# CHARACTERIZATION & SEPARATION OF TUNGSTEN IN CASSITERITE (TIN MIDDLING) FROM BUKIT KACHI MINE

# MUHAMMAD DANIAL HAZIQ BIN NOR ASIM

# UNIVERSITI SAINS MALAYSIA

2022

# SCHOOL OF MATERIALS AND MINERALS RESOURCES ENGINEERING

# **UNIVERSITI SAINS MALAYSIA**

# CHARACTERIZATION & SEPARATION OF TUNGSTEN IN CASSITERITE (TIN MIDDDLING) FROM BUKIT KACHI MINE

By

## MUHAMMAD DANIAL HAZIQ BIN NOR ASIM

## Supervisor: Assoc. Prof. Dr. Hashim bin Hussin

Dissertation submitted in partial fulfilment of the requirements for the degree of Bachelor of Engineering with Honours (Mineral Resources Engineering)

Universiti Sains Malaysia

# AUGUST 2022

### DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "Characterization and Separation of Tungsten in Cassiterite from Bukit Kachi Mine". I also declare that it has not been previously submitted for the award of any degree nor diploma or other similar titlr of this for any other examining body or University.

Name of Student: Muhammad Danial Haziq Bin Nor AsimSignature:Date:  $16^{th}$  August 2022

Witnessed by:

Name of Supervisor : Assoc. Prof. Dr. Hashim bin Hussin Signature:

Date  $: 16^{th}$  August 2022

#### ACKNOWLEDGEMENT

Let me begin by expressing my special thanks to my supervisor, Assoc. Prof. Dr. Hashim bin Hussin for his guidance, encouragement, and support. His time, effort, and knowledge allowed me to finish this project, and I cannot thank him enough for his assistance.

In addition, I would like to thank the engineers from Bukit Kachi Mine, Mr. Hafiz and Mr. Muaz provided samples for this research. I am extremely grateful to the staff and technicians of the School of Material and Mineral Resources Engineering who helped me with this research and allowed me to access to the facilities and machines that experiment work. I appreciate them helping to make this project a reality.

Likewise, I would like to extend my gratitude to my friends for their stimulating discussion and opinions that helped me in writing this thesis. I am thankful for their existence since they are always there to lift me up when I feel stressed out and unable to deal with my feelings.

As a final note, I would like to thank my beloved family for their support and encouragement in this endeavor. It has been more important to me to complete this project than anyone else. Special thanks goes to my parents who keep supporting me spiritually and mentally throughout this project. Their love and guidance are with me in whatever I do. Thank you so much.

## TABLE OF CONTENTS

DECI	LARATIC	DNii	
ACK	NOWLEI	DGEMENTiii	
TABI	LE OF CO	NTENTSiv	
LIST	OF TAB	LESvii	
LIST	OF FIGU	RESviii	
LIST	OF SYM	BOLSx	
LIST	OF ABBI	REVIATIONS xi	
LIST	OF APPE	ENDICES xii	
ABST	<b>TRAK</b>	xiii	
ABST	RACT	xiv	
CHAI	PTER 1	INTRODUCTION1	
1.1	Research	Background1	
1.2	Problem Statement 3		
1.3	Study Area		
1.4	Objectives		
1.5	Project Outline		
1.6	Thesis Outline		
CHAI	PTER 2	LITERATURE REVIEW11	
2.1	Introduct	ion 11	
	2.1.1	Tungsten ores	
	2.1.2	Tin ores18	
2.2	Regional	Geology	
	2.2.1	Tectonic Background	
	2.2.2	Regional stratigraphic feature	
	2.2.3	Regional structure	

	2.2.4	Regional magmatite	22
	2.2.5	Regional distribution of mineral resources	23
2.3	Benefici	ations of Tungsten and Tin Ores and Technical Challenges	24
	2.3.1	Tungsten ores	24
	2.3.2	Tin ores	27
2.4	Mineral	Characterization	29
	2.4.1	Visual Assessment and Morphology Study	29
	2.4.2	X-Ray Diffraction (XRD)	31
	2.4.3	X-Ray Fluorescence (XRF)	33
	2.4.4	Mineral Liberation Study	34
2.5	Mineral	Processing Method	36
	2.5.1	Mozley Table	36
	2.5.2	Magnetic Separator	38
	2.5.3	High Tension Roll Separator (HTRS)	39
СНА	PTER 3	METHODOLOGY	44
<b>CHA</b> 3.1	<b>PTER 3</b> Introduc	METHODOLOGY	. <b> 44</b> 44
<b>CHA</b> 3.1 3.2	PTER 3 Introduc Flow Re	METHODOLOGY	<b> 44</b> 44 44
<ul><li>CHA</li><li>3.1</li><li>3.2</li><li>3.3</li></ul>	PTER 3 Introduc Flow Re Raw Ma	METHODOLOGY	<b> 44</b> 44 44 46
<ul><li>CHA</li><li>3.1</li><li>3.2</li><li>3.3</li></ul>	PTER 3 Introduc Flow Re Raw Ma 3.3.1	METHODOLOGY	<b>44</b> 44 44 46 46
<ul><li>CHA</li><li>3.1</li><li>3.2</li><li>3.3</li></ul>	PTER 3 Introduct Flow Re Raw Ma 3.3.1 3.3.2	METHODOLOGY estion essearch Work aterial Sampling Polished Section	44 44 46 46 47
CHA 3.1 3.2 3.3 3.4	PTER 3 Introduc Flow Re Raw Ma 3.3.1 3.3.2 Mineral	METHODOLOGY esearch Work esearch Work nterial Sampling Polished Section Characterization	44 44 46 46 47 48
<ul> <li>CHA</li> <li>3.1</li> <li>3.2</li> <li>3.3</li> <li>3.4</li> </ul>	PTER 3 Introduct Flow Re Raw Ma 3.3.1 3.3.2 Mineral 3.4.1	METHODOLOGY	44 44 46 46 47 48 48
<ul> <li>CHA</li> <li>3.1</li> <li>3.2</li> <li>3.3</li> <li>3.4</li> </ul>	PTER 3 Introduc Flow Re Raw Ma 3.3.1 3.3.2 Mineral 3.4.1 3.4.2	METHODOLOGY essearch Work terial Sampling Polished Section Characterization Mineralogical Study Ore visual assessment and ore morphological study	44 44 46 46 46 48 48 48
<ul> <li>CHA</li> <li>3.1</li> <li>3.2</li> <li>3.3</li> <li>3.4</li> </ul>	PTER 3 Introduct Flow Re Raw Ma 3.3.1 3.3.2 Mineral 3.4.1 3.4.2 3.4.3	METHODOLOGY esearch Work	44 44 46 46 47 48 48 48 48
<ul> <li>CHA</li> <li>3.1</li> <li>3.2</li> <li>3.3</li> <li>3.4</li> </ul>	PTER 3 Introduc Flow Re Raw Ma 3.3.1 3.3.2 Mineral 3.4.1 3.4.2 3.4.3 3.4.3	METHODOLOGY etion	44 44 46 46 46 48 48 48 48 49 49
<ul> <li>CHA</li> <li>3.1</li> <li>3.2</li> <li>3.3</li> <li>3.4</li> </ul>	PTER 3 Introduct Flow Re Raw Ma 3.3.1 3.3.2 Mineral 3.4.1 3.4.2 3.4.3 3.4.3 3.4.4 Physical	METHODOLOGY tion	44 44 46 46 46 47 48 48 48 48 49 49 50

	3.5.2	Magnetic Separator	. 51
	3.5.3	High Tension Roll Separator (HTRS)	. 52
CHAI	PTER 4	RESULTS AND DISCUSSION	. 54
4.1	Introduct	tion	. 54
4.2	Sample G	Characterization	. 54
	4.2.1	Visual Assessment	. 54
	4.2.2	Ore Morphological Analysis	. 56
	4.2.3	X-Ray Fluorescence Analysis	. 58
	4.2.4	X-Ray Diffraction Analysis	. 60
4.3	Physical	Processing	. 63
	4.3.1	Mozley Table	. 63
	4.3.2	Magnetic Separator	. 68
	4.3.3	High Tension Roll Separator (HTRS)	. 72
CHAI	PTER 5	CONCLUSION AND RECOMMENDATIONS	. 78
5.1	Conclusi	on	. 78
5.2	Recommendations for Future Research		. 80
REFE	RENCES	5	. 81
APPE	NDICES		

## LIST OF TABLES

## Page

Table 1: Typical grades of (WO <sub>3</sub> %), tungsten minerals, accompanying minerals
and mines of these deposits16
Table 4.1: The XRF analysis result for raw sample A1
Table 4.2: The XRF analysis result for raw sample B1    59
Table 4.3: Detail data for calculation recovery Sample A1    63
Table 4.4: Detail data for calculation recovery Sample B1    64
Table 4.5: The XRF analysis result of concentration for Sample A1 and B1 65
Table 4.6: The detail data of weight of Sample A1 for magnetic separator 68
Table 4.7: The detail data of weight of Sample B1 for magnetic separator 69
Table 4.8: The XRF analysis result of magnetic for Sample A1 and B170
Table 4.9: The detail data of Sample A1 for High Tension Roll Separator72
Table 4.10: The detail data of Sample B1 for High Tension Roll Separator73
Table 4.11: The XRF analysis result for conductor for Sample A1 and B1 74

## LIST OF FIGURES

## Page

Figure 1.1: Location plan PML5
Figure 1.2: Topography Plan
Figure 1.3: Entrance Route7
Figure 2.1: The distribution diagram of the metallogenic belts in Malays Peninsula
Figure 2.2: Beneficiation flowsheet of Tungsten minerals (scheelte & wolframte)
at the Shizhuyuan mine27
Figure 2.3: a) Mozley table. b) Particle with low specific gravity move farther than
the particle with high specific gravity. c) The particle produce
circular motion
Figure 2.4: Operating principle of a roll-type electrostatic separations
Figure 3.1: Processing Flow Chart
Figure 3.2: John Riffle Splitter
Figure 3.3: Sample after mould
Figure 3.4: Optical Microscope
Figure 3.5: Mozley Table
Figure 3.6: Magnetic Separator
Figure 3.7: High Tension Roll Separator
Figure 4.1: 60% Tungsten
Figure 4.2: 40% Tungsten
Figure 4.3: Raw Sample A1
Figure 4.4: Raw Sample B1
Figure 4.5: The XRD analysis result raw sample A1 by X-Pert HighScore 61
Figure 4.6: The XRD analysis result raw sample B1 by X-Pert HighScore 62

Figure 4.7: Sample A1	66
Figure 4.8: Sample B1	67
Figure 4.9: Magnetic Sample A1	71
Figure 4.10: Magnetic Sample B1	71
Figure 4.11: Conductor Sample A1	75
Figure 4.12: Conductor Sample B1	76
Figure 4.13: Graph composition for recovery of tungsten in Cassiterite	77

## LIST OF SYMBOLS

- A Micron
- °C Degree Celcius
- **Θ** Theta
- Al Aluminium
- Pb Plumbum
- O Oxygen
- Fe Iron
- W Wolframite
- Sn Tin
- Si Silicon
- Zn Zinc
- Cd Cadmium

## LIST OF ABBREVIATIONS

SEM	Scanning Electron Microscopy
EDX	Energy Dispersive X-Ray
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
HTRS	High Tension Roll Separator

## LIST OF APPENDICES

Appendix A Equipment Used

Appendix B XRD Data Analysis

# PENCIRIAN DAN PEMISAHAN TUNGSTEN DALAM KASITERIT (PERTENGAHAN TIN) DARI LOMBONG BUKIT KACHI

#### ABSTRAK

Kajian ini meliputi pencirian dan pengasingan tungsten dengan menggunakan meja mozley, pemisah magnetik dan pemisah tegangan tinggi (HTRS). Penyelidikan ini bertujuan untuk mencirikan sampel dan mendapatkan pemulihan tungsten yang tinggi dengan mengasingkan tungsten dalam kasiterit (pertengahan tin) yang mengandungi 40% dan 60% tungsten dari Lombong Bukit Kachi. Pertama, penilaian visual, analisis mikroskopik, analisis XRD, dan analisis XRF telah dijalankan ke atas sampel mentah pada peringkat awal penyiasatan. Daripada keputusan analisis XRF, didapati bahawa mineral yang paling berharga ialah timah, besi dan tungsten. Sampel mentah dipisahkan dengan menggunakan meja mozley dan menghasilkan dua produk: ketumpatan tinggi dan ketumpatan rendah. Selepas proses mej mozley selesai, sampel berketumpatan tinggi menjalani pemisah magnet dan menghasilkan dua produk iaitu bermagnet dan bukan bermagnet. Akhir sekali, selepas proses magnet selesai, sampel bermagnet menjalani HTRS dan menghasilkan dua produk iaitu konduktor dan bukan konduktor. Setiap sampel daripada proses yang diperlukan menjalani kaedah pengisaran kerana pemerhatian SEM-EDX menunjukkan terdapat mineral yang megisi dengan mineral lain. 'Ring Mill' dipilih untuk mengurangkan saiz sampel, dan sampel dianalisis dengan XRF dan XRD. Daripada keputusan XRF dan XRD, kita tahu bahawa Berjaya dipisahkan tungsten daripada kasiterit (pertengahan tin) dan daripada setiap proses kita dapat melihat bahawa perolehan tungsten dalam sampel meningkat iaitu 72.03% dalam Sampel A1 dan 38.89% dalam Sampel B1.

# CHARACTERIZATION AND SEPARATION OF TUNGSTEN IN CASSITERITE (TIN MIDDLING) FROM BUKIT KACHI MINE

#### ABSTRACT

This study covers characterization and separation of tungsten in by using mozley table, magnetic separator and high tension roll separator (HTRS). This research aims to characterize the sample and get the high recovery of tungsten by separating the tungsten in cassiterite (tin middling)which contain 40% and 60% tungsten in cassiterite from Bukit Kachi Mine. Firstly, the visual observation, microscopic analysis, XRD analysis, and XRF analysis were carried out on the raw sample at the initial stage of investigation. The XRF analysis results, indicated that the most valuable minerals are casssiterite, hematite and wolframite for Sample A1 and B1. The raw samples were separated by using a mozley table and produced two products: high specific density and low specific density. After the mozley table process are completed, the high specific density samples undergo the magnetic separator and produce two products which are magnetic and non-magnetic. Lastly, after the magnetic process is completed, the magnetic samples undergo the HTRS and produce two products which are conductor and non-conductor. Sample from every physical process required undergoes the grinding method since SEM-EDX observation shows there is mineral interlock with other minerals. The ring mill was chosen to reduce the size of samples, and the results were subjected to XRF and XRD analysis. From XRF and XRD results, we know that it successfully separates tungsten from cassiterite and from each process we can see that the recovery tungsten (WO<sub>3</sub>) in the sample increases which is 72.03% for Sample A1 and 38.89% for sample B1.

### **CHAPTER 1**

## **INTRODUCTION**

### 1.1 Research Background

Beginning in the early 19th century, the Kedah area began producing tin. In the mining history of tungsten and tin, the most important period is about 100 years ago. The Bukit Kachi mine, located in the Temin area of the Sintok mountain, is famous in Sintok. The mine was owned by J A Russel Co. Ltd. The company carried out continuous mining activities from 1916 to 1940 based on previous geological data collected (Aras Kuasa, 2017).

As of October 2015, China Nonferrous Metal (Guilin) Geology And Mining Co. is authorized by the company Aras Kuasa (AK) which holds the mine lease for the area at that time to perform geological, geophysical, geochemical, and engineering logging work in the mining area. Until 2017, this company is in operation (Aras Kuasa, 2017).

The mining operations taken over by a new company in 2017, Malamet Sdn Bhd, a subsidiary of Wolfram Group Company. Moscow is home to Wolfram Group Company, the biggest tungsten manufacturer and producer in Russia. Specifically, the company's main products are tungsten and tin.

Subsidiary company, Hundred Gold Properties Sdn Bhd, now operates a full mining and manufacturing operation in Bukit Kachi, Kedah. In Malaysia, the company is growing and gaining potential to be one of the top companies in the mining industry.

Important tungsten mines are in California, Colorado, South Korea, Bolivia, Russia, and Portugal. Even China reportedly has supply of 75% of the world's tungsten. Tungsten metal is silver-white and shiny or shiny, but this metal is usually obtain in the form of a grey powder (Olumbambi, 2004).

In other references states that pure tungsten is a metal that is tin white to steel grey. Very pure tungsten can be cut with a hacksaw and can be shaped easily. In its impure state, tungsten is brittle and requires hard work to form. Tungsten has the highest melting point (3,422 °C) of all metal elements, and at 314°C has the highest tensile strength. Tungsten oxidized in the air and must be protected when stored at elevated temperatures. Its thermal expansion is almost the same as borosilicate glass, which makes it helpful in sealing from glass to metal (Editorial, 2008).

Tin is a soft metal that is silvery-white and easy to forge. It is also corrosion resistant and is used to plating other metals for corrosion resistance. Tin is also an element in many alloys, for example, with copper to produce bronze. It is also the important metal to produce pewter (Abrahman, 2019).

Main mineral in tin ore is cassiterite, while quartz, xenotime, monazite are secondary minerals and a naturally occurring oxide of tin containing about 78.8% Sn. Of less importance are two complex sulphide minerals, stannite (Cu<sub>2</sub>FeSnS<sub>4</sub>), a copper-iron-tin sulphide, and cylindrite (PbSnFeSb<sub>2</sub>S<sub>14</sub>), a lead-tin-iron-antimony sulphide. These two minerals occur chiefly in lode deposits in Bolivia, often associated with other metals such as silver (Barry, 2017).

Recent studies have shown that tungsten alloys could be the most promising materials as plasma-facing first walls in future commercial nuclear fusion devices (Zheng, 2018).

## **1.2 Problem Statement**

Every mineral has its own set of characteristics and challenges. The selection of optimal technical processing of minerals necessitates a thorough understanding of chemical and mineralogical components (Olubambi, 2006). The statement of the problem associated with it is impossible to distinguish the elements present in the ore simply by looking at hand specimens. In addition, several processing methods need to use to isolate tungsten ores from the sample.

Therefore, a detailed characterization study needed to solve this problem and optimize the ore separation process with the actual purpose. Tungsten residues contain abundant valuable minerals that are difficult to recover by traditional gravity and flotation process. This study presents a route, centrifugal concentration for cassiterite recovery from tungsten residues through centrifugal concentration.

## 1.3 Study Area

The raw sample used for the study is a tin middling in Bukit Kachi Mine, Kedah. The sample collected at Bukit Kachi Mine belongs to Hundred Gold Properties Sdn. Bhd. which is a part of Malamet Sdn. Bhd. This company is a subsidiary of Wolfram Group Company.

Hundred Gold Properties Sdn. Bhd. is located at Bukit Perangin, Mukim Temin,Kubang Pasu, Kedah Darul Aman. This mine site is on 3 Lot of land which include area of 195.163 hectares (482.25 acres). This location is about 6.5 km from southeast Universiti Utara Malaysia.

Town that are nearby is Sintok which is northeast from this mine. Grid Topography is U 06<sup>o</sup> 24' 45.7" and T 100<sup>o</sup> 32' 0.61" is one of the tin mine company

in Malaysia. This company has a mining lease about 195.163 hectares. Land area which area potential of deposit is about 113.06 hectares (279.37 acres). This areas is rich with minerals like tin tungsten, and quartz.

The location of mine is estimated 3 km from the main road before entering the reserve forest. The road is unpaved and not even which need to travel through some small rivers. Generally, the topography is highland and wavy that surrounded by secondary forest and some rubber trees plantation. The altitude from the sea level is between 300 m to 700 m. the highest altitude level is 711 m at the southwest, while Bukit Kachi located in northeast in Lot 6720 with altitude of 448 m.

Sungai Pinang flows in the north region and Sungai Pdg Pelanduk in the south region from the project area. Based on figured below shows the location (Figure 1.1), topography plan (Figure 1.2) and entrance route (Figure 1.3).



Figure 1.1: Location plan PML



Figure 1.2: Topography Plan



Figure 1.3: Entrance Route

### 1.4 Objectives

The goals of this study are to analyse the composition of the obtained 60% and 40% of tungsten in tin middling sample and separate the precious mineral from it. As a result, the following objectives are set for this research:

- a) To characterize the tin tungsten ore in tin middling from sample Bukit Kachi Mine.
- b) To know the ability and recovery of the separation tungsten in tin middling.

### **1.5 Project Outline**

The aim of this experiment is to isolate useful minerals using a magnetic separator, high tension roll separator and gravity. To achieve the objective of this project, there are many stages of review must completed. For example, by using scanning electron microscopy (SEM), X-ray Fluorescence (XRF), and X-Ray Diffraction (XRD) for mineralogical and chemical composition studies including grade analysis and process selection. The following is a compilation of necessary step and analysis:

- a) **Visual Assessment:** Observe the samples visually, knowledge may gathered with naked eye, hand or sense of smell.
- b) Sampling: Use riffle box for homogenous sampling
- c) Mineral characterization analysis: X-ray diffraction (XRD). X-ray Fluorescence (XRF) and Scanning Microscope Electron with Energy Dispersive X-ray Analyzer (SEM-EDX).
- d) Mineral Processing: Gravity method (Mozley Table), Magnetic Separator and High Tension Roll Separator (HTRS).

### **1.6** Thesis Outline

Systematic writing in this study including several things.

### I. CHAPTER 1: INTRODUCTION

This chapter describes the research background of the project, study area, problem statement and objectives of the project.

## II. CHAPTER 2: LITERATURE REVIEW

This chapter describes more on the beneficiations of the tungsten and tin ores, and the principle working of the SEM-EDX, XRD and XRF. There is also theoretical explanation on operating parameters of Mozley Table, Magnetic Separator and High Tension Roll Separator (HTRS) and information of the machines used for sample processing.

## III. CHAPTER 3: METHODOLOGY

In this chapter, we describe the theoretical relationship that has been described in the previous chapter with problems, a detailed description and flowchart of the research activities, in-depth explanations of how the research was conducted.

## IV. CHAPTER 4: RESULTS AND DISCUSSION

In this chapter, you will find the results of XRD, XRF, and SEM-EDX characterization, along with the data obtained from the physical processing method. In order to accomplish the study's objectives, the data will be analyzed and discussed.

## V. CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

This chapter contains conclusions and recommendations for future work in light of the results of the analysis.

## VI. REFERENCES

List the libraries that were consulted during the preparation of the study and the review of the research report.

## VII. APPENDIX

Comprises all the data that was used in the study, as well as any documents that needed to be addressed as part of the research report.

#### **CHAPTER 2**

### LITERATURE REVIEW

### 2.1 Introduction

Tungsten, which is a hard, refractory, and rare metal, is important in many commercial and industrial applications. Tungsten's primary application for over 100 years has been as the filament in incandescent light bulbs. However, tungsten production in the world is not as much as tin, due to low demand by the industry. But as known tungsten is also very important all over the world. There is also tungsten oxide in cassiterite, which can make that mineral economical and valuable. As well as can also earn ancillary income by selling tungsten oxide to the industry. Some industries do not take tailings as valuable minerals, that is why before we throw out that tailings.

It is mostly known for forming highly durable and hard carbides out of tungsten. It is due to this property that tungsten is most commonly used in steels as a component for high-speed and other tooling steels. Tungsten makes up 30 percent of the world's tungsten production. (Giena, 2014).

In almost equal amounts, tin is extracted from mineral (mainly traditional mining and artisanal mining), as well as from secondary extraction (recycled materials). Around three hundred tonnes extracted annually. Generally, tin concentrated by gravity-splitting methods due to variations in the composition of gangue (usually silicates) and flotation due to cassiterite (SnO<sub>2</sub>) (Rimaszeki, 2012).

Tinplate, solder alloys, bearing materials, tin and alloy coatings (both plated and hot-coated), pewter, bronzes, and fusible alloys are the most common commercial applications of tin. The chemical properties of tin include its presence in two valence states (II and IV) and amphoteric properties (its ability to act as an acid as well as a base). Furthermore, it can form organometallic compounds directly with carbon. In addition to these properties, tin chemicals are used for a number of important applications, such as in electroplating, agricultural and pharmaceutical products, and plastics and ceramics. (Barry, 2017)

The properties of the mineral are important for the separaton of minerals. Specific gravity, conductivity and magnetism are the properties that are usually taken into consideration while producing efficiently at a factory. The devices usually used to manufacture tin and tungsten are shaking table, magnetic separator and froth floating (Wills, 2005).

### 2.1.1 Tungsten ores

Tungsten, commonly known as wolfram, has the highest melting point of all metals ( $3422 \pm 15$  °C). With the symbol W and atomic number 74. Tungsten is also one of the heaviest metals, with a density of 19.25 g/cm3. Tungsten has the lowest vapour pressure of any metal, extremely high moduli of compression and elasticity, extremely strong thermal creep resistance, and extremely high thermal and electrical conductivity. Tungsten is the most essential metal for thermo-emission applications, not only because to its strong electron emissivity generated by tiny additions of other metals, but also due to its great temperature and chemical stability. Tungsten often includes trace amounts of carbon and oxygen, which provide significant hardness and brittleness (ITIA, 2017).

Tungsten is an essential raw element with a wide range of uses in industries such as energy, manufacturing, computer technology, and consumer goods. Tungsten, in particular, has found widespread application in metalworking, mining and stone-cutting equipment, high-temperature technologies, lighting, catalyst and pigment, petroleum, weaponry, and aerospace sectors (Shen, 2019). Tungsten carbide is a solid, metal-like substance that is widely utilised in automobile and aircraft manufacture, building, electronics manufacturing, oil and gas drilling, and military (Shedd, 2018). According to recent research, tungsten alloys may be the most viable materials for plasma-facing initial walls in future commercial nuclear fusion devices (Zheng, 2018).

Cemented carbides, also called hardmetals, are the most important applications of tungsten today. Tungsten monocarbide (WC) is the main constituent and has a hardness close to diamond. Hardmetal tools are used for the shaping of metals, alloys, ceramics and other materials. About 54–72% of the tungsten produced globally is used for hardmetals. Steel and alloys, mill products such as lighting filaments, electrodes, electrical and electronic contacts, wires, sheets, rods and a widespread variety of chemicals represent other important uses of tungsten.

Because of its unique qualities, extensive applicability in a variety of industries, scarcity of prospective alternatives, and geographically concentrated production, tungsten is a crucial component and strategic resource in the global economy (Calvo, 2019). The United States Department of Interior issued the Final List of Critical Minerals 2018 (83 FR 23295) in May 2018, and tungsten was among the 35 minerals (or mineral material groupings) designated as critical (Doi, 2018). Since 2011, the European Union has also identified tungsten as a vital raw material (Martins, 2019). Except for Australia, tungsten is regarded as a vital element in all regions other than the United States and the European Union (Hayes, 2018).

Because of its vital economic importance and considerable supply risk, tungsten has been designated as one of Europe's 20 crucial commodities (EC, 2014). The world's tungsten concentrate production is spread across a number of nations, although China produces more than 80% of it. According to a 2016 USGS report (Jewell and Kimball,

13

2016), total worldwide mine output of tungsten in 2015 was 87, 000 t, with China accounting for 71,000 t. Currently, four EU nations, including Austria, Portugal, Spain, and the United Kingdom, manufacture tungsten concentrate, with a total of 2830t produced in 2015. The EU consumes roughly 10,000t of tungsten each year, and demand expected to rise somewhat over the next decade (Starck, 2013). As a result, boosting tungsten production from basic resources should be one of the key approaches to meeting the metal's demand in the EU market.

The typical abundance of tungsten in the earth's crust believed to be 1.25–1.5 ppm, which is similar to the abundance of tin and molybdenum. It found in higher concentrations in granite (approximately 2 ppm) than in basaltic (1 ppm) and ultramafic rocks (0.5 ppm). Only scheelite (CaWO<sub>4</sub>) and wolframite ((Fe, Mn)WO<sub>4</sub>) are economically important tungsten minerals (Schmidt, 2012). Wolframite, on the other hand, is a mineral series formed of ferberite (FeWO<sub>4</sub>) and hubnerite (MnWO<sub>4</sub>). Iron or manganese dominance would result in the formation of one of two minerals. The iron-dominated one will make ferberite, whereas the manganese-dominated one will form hübnerite (Errandonea and Segura, 2010).

China started to dominate the world tungsten market in 1949 and has been the primary tungsten producer for over 70 years. China produced more than 40% of tungsten concentrates between 1949 and 1985 and more than 66% between 1986 and 2008 (Brookes, 2011). In 2020, China held 82% of the world's tungsten mine production and 56% of the world's tungsten reserves (U.S.G.S, 2021). Meanwhile, China has adopted stricter 6 pollution control and safety regulations on tungsten production and shut down numerous tungsten mining facilities since 2017, which resulted in a reduced supply of tungsten to the world market and high volatility in prices

for tungsten commodities (Liu,H, 2020). Consequently, to balance the global tungsten demand and supply, markets would need to rely on exploring new primary deposits around the world and utilizing secondary tungsten resources (Dvoracek, 2017). Currently, tungsten waste contamination to the environment has also been a concern. For example, the Panasqueira mine, the largest Sn–W deposit in Western Europe, had stored a significant amount of tungsten tailings in tailing dams. These tailings generate low pH (~3) and are enriched in toxic elements acid mine drainage (AMD), leaking into the nearby river (Candeias, 2014).

At the Lianhuashan mine, one of the largest tungsten mines in China, it was found that surface water, soil, and plants around the tailing dam were severely contaminated by heavy metals and arsenic (Lin,Chen, 2013). Further study in the same area showed that tungsten tailings have potential health risks to the surrounding residents (Liu,Luo, 2010). Consequently, appropriate treatment for tungsten tailings to prevent potential contamination may be required. Meanwhile, tungsten tailings may contain numerous valuable elements and minerals and could be used as a secondary resource for metal recovery. This paper focuses on a comprehensive literature review of tungsten properties and mineralogy, potential risks of tungsten to the environment and humans, tungsten primary and secondary resources, and potential reprocessing approaches for tungsten tailings.

The world reserves of tungsten are estimately 4.000.000 t W of which China holds about 40% (Bernhart, 2015). The five major types of tungsten ore deposits from which most ore is currently produced are skarn, vein/stockwork, porphyry, disseminated or greisen, and stratabound (BGS, 2011). Typical grades (WO<sub>3</sub>%),

tungsten minerals, accompanying minerals and mines of these deposits are shown in Table 1. Other deposit types include pegmatite, placer, brine/evaporate and hot springs.

Deposit type	Typical grade	Tungsten	Accompanying	Mine
	WO3%	Mineral	Metals	
Stratabound	0.3-1.4	Scheelite	Cu, Mo, Zn and	Cantung (Canada),
(deposit size <			Bi	Los Santos (Spain)
106 –107 t)				Pasto Bueno (Peru),
Vein/stockwork	Variable	Wolframite	Sn, Cu, Mo, Bi and Au	Panasqueira(Portugal)
deposit size <				San Fix (Spain)
105 –108 t)				Sui I M (Spuil).
Porphyry	0.1-0.4	Wolframite or	Mo, Bi and Sn	Xingluokeng (China),
(deposit size <		scheeelite		Northern
107 –108 t)				Dancer(Canada),
				Climax (USA)
Disseminated	0.1-0.5	Wolframite	Sn, Bi and Mo	Shizhuyuan (China)
(deposit size <		and scheelite		
107 –108 t)				
Stratabound	02-1.0	Scheelite	N/A	Mittersill(Austria);
(deposit size <				Damingshan (China);
106 –107 t)				Mulgine (Austra

Table 1: Typical grades of (WO<sub>3</sub>%), tungsten minerals, accompanying minerals and mines of these deposits

As the largest producer of tungsten, China has more than ten major tungsten mines with an annual output over 1300 tonnes of WO<sub>3</sub>. Most of these mines are located in Jiangxi and Hunan, in the south of China. The Xianglushan deposit located in Jiangxi is the largest tungsten mine in China with an annual output of over 5700 tonnes of WO<sub>3</sub>. The Shizhuyuan in Hunan is a large polymetallic tungsten mine with an annual output of 5500 tonnes of WO<sub>3</sub>. It is a W-Sn-Mo-Bi polymetallic deposit and characterized by low grade and complicated composition (Han, 2017).

The ore contains scheelite, wolframite, molybdenite, cassiterite, bismuthinite, and fluorite. The Nui Phao mine in Vietnam is the largest tungsten mine outside of China and unique polymetallic mine with significant amounts of tungsten, fluorspar, bismuth and copper. The mining reserves are 66 million tonnes of ore with an average grade 0.21% WO<sub>3</sub> (Masan Resources, 2012). The Vostok-2 is Russia's largest skarn deposit containing high grade sulfide–scheelite ore with substantial base metal and gold mineralization. It has been mined since 1969, firstly from an open pit, and subsequently by means of underground mining operations (Soloviev and Krivoshchekov, 2011). The Cantung mine located in western Northwest Territories of Canada is a skarn type of deposit with the reserves of 1.8 million tonnes at the grade 0.81% WO<sub>3</sub>. It is continuously operating underground, with seasonal mining from an open pit.

The Mittersill mine in Austria hosts the largest tungsten deposit in Europe producing scheelite concentrates. The deposit consists of two parts, the Ostfeld open pit mine and the Westfeld underground mine (Holzer and Stumpfl, 1980).

#### 2.1.2 Tin ores

Tin deposits are divided into two types: primary and secondary ore deposits. The primary tin ore deposits are associated with magmatic-hydrothermal systems (tin granites, pegmatites, tin porphyries). Cassiterite is very dense and may be dispersed by exogenic processes (weathering, erosion) and eventually form placer deposits within a few kilometers of their primary source due to its hardness and chemical stability (Lehmann, 2020).

Tin was historically mined mainly from placer deposits, with approximately 85% of the metal recovered from these deposits (±27 million tons of Sn). Typically, such deposits are found only in a few provinces within larger granite belts. In decreasing order of importance, they are Southeast Asia (Indonesia, Malaysia, Thailand, Myanmar), South China, the Central Andes (Bolivia, southern Peru), and Cornwall, UK.

Indonesia has been operating a tin placer mine for more than half a century and is one of the largest tin producers in the world. Because the secondary tin deposits are gradually being depleted, PT Timah, Tbk (the country's largest tin miner) has begun exploring and mining the primary deposits in Belitung (tin-bearing iron ores). In the near future, tin's new source/substitute is anticipated to be the primary deposit.

The properties of primary and secondary ores are different. Secondary ores contain tin in the form of cassiterite, SnO<sub>2</sub>, which can be separated physically. In primary ore, tin was often associated with other minerals requiring advanced chemical separation/processing rather than physical. Depending on the ore's properties and components, hydrometallurgy or pyrometallurgy is used in the chemical processing of

primary tin ore. Low-grade tin ores, on the other hand, were often treated using hydrometallurgy.

Some research has been done on the hydrometallurgy processing of tin ore; dissolved tin from pure tin and Sn–Fe alloys in sodium hydroxide solutions and discovered that the dissolution rate of tin from a 50 wt. percent Sn–50 wt. percent FeSn<sub>2</sub> mixture in sodium hydroxide solutions was higher than that of pure tin (JunW,2004). Tin extraction from Pb-free solder waste through hydrochloric acid leaching (Yoo K, 2017). Lalasari investigated the use of HCl to dissolve cassiterite's related minerals such as iron (Fe), lanthanum (La), cerium (Ce), and titanium (Ti) (Lalasari, 2020).

Tin has also been extracted from hematite iron ore using pyrometallurgy processes such as sulfidation roasting with high sulphur coal and reduction roasting with pyrite (FeS<sub>2</sub>) (Sang, 2016).

Primary tin ores are extracted by underground mining. In exceptional cases, depth has exceeded 1000m; most nonferrous metal extraction technologies are applied. The procedure in a given setting is determined by the weight, shape, and inclination of the ore body, as well as geological factors (Guzzman, 2017).

Secondary deposits of loosely packed hard mineral rock containing cassiterite are obtained utilising high-production loading techniques that usually undertake preliminary classification. Mining circumstances have a substantial impact on general local conditions, especially the degree of economic growth in the area. In Zaire, for example, classic open-pit techniques recover alluvial deposits (wetted pegmatites) containing up to 0.15 percent tin (Guzzman, 2017). Dredging shovels, dragline excavators and bucket excavators, and other locally adapted equipment are used to recover loose alluvial and marine deposits in river valleys and underwater regions in Thailand, Malaysia, and Indonesia. This apparatus initially separates the gangue and other minerals such as wood (Pawlek, 2013).

Cassiterite is extracted from alluvial deposits at depths of up to 40 metres off the shores of Indonesia, Thailand, and Malaysia using chain and bucket excavators. This situation also has an immediate advantage. Beneficiation of primary tin ore is challenging. Because the principal material, cassiterite, is nonmagnetic and hence unsuitable for flotation, gravity must be utilised instead. Cassiterite is also often intergrown, and the minerals that surround it react similarly to cassiterite during processing. (Leube, 2012).

Native tin is exceedingly uncommon, occurring solely in Canada. In terms of commercial importance, cassiterite is the most significant tin mineral (SnO<sub>2</sub>). It has a hardness of 6-7 on the Mohs scale, a density of 6.8-7.1 g/cm3, and a tin content of up to 79 percent Sn. The most typical colour is brown to brownish-black. The addition of Ti, Fe, Nb, Ta, or Mn can generate colours ranging from grey to white. Contact deposits of cassiterite may be linked with other elements such as magnetite, arsenical iron pyrites, or zinc blende (Leube, 2012).

## 2.2 Regional Geology

#### 2.2.1 Tectonic Background

The Malay Peninsula is divided into two crustal blocks for Bentong-Raub deep fault zone as a boundary. The east one is called as Indo-China block (Eastern Belt), the west region of the deep fault zone is belonged to China-Myanmar SibuMaSu block (Western belt). During the Indosinian movement period the two blocks colluded and joined with each other. Sintok district is located at the China-Myanmar MaSu block in the west of Bentong-Raub deep fault. Bentong-Raub deep fault are constituted of the main fault zone and a series of parallel north-south linear structure, companying the outcrops of serpentinized mafic-ultromafic magmatic rocks of small scale. Bentong-Raub deep fault constitutes the boundary of the Indo-China block and China-Myanmar MaSu block. The orogenic movement of Malay Peninsula began in the Late Permian period when Indo-China block colluded with the China-Myanmar MaSu block until early Triassic. In this period, tectonic unconformity phenomenon took place in the whole Peninsula (Aras Kuasa, 2017)

#### 2.2.2 Regional stratigraphic feature

The strata, exposed in the Malay Peninsula area, from the old to the new, mainly include Precambrian system, Cambrian-Devonian system, Carboniferous-Permian system, and Triassic-Cretaceous system. With Bentong-Raub deep fault as the boundary, the stratum assemblage characteristics are significantly different in the east and west parts of the Malay Peninsula. By comparison of the strata in the east and west blocks in the Malay peninsula, it is indicated that in the Indosinian tectonic stage, the strata in the eastern coastal are mainly sedimentary rock of carbonate formation of shallow coastal faces, as the strata of central gold metallogenic belt in the east are mainly marine volcano sedimentary assemblage. During the tectonic stage, the sedimentary environment in the whole peninsula changed from a marine environment to a continental environment (Aras Kuasa, 2017)

#### 2.2.3 Regional structure

The main faults in the Malay Peninsula are Bentong-Raub deep fault and Lebir deep fault. The central area between the two deep faults was under platform - arc environment in the margin of Indo-China continental paleocraton from the Early Carboniferous to Lateli Triassic period. The length of Bentong-Raub fault is more than 300 km, to the north it connects with ChiangRai-ChiangMai fault in Thailand. The main fault shears along the right. The strike slip is about 10 km. It is considered to be one of the most important tectonic fault in the Malay Peninsula. The deep fault is composed of a series of linear NS structures in parallel, accompanying by tectonic melange and ophiolite of strong schistosity. The striking trend of Lebir deep fault is near in north-south direction across the northeast Malay Peninsula with a total length of more than 320 km. The topography on both sides of the fault shows that the east is high and the west is low, the contrast is very obvious (Aras Kuasa, 2017).

#### 2.2.4 Regional magmatite

The Malay Peninsula granites are widely developed. The whole peninsula is mainly divided into three granite provinces, including the central, eastern and western province. Granite formation in central and eastern provinces is closely related with the oceanic crust sub-duction and collision and orogeny movement during Permian-Triassic period. The western granite province is difference from the eastern and central granite provinces in the peninsula, which is inferred to be the cause of the northeast reduction of Tethys in Tertiary period. It is a set of I type granite in late Cretaceous to Tertiary period in the west granite province. Sintok area is located in the western granite province (Aras Kuasa, 2017).

### 2.2.5 Regional distribution of mineral resources

According to the metal deposit types, the Malay Peninsula is divided into three metallogenic belts, West metallogenic belt, Central metallogenic belt and East metallogenic belt for the boundary of Bentong-Raub fault and Lebir fault (Figure 2.1). The middle belt area is call as the Central Au metalligenic belt for the distribution of main gold deposits. The west area of Lebir fault and the east area of Bentong-Raub are called as West metallogenic belt and East metallogenic belt individually for the distribution of main tin deposits. Sintok mining area is located in the West Tin metallogenic belt, which is in the west of Bentong-Raub fault (Aras Kuasa, 2017).



1. Bentong-Raub fault, 2. Lebir fault

Figure 2.1: The distribution diagram of the metallogenic belts in Malays Peninsula

## 2.3 Beneficiations of Tungsten and Tin Ores and Technical Challenges

#### 2.3.1 Tungsten ores

To fulfil the criteria of international commerce, the beneficiation process of scheelite and wolframite ores normally consists of pre-concentration after crushing and grinding, followed by roughing, cleaning, and final purification stages to create a concentrate with 65–75 percent WO<sub>3</sub>. Only scheelite lends itself well to floating. In contrast to scheelite, wolframite is paramagnetic. Thus, gravity concentration and flotation are used to beneficiate scheelite ore, whereas gravity and/or magnetic separation is used to beneficiate wolframite ore (Lassner and Schubert, 1998).

Due to the brittle nature of both scheelite and wolframite, comminution is carefully designed to avoid overgrinding, that is, to minimise fines formation; appropriate sizing techniques (screening, hydro-classifications using hydrocyclones or classifiers) are used at every stage of comminution, and rod milling is more commonly used than ball milling. According to a study (Li and Gao, 2017), rod milling of scheelite has additional advantage over ball milling because the rodmilled scheelite particles are more hydrophobic and have a greater flotation recovery due to stronger contact with the collector and easier attachment to air bubbles. In recent years, quantitative mineralogical analyses techniques such as mineral liberation analysis (MLA) have been used to compare the liberation performance during comminution of different tungsten ores (Hamid, 2017).

For pre-concentration, X-ray sorting and gravitational procedures are commonly utilised. For pre-concentration of wolframite ore, optical sorting and/or hand-picking procedures are also utilised. The high density of scheelite and wolframite allows them to be separated from the gangue minerals using gravity methods. Jigs, spirals, shaking