP)

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Goitom Gebreyohannes Berhe

SUMMARY

The aim of this dissertation was to examine various beneficiation, leachingand extraction approaches for tantalum and niobium from the Ethiopian Kenticha pegmatite ore. The Kenticha rare-earth element pegmatite, an internationally imperative tantalite spring in the Neoproterozoic rocks of the Adola greenstone belt, of Southern Ethiopia, is normally called a Kenticha pegmatite field. Three zones have been identified for the Kenticha pegmatite in previous studies: the granitic, the Spodumene-free, and Spodumene-bearing zones. The beneficiation methods for Ethiopian Kenticha pegmatite-Spodumene ores have been assessed through mineralogical and quantitative analyses with X-ray Diffraction (XRD) and Energy Dispersive X-ray Fluorescence (EDXRF). The upper zone deposit of Kenticha pegmatite-Spodumene deposit contains up to 58.7 weight%, more tantalite than the inner zone. XRD analysis revealed that the upper zone is dominated by manganocolumbite (tantalite) while the inner zone is predominantly tantalite-Mn. Repeated cleaning and beneficiation of the upper zone ore resulted in concentrate compositions of 57.34 weight% of Ta_2O_5, and 5.41 weight% of Nb_2O_5. Washing the tantalite concentrates using 1 volume% KOH, and 1 M H_2SO_4 leads to the complete removal of thorium and radioactive uranium oxides from the concentrate at a time. The findings of this study suggest that the beneficiation and alkaline washing of Kenticha pegmatite-Spodumene ore produces a high-grade export quality tantalite concentrate with negligible radioactive oxides.

Afterwards, acid and alkaline leaching agents were used to decompose Kenticha tantalite ore. The decompositions of tantalite ore were carried out using HF-to-H_2SO_4 and KOH. The different factors that would affect the decomposition product and residue, such as fusion time, ratio of concentration, particle size of the ore and mass of KOH towards the retained mass of the residues in the fusion and digestion media were investigated. The residues were analyzed by EDXRF, FT-IR, and XRD. The EDXRF analysis showed that the percent composition of Nb_2O_5 was less than Ta_2O_5 in both the residues obtained using 6 N HF: 2 N H_2SO_4 and 10 g KOH as decomposition agents. 14.20 weight% Ta_2O_5 was obtained in the residue using alkaline fusion has, followed by water leaching, while only 0.23weight% Ta_2O_5 was obtained using the acidic decomposition step. The XRD diffraction patterns indicated that the residue from the primary chemical fusion method shown similarity with crystalline patterns of $KTaO_3$. No $KNbO_3$ phase was observed in the residues obtained using both decomposition approaches.

Finally, the dissolution of Kenticha tantalite ore in KOH fusion and the hydro leaching systemwas studied at 400 ^{0}C for one hour reaction time. From the dissolved solution, niobium and tantalum were extracted from the neutralized alkaline dissolved and hydrolyzed solution with a new greener process, i.e., EMIC/$AlCl_3$ media, as the ionic liquid extractant. The new process, using selective stripping, precipitation and calculations resulted in a highly crystalline 99.84 weight% pure Nb_2O_5 and amorphous 90.81 weight% Ta_2O_5. The compositions of the dissolved metal ions and solids were analyzed by ICP-OES, EDXRF, XRD, and FT-IR.

Keywords: Beneficiation; Decomposition; Ionic Liquid; Kenticha;Leaching Agents Manganocolumbite; Pegmatite-Spodumene; Radioactive Oxide and Tantalite.

OUTLINE OF THE DISSERTATION

The work undertaken is entitled “Beneficiation, Decomposition and Solvent Extraction of Nb and Ta of Ethiopian Kenticha Pegmatite ore," and is presented in seven chapters. Each chapter has references based on **Harvard referencing system** inserted using **EndNote software**. A brief chapter-based summary is given below. :-

Chapter 1 deals with general introduction of the study, including background, rational, statement of the problem, scope and significant of this study were discussed.

Chapter 2 describes the conceptual framework of this study begins with review of related literatures to the study. Firstly, chemistry, occurrences and physicochemical properties of niobium and tantalum, the global geologic occurrence of Nb and Ta is presented. The next section describes the principles of mineral processing of Nb and the parent Kenticha pegmatite ore including beneficiation, extraction, precipitation, the uses of ionic liquids in hydrometallurgy in the last section the gap, objective and hypothesisof the study were discussed.

In **Chapter 3** the apparatus, instruments, and methodology used in this study are listed. Various variables for beneficiation, decomposition and separation processes were presented.

The results and discussion of this study are presented based on articles either published or accepted for publication from data generated during this study as chapters 4, 5 and 6. The instrumentation was discussed in the appendix II.

In **Chapter 4** the first section of the published paper of this study describes an alternative beneficiation of pegmatite-spodumene ore and the removal of radioactive oxides from samples collected in the upper zone and those from 20-meter depth.

In **Chapter 5** the accepted manuscript presents detailed discussions of decomposition of tantalite ore using acidic (HF-H_2SO_4) and alkaline media (KOH). It was shown that the rate of digestion is affected by some factors such as; particle size, the nature of the solvent, decomposition temperature, agitation time, liquid-to-liquid ratio and amount of KOH and HF-H_2SO_4 added during the decomposition processes.

In **Chapter 6** accepted manuscript gives a detailed description of the decomposition process of the tantalite ore by molten KOH followed by hydrolysis and isolation of Nb and Ta by ionic liquids as extractant.

Finally, the methods used to extract, to strip and to precipitate the oxides of Nb and Ta were presented.

In **chapter 7** the evaluations, strength and limitations, and recommendations were discussed.

Finally, in **Appendix** the CV, of author, supervisors, and principles of instruments used in this dissertation and data's were discussed, copied and attached to the hard copy.

PUBLICATIONS, CONFERENCES, ABSTRACTS AND POSTERS

1. Articles In press papers

- **Berhe Goitom Gebreyohannes**, Velázquez del Rosario Alberto, Abubeker Yimam, Girma Woldetinsae, and Bogale Tadesse. Alternative beneficiation of tantalite and removal of radioactive oxides from Ethiopian Kenticha pegmatite–Spodumene ores, International Journal of Minerals, Metallurgy and Materials, Volume 24, Number 7, July 2017, Page 727. DOI: 10.1007/s12613-017-1456-8. IF= 0.943, © Thomson Reuters Journal Citation Reports 2017.
- **Goitom Gebreyohannes Berhe**, Velázquez del Rosario Alberto, Abubeker Yimam, Girma Woldetinsae, and Bogale Tadesse. Decomposition of Ethiopian Tantalite Ore using Acidic and Alkaline Media, Physicochemical Problems of Mineral Processing.
  DOI: http://dx.doi.org/10.5277/ppmp1840.IF= 0.901, © Thomson Reuters Journal Citation Reports 2017
- **Berhe Goitom Gebreyohannes**, Yonas Chebude and V. J. T. Raju, Synthesis and Characterization of Metal Complexes of Derivative of 1,10-phenanthroline, International Research Journal of Pure & Applied Chemistry, 12(4): 1-8, 2016, Article no.IRJPAC.18137, ISSN: 2231-3443, NLM ID: 101647669.

2. International conferences, abstracts and posters

Conference

- **GKEN 7th International Conference and Workshop**, Mineral Processing of Tantalum and Niobium from Ethiopian Kenticha Tantalite Ore, in Jimma University. December, 2017. (Oral presenter).
- **GKEN 5th International Conference and Workshop**, A Proposal: Investigation on Separation, Purification and Refining of Tantalum and Niobium using Ionic Liquids from Ethiopian Kenticha Tantalite Ore, in Jimma University. December, 2015. (Oral presenter).

Abstract

- **Berhe, Goitom Gebreyohannes**. A Review Approaches for Extractive hydrometallurgy of niobium and tantalum from Ethiopian Kenticha Ores. ECS. Web: Abstract MA2016-02 3906. 2016/09/01. http://ma.ecsdl.org/content/MA2016-02/53/3906.abstract.

3. National conferences, abstracts and posters

Conference

- The 8th Annual Research Conference of Jimma University, April 27-28, 2017, Perspectives on Beneficiation, Separation and Purification of Niobium and Tantalum from Ethiopian Kenticha Ore.

Abstracts and Posters

- The 8th Annual Research Conference of Jimma University, April 27-28, 2017 (Book of Abstracts):
    1. Alternative Beneficiation of Tantalite and Removal of Radioactive Oxides; from Ethiopian Kenticha Pegmatite-spodumene Ore;
    2. Decomposition of Ethiopia Tantalite Ore Using Acidic and Alkaline Media; and
    3. Separation and Purification of Niobium and Tantalum Using Alkaline Fusion Tantalite Ore of Ethiopia

Community-Based Participation

- Jimma Institute of Technology Awarded in Effective University Community Service of 2016/17 Academic year. The certificate is awarded to **Goitom Gebreyohannes Berhe**.

1

GENERAL INTRODUCTION

CHAPTER 1: GENERALINTRODUCTION

1.1 Background and Rationale of the Study

Granitic rocks such as pegmatite often contain anacceptable composition of tantalum and niobium. Other minerals such as Microcline, Quartz, Spodumene, Beryl, Lepidolite, Tourmaline, Muscovite, Cassiterite are found in association with pegmatite. The decomposition and erosion of these rocks may lead to the concentration of Ta and Nb in alluvial deposits (Baba et al., 2007; Küster, 2009; Melcher et al., 2015). At present, economically exploitable tantalite ores are found only in few countries of the world such as Australia, Brazil, Canada, Ethiopia, Mozambique, Nigeria, Portugal, Thailand, and Democratic Republic of the Congoand almost the deposit are found in Africa. Ethiopia has world-class tantalite deposit at Kenticha on the Adolagreenstone belt, Southern Ethiopia. The belt is known for many kinds of metallic and nonmetallic minerals, such as; gold, emeralds, dolomite, calcium carbonate, alkaline metal containing minerals, etc. Opportunities for tantalum investment as well as to all minerals and gems have been reported(Gaballah et al., 1997; G. D. C. O. f. t. r. d. i. E. G. S. o. E. R. D. GSE et al., 2014; G. D. C. GSE, 2010; Küster et al., 2009). Highly concentrated tantalite, is currently mined by the Ethiopian Mineral Petroleum and Biofuel Corporation (EMPBC) (Baba et al., 2007; Küster, 2009; Melcher et al., 2015).

The production and exporting of Kenticha Ta deposit in Ethiopia is about 100 tons/year concentrate containing up to 60% Ta_2O_5. All the production is exported by governmental and non-governmental sectors. In addition to a world-class reserve of tantalum, the Kenticha pegmatite also contains appreciable quantities of niobium, lithium, and beryllium-bearing minerals (including the recently discovered premium grade emerald) as well as other industrial minerals. The disadvantage Ethiopian licensing for exporting tantalite ore is only per purity Ta_2O_5 (Melcher et al., 2015). This has been without including the cost of transport of the rest 40-50% which is considered as the impurity as well niobium. The revenue from the export has produced a significant benefit in the Ethiopian economy. The most common worldwide metallurgical applications of both Nb & Ta are for electronic devices. Up to 60% of the world’s Ta production is currently used in capacitor manufacturing (Nikishina et al., 2014). Pure forms of Ta and Nb still required for various applications, particularly for the production of nuclear energy.

The beneficiation of tantalite ores affected by its Mn/Fe and Ta/Nb ratios, response to magnetic fields, the presence of radioactive materials, the nature of the ore and particularly the percentage of Ta_2O_5 in the ore and impurities. The primary choice of beneficiation stage usually starts with upgrading processes, such as sizing and classification, washing, gravity separation and magnetic separation steps (Nete et al., 2014a).

Pegmatite ore dissolution has usually done with concentrated hydrofluoric acid and sulfuric acid (H_2SO_4) at high temperature. Dissolution is followed by solvent extraction (SX) to separate various dissolved metals from one another. SX was a method by which two or more compounds areseparated from each other into two immiscible or partly immiscible liquids based on their relative solubility. Various solvent extractants were employed on a commercial scale for extraction. A comparison of the properties of various commercial extractants suggests that methyl isobutyl ketone has low cost, and low density compared to other extractants and that is why it is employed widely. However, due to low flash point and high volatility, methyl isobutyl ketone may result in operational hazards with high losses (Bright et al., 2013; O. El-Hussaini, 1996; O. M. El-Hussaini & Mahdy, 2002; El Hazek, 2001; Ungerer, 2012).

Numerous explores have been done, concerning Nb and Ta recuperation from tantalite mineral. Utilizing octanol as extractant and 95.7% and 84.1% of Ta and Nb were recuperated from HF and HF-H_2SO_4 acidic arrangements fluoride– sulfuric corrosive arrangements, individually (Adekola, 2011; Agulyansky, 2004; Ayanda & Adekola, 2011; Deblonde et al., 2015; Htwe & Lwin, 2008; Zhu & Cheng, 2011). On the other hand, El Hussaini, 1996, studied the separation of Nb and Ta from columbite–tantalite ore using either methyl iso butyl ketone or Tri-butyl phosphatefrom HF/HNO_3 and HF/H_2SO_4 leach liquors. Also, the extraction of Nb from pre-processed ore material (after removing U, Th, rare earth elements (REE) and Ta) using solvent extractants such as tri-butyl phosphate, 2-Octanol, cyclohexanone and methyl iso-butyl ketone, from HF/H_2SO_4 leach liquor has been reported (O. El-Hussaini, 1996; O. M. El-Hussaini & Mahdy, 2002). Nowadays, HF is mostly employed for the Nb and Ta extraction and an appreciable quantity of fluorspar sludge is formed in the HF processes which need a proper area for its disposal as the emissions of HF based processes causes serious environmental problems, increases the cost of operation and makes the retrieval of Nb and Ta products difficult. In order to reduce the emission of HF fumes, a cleaner process was developed for separation of Nb and Ta from low-grade ore using KOH. However, this process needs further investigations on mechanism of reaction of the fusion; for high grade and possible of recovery of N bans Ta from the KOH fused solution(Huddleston et al., 1998; X.-H. Wang et al., 2010; X. Wang et al., 2009; H.-m. Zhou et al., 2005; H. Zhou et al., 2005; Zhu & Cheng, 2011).

Currently, there is a lack of extensive research on alternative thermally stable and environmentally friendly solvents to HF, H_2SO_4 that can be used for both high and low quality of tantalite ore decomposition and extraction. Therefore, this research was proposed with the aim of investigating reagents suitable for decomposition and separation of Ta and Nb in laboratory scale with due consideration to cost and environmental footprint. In this sense, the key approaches employed are: **replace the use of hydrofluoric acid for dissolution of tantalite using alkaline salts, replace the petroleum derived solvents by new "environmentally friendly" solvents using ionic liquids from high-grade ores and minimize the waste produced by process integration and added value sub-products recovery**. The experimental plan has been classified into four categories: namely, **beneficiation, decomposition, separation, and purification.**

1.2 Statement of the problem

Hydrometallurgical techniques for preparing tantalite concentrates have the accompanying issues: decay of Ta and Nb containing solvents from pegmatite mineral, and from HF combination have particular challenges like the loss of reagents, the co-disintegration of abnormal state of polluting influences with tantalum and niobium, and the loss of generous amounts of fluorine all the while, us of unpredictable natural extractants and so on (Huddleston et al., 1998; X.-H. Wang et al., 2010; X. Wang et al., 2009; H.-m. Zhou et al., 2005; H. Zhou et al., 2005; Zhu & Cheng, 2011).To overcome these problems different aspects could appropriated in the push of the hydrometallurgical processing to greener technology. For example the application of environmentally friendly fusion agents, the introduction of higher stability, lower solubility, versatile and non-volatile green extractant, alternative HF free decomposition of tantalite; and very low amount of liquid and solid wastes.

Currently, five alternative approaches exist for the production of TNO from tantalite ore; these are beneficiations, decompositions, separations, precipitations, and calcination. According to D Kuster et al., 2009; Ethiopian Kenticha tantalite ore has various elemental compositions, and the sophisticated processing approaches will be needed to concentrate high-grade tantalite(Küster et al., 2009). After beneficiation; which is the first enrichment step of the mineral processing, the concentrated ore will need different approaches to breakdown into soluble and insoluble products. This requires several chemicals and careful handling during processing. New or alternative, environmental, green, more efficient and effective reagent schemes are desirable to separate the TNO. Therefore; alkaline fusion agents and green extractants such as; ionic liquids (ILs) will be chosen for this study to strengthen the search for alternative environmental green extractants. Thus, this study entails the alternative beneficiations, decompositions, removal of radioactive oxides from pegmatite ore, decomposition using alkaline fusion, extraction and separation of Ta and Nb by ionic liquid in the presence of Lewis acid. The effect of variables such as particle size of the ore, leaching agents and their concentration, solid-to-liquid and solid-to-solid ratio, extractant, decomposition time, speed and time of stirring, and reaction temperature were investigated.

1.3 Background of the study area

The Kenticha pegmatite field is situated in the Adola area, southern Ethiopia, within Neoproterozoic rocks in an area of about 2.5 km long and 40-70 m wide with various thicknesses and is emplaced at or near a significant NNE-SSW-trending shear zone(sees Figures 2.3). Ethiopian Kenticha pegmatite ore ismainly rich in, Fe-columbite (magnetic) and Mn-tantalite/tantalite (nonmagnetic). Kenticha pegmatite contains various oxides and trace impurities such as; SiO_2, Al_2O_3, Fe_2O_3, MnO, CaO, Na_2O, K_2O, Li_2O, TiO_2, P_2O_5 and in ppm Ga, Be, Sn, Nb, Ta, Zr, Hf, Zn, Th, Li, U. In contrast to most equivalent rare-element pegmatites (e.g., Tanco, Canada), the Kenticha pegmatite contains little or no cassiterite and pollucite (Baba et al., 2007; Küster, 2009; Tadesse & Zerihun, 1996; Tessema, 2003; Zerihun et al., 1995).

The Kenticha tantalum deposit is currently mined and exported from Kenticha mining plant by EMPBC about 70 tons/year. The probable reserve of primary ore is 2400 tons at a grade of 0.015% Ta_2O_5 from 1:1 to up to 3:1 of Ta and Nb ratio from upper to lower zones of the deposit in the spodumene unit, which is, this spodumene ore is the focus of this study(Baba et al., 2007; Küster, 2009; Tadesse & Zerihun, 1996; Tessema, 2003; Zerihun et al., 1995).

1.4 Scope and Delimitationsof the study

The main focus of the study was the replacement of fluoride decomposition of tantalite ore by alkaline fusion and to investigate alternative and green beneficiation and separation of niobium and tantalum from tantalite ore. The proposed systems is limited only replacement of fluoride containing decompositions and organic extractants in solvent extraction of niobium and tantalum from Kenticha pegmatite-spodumene ore. Some parameters and instruments were made as a consideration of a proper availability or access of chemicals, instruments and research laboratory.

1.5 Significance of the study

The scope of this dissertation was applying greener technology in beneficiation, decomposition, and solvent extraction technology of niobium and tantalum from Ethiopian Kenticha pegmatite ore in laboratory scale.

Still, now, Ethiopiaexports tantalite ore to China only. The reason is Kenticha tantalite ore has Th and U radioactive and Li oxides above the "Coltan" (columbite-tantalite)criteria(Barros & Willersinn; BGS, 2011; Dinkneh, 2012; GSE, 2010; GSE et al., 2014; G. D. C. GSE, 2010). Therefore; it is important to investigate alternative methods of beneficiation and removal of radioactive oxides from the ore for exporting to worldwide and further extraction of Nb and Ta from Kenticha ore.

Nowadays, HF and KOH are mostly under development for the Nb and Ta extraction from high and low-grade tantalite ores, by using volatile organic extractants. An appreciable quantity of fluorspar sludge is formed in the HF processes which need a proper area for its disposal.

The emission of HF and organic solvents based processes cause serious environmental problems, increases the cost of operation and makes the retrieval of Nb and Ta products difficult. Therefore, this research was proposed with the aim of investigating reagents suitable for decomposition and separation of Ta and Nb in laboratory scale with due consideration to cost and environmental footprint. In light of this, the key and important approaches employed are: replace the use of hydrofluoric acid for dissolution of tantalite using alkaline salts, replace the petroleum-derived solvents by new "environmentally friendly" solvents using ionic liquids for low and high-grade ores.

Finally, the potential contribution of the dissertation is to communicate the findings to the scientific community and pave the way for employment of the green technology on an industrial scale.

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2

REVIEW OF RELATED LITERATURE AND OBJECTIVES

CHAPTER 2: REVIEW OF RELATED LITERATURE AND OBJECTIVES

The beneficiations, decompositions, and separations of Nb and Taof tantalite ore were reviewed from related kinds of literatures in this dissertation. To plan the relevant laboratory experiments, information available in the literatures were reviewed on physicochemical properties, beneficiations, separations, purifications, refining, and applications of niobium and tantalum from tantalite ore and were presented in the following sub-topics.

2.1 Chemistry of niobium and tantalum

Knowledge of the chemistry of elements helps to understand the physical and chemical properties of a components, relationship with other features and reaction conditions at different states such as; liquids, gases, and solids. In the modern periodic table of elements, both niobium and tantalum are group VB transition metals with a chemical symbol of Nb and Ta, respectively. All group VB metals (d-block and they found in the middle of the periodic table of elements) were mostly found in nature as oxide compounds having +V oxidation state, and they are hard refractory metals. The chemistry of Nb and Ta are dominated by +V oxidation state, and these group VB elements shows they have similar chemical properties, implying their naturallyoccurrence are together and also reaction with air, water, acids, and alkaline are similar, so that it becomes challenging to separate them from their mineral or parent ore (AAS, 2001; Agulyansky, 2004; Alves & Coutinho, 2015; Gibalo & Schmorak, 1970; Nowak & Ziolek, 1999).

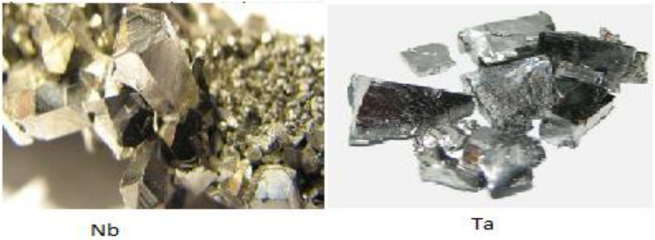


Figure 2.1 Crystals of niobium and tantalum metals (Melcher et al., 2015; Melcher et al., 2008; Simandl et al., 2012; Zerihun et al., 1995)

Nb metal is a lustrous, gray, ductile, ferromagnetic metal and it has a high melting point of around 2,500 °C and a boiling point of 4,800 °C. Similarly, Ta metal is a tough, malleable and ductile metal (malleability and ductility is the only property of metals which reflects readily flexible into wire and different mechanical shapes), and it has a very high melting and boiling points of around 3,000 °C and 5,460 °C, respectively and comparatively to all metals, Ta metal has the third highest melting point after tungsten and rhenium. And also, density of Nb and Ta metals are 8.57 and 16.69 grams per cubic centimeter, both are non-radioactive, non-toxic and bio-compatible metals and shows variable oxidation states such as; V, VI, III, II and I during chemical reactivity and 53.7 and 57.5 W(m.K) thermal conductivity, respectively (Agulyansky, 2004; Alves & Coutinho, 2015; Nowak & Ziolek, 1999).

It is clear from above physical and chemical properties that there are the similarity between tantalum and niobium. Both the metals have similar mechanical and physical properties, such as; very high malleability, ductility, melting and boiling points, and thermal conductivity that style them exceptionally nice-looking to rummage-sale in self-protective weaponry, modern generation airplanes as well as nuclear engine, in the electronic devices and alloying industry (Agulyansky, 2004). However, tantalum's high physical strength, high melting point, protective resistance and high electrical capacitance, makes the most economic metal over niobium's in the nuclear reactor and capacitor industries, and the different densities of Ta and Nb can be utilized to isolate each other by shaking and gravitational separation processes when existing together in solutions (Chiranjib Kumar Gupta, 2006; Huddleston et al., 1998; Tessema, 2003; Zerihun et al., 1995).

Niobium has ^{93}Nb the most stable isotope in the Earth's crust and unstable isotopes such as; ^{113}Nb, ^{81}Nb, ^{82}Nb, ^{84}Nb, ^{92}Nb, ^{96}Nb, ^{101}Nb, and ^{103}Nb. There are two naturally occurring isotope of tantalum which is ^{180}Ta and ^{181}Ta (Gaballah et al., 1997; Chiranjib Kumar Gupta, 2006).

Tantalum is also a rare and refractory transition metal with unique physical properties, such as; high strength; ductility and resistance to corrosion and working temperature, and inertness (used in replacement metal in the human body). Tantalum also used in many new generation alloys and numerous industrial applications such as; electronic and nuclear (Gibalo & Schmorak, 1970; Chiranjib Kumar Gupta, 2006; Xie et al., 2014).

2.2 Occurrence of niobium and tantalum

Nb ranks 34th, with 20 ppm, and Ta ranks the 50th,with 1.7 ppm in relative abundance among elements found in the Earth's crust. Both are not foundnaturally as free elements, but are found in minerals that contain Nb and Ta also known as columbite-tantalite (“Coltan”)which have a chemical formula of [(Fe, Mn)(Nb, Ta)$_2$O$_6$] (see Table 2.1 and Table 2.2) (O. El-Hussaini, 1996; El Hazek, 2001; Patel & Khul'ka, 2001; Pienaar, 2015).

2.3 Chemical reactions of niobium and tantalum

2.3.1 Chemical reactions of niobium

From numerous points of view of chemical reaction behaviors, the chemical property of Nb is similar to Ta; Nb does not react with air and water under typical conditions. However, Nb reacts with F_2, Cl_2, Br_2, and I_2 amid warming to form NbF_5, (white), $NbCl_5$, (yellow), $NbBr_5$, (orange), and NbI_5 (brass-hued). Nb is resistant to numerous acids; however, it dissolves in HF, or in a blend of HF and HNO_3 at room temperature and Nb will break down into a liquid soluble base, gradually. Despite the fact that Nb shows the greater part of the formal oxidation states from +V to −I, and characteristically, the pentoxide is antecedent to all Nb mixtures and compounds (Agulyansky, 2004; Ayanda & Adekola, 2011; El Hazek, 2001; Chiranjib Kumar Gupta, 2006; Tessema, 2003; Zhu & Cheng, 2011) and see sub-section 2.6 for more details.

2.3.2 Chemical reactions of tantalum

Ta is inert with air and water at normal temperature and reacts only with fluorine gas and certain most reactive halogen such as; fluorine compounds at room temperature, but Ta react with halogens while heating to form tantalum (V) halides such as; TaF_5 (white), $TaCl_5$ (white), $TaBr_5$ (pale yellow), and TaI_5 (black). Ta appears not too attacked by many acids but dissolves in hydrofluoric acid, HF, or oleum at room temperature and Ta metal attacked by molten alkali. At higher temperature (above 150°C), Ta becomes more active, it reacts with acids and alkalis (Agulyansky, 2004; Ayanda & Adekola, 2011; El Hazek, 2001; Chiranjib Kumar Gupta, 2006; Tessema, 2003; Zhu & Cheng, 2011) (see section 2.6 for more details).

2.4 Global geologic occurrence of niobium and tantalum

2.4.1 Occurrences and deposit types

Niobium and tantalum naturally occurs combination with oxygen and one or more other metals as niobates and tantalites in various sources of deposits. Of these, the important minerals are niobates-analytes as pegmatite, pyrochlores as carbonites, and niobium-tantalum bearing cassiterite and columbo-tantalite as core deposits (Table 2.1 and 2.2) (Baba et al., 2007; Küster, 2009; Tadesse & Zerihun, 1996; Tessema, 2003; Zerihun et al., 1995). Although, the twins elements have been produced worldwide from mined pegmatite ores (Tessema, 2003).

	Formula	%Nb_2O_5	%Ta_2O_5	%TiO_2	%Fe_2O_3
hlore	$(Na,Ca)_2Nb_2O_6(O,OH,F)$	40-75	0-2	1-6	0-6
erite	$(Ti,Ta,Nb,Fe)_2O_6$	10-15	30-50	30-50	10-30
nbo-tantalite	$(Fe,Mn)(Ta,Nb)_2O_6$	25-60	20-50	0,5-3	28-58
nbite	$(Fe,Mn)(Ta,Nb)_2O_6$	40-75	1-40	0,5-3	28-58
lite	$(Fe,Mn)(Ta,Nb)_2O_6$	2-40	42-84	0,5-3	28-58
m loparite	$(Ce,Na,Ca)_2(Ti,Nb)_2O_6$	16,2	Traces	38,8	Trace
lite	$(Na,Ca)_2Ta_2O_6(O,OH,F)$	83,5	Traces	Traces	Traces
erite	$(Ti,Ta,Nb,Fe)_2O_6$	30-50	10-15	30-50	10-30
ginite	Man $(Sn, Ta)(Ta,Nb)_2O_8$	69,5	8,4	Traces	1,3

Table 2.1Niobium and tantalum ores (Tessema, 2003)

Table 2.2Major deposits of Nb and Ta (Achebe, 2016)

osit type	Deposit grade	Major examples
ritic regolith above carbonated	Up to 3% Nb_2O_5	Araxa and Catalano, Brazil; Tomtor, Russia; Lueshe. Democratic Republic of Congo
d rock carbonate or nepheline ite with pyrochlore	Up to 0.59% Nb_2O_5	Niobec and Oka, Canada
-element granites with tantalum- magmatic columbite and iterite	< 0.05% Ta_2O_5	Abu Dabbab and Nuweiba, Egypt; Yichun, Ch
-element pegmatites of the Li-Cs- pe	< 0.05% Ta_2O_5	Green bushes and Wodgina, Australia; Tanco, Canada; Volta Grande, Brazil; Kenticha, Ethiopia; Mo Marropino, Mozambique
ial, alluvial and coastal tin placers	< 0.01% Ta_2O_5	Malaysia, Nigeria, Central Africa

2.4.2 Global production of niobium and tantalum

Worldwide mine productions of concentrated ores containing oxides of Nb and Ta are more prominent than 100,000 tons/year and the vicinity of 500 and 2,000 tons/year, individually (Brown et al., 2010). Around 90% of niobium manufactured was originated from Brazil and Canada. Tantalum is Masculine delivered in Australia, Brazil and Canada and very few manufacturing plants are situated in Ethiopia, Democratic Republic ofCongo, Mozambique, Nigeria, and Rwanda. Niobium is mostly extracted from pyrochlore ore which is exceptionally hard to prepare because of the similarity between niobium and tantalum elements. Niobium and tantalum are the basic components, valuable for some segments of the worldwide economy, and unevenly spread out over the world. Hence, many mining ventures attempt to differentiate the niobium and tantalum supply (KEBEDE, 2012; Mackay & Simandl, 2014; Melcher et al., 2015; Melcher et al., 2008).

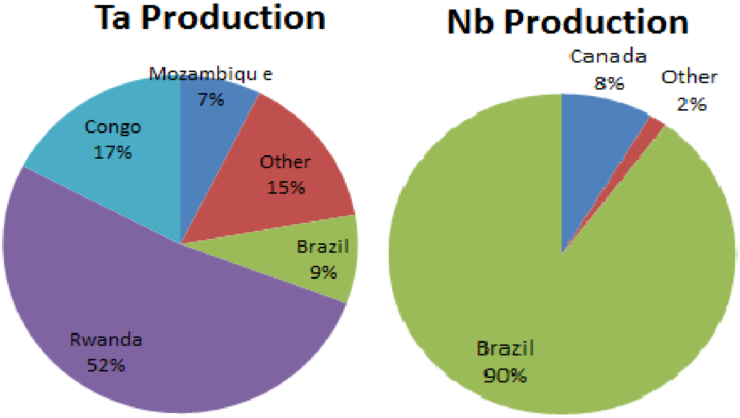


Figure 2.2 World mine production (metric tons) of contained Ta metal by country in 2015 (KEBEDE, 2012)

2.4.3 Tantalum in Ethiopia

According to several reports (Baba et al., 2007; Küster, 2009; Tadesse & Zerihun, 1996; Zerihun et al., 1995) and Geological Survey of Ethiopia (Melcher et al., 2015) at exhibit Ethiopia supplies near 10% of the worldwide utilization of tantalum. The Kenticha tantalum deposit has Ta/Nb proportions from 1:1 up to 3:1, which makes the deposit monetarily imperative. This deposit is marked with high quality Ta-Nb and made it one of the best of the like deposits elsewhere in the world. This has warranted commissioning of the Kenticha mining pilot plant and processing local by utilizing very simple enrichment processes in the grade of 40-60% of Ta_2O_5.

2.4.4 Geological setting of Kenticha pegmatite field

The Kenticha pegmatite field pegmatite isboundless in the Adola territory in southernmost Ethiopia in a zone of around 2,500 km^2. The pegmatite is emplaced at a noteworthy NNE-SSW-inclining shear zone (Figure 2.3) (Küster, 2009; Melcher et al., 2015). The Ta bearing pegmatite supply in Kenticha field weathering has influenced the feldspars and the more significant part of the lithium-bearing minerals, though the tantalite ore is unaffected by the weathering. The Kenticha tantalum ore has been mined by EMPBC and mining is so far bound to the weathered some portions of the mineral. The mineral is uncovered by a bulldozer, gathered up onto trucks and headed to a beneficiation plant where the tantalite is blended with water. At that point the tantalite concentrate is produced through a progression of the ventures of screening, jigging, shaking tables, gravity separation and last treatment on magnetic separation. The recovery of non-magnetic concentrated tantalite has been in the grade of 20 to 70% of Ta_2O_5. According to Tanatlum-Niobium International-Study Center (T.I.C), this grade is considered as high grade of tantalite concentrate (Barros & Willersinn; Barume et al., 2016; Schulz & Papp, 2014). The remaining is put away in an immense tailings lake for later utilization and the magnetic portion of the concentrated is stored in the camp (Mackay & Simandl, 2014; Zerihun et al., 1995). The Kenticha pegmatites show complex zoning, aside from tantalite, various lithium minerals, for example, Lepidolite and Spodumene are discovered and uranium is a bottomless follow component in some portion of the ore deposit. Although, the concentrated tantalite contains over 0.5% uranium, well over the adequate to the market criteria of the European and North American, mainly on the percentage composition of metal oxides of Li, Th and U (also see Tables 4.1 and 4.2 exported lots samples of tantalite by EMPBC) (Baba et al., 2007; Gebreyohannes et al., 2017; Küster, 2009; Mackay & Simandl, 2014; Tadesse & Zerihun, 1996; Tessema, 2003; Zerihun et al., 1995).

2.4.5 The Kenticha pegmatite.

Figure 2.3Weathered tantalum ore body (Mackay & Simandl, 2014; Melcher et al., 2015).

According to works of D. Kuster et al., 2009 and Tadesse and Zerihun, 1996 on Kenticha pegmatite ore, the most economically significant component mineralization in Kenticha pegmatite focuses on the upper zone of the Kenticha deposit specific area, which encompasses up to 3.0 wt% Li_2O, 3,780, 111, 1,320, 332 ppm of Rb, Cs, Ta, and Nb, respectively. Minerals in Kenticha pegmatite, for the most part, incorporate tantalite in Spodumene unit deposit. The tantalite, is characterized into Mangano-tantalite and advanced in Ta and drained in Nb (Huddleston et al., 1998; Patel & Khul'ka, 2001; Tadesse & Zerihun, 1996; Tessema, 2003; X. Wang et al., 2009)

2.5 Principles for mineral processing and extraction of Nb and Ta

2.5.1 Introduction to mineral processing

To accomplish the objective of recuperating concentrates of essential metals from the deposited mineral, the ore mineral particle size must be reduced to finalize other partition. This procedure is called "comminution" or size diminishment. There are two noteworthy targets for comminution in mineral beneficiation: The primary goal of comminution is ‘liberation.' Liberation is the procedure to open composite minerals in the deposit ore into more autonomous particles, and without it we can't gather the needed segments as it were. The second target of comminution in mineral preparing is to alter the measure of mineral particles to adjust to the ideal size for the progressive division forms and see Figure 2.4 (Beyecha, 2016).

Mineral beneficiation is the initial phase in the extraction of metal from common assets. With the exhaustion of high review metal minerals, it is essential to building the metal review by physical techniques; which are named mineral beneficiation. The destinations of mineral beneficiation are: to increment the metal review of mineral; to lessen the measure of gangue minerals with the goal that lower volume of slag shapes in the pyrometallurgical extraction of metals and slag contains gangue minerals; to diminish the warm vitality required to isolate the fluid metal from gangue minerals; and to reduce the liquid arrangement necessity in the hydrometallurgical extraction of metals.

2.5.2 Mineral processing of tantalite ore

Tantalite has specific gravity of, 8.0 $g.cm^{-3}$ in contrast to columbite with 5.2 $g.cm^{-3}$. This distinction can be utilized to separate tantalite from columbite using shaking table and gravity separation after washing the mined ore. Tantalite has its very own progression structure of Fe, and Mn bases shift significantly without much impact on properties to have a kind name of ferrotantalite (colombite) and manganotantalite (tantalite), individually. Mn-rich tantalites can be dark colored, translucent, fragile, feeble magnetic, insoluble in concentrated acids such as; hydrochloric, nitric and sulfuric, dissolvable in hydrofluoric and phosphoric acids (see section 2.1, 2.3 and Figure 2.5 (a) and (b), whereas, (c) is Fe-rich tantalite) (Mitchell, 2015; Nete, Koko, et al., 2014; Pienaar, 2015; Ungerer, 2012).

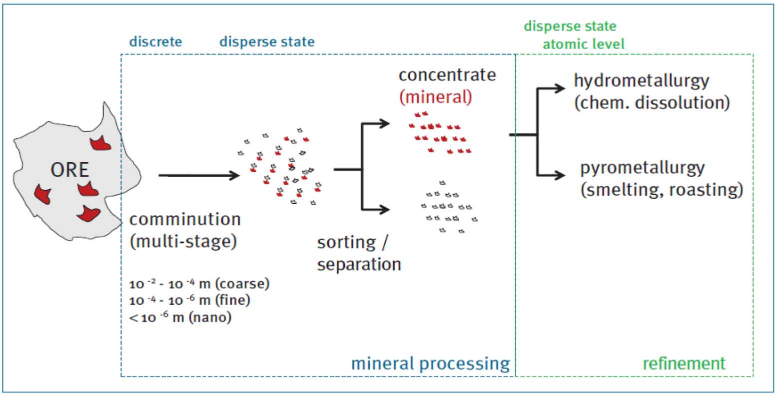


Figure 2.4Systematic representation of mineral processing (Beyecha, 2016).

Figure 2.5 Tantalite ore (black) in pegmatite-spodumene mineral (a), concentrated Kenticha non-magnetic or tantalite (b) and magnetic or columbite (Mackay & Simandl, 2014; Nikishina et al., 2014)

‘Mineral processing of tantalite ore from the pegmatite ore is depends on the presence of radioactive oxides, response to the magnetic field, Nb-Ta content and grade of tantalite. The present treatment techniques for tantalite concentrates, among the most part: flotation, buoyancy, planktonic electric detachment and chemical treatment, incorporate gravity and magnetic separation are the most well-known and financial technique to advance a high grade and quality tantalum and niobium minerals.’

2.6 Beneficiation, decompositions and separation processes of Nb and Ta from tantalite ore

The extraction of Nb and Ta from tantalite ore were the primary aims of this study. Both metals exist in the form of oxides with a lot of metal oxide (considered as impurities). Therefore, to improve the efficiency of extraction, the following processes are needed: beneficiation, digestion, separation and precipitation stages.

2.6.1 Primary beneficiation of tantalite

As per works of Nete et al., 2014, on Mozambique tantalite; the mined production of neat oxides Nb and Ta from pegmatite ore involves the expulsion of related contaminations and the consequent separation of these metals from each other and its prosperity typically relies on upon the physical and chemical properties of both the ore and their impurities, for example, the nearness of radioactive oxides, its magnetic property, involvement of Nb and Ta on the mineral and the amount of metal oxide and impurity of the ore. These can affect the quality, the separation and extraction processes as well as the cost of the concentrated and the fabricated metal. The beneficiation procedure of a mineral, for the most part, begins with an advancement step, which may include gravity and magnetic separation stages of concentration of the target ore after crushing, sizing, washing and classification levels (Nete, Purcell, et al., 2014).

These steps, remove almost all magnetic ores. The magnetic ores are known as columbite ores whereas the non-magnetic ores are known as tantalite concentrated ores. Practically almost all light ores from the impurities containing titanium are separated and deposited in the light waste portion of the process and stored as tail (Nete, Purcell, et al., 2014). Additional, the presences of radioactive components in the concentrated tantalite confounds the transportation for exporting, dealing with, and handling of these minerals (Küster et al., 2009). The Kenticha tantalite ore needs proper removal of what and separation from the metal(H.-m. Zhou et al., 2005; H. Zhou et al., 2005; Zhu & Cheng, 2011).Based on the works of O. El-Hussaini et al, 2002, on Egypt tantalitedeclared that, washing and filtering of tantalite using H_2SO_4 at various temperatures. The outcomes acquired showed that most oxides composition of Th and half oxide composition of U were expelled from the tantalite ore (O. El-Hussaini, 1996; O. M. El-Hussaini & Mahdy, 2002)

The next step after enrichment step is digestion or decomposition of the constituents of the ore to form a solution. The method of extraction mainly depends on the absorption or dissolution of the highly concentrated targeted tantalite ore. The difficulty of decomposition of these metals from the ore is due to the fact that only in HF and salts as fusion agents can leach the ore (O. M. El-Hussaini & Mahdy, 2002; Gibalo & Schmorak, 1970; Maina et al., 2007; X.-H. Wang et al., 2010; X. Wang et al., 2009; H.-m. Zhou et al., 2005; Zhu & Cheng, 2011). This method used for the solvent extraction and determined by the amount of Nb and Ta metal ions in the dissolved solution, undissolved amount of Nb and Ta in the residue, its distribution through the solid, the nature of the stable, digestion temperature, concentration of the digestive agent, and the particle size of the ore(Maina et al., 2007). The mechanism of leaching involves complex chemical reactions. These may be affected by the rate of transport of solvent or melting of salt to be fuse into the mass of to be leached or soluble and insoluble metal ions. Some combination of these rates may be significant. The process can be considered generally to comprise of three stages: the change of phase, its diffusion and rate of the solute from the solution and mixture of ore and molten salt (Chiranjib Kumar Gupta, 2006).

2.6.2 Digestion and extraction processes of Nb and Ta

As discussed the physicochemical properties of both Nb and Ta in section 2.3; Ta_2O_5 is more soluble and stable in alkaline than in acidic media whereas; Nb_2O_5 is more soluble in acids and fluxes, relatively (Gibalo & Schmorak, 1970). Comparatively, both Nb and Ta are more soluble in KOH than NaOH. An acidic and alkaline decomposition and fusion of Nb(V) and Ta(V) tend to hydrolyze and to result in hydrophilic (or water-loving or polar) colloids solutions. Therefore; the following specific reactions of oxides of tantalum and niobium (OTN) (Eq. 2.1 to 2.19) are described based on the theme of the study which means chemical reaction with acids and alkaline solution by looking the final output of the survey to prepare OTN by solvent extractions (O. El-Hussaini, 1996; O. M. El-Hussaini & Mahdy, 2002; El Hazek, 2001; Chiranjib Kumar Gupta, 2006; Ungerer, 2012; X.-H. Wang et al., 2010; X. Wang et al., 2009; H.-m. Zhou et al., 2005; H. Zhou et al., 2005; Zhu & Cheng, 2011).

2.6.2.1 Acidic decomposition of tantalite ore

Nb and Ta metal ions are precarious in dissolved solvent systems and activities as they can be promptly hydrolyzed even in extremely acidic decomposed solutions, for example, HF, HCl, H_2SO_4, and in some natural acids as well in solutions containing hydrogen peroxide, thus, subsequent in the formation of complex matrixes (Brown et al., 2010; O. M. El-Hussaini & Mahdy, 2002; Gibalo & Schmorak, 1970; Küster, 2009; Maina et al., 2007; Melcher et al., 2015; Nete, Purcell, et al., 2014; Nikishina et al., 2014; Patel & Khul'ka, 2001; Pienaar, 2015). Recommending the conceivable arrangement of blended buildings of fluoro-bisulfate (a mixture of HF and H_2SO_4) with Nb and Ta are inclined to water leaching, yielding immaculate fluoride networks and sulfuric corrosive. Be that as it may; the fluoride arrangements of Nb and Ta are less inclined to form poly and multiple species (H.-m. Zhou et al., 2005; H. Zhou et al., 2005; Zhu & Cheng, 2011). The accompanying response (Eq. 2.1 to 2.12) wonders could be formed amid disintegration, separation and cleansing procedures of tantalite ore with HF (Tessema, 2003).

$Ta_2O_5 + 14\ HF \rightarrow 2\ H_2[TaF_7] + 5\ H_2O$ ………………………………………………Eq. 2.1

$Nb_2O_5 + 10\ HF \rightarrow 2\ H_2[NbOF_5] + 3\ H_2O$ ……………………………………………Eq. 2.2

As soon as, low concentrations of HF predominant$NbOF_5^{2-}$, $NbF_6^-$and TaF_7^{2-}, TaF_6^- were be formed and when 35% or higher $NbF_6^-$and $TaF_6^-$was be formed (Brown et al., 2010; Maina et al., 2007; Nete, Purcell, et al., 2014).

$NbOF_5^{2-} + 3HF \leftrightarrow NbF_6^- + HF_2^- + H_2O$ …………………………………………Eq. 2.3

$TaF_7^{2-} + HF \leftrightarrow TaF_6^- + HF_2^-$……………………………………………………Eq. 2.4

The concentration of HF could affect the Nb and Ta poly complex matrixes, and these indicate to the formation of oxy-complexes of Nb and fluoride complexes of Ta (Baba et al., 2007; X.-H. Wang et al., 2010; H. Zhou et al., 2005).

$NbOF_n^{3-n} + H^+ \leftrightarrow NbOF_{n-1}^{4-n} + HF$ ………………………………Eq. 2.5

And

$NbOF_n^{3-n} + 2H+ \leftrightarrow NbF_n^{5-n} + H_2O$ ……………………………Eq. 2.6

$TaF_n^{5-n} + H^+ \leftrightarrow TaF_{n-1}^{4-n} + HF$ ……………………………………………Eq. 2.7

After the above formations of poly complexes matrixes, knowledge of the reactivity difference of Nb and Ta metal ions is essentially required. Therefore; in the introduction of the very dilute concentration of acid, for example, 1M H_2SO_4 resulting in the formation of biphase dissolved solution after addition of organic solvents or is known as extractant (Eq. 2.5 – 2.7). The upper and lower phases of the dissolved solution are Ta metal ions and Nb metal ions, respectively. Thus resulting in separated hydrogen fluorides and oxy-fluorides of both Ta contain and Nb containing phases, respectively are expelled from the dissolved solution which was formed by acidic decomposition (Eq. 2.1 and 2.2) utilizing organic solvents are known as extractants. Alternatively, Nb requires a larger amount of acidity in the solution to stay in the organic stage and can henceforth be specifically evacuated by separation into less acidic solution or into pH 6.2 to 6.8 the broke up containing solution of Nb and Ta metal ions and then accomplished by pH change or called by precipitation to give $Ta(OH)_5$ and $Nb(OH)_5$, which is calcined to create Ta_2O_5 and Nb_2O_5(Achebe; Mackay & Simandl, 2014; Zhao et al., 2005).

$H_2[TaF_7] + 5H_2O + 7NH_3 \rightarrow Ta(OH)_5\downarrow + 7NH_4F$ ……………………………………Eq. 2.8

$2Ta(OH)_5 \rightarrow Ta_2O_5 + 5H_2O$ ………………………………………………………Eq. 2.9

$H_2[NbOF_5] + 2HF \rightarrow H_2[NbOF_5] + 2HF$ ………………………………………Eq. 2.10

$2H_2[NbOF_5] + 10NH_4OH \rightarrow 2Nb(OH)_5\downarrow + 10NH_4F + 2H_2O$ ……………………… Eq. 2.11

$2Nb(OH)_5 \rightarrow Nb_2O_5 + 5H_2O$ ……………………………………………………Eq. 2.12

The first strides of the marketed hydrometallurgical procedures are schematically appeared in Scheme 2.1 and the science required in the process can be portrayed by the accompanying equations 2.13 to 2.19 (Davris et al., 2014; Graedel et al., 2011; Ungerer, 2012; Zhu & Cheng, 2011).

The chemistry involved in the process reported in Scheme 2.1 can be described by the following equations (Tessema, 2003):

Dissolution: $Nb_2O_5, nH_2O_{(s)} + 10\ HF \leftrightarrow 2\ [NbOF_5]^{2-} + 4\ H^+ + (3 + n)\ H_2O$....Eq. 2.13

$Ta_2O_5, nH_2O_{(s)} + 14\ HF \leftrightarrow [TaF_7]^{2-} + 4\ H^+ + (5 + n)\ H_2O$............Eq. 2.14

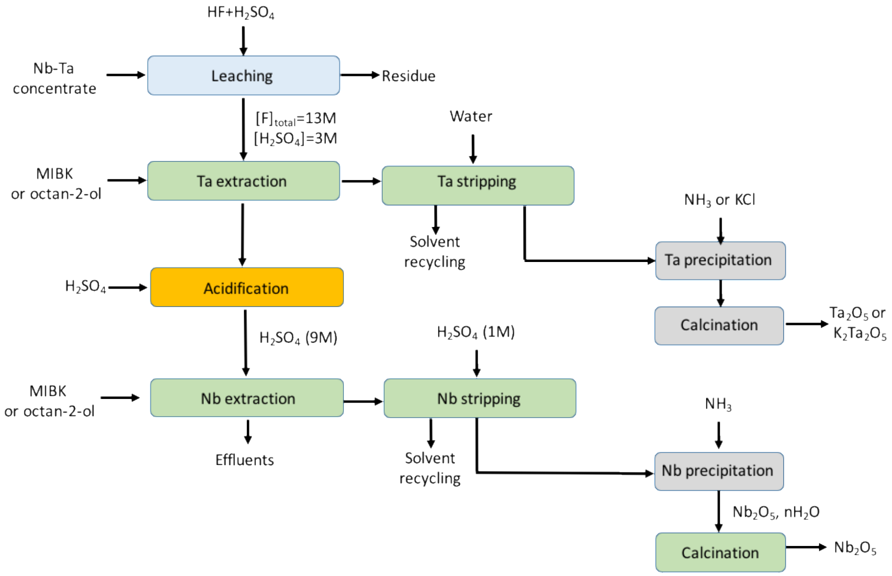
Tantalum extraction: $[TaF_7]^{2-} + 2\ H^+ + \overline{MIBK} \leftrightarrow \overline{H_2TaF_7MIBK}$ ………………Eq. 2.15

Tantalum stripping: $\overline{H_2TaF_7MIBK} + 2\ H_2O \leftrightarrow \overline{MIBK} + [TaF_7]^{2-} + 2\ H_3O^+$….Eq. 2.16

Acidification: $[NbOF_5]^{2-} + HF + H_3O^+ \leftrightarrow [NbF_6]^- + 2\ H_2O$ …………Eq. 2.17

Niobium extraction: $[NbF_6]^- + H^+ + \overline{MIBK} \leftrightarrow \overline{HNbF_6MIBK}$……………………....Eq. 2.18

Niobium stripping: $\overline{HNbF_6MIBK} + H_2O \leftrightarrow [NbOF_5]^{2-} + 2\,H^+ + HF + \overline{MIBK}$...Eq. 2.19



Scheme 2.1 Flow sheet of the conventional oxides of Ta-Nb separation process (Tessema, 2003)

2.6.2.2 Evaluation of extractants used for traditional separation of Nb and Ta metal ions

Even though; an organic extractant has negative impact on the environment, they need to evaluate the selectivity of isolation in the formation of biphase systems from the decomposed solution containing both Nb and Ta metal ions for further precipitation and calcination steps. Knowledge of these extractant has an evident in selecting "GREEN" extractant for the fabrication of oxides of tantalum and niobium.

The properties of a few solvents used as extractants utilized for niobium extraction are thought about and reviewed (Achebe; Ayanda & Adekola, 2011; Davris et al., 2014; G. J. Deblonde et al., 2016; El-Hazek et al., 2012; Graedel et al., 2011; Rodriguez et al., 2015; Zhu & Cheng, 2011). The primary parameters of the physical properties are molecular weight, flash point, density, splash point, consistency, dissolvability in water and toxicity. The primary organic extracts are octanol (OCL), methyl iso butyl ketone (MIBK), cyclohexanone and (CHO) Tri-butyl phosphate (TBP), contrasted with different extractants in Table 2.3. Comparatively, 2-octanol ought to be the best choice for mechanical practices and to be the savvy extractant (Achebe; Ayanda & Adekola, 2011; El Hazek, 2001; Graedel et al., 2011; Chiranjib Kumar Gupta, 2006; Maina et al., 2007; Nete, Purcell, et al., 2014; Nikishina et al., 2014; Ungerer, 2012; X. Wang et al., 2009; H.-m. Zhou et al., 2005; H. Zhou et al., 2005; Zhu & Cheng, 2011).

Table 2.3 Evaluation of organic extractant in extraction of Nb and Ta ions (Zhu & Cheng, 2011)

Physicochemical property	Order			
	1st	2nd	3rd	4th
Flame risk	MIBK	CHO	OCL	TBP
Stability	TBP	CHO	MIBK	OCL
Selectivity	TBP	OCL	CHO	MIBK
Cost	TBP	MIBK	CHO	OCL
Solubility in water	CHO	MIBK	OCL	TBP

2.6.2.3 Alkaline fusion of tantalite ore

The inquiry of new maintainers and safe procedures to recuperate and isolate tantalum and niobium rather than regular methods utilizing acidic fluoride media is profoundly imperative. The basic arrangement shows up as an option medium for the hydrometallurgy of niobium and tantalum. Transmittable considerations were given for the decomposition and precipitation of Nb and Ta metal ions and metals utilizing the higher amount of alkaline salts of KOH or NaOH taken after fusion followed by dissolving with water were formed complex species in the dissolved solutions containing Nb and Ta metal ions at higher than pH=10 are called soluble hexametalate (a complex species of alkaline Nb and Ta metal ions are called hexaniobate and hexatantalate, respectively) can be formed (Eq. 2.31 to 2.33). These hexametalate salts are of specific significance to create $Nb_2O_{5(s)}$ and $Ta_2O_{5(s)}$ of separation and precipitationimprovement processes. Subsequent to the above solvent extraction using acidic decomposition, the alkaline digested solutions containing Nb and Ta ions may be created by diminishing or neutralizing the strength of acidic solutions followed by customary Nb–Ta solvent extraction process, separation of the multiple strip stages followed by neutralized and precipitation steps (Nyman et al., 2006; X.-H. Wang et al., 2010; X. Wang et al., 2009; Zhu & Cheng, 2011).

In a current work by Gauthier et al. 2016, play a noteworthy part in the solvency of Nb in KOH fused solutions, the dissolved efficiency of both Nb and Ta metal ions has been checked at various pH ranges (G. J.-P. Deblonde et al., 2016). In this manner, the higher solvency of solid oxides of Ta and Nb in alkaline media may emerge from the most noteworthy steadiness of tantalum oxide contrasted with niobium oxide in alkaline media. This approach may consider as an environmental process as compared to volatile HF and H_2SO_4 acids.

To talk about the chemical responses of alkaline fusion marvel and stage investigation based research works of Wang et al., (2009 and 2010), alkaline fusion, mostly depend on the fusion of the metal ions by amount of KOH salt taken before by hydrolysis to solvent form which is drained in water of the filtering deposit which demonstrated for the most part as an insoluble solid solutions of $KTaO_3$ and $KNbO_3$ and dissolvable K_3NbO_4, K_3TaO_4, K_2SiO_3, K_2SnO_3, $KFeO_2$ and K_2MnO_3 and K_2TiO_3 (Eq.2.20 to 2.24(X.-H. Wang et al., 2010; X. Wang et al., 2009).

$(Fe, Mn)O.(Ta, Nb)_2O_5 + 2KOH \leftrightarrow 2K(Ta,Nb)O_3 + (Fe,Mn)O + H_2O$ …………Eq.2.20

$(Fe, Mn)O.(Ta, Nb)_2O_5 + 6KOH \leftrightarrow 2K_3(Ta,Nb)O_4 + (Fe,Mn)O + 3H_2O$ ……….Eq.2.21

$6K_3(Ta,Nb)O_4 + (5+n)H_2O \leftrightarrow K_8(Ta,Nb)_6O_{19}.nH_2O + 10KOH$ ...…….…………Eq.2.22

$Fe_2O_3 + 2KOH \leftrightarrow 2KFeO_2 + H_2O$ …………………………………..…………..Eq.2.23

$MnO_2 + 2KOH \leftrightarrow K_2MnO_3 + H_2O$ ……………………………………………..…Eq.2.24

Such interactions between niobium or tantalum and cations might be in charge of noteworthy changes of solvency. For example, the utilization of calcium-bearing reagents is rather than the utilization of mineral acids for neutralizing niobium and tantalum solutions prompts quantitative precipitation of Nb and Ta (Elemental, 2001). High precipitations yields can be acquired in a wide pH extend, and in any case, selective separation of tantalum and niobium can't be accomplished by precipitation in basic media. Dissolvable extraction forms should then be developed to separate niobium and tantalum. Such separation may be hard to accomplish because of the possible development of blended niobium-tantalum networks since niobium and tantalum have the comparative sweep and can without much of a stretch substitute.

2.6.3 Refining of niobium and tantalum

Countless treatment methodology for the breakdown of essential sources has been created. Every one of these procedures can be partitioned into a reduction of metallic or compound shape is called metallothermic reduction or specifically using aluminothermic, carbothermic, magnesiothermic, etc. reduction processes (the process producing of metal forming their oxide compound using reduction). A few strategies were utilized for the diminishment to metallic niobium. In huge scale creation, Nb_2O_5 is diminished with hydrogen or carbon (Arcos et al.; Balaji et al., 2002; Choudhury & Hengsberger, 1992; El Hazek, 2001). In the aluminothermic response, a blend of tantalum oxide or niobium oxide and iron oxide are responded with Al:

$3Nb_2O_5 + Fe_2O_3 + 12Al \rightarrow 6Nb + 2Fe + 6Al_2O_3$ ………………………………….…. Eq. 2.25

Agreeing with literature review (Nete et al., 2012), the three commonplace niobium/tantalum metal oxide lessening forms is calciothermic decrease, aluminothermic diminishment, and magnesiothermic and metal vapor decrease processes. In calciothermic reduction, niobium oxide is diminished with calcium within sight of iodine/sulfur as a warm sponsor. This procedure can be connected with a specific end goal to acquire little amounts of genuine unadulterated high-grade metal. The other vital method for metal oxide lessening is an aluminothermic reduction process. The metallothermic reduction of niobium oxide with aluminum is the most monetarily reasonable practice for creating niobium metal. The crude material for delivering niobium metal is high immaculateness niobium oxide which is set up through dissolvable separation and calcination forms. Small measures of oxidizers (for example, sodium nitrate) are added to improve the response and the outcome was utilized as a part of the steel superconductive amalgams creation (Agulyansky, 2004; Choudhury & Hengsberger, 1992).

Tantalum powder for capacitors is delivered by the diathermic and calciothermic diminishments of halide salts or named the Hunter procedure. This procedure is appropriate for providing high-immaculateness niobium/tantalum with controlled powder morphology and mainly utilized for the capacitors (Agulyansky, 2004; Balaji et al., 2002; Choudhury & Hengsberger, 1992; Chiranjib K Gupta & Suri, 1993; Lakshmanan et al., 2016) with the point of building up an efficient creation process for fine niobium and tantalum powder with controlled morphology and molecule estimate. Nonetheless, there were a few disadvantages that must be overcome before the procedure can be commercialized(Agulyansky, 2004; Choudhury & Hengsberger, 1992).

2.7 Ionic liquids in hydrometallurgy

In the view of recent emerging technology and innovation, the application of organic solvent in extraction technology is the oldest method of extraction. Since the environmental concern is the primary topic of all developing and non-developing countries. The main reasons of these organic solvents are they are volatile at normal condition, and they have not a large range of working temperature. At present, there is a great interest and attention onsearching alternative solvent, media, and technology to reject the use of organic extractant solvents and utilization of acids to digest minerals from their deposits. The newest findings are possibly groups to "GREEN TECHNOLOGY."

To solve the above current concern of extraction of metals from their ores, this dissertation aims to find alternative and green solvents are known as ionic liquids (ILs). There have been some reviews on applications of ILs in the extraction of metals and electrodepositing of Nb and Ta. The developments, new, rapid, efficient and green analytical methods of solvent extraction of metal ions from digested ores are the core concern of all researchers. Also, this study finds ILs for a separation purpose alternative to the behavior of organic extraction for Nb and Ta separation from dissolved solutions.

Currently, the definition of the green solvents or ILs are liquids below the boiling point of water and are liquids to a wide range of working temperature (up to 400 °C) without volatilization. These green solvent may including imidazolium, pyridinium, ammonium, phosphonium, thiazolium, and triazoliumcations ILs (Figure 2.6) and these ILs are grouped on their functional group present in their chemical formula (Dadfarnia et al., 2010; Dai et al., 1999; Davris et al., 2014; Dharaskar Swapnil, 2012; Zhang et al., 2007). The physicochemical properties of the ILs are dependent on the nature of ions present in their functional group which is the cation or the anion (Figure 2.6) (Balaji et al., 2002; Gebreyohannes et al., 2017; Chiranjib K Gupta & Suri, 1993; Rodriguez et al.).

2.7.1 Characteristics of ionic liquids

The compressed physicochemical properties of IL is a salt, high thermal stable, having below 30 and 10 Scm^2 mol^{-1} dielectric constant and molar conductivity, respectively, having wide range of electrochemical window (>2V to 4.5V), negligible vapor pressure and excellent for many organic reactions and as a result of their unmistakable properties, ionic fluids are pulling in expanding consideration in many researches, including natural science, electrochemistry, catalysis, physical science, and engineering (G. J.-P. Deblonde et al., 2016; Friese et al., 1996; Gaballah et al., 1997; Gebreyohannes et al., 2017; Chiranjib K Gupta & Suri, 1993; Rodriguez et al.). Ionic liquids have gained extensive interest recently due to their versatility, and low environmental impact (Chiranjib K Gupta & Suri, 1993).

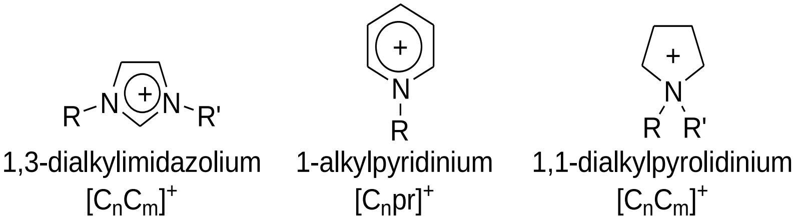


Figure 2.6 Common functional groups in ILs

An assortment of uses of ILs is additionally because of the likelihood of outlining their physicochemical properties by choosing suitable cation and anion. For instance, their solvency in liquids depends for the most part on the anion and cation, yet may likewise be changed or displaced by the length and the element of the cations alkyl substituent organic chains. ILs was having in its structure such polar anions is soluble in water. Which are these anions ILs are soluble in polar aqueous and non-aqueous solvents as well soluble and insoluble in nonpolar solvents and can form biphase with these solutions having polarity difference? Like this, these polar ILs expands the hydrophobicity and cutoff point's miscibility with polar solvents such as; water. Besides; the solvency of various species in imidazolium ionic fluids depends for the most part on extremity and hydrogen holding capacity. Immersed aliphatic mixes are for the most part just sparingly dissolvable in ILs, while olefins indicate fairly more noteworthy dissolvability, and aldehydes can be miscible. Diverse diagnostic methods have yielded to some degree distinctive total solvency esteems (Deblonde et al., 2015; El-Hazek et al., 2012; Espinoza, 2012; Gaballah et al., 1997; Gebreyohannes et al., 2017; Chiranjib K Gupta & Suri, 1993).

One of the primary room temperature ILs and a blend of 1-Ethyl-3-methylimidazolium chloride (EMIC) with $AlCl_3$ is not water stable and mostly have the application in electrodepositing of Nb and Ta from dissolved solutions (Gaballah et al., 1997; Hirayama et al., 2005; Huddleston et al., 1998; Liu et al., 2003; Regel-Rosocka & Wisniewski, 2011; Wei et al., 2003; Zhang et al., 2007; Zhao et al., 2005). The disclosure of nonpolar EMIC was permitted the advancement of new and green strategies, including the separation of water-dissolvable.Selected transition metal ions that are dissolvable in ILs might be reused self-possessed with the IL, after removal with polar solvents and the non-polar natural dissolvable utilized for item liquid-liquid separation. The metal ions and IL might be reused a few times (Espinoza, 2012; Friese et al., 1996; Gaballah et al., 1997; Gebreyohannes et al., 2017).

EMIC is an imidazolium IL having a chemical formula of $C_6H_{11}ClN_2$, the molar mass of 146.62 $g{\cdot}mol^{-1}$ and melting point of 77 to 79 °C (G. J.-P. Deblonde et al., 2016; Gaballah et al., 1997). The investigation of dissolvable consequences for responses is one of the longest and challenging settled zones of complex findings. Normally, ILs considers solvents regarding their extremity as communicated by the dielectric constant. Be that as it may, it is impractical to quantify the dielectric constant of an ILs specifically, so this can't help us for separation purpose.

2.7.2 Ionic liquids in liquid extraction

Water-insoluble ILs assumes a vital part particularly in the scaled down variant of liquid-liquid extraction method (Espinoza, 2012; Nete, Koko, et al., 2014; Rodriguez et al.), for example, small scale extraction or and as modifiers of stationary phases. Thus, water-dissolvable hydrophilic ILs can likewise be utilized as extricating dissolvable, as they prompt arrangement of watery biphasic frameworks with appropriate salting-out specialists (Balaji et al., 2002; Burt, 1996; Deblonde et al., 2015; El-Hazek et al., 2012; Espinoza, 2012; Nete, Koko, et al., 2014)

In many water immiscibility ILs, is reached by using a hydrophobic phases unlike hexafluorophosphate ([PF_6]) there are commercially available none fluorinated ILs such as; tricaprylmethyl ammonium chloride (Aliquats 336), Tri-butyl phosphate (TBP) and trihexyltetradecyl phosphonium chloride (Cyphoss IL 101). However; the hydrophobicity is formed by a long and bulky alkyl cation chains significantly by increase the viscosity of these Ils. This high viscosity can cause difficulties in solvent extraction applications, because intensive mixing and heating are required to increase mass transfer and speed up the kinetics (Beurlen et al., 2011; Kim et al., 2013; Mitchell, 2015). Moreover; PF_6 anion IL resulting in generating toxic HF due to the presence of fluorinated anion and their hydrolysis in water (Beurlen et al., 2011; Melcher et al., 2008; Mitchell, 2015).

Imidazolium ILs with non-fluorinated anions are only water immiscible if the alkyl chain on the 1-position is sufficiently long, but this leads to unwanted surfactant behavior and formation of emulsions during solvent extraction (Beurlen et al., 2011; Burt, 1996; Kim et al., 2013; Melcher et al., 2008).10 These ILs as extractant in liquid-liquid separation frameworks have been most extensively depicted in literatures, up until now. The solvent separations of metal ions into two stages are required expansion of unique legend with the plan to improve liking of unequivocally hydrated ions to hydrophobic ILs stage and hydrophilic stage. A system of metal ions separation with imidazolium based ILs can be portrayed by cation-trading as per the accompanying to the following equation (Balaji et al., 2002; Beurlen et al., 2011; Burt, 1996; El-Hazek et al., 2012; Gaballah et al., 1997; Gebreyohannes et al., 2017; Melcher et al., 2008; Nete, Koko, et al., 2014):

$$M^{m+}_{(a)} + \mathrm{m}_{(0)} + \mathrm{m[Emi^{+}]}_{(0)} \leftrightarrow ML^{m+}_{m(0)} + \mathrm{m[Emi^{+}]}_{(a)} \quad \text{Eq. 2.20}$$

2.7.3 Mechanism of phase separation

The mechanism of the aqueous bi-phase system (ABS) may be explained as the ionic liquid competes with the salt ions for water molecules and greater affinity of salt particles for water molecules causes their mutual attraction. This forces reduction of ILs is ions hydration and consequently decreases its water solubility. This leads to phase formation, consisting of ionic liquid and a small amount of water. This mechanism can also be explained on the basis of the thermodynamic theory of Gibbs 'free hydration energy'. Kosmotropic ions having a large negative energy of hydration exhibit high affinity to water particles and attract them stronger than ionic liquids (Adetunji et al., 2005; Beurlen et al., 2011; Melcher et al., 2008; Mitchell, 2015; Theron, 2010).

The presence of two charged species from the ionic solvent itself, in an IL/ABS, makes metal ion separation a much more complex process than in traditional solvents. This does not necessary mean that ILs are not suitable for separation processes, but one needs to find the right combination of IL and ligand to obtain similar behavior as in organic solvents or one needs to use the differences from organic solvents for achieving more advantageous separations (Adetunji et al., 2005; Beurlen et al., 2011; Kim et al., 2013; Melcher et al., 2008; Mitchell, 2015).

2.7.3.1 The density of imidazole ILs

The density of ionic liquids is related to the volumes of anions and cations. Comparison with the density of chlorine aluminate which included different substituent-imidazole cations, shows that the density of ionic liquids has a linear relationship with the length of the N-alkyl chain which is in the imidazole cations. The larger volumes of organic cations are the smaller density of ionic liquids. The density of ionic liquids can be slightly adjusted by the structure of cations. Anions have more obvious effects on the density of the ionic liquids. When the volumes of anions become larger, the density of ionic liquids will be higher. Therefore, designing different density of ionic liquids can select different cations and anions. In fact, the pH of ionic liquids is determined by the anion which is in the ionic liquid(C., 2007).

2.7.3.2 The viscosity of imidazole ILs

The viscosity of ionic liquids mainly depends on the capacity of hydrogen bonds formation in ionic liquids and the magnitude of van der Waals forces. For example; the relationships between the van der Waals forces and the viscosity of ionic liquids can be found by changing the anions of 2,3-dibutyl-2-methyl-imidazolium ionic liquid. When the anion CF_3SO_{3-} is changed into $C_4F_9SO_3^-$ and CF_3COO^- is also changed into the C_3F_7COO-, it will significantly increase the viscosity of ionic liquids because $C_4F_9SO_{3-}$ and $C_3F_7COO^-$ anions have stronger van der Waals forces(Dymek, 1989).

2.7.4 Extraction of metal ions using ILs

Ionic liquids have been used for extraction of metals after addition of appropriate complexation reagent. Imidazolium ILs as solvents in liquid-liquid extraction systems have been most broadly described in literatures, so far. The most promising examples of ionic liquids used for this purpose are 1-alkyl- 3-methylimidazolium hexafluorophosphate, tetrafluoroborate and bis (trifluoromethylsulphonyl) imide. Extraction of metal ions into ionic liquid phase requires addition of special ligand with the aim to enhance affinity of strongly hydrated ions to hydrophobic ILs phase (Adetunji et al., 2005; Beurlen et al., 2011; Kim et al., 2013; Mitchell, 2015; Nete, Koko, et al., 2014; Theron, 2010).

Owing to above liquid-liquid extraction systems, significant improvement in extraction of alkali metals and lanthanides in comparison to traditional molecular organic solvent has been reported. It has been also established that the distribution coefficients for metal cations were the most advantageous for shorter 1-alkyl-3-methyl imidazolium ILs (Burt, 1996; Melcher et al., 2008; Mitchell, 2015).

The most popular imidazolium ionic liquids are the 1-alkyl-3-methylimidazolium salts due to the easy alkylation of commercially available. The benefit of using this method over the conventional quaternization of imidazole with a haloalkane is twofold: (1) this procedure is completely halogen-free, avoiding potentially toxic chloride imidazolium precursors, and (2) higher yields can be reached in shorter reaction times and at lower temperatures.

In this study, based of disadvantages and availability, which is selected only 1-Ethyl-3-methylimidazolium chloride (EMIC) for aqueous bi-phase separation (ABS) or for hydrophobic and hydrophilic phases (Adetunji et al., 2005; Burt, 1996; Theron, 2010).

The physicochemical properties of EMIC such as conductivity and viscosity depend on the structural changes of the melt (Friese et al., 1996). Characterization of the melt has revealed the presence of chloroaluminate anions $[AlCl_4]^-$and $[Al_2Cl_7]^-$ depending on the aluminum chloride concentration (Friese et al., 1996; Rodriguez et al., 2015). These species are formed according to reactions Eq. 2.21 and Eq. 2.22 (Deblonde et al., 2015; Friese et al., 1996; Gaballah et al., 1997; Theron, 2010).

$EMI^+Cl^- + AlCl_3 \leftrightarrow EMI^+[AlCl_4]^-(0 < x(AlCl_3) < 0.5$……..……..…………..….Eq. 2.21

$EMI^+[AlCl_4]^- + AlCl_3 \leftrightarrow EMI^+[Al_2Cl_7]^-(0.5 < x(AlCl_3) < 0.67)$ (II)………..……Eq. 2.22

It is possible to buffer acidic melts to neutrality by the addition of solid alkali metal chlorides, MCl, to acidic melts may be occurred in the following Eq. 2.22 - Eq. 2.23.
$Al_2Cl_7^- + MCl \quad M^+ + 2AlCl_4^-$ ………………………………………………. Eq. 2.22
$CaCl_2$ can be used to buffer acidic melts, while basic melts can be buffered using $CdCl_2$ or $MgCl_2$. The expected buffering reaction would be:
$Al_2Cl_7^- + MX \qquad AlCl_4^- + AlXCl_3^- + M^+$ where; X= Br or I ……………..…. Eq. 2.23

It is also possible that ions such as $AlCl_2Br_2^{-2}$, $AlClBr_3^-$, or $AlBr_4^-$ may be formed (Jehng & Wachs, 1991; Jesik Park; Philipp Keil, 2011; Regel-Rosocka & Wisniewski, 2011; Ren et al., 2011; Wei et al., 2003).

2.7.5 Solvent Extraction of Nb and Ta using ILs

Still now there is no any literature data on solvent extraction of Nb and Ta using ILs from alkaline fusion of tantalite ore system. However; there are few literatures on the solvent extraction of Nb and Ta from fluoride fused tantalite ore system.

The most extractant used in separation of Nb and Ta from the aqueous phase of fluoride system are tributhyl phosphate (TBP) and aliquot 336. The extraction of Nb with TBP was smaller compared to Ta from HF-H_2SO_4 system and the Niobium extraction decreased with the decrease in concentration of tri butyl phosphate (El-Husaini & El-Hazek, 2005; Gebreyohannes et al., 2017; Mackay & Simandl, 2014; Nete, Purcell, et al., 2014). During Niobium extraction the phase separation for niobium extraction using TBP was difficult for tri butyl phosphate due to its high density (Nikolaev & Maiorov, 2007).

Niobium extraction was performed with tertiary amines alamine by Markland (Pitfield et al., 2010). Alamine (aliquot 336) was employed to extract Niobium from Hf-H_2SO_4 system. During extraction, Nb extraction was increased and it decreased with increase in H_2SO_4 concentration and Nb higher in tertiary amine than secondary amine (Pitfield et al., 2010).

2.8 Recovery and recycling of the metal ions and Solvents

Most of disposal of metals contained wastes meets environmental equipment's produced worldwide. Therefore, recycling and recovery of metals and solvents are must essential to assure green and sustainable environment. Among technologies, solvent extraction (SX) is a powerful method of recycling of metal ions, polar and non-polar solvents have been used in solid-liquid separations production of hydrometallurgical processing technologies (Marcelo & Ouro, 2011).

In the separation step of SX or simply, consisting of the transfer of a solute from one solvent to another (the two solvents being immiscible or partially miscible), with each other, the dissolved solution containing metal ions or feed solution is conducted with extractant (organic or ionic liquid). The target metal ions are separated to interest extractant phase (mostly, the upper phase). The liquid or untargeted phase (mostly, lower phase) is then separated or submitted or stored for recovery and recycling of other metals and fusing agent solvent(El Hazek, 2001; Graedel et al., 2011; Philipp Keil, 2011; Schubert, 2011).

For effective and efficient separation in SX successive stripping steps are needed. The successive extractant used in the stripping steps produces lower phases to be recycled and recovered.

Finally, according to Marcelo and Ouro (2011), the SX is a simple operation and very efficient method to recover both metals from the feed solutions or from industrial effluents, from residues and from extractants is self (Marcelo & Ouro, 2011).   SX might contribute to eliminating and reducing the energy and costs required transporting hazardous materials to waste sites, to produce and process the raw metals in waste sludge or residues, and replacement or recycling of the discharged wastewater. Generally, SX covers the selection of solvents in terms of "use of clean technology" is the core criteria for minimized wastes and highest recovery and recycling.

Ionic liquids have a very good solubility with organic materials and inorganic salts. They can be miscible with a variety of compounds. Ionic liquids are usually recycled in two ways, such as liquid-liquid and solid-phase extraction. Therefore; in this study the first recovery and recycling method is discussed as follow:

2.8.1 Liquid-liquid extraction

For example; firstly, if the mixture solution of IL only contains water, ethanol, acetone or other common solvents, by reducing pressure and distillation, they will be removed and ionic liquid will be pure and then reused and if the mixture solution of cellulose and ILs, the mixture solution and the ILs could be purified and recycled by this method (Turner, 2003). It means: cellulose is dissolved in the ionic liquid and the solution will be heated to 70~130 ºC in an oil bath. Vacuum degassing of the warm cellulose ionic liquid solution is coated on a glass plate and use another piece of glass plate is used to cover on the top. Then the system is put into distilled water and soaked a period of time. After that the template was opened slowly and the ionic liquid is washed and the regenerated cellulose membrane is removed. The mixture of water and ionic liquid is decompressed and distillated, and then it is placed in a vacuum dryer for more than 24 h in order to remove water. The recovery rate of ionic liquids is 96.120%. The result of Swatloski et al., 2002, work shows that the recovery rate of ionic liquids is high. The recovered ionic liquids can be re-used (Swatloski, 2002).

Secondly, the mixture solution of the ionic liquid contains inorganic salts. Some K_3PO_4 solution can be added into the mixture solution. After that salting-out will happen. The upper layer is the ionic liquid and the lower-layer is K_3PO_4 solution with salt. Through the liquid seperation treatment, a pure ionic liquid is obtained by further purification steps (Swatloski, 2002; Turner, 2003)

2.8.2 Solid-phase extraction

In solid phase extraction, the cations in the mixture solution of the ionic liquids are exchanged by ions in resin. Firstly, ionic liquids are diluted by distilled water, and then SCX cartridges are used to ion exchange. Secondly, after solid phase extraction pre-concentration, the samples are eluted by orthophosphoric acid. If there are some salts or organic solvents in the solution such as methanol or acetonitrile and acid solutions, they will be extracted by using phosphoric acid in the ionic liquid solution. Finally, the acidification of a saturated salt solution has a very effective elution system. This also shows that ionic liquid resins have certain hydrophobicity and it is used for solid-phase interactions. In solid–phase extraction, the breakthrough volume is very important, because it limits the attainable detection (Swatloski, 2002).

2.8.3 Recycling of immiscible solvents

Once a solvent has is contaminated and mixed with other solvents and become in a position not to use for required operations, there are two options: disposing as hazardous waste or it can be recycled. Distillation is one of the techniques implemented to safely and efficiently turn solvent-based waste into a reusable solvent. Recycle and reuse of solvent minimizes operating cost and allow profitable operation of a recovery system (K. L. Shivabasappa, 2008).Thermodynamics offers an alternative value system to bring clear understanding and insights to the issues of recycling. It highly prevents loss of resources too. Furthermore, thermodynamics deduces the minimum amount of work required to separate a mixture and to recycle the original value of the materials. Enthalpy of mixing that refers to the change in the enthalpy per mole of solution formed when pure components are mixed at the same temperature and pressure, is one of the important parameters. Reports show that there is lack of date in enthalpy of mixing especially in mixed-solvents systems. The equation of Pitzer’s can be used to analyze molar excess enthalpy of mixing data. These kinds of data can be also examined in the light of Young’s Cross Square rule (B.R. Deshwal, 2003; Gutowski, 2008).

2.9 Gap analysis of the study

The world resources available today may not meet future demand for Ta and Nb. These metals are recovered mainly from the minerals of “Coltan” (columbite-tantalite ore), which consists oxides of Ta and Nb (OTN) (Amuda et al., 2007; Bernstein et al., 2008; Beurlen et al., 2011; Htwe & Lwin, 2008; Melcher et al., 2015; Melcher et al., 2008; Mitchell, 2015). The concentrates from this ore typically contain between 10 wt% and 60 wt% Ta_2O_5 in the case of concentrates from leading producers such as Greer Lake (Manitoba), Tanco pegmatites

(Canada), Kenticha pegmatites (Ethiopia), Greenbushes and Wodgina (Western Australia), Yichun (SE China), Pampean Ranges (Argentina), and the Eastern Desert (Egypt) (Melcher et al., 2015).

According to the mineralogical composition of Kenticha pegmatite, it is classified into beryl, feldspar-muscovite, albite–spodumene, and spodumene. Spodumene contains the highest compositions of Mn-tantalite, along with radioactive elements such as Th and U, which require careful removal for the concentrate product to meet export standards (Küster, 2009). The beneficiation of OTN also requires the removal and separation of associated impurities from each other because Nb, Ta, Fe, and Ti are usually associated with one another in minerals. Because of their similar chemical properties, these elements they are separated with difficulty (Adetunji et al., 2005). Therefore; to date, no work has been reported on washing as well as decomposition for high-grade tantalite ore using low concentrations of acids and alkaline solutions; therefore, in this study, low concentration of H_2SO_4 and KOH will be used to remove radioactive oxides from the Kenticha ore.

Following the beneficiation of the ore, a number of processes may be required based on the mineralogy and the chemical composition of the Kenticha ore. The primary step in hydrometallurgical processes is to breakdown the constituents of the ore to solution. This may depend on the rate of the decomposition and leaching of the tantalite ore and/or the solubility of the solute to be extracted (Agulyansky, 2004; Nete, Koko, et al., 2014; Nete, Purcell, et al., 2014; Zhu & Cheng, 2011). The decomposition of the concentrated Mn–tantalite may be carried out via several complicated procedures, such as alkali fusion, chlorination, reduction and acid leaching. Currently, most of the tantalite ores are digested concentrated HF (Rodriguez et al., 2015; X. Wang et al., 2009).

However, these decomposition processes are associated with the loss of HF due to volatilization (Agulyansky, 2004; Nete, Koko, et al., 2014; Nete, Purcell, et al., 2014; Zhu & Cheng, 2011), which is toxic to plant operators and causes equipment corrosion. A sum of studies have been reported in the literature with the aim of eliminating HF pollution at the source leading to cleaner Ta and Nb production processes (El-Hazek et al., 2012; X.-H. Wang et al., 2010). For example, the decomposition of niobium–tantalum ores with KOH sub-molten salt has been proposed as an alternative method with the objective of eliminating HF(Zhao et al., 2005; Zhu & Cheng, 2011).

In light of the above phenomena, the present study aims to compare the performance of both HF and KOH fusion methods on the decomposition efficiency mangano-tantalite, and subsequent leaching of Ta and Nb in aqueous solutions. However, the beneficiation methods employed prior to KOH fusion may play a key role in the removal of associated heavy minerals such as hematite, manganese oxides and rutile as well as radioactive oxides such as U_3O_8 and ThO_2(Bernstein et al., 2008; Melcher et al., 2015).

Assortments of organic solvents have been extensively studied in recent years in solvent extraction (SX) of Ta and Nb containing liquors. Examples include methyl iso-butyl ketone, tri-butyl phosphate, cyclohexanone, and 2-Octanol (Amuda et al., 2007; Chiranjib Kumar Gupta, 2006) and high molecular weight amines (O. M. El-Hussaini & Mahdy, 2002). Comparatively, due to its solubility, selectivity and stability methyl iso-butyl ketone is the most commonly used worldwide (Zhu & Cheng, 2011). Ionic liquids (ILs) or the so-called “green solvents” can be considered as suitable alternatives for SX of Ta and Nb as they possess very low vapor pressure, versatility, and high capacity for separating organics and metal ions from aqueous phases. The potential benefits of ILs in the recovery of metal ions have been summarized in a number of reviews elsewhere (Hirayama et al., 2005; Huddleston et al., 1998; Li et al., 2007; Wei et al., 2003; Zhao et al., 2005). Further studies on the separation and determination of Nb and Ta are required regarding efficiency, selectivity and sensitivity. This study aims to demonstrate the feasibility of using ionic liquids (ILs) as an extracting phase following the decomposition of tantalite ore by KOH fusion in the presence of Lewis acids.

In sum, to the best of the authors’ knowledge, there is no previous study on the removal radioactive oxide form radioactive oxide containing tantalite ore, KOH fusion of high grade tantalite and separation of Ta and Nb from dissolved alkaline solutions using ionic liquids. In addition, there still exists a lack of quantitative data on the solubility, separation and precipitation of the Ta and Nb from low grade ores.

2.10 Objective of the study

2.10.1 General objective

The aim of this study was to investigate **alternative method and green technology for the hydrometallurgical processing of niobium and tantalum from Ethiopian Kenticha pegmatite ore, through the replacement of hydrofluoric acid by roasting and high-temperature leaching alkaline salts and solvent extraction using ionic liquids extractant in the presence of Lewis acid** at a laboratory scale.

2.10.2 Specific objectives

The specific objectives of the study were:

- To investigate separation, purification and refining methods of Nb & Ta from tantalite by removing the use of hydrofluoric acid to dissolve niobium and tantalum, and replace it by the roasting and high-temperature leaching using alkaline fusion with highly concentrated potassium hydroxide salt.
- To determine the effect of the mass of alkaline fusion agent to tantalite ore ratio, concentrations of decomposition agents to ore ratio, decomposition and stirring time, decomposition temperature and calcination of the ore and oxides of Nb and Ta.
- To characterize and analyze the particle sizes of the ores, purity of oxides of Nb and Ta and residues of acidic and alkaline fusion by ICP-OES, EDXRF, AAS, XRD, XRF, and FT-IR.
- To replace the petroleum-derived solvents, for the separation of both metals by new "environmentally friendly" solvents as ionic liquids using solvent extraction, minimize the waste production by process integration and added value sub-products recovery.

2.11 Hypothesis

The replacement of hydrofluoric acid as a decomposition agent for Kenticha tantalite ores by roasting and high temperature water leaching and extraction using ionic liquids, leads to a new “environmental friendly” solvent extraction technology without increasing the decomposition time, incrementing the dissolution of metals and the percentage of recovery of Nb and Ta and minimizing of waste produced by process integration bringing added value sub-products recovery.

From these hypotheses, the following research questions are arising:

1) Is the leaching solute effective and alternative hydrofluoric acid to dissolve tantalite?
2) Is a combination of alkaline fusion best leaching solute over hydrofluoric acid?
3) Do the ionic solvents have higher selectivity to dissolve Nb & Ta from the leach solutions than traditional extractant?
4) Could the combination of ionic solvent extraction and alkaline fusion produce acceptable pure Ta & Nb metals from the leach solution?
5) Could the solvents and impurities separated, treated and recycled be handled in convenient manner?
6) Is the investigation novel, environmental friend & applicable to Ethiopia?

The research questions have arisen from the hypotheses should be correspondingly answered in specific moments, except hypothesis number 6.

The research questions have arisen from the hypotheses should be correspondingly answered in specific moments.

2.12 Conclusions

The primary beneficiation methods, acidic and alkaline leaching and organic and ionic solvent extraction and refining techniques discussed in this literature review indicate that effective procedures have been settled for the extraction of Nb and Ta of tantalite ores. However, effective extraction of Nb and Ta depends on the competence of each unit operation (beneficiation to refining) and the direct links between these procedures, in addition to the mineralogy of the ore.

Most of the available beneficiation and extraction methods do not adequately deal with radioactive oxides in the tantalite ore, are energy intensive and/or use environmentally unfriendly toxic reagents. Thus, the current study aims to investigate alternative beneficiation, digestion, separation and purification of Nb and Ta from Ethiopian Kenticha pegmatite ore deposit with the focus of reducing radioactive oxide contamination, cost and environmental footprint. This dissertation wasinvestigating the feasibility of using ionic liquids (ILs) for solvent extraction in promoting the application of green technology in mineral processing and metal extraction.

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3

GENERAL METHODS AND MATERIALS

CHAPTER 3: GENERAL METHODS AND MATERIALS

Diverse experiments were performed keeping in mind the end goal to control the best conditions on alternative and effective beneficiation and removal of radioactive oxides, decomposition or digestion of concentrated solid tantalite to solution, separation of targeted Nb and Ta metal ions from the dissolved solution and purification of tantalum and niobium from the striped solutions. These ideal states of beneficiation, extraction and separation are controlled by various parameters. They incorporate the particle sizes, decomposition temperature, decay time, the proportion of acids and alkaline solutions with tantalite ore of the nourish solutions, the nature of the buildup, and the idea of the stripping agents. Ammonium hydroxide was utilized as the precipitation agent. All investigations were in box bunch tests. Here, every one of the systems to get the test information and data used to examine the procedures explored is clarified and all the mechanical assembly or instruments; utilized. The methods used to characterize and analyze the samples acquired are additionally clarified underneath:

3.1 Apparatus and instruments

The apparatus, instruments and raw materials used are bulleted below:

- Flasks and bottles made in polytetrafluroethylene (PTFE), perfluoroalkoxy (PTA), or polyethylene because glass apparatus cannot be used since HF dissolve silica.
- Beakers made of PTFE
- Separation funnel
- Furnace
- Stirring bar
- Magnetic stirrer
- Sampling pipette
- A measuring cylinder
- Sartorius ENTRIS323-1S chemical weighing balance
- Frantz model LB1 magnetic barrier laboratory separator
- Thermometer
- Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES)
- X-ray Diffractometry (XRD)

- Energy-dispersive X-ray fluorescence spectrometer (EDXRF)
- Fourier-transform Infrared Spectroscopy (FT-IR)

3.2 Planning

The aim of this dissertation was to eliminate the practice of HF by introducing green solvent and environmental friend hydrometallurgical process and to find optimum conditions for extracting and separating tantalum and niobium from Ethiopian-Kenticha pegmatite and to produce enriched tantalum oxide and niobium oxide from the typical tantalite concentrate.

The experiment design ensures higher accuracy with lower costs. With a laboratory scale study, experiments were carried out by manipulating or controlling variables such as: mass and purity of salt, particle sizes, temperature for roasting and leaching, contact time, speed and reaction times, metal ratio, percentage of retrieval of Nb and Ta, types and amount of waste production and added value of sub-products recovery. All the results were characterized by ICP-OES, XRF, XRD, and FT-IR. This research work has four packages detailed on Table 3.1. Each package corresponds to one article in chapter 4, 5 and 6 respectively. Each separate activities aiming to get novel, alternative and environmental friend manner within high purity by showing the gab up to date. The experimental works were conducted in Mekelle University, postgraduate research center of Department of Chemistry and Ezana Mining Laboratory and also, the analysis parts were conducted in Adama Science and Technology University, Department of Material Engineering, laboratory of Geological Survey of Ethiopia and Ethiopian Mineral Petroleum and Biofuel Corporation (EMPBC), in the research center of Poly Technology Institution of Behrdar University, the Federal Democratic Republic of Ethiopia, Ministry of Mines, Petroleum and Natural Gas and Kenticha Tantalum Plant and Addigrat Pharmaceuticals Factory.

3.3 General Methodology of the study

This dissertation paper theory is a combination of two published journals, (Berhe et al., 2017; Gebreyohannes et al., 2017), one submitted manuscript and one accepted min-review manuscript. While the main intend being to discover better than ever green techniques to digest and separate Nb and Ta metal ions from the dissolved solution and to isolate and precipitate Nb and Ta metal ions and oxides from separated dissolved solutions. These studies explored distinctive elements of niobium and tantalum chemistry, for example, the methodologies of beneficiation and evacuation of radioactive oxides, the correlation of green strategies for the tantalite and assurance of the Nb and Ta metal ions also the impurities introduce in the mineral utilizing alkaline and acidic draining procedures and solvent extraction and striping stages of niobium and tantalum from the digested solutions. The beneficiation, decomposition and solvent extraction technique of this study done by adjusting the methodologies is followed by replacing new green solvents. Every original copy is portrayed in detail in section 4, 5 and 6, separately.

The point of this exploration was to discover ideal conditions for beneficiations, removing and isolating tantalum and niobium from Ethiopian Kenticha tantalite and deliver tantalum oxide and niobium oxide as conceivable beginning with a run of the mill Kenticha pegmatite-spodumene ore. The selected procedures to finish as indicated by the accompanying perception of every approach are as per the following:

3.3.1 Method studied observation I: Beneficiation and removal of radioactive oxides

A more point by point system in the beneficiation and expulsion of radioactive oxides from pegmatite mineral is given in **Article I ofChapter 4**.

Tantalite mineral was first crushed; the particle size distribution and washed utilizing tap water as dispersant taken after, by shaking table. At last, the overwhelming minerals were isolated by gravity and magnetic separation to isolate manganocolumbite than ferrocomlumbite. The nearness of radioactive oxides in the tantalite mineral were expelled by dilute alkaline solutions as opposed to by dilute acidic washing by keeping the composition of tantalite pentoxide and this is best approach for facilitate extraction procedures and sending out. Furthermore, the ore deposit, magnetic and nonmagnetic bits, basic and acidic washed minerals were analyzed utilizing EDXRF, FT-IR and XRD spectroscopies.

3.3.2 Method studied observation II: The dissolution techniques

A more detailed framework in the decomposition process is given in **Article II of Chapter 5.**

The chemical liquid-liquid extraction and evaluation of the diverse components require the samples must be in the form dissolved solutions. The literature studies in Chapter 2, has demonstrated that energetic conditions, for example, the utilization mixture of acids of HF-H_2SO_4 and alkaline salt digestion methods are normally utilized for mineral disintegration. Acidic draining of the mineral sample was utilized as a part of this study for the particular disintegration of target metals from solid and liquid samples.

These techniques includes the transformation of the untargeted undissolved metal oxides and considered as an impurities and can be isolated and separated physically from the solid buildup by solid-liquid separation such as; filtration by washing to pH 7, decantation or centrifugation. Acidic leaching is a simple procedure to perform and is a great deal less destructive (contingent upon the acid utilized). The detriments of acidic leaching incorporate the exceptionally acidic and sometimes harmful remaining emanating.

Flux/alkaline fusion is frequently utilized as another option to acidic decay. This decomposition technique is frequently utilized for the digestion of the solid tantalite to liquid samples, for example, ores, wastes of high temperature furnaces or slags and electronic capacitors which are impervious to corrosive assault. Alkaline fusion methods include the warming a homogenous digestive agent which involves a plenty of salt added to a concentrated mineral sample at a given temperature which surpass the melting point and volatility of the flux in a fitting holder, for example, a crucible. The digestive salt and the sample ore react with each other at the given lifted temperature as a liquid blend in distilled water draining. The decision of the mass flux is chosen based delivering the lower mass of residue and hence critical for this dissolution strategy might be influenced by enthusiastic parameters, for example, particle size of the mineral, synthesis of the ore, temperature, pressure and amount of KOH. At long last, the alkaline fusion products are contrasted and acidic dissolution of tantalite ore. The efficiency of dissolution of the ore by salt is typically subject to the ore: salt weight proportion also decomposition temperature. At the point when the reaction is finished, judged by visual assessment which is demonstrated by the vanishing of altogether the beginning ore and salt samples, the liquidized is permitted to cool down and after that hydrolyzed with plenty of distilled water. The alkaline salt fusion procedure is regularly utilized for digestion of mineral solid samples because of it maintains a strategic distance from the utilization of the possibly harmful and volatile HF.

3.3.3 Conceptual framework of the research work

Table 3.1 Summary of study by packages

ives	**Activities**	**Parameters to checked**
t purity and reliable compositions of unds of Kenticha tantalite with pure e	sizing, shaking table, gravity , and magnetic separation separation, and washing	particle sizes and approach
ecomposition of tantalite on alkaline optimum decomposition ature and optimum tantalite to solute	Decomposition of tantalite with potash and Acid	Particle size, temperature, tantalite ratio, ratio of HF and H_2SO_4, mass and contact time
ved solutions of Nb & Ta in ionic from the feed solution, separated ns of Nb & Ta from the organic and determined the number of stages action	Dissolution in ionic liquids, stripping with water, stripping with sulfuric acid, and Separation of Nb & Ta rich strip solutions.	Concentration of H_2SO_4, stripping contact time, distribution coeffici separation coefficient (β) and e factor (%E) and McCabe-Thiele diag
tion of high purity and quality of n pentaoxide decomposition of e on alkaline fusion and optimum Nb rip solution and ammonia solution	Precipitation of niobium pentaoxide from niobium rich strip solutions, calcination of niobium pentaoxide, and compassion of the dried with the purchased niobium pentaoxide by XRD and SEM	Amount of ammonia solution; contac distribution coefficient (α), se coefficient (β) and extraction facto and McCabe-Thiele diagrams
tion of high purity an d quality of m pentaoxide decomposition of e on alkaline fusion and optimum Ta rip solution and ammonia solution	Precipitation of tantalum pentaoxide from niobium rich strip solutions, calcination of tantalum pentaoxide, and compassion of the dried with the purchased tantalum pentaoxide by XRD and SEM	Amount of ammonia solution; contac distribution coefficient (α), se coefficient (β) and extraction facto and McCabe-Thiele diagrams

3.3.4 Method studied Observation III: Separation, purification and precipitation techniques

A more detailed framework in the solvent extraction process is given in **Article III of Chapter 6**.

3.3.4.1 Solvent extraction

Liquid–liquid or solvent extraction is an extremely well known and viable strategy to separate and isolate metal ions from each other or from meddling matrices. This solvent separation technique prompts the specific exchange of substances or metal ions starting with one dissolvable then onto the next immiscible dissolvable. The dissolved solution was isolated to diphase by adding ionic liquids and H_2SO_4 to modify the pH for higher dissolved niobium and tantalum metal ions in one of the isolated stages. The liquid samples were investigated utilizing ICP-OES and the residue was analyzed utilizing EDXRF and FT-IR

3.3.4.2 Selection of stripping agent

Diverse stripping agents, for example, distilled water and sulfuric acid was utilized to purify niobium and tantalum from the dissolved solvent. The stripping tests were directed at the same contact time and at A/O (i.e. aqueous to organic) proportion of 1/1. The organic stages from the extraction procedure were washed with distilled water and dilute sulfuric acid to get niobium by separating extraction. The acidity of the aqueous stage niobium solution was balanced and afterward reached with EMIC/$AlCl_3$ to remove niobium ions from tantalum ions. The dissolved metal ions of solutions in each staged were analyzed by ICP-OES.

3.3.4.3 Precipitation

A 30% of ammonium hydroxide (NH_4OH) was added to the pregnant solutions from the stripping procedure, to set niobium and tantalum into oxide forms. The precipitate was permitted to relax for one day for tantalum and three days for niobium and after that filtered in the reaction box. The precipitate were washed with distilled water to pH 7 and dried at 100°C in an oven to remove moistures from the solid oxides. The dried precipitate was placed in a porcelain pot and after that set in the furnace to 1200 ^{0}C for an hour to evacuate impurity which have lower boiling point than oxides of Nb and Ta. The calcinated solid samples were then analyzed by XRD, EDXRF and FT-IR analysis.

3.5 Instruments implemented in this study

The accomplishment of most processes of digestion, separation and purification procedure is at long last assessed by the rate recuperation and the immaculateness of the objective elements. It is in this way critical that each progression of the beneficiation method is checked and evaluated for its prosperity. This is accomplished by the measurement of the considerable number of components segregated amid that particular step. These assurances of the chemical reactions and separation efficiencies at each stages and steps likewise helps with the percentage composition of altogether the principle oxides and additionally that of the impurities acquired amid the entire procedure which is critical for the enhancement of the distinctive procedures or ventures in the beneficiation, separation and purification processes. Accordingly, the choice of the strategies that are reasonable for the exact assurance of tantalum and niobium in this investigation, and also that of the contaminations included is essential.

The abrogating influence in the technique choice in this investigation was the multifaceted nature of the Kenticha tantalite ore as far as the basic naturally occurred elemental composition, the great level of inactivity of tantalum and niobium towards numerous compound reagents and additionally the substance likenesses of the two primary components. The systematic procedures utilized as a part of this investigation were chosen on the premise of their accessibility and also their pertinence for the diverse phases of the beneficiation and solvent extraction procedures. Besides, due inaccessibility of research center, instruments and chemicals in the Jimma Institution of Technology, this experimentation was compelled to work in various legislative associations, for example, Mekelle University, Research center of the Department of Chemistry, Adama Science and Technology University, Department of Material Engineering, laboratory of Geological Survey of Ethiopia and Ethiopian Mineral Petroleum and Biofuel Corporation (EMPBC), in the research center of Poly Technology Institution of Bahir dar University, Kenticha Tantalum Plant and non-governmental organizations such as; Ezana Mining PLC and Adigrate Pharmaceutical Factory.

Detailed description of instruments used for analysis in this study is relegated to Appendix II.

Table 3.2 Instruments of the study

Type of analysis	Target samples	Instruments
Molecular bond	Solis samples, such as; pegmatite, tantalite, residues and Nb_2O_5 and Ta_2O_5	FT-IR
Structure	Solis samples, such as; pegmatite, tantalite, residues and Nb_2O_5 and Ta_2O_5	XRD
Elemental composition (major metal oxide of tantalite ore)	Solis samples, such as; pegmatite, tantalite, residues and Nb_2O_5 and Ta_2O_5 and dissolved and striped liquid sample.	ICP-OES and EDXRF

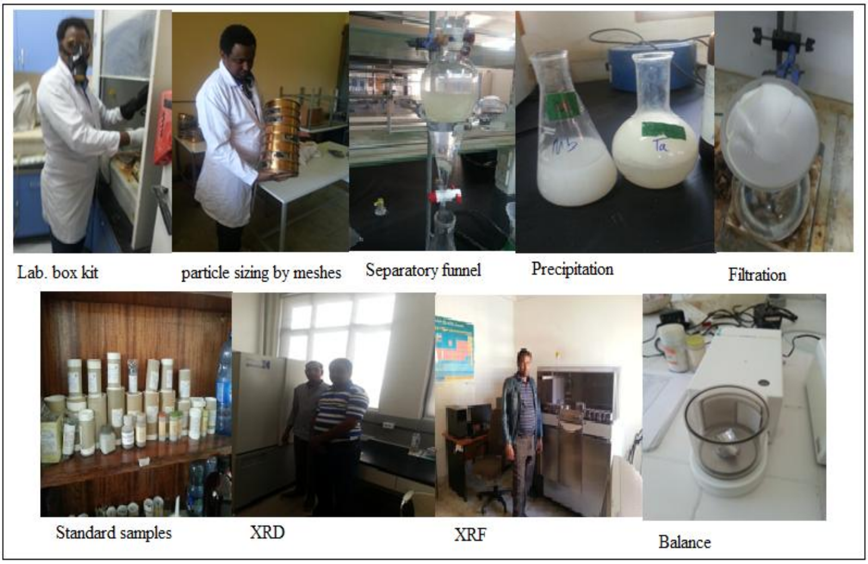

Figure 3.1 Sample photos of laboratory techniques and instruments

3.6 Conclusion

In light of the outcomes from different reviews (see Section 2.5), other preparing strategies, for example, magnetic separation for the expulsion of magnetic impurities and washing with extremely dilute H_2SO_4 and

KOH for radioactive material evacuation were additionally examined for the beneficiation of tantalite. Other separation, stripping and solidification systems examined incorporate precipitation, dissolvable extraction utilizing ionic liquids. The comprehension of the working standards and in addition the qualities and restrictions of these systems are critical to the enhancement of the procedures.

XRD, ICP-OES and EDXRF were the principal strategies for the quantification of the concentrated tantalite ore. By and large the separation of Nb and Ta from the tantalite ore, in this dissertation was expert utilizing a blend of painstakingly chose decomposition procedure(s), separation and assurance methods. All data and scanned instrumental results are in Appendix II.

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4

ALTERNATIVE BENEFICIATION OF TANTALITE AND REMOVAL OF RADIOACTIVE OXIDES FROM ETHIOPIAN KENTICHA PEGMATITE–SPODUMENE ORES

CHAPTER 4: ALTERNATIVE BENEFICIATION OF TANTALITE AND REMOVAL OF RADIOACTIVE OXIDES FROM ETHIOPIAN KENTICHA PEGMATITE–SPODUMENE ORES

Abstract

The beneficiation methods for Ethiopian Kenticha pegmatite–Spodumene ores were assessed through mineralogical and quantitative analyses with X-ray diffraction (XRD) and energy-dispersive X-ray fluorescence (EDXRF). The upper zone of the Kenticha pegmatite–spodumene deposit contains up to 58.7 wt% more tantalite than the inner zone. XRD analysis revealed that the upper zone is dominated by manganocolumbite, whereas the inner zone is predominantly tantalite-Mn. Repeated cleaning and beneficiation of the upper-zone ore resulted in concentrate compositions of 57.34 weight% of Ta_2O_5 *and 5.41 wt% of* Nb_2O_5*. Washing the tantalite concentrates using 1 vol% KOH and 1 M* H_2SO_4 *led to the removal of thorium and uranium radioactive oxides from the concentrate. The findings of this study suggest that the beneficiation and alkaline washing of Kenticha pegmatite–spodumene ore produces a high-grade export-quality tantalite concentrate with negligible radioactive oxides.*

Keywords*: Beneficiation; Kenticha;* Manganocolumbite*; Pegmatite-spodumene; Radioactive Oxide; Tantalite*

4.1 Introduction

In the modern electronics and nuclear industries, both tantalum (Ta) and niobium (Nb) are key and critical metals (Baba et al., 2007; Bernstein et al., 2008). Columbo–tantalite, which is the major source for these rare metals, occurs mainly in pegmatites associated with granites. The common name for the mineral is tantalite when tantalum predominates over columbium (Nb) and columbite/niobite when columbium is dominant (Baba et al., 2007; Melcher et al., 2015). The world resources available today may not meet future demand for Ta and Nb. These metals are recovered mainly from the minerals of “Coltan” (columbite-tantalite ore), which consists oxides of Ta and Nb

(OTN) in the form of ($(Fe,Mn)(Ta,Nb)_2O_6$) and insignificant in the form of microlite, ixiolite, and wodginite (Amuda et al., 2007; Bernstein et al., 2008; Beurlen et al., 2011; Htwe & Lwin, 2008; Melcher et al., 2015; Melcher et al., 2008; Mitchell, 2015). The concentrates from this ore typically contain between 10 wt% and 60 wt% Ta_2O_5 in the case of concentrates from leading producers such as Greer Lake (Manitoba), Tanco pegmatites (Canada), Kenticha pegmatites (Ethiopia), Greenbushes and Wodgina (Western Australia), Yichun (SE China), Pampean Ranges (Argentina), and the Eastern Desert (Egypt) (Melcher et al., 2015). The classification of pegmatite ores is based on the metamorphic environment, mineralogy, elemental composition, and texture; the ores are divided into different classes. On the basis of their mineralogical composition, the LCT (Li–Cs–Ta) family of the rare-element class is the economically most important family for Ta and Nb, and four pegmatite types (beryl, complex, albite-spodumene, spodumene) exist (Adetunji et al., 2005; Kim et al., 2013; Küster, 2009; Melcher et al., 2015; Tadesse & Zerihun, 1996; Tessema, 2003; Zerihun et al., 1995). According to the mineralogical composition of Kenticha pegmatite, it is classified into beryl, feldspar-muscovite, albite–spodumene, and spodumene. Spodumene contains the highest compositions of Mn-tantalite, along with radioactive elements such as Th and U, which require careful removal for the concentrate product to meet export standards (Küster, 2009). The beneficiation of OTN also requires the removal and separation of associated impurities from each other because Nb, Ta, Fe, and Ti are usually associated with one another in minerals. Because of their similar chemical properties, these elements they are separated with difficulty (Adetunji et al., 2005). This Kenticha pegmatite is the main subject of this paper.

According to D. Küster (Küster, 2009) and Kim (Kim et al. 2013), the Kenticha rare-element pegmatite (Ta–Li–Nb–Be–Cs) mineralized zone is located ,southern (Oromia Regional State) Ethiopia, spanning approximately 2.5 km in length and up to 700 m in width, which denotes a globally important tantalum source and deposit (Kim et al., 2013; Küster, 2009). Exploration by Ethiopian Mineral Petroleum and Biofuel Corporation (EMPBC) under the Federal Democratic Republic of Ethiopia, Ministry of Mines, Petroleum and Natural Gas is ongoing exporting high-grade or 50–60 wt% Ta_2O_5. The possible standby resource of primary Kenticha pegmatite ore is 17,000 tons at Ta_2O_5

grade of 0.017 wt%, whereas it was estimated to be 2400 tons at 0.015% Ta_2O_5 in the weathered zone. The deposit of Kenticha is related to late Neoproterozoic I-type granites, a highly complex sub-horizontal pegmatite sheet with a thickness approaching 100 m and classified into three zones-the upper zone (UZ), the inner zone (IZ), and the lower zone (LZ)-on the basis of the scheme of Černý and Ercit (Kim et al., 2013; Küster, 2009). The exploitable and highly concentrated tantalite occurs in the UZ and is characterized by spodumene. Spodumene-bearing pegmatite crystal is white (Fig. 4.1) and occurred up to 4 m in length and with various Ta/Nb ratios from 3:1 to 1:1 and lower, which imitates the Ta mineralization potential. The Ta/Nb ratio is the highest in the spodumene unit, which is the focus of the present mining by governmental EMPBC corporation, local farmers and future development for the extraction of Ta (Kim et al., 2013; Küster, 2009; Tadesse & Zerihun, 1996; Zerihun et al., 1995).

The beneficiations of tantalite ores often involves pre-concentration, feather concentration, and concentrate clean-up for less than 0.1 wt% Ta_2O_5. The choice of any or all of these processes and their success would normally depend on the physiochemical properties of the ore, its Mn/Fe and Ta/Nb ratios, its response to magnetic fields, the presence of radioactive materials, the nature of the ore, and grade of Ta_2O_5 and impurities (or associated minerals). The primary choice of commination and concentration process of an ore containing OTN usually upgrading stage is called beneficiation, which encompass mineral processing steps such as sizing and classification, washing, gravity separation, and magnetic separation steps (Baba et al., 2007; Bernstein et al., 2008). However, the most well-known beneficiation processes for concentrating tantalite ore are gravity and magnetic separations. Secondary ore concentration stages are generally required to increase the content of Ta_2O_5 before further processing to recover Ta and Nb and to remove associated Ta-bearing minerals, impurities, and radioactive elements to acceptable levels (Baba et al., 2007; Bernstein et al., 2008; Burt, 1996). The separation process of Ta and Nb is a complex and difficult process from dissolved solutions and parent mineral, mainly because of the similarities between both elements in physicochemical properties, that’s way they are found in the same group of the periodic table of elements (Nete, Koko, et al., 2014; Nete, Purcell, et al., 2014). Associated magnetic heavy minerals are subsequently separated by magnetic separation (Amuda et al., 2007).

Some studies have indicated the successful removal of up to 97 wt% Fe and 86 wt% Ti from tantalite using magnetic separation and 76.32 wt% ThO_2 and 44.98 wt% U_3O_8 radioactive elements using acid leaching from high-grade ores. In addition, 93.65 wt% Nb and 93.6 wt% Ta were recovered from lesser grade ore by using a KOH digesting agent and followed by systematic addition of water. However, approximately 80 wt% Sn, 50 wt% Ti, 20 wt% Fe, and 20 wt% Mn were also leached from low-grade ores (El-Husaini & El-Hazek, 2005; O. M. El-Hussaini & Mahdy, 2002; Htwe & Lwin, 2008; Theron, 2010; X.-H. Wang et al., 2010). The separation of thorium from uranium was carried out using two different stripping steps to achieve recoveries of 99.6% ThO_2 and 91.2% U_3O_8(El-Husaini & El-Hazek, 2005; Nete, Koko, et al., 2014). Similarly, a process involving acid digestion extraction of niobium oxide from columbite–tantalite concentrate and resulted in 74% Nb_2O_5(Htwe & Lwin, 2008). El-Hussaina and Mahdy reported that a final product of 100% Nb_2O_5 and Ta_2O_5 was obtained when an Egyptian ore was leached using 4.3 N HF and 5.7 N H_2SO_4(O. El-Hussaini, 1996). Another study on the digestion behaviors of oxides OTN by using KOH and water leaching process showed that the dissolution rate of tantalum increased and the dissolution rate of niobium decreased at 400 °C (X.-H. Wang et al., 2010). Notably, however, these processes were carried out under relatively higher concentrations of acids and at a higher temperature of the KOH digestion agent. The literature contains a few studies on the dissolution behavior of Ta_2O_5 and Nb_2O_5 with acids for high-grade tantalite ore and with alkaline solutions at room temperature for low-grade tantalite ore. However, to date, no work has been reported on washing as well as decomposition for high-grade tantalite ore using low concentrations of acids and alkaline solutions; therefore, in this work, we used 1 M H_2SO_4 and 1 vol% KOH to remove radioactive oxides from the ore.

In this paper, we propose an alternative approach to the beneficiation of two different OTN-bearing spodumene white sands from the same deposit. The efficiency of gravity and magnetic separation methods and the suitability of acid and alkaline washing for radioactive material removal from Ethiopian Kenticha tantalite sample ores are also studied.

4.2 Experimental materials and methods

4.2.1 Materials

The tantalite ore used for this investigation was sourced from the Kenticha tantalite mine in the regional state of Oromia, Ethiopia. The mineralogical purity of the ore was investigated using a Shimadzu Maxima-XRD-7000 X-ray diffractometer equipped with a Cu K_α radiation source ($\lambda = 1.540600$ Å) operated at 40.0 kV and 30.0 mA. The resulting diffractograms were interpreted using the Diamond (version 4.2.2) software, the Match! (Version 3.2.2) software and the COD reference database. An energy-dispersive X-ray fluorescence (EDXRF 2800) was used for compositional analysis of the solid mineral and was calibrated using high-grade samples. The beneficiation of the ores was carried using a Frantz model LB1 magnetic barrier laboratory separator and a Laboratory LY model LY1000 × 450 shaking table. The mass of the ores was measured using a Sartorius ENTRIS323-1S chemical weighing balance. Analytical-grade H_2SO_4 and KOH (Sigma-Aldrich) without further purification and doubly distilled water were used in this research.

4.2.2 Methods

As suggested by (Küster, 2009) to obtain an ore which have highest tantalite content, we collected the sample ores from the currently mined by EMPBC from the UZ and the 20-m-depth IZ of Kenticha pegmatite–spodumene ore deposit (Fig. 4.1, white-colored ore). Ten-kilogram samples (sample 1A and 1B) were milled manually with a mortar and pestle to less-than-200 to 400 and above-400 mesh sizes. This step was followed by washing and decantation to reject residues. The samples were then treated using shaking tables to recover the heavy brown–black portion of the ore. Further beneficiation was conducted by gravity separation (25 °C, 250 rpm and 1 hour) and magnetic separation according to schemes 1 and 2. The presence of magnetic minerals in the nonmagnetic samples was checked using a permanent hand-held magnet.

The next and US acceptable grading step of beneficiation elaborates the elimination of radioactive oxides such as uranium and thorium from the nonmagnetic portion of the sample. Approximately 2.0 g of nonmagnetic fraction (sample 6) was weighed and subsequently shifted to a pre-weighed beaker.

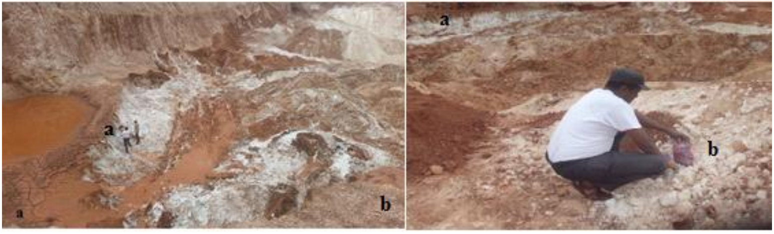
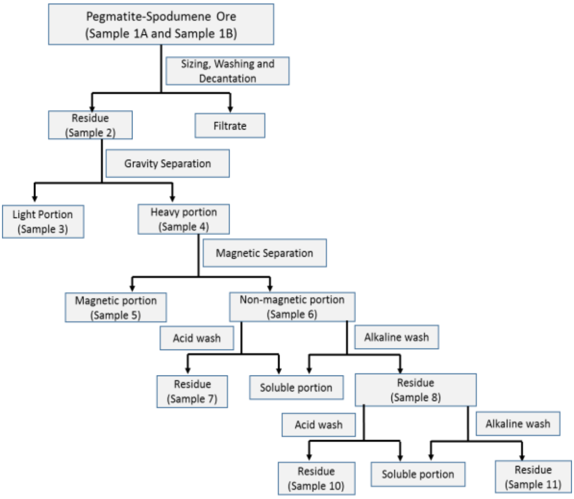
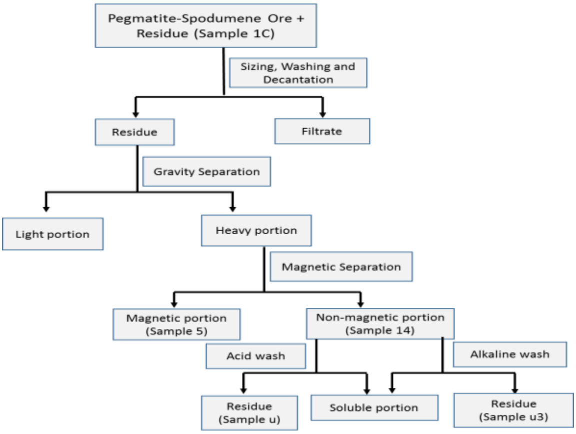


Figure 4.1 View of the Kenticha pegmatite mine (EMPBC): Region (a) 20-m inner zone and region (b) upper zone of mined spodumene.

The washing was carried out using 1 M acid (H_2SO_4) and 1 vol% alkaline (KOH) solutions at room temperature (20 °C) and for a washing time of 1 min. The obtained slurry was separated, stored for further study. The solid non-magnetic samples (samples 7 and 8) were dried in the open air for 2 days. Sample 8 was washed again with 1 M H_2SO_4 and 1 vol% KOH solutions to obtain sample 10 and sample 11, respectively, to investigate whether further removal of radioactive materials could be achieved. The validity of the primary beneficiation was tested by mixing the light portion from Scheme 1 (sample 3) with the original ore in a 1:1 ratio to obtain sample 1C (see Scheme 4.2). All samples except the low grades such as pegmatite–spodumene and residues were analyzed by powder XRD and EDXRF. All measurements were carried out in triplicate.



Scheme 4.1 Systematic separation approach for the beneficiation of Kenticha pegmatite–spodumene ore. Sample 1A was taken from the upper zone of the deposit, and sample 1B was from the 20-m-deep inner zone of the currently mined deposit.



Scheme 4.2 Systematic connected approach for the beneficiation of Kenticha pegmatite–spodumene ore. Sample 1C was prepared by mixing a 1:1 ratio of pegmatite–spodumene ore with sample 3 of Scheme 4.1.

4.3 Results and discussions

4.3.1 Mineralogical studies of the Ethiopian Kenticha ore

EDXRF quantitative analysis of ore samples from different mining zones revealed that the composition of the Kenticha ore deposit varies substantially depending on the mining locations. As evident from Tables 1 and 2, the Ta_2O_5 content in the highly concentrated zones was as high as 70 wt%, whereas the Ta_2O_5 content in other zones was as low as 26 wt%. However, the composition of Nb_2O_5 in the low-Ta_2O_5-concentration zones was as high as 31 wt%, although Nb_2O_5 contents as low as 7 wt% have been reported. The amounts of U and Th oxides in the ore were noted because these are the major penalty elements. In the Kenticha pegmatite ore, certain parts of the coltan mineralization contain low levels of uranium and lithium. In most parts of the Kenticha coltan, the uranium content was above the critical level of 0.5 wt% (Tables 4.1 and 4.2) and the lithium grade greater than 1.64 wt% was obtained in the spodumene (results not shown) (Burt, 1996; Hayes & Burge, 2003; Mackay & Simandl, 2014; Mroueh et al.; Patel & Khul'ka, 2001; Tadesse & Zerihun, 1996).

Table 4.1EDXRF mineralogical analysis of tantalite ore samples from the Kenticha deposit in Ethiopia (high-concentration lots). Source: EMPBC, Feb. 2016.

Lot Number	Ta_2O_5 wt%	Nb_2O_5 wt%	U_3O_8 wt%	TiO_2 wt%	SnO_2 wt%	ThO_2 wt%	Sb ppm
36	69.71	7.21	0.30	0.25	0.085	0.026	<20
52	67.42	10.84	0.56	0.28	0.210	0.088	<20
37	62.98	11.61	0.61	0.32	0.090	<0.005	<20
53	61.57	12.95	0.86	0.39	0.320	0.086	<20
39	60.63	9.81	0.56	0.52	0.070	0.015	<20
54	60.23	12.55	1.19	0.41	0.340	0.091	<0.001
32	60.13	15.19	0.55	0.24	0.090	0.025	<20
33	59.23	17.38	0.80	0.15	0.081	0.017	<20
35	58.93	9.06	0.42	0.42	0.079	0.024	<20
29	57.76	13.93	0.67	0.64	0.037	<0.01	<20

Table 4.2 EDXRF mineralogical analysis of tantalite ore samples from the Kenticha deposit in Ethiopia (low-concentration lots). Source: EMPBC, Feb. 2016

Lot Number	Ta_2O_5% wt%	Nb_2O_5% wt%	U_3O_8% wt%	TiO_2% wt%	SnO_2% wt%	ThO_2% wt%	Sb ppm
67	34.89	10.56	0.44	2.53	0.45	0.068	<20
80	34.86	21.87	<0.2	1.58	0.15	<0.022	<20
68	34.83	13.32	0.90	0.90	0.69	0.019	<20
70	33.75	21.34	0.77	0.43	0.61	0.049	30
81	33.27	24.24	0.40	0.85	0.11	<0.02	<20
71	33.01	26.33	0.52	0.39	0.63	0.015	<20
76	32.07	18.92	0.48	5.17	0.13	0.034	<0.002
72	31.80	23.03	0.85	0.30	0.63	0.044	<20
83	30.87	26.72	0.43	1.31	0.10	0.200	<20
82	26.33	31.01	0.26	1.24	0.07	0.023	<20

4.3.2Gravity and magnetic separation

The industrial and local methods for the beneficiation of a tantalite ore is gravity separation, which allows Ta- and Nb-bearing minerals to be concentrated together with other heavy minerals (Amuda et al., 2007). However, in the existing study, the focus is the beneficiation of OTN with a view of economic value from the Ta-bearing minerals and tails. The other associated magnetic heavy-metal-containing minerals were separated by using magnetic separation, where the hematite transformed to ferromagnetic magnetite was concentrated from the nonmagnetic minerals (Amuda et al., 2007). Gravimetric analysis was carried out to determine the particle size distribution of the sample used for this study is given in Table 4.3.

Table 4.3 Particle size distribution of pegmatite–spodumene ore

Sieve size	Mass retained (kg)		Percentage retained (wt%)	
	Sample 1A	Sample 1B	Sample 1A	Sample 1B
200	0.022	0.017	0.22	0.17
250	0.015	0.012	0.15	0.12
300	0.011	0.008	0.11	0.08
350	0.008	0.005	0.08	0.05
400	0.007	0.004	0.07	0.04
>400	0.001	0.001	0.01	0.01
Sum	**0.064**	**0.047**	**0.64**	**0.47**

As shown in Table 4.4, the nonmagnetic (tantalite) fraction is higher in sample 1A than in sample 1B; in addition, the beneficiation with mesh size of 200 produces highest weight of retained tantalite. The gravimetric results indicate that sample 1A produces higher (58.7 wt%) tantalite than sample 1B because of the meteorological conditions of the Kenticha deposit. The 20-m-deep mined samples have a lower tantalite mass% than the samples from the upper part of the deposit (sample 1A), as shown in Table 4.1 and Table 4.2 (Kim et al., 2013; Küster, 2009). Further studies using XRD (Fig. 4.2) indicate that the dominant phases in sample 1A are $Mn_{0.3}Nb_{0,24}O_2Ta_{0.42}$ (76%) and $Nb_{0.61}Ta_{2.39}TeI_7$ (20.6%). However, the primary phase in sample 1B was found to be a tantalite-(Mn) ($(Fe_{0.09}Mn_{0.88}Nb_{0.28})_6Ta_{1.72}$). Surprisingly, because of the absence of the fingerprint of OTN in the 30° of sample 1B, the chemical composition of sample 1A is expected to belong to manganocolumbite, including associated minerals (considered as residue in this study) (Baba et al., 2007; Kabangu & Crouse, 2012; Nete et al., 2012; X. Wang et al., 2009; H.-m. Zhou et al., 2005).

Table 4.4 Concentrated mass of pegmatite–spodumene ore**.**

Sample code	**Mass (kg)**
Sample 1A *Theoretical	0.015
Magnetic (5)	0.046
Nonmagnetic (6)	0.022
Nonmagnetic (sample 1 + residue) (14)	0.045
Sample 1B *Theoretical	0.015
Magnetic	0.027
Nonmagnetic	0.017

**Theoretical data are basedon (Küster, 2009)*

The general differences in the XRD patterns of sample 1A and sample 1B (Fig. 4.2) indicate differences in mineralogy and the existence of additional elements in the tantalite ore. These results suggest that better enrichment of OTN requires removal and separation of associated impurities to improve the overall grade of Ta in the concentrate. Beneficiation of a mixture of pegmatite–spodumene ore with the residues (light and magnetic portions) (Scheme 4.2) is the best alternative approach for higher grades of tantalite ore over the primary beneficiation of pegmatite ore (Scheme 4.1). As shown Table 4.5, sample 14 scored 57.34 wt% of Ta_2O_5.

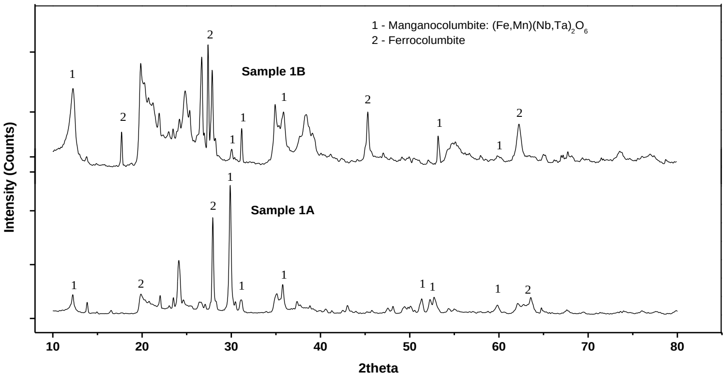


Figure 4.2 Compositional XRD pattern of pegmatite–spodumene ore sample 1A from the upper zone and sample 1B from the 20-m-deep inner zone on the current under mined condition by EMPBC.

4.3.3 Acid and alkaline washing

The presence of radioactive oxides in Kenticha tantalite concentrate requires further purification processes and stages (see Th and U quantities from Tables 4.1 and 4.2) (Burt, 1996; Hayes & Burge, 2003; Kim et al., 2013; Küster, 2009; Mackay & Simandl, 2014; Mroueh et al., 2015; Patel & Khul'ka, 2001; Tadesse & Zerihun, 1996). Acid and alkaline washing were used to assess the extent of removal of radioactive elements from the tantalite concentrates. Following washing with low-concentration acid and alkaline solutions, the chemical composition of the samples were analyzed by EDXRF; the results are presented in Table 4.5. Table 4.5 reveals that samples 6, 8, 11, 14, and u3 are mainly composed of Ta_2O_5 (> 45 wt%), suggesting that the samples represent tantalite ores. According to the grades defined by the Tantalum-Niobium Study Center (Gibalo & Schmorak, 1970), such ores are considered to have excellent grades of tantalum. Samples 7, 10, and u represent columbite because they contain more Nb_2O_5 than Ta_2O_5 and also negligible amounts of Fe, Ti, Th, and U oxides. These results indicate that washing with dilute H_2SO_4 and KOH at room temperature resulted in the removal of the majority of the radioactive oxides. However, washing the tantalite with 1 M H_2SO_4 solution resulted in a decrease in the percentage of Ta_2O_5 and an increase in the percentage composition of Nb_2O_5. By contrast, washing of tantalite with 1 vol% KOH alkaline solution resulting in an increase in the percentage composition of Ta_2O_5 and a decrease in the percentage of Nb_2O_5. Therefore, washing the tantalite concentrate using dilute KOH is advisable to increase the percent of Ta_2O_5 before further extraction and to reduce the amount of radioactive elements. Notably, the limits for Th and U contents allowed in exportable concentrates are 0.1 wt% ThO_2 and 0.1 wt% U_3O_8(Baba et al., 2007). The beneficiation and washing procedures carried out in this study produce tantalite concentrates of acceptable quality that meet the essential requirements for safe handling, transport, and storage.

Table 4.5 Elemental analysis of concentrates by XRF

Sample (code)	Percentage, wt%							
	Ta_2O_5	K_2O	Nb_2O_5	TiO_2	Fe_2O_3	ThO_2	U_3O_8	Ta/Nb
c (5)	6.25	0.41	10.15	5.33	80.23	0.06	0.10	0.62
netic (6)	45.71	0.67	5.51	Nd	Nd	0.04	Nd	8.30
shed (7)	12.73	0.25	21.15	Nd	Nd	0.05	Nd	0.60
washed (8)	45.04	0.41	5.49	Nd	Nd	0.00	Nd	8.20
shed (10)	12.08	0.16	20.97	Nd	Nd	0.09	Nd	0.58
washed (11)	45.09	0.65	5.41	Nd	Nd	0.00	Nd	8.33
residue (14)	57.34	1.66	5.41	Nd	Nd	0.09	Nd	0.59
shed (u)	11.31	1.36	14.13	Nd	0.00	0.08	Nd	0.80
washed (u3)	62.12	1.32	5.15	Nd	0.00	0.00	Nd	12.06

The predominant compound identified from samples 8, 11, and 14 upon washing was manganocolumbite, as evidenced by XRD analysis (Fig. 4.3) and the presence of Fe, Mn, Nb, Ta, and O (Baba et al., 2007; X. Wang et al., 2009). The main mineral constituents of the residues were similar to those of the raw ore (sample 1A) with undissolved Ta_2O_5 peaks at 30° and 60°, which supports the elemental composition shown in Table 3 (Baba et al., 2007; Kabangu & Crouse, 2012; X. Wang et al., 2009; H.-m. Zhou et al., 2005). The absence of the core peak at 25° and the presence of a medium-intensity peak at 30° and a low-intensity peak at 60° in the XRD pattern of sample 5 are observed due to reduced Ta_2O_5 composition, whereas the existence of a sharp peak at 44° is attributed to a higher Fe_2O_3 concentration as compared to sample 1A and 14. These observations are in agreement with EDXRF results that confirm the main characteristics of magnetic materials (Baba et al., 2007; Kabangu & Crouse, 2012; X. Wang et al., 2009; H.-m. Zhou et al., 2005). Again, the results from sample 8 and sample 11 shows that washing with dilute alkaline solution produce Kenticha tantalite concentrate of high quality that satisfies the “Coltan’s” criteria for exports.

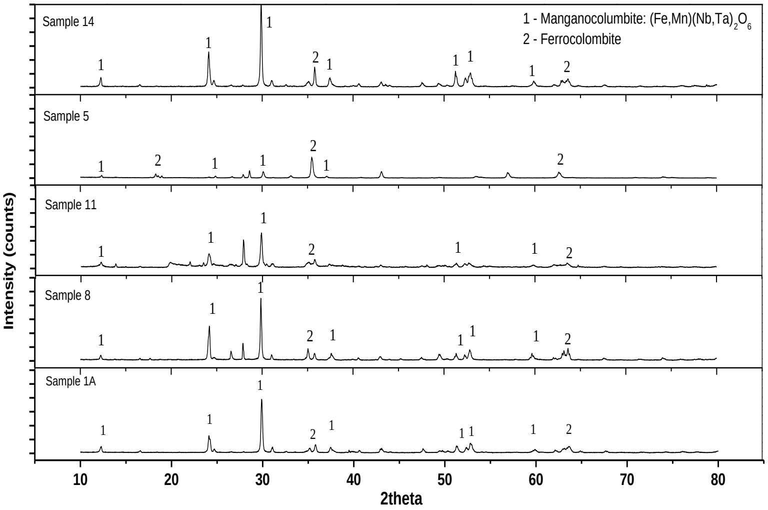


Figure 4.3 XRD spectra of Kenticha pegmatite–spodumene ore (sample 1A); nonmagnetic fractions washed using 1% KOH (samples 8 and 11); ore and residue mixture after concentration (sample 14), and the magnetic fraction (sample 5).

4.4 Conclusions

In this study, the primary beneficiation methods of Kenticha pegmatite–spodumene ore were examined. The results led to the following conclusions:

1) Ethiopian Kenticha pegmatite–spodumene beneficiates relatively easily with gravity and magnetic separation techniques, producing high-grade Ta and Nb oxide concentrates. The upper geographical zone of the deposit resulted in better quality tantalite concentrate as compared with the 20-m-deeper zone.

2) Beneficiation of mixture of pegmatite–spodumene ore with the residues has shown best alternative approach for higher grade of tantalite ore over the primary beneficiation of pegmatite ore.

3) When the tantalite concentrate was washed using 1 M H_2SO_4, high yields of Nb_2O_5 with low levels of Th and U were obtained; by contrast, washing with 1 vol% KOH resulted in the highest level of Ta_2O_5, with almost no oxides of Th and U present.
4) The EDXRF analysis of the magnetic fraction of tantalite concentrate indicated a low content of Th and U.
5) The analysis of Kenticha pegmatite–spodumene ore using EDXRF and XRD has shown that the Ethiopian tantalum ores are of high grade and can therefore be subjected to direct processing for tantalum and niobium products without the need for complex and costly concentration procedures.
6) Knowledge of the presence of very low concentrations of radioactive oxides in the samples would assist in the design of appropriate beneficiation and extraction routes for similar deposits in Ethiopia.

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5

DECOMPOSITION OF THE KENTICHA MANGANO-TANTALITE ORE BY HF/H_2SO_4 AND KOH FUSION

CHAPTER 5: DECOMPOSITION OF THE KENTICHA MANGANO-TANTALITE ORE BY HF/H_2SO_4 AND KOH FUSION

Abstract

The decomposition behavior of Ta and Nb from mangano-tantalite ore was investigated using HF/H_2SO_4mixture and KOH fusion. The effects of reaction time, decomposition temperature, acid and alkaline concentrations and particle size of the dissolution process were examined. At high HF and KOH concentrations, higher decomposition rates were observed. The highest decomposition rates were achieved in 6:2 molar ratios of HF and H_2SO_4 and upon the addition of 10 g KOH in the alkali fusion step. In addition, similar trends in decomposition rates between the two agents (HF/H_2SO_4 and KOH) and comparable the dissolution performances were observed. Increasing the decomposition temperature initially increases the decomposition rate of mangano-tantalite for the two systems considered in this study. However, no significant change in water dissolution rate of Ta and Nb was observed beyond 50 °C for HF/H_2SO_4 system and above 400 °C when using KOH fusion process. The elemental and compositional analyses of the leached residues using XRF, XRD and FT-IR spectroscopy indicate that acid (mixture of HF and H_2SO_4) decomposition has resulted in better dissolution performance for Nb and Ta compared with the alkaline fusion method.

Key words: Decomposition; Kenticha pegmatite; mangano-tantalite; Ta; Nb.

5.1 Introduction

Tantalum and niobium are widely used in many cutting edge technologies such as in the aerospace industry for jet engines and turbine parts, as skin for spacecraft and missiles, rocket nozzle, and in the modern electronics due to their good mechanical strength, ductility and high melting points (El-Hazek et al., 2012; Chiranjib Kumar Gupta, 2006). The estimated annual global production of tantalum has increased from 765 metric tons in 2012 to 1,200 metric tons in 2014 (Küster et al., 2009). Identified resources of tantalum, most of which are found in Australia, Brazil, Canada and Ethiopia amount to

>150,000 Mg. Brazil and Canada are by far the world's leading niobium producers accounting for 99% of production in 2013 and 2014 (Küster et al., 2009).

The most important tantalum containing minerals are generally columbite–tantalite, microlite, ixiolite, pegamatites and wodginit (Černý & Ercit, 2005; Küster, 2009). The Ethiopian Kenticha pegmatite is the main subject of this study. The Kenticha pegmatites are characterized by Fe–columbite and Mn–tantalite, targetly (Černý & Ercit, 2005; Kim et al., 2013; Küster, 2009; Tadesse & Zerihun, 1996; Zerihun et al., 1995). The Fe–columbite (composition of niobium > tantalum) and Mn-tantalite (composition of niobium < tantalum) are separated by the use of magnetic field and the resulting non-magnetic ore is mainly Mn-tantalite (Zerihun et al., 1995). Kenticha pegmatite contains SiO_2, Al_2O_3, Fe_2O_3, MnO, CaO, Na_2O, K_2O, Li_2O, TiO_2, P_2O_5 and trace amounts of Ga, Be, Sn, Nb, Ta, Zr, Hf, Zn, Th, Li, U (Kim et al., 2013; Küster, 2009) in contrast worldwide pegmatite deposits (e.g., Tanco, Canada and Greenbushes', Australia) (Küster, 2009; Zerihun et al., 1995).

Following the beneficiation of the ore, a number of processes may be required based on the mineralogy and the chemical composition of the ore. The primary step in hydrometallurgical processes is to breakdown the constituents of the ore to solution. This may depend on the rate of the decomposition and leaching of the tantalite ore and/or the solubility of the solute to be extracted (Agulyansky, 2004; Nete, Koko, et al., 2014; Nete, Purcell, et al., 2014; Zhu & Cheng, 2011). The decomposition of the concentrated Mn–tantalite may be carried out via several complicated procedures, such as alkali fusion, chlorination, reduction and acid leaching. Currently, most of the tantalite ores are digested concentrated HF (Rodriguez et al., 2015; X. Wang et al., 2009). The dissolution of columbite–tantalite in HF can be represented by the following reactions (Eq. 5.1 to Eq. 5.4) (Chiranjib K Gupta & Suri, 1993):

$$FeNb_2O_6 + 16HF \rightarrow 2H_2NbF_7 + FeF_2 + 6H_2O \quad \text{Eq.5.1}$$

$$FeTa_2O_6 + 16HF \rightarrow 2H_2TaF_7 + FeF_2 + 6H_2O \quad \text{Eq.5.2}$$

$$MnNb_2O_6 + 16HF \rightarrow 2H_2NbF_7 + MnF_2 + 6H_2O \quad \text{Eq.5.3}$$

$$MnTa_2O_6 + 16HF \rightarrow 2H_2TaF_7 + MnF_2 + 6H_2O \quad \text{Eq.5.4}$$

However, these decomposition processes are associated with the loss of HF due to volatilization (Agulyansky, 2004; Nete, Koko, et al., 2014; Nete, Purcell, et al., 2014; Zhu & Cheng, 2011), which is toxic to plant operators and causes equipment corrosion. A sum of studies have been reported in the literature with the aim of eliminating HF pollution at the source leading to cleaner Ta and Nb production processes (El-Hazek et al., 2012; X.-H. Wang et al., 2010). For example, the decomposition of niobium–tantalum ores with KOH sub-molten salt has been proposed as an alternative method with the objective of eliminating HF(Zhao et al., 2005; Zhu & Cheng, 2011). The digestion reaction of tantalite ore with KOH has been suggested to proceed through the following steps (Eq .5.5 to Eq.5.6) (Zhao et al., 2005):

$3(Fe,Mn)O.(Ta,Nb)_2O_5 + 8KOH + (n-4)H_2O \rightarrow K_8[(Ta,Nb)_6O_{19}.nH_2O] + 3(Fe,Mn)O$ ……..…...Eq.5.5

$K_8[(Ta, Nb)_6O_{19}.nH_2O] \leftrightarrow 6K(Ta, Nb)O_3 + 2KOH + (n-1)H_2O$ …………….....Eq.5.6

The $K_8[(Ta, Nb)_6O_{19}.nH_2O]$ produced in the Eq. 5.5 is soluble while the $K(Ta, Nb)O_3$ produced in the next reaction in Eq. 5.6 is insoluble, and whichever of these two species present in the leaching system is determined by the reaction conditions. The niobates and tantalates species produced during the alkaline decomposition of columbite–tantalite mineral are readily converted to more soluble species as shown below (Eq. 5.7 to Eq. 5.10):

$Fe(TaO_3)_2 + 6KOH \rightarrow 2K_3TaO_4 + FeO + 3H_2O$ ………...………..………..Eq.5.7

$Fe(NbO_3)_2 + 6KOH \rightarrow 2K_3NbO_4 + FeO + 3H_2O$ ……………………………....Eq.5.8

$Mn(TaO_3)_2 + 6KOH \rightarrow 2K_3TaO_4 + MnO + 3H_2O$………..……………………..Eq.5.9

$Mn(NbO_3)_2 + 6KOH \rightarrow 2K_3NbO_4 + MnO + 3H_2O$……………………………Eq.5.10

In light of the above reaction mechanism (Eq. 5.1 – Eq. 5.10) the present study aims to compare the performance of both HF and KOH fusion methods on the decomposition efficiency mangano-tantalite, and subsequent leaching of Ta and Nb in aqueous solutions. The optimum decomposition and leaching conditions for Kenticha pegmatite ore using acidic (HF and H_2SO_4) and alkaline (KOH) at various decomposition time, temperature and concentrations of alkaline and acid leaching agents will be presented.

5.2Experimental

5.2.1 Materials

The pegmatite ore was sourced from the Kenticha processing plant in the regional state of Oromia, Ethiopia, currently mined by EMPBC. The mineralogy of the ore was investigated using a Shimadzu Maxima-XRD-7000 X-Ray Diffractometer (XRD) with CuKα (1.540600A) radiation. The XRD analysis revealed that the Kenticha pegmatite ore is dominated by a mangano-tantalite phase as can be seen from Fig.5.1. An Energy Dispersive X-Ray Fluorescence (EDXRF 2800) was used for the compositional analysis of the solid minerals. The sample is mainly composed of Ta_2O_5, Nb_2O_5, TiO_2, Fe_2O_3, and other radioactive impurities such as ThO_2 and U_3O_8 (Table 5.1). A more detailed mineralogical analysis and suggested methods for the removal of radioactive oxides from the ore have been discussed elsewhere (Gebreyohannes et al., 2017). A Shimadzu FT-IR-8400S spectrophotometer was used to check the presence or absence the Nb/Ta oxygen bond frequency. The particle size distribution was analyzed using mesh sieves (PAT). The decomposition process was carried out in stainless batch reactor (SUS316) in high temperature furnace at 400 °C. Analytical grade HF, H_2SO_4 and KOH (Sigma-Aldrich) without further purification, de-ionized, doubly distilled water was used in this study.

Table 5.1Typical chemical composition of Kenticha pegmatite ore and beneficiated non-magnetic tantalite fraction.

mple code)	Percentage, wt%						
	Ta_2O_5	K_2O	Nb_2O_5	TiO_2	Fe_2O_3	ThO_2	U_3O_8
te ore (1)	2.32	3.47	0.45	3.56	25.54	0.09	0.80
e concentrate (3)	55.71	0.67	5.51	0.36	4.31	0.03	0.68

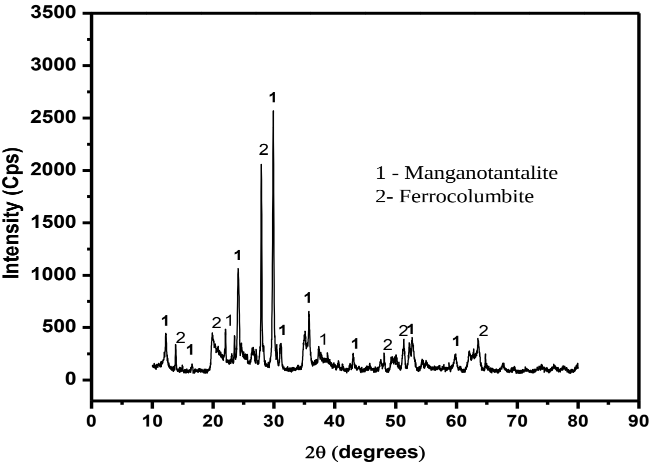
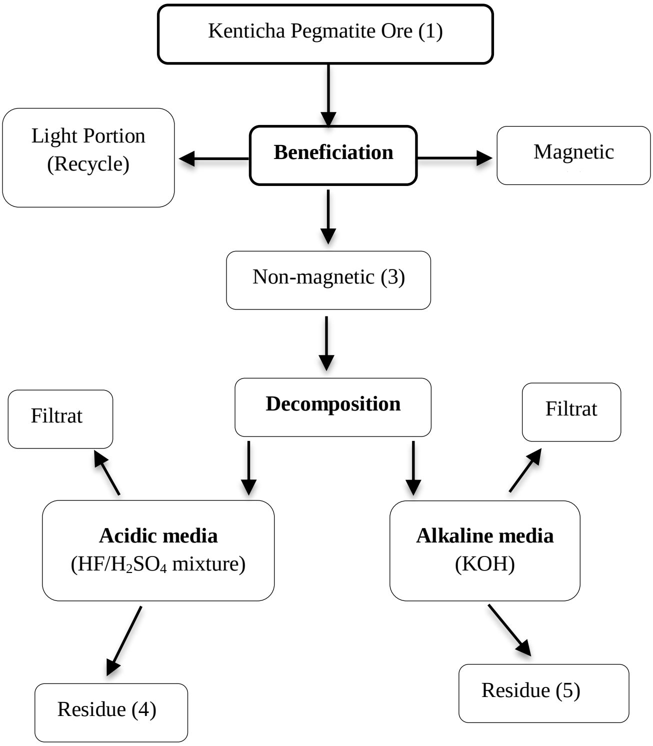


Figure 5.1 XRD pattern of the Kenticha pegmatite ore (sample 1).

5.2.2 Methods

A 10 kg Kenticha pegmatite ore (sample 1) was milled manually with mortar and pestle to obtain desired particle sizes (Table 5.1 and Fig. 5.1). This was followed by washing and decantation to reject filtrate. The residues were then treated by gravity separation using a shaking table to separate the heavy brown-black portion from the light fraction. Further beneficiation was conducted on the heavy portion by magnetic separation method. The non-magnetic fraction of the mineral was then taken for decomposition studies according to the scheme in Scheme 5.1. In order to conduct acid digestion tests at various temperature, acid and alkaline concentrations and particle sizes, 2.5 g of non-magnetic sample (sample 3) was used. Filtration was carried out following acid digestion to obtain residue (sample 4) and filtrate. The alkaline fusion steps were carried out in accordance with previously published procedure (X.-H. Wang et al., 2010). The KOH was transferred to a batch reactor using ceramic crucibles. When the desired temperature was reached, a mechanical stirrer was started and 2.5 g of tantalite (sample 3) with a known particle size distribution was added. The mixture was then placed inside a furnace, heated to 400 °C and allowed to fuse for 80 mins. The product was cooled and was then leached with 100 cm^3 de-ionized water. The filtrate and residue (sample 5) were obtained by filtration. All residues were compared by gravimetric, XRF, XRD and FT-IR analyses.



Scheme 5.1 Schematic diagram of a connected approach for the beneficiation and decomposition of Kenticha pegmatite ore.

5.3 Results and discussion

5.3.1 Beneficiation of the ore

The rate of leaching is affected by a number of parameters such as particle size, the nature of the leaching agent, temperature, agitation time and degree of acidity or alkalinity of leaching agents (Nete, Purcell, et al., 2014; X. Wang et al., 2009; Zhu & Cheng, 2011). However, prior to direct leaching repeated beneficiation of the pegmatite-spodumene ore is required to upgrade the tantalite portion (Černý & Ercit, 2005; Küster, 2009). In this study, gravity and magnetic separation methods were used to upgrade the ore and separate the magnetic and non-magnetic constituents in the ore. Fig. 5.2 shows the distribution of magnetic and non-magnetic minerals within the parent ore with respect to particle size. The magnetic and non-magnetic mass fractions shown in Fig. 5.2 were obtained from a 10 kg portion of each mesh size according to the beneficiation scheme shown in Scheme 5.1. It can be seen that higher magnetic fraction is recovered in the finer size fraction (>400 mesh) while the non-magnetic portion tends to be slightly concentrated in the coarser size fraction (<200 mesh size).

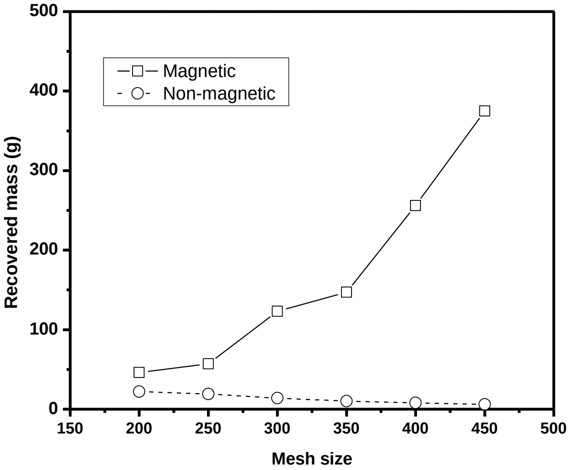


Figure 5.2 Distribution of magnetic and non-magnetic mineral fractions of pegmatite ore with particle size after beneficiation according to scheme in Fig. 5.1. Initial sample mass is 10 kg.

The XRD diffraction patterns (and dominant phases) of the magnetic and non-magnetic components of the ore concentrated Mn-tantalite and Fe-tantalite from different size fractions are shown in Fig. 5.3. The non-magnetic portion (tantalite ore) is the main subject of this study, and because it is slightly concentrated in the <200 mesh particle size range, this size range was used for further studies.

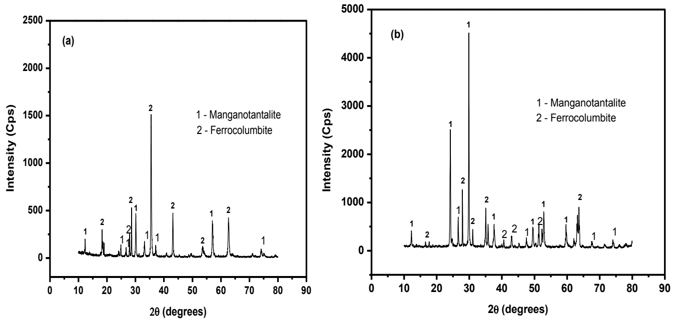


Figure 5.3 XRD diffraction of (a) magnetic (sample 2) and (b) non-magnetic (sample 3) fractions of the Kenticha pegmatite ore after magnetic separation.

5.3.1.1Effect of HF:H_2SO_4 ratio and KOH concentration on decomposition of tantalite

The effect of HF:H_2SO_4ratio and KOH concentration on the decomposition behavior and water leaching of tantalite ore was carried out in the <200 mesh particle size range. The decomposition studies were initially carried out at 400 °C and 80 mins reaction time. In high acid concentration with higher HF proportions, higher decomposition efficiency was observed (Fig. 5.4(a)). Similarly, higher KOH concentration (10 g) leads to higher decomposition as can be seen from the smallest amount of residue in Fig. 5.4(b). In addition, similar trends in decomposition rates and comparable dissolution performances between HF:H_2SO_4 and KOH were observed. The remaining small amount of residues with the use of 6:2 molar ratios of HF and H_2SO_4 and upon the addition of 10 g KOH suggests that the majority of the tantalite ore was effectively dissolved. Thus, 6:2 H to H_2SO_4 ratio and 10 g KOH were chosen for subsequent studies on the effect of time and digestion rate of tantalite ore.

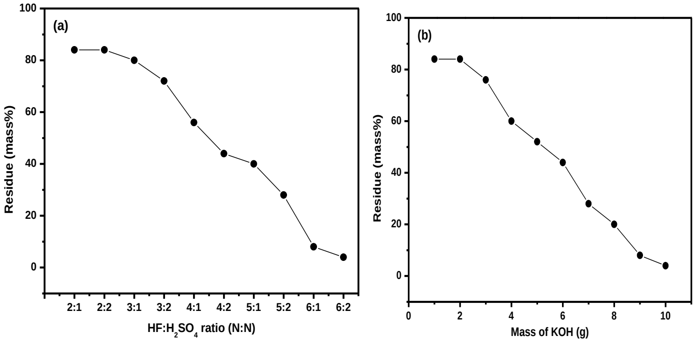


Figure 5.4 Effect of acid and alkaline concentration on the decomposition of tantalite using a) various HF:H_2SO_4ratios and b) various KOH proportions

5.3.1.2 Effect of reaction time on decomposition of tantalite

Fig. 5.5 shows the effects of time on the digestion of tantalite using HF and H_2SO_4 in 6:2 molar ratio and using alkaline fusion in 10 g KOH. It can be seen that the rate of digestion increases with time until a decomposition time of 80 mins, after which it reaches a steady state. Thus, decomposition time of 80 mins appears to be the most efficient condition for tantalite ore dissolution in both acidic and alkaline media with similar behavior for the amount of residues.

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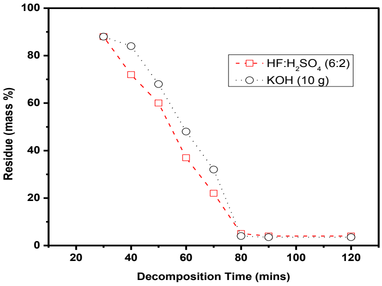

Figure 5.5 Effect of reaction time on decomposition of tantalite using 6:2molar ratio of HF to H_2SO_4 and alkaline fusion in 10 g KOH

5.3.2 Effect of temperature on tantalite dissolution

The consequence of reaction temperature on the decomposition of tantalite was studied in the range of 20 - 90 °C for HF/H_2SO_4 system and in the range of 200 - 500 °C using the KOH fusion method. A 2.5 g tantalite ore sample, 200 mesh size particle, 6:2 mole ratio for HF/H_2SO_4, 10 g KOH, 300 rpm string speed and 80 mins reaction time were used at each of the decomposition temperature investigated. Fig. 5.6(a) and (b) show that for both acidic and alkaline fusion systems, increasing the decomposition temperature initially increases the rate of dissolution of Ta and Nb.

However, increasing the decomposition temperature beyond 50 °C for HF/H_2SO_4 system did not result in significant changes in dissolution of Ta and Nb (Fig. 5.6 (a)).Similarly, no substantial change in % metal dissolution was observed upon increasing the temperature above 400 °C when using 10 g KOH as can be seen from Fig. 5.6 (b). While no significant change in % dissolution was noted for Nb between the two systems, the % dissolution of Ta in the acidic leaching agent was slightly higher than in alkaline fusion. Nevertheless, in the current experimental conditions, decomposition of tantalite ore with KOH fusion at 400 °C and with HF/H_2SO_4 mixture at 50 °C appear to be effective.

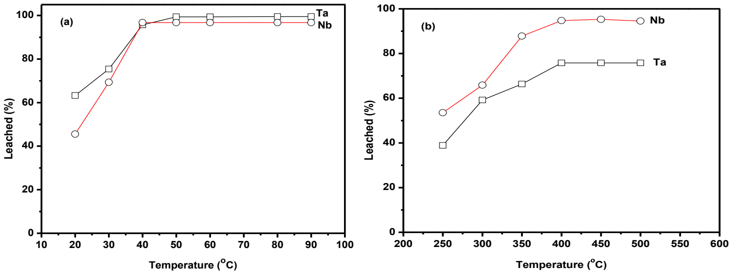

Figure 5.6 Effect of decomposition temperature on the % dissolution of Nb and Ta: (a) using 6:2 molar ratio of HF:H_2SO_4 and (b) using 10 g KOH

5.3.3 Characterization of ore and residues

The chemical composition of the both potions (magnetic and non-magnetic) of the ore, and the residues leftover after decomposition by acidic media and alkaline fusion followed by water leaching were determined using XRF, XRD and FT-IR. Table 5.2 shows that the composition of the target metals (Nb and Ta) is higher in the water leached alkaline fusion residue as compared with the residue from acidic decomposition. This implies that the acidic leaching agent (mixture of HF and H_2SO_4) would be a better option for the dissolution of Nb and Ta from Mn-tantalite. The residue of alkaline fusion had higher amount of Ta (14 wt% of Ta_2O_5) suggesting that not all of the tantalite is decomposed by alkaline fusion and water leaching.

Table 5 2 Elemental analysis of beneficiated ore, and residues after decomposition with 6:2 molar ratio of HF and H_2SO_4, and using 10 g KOH.

Sample (code)	Wt%						
	Ta_2O_5	K_2O	Nb_2O_5	TiO_2	Fe_2O_3	ThO_2	U_3O_8
Magnetic 2)	6.25	0.41	10.15	5.33	80.23	0.06	0.10
Non-magnetic 3)	55.71	0.67	5.51	0.36	4.31	0.03	0.68
Acidic residue (4)	0.23	15.56	0.01	Nd	Nd	Nd	Nd
Alkaline residue (5)	14.20	15.61	0.35	Nd	0.22	0.01	Nd

Nd – Not Detected.

The XRD spectra of the residues after alkaline fusion (sample 5) and acidic decomposition (sample 4) are shown in Fig. 5.7(a) and (b), respectively. Additionally, it can be seen that crystalline phases in the residues are different from the original ore shown in Fig. 5.1 and the non-magnetic tantalite fraction shown in Fig. 5.3(b). The main phase in the residues was attributed to $KTaO_3$ instead of $KNbO_3$. This observation is in agreement with previous studies published on the alkaline fusion related tantalite ore decomposition processes (X.-H. Wang et al., 2010; X. Wang et al., 2009).

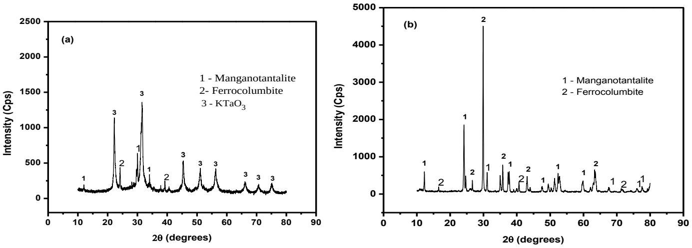

Figure 5.7 XRD spectra of leaching residues from (a) KOH fusion (sample 5) and (b) HF:H_2SO_4decomposition (sample 4)

The observations from the XRF and XRD analyses are also supported by FT-IR stretching frequencies in the range of 1665 to 655 cm^{-1} for the residues (Table 5.3) which implies differences in structure of metal oxide bonds between both residues and the tantalite ore. As indicated in Table 5.2, only 0.23 wt% Ta_2O_5 was detected in the residue after acid leaching (sample 4). Thus, the absence of stretching spectra at 721 cm^{-1} for the acid leached residue as compared with that of the tantalite ore (with 55.71 wt% Ta_2O_5) confirms the very low wt% of Ta_2O_5 in the acid leached residue. The 721 cm^{-1} stretching frequency corresponds to Ta-O bond in samples of pegmatite ore, tantalite ore and alkaline leached residue.

Table 5.3 FT-IR analysis of pegmatite ore, tantalite concentrate, and water leached residues collected following acidic decomposition and alkaline fusion.

Sample (code)	Frequency, cm^{-1}
Pegmatite ore (1)	3520 (vs); 2954 (s); 1774 (s); 1665(s); 1454 (vs); 732(vs); 657(v
Tantalite (3)	3520 (vs); 2954 (s); 1774 (s); 1665(s); 1454 (s); 721(vs); 655(v
Acidic residue (4)	3520 (w/0;2954 (s); 1774 (s); 1685(s); 1465(s); Nd; 655(w); 5
Alkaline residue (5)	3520 (vs); 2954 (s); 1774 (s); 1685(s); 1454 (s); 721(vs); 655(w

From the XRF, XRD and FT-IR analyses, it can be concluded that the residues from the acidic decomposition and alkaline fusion routes are chemically different from each other and thus each system follows a characteristic dissolution reaction.

5.4 Conclusions

In this study, the performance of HF/H_2SO_4 mixture and KOH fusion as decomposition agents for tantalite ore was investigated. The decomposition step was followed by water leaching to study the rate of dissolution of Ta and Nb. The dissolution rate was found to depend on the proportion of HF and H_2SO_4, the concentration KOH, decomposition time and temperature. The non-magnetic tantalite fraction appears to be slightly concentrated in <200 mesh particle size range. Higher ratio of HF to H_2SO_4 in the acidic system and higher KOH concentration during alkaline fusion, lead to smaller amounts of residues leftover after decomposition. Elemental and compositional analyses of the residues after leaching by water suggests that the acidic decomposition approach results in better dissolution of Nb and Ta metal ions overall compared with the alkaline fusion approach.

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6

GREEN EXTRACTION OF NIOBIUM AND TANTALUM FROM KOH FUSED TANTALITE USING IONIC LIQUID

CHAPTER 6: GREEN EXTRACTION OF NIOBIUM AND TANTALUM FROM KOH FUSED TANTALITE USING IONIC LIQUID

Abstract

The separation and extraction efficiency of Ta and Nb from KOH fused tantalite using EMIC/$AlCl_3$ *ionic liquid was investigated. The KOH fusion was carried out at 400* ^0C *and reaction time of 1 h using 5:1 KOH-to-tantalite mass ratio. Under the experimental conditions considered in this study, 27 wt% of the* Ta_2O_5 *was transformed into insoluble* $KTaO_3$ *during the KOH fusion step while the conversion of* Nb_2O_5 *into the insoluble* $KNbO_3$ *has not been observed. The extraction of both Ta and Nb from leached liquor at pH 6 using EMIC/*$AlCl_3$ *as extraction resulted in the separation of 99.23 Vol%* Nb_2O_5 *and 97.84 Vol%* Ta_2O_5*. The separation of Nb and Ta from each other resulted in the extraction of 81.46 vol% of* Nb_2O_5 *into the aqueous lower phase and 91.69 vol% of* Ta_2O_5 *into the organic upper phase. The final precipitate contained, 99.84 wt% pure crystalline* Nb_2O_5 *and an amorphous 90.81 wt% purity* Ta_2O_5*. These observations suggest that KOH fusion of tantalite followed by solvent extraction of Ta and Nb using EMIC/*$AlCl_3$ *can be considered as an environmentally friendly alternative to HF-based lixiviants and organic extracts in the hydrometallurgical processing of tantalite ore. The compositions of the dissolved metal ions and solid samples were analyzed by ICP-OES, EDXRF, XRD and FT-IR.*

Key words: Ionic liquids, tantalite ore, tantalum, niobium, solvent extraction.

6.1 Introduction

Niobium (Nb) and tantalum (Ta) are grouped VB transition metals that have attracted a high demand in recent years due to their applications in many industries(Nikishina et al., 2014; H.-m. Zhou et al., 2005). These critical and economic elements occur together in leading types of ores, such as “Coltan”, manganocolumbite, ferrocolumbite, and pyrochlore. The chemical separation of the two metals from these areas and from each other is usually challenging but feasible (Chiranjib Kumar Gupta, 2006; Nete, Purcell, et al., 2014; Zhu & Cheng, 2011). The decomposition of the host ore is the key step in the extraction of Nb and Ta from the target ore. Currently, the major hydrometallurgical process used to produce of Ta and Nb involves the use of fluorinated media and a mineral acid (Chiranjib Kumar Gupta, 2006; Nete, Purcell, et al., 2014; Zhu & Cheng, 2011). However, the fluoride solutions (F^-) are highly poisonous and a large amount of sewages is released from processing plants which pose significant environmental problems due to the high volatility (up to 7 vol%) of these wastes (X. Wang et al., 2009). In particular, the use of fluoride solutions is appropriate for only high-grade tantalite ores, and it is difficult to decompose low-grade ores by hydrofluoric acid (X. Wang et al., 2009). Other alternative processes with lower environmental impact compared with fluoride solutions have gained increasing attention recently for the production of Nb and Ta from low grade tantalite ores (Deblonde et al., 2015; G. J.-P. Deblonde et al., 2016; X.-H. Wang et al., 2010; X. Wang et al., 2009; H.-m. Zhou et al., 2005). For instance, the use of KOH sub-molten salt for leaching of low-grade refractory niobium–tantalum ores has been proposed (Nikishina et al., 2014). The decomposition of niobium–tantalum ore with KOH fusion proceeds through the following general reactions (Eq. 6.1 to Eq. 6.2)(H. Zhou et al., 2005):

$$3(Fe, Mn)O.(Ta, Nb)_2O_5 + 8KOH + (n - 4)H_2O \rightarrow K_8[(Ta, Nb)_6O_{19}.nH_2O] + 3(Fe,Mn)O \text{............Eq.6.1}$$

$$K_8[(Ta, Nb)_6O_{19}.nH_2O] \leftrightarrow 6K(Ta, Nb)O_3 + 2KOH + (n - 1)H_2O \text{.................................Eq.6.2}$$

It is important to note that the decomposition rate depends on whether the soluble $K_8[(Ta, Nb)_6O_{19}.nH_2O]$ or the insoluble $6K(Ta, Nb)O_3$ predominate in the system. The formation of these two species during the decomposing step is determined by various reaction conditions. A recent study of various reaction times, decomposition temperature, acid and alkaline concentrations, and particle size has shown that KOH fusion can be a suitable alternative decomposition agent to the volatile, corrosive and toxic HF in the hydrometallurgical processing of manganotantalite ores (Baba et al., 2007). The KOH fusion step is often followed by water leaching for the dissolution of Nb and Ta containing species. However, the beneficiation methods employed prior to KOH fusion play a key role in the removal of associated heavy minerals such as hematite, manganese oxides and rutile as well as radioactive oxides such as U_3O_8 and ThO_2(Bernstein et al., 2008; Melcher et al., 2015).

Assortments of organic solvents have been extensively studied in recent years in solvent extraction (SX) of Ta and Nb containing liquors. Examples include methyl iso-butyl ketone, tri-butyl phosphate, cyclohexanone, and 2-Octanol (Amuda et al., 2007; Chiranjib Kumar Gupta, 2006) and high molecular weight amines (O. M. El-Hussaini & Mahdy, 2002). Comparatively, due to its solubility, selectivity and stability methyl iso-butyl ketone is the most commonly used worldwide (Zhu & Cheng, 2011). Ionic liquids (ILs) or the so-called “green solvents” can be considered as suitable alternatives for SX of Ta and Nb as they possess very low vapor pressure, versatility, and high capacity for separating organics and metal ions from aqueous phases. The potential benefits of ILs in the recovery of metal ions have been summarized in a number of reviews elsewhere(Hirayama et al., 2005; Huddleston et al., 1998; Li et al., 2007; Wei et al., 2003; Zhao et al., 2005).

Further studies on the separation and determination of Nb and Ta are required regarding efficiency, selectivity and sensitivity. This study aims to demonstrate the feasibility of using 1-ethyl-3-methyl imidazolium chloride (EMIC) as an extracting phase following the decomposition of tantalite ore by KOH fusion. Metal extraction was performed by varying acid concentration with constant mass of EMIC in the presence of a Lewis acid ($AlCl_3$) in the KOH feed solution. The separation and purification of Nb and Ta from other metal ion impurities in ILs are investigated with the aim further prospective development (Roeper et al., 2013; Zhou et al., 2012). To the best of the authors’ knowledge, there is no previous study on the separation of Ta and Nb from dissolved alkaline solutions. In addition, there still exists a lack of quantitative data on the solubility, separation and precipitation of the Ta and Nb from low grade ores.

6.2 Experimental

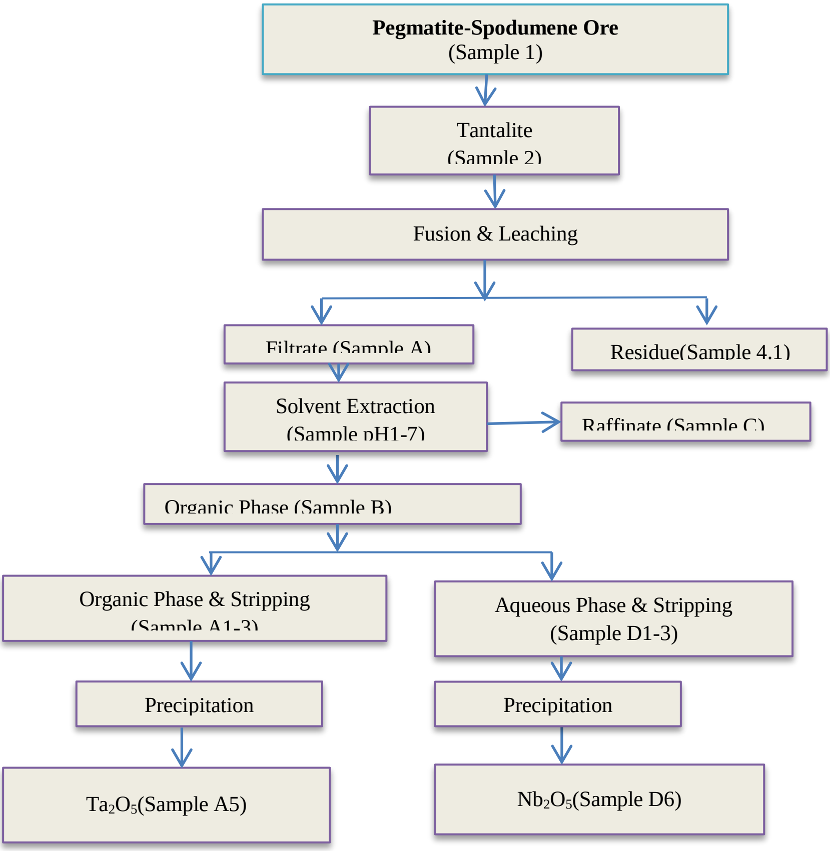
6.2.1 Materials

The sample ore was obtained from the Kenticha tantalum mine in the regional state of Oromia, Ethiopia. The mineralogical purity of the ore was investigated using X-ray Diffractometer (Shimadzu) with Cu anode. The resulting spectra were interpreted using Diamond (Version 4.2.2), and Match (Version 3.2.2) with COD reference database. An Energy Dispersive X-ray Fluorescence (EDXRF 2800) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) from PerkinElmer were used for elemental analysis of the mineral ores. High temperature furnace was used for calcination in order to decompose associated oxides and Shimaduzu FTIR-8400S spectrophotometer in KBr was used to support the presence or absence the Nb/Ta oxygen bond frequency. The particle size was analyzed using standard mesh sieves (No 72 PAT). Solution pH measurements were performed with a pH-meter (827) and calibrated with standards at pH 4 – 9. The dissolution process was carried out in high temperature furnace at 400 °C temperature inside the stainless batch reactor (SUS316). Analytical grade EMIC, H_2SO_4 and KOH (Sigma-Aldrich) without further purification, and de-ionized were used in this study. The EMIC/$AlCl_3$ was prepared in accordance procedure reported elsewhere (Roeper et al., 2013).

6.2.2 Methods

A schematic representation of the fusion, separation, precipitation and calcination procedures used in this study is given in Scheme 6.1. The tantalite was obtained by beneficiation of pegmatite-Spodumene ore (sample 1) based on previously developed procedure (Bernstein et al., 2008). The alkaline fusion steps were carried out in accordance with previously published studies(Berhe et al.; X. Wang et al., 2009). A given mass of KOH and tantalite ore (sample 2) was used to obtain a mass ratio of 5:1. The mixture was placed inside a furnace, heated to 400 °C at the constant stirring speed at atmospheric pressure and allowed to fuse for one hour. The product was then cooled to room temperature and leached with 100 ml de-ionized water. The filtrate (sample A) was transferred to another 100 ml volumetric flask while the residue (sample B) obtained upon filtration was washed with de-ionized water. The chemical composition of the residues was analyzed by EDXRF and FT-IR analyses. The concentrations of Nb and Ta in the filtrates were determined by ICP-OES.

The solvent extraction process was carried out in accordance works of El.-Husaini and El-Hazek (El-Hazek et al., 2012; O. El-Hussaini, 1996)with the following procedure. A 50/70 ml filtrate solution (sample A) was neutralized using H_2SO_4 to obtain solutions with pH values of 1 – 7. Then, 10 ml of the neutralized filtrate was mixed with 2 g of EMIC/$AlCl_3$ by shaking for 30 minutes in an atmosphere dry box. The organic phase (sample D) was separated using separatory funnel and the raffinate (sample C) was stored for further study. Bi-phases were obtained upon adding 6 N H_2SO_4 and 2 g EMIC/$AlCl_3$ into the organic phase, which was then separated into the aqueous phase (sample D1) and organic phase (sample A1). Stripping of the aqueous and organic were conducted by adding 2 N H_2SO_4 and deionized water (labeled as sample D2 and A2), respectively. Stripping was repeated again to obtain D3 and A3. Both stripped phases were precipitated by adding 30% ammonia solution. The precipitates were then dried in an oven for 3 days at 100 °C and calcined in a furnace at 1,200 °C for an hour to obtain sample D6 and sample A5. The concentrations of dissolved Nb and Ta were analyzed for by ICP-OES while the calcined solids were analyzed by EDXRF.



Scheme 6.1 Systematic process of fusion, extraction, stripping and precipitation of tantalite.

6.3. Results and Discussion

6.3.1 KOH fusion and leaching of tantalite ore

Prior to SX by the EMIC/$AlCl_3$, the molten KOH fusion was applied for the decomposition of the tantalite ore. The decomposition rate has been found to depend on a number variables, including particle size, alkaline-to-tantalite ratio, reaction time and temperature (Berhe et al.; X. Wang et al., 2009; Zhao et al., 2005).

Based on the optimum conditions obtained in previous studies by the authors, the KOH fusion was done at a particle of 5:1, reaction time of 80 mins, and decomposition temperature of 400°C at 330 rpm stirring speed. Analysis of the residue remaining after leaching by de-ionized water showed the presence of insoluble $KTaO_3$ and $KNbO_3$, and soluble K_3NbO_4 and K_3TaO_4 which may have formed according to reactions 3 and 4, respectively. Other impurities such as K_2SiO_3, K_2SnO_3, $KFeO_2$, K_2MnO_3, and K_2TiO_3 were also found which is in agreement with similar studies (X. Wang et al., 2009) (Eq.6.3 to Eq. 6.4).

$6K_3(Ta,Nb)O_4 + (5+n)H_2O \leftrightarrow 6K(Ta, Nb)O_3 + 12KOH + (n - 1)H_2O$……………………Eq.6.3

$(Fe,Mn)O.(Ta,Nb)_2O_5 + 6KOH \leftrightarrow 2K_3(Ta,Nb)O_4 + (Fe,Mn)O + 3H_2O$…………………....Eq.6.4

Table 6.1 shows the EDXRF analysis of the host pegmatite ore (sample 1), the beneficiated tantalite before KOH fusion (sample 2) and residue after KOH fusion and water leaching (sample B). From the results, it can be seen that the sample B contains significant amounts of undissolved Ta_2O_5 (15.22 weight %) while the Nb_2O_5 has been dissolved with only a little fraction remaining in residue. In comparison with the initial concentrations, 72.68% wt% and 88.39 wt% Ta_2O_5 and Nb_2O_5 were leached in the dissolved solution, respectively, when using a mole ratio of 5:1 of KOH-to-tantalite in the fusion process. The essence of the fusion was to facilitate the leaching of tantalum and niobium, which will then be separated from the aqueous bi-phase.

Table 6.1 Chemical analysis of host pegmatite ore (sample 1), the beneficiated tantalite before KOH fusion (sample 2) and residue after KOH fusion and water leaching (sample B).

Sample code	wt%			
	Ta_2O_5	Nb_2O_5	TiO_2	Fe_2O_3
1	2.32	0.45	3.56	25.54
2	55.71	5.51	0.36	4.31
B	15.22	0.64	Nd	Nd

It is known that increasing the temperature in the alkaline fusion process increases the dissolution of target metal ions as well as impurity metal ions due to the increase in the rate of decomposition of the ore(Berhe et al.). The major oxide species in the leached liquor (sample A) with respect to fusion temperature are given in Table 6.2. It is evident that increasing the decomposition temperature initially increased the rate of dissolution of both Ta and Nb. However, no significant change metal dissolution was observed upon increasing the temperature above 400 °C. In addition, it can be seen from Table 6.2 that the decomposition and leaching efficiency of Nb oxide was higher than that of Ta oxide in the temperature range investigated. This suggests that the KOH fusion and water leaching may be more effective in the separation of Nb ions from high grade tantalite ore than for the ions.

Table 6.2 Major oxide composition of the alkaline fused filtrate obtained at various fusion temperatures.

Fusion Temperature, ^{0}C	Vol%			
	Ta_2O_5	Nb_2O_5	TiO_2	Fe_2O_3
250	21.67	2.95	4.31	3.31
300	32.98	3.63	4.81	3.40
400	42.23	5.22	5.20	5.11
500	42.24	5.21	5.33	5.10

6.3.2 Analyses of residue after KOH fusion and leaching

The composition of the residue (sample B) leftover after alkaline fusion and water leaching was analyzed usingXRD and FT-IR. Figure 6.1 shows that the XRD diffraction patterns obtained for sample B show different patterns as compared with the tantalite concentrate (sample 2). In particular, sample B contains $KTaO_3$ specieswhich is in agreement with previous studies on the alkaline fusion processes of tantalite ores (X.-H. Wang et al., 2010). This indicates that besides converting into soluble K_3TaO_4, a fraction of tantalum is directly converted into insoluble $KTaO_3$ in the KOH decomposition procedure which consequently leads to low dissolution rate of Ta_2O_5 during leaching.

A comparison between the FT-IR spectra of pegmatite ore (sample 1), tantalite concentrate (sample 2) and KOH fusion residue (sample B) shown in Figure 6.2 reveal similar stretching frequencies in the region of 1500 to 3600 cm^{-1} . This suggests the possibility of the presence of similar oxide types in all samples. However, the compounds formed during the KOH fusion step are chemically and structurally different as can be seen from the differences in stretching frequency of Nb_2O_5 at about 1483 cm^{-1} in samples 1, 2 and B. The absence of Nb-O stretching corresponding to Nb_2O_5 in the residue (B) which is in agreement with XRD diffraction patterns of sample B shown in Figure 6.1. The presence of stretching frequencies at 555, 655 and 721 cm^{-1} in are attributed to the Nb-O and Ta-O bonds.

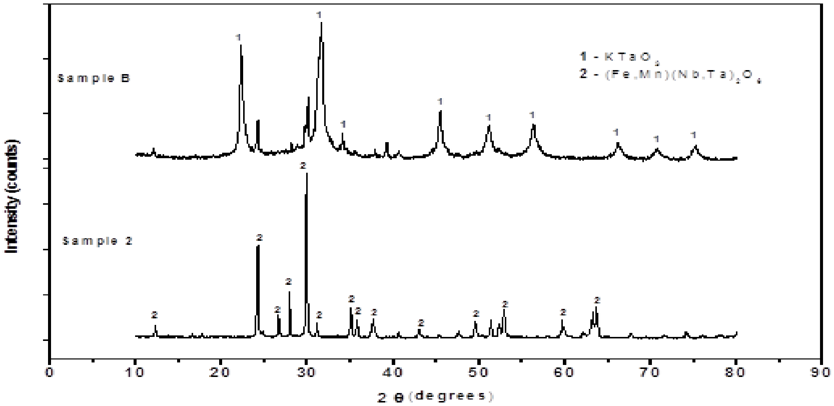


Figure 6.1 XRD spectra of tantalite concentrate (sample 2) and residue (sample B) obtained after alkaline fusion and leaching.

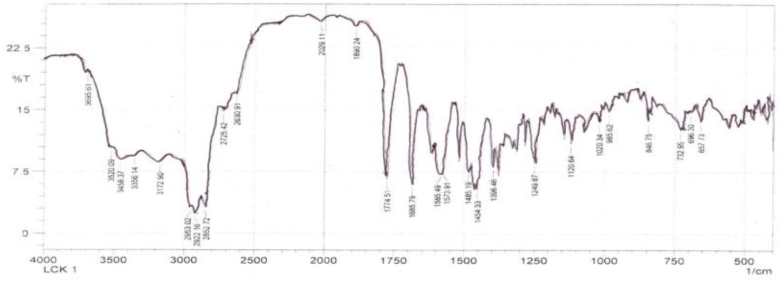
Table 6.3FT-IR result of solid sample

Sample code	Frequency (cm^{-1})
1	3520(vs); 2954(s); 1774(s); 1665(s); 1454(vs); 732(vs); 657(vs), 555(w)
2	3520(vs); 2954(s); 1774(s); 1665(s); 1454(s) 721(vs); 655(vs); 555(vs)
B	3520(vs); 2954(s); 1774(s); 1685(s); 1454(s); 721(vs); 655(w); 555(vs)

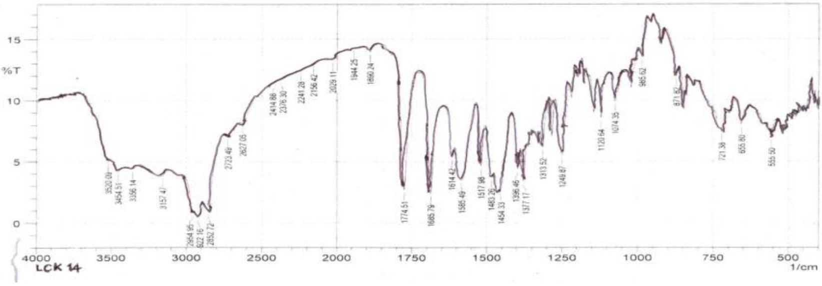
6.3.3 Solvent Extraction of Nb and Ta from KOH fused solution

6.3.3.1 Separation and precipitation

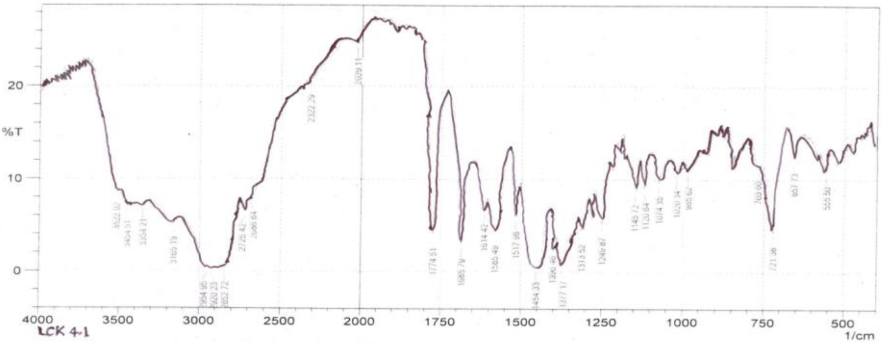
In order to ensure the soluble $K_8[(Ta, Nb)_6O_{19}.nH_2O]$ was formed during the KOH fusion step instead of the insoluble $6K(Ta, Nb)O_3$ according to equations 3 or 4, it was essential that the fusion was done in excess KOH (H. Zhou et al., 2005). The alkaline Nb or Ta solutions obtained from the leaching of the KOH fusion product were neutralized by the addition of 6 N H_2SO_4 to obtain solutions with pH of 1 – 7. Acidification with H_2SO_4 also helps to produce a purified Nb-Ta hydrous oxide, $(Nb,Ta)_2O_5.nH_2O$ (Gauthier Deblonde, 2016). For better extraction of both elements, collective extraction can be done by adding EMIC/$AlCl_3$ to the feed solution (sample A) to recover both elements in the upper phase (UP) while other impurities are rejected to the lower phase (LP). In order to determine the optimum pH conditions for an efficient bi-phase separation, the composition of the UP was analyzed at various pH as shown in Figure 6.3. It can be seen from Figure 6.3 that pH 6 is suitable for bi-phase separation of Nb_2O_5 and Ta_2O_5 from UP. In comparison with the concentrations of Nb_2O_5 and Ta_2O_5 in the filtrate (sample A), 99.23-



a) Sample 1



b) Sample 2



c) Sample B

Figure 6.2 FT-IR spectra of pegmatite ore a) (sample 1), b) tantalite concentrate (sample 2), and c) KOH fusion residue (sample B) following water leaching.

-vol% Nb_2O_5 and 97.84 vol% Ta_2O_5 have been recovered into the organic phase (sample D) as shown in Table 6.4. This high dissolution of Nb and Ta ions at pH 6 may be due to the mineralogical composition of the pegmatite ore and the product formed by excess KOH fusion. The possible mechanism for the extraction of fused tantalite with EMIC/$AlCl_3$ is shown in Eq. 6.5 to Eq. 6.7 (Amarasekara, 2016).

$EMIM^+Cl^- + AlCl_3 \leftrightarrow EMIC^+[AlCl_4]^-$ ……………………………………..……......Eq.6.5

$EMIM^+[AlCl_4]^- + AlCl_3 \leftrightarrow EMIM^+[Al_2Cl_7]^-$……………………………………….Eq.6.6

$\mathrm{Ta/Nb}^{m+}_{(w)} + m_{(0)} + m[EMIM^+[Al_2Cl_7]^-]_{(0)} \leftrightarrow \mathrm{Ta/Nb}^{m+}_{m(0)} + m[EMIM^+[Al_2Cl_7]^-]_{(w)}$ …Eq.6.7

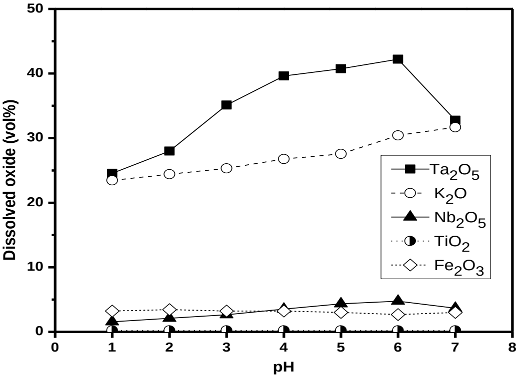


Figure 6.3 Effect of pH on the composition of UP after SX of leached liquor with EMIC/$AlCl_3$

The second stage of extraction involves the separation of Ta and Nb from each other. In order to achieve this objective, 6 N H_2SO_4 and 2 g EMIC/$AlCl_3$ was added to the organic phase (sample D) which was then separated into the aqueous phase (D1) and organic phase (A1). As shown in Table 6.3, the aqueous LP is composed of 4.22% Nb_2O_5 (81.46 vol% of Nb_2O_5 in sample D) while the organic UP contained 37.89 vol % Ta_2O_5 (91.69 vol% of the total Ta_2O_5 in sample D). Stripping the Nb and Ta loaded liquor with 2 N H_2SO_4 and double distilled water resulted in the removal of 99 Vol% Nb and 96.51 Vol% Ta ions from the LP and UP solutions. The extraction efficiencies of Nb ion from the feed solutions obtained in this study is higher, higher in comparison with fluoride based leaching and organic phase extraction methods reported in the literature (El-Hazek et al., 2012; O. M. El-Hussaini & Mahdy, 2002; Nete, Koko, et al., 2014; Stevenson & Hicks, 1953) These results suggest that alkaline fusion followed by leaching and ionic liquid extraction is more efficient for extraction of Nb as compared with Ta.

Table 6.4Chemical analysis of filtrate before SX (A), UP after SX (D), LP and UP after second stage SX and stripped solutions of aqueous and organic phases.

Sample code	vol%			
	Ta_2O_5	Nb_2O_5	TiO_2	Fe_2O_3
A	42.23	5.22	5.20	5.11
B	41.32	5.18	1.09	3.78
D1	0.01	4.22	0.00	0.00
D2	0.01	0.23	0.00	0.00
D3	0.01	0.02	0.00	0.00
A1	37.89	0.41	1.10	1.56
A2	1.13	0.02	0.11	1.23
A3	0.29	0.01	0.11	1.01

The strip solutions containing Nb and Ta were directed to precipitation by adding 30 vol% ammonia solution at pH 9. The precipitates of Nb and Ta were filtered, dried and calcined to obtain sample D4 and sample A4, which are composed of 99.84 wt% Nb_2O_5 and 90.81 wt% Ta_2O_5, respectively, as shown in Table 6.5.

Table 6.5 analysis of Nb_2O_5 and Ta_2O_5 precipitate obtained by ammonia addition

Sample code	wt%			
	Ta_2O_5	Nb_2O_5	TiO_2	Fe_2O_3
D4	0.01	99.84	0.00	0.00
A4	90.81	3.05	0.00	0.53

6.3.3.2 Characterization of Nb_2O_5 and Ta_2O_5 precipitate

Figure 6.4, presents XRD spectra of Ta_2O_5 (sample A4) and Nb_2O_5 (sample D4) after precipitation. The spectrum of Ta_2O_5 reveals its non-crystalline nature. This may be due to the presence of other metal oxides or impurities in the Ta_2O_5 precipitate as Ta_2O_5 is<91 wt%. By contrast, XRD analysis of the Nb_2O_5 precipitate suggests that it exhibits totally crystalline behavior (and 99 wt% Nb_2O_5 purity).

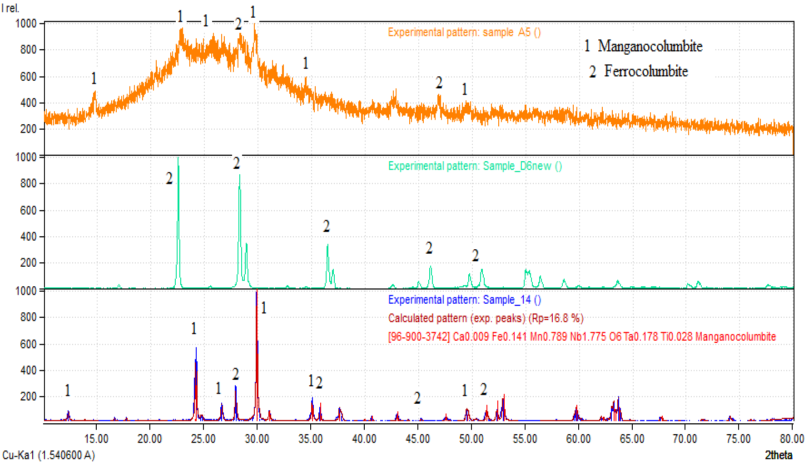
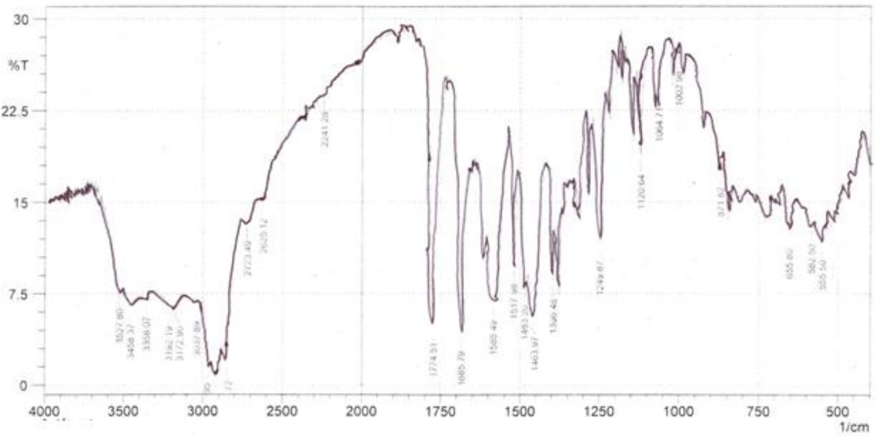
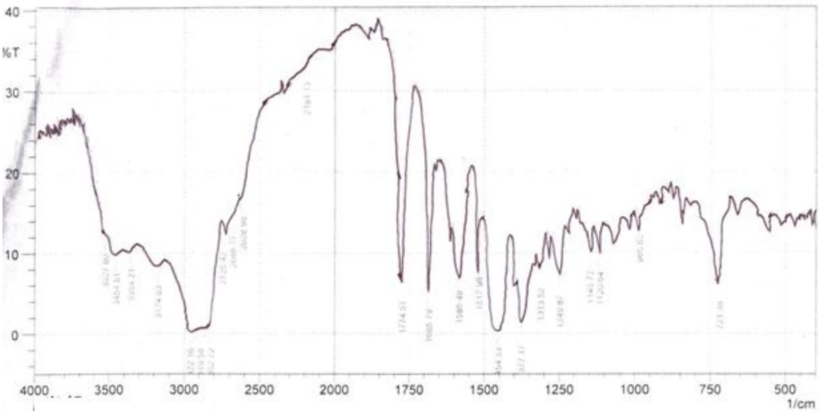


Figure 6.4 XRD spectra of Ta_2O_5 (sample A4) and Nb_2O_5 (sample D4) precipitate in comparison with the tantalite concentrate (sample 2).

It can be seen from the FI-IR stretching frequencies of Ta_2O_5 (sample A4) and Nb_2O_5 (sample D4) shown in Table 6.6/Figure 6.5 (a, b) that the region of 1500 to 3600 cm^{-1} are mostly similar with each other, and comparable with that of the tantalite concentrate (Fig. 6.2b). The strong stretching frequencies at 555 to 721 cm^{-1} and at 800 to 1000 cm^{-1} for the vibrations of M-O-M bridges and M-O bond of the metal oxide, respectively, are similar other studies indicating a possible frequency of tantalate and niobate oxides (Deblonde et al., 2015; G. J. Deblonde et al., 2016). The characteristic stretching frequencies observed at 1463 cm^{-1}, 655 cm^{-1} and 555 cm^{-1} in D4 is attributed to the presence of Nb-O bending deformation and Nb-O stretching frequencies in Nb_2O_5. The very clear stretching frequencies in the 1,500 to 1,000 cm^{-1} region shows that there is a homogeneous distribution of Nb_2O_5 in sample D4. The presence of stretching frequency at 721 cm^{-1} in A4 is attributed to the Ta-O stretching in Ta_2O_5.



a) Sample D4



b) Sample A4

Figure 6.5 FT-IR spectra of precipitates ofa) Nb_2O_5 (sample D4) and b) Ta_2O_5 (sample A4).

Table 6.6FT-IR result of solid sample

Sample code	Frequency (cm^{-1})
2	3520 (vs); 2954 (s); 1774 (s); 1665(s); 1454 (s) 721(vs); 655(vs); 555(vs)
D4	3520 (vs); 2954 (s); 1774 (s); 1685(s); 1463(s); 655(w); 555(s)
A4	3520 (vs); 2954 (s); 1774 (s); 1685(s); 1454(s); 721(s)

6.4 Conclusions

1. This study shows that KOH fusion of tantalite followed by solvent extraction of Ta and Nb using EMIC/$AlCl_3$ can be considered as a suitable alternative to HF-based lixiviants and organic extracts in the hydrometallurgical processing of low grade tantalite ores.
2. The extraction efficiency of EMIC/$AlCl_3$ for Nb and Ta from KOH fusion is dependent on the pH of leached liquor and the highest separation of Nb than Ta was achieved at pH 6.
3. In comparison with the pregnant solution, extraction efficiencies of 81.46 vol% of Nb_2O_5 and 91.69 vol% of Ta_2O_5 were achieved using EMIC/$AlCl_3$ as extractant.
4. Precipitation of the stripped solutions with 30% ammonia solution resulted in crystalline Nb_2O_5 (99.84 wt%) and amorphous Ta_2O_5 (90.81 wt%) as final products.
5. Further kinetics and thermodynamic studies and state-of-the-art research are required to realize the application of ionic liquids as Nb and Ta extracting agents. Their application in real water systems is still limited due to the lack of basic knowledge regarding their stability, solubility and metal-uptake mechanisms.

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7

GENERAL CONCLUSIONS, STRENGTHS AND LIMITATIONS, AND RECOMMENDATIONS

CHAPTER 7: GENERAL CONCLUSIONS, STRENGTHS AND LIMITATIONS, AND RECOMMENDATIONS

7.1 Conclusion

In this study, the primary beneficiation, decomposition and separation methods of Kenticha pegmatite–spodumene ore were examined. The results led to the following conclusions:

In **chapter 4**, Ethiopian Kenticha pegmatite–spodumene beneficiates relatively easily with gravity and magnetic separation techniques, producing high-grade Ta and Nb oxide concentrates. The upper geographical zone of the deposit resulted in better quality tantalite concentrate as compared with the 20-m-deeper zone. Beneficiation of the mixture of pegmatite–spodumene ore with the residues has shown the best alternative approach for the highest grade of tantalite ore over the primary beneficiation of pegmatite ore. When the tantalite concentrate was washed using 1 M H_2SO_4, high yields of Nb_2O_5 with low levels of Th and U are obtained; by contrast, washing with 1 vol% KOH resulted in the highest level of Ta_2O_5, with almost no oxides of Th and U present. The EDXRF analysis of the magnetic fraction of tantalite concentrate indicated a low content of Th and U. The study of Kenticha pegmatite–Spodumene ore using EDXRF and XRD has shown that the Ethiopian tantalum ores are of high-grade. Therefore, it can be subjected to direct processing for tantalum and niobium products without the need for complicated and costly concentration procedures. Knowledge of the presence of deficient concentrations of radioactive oxides in the samples would assist in the design of suitable beneficiation and extraction rates for similar deposits in Ethiopia.

In **chapter 5,** the performance of HF/H_2SO_4 mixture and KOH fusion as decomposition agents for tantalite ore was investigated. The decomposition step was followed by water leaching to study the rate of dissolution of Ta and Nb. The dissolution rate was found to depend on the proportion of HF and H_2SO_4, the concentration KOH, decomposition time and temperature. The non-magnetic tantalite fraction was appeared slightly concentrated in <200 mesh particle size range. A higher ratio of HF to H_2SO_4 in the acidic system and higher KOH concentration during the alkaline fusion lead to smaller amounts of residues left over after decomposition. Elemental and compositional analysis of the residues after leaching by water suggests that the acidic decomposition approach results in better dissolution of Nb and Ta metal ions overall compared with the alkaline fusion approach.

In **chapter 6** of this study confirms that alkaline fusion was used as an alternative to fluoride media in the extraction and separation of Nb and Ta as GREEN and new process. The dissolution of tantalite in KOH fusion and H_2O leaching is reacted at 400 ^{0}C for one h, 15.22 wt% of Ta_2O_5 converted into insoluble $KTaO_3$, and around 94 vol% of Nb_2O_5 and 75 vol% of Ta_2O_5 are dissolved for beneficial solvent extraction processes. The ability of extraction using EMIC/$AlCl_{3,}$ IL for Nb and Ta from KOH fusion is dependent on the neutralization pH, and highest separation of Nb than Ta was achieved at pH 6. The extraction improved considerably with the introduction of sulfuric acid and water into the feed solution. For nearly complete removal of tantalum and niobium with IL as green extraction and recovery of 99.84 weight% Nb_2O_5 and 90.81wt%, Ta_2O_5 was attained by precipitation and calcination from the strip solution. That alkaline fusion is a robust approach for solvent extraction of niobium than tantalum from high-grade tantalite ore. However, considering the state of the art of EMIC/ $AlCl_3$ ionic liquids as Nb and Ta extracting agents, their application in real water systems is still limited to basic knowledge regarding their stability, solubility and metal-uptake mechanism.

7.2 Strengths and Limitations of the study

This PhD dissertation gave an alternative beneficiation to Li bearing and radioactive oxide containing Kenticha pegmatite ore, alternative and green decomposition of the enriched tantalite ore and green and novel separation method of niobium and tantalum from the dissolved tantalite ore.

In order to conduct such laboratory research an updated scientific laboratory instruments and facilities in Jimma and as well in the country are required. However, it was tried to offset the short comings in facilities by conducting the research at different governmental and non-governmental research laboratories.Despite the lack of the necessary laboratory facilities it was able to produce two publications and one accepted papers in the web of sciences.

In this strength and limitation, an assessment of the present study in addressing the initial project aimwas addressed. The objectives were mainly accomplished as revealed by the results obtained in **Chapters 4 to 6**.

The results in **Article I ofChapter 4** the mineralogy composition of Kenticha ore needs to beneficiate primary before further decomposition and extraction processes of **Chapter 5** and **6**, respectively. The presence of radioactive elements such as Th and U in Kenticha tantalite complicates the transportation, handling, and processing of concentrating. Acid and alkaline washing were employed to assess the extent of removal of radioactive elements from tantalite concentrates. The remaining enriched ores were washed by usinglow concentrations of acid and caustic the chemical composition of the samples were analyzed. According to the grade of Tantalum-Niobium International Study Center, such ores are considered to have excellent grades of tantalum. Therefore, it is advisable to wash the tantalite concentrate using dilute KOH to increase the percent of Ta_2O_5 before further extraction and to reduce the number of radioactive elements. The beneficiation and washing procedures carried out in this study produce tantalite concentrates of acceptable quality that meet the essential requirements for safe handling, transportation, and storage. However, in this study due to unavailability of electronic microscopies such as SEM and TEM, the grain sizes of Kenticha ore and concentrated tantalite ores were not studied.

In Article II of chapter 5, this study also shows that breakdown of the tantalite ore using acidic and alkaline media in various parameters such as; particle size, the nature of solvent, temperature and agitation time. The particle size affects significantly for the decomposition of tantalite ore in various ranges of concentration ratio, and the higher rate of HF to H_2SO_4 and grams of KOH in 1 g of tantalite resulted in a minimum mass of residue and most percent's of Ta and almost all Nb are dissolved. Therefore, decomposition using KOH is a better alternative by replacing the use of HF for environmental reason. Because the volatility of HF in decomposition step the alkaline fusion is the better alternative with higher content of $KTaO_3$ in the residue. However, in this study due to unavailability of instruments, electronic microscopy and kinetic and thermodynamics effect of Kenticha ore and concentrated tantalite ores were not studied.

In Article III of chapter 6, this study confirms that alkaline fusion was used as an alternative to fluoride media in the extraction and separation of Nb and Ta as GREEN and new process. The dissolution of tantalite in KOH fusion and H_2O leaching was reacted at 400 ^{0}C temperature, and around 94 vol% of Nb_2O_5 and 75 vol% of Ta_2O_5 was dissolved and for beneficial solvent extraction processes compared the composition of rich tantalite in **Chapter 4**. The ability of solvent extraction using EMIC/$AlCl_3$ ionic liquid as replacement of organic extractants for Nb and Ta from KOH fusion was dependent on the neutralization pH. Highest separation of Nb than Ta was achieved at pH 6, and also shown that recovery of 99.84 wt% Nb_2O_5 and 90.81 wt% Ta_2O_5 were attained by precipitation and calcination from the strip solution as compared with the percent of dissolved of tantalite ore using KOH in **Chapter 5**. That alkaline fusion is powerful approach for solvent extraction of niobium than tantalum from high-grade tantalite ore. However, the consumption of large quantities of water for neutralization presents the high costof recovering Nb and Ta from alkaline solutions. Therefore, new methods for precipitating these valuable metals in alkaline pH need to be developed, and the development of further works on the loading, kinetics, and thermodynamics of solubility, scrubbing and increasing the purity of Ta_2O_5 is required. Moreover, considering the state of the art of EMIC/$AlCl_3$ ionic liquids as Nb and Ta extracting agents, their application in real water systems is still limited to basic knowledge regarding their stability, solubility and metal-uptake mechanism and the recovery of the solvents such as ionic liquids and waters are still requires further recycling methods and instruments.

The success of the study is further underlined by the characterization and isolation of the main elements as relatively pure products after successive beneficiation, decomposition, separation, stripping and precipitation processes from the Kenticha pegmatite-spodumene ore.

This study thinks the strengths, based on the scientific contributions, could be:

1) General, specific objectives, research tasks and scientific hypothesis were 100 % completed using consistent and systematic scientific approach, advanced characterization techniques and new generation Lab equipment’s to conduct and validate test results at the highest accuracy.

2) An alternative scientific local solution using “green technology” approach and feasible to be implemented in Ethiopian context, was investigated and proved at laboratory scale for the hydromel

3) Metallurgical processing of niobium and tantalum from Ethiopian Kenticha pegmatite;

4) The establishment and validation of a new technology to replace hydrofluoric acid as leaching agent of tantalite by alkaline salts was produced, what is, at the same time, our first new scientific contribution;

5) The viability to replace the petroleum derived solvents by new “environmental friendly” solvents using ionic liquids from high grade ores is confirmed, what is our second new scientific contribution;

6) The minimization of wastes production by process integration and added value sub-products recovery -what is also a new technological contribution- was not totally accomplished. However, the recycling processes have been to recover by green processes.

7.3 Recommendations

The following recommendations are suggested for further investigations which could help the beneficiation, decomposition and separation of niobium and tantalum from Ethiopian pegmatite ore by KOH fusion agent and an extractant EMIC/$AlCl_3$, ionic liquid system to be used efficiently.

Initially, in the beneficiation experiments, the deposited impurity is stated as light and magnetic ores separated by decantation, shaking tables, gravity and magnetic separation from the tantalite ores could be better to undertake investigations other valuable metals from tails.

In the decomposition of tantalite ore experiments, the residues and 15.22 weight% of $Ta_2O_5$from the residue could be better to undertake investigations other valuable metal oxides from residues.

In the solvent extraction experiments, the dissolved metal ions in the aqueous phase, the huge amounts of water in neutralization producer and impurity involved in the produced 90.81wt% Ta_2O_5 could be better to undertake investigations other valuable metals from dissolved metal ions. Also, further processing is necessary in order to produce a high purity tantalum and niobium pentoxide suitable for electronics industries for manufacturing capacitors, superconductivity and other specific applications.

Considering the state of the art of EMIC/$AlCl_3$ ionic liquids as Nb and Ta extracting agents, their application and recovery in real water systems is still limited to basic knowledge regarding their stability, solubility and metal-uptake mechanism. Therefore, further knowledge and alternative ionic liquids as extractants and salting-out agents are necessary in order to produce very highly pure tantalum and niobium pentoxide. Further recycling process is necessary in order to manage the cost of ionic liquid.

Considering, managements of chemicals and environmental concern could be better to undertake investigations in recycling and handling of untargeted dissolved metal ions and residues, which was considering as impurity and to produce efficient separation, recycling and handling in convenient manner.

Considering checking the validity of the methodology of the study further investigation on alkaline fusion and solvent extraction of niobium and tantalum from African tantalite and capacitor scraps will be required.

Finally, the Ethiopian government through appropriate authority shouldconsider an industrial scale alternative green methods of processing of tantalite ore such as this study into valuable and economical metals and other mineral deposits to maximize economic benefits.This is in line with the government policy for value addition, safe guarding the environments, practical industry university linkages and building capacity and skills of scientists and professionals in the field of metallurgy.

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