

TITANIUM RECOVERY FROM Ti-BEARING MINERALS IN ORE DEPOSIT AND MINE TAILINGS

by

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Declaration

I **Beverley Andile Marufu** hereby declare that this dissertation titled “Titanium recovery from Ti-bearing minerals in ore deposit and mine tailings”, submitted by me for the Master of Science degree at the University of the Free State is my own original and independent work and has not been previously submitted to another university and/or faculty. The information derived from the literature has been duly acknowledged in the text, and a comprehensive list of references has been provided.



Beverley Andile Marufu

2 July 2025

Date

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Summary

Titanium (Ti) is a valuable element that is difficult to extract from its minerals, whether high-grade ores rich in rutile and ilmenite or from low-grade ores and tailings. Simplifying the extraction of vanadium from low-grade sources, such as tailings and vanadium-bearing titanium minerals, which are primarily available in South Africa, would be of economic interest to the mining industry. This research focused on recovering titanium from ore deposits and mine tailings through scalable chemical leaching methods. Both ore and tailing samples were characterised using XRD, SEM-EDS, and XRF to identify the minerals present and semi-quantitatively analyse their Ti content, revealing the presence of silicates and oxides in the vanadium-bearing titanomagnetite (VBT) and oxides only in the vanadium tailings. Sequential extraction was also performed on the samples. The study identified lithium metaborate flux fusion as the most effective dissolution method, surpassing sodium sulphate and ammonium sulphate. H_2SO_4 was the most effective leaching acid compared to HNO_3 , HCl , H_3PO_4 , NaOH , and NH_4OH . Aqua regia was also effective. However, it had high coextraction of impurities. Physical separation using magnetic separation and density separation was performed, and the sub-samples were also characterised using the same non-destructive methods as the ore and tailings. The vanadium-bearing titanomagnetite ore was found to be very magnetic, while the tailings were non-magnetic. Magnetic separation revealed high magnetite content in the ore, while tailings contained non-magnetic and weakly magnetic ilmenite, hematite and pseudobrookite minerals. LiBO_2 flux fusion showed that the VBT ore contained 3.0 % Ti while the tailings contained 5.2 % Ti. Roasting using NaOH and NaHCO_3 and adding oxidising (H_2O_2) and reducing agents showed no significant improvement in leaching efficiency for Ti, deeming the extra step unnecessary. Optimal leaching conditions were identified as 7 M H_2SO_4 at 90 °C, 600 rpm for 5 hours, achieving a selective leaching efficiency of 95.6 % and 85.5 % for Ti for the VBT ore and tailings, respectively, alongside minimised recovery percentages for vanadium (V) and iron (Fe). The concentration of Ti in the final leach liquor of the ore and the tailings was 2.8 % and 4.3 % respectively.

Chapter 1: Motivation of the study

1.1 Introduction

Titanium is the ninth most abundant element in the Earth's crust (Tarselli, 2013). Its high strength elicited its name, and Martin Heinrich Klaproth named it after the strong 'Titans', which were the sons of the earth goddesses in Greek mythology, which referred to 'their incarnation of natural strength' (Holden, 2019). The element naturally occurs in about 45 minerals, mainly rutile, ilmenite, and titanomagnetite. Rutile and ilmenite are the two most crucial Ti minerals due to their high Ti concentrations. Titanium also occurs in other silicate and oxide minerals. The earth's crust comprises 90 % silicate minerals that contain low Ti concentrations (between 0 and 1 %), rendering these minerals uneconomical for beneficiation (value addition). Meanwhile, titanium oxides such as rutile and anatase have Ti concentrations between 15 and 95 %, making these minerals also more economically viable for beneficiation (Van Gosen *et al.*, 2014).

Other valuable sources of titanium are tailings left behind from previous mining activities. Although these sources are less common, they still play an essential role in the production of titanium. (U.S. Geological Survey, 2021). These tailings consist of processed rock or minerals that remain after other valuable elements are removed from the original minerals. The remaining fractions, initially considered worthless and economically unimportant, are the waste products produced after the crushing, grinding, and processing of the original ore, which sometimes creates an exploitable concentrate. Examples of secondary titanium-rich sources include vanadium ores, such as vanadium-bearing titanomagnetite (VBT) and its associated tailings. The ore is primarily mined and processed for vanadium, but it also contains significant amounts of titanium. (Bian *et al.*, 2021; Zhao *et al.*, 2015).

In 2024, the top five global titanium producers were as follows, China (3.3 million Mt), Mozambique (1.9 million Mt), South Africa (1.3 million Mt), Australia (0.4 million Mt) and Norway (0.36 million Mt), with China having the largest reserves of titanium minerals (ilmenite) worldwide. Although rutile resources are being depleted, Australia, India, Ukraine, and South Africa still have significant rutile reserves (**Figure 1.1**). The world's total titanium production reached an estimated 9.35 million Mt, with ilmenite being the dominant mineral, accounting for over 90 % of this (U.S. Geological Survey, 2025).

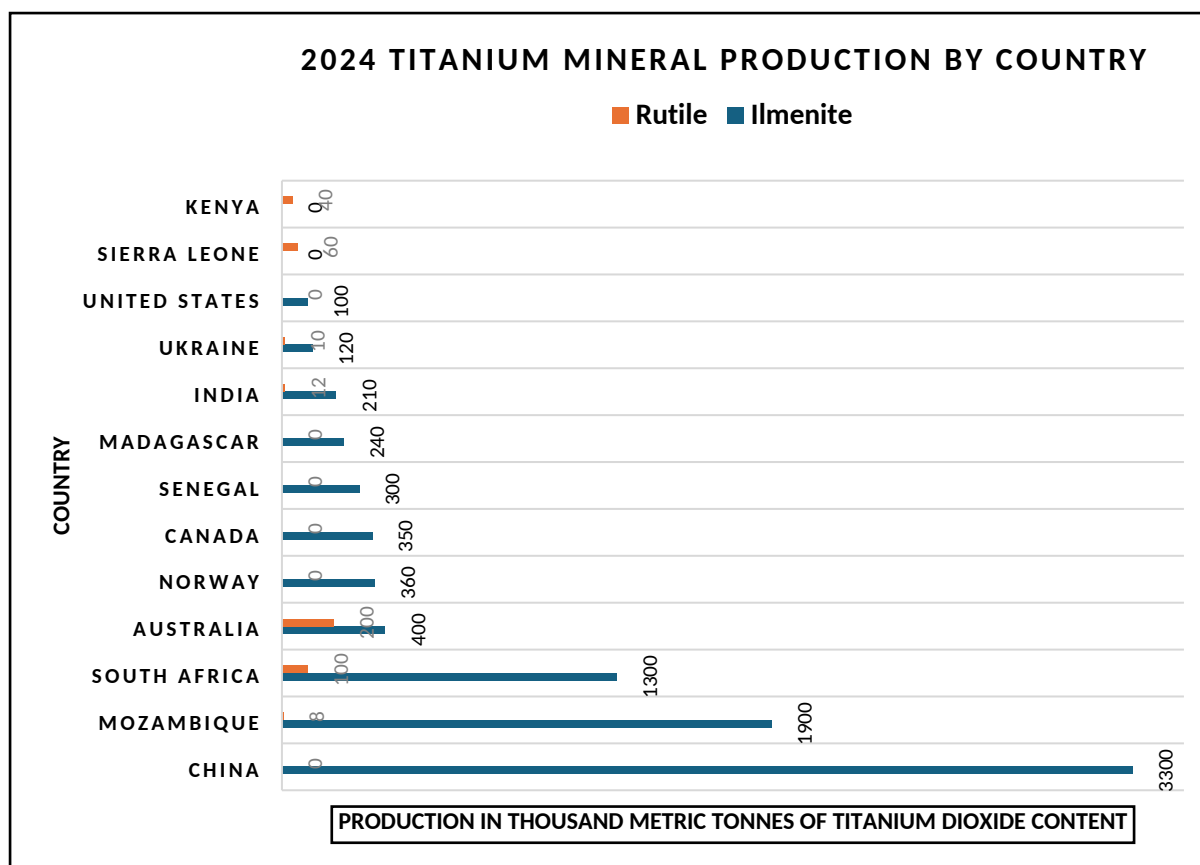


Figure 1.1: 2024 titanium minerals worldwide mine production by country (in 1 000 Mt of TiO_2 content) (U.S. Geological Survey, 2025)

South Africa is the third-largest producer of titanium minerals, primarily processing ilmenite and rutile as sources of titanium. The element has been identified as one of South Africa's most abundant natural resources and is potentially a vital driver of economic growth (De Bryne *et al.*, 2023). Titanium-rich ores in South Africa are found in the Bushveld Complex, which is also renowned for its platinum group metals, chromium, and vanadium content. The Phalaborwa Igneous Complex is also rich in tin, copper, feldspar, and zirconium (Ahiakwo *et al.*, 2018). Another mineral source rich in Ti is the heavy-mineral deposits in South Africa's Holocene high dunes near Richards Bay, situated 160 kilometres north of Durban (Motsie, 2010). Namakwa Sands on the west coast is also another source of the heavy minerals, which are rich in titanium.

Titanium is widely used in various industries, including the paper and plastics industry, cosmetics, and alternative energy production, among others. The pigment sector is the primary driver of titanium products, consuming approximately 95 % of all titanium feedstock (U.S. Geological Survey, 2022). Rutile (TiO_2) and ilmenite (FeTiO_3) are the principal ores used to produce white pigments for the paper, plastic, and paint industries. The paint industry consumes 60 % of the total titanium dioxide produced worldwide. The plastic, paper, and other industries consume approximately 20 %, 5 %, and 15 % of the TiO_2 produced, respectively (Haverkamp *et al.*, 2022). The steel industry and other industries, such

as cosmetics, also use a large portion of the remaining titanium dioxide produced. The photocatalytic splitting of water also utilises titanium dioxide (Eidsvåg *et al.*, 2021) due to the ease of oxygen and hydrogen separation, and applicability in both small- and large-scale facilities (Jafari *et al.*, 2016).

The titanium steel industry uses less than 5 % of the total titanium produced, but its applications are gaining popularity due to its high tensile strength and low density, which allows for a very high strength-to-weight ratio, and metal alloy production (Department of Mineral Resources RSA, 2011). The most common alloy is Ti6Al4V (6 % aluminium, 4 % vanadium, 90 % titanium), also known as Grade 5, and is used in additive manufacturing (Roux *et.al.*, 2019). It is used in the medical industry for knee replacement implants (**Figure 1.2**). This is because the alloy possesses excellent strength, high corrosion resistance, good weldability, low modulus of elasticity, and heat-treatable characteristics (Mohammed *et al.*, 2014).



Figure 1.2: Ti-6Al-4V medical application examples (Dziubińska *et.al.*, 2017)

Although titanium is essential in various industries, its extraction processes are often complex, energy-intensive, and costly, particularly when dealing with low-grade ores or tailings. These challenges underscore the need for technological innovation and alternative beneficiation approaches to harness the potential of titanium sources that are currently underutilised or considered waste. Addressing these inefficiencies is crucial for maximising titanium's economic, social and industrial value while mitigating environmental impacts associated with conventional extraction methods.

1.2 Problem Statement

South Africa is a major global exporter of titanium ore and concentrate, selling partially beneficiated titanium slag for approximately USD 0.20/kg. In contrast, pure titanium metal is imported at USD 30/kg or more (Vilakazi, 2017). This disparity has a significant impact on potential foreign income and capital that could greatly benefit the country. Data from the United States Geological Survey (U.S. Geological Survey, 2019) indicates that South Africa supplies the titanium industry with approximately 20 % of raw titanium-bearing materials, valued at around USD 9 billion.

Approximately 95 % of South Africa's titanium mineral concentrates and by-products are exported to other countries, leaving only 5 % for domestic use. Despite having the second-largest titanium deposits globally, there is no known producer of titanium metal and only a handful produce titanium dioxide. Therefore, the country and its industries contribute very little to the important downstream beneficiation activities such as titanium metal and titanium dioxide production, among other value-added products (Rokita, 2017).

The lack of titanium industries in South Africa is partially due to the high electricity demands of pyrometallurgical (Kroll Process) and electrochemical (Cambridge FFC) methods that are mainly used to extract titanium from its ores (el Khalloufi *et al.*, 2021). The decreased availability and unpredictability of electricity in South Africa lately have discouraged the development of Ti-final product industries because of their high energy consumption using the above-mentioned methods (Durr, 2016). This has drastically increased local titanium prices, creating a need for technological innovation that can aid titanium extraction (de Bryne *et al.*, 2023).

Available methods for titanium beneficiation are usually not feasible for all titanium sources, such as low-grade mineral ores and tailings. Several titanium minerals, such as titanomagnetites, sphene (titanite), perovskite, and low-grade ilmenites with higher quality-degrading impurities, are unexploitable due to the lack of appropriate technology. The general commercial extraction methods used to produce titanium dioxide are the 'Sulphate and the Chloride processes', but these require high titanium percentages in the minerals. The 'Chloride process' technology requires pure-grade ore such as rutile (95-100 % TiO_2). In addition, only a few economically viable methods for Ti extraction (isolation) from tailings and titanium-containing ores/low-grade ores have been developed (Zhao *et al.*, 2015), rendering substantial amounts of titanium useless, resulting in the loss of this valuable element.

Another concern is that current titanium beneficiation methods are not environmentally friendly and wasteful due to the large amounts of highly concentrated acids used during the beneficiation process,

and large amounts of waste produced (Gázquez *et al.*, 2014). The corrosion and toxicity properties of waste products, including tailings and solutions, are major concerns in the titanium dioxide industry (Doan, 2003). With global demand for titanium dioxide spiralling, prices continue to escalate as consumption is expected to reach production capacity soon.

The largest waste producer worldwide is the mining industry, generating an estimated 5-7 billion tonnes of tailings per annum (Adiansyah *et al.*, 2015; Jones and Boger, 2012). This figure has been increasing due to the expansion of mining operations and the extraction of lower-grade ores. Contributing factors to the generation of larger quantities of tailings are that the ores which are mined, a) produce larger quantities of waste product (Kinnunen and Kaksonen, 2019), b) consumer demand also leads to an increase in industrial demand, thus necessitating the mining of additional ores. These factors all indicate that it will become inevitable to revisit mine waste products for titanium and other valuable metals (Green Action Task Force, 2019).

Mine tailings are not only unsightly but also cause environmental problems. Tailing storage facilities are prone to landslides and dam collapse (Nejeschlebová *et al.*, 2015; Kossoff *et al.*, 2014). Fatalities, community displacement, infrastructure damage, health issues, and loss of ecosystems and habitats have all been severe consequences of failing to manage tailings properly. The mining industry has been hit by a vast number of claims and lawsuits, resulting in billions of dollars in lost revenue following these accidents. The catastrophic 1966 avalanche of coal waste in Aberfan, Wales, engulfed the landscape, buildings, including an entire schoolhouse, leaving a deadly trail that resulted in the death of one hundred and forty-four people (Williams and Parkes, 1975). Recently, in Brumadinho, Brazil, a fatal collapse of a tailing dam occurred in January 2019 at the Córrego do Feijão iron ore mine (Owen *et al.*, 2020).

South Africa has also been affected by such disasters. The Zululand Anthracite Colliery in Ulundi, KwaZulu-Natal, collapsed in December 2021. In September 2022, a tailings dam in Jagersfontein collapsed due to the structural failure of the dam wall. The toxic mine waste and mud from this incident displaced many locals, creating an accommodation problem that is still being felt to this day. According to the Daily Maverick local newspaper, nine houses were swept away by the mudslide shown in **Figure 1.3** (Stoddard, 2022), and more than twenty were severely damaged, while four bodies were found buried under mud. A further seventy people were hospitalised due to injuries sustained during the collapse (Drage-Dlodlo, 2022).



Figure 1.3: Affected houses in Jagersfontein diamond mine tailings dam (Dlangamandla, 2022)

1.3 Rationale

Industrialisation of countries needs locally available raw materials to manufacture products and export them to global markets, propelling economies to greater heights. Titanium is abundant in South Africa, but its extraction is expensive. Given this challenge, it is imperative to develop more cost-effective and efficient alternatives to the current beneficiation processes. This will facilitate and help develop the industry's value by developing end-user markets such as the aerospace and medical sectors (Roux, 2020). **Figure 1.4** illustrates TiCoC's (S.A. Titanium Centre of Competence) envisioned consolidated titanium industry, comprising four levels: supportive platforms, technology development, industrialization, and commercialization, as well as the development of South African suppliers. Supportive platforms, such as titanium research and development in universities and government-subsidized laboratories, and necessary technology development, as exemplified by the development of the world's largest titanium printer, have been the country's primary focus (De Bruyne, 2023). The diagram shows that moving up the levels will benefit the S.A. Titanium industry development.

According to the New Growth Plan (NGP), mineral beneficiation is also one of the primary growth nodes for employment generation. The authors discussed the local titanium industry's potential national and socio-economic benefits (van Vuuren *et al.*, 2005; du Preez, 2014) such as revenue generation, permanent job creation, increased annual imports, and generation of foreign currency. (van Vuuren, 2009b).

Recent titanium metal industry research is pushing forward the limits in the hunt for more energy-cost-effective titanium recovery technologies than the currently used non-energy-efficient pyrometallurgical methods (Li *et al.*, 2022; Qiu and Guo, 2022). South Africa needs cost-effective,

relatively energy-efficient hydrometallurgical methods suitable for low-grade ores or tailings. (Department of Mineral Resources RSA, 2011).

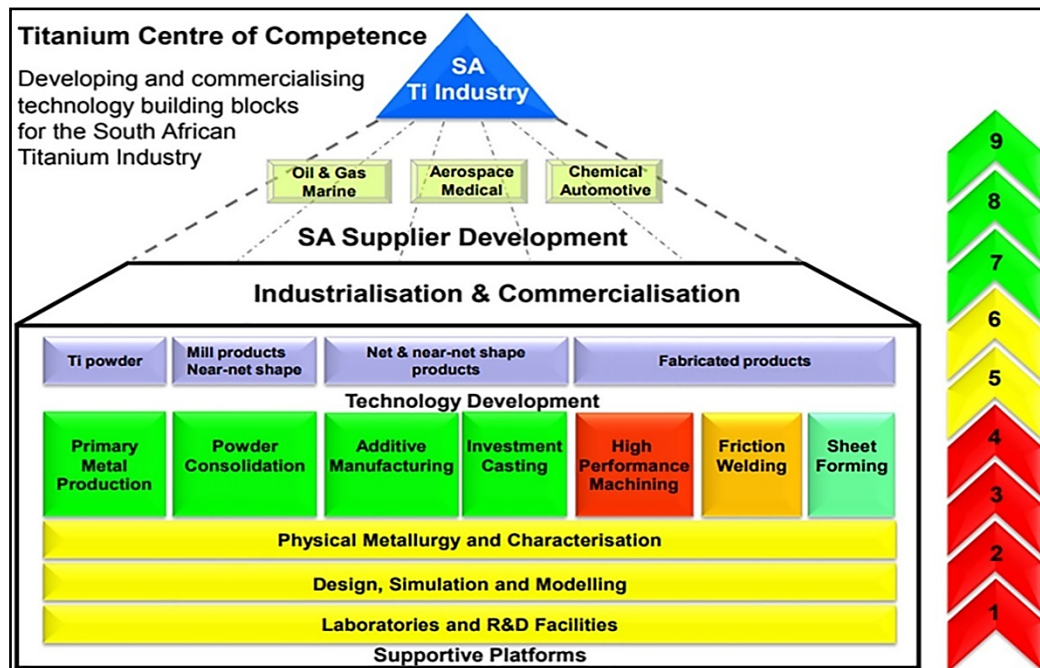


Figure 1.4: Consolidated South African titanium industry (du Preez, 2014)

Developing a commercially acceptable method for the pigment industry should be straightforward, environmentally friendly, suitable for low-grade ores and tailings, and compliant with regulations. It should reduce the extensive use and loss of expensive and corrosive chemicals through recycling, be suited for all ore grades, generate manageable intermediate products, and be economically beneficial. (Agboola *et al.*, 2020; Tayebi-Khorami *et al.*, 2019). A novel hydrometallurgical technique is required that uses lower quantities of electricity and less concentrated acids for extracting titanium dioxide from available raw materials with the lowest accessible proportion of titanium, in order to maximize the total recovery of titanium from low-grade ores and tailings, thereby increasing production capacity. It will enable cheaper and complete titanium beneficiation, (Moosakazemi *et al.*, 2020).

The social, health, and environmental impact of mine tailings and the potential for man-made disasters adds increased motivation to find alternatives to mine tailing management and beneficiation, which is a necessary by-product of mining and metals processing and will remain so in the near future (Owen *et al.*, 2020). Treatment of tailings also has a long-term impact on the mines' economic and ecological efficiency. The mitigation hierarchy is an excellent system for directing risk management and impact reduction by addressing potential sources of pollution, such as minimizing the production of unnecessary tailings. A goal of International Finance Cooperation (IFC) Performance

Standard 1 underscores the importance of Risk Assessment and Management of Environmental and Social Risks and Impacts is *“To adopt a mitigation hierarchy to anticipate and avoid, or where avoidance is not possible, minimise, and, where residual impacts remain, compensate/offset for risks and impacts to workers, affected communities, and the environment,”* (International Finance Corporation, 2012).

This concept supports the beneficiation of titanium from low-grade ores and tailings, thereby reducing waste and minimizing the harmful side effects associated with tailings. Contextually, many mining activities concentrate on only one target element. For example, in the vanadium industry, tailings contain high quantities of titanium, which is worthwhile to recover after the vanadium has been removed. Reclamation is sensible because the mineral has already been mined with little to no additional cost. Beneficiation of these tailings will reduce production costs while also improving environmental sustainability and generating valuable elements and products. It is therefore highly recommended to revisit certain mine tailings to recover the titanium. Reprocessing may be more cost-effective than processing virgin materials, and converting waste into value is essential (Palmer, 2023).

1.4 Aim and Objectives

The focus of this study is to establish whether a less expensive and complex procedure for titanium beneficiation from vanadium ore, as well as mine tailings, can be developed to produce a titanium product by selectively removing impurities and producing a titanium-enriched product. Extensive research is required to improve titanium beneficiation from different ores that contain significant percentages of titanium, which would otherwise be overlooked due to their non-conduciveness to normal beneficiation processes. The study also entails an extensive investigation of relevant literature on beneficiation and analytical techniques for extracting and quantifying titanium in typical titanium sources and ores containing a significant and valuable amount thereof. The objectives of this study include;

- an in-depth search of relevant literature on beneficiation techniques and processes for the extraction of titanium from different titanium sources
- perform physical characterisation of both mineral ore and the mine tailings
- complete chemical characterisation of both types of samples
- compare the physical and chemical characteristics of mineral ore and tailings
- investigate and evaluate different dissolution/leaching methods for Ti/V separation
- develop a simple hydrometallurgical method for maximum titanium leaching using different leachants

Chapter 2: Review of the element titanium

2.1 Discovery of titanium

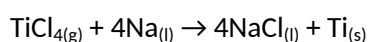
In 1791, while analysing the black magnetic sands near Manaccan (**Figure 2.1**) in Cornwall, England, the British clergyman and mineralogist William Gregor discovered a mineral that he named manaccanite (nowadays known as ilmenite, FeTiO_3). It contained a mixture of iron, oxygen, and an unknown element that he called manachite (titanium). Manaccanite or ilmenite was a significant source of what would later become known as titanium. The term "ilmenite" was coined after the Ilmen Mountains in the Southern Urals (Cahen and Wootton, 1920).



Figure 2.1: Location of Manaccan (Boothe, 2020)

Two years after Gregor's discovery was published, a renowned German scientist called Martin Heinrich Klaproth (1743-1817) isolated rutile, TiO_2 , from a piece of red schorl found in Boinik, Hungary. Klaproth published his findings in 1795, citing Gregor's study and the similarities between the two oxides, and Klaproth termed his product "iron-shot titanite from Cornwall." He stated that Manaccanite "is composed of iron and an unknown metallic oxide." (Housley, 2007). He discovered the same metal oxide in the mineral titanate and named it titanium. He studied a Manaccan sand sample and found that it contained approximately 51 % iron oxide, 42.3 % titanium dioxide, 3.5 % silica, and 0.25 % manganese oxide. Aware of Gregory's previous study, he concluded that the Cornwall and Hungary samples contained the same metal oxide, TiO_2 (Weeks, 1932).

Although W. Gregor in England and M.H. Klaproth in Hungary independently discovered titanium, its discovery remained largely insignificant for more than a century. It was only after this period that different scientists made tremendous progress in both its use and extraction processes throughout the 19th and 20th centuries. J.J. Berzelius, a Swedish chemist, accomplished a crude separation and isolated impure titanium in 1825 (Gázquez *et al.*, 2014). D. K. Kirillov, a Russian chemist, extracted very pure metallic titanium in 1875. In 1887, Lars Fredrik Nilson and Otto Pettersson, chemistry professors at Uppsala and Stockholm Universities, respectively, reported the isolation of 95 % pure titanium by reducing titanium tetrachloride with sodium in an airtight steel cylinder, as shown in **Equation 2.1**, producing yellow scales with a bluish surface (Weeks, 1932).



Equation 2.1

The advent of electricity altered the nature of laboratory equipment and procedures. In 1896, Henri Moissan, a French chemist, devised an electric furnace that he used to purify many previously impure elements. The combustion of metal oxides in the presence of carbon successfully produced 98% pure titanium. The isolated product was nitrogen- and silicon-free, containing 2% carbon. However, these impure titanium products were brittle due to the presence of oxygen and carbon, and processes had to be developed that excluded these elements during the production steps (Sehhat *et al.*, 2022; Jackson, 2021).

Early attempts to make pure titanium from its compounds led to the formation of nitrides (TiN), carbides (TiC), or carbonitrides (TiCN), which, because of their metallic lustre and appearance (**Figure 2.2**), were often mistaken as the metal itself (Froes, 2015).

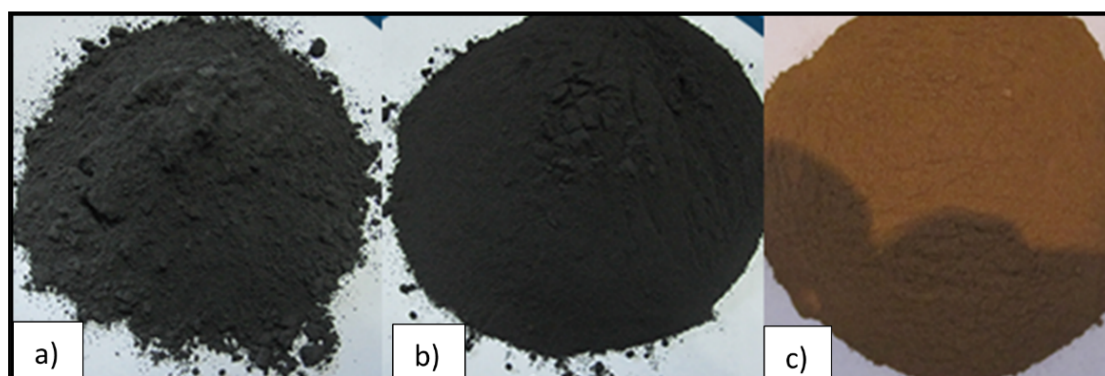
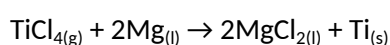


Figure 2.2: Titanium compounds (a) Titanium carbide (TiC), (b) Titanium carbonitride (TiCN) and (c) Titanium nitride (TiN) (HNJC Metal, 2020)

Pure titanium metal (99.9 %) was first isolated in 1910 by American chemist Matthew A. Hunter, who collaborated with the General Electric Company. Their process improved the Nielsen and Petterson process by creating an inert atmosphere at 1 000 °C to reduce titanium tetrachloride using sodium. Dilute hydrochloric acid was used to leach the titanium and remove sodium chloride from the product,

thereby obtaining metallic titanium that is practically free of impurities (Panigrahi *et al.*, 2010). This process was the first industrial process used for titanium metal production until the Kroll Process was developed.

In 1925, the van Arkel-de Boer (Crystal-bar or Iodine) process was used to obtain small quantities of ultrapure titanium developed by Antonne Eduard van Arkel and Jan Hendrik de Boer. They also successfully isolated zirconium, hafnium, and thorium using the same process (Binnewies and Schmidt, 2012). In 1932, William J. Kroll from Luxembourg initially reduced titanium tetrachloride with calcium to produce ductile titanium metal. In 1938, Kroll refined his initial process, replacing calcium with magnesium, and industrially produced 50 pounds of titanium. This method remains the preferred method for producing titanium metal to this day. The reaction equation is shown in **Equation 2.2**. It is now known as the Kroll process and produces a “titanium sponge” as its product, which serves as a feedstock for titanium alloys or titanium components (**Figure 2.3**). William Kroll devoted his entire life to this breakthrough commercial pyrometallurgical process, which still dominates the titanium production landscape, even though research continues to seek cheaper and more efficient methods to obtain pure titanium. Vacuum distillation where the sponge is heated under vacuum to vaporize the MgCl_2 and excess Mg is used to separate the MgCl_2 from Ti.



Equation 2.2



Figure 2.3: Titanium sponge (Stanford materials, 2023)

The titanium timeline indicates that it took approximately 150 years (from 1791 to 1938) to develop an economical procedure to produce pure Ti metal suitable for industrial usage. The U.S. Bureau of Mines improved the process for manufacturing large quantities of titanium metal and successfully

produced 2 tonnes in 1947. By 1953, the annual Ti production had reached 1,000 tonnes Peterson, 1954). **Figure 2.4** shows the current Ti sponge production by country.

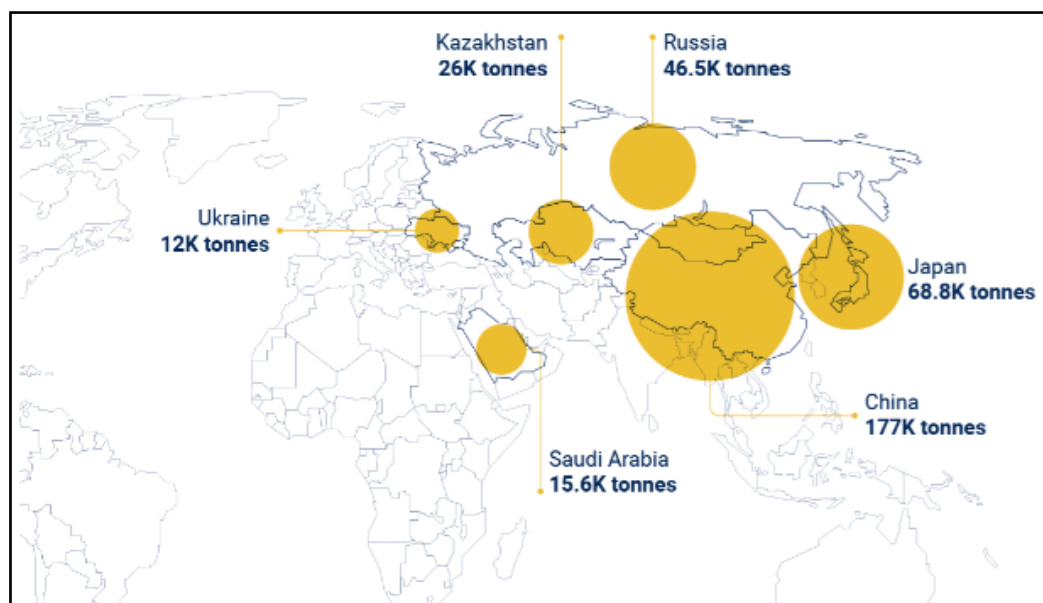


Figure 2.4: Titanium sponge production capacity by country in 2021 (Bhutada, 2023)

Ti product development also took place in the pigment industry. Initially, the adoption of titanium dioxide-containing paints was slow, so the history of the presence of titanium white in modern painting is poorly documented. Although the titanium pigment was discovered in 1821, the first white titanium dioxide pigment manufacturing company was established in 1916. The Titanium Pigment Corporation of Niagara Falls, New York, and the Titan Co. AS, of Norway, were instrumental in improving the technology (Sulphate process) that enabled mass production. At the same time, they began to commercially produce this new white pigment. It is estimated that 165.05 million Mt of titanium dioxide pigment were manufactured worldwide in the period between 1916 and 2011 (**Figure 2.5**). The largest application for Ti is in pigment industry. Currently, above 60 %. Nearly all companies use the chloride process.

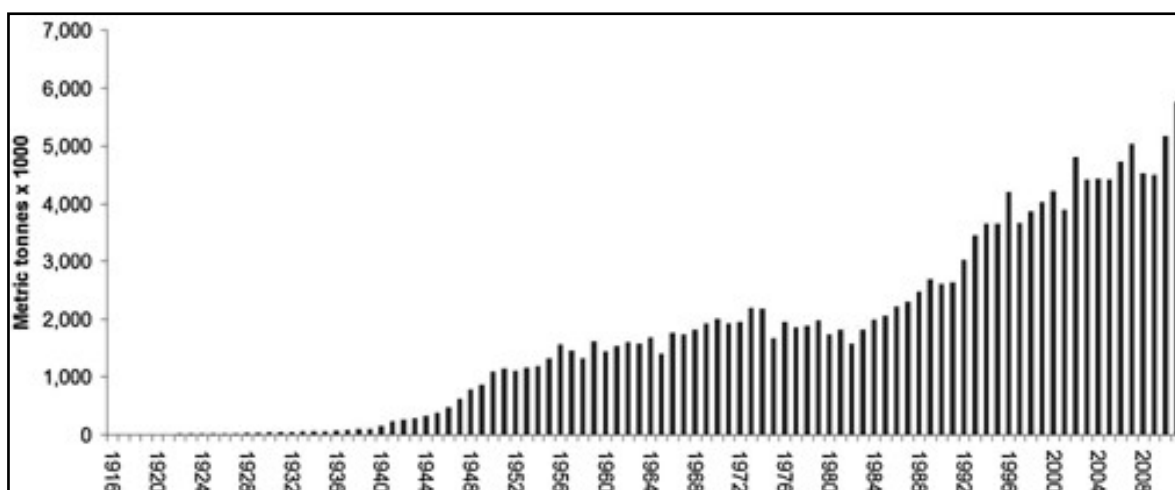


Figure 2.5: The historical production of titanium dioxide pigments worldwide, combined, 1916-2011 (Jovanović, 2015)

2.2 Natural occurrence of titanium

Initially, titanium was estimated to have an elemental abundance of about 0.45 % elemental titanium and 0.75 % as TiO_2 of the entire earth's crust (Wedepohl, 1995; Vinogradov, 1962; Goldschmidt, 1954; and Clarke and Washington, 1924). Elemental titanium was also estimated to be 0.9 % in a different study (Turekian and Wedepohl, 1961). Lee and Yao (1970) later revised the elemental abundance to 0.64 % and the titanium dioxide abundance to 1.07 %. The current estimate is 0.6% (Prando *et al.*, 2017; Sibum, 2003).

Rutile, ilmenite, leucosene, anatase, brookite, perovskite, sphene (titanite) and pyrophanite (MnTiO_3) are the main Ti-ore minerals. Commercial ilmenite deposits are broadly classified into three types: large-scale hard-rock deposits, alluvial tin-associated deposits, and beach sand-associated deposits (Sampath *et al.*, 2023). The massive hard rocks are found at Canada's Allard Lake deposit, the United States' Sanford Lake deposit, and Norway's Tellnes deposit (Charlier *et al.*, 2010; Diot *et al.*, 2003). Ilmenite deposits associated with tin have been identified mainly in Nigeria and Malaysia. Many nations have deposits of ilmenite beach sand (black sand), including Sri Lanka, India, South Africa, Australia, and Brazil (Premaratne and Rowson, 2003). Most deposits are found in Asia (China, Japan, and India), North America (the USA and Canada), Australia, and New Zealand (**Figure 2.6**). The leading producers in Africa are Mozambique and South Africa. Australia, South Africa, and Ukraine are the biggest rutile producers, while China and the USA mainly produce ilmenite. South Africa is currently the second biggest Ti mineral producer in the world (after Australia) from Heavy Mineral Deposits, KZN (South Coast) and Namakwa Sands (West Coast).

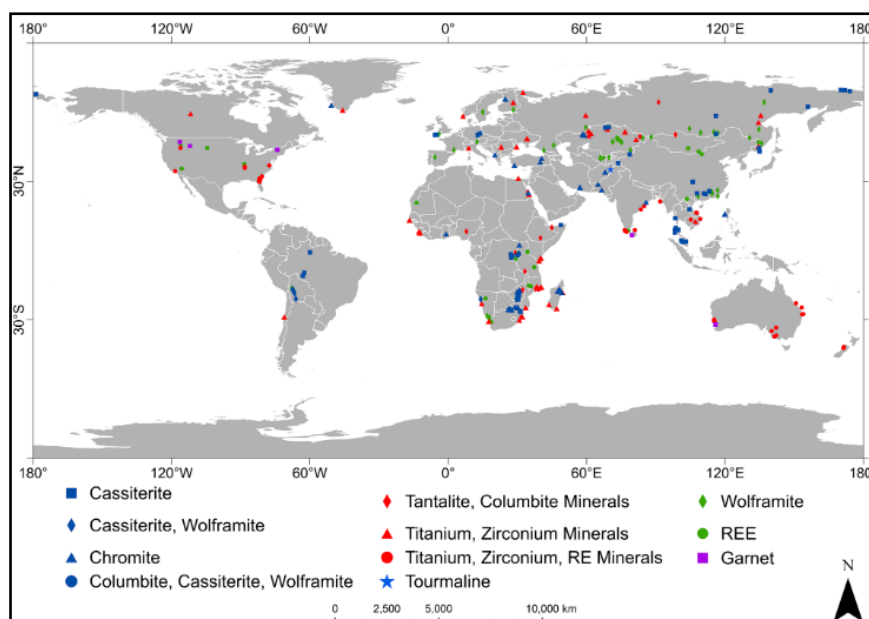


Figure 2.6: The global distribution of heavy mineral deposits and the main commodities in each occurrence (Subasinghe *et al.*, 2022)

Commonly found in black sand, ilmenite is the primary source of titanium. Black sand is a type of sand that is characterized by a dark hue and consists of heavy, glossy and a partially magnetic combination of generally fine grains found as part of a placer deposit (Hebatalrahman *et al.*, 2019). Sands with a specific gravity greater than 4.0 g/cm³ are referred to as heavy mineral sands (HMS) or simply heavy minerals. The term ilmenite also encompasses the entire range, from unweathered ilmenite (TiO₂ content of less than 50 %) to altered ilmenite (TiO₂ content of more than 60 %). Altered ilmenite, containing more than 70 % TiO₂, is commonly referred to as leucoxene (Contreras *et al.*, 2017).

Both Ilmenite (TiFeO₃) and rutile (TiO₂) are found in HMS, where chemical weathering has concentrated the extremely resistant titanium minerals under conditions such as those created by ocean waves. Weathering of host rocks releases minerals, but only the durable and chemically stable minerals, such as titanium oxides and ilmenite, resist the transport by wind and water to become part of a new deposit (Degryse and Braekmans, 2014). The chemically inert and physically robust titanium mineral fractions are released in the ocean and wave actions deposit these minerals onto beaches forming the HMS which commonly include also zircon (Zr/Hf)SiO₄ and monazite (Ce,La,Nd,Th)PO₄, and garnet (A₃B₂(SiO₄)₃ where A is a bivalent metal and B is a trivalent metal), among others Ti-minerals (Table 2.1).

Table 2.1: Minor titanium minerals naturally occurring in heavy minerals beach sands (Mackey, 1994)

Mineral	Formula	Ti (%)	Mineral	Formula	Ti (%)
Anosovite	Ti ₃ O ₅	64.2	Hydrorutile	TiO ₂ .xH ₂ O	48.9

Crichtonneite	$(\text{Ca,Ln,Ac})_{2,x}(\text{Ti,Mg,Al,Fe.Tr})_{21}\text{O}_{38}$	12.1	Kalkowskyn	$\text{Fe}_2\text{Ti}_3\text{O}_9$	35.9
Knopite	$(\text{Ca,Ti,Ce}_2)\text{O}_3$	11.5	Doetlerite	TiO_2	59.9
Pyrophanite	MnTiO_3	31.7	Fulvite	TiO	74.9
Mananilmenite	$(\text{Fe,Mn})\text{TiO}_5$	20.1	Gelkielite	MgTiO_5	31.5
Picroilmenite	$(\text{Mg,Ge})\text{TiO}_5$	21.3	Tielite	AlTiO_5	30.9
Yttrocrasite	$\text{YTh}_2\text{Ti}_4\text{O}_{11}$	35.1			

*Ti maximum % composition according to percentage composition calculations.

In addition to ilmenite and rutile, titanomagnetite is also a source of titanium (**Figure 2.7**), Gázquez *et al.*, 2014). Ilmenite has a titanium dioxide content ranging from 40 % to 65 %. Other components include ferrous oxide or ferric oxide, as well as trace quantities of vanadium, magnesium, and/or manganese (el Khalloufi *et al.*, 2021). Natural forms of TiO_2 are frequently coloured due to the presence of impurities. The titanium in the ilmenite is present in the +4 oxidation state. In contrast, only about 20 % of the iron is in the +3 oxidation state, while the remainder of the Fe is in the +2 oxidation state (Samal *et al.*, 2009). It is this combination of iron oxidation states that renders ilmenite magnetic due to the presence of unpaired electrons in the Fe^{2+} valence orbitals.

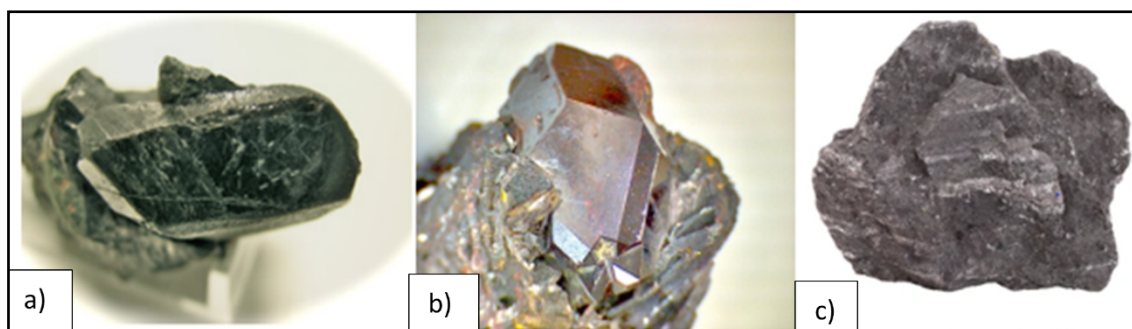


Figure 2.7: Ilmenite (a), rutile (b) and titanomagnetite (c) (Gázquez *et al.*, 2014)

Natural rutile (TiO_2) is a precious and scarce Ti-containing mineral, and worldwide, no other substantial rutile-dominant deposits have been identified in over a century. Kasiya, a region in Malawi, is currently recognised as having the world's largest single rutile deposit. The mineral resource estimate encompasses extensive zones of very high-grade rutile that span a vast region of over 200 km². Sierra Leone, Australia, and Kenya also possess rutile deposits. **Figure 2.8** shows its quantity distribution in these countries. Current natural rutile supplies are dwindling as reserves at numerous deposits are being depleted for product development, coinciding with deteriorating ore grades. Sierra Rutile in Sierra Leone and Base Resources' Kwale operations in Kenya are two examples. Furthermore, with only a few new deposits expected to come online, natural rutile supplies are likely to remain severely scarce as a Ti source (Svm, 2023). Different mineral resource categories for Kasiya are shown, while the total is shown for its competitors.

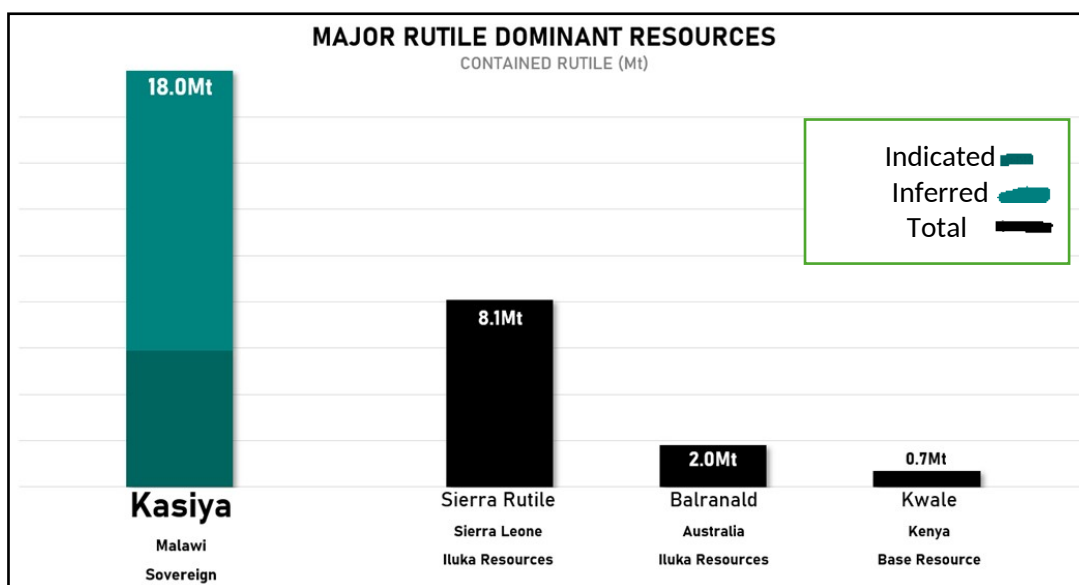


Figure 2.8: Major rutile resources (Svm, 2023)

There are minerals with a higher content of Ti than ilmenite, such as anatase, brookite, perovskite, and sphene, among others (Table 2.2). However, they are not the primary industrial source of titanium due to their instability and scarcity. Anatase is known to occur with brookite, and the former is utilised in nanotechnology, while the latter has limited economic value. Sphene and pyrophanite are minerals that are unlikely to be used as ores for titanium metal recovery, due to the high processing costs.

Titanomagnetite is a mineral that contains titanium and iron oxides, with the formula $\text{Fe}^{2+}(\text{Fe}^{3+}, \text{Ti})_2\text{O}_4$. Titaniferous magnetite, mogensenite, Ti-magnetite, and titania magnetite are other names for it. Titanomagnetite ores containing vanadium are among the most promising unconventional ores, serving as a significant source of titanium, vanadium, and iron. Its deposits total tens of billions of tonnes worldwide (Deryabin, 2007). Titanomagnetite ore utilisation for the metallurgical processing of Ti is crucial owing to the depletion of rich magnetite reserves. Furthermore, processing titanomagnetite can help alleviate the titanium raw material shortage (Sachkov *et al.*, 2017).

Table 2.2: Estimated TiO_2 content in titanium-containing minerals (Van Gosen, 2014; Pownceby *et al.*, 2008; Murphy and Frick, 2006; Grey and Reid, 1975; Teufer and Temple, 1966)

Mineral	Formula	TiO ₂ %	Characteristics
Rutile, Anatase, Brookite	TiO ₂	95-100	Polymorph of rutile. Crystallise as blue or black tetragonal crystals. Titanium mineral alteration result.
Leucoxene	FeTiO ₃	70-100	An uncommon orthorhombic polymorph of rutile formed by the alteration of ilmenite minerals.
Altered ilmenite	FeTiO ₃ -Fe ₂ TiO ₉	53-70	Arizonite is an altered ilmenite having rutile-like characteristics. Crystallises in a hexagonal shape.
Pseudorutile	FeTiO ₉	60-65	Alteration in the composition of ilmenite and pseudorutile. Optically homogenous and amorphous.

Perovskite	CaTiO ₂	58	Altered form of all titanium-containing minerals with a high TiO ₂ content. Internal reflection optically distinguishes them from rutile and anatase.
Ilmenite	FeTiO ₃	45-53	A reddish brown, grey, yellow, green, or red gem. It occurs as an accessory mineral in a variety of rocks and minerals.
Titanate (Sphene)	CaTiSiO ₅	40	Somewhat uncommon accessory mineral. It is found as a secondary mineral in metamorphic and igneous rocks.
Ulvospinel	FeTiO ₄	36	A black, brown to reddish-brown accessory mineral found in igneous rocks. Often occurs in titaniferous magnetite iron ores, kimberlites, and strongly reduced iron-bearing basalts, among other places.
Pseudobrookite	Fe ₂ TiO ₅	33	A rare, dark black mineral having needle-like acicular prismatic crystals, found in the presence of pyroxenes, hornblende, tridymite, topaz, hematite, and bixbyite.
Titanohematite	(Fe, Ti) ₂ O ₃	0-34	A homogeneous cubic mineral with the main phase Fe ₂ O ₃ . Consists of more than 5 % TiO ₂ . It is a solid solution of ulvospinel and magnetite.
Titanomagnetite	(Fe, Ti) ₂ O ₄	0-30	It is a hematite-ilmenite solid solution. It is light grey to white. It has a lower reflectivity.

Titanium is not only limited to the Earth's crust, but is found in human blood, bones, and tissues. Humans are estimated to consume approximately 0.8 mg daily, but these minute quantities are not absorbed into the bloodstream. An early study also showed the presence of titanium dioxide in plant ash (Table 2.3).

Table 2.3: Titanium dioxide percentages in some vegetable ash (Wait, 1896)

Plant ash	Titanium dioxide (%)
Oak wood	0.31
Apple and pear wood mixed	0.21
Apple	0.11
Cow peas	0.01
Cottonseed meal	0.02

The vanadium-bearing titanomagnetite mineral is a strategic source of titanium, iron, vanadium, and other valuable elements (Zhang *et al.*, 2018). However, its complex mineralogy and low TiO₂ grade have made it difficult to comprehensively utilise titanomagnetite concentrates in the extraction and isolation of titanium. It has commonly been considered that the recovery of TiO₂ from vanadium-bearing titanomagnetite is industrially impossible and uneconomic. Nevertheless, extensive research has continued to be carried out on this subject matter. Large reserves of vanadium-bearing

titanomagnetite are available worldwide with TiO_2 grades ranging between 1 and 20 % wt (Taylor *et al.*, 2006). The Panzhihua Complex in the Sichuan Province, in China, also has the largest deposits (Pang *et al.*, 2010), followed by the Windimurra Complex in Australia (Ivanic *et al.*, 2010). The Bushveld Complex in South Africa, the largest known deposit of its kind in the world, is renowned for its comparatively high titaniferous magnetite concentrations, which also have a high vanadium content that can be processed for its titanium content.

2.3 Physical properties of titanium metal

Titanium is the fourth most abundant structural metal after aluminium, iron, and magnesium. Although it is more abundant than zinc, copper, and lead, it is more difficult to recover (De, 1993). This is because the extraction process is slow, expensive (magnesium and sodium used are expensive), energy and labour-intensive. In its metal form, it is a silvery grey metal, a light and strong metal with a rough and sharp texture (**Figure 2.9**).

Titanium has low density, very low electrical and thermal conductivity, good strength, and excellent corrosion resistance. It has the same strength as steel but is 45 % lighter, and it has twice the strength of aluminium but is only 60 % heavier. Pure titanium is ductile, malleable, and lustrous, and becomes brittle when contaminated by carbon and nitrogen. Natural titanium has five stable isotopes, ^{46}Ti (8 %), ^{47}Ti (7.3 %), ^{48}Ti (73.8 %), ^{49}Ti (5.5 %) and ^{50}Ti (5.4 %), but several unstable isotopes (radioactive) like ^{51}Ti are also known (Frost and Lindsley 1991; Froes 2015). A comprehensive list of titanium metal's physical and mechanical properties is presented in **Table 2.4**.

Table 2.4: Titanium metal physical and mechanical properties (Froes, 2015)

Physical Property	Description
Natural state	Solid
Atomic Number	22
Atomic mass (amu)	47.867
Electronic configuration	[Ar] 3ds ² 4s ²
Stable Isotopes	^{46}Ti , ^{47}Ti , ^{48}Ti , ^{49}Ti , ^{50}Ti
Atomic radius (pm)	187
Melting point (°C)	1660
Boiling point (°C)	3287
Density (g/cm ³)	4.51
Electronegativity	1.54
Van de Waals radius (pm)	187
Atomic radius (pm)	147
First ionisation energy (kJ mol ⁻¹)	658

Thermal conductivity (W/m-K)	17
Thermal expansion (0-315 °C), $\mu\text{m/m.}^\circ\text{C}$	≈ 3
Specific heat capacity (J/g. $^\circ\text{C}$)	2173
Electrical resistivity ($\mu\Omega\cdot\text{cm}$)	42
ΔH fusion (J/g)	435.4
Heat capacity, (J/mol $^\circ\text{C}$)	26.06
Poisson's ratio	≈ 0.4
Magnetic susceptibility (emu/g)	3.17
Tensile modulus $\times 10^3$ (MPa)	≈ 101
Compression modulus $\times 10^3$ (MPa)	≈ 103
Shear modulus $\times 10^3$ (MPa)	≈ 44
Tensile strength (MPa)	240
Tensile yield strength (0.2 %) MPa	170
Compression yield strength (0.2 %) MPa	170
Shear strength (MPa)	≈ 140
Elongation in tension (%)	35
Hardness (1500 kg load) HB	≈ 65
Bend radius (R/t)	≈ 4



Figure 2.9: Pure titanium metal (Rhj, 2021)

2.4 Chemical properties of titanium

Titanium chemistry shares many similarities with zirconium due to being in the same group on the periodic table (Group 4), although its aqueous solution chemistry is analogous to that of vanadium and chromium due to similarities in oxidation states and their shared occurrence in ore deposits like titanomagnetite. Titanium phosphate, sulphate, and nitrate display metallic properties, while titanates of calcium, iron, and sodium exhibit non-metallic characteristics (Stamper, 1970; Vinogradov, 1959). Titanium has the electronic configuration $[\text{Ar}]3d^24s^2$, and it loses 2 to 4 electrons in the 3d and 4s orbitals to form relatively stable Ti^{2+} , Ti^{3+} , and Ti^{4+} oxidation states. This results in the formation of several complexes with s- and p-donating ligands such as O^{2-} , OH^- , and halides (X^-), which stabilise this high oxidation state of the element.

2.4.1 Ti⁴⁺ oxidation state

The most stable and common oxidation state is +4. However, compounds of a range of lower oxidation states, such as -1, 0, +2, and +3, are also known (Tian *et al.*, 2006). These are readily oxidized to Ti⁴⁺ by air, water, or other reagents such as hydrogen peroxide, permanganate, and nitric acid. In nature, Ti forms a variety of titanium dioxides such as rutile, anatase, and brookite, which are attributed to its stable +4 oxidation state. Titanium is predominantly present in these minerals as titanium dioxide; therefore, it is commonly reported as TiO₂ in chemical analyses rather than the titanium element, Ti. Out of the many +4 compounds (some of them listed in **Table 2.5**), TiO₂ is the most important. It is used as a precursor to make titanium metal directly or by first being converted into titanium tetrachloride (TiCl₄). The production of TiCl₄ involves heating TiO₂ in the presence of Cl₂ gas, which acts as a reducing agent and a source of Cl⁻ ion ligands. This is because Ti⁴⁺, which has the electron configuration [Ar]3d⁰4s⁰, has the 3d orbitals available for Cl⁻ ion ligands to form a complex and stabilise its high oxidation state. The +4 oxidation state can be reduced to +3, +2, and 0 (**Figure 2.10**) with reduction potentials that strongly depend on the ligand environment and conditions.

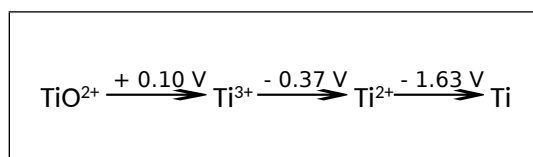


Figure 2.10: Scheme illustrating the reduction process from Ti⁴⁺ to T⁰ and the respective standard reduction potentials

The +4 aqueous chemistry is confined to strongly acidic liquids. The Ti⁴⁺ ion cannot exist in water, but the titanyl ion (TiO²⁺) (aq) exists at very low pH. The actual ion, present in strongly acidic solutions, however, is probably not TiO²⁺(aq), but TiO(OH)⁺(aq) or Ti(OH)₂²⁺(aq). A solution containing titanium in its +4 oxidation state can only remain colourless if it is kept highly acidic. When an acidic solution of the colourless titanyl ion compound is diluted, a white precipitate of hydrous titanium (IV) oxide (TiO₂·nH₂O) is formed. Even at higher pH levels on the acidic side, TiO²⁺(aq) remains highly prone to hydrolysis. Ti⁴⁺ is a highly stable, intensely red peroxo complex at low pH, which retains its colour even under extreme dilution, appearing yellow. If a few drops of 20 % H₂O₂ are added to the purple Ti³⁺ solution in dilute HCl, two distinct colours are formed due to the oxidation of the Ti³⁺ to colourless Ti⁴⁺, then orange when excess hydrogen peroxide is added due to the formation of a +4 complex with hydrogen peroxide with the formula [Ti(OH)₂(H₂O)(H₂O₂)]⁺ (Mori, 1956).

Aqueous solutions of Ti^{4+} are colourless. This is because its electron configuration $[\text{Ar}]3d^0$ has no unpaired electrons; therefore, there are no d-d transitions, resulting in the formation of the colourless $\text{Ti}(\text{H}_2\text{O})_6^{4+}$ complex.

2.4.2 Ti^{3+} oxidation state

The +3 oxidation state is relatively common. Ti^{3+} forms several stable compounds, which can be obtained from Ti (IV) salts using a zinc/dilute sulphuric acid reducing agent. The most important +3 compound is the crystalline titanium trichloride, which is particularly useful as a catalyst in industrial stereospecific polymerisation. Other compounds include Ti_2O_3 , $\text{Ti}(\text{OH})_3$, and Ti_2CO_3 , among others. The +3 oxidation state is relatively stable in acidic conditions, thereby widening its aqueous chemistry, as discussed in this section.

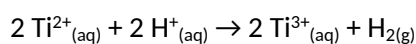
Titanium exists in aqueous solutions in the +3 oxidation state. Slow oxidation occurs when Ti^{3+} is exposed to air, resulting in the conversion of Ti^{3+} to Ti^{4+} . The process occurs under acidic conditions at a temperature of 20 °C and 1 atm pressure, and it takes several days for the conversion of Ti^{3+} to Ti^{4+} to occur.

Ti^{3+} is purple in an aqueous medium. The purple colour of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ (H_2O is the ligand in an aqueous medium) disappears and changes to colourless. The Ti- H_2O metal complex formation leads to d-d orbital splitting, where some d-orbitals move to higher energy levels, while the remaining orbitals move to lower energy levels. The transmission of the unpaired electron in the Ti^{3+} complex ($[\text{Ar}]4s^0d^1$) from the t_{2g} (lower energy) to the e_g orbitals (higher energy) results in the observation of the violet colour in solution at 500 nm.

Titanium is relatively labile in its common oxidation states. Water exchange is used as a convenient benchmark. The rate constant for water exchange in the Ti(III) species $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is $1.8 \times 10^5 \text{ s}^{-1}$ at room temperature (Hugi *et al.*, 1987).

2.4.3 Ti^{2+} oxidation state

The chemistry of the +2 oxidation state is limited. The +2 oxidation state cannot exist in an aqueous solution due to its high reduction power, producing hydrogen gas and an alkaline Ti^{3+} species. A known +2 oxidation state compound is titanium (II) oxide. It can be prepared by heating titanium dioxide and titanium metal at 1,500 °C. Acidic solutions of TiO are stable for a short time as they decompose, producing hydrogen according to **Equation 2.3** (Holleman *et al.*, 2001).



Equation 2.3

2.4.4 Ti metal

Titanium metal is insoluble in water, and it is not attacked by cold mineral acids or by hot aqueous alkali. However, it dissolves readily in HF, hot HCl, hot HNO₃, hot H₂SO₄, and hot concentrated H₃PO₄. The dissolution accelerates as the acid concentration increases (Hung *et al.*, 2017). Titanium reduces water vapour to form Ti dioxide and hydrogen, and it reacts similarly with hot concentrated acids, although it forms trichloride with hydrochloric acid.

The metal reacts with many other metals such as Al, Be, Cr, Fe, and metalloids such as Sb and B, forming intermetallic or interstitial compounds (Valentine 2011) such as titanium aluminide (TiAl), titanium antimonide (Ti₄Sb), titanium diboride (TiB₂), TiCr₂ and TiFe₂ (Ziemnicka-Sylwester, 2013; Ivanchenko and Pryadko, 2008; Abe and Tsuji, 1983). It is also highly reactive towards oxygen and readily forms a passive, protective TiO₂ coating (leading to corrosion resistance) when exposed to elevated temperatures in air; however, at room temperature, it resists tarnishing.

Titanium reacts with various non-metals such as halogens, carbon, nitrogen, silicon, and sulphur at very high temperatures. The reactions produce very stable, hard, and refractory compounds such as TiN, TiC, TiB, and TiB₂. Titanium's strong affinity for carbon, nitrogen, and hydrogen affects its mechanical properties. Therefore, it is important to process titanium in their absence (Zadra, 2013). The metal absorbs hydrogen to give TiH₂. It forms the nitride, TiN, and the carbide, TiC, in the presence of nitrogen in a high-energy, vacuum environment.

2.4.5 Titanium halides

Titanium is combined with halogens at 200 °C, and Ti (IV) halides are formed. **Table 2.5** presents the physical properties of Ti (IV) halides. All titanium tetrahalides behave as Lewis acids, dissolving in polar solvents to give a series of addition compounds and adducts. The trihalides of titanium can be prepared by reducing the tetrahalides with the metal. The dihalides TiX₂ (X = Cl, Br, I) are black solids (Valentine, 2011).

Table 2.5: Titanium tetrahalides physical properties (Libretexts, 2023)

Formula	Colour	Melting point (°C)	Boiling point (°C)
TiF ₄	White	-	284
TiCl ₄	Colourless	-24	136.4
TiBr ₄	Yellow	38	233.5
TiI ₄	Violet black	155	377

Titanium (IV) chloride is an example of a covalent chloride. It is a colourless liquid that emits fumes in moist air when it reacts with water, resulting in titanium (IV) oxide and hydrogen chloride fumes. To avoid this, everything must be kept completely dry (Titanium Dioxide Manufacturers Association, 2017).

2.4.6 Ti compounds

Titanium forms a wide range of organic and inorganic compounds. The salts are known in the three oxidation states. Titanium coatings are also a special group of titanium compounds. These are titanium carbonitride TiCN, titanium nitride (TiN), and titanium carbide (TiC). These are very hard cermets used for drilling and reaming. TiC is formed by heating pure TiO₂ with carbon black under high temperatures (1700-2100 °C) (Wolfe *et al.*, 2014). Other known compounds are the sulphur-containing compounds such as TiS₂, Ti₂S₃, and TiS, as well as the lower metal oxides, Ti₂O₃ and TiO. **Table 2.6** shows a list of well-known inorganic and organometallic titanium compounds.

Table 2.6: Chemical inorganic and organometallic compounds of titanium in different oxidation states (ChemEurope, no date)

Titanium compound	Oxidation state
TiO ₂	+4
TiCl ₄	+4
TiC	+4
(NH ₄) ₂ [TiF ₆]	+4
TiOCl ₂	+4
Ti{OCH(CH ₃) ₂ } ₄	+4
TiN	+3
Ti ₂ O ₃	+3
Ti ₂ S ₃	+3
TiCl ₃	+3
((C ₅ H ₅) ₂ TiCl ₂)	+2
TiCl ₂	+2
TiO	+2

2.4.7 Titanium complexes

The most common coordination number of titanium is six (recognised by all metal oxidation states), although four-, five-, seven-, and eight-coordinate compounds are known. **Table 2.7** presents the common oxidation states of titanium, along with their associated coordination numbers and stereochemistry. This highlights titanium's ability to exist in multiple oxidation states—a feature that fuels significant interest in its coordination chemistry, particularly given its vital roles in materials science and catalysis. An example of the synthesis of one of the compounds is when hydrated TiO₂ is dissolved in concentrated HF, a colourless hexafluorotitanate(IV) octahedral complex with the formula [TiF₆]²⁻_(aq) is formed.

Table 2.7: Titanium Oxidation states and stereochemistry (Wilkinson *et al.*, 1987)

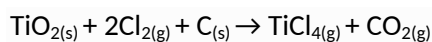
Oxidation state	Coordination number	Geometry	Examples
Ti ^{-I}	6	Octahedral	[Ti(bipy) ₃] ⁻
Ti ⁰	6	Octahedral	[Ti(bipy) ₃]
Ti ^{II} , d ²	4	Distorted tetrahedral	(η^5 -C ₅ H ₅) ₂ Ti(CO) ₂
	6	Octahedral	TiCl ₂
Ti ^{III} , d ¹	3	Planar	Ti{N(SiMe ₃) ₂ } ₃
	5	Trigonal bipyramidal	TiBr ₃ (NMe ₃) ₂
	6*	Octahedral	TiF ₆ ³⁻ , TiCl ₃ (THF) ₃
Ti ^{IV} , d ⁰	4*	Tetrahedral, Distorted tetrahedral	TiCl ₄ , (η^5 -C ₅ H ₅)TiCl ₂
	5	Distorted Trigonal bipyramidal, Square planar	K ₂ Ti ₂ O ₅ , TiO(porphyrin)
	6*	Octahedral	TiF ₆ ²⁻ , Ti(accac) ₂ Cl ₂
	7	ZrF ₇ -type, Pentagonal bipyramidal	[Ti(O ₂)F ₅] ³⁻ , Ti ₂ (ox) ₃ ·10H ₂ O
	8	Distorted dodecahedral	TiCl ₄ (diars) ₂ , Ti(S ₂ CNEt ₂) ₄

d^x - number of electrons in the d orbital

2.5 Titanium metal manufacturing from titanium mineral concentrate

The preferred techniques for manufacturing titanium metal are based on the reduction of titanium tetrachloride. This is because it is not feasible to generate titanium metal using the conventional approach of reducing the dioxide with carbon due to the development of a very stable carbide (TiC). Furthermore, the metal reacts with both dioxygen and dinitrogen at high temperatures. At 900 °C, hydrogen reduction only reduces TiO₂ to Ti₂O₃, whereas common reducing metals such as Na, Al, Ca, or Mg seldom provide pure products (Valentine, 2011).

The Kroll process (summarised in **Figure 2.11**) is the primary industrial method of obtaining titanium metal from minerals (Kroll, 1965; Kroll, 1940). Rutile ore with a TiO₂ grade of around 95 %, upgraded ilmenite (UGI), or upgraded titanium slag (UGS) are used as feed materials for titanium metal production. The powder is heated at 1 027 °C while adding chlorine and carbon to generate crude titanium tetrachloride according to **Equation 2.4**. The TiCl₄ is subsequently reduced with magnesium in either a vacuum furnace or an argon environment at red-hot temperatures of 800 - 850 °C to remove the chlorine and leave behind the pure metal. The reaction is shown in **Equation 2.5**. Condensation is used in this method to eliminate impurities such as FeCl_x and AlCl₃, which have higher boiling temperatures than TiCl₄ (136 °C). Impurities with similar boiling temperatures to TiCl₄, such as vanadium oxychloride (VOCl₃), tin tetrachloride (SnCl₄), and silicon tetrachloride (SiCl₄), stay in the TiCl₄ intermediate. A multistep distillation method removes SnCl₄ and SiCl₄, while VOCl₃ is challenging to remove because it has a boiling point of 127 °C, close to that of titanium tetrachloride. Therefore, it is reduced with a reducing agent such as hydrogen sulphide (H₂S) to form vanadium tetrachloride (VCl₄), which has a higher boiling point (154 °C) than VOCl₃. After the distillation procedure, high-purity (>99.98 %) TiCl₄ is achieved.



Equation 2.4

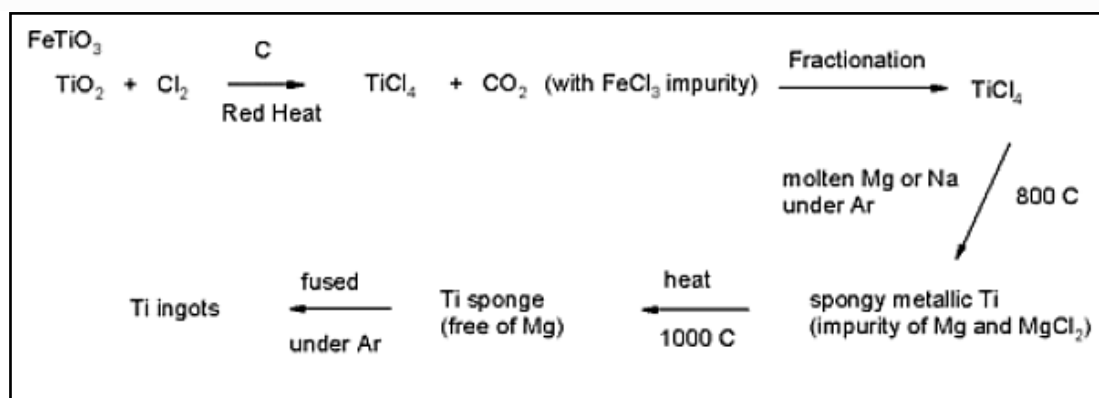
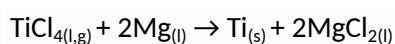


Figure 2.11: Kroll process flow diagram (Libretexts, 2023)

Titanium sponge is the most basic form of titanium metal obtained through the Kroll process. It is known as a “sponge” metal due to its numerous pores. **Figure 2.12a** depicts a schematic illustration of a steel reduction container used for titanium metal production from TiCl_4 feed. The following process is electrolysis, which separates magnesium chloride through the reduction and separation processes by electrolyzing it into Cl_2 gas and magnesium metal. The diagram of the vacuum distillation cell used to remove Mg and MgCl_2 is shown in **Figure 2.12b** (Takeda *et al.*, 2020). The magnesium and chlorine gases are reused in the reduction and chlorination processes. Lastly, the magnesium-free sponge is melted into ingots under argon.



Equation 2.5

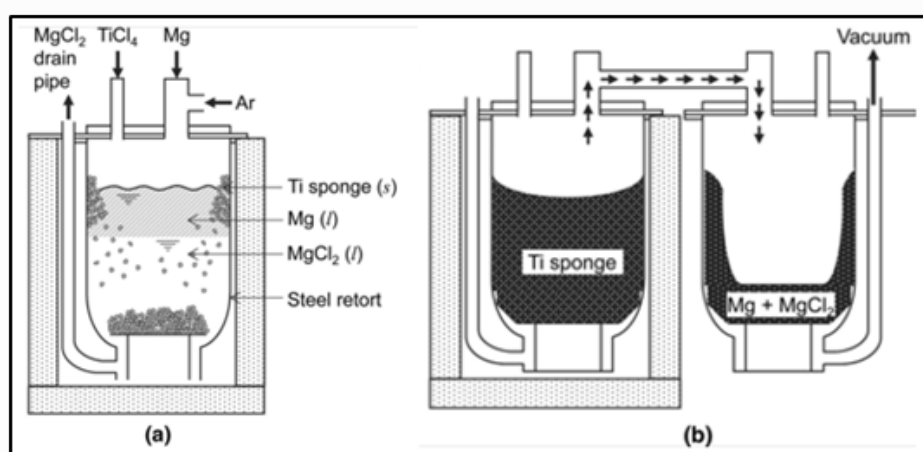


Figure 2.12: The schematic depiction of the reaction system of the Kroll process (a) Magnesiothermic TiCl_4 reduction (b) Vacuum distillation is used to remove Mg and MgCl_2 from titanium sponge (Takeda *et al.*, 2020)

However, the Kroll technique has limitations, including a lengthy production time frame, high production temperatures, and extensive energy consumption (van Vuuren, 2009). Another significant

barrier to making low-cost titanium goods is that the Kroll process produces titanium sponge. According to Kraft (2004), the entire cost of conventional titanium components comprises 38 % for Ti sponge production *via* the traditional Kroll process, 15 % for Ti sponge refinement, and the remaining 47 % for the machining step, which creates nearly 75 % of the Ti sponge scrap. As a result, it was proposed that powder metallurgy techniques, such as additive manufacturing, be used to produce near-net-shape objects. Other procedures, such as the hydride-dihydride (HDH) process, could convert the Ti sponge to Ti powder. However, this is also expensive (Van Vuuren *et al.*, 2011; McCracken *et al.*, 2010). This highlights the need for further research on more cost-effective methods for obtaining titanium powder. Potential processes such as the Ono and Suzuki process (Suzuki *et al.*, 2021; Suzuki *et al.*, 2003), the Fray-Farthing-Chen Cambridge process (Oosthuizen, 2011), the Armstrong process (Chen *et al.*, 2012), the Council for Scientific and Industrial Research Ti process (van Vuuren, 2015), the direct reduction of titanium slag process (Fang *et al.*, 2013), and hydrogen-assisted magnesiothermic reduction (HAMR) (Zhang *et al.*, 2017) are being investigated and refined. The HAMR could reduce the Kroll process energy by 62 % (Oosthuizen, 2011).

These methods also have their limitations. Titanium's high chemical affinity for oxygen makes it more difficult to remove the oxygen from TiO_2 to give Ti, compared to reducing chlorine from TiCl_4 to make Ti. Furthermore, during the reduction of TiO_2 to Ti, the synthesised byproducts of oxides are challenging to remove due to their high melting point. On the other hand, the chloride species formed as byproducts during the reduction of TiCl_4 can be easily removed. Therefore, TiCl_4 is more favourable as a precursor for continuous production. A novel method for producing titanium powder has been proposed, where TiCl_4 is reduced using MgH_2 in a hydrogen atmosphere to yield TiH_2 powder, which is subsequently dehydrogenated to produce titanium powder. The study has shown that producing Ti powder *via* the TiH_2 route from ilmenite at the low-temperature range is economically feasible (Ardani *et al.*, 2021).

Several efforts have been made worldwide to develop a simple, energy-efficient, cost-effective, and eco-friendly titanium extraction technique. Most of these initiatives aim to shorten the process steps, develop a continuous method, and/or directly extract titanium from TiO_2 . The bulk of these sophisticated methods give titanium powder, which may be used to manufacture desired goods *via* additive manufacturing or 3D printing (Nagesh, 2022). **Figure 2.13** is a flow diagram illustrating the methods used to obtain and purify various types of titanium to produce the final products. Review papers by Takeda *et al.* (2020) and Suzuki *et al.* (2021) summarise recent technologies utilised to obtain Ti metal. The Armstrong/ITP technique, developed by International Titanium Powder (ITP) and promoted by Armstrong, is currently the top-ranked process for producing titanium metal from TiCl_4

(Araci *et al.*, 2015). It features several innovations designed to consistently produce high-quality titanium powder particles.

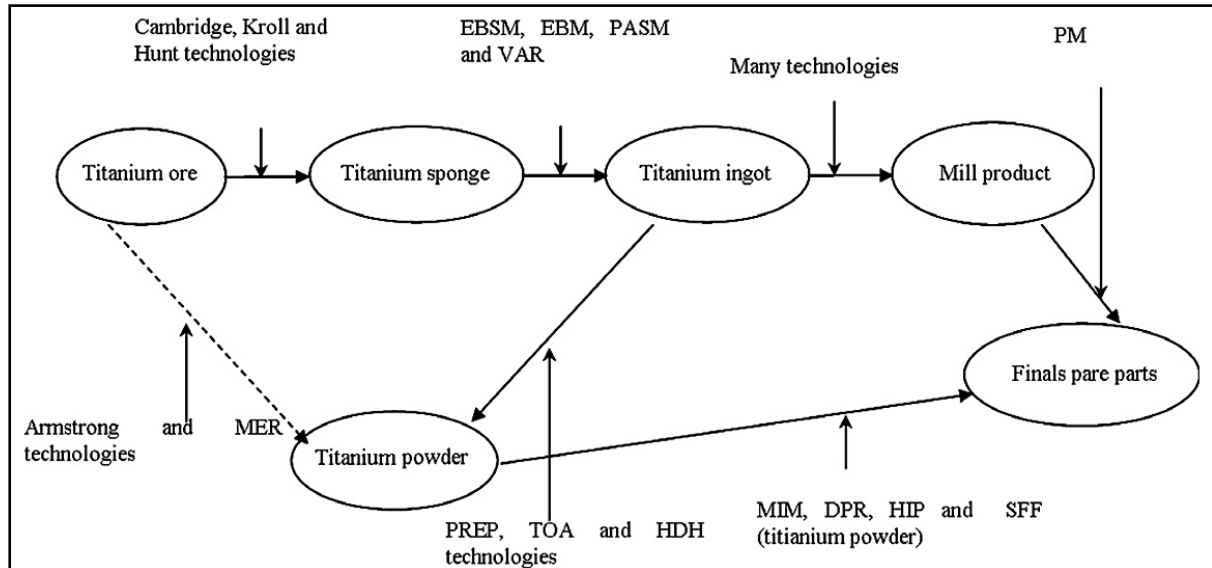


Figure 2.13: Alternative methods being used in the titanium metal industry (Cui *et al.*, 2011).

Patent activity on titanium metal production has remained relatively steady since 2002, indicating a constant but not significantly growing interest in the topic (WIPO, 2022). However, various studies continue to investigate different economic methods for manufacturing titanium from a range of sources, including tailings, low-grade ores, and even metal scrap.

2.6 Possible recovery of titanium from metal scrap

Titanium is extensively recyclable, which significantly reduces the production costs. On the other hand, titanium does not corrode and preserves its shiny appearance for extended periods. This allows it to be recycled further down the line (Ti-Tek, 2019). The scrap rate (percentage of goods or materials that can be recycled) of completed titanium materials is relatively low, typically around 50 %, due to the unique production techniques of titanium and its alloys. When final parts are manufactured, the finished product scrap rate is only 10-20 %. As a result, recovering titanium metal waste is crucial for preserving resources and cutting costs. Titanium scrap (**Figure 2.14**) is obtained from various sources.

Titanium scrap generated during the production of sponge titanium, for example, must be disposed of and reprocessed, as it may contain impurities such as iron, chlorine, oxygen, and nitrogen that do not meet the final product quality standards. Furthermore, titanium scrap generated during titanium ingot casting and titanium trash produced when converting titanium material into titanium goods are also significant sources of titanium scrap (Advanced Refractory Metals, 2023).



Figure 2.14: Titanium metal scrap (Stockholm, 2013)

Industrial waste is released into the atmosphere, wastewater is discharged into water bodies, and solid waste is stored in sludge storage facilities, polluting soils and natural waterways (Ospanov *et al.*, 2022). As a result, it is crucial to extract valuable components from them and identify strategies to reduce the generation of titanium production waste (Karshyga *et al.*, 2022). Currently, such metal scrap is usually used to make ferroalloys, but it would be beneficial if it could be reused in the Ti smelting process to get pure Ti (Zheng and Okabe, 2008).

Low-grade titanium scraps, highly contaminated with oxygen and iron, are being used in the steel industry to produce additive alloys, such as ferro-titanium. If the demand for titanium metal rises rapidly, the market may soon see an oversupply of low-grade titanium scrap. As a result, developing anti-contamination and effective techniques for removing oxygen and iron is critical for efficiently exploiting titanium. These technologies are critical for expanding the titanium sector through advancements in titanium smelting and recycling technologies (Takeda *et al.*, 2020).

There are several ways to recycle titanium scrap metal. Uncontaminated titanium scrap can be utilised as an addition for smelting titanium ingots or combined with sponge titanium and pressed into titanium blocks. Waste titanium sponges, waste titanium heads, and waste titanium scraps can be used as alloy additives in the ferrotitanium industry or as raw materials for titanium powder, depending on their purity and composition. Titanium scrap with high impurity content can be treated into high-titanium iron (Maldybayev *et al.*, 2024). Waste titanium powder can be utilised as

pyrotechnic deflagration agents, additives in the aluminium processing sector, and raw materials for powder metallurgy titanium products (Advanced Refractory Metals, 2023).

Electrolytic refinement and chemical reaction using MgCl_2 molten salt electrolysis can be used to deoxidize Ti scrap. The electrochemical and chemical processes generated by applying varying voltage ranges to the cathode electrode, which is set up with target brittle Ti scraps linked to the Ti wire, reduce the oxygen content in the Ti scraps. After deoxidation, the Ti scrap is washed with a 1 M citric acid solution, a 0.5-8 M HCl solution, and a 12 M H_2SO_4 solution for 30 minutes on a magnetic stirrer at 150 rpm to remove the MgO and remaining chlorides. The cleaned Ti scrap is then dried under a vacuum. The following mechanism governs the Ti deoxidation process. The oxygen in the titanium scrap cathode combines with Mg ions in the MgCl_2 molten salt flow to form MgO, thereby eliminating oxygen from the Ti (Kwon *et al.*, 2021). **Figure 2.15** shows a schematic diagram of the deoxidation process.

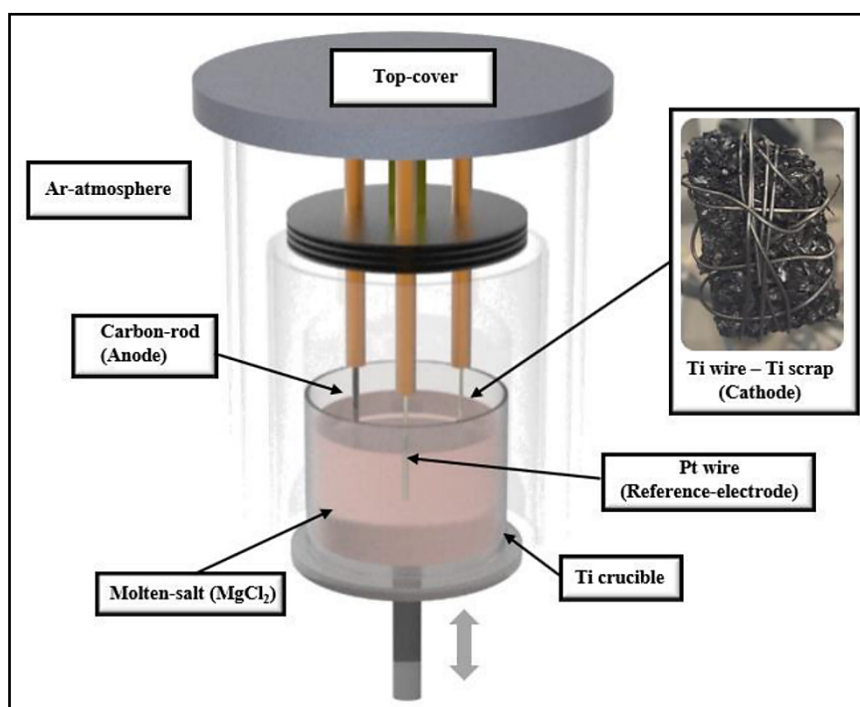


Figure 2.15: Schematic diagram of device structure for electrolytic deoxidation process (Kwon *et al.*, 2021)

Titanium can also be recovered from chloride waste generated from the Kroll process. Metallic Ti can be recovered as TiCl_4 by using FeCl_2 , and the reaction products of TiCl_4 and Fe may be easily recovered individually (Zheng and Okabe, 2008). Other remelting procedures, including electron-beam melting (EBM), plasma arc melting (PAM), and vacuum arc remelting (VAR), are used to recover titanium scrap since they can minimize oxygen contamination (Tekeda and Okabe, 2018).

2.7 Industrial applications of Ti metal and Ti compounds

Titanium is mined and processed to manufacture various high-value industrial products, including pigments, super alloys, sports equipment, and medical devices. The popularity of titanium as a metal and its metal compounds in the manufacturing industry has progressively risen over the last 80 years, not only due to its diverse applications but also due to its unique and sought-after properties, such as its weight-to-strength ratio and inertness towards corrosion. Before World War II, titanium was primarily processed as its oxide for use in the titanium dioxide pigment industry. During the war, the U.S. and the Soviet Union sought to resolve their need for lightweight and durable metals for their aerospace industries, and the use and applications of titanium metal gained popularity. Since the end of the Cold War, the use of titanium has shifted from primarily military to commercial applications (Housley, 2007). Approximately 5 % of the titanium consumed annually in the U.S. is in the form of titanium metal for high-performance applications (**Figure 2.16**).



Figure 2.16: Titanium metal high-performance applications (Bhutada, 2023)

Titanium is the metal of choice for many applications, primarily in aviation and aerospace, the construction industry, and automotive manufacturing, due to its strength and weight properties. It has the highest strength-to-density ratio of any metal on the periodic table. Titanium metal has a low density, making it incredibly lightweight (40 % lighter than copper and 60 % lighter than iron) (Ti-Tek UK, 2023). Spaceships, turbine engines, and missiles all use titanium metal (Blakey-Milner *et al.*, 2021). Unlike other construction metals, titanium has a long lifespan with a lower lifetime cost than other

metals used in architecture and construction. It withstands possible corrosion, which can emanate from gases produced by industries, and remains inert in both marine habitats and in sulphur-rich industrial environments. Its corrosion resistance is attributed to the formation of the passive and protective titanium oxide layer on its surface when exposed to air (Bocchetta *et al.*, 2021). It is also widely employed in power generation, military, sports goods, and dentistry, due to its exceptional qualities.

Titanium metal can also be easily machined and fabricated into various metal parts and components because it is a refractory metal that is relatively soft and ductile. It may also be seam welded in open air without a flux agent, and the weld zone does not require extra protection. Titanium's low thermal expansion coefficient helps it withstand extensive expansion and contraction compared to other manufacturing metals, expanding 50 % less than steel, under extreme temperatures, providing better structural stability. One of titanium's sought-after advantages is its excellent temperature resistance, which makes it ideal for use in high-temperature applications, such as foundries, turbine jet engines, and certain satellites, due to its high melting point. Superstructures that require a rigid yet lightweight framework, as well as buildings where fire safety is crucial (such as skyscrapers), extensively utilise this advantage of titanium as a manufacturing material. It is a noble metal; thus, joining it with other metals that are different from it reduces its galvanic corrosion. Titanium alloys are also used to manufacture golf club heads due to their characteristic high strength and ease of welding. It is also used in the manufacturing of batteries, functional fillers, and chemical feedstock, to name a few.

Titanium is also utilised in the medical field. Its bio-inertness, compatibility with bone formation, high strength, flexibility, and resistance to extreme physiological fluid conditions make it the most biocompatible of all metals and thus extremely useful in the medical industry (Hoque, 2022). It is entirely non-toxic to both humans and animals (partially due to its corrosion resistance), which allows it to be introduced into the human body without causing an adverse reaction. As a result, titanium is often used to permanently reinforce fractured bones, as well as for artificial hip and knee replacements, heart valves, pacemakers, bone plates and screws, cranial plates for skull fractures, spinal and maxillofacial dental implants, and other implants. Medical research also indicates that the human body can withstand enormous doses of titanium without any adverse effects.

The chemical and paint industries also extensively use titanium as titanium dioxide. TiO_2 is often used as a white pigment in exterior paints due to its chemical inertness, strong coating ability, opacity against UV radiation damage, and ability to self-clean. Its inertness also allows it to withstand weathering. Furthermore, titanium dioxide was initially used as a bleaching and whitening agent in porcelain enamels, imparting them a finishing touch of exceptional brightness, hardness, and acid

resistance (Martín-Martínez, 2002). Paints and coatings, plastics, paper, fibres, building supplies, cosmetics (including sunscreen and lipstick products), toothpaste, optical coatings (such as beam splitters and anti-reflective coatings), medications, inks, and many other industrial items all utilise TiO_2 pigments.

Titanium dioxide nanoparticles have shown enormous potential due to their intriguing features and applications in water treatment, coating materials, the porcelain and ceramics industries, energy device manufacturing, and soil remediation. The impressive photocatalytic capacity, biocompatibility, and low toxicity of TiO_2 nanoparticles have been utilised in nanobiotechnology and nanomedicine for genetic and tissue engineering, the production of healthcare items, bioimaging, and the treatment of diseases such as cancer (Akakuru *et al.*, 2020).

TiO_2 is one of the top five nanoparticles utilised as antimicrobial photocatalytic coatings. These nanoparticles prevent microbial proliferation or significantly reduce the number of microorganisms that grow on the surfaces of building materials. A photocatalyst study indicates that it is also a viable technology for decomposing organic contaminants in air and water, utilising pure solar energy without producing harmful byproducts (Haider *et al.*, 2017). Since Pilkington commercialised self-cleaning glass in 2001, semiconductor photocatalysis (SPC) has been on the rise. It is a process in which light activates a surface coating, typically titanium dioxide, to facilitate the breakdown of organic debris (Holder, 1994). A self-cleaning wall is shown in **Figure 2.17**.



Figure 2.17: Self-cleaning TiO_2 -coated high building (Haider *et al.*, 2019)

Titanium dioxide nanoparticles have numerous applications in industry and show potential for use in additional areas. **Figure 2.18** illustrates the current applications of titanium dioxide and its prospects. Titanium dioxide also serves as a catalyst support. Its application as a high-temperature oxygen sensor and humidity sensor is being considered.

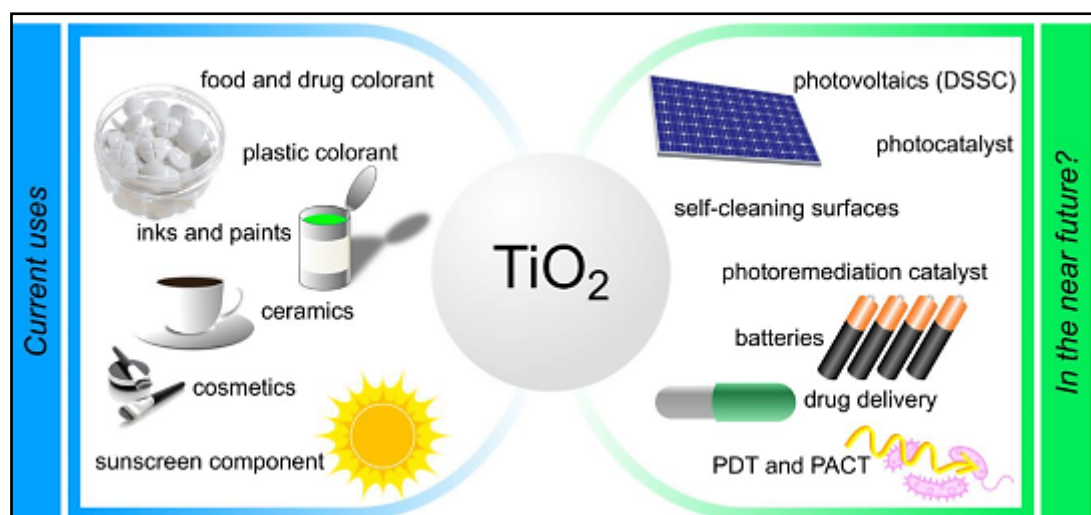


Figure 2.18: TiO_2 current and anticipated future applications. PDT-photodynamic therapy; PACT-antimicrobial photodynamic therapy; DSSC-dye-sensitized solar cell (Ziental *et al.*, 2020)

Other honourable mentions of titanium compounds are titanium tetrachloride, titanium trichloride, titanium carbide, and organic titanium compounds. Titanium tetrachloride is primarily an intermediate in the production of titanium metal. It is used as a starting material for synthesis reactions of most organic compounds, such as alkyl esters of titanium, alkyl titanates, and as a component in Ziegler-type catalyst polymerization. This substance fumes in moist air, producing a dense white smoke, and is thus employed as a smokescreen and skywriting. Titanium trichloride is prepared by reducing titanium tetrachloride and is used as a colouring agent in molasses. TiCl_3 is a beneficial catalyst in the manufacture of polypropylene through the polymerisation of propylene. For co-polymerization, trialkyl aluminium is used as a co-catalyst and displays high catalytic activity (Makino *et al.*, 1991). Cross-linking agents and catalysts are found to be beneficial for organic titanium compounds (United Nations Environment Programme and World Health Organization, 1982). Titanium carbide is used in structural metals and alloys.

Titanium is considered the metal of the future. Cost-competitive production could be expanded from specialised products to everyday goods such as consumer electronics, luxury items, and electric vehicles (Bhutada, 2023). Its manufacturing can be considerably increased thanks to technological advances, making it a “common metal” (Froes, 2015). In September 2023, Apple released its high-end cell phone versions, the iPhone 15 Pro and iPhone 15 Pro Max. They were the first to be made of titanium grade 5 alloy frames. This made them the lightest Pro and Pro Max cell phone models and provided better heat dissipation than any previous models made of stainless-steel frames (Rossignol, 2023).

2.8 Beneficiation of titanium from primary ores and secondary resources

2.8.1 Mining and processing of titanium ores

Ilmenite is the most commonly used titanium mineral, and it accounts for approximately 92 % of the world's titanium mineral production (El Khalloufi *et al.*, 2021). World anatase, ilmenite, and rutile resources total more than 2 billion tonnes (U.S. Geological Survey, 2022). It is interesting to note that the majority of the world's titanium reserves are in the form of titanomagnetite and anatase (and not ilmenite), which account for approximately 50 % of the total reserves. However, titanium is not easily recovered from these minerals, and they are therefore not currently economically viable. Ilmenite and rutile are therefore the two primary mineral sources of titanium with commercial importance. Lower-grade titanium sources are also currently processed because these ores are abundant, as high-grade ores such as rutile are becoming depleted. For pigment production, the chromium oxide and vanadium pentoxide content in the lower-grade ores must be less than 0.2 % and 0.5 %, respectively.

The mining technique used is determined by the type of mineral resource, its location on or below the surface, its concentration, and whether it is economically viable to justify extraction. A TiO_2 content of 5-7 % is necessary for the commercial exploitation of ore resources. The dredging of dunes is employed on a big scale, whereas dry mining is used on a small scale or when there is insufficient water available, such as in hard rock deposits or where the clay content of the Ti source is high (Habashi, 1997; Murphy and Frick, 2006; Stamper, 1970). Dunes or deposits with 1-10 % heavy mineral content are often wet-dredged and sieved. The slurry, a mixture of ore concentrates and water, is pumped to a wet concentrator. The concentrator and the dredger are in a significant body of water and are moved as operations progress. The concentrator removes silica through gravity concentration, which is achieved by the difference in terminal velocity between the silica and the heavy mineral. As a result, the heavier mineral particles settle to the bottom. In contrast, the lighter silica floats to the top and is removed, thereby increasing the concentration of heavy minerals from 90 % to 98 %. The separated silica and rocks are returned to the mining site, and some of the water is recovered and reused (Murphy and Frick, 2006; Habashi, 1997; Stamper, 1970).

Dry mining operations are carried out conventionally, using scrapers, excavators, and trucks. For rock mining, the first step involves blasting the mineral body to liberate the target mineral from the host rock, producing smaller, manageable particles, which are transferred for crushing and subsequent separation processes. Conversely, Ilmenite has magnetic properties and is separated from the mass mineral samples employing electromagnetic equipment to produce Ti-enriched sand. High-intensity magnetic separators are used to recover leucoxene and other weathered ilmenite fractions. Electrostatic separation of rutile and zircon is utilised due to their difference in resistivities to electric

current. Rutile has a lower resistivity of the two and is therefore regarded as the conducting mineral, while zircon is the non-conducting mineral (Venter *et al.*, 2008). Usually, gravity concentration or magnetic separation methods are employed to separate the two natural compounds. However, rutile and zircon have similar gravity and magnetic properties which makes it difficult to separate the zircon in the heavy sands from rutile by gravity concentration or magnetic separation (Murphy and Frick, 2006; Habashi, 1997).

Mineral sands are often mined and separated using open-pit techniques, including both wet and dry methods, such as dredge mining operations. Richards Bay Minerals (RBM) in South Africa (**Figure 2.19**) uses dredging and concentration on a floating gravity separation plant. The floating separator is typically located in a man-made freshwater pond adjacent to the ocean, and the mineral sands from the coastal dunes are then separated into ilmenite, rutile, and zircon at the smelter's mineral separation facility. The dredger takes material from the pond's front end, while the tailings are separated at the rear of the floating plant, resulting in movement of the man-made pond in a forward direction. The floating dredge is equipped with a suction bucket that transfers the mineral-rich sand to a set of screens, known as trommels, which remove the unwanted materials. The dredger trudges forward at a pace of 2-3 meters daily as it mines through the dune (Jones and Curr, 2006). The smelting of the isolated ilmenite occurs in an electric arc furnace, yielding titanium slag with a TiO_2 content of over 85% and high-quality pig iron as a byproduct.



Figure 2.19: Rio Tinto's Richards Bay Minerals (Contributor, 2019)

Australia, which is rich in rutile and ilmenite, uses a similar mining method. Their method involves dredging the sand using a massive suction pipe, which separates the heavy minerals from the lighter sand particles. The unwanted material (gangue) is returned to the mined area while the dredge travels

steadily forward. Excavating higher-grade deposits containing relatively hardened material or strata requires the use of specialized mining equipment, such as self-loading scrapers, bucket-wheel excavators, bulldozers, and front-end loaders.

2.8.2 Beneficiation

In extractive metallurgy, beneficiation is the process of removing gangue from the target ore deposits to increase their economic value (Dworzanowski, 2013). This is especially important for low-grade ores to improve valuable element composition to economically exploitable levels. This value-addition process also reduces freight and shipping costs as less space and resources are needed to transport the ore from one place to another. The concentration of the elements of interest increases with the removal of the gangue in the ore, making it possible to extract it at lower costs with lower quantities of impurities (Warui, 2015).

Titanium occurs in many low-grade ores. Magnetic separation, gravity separation (**Chapter 4**), milling (crushing and grinding), washing, filtration, sorting, sizing, jigging, agglomeration (pelletising, sintering or nodulizing) and froth floatation are standard methods used in the beneficiation process (Sharma, 2004; United States Environment Program Agency, 1994). Most of these processes are also used to beneficiate iron ore deposits, a significant source of titanium. Titanium ores also contain large amounts of unwanted silica, which is magnetically separated from the titanium and iron that are closely bonded in a mineral such as ilmenite.

The most significant impediment and primary cause of the high titanium commodity prices is outdated and costly techniques used to extract the metal from raw sources (Van Vuuren, 2009). Many alternative replacement processes are being researched worldwide, notably in South Africa, where the Council for Scientific and Industrial Research (CSIR) funded by the Department of Science and Technology (DST) is involved. The CSIR-Ti process produces high-purity titanium powder by reducing TiCl_4 with an alkali or alkaline earth metal in a molten salt bath, thereby facilitating its application in fields such as powder metallurgy. The Anglo-American firm is developing the Peruke method, which involves preparing a fluotitanate salt from titanium dioxide, which is then reduced with aluminum to produce titanium metal and aluminum fluoride as a byproduct. To date, no viable approach has been established for replacing the Kroll process on an industrial scale (Roux *et al.*, 2019). The most prevalent method performed worldwide is the expensive Kroll procedure. Thus, if the Peruke process or CSIR-Ti approaches are commercialised effectively, these less expensive alternatives might considerably help to develop the South African titanium industry as a net income generator (Durr, 2016).

2.8.3 Tailings

Beneficiation of low-grade ores can increase the target mineral's content in commercially viable deposits. Several ores (excluding ilmenite and rutile) contain titanium in relatively small quantities. Vanadium-rich ores, which contain substantial amounts of titanium, can increase the economic value of the ore bodies by removing unwanted materials (Dworzanowski, 2013). The tailings produced from the processing of vanadium ore bodies accumulate and pose severe environmental problems; however, they still contain valuable elements such as titanium and iron.

Mining practices generate a significant amount of tailings, which give rise to various problems. Hence, further beneficiation of tailings should be important to reduce these problems. Large piles of tailings deposits cause three main environmental problems, namely:

- a) the risk of hazardous landslides,
- b) the release of potentially hazardous dust particles, and
- c) the leaching of potentially poisonous elements from tailings into natural water bodies.

The build-up of large mountains of waste, associated with unseasonable heavy downpours of rain, also has the potential to destabilise the mine tailings, turning them into sources of dangerous mudslides. Airborne particles, which may contain poisonous heavy metals such as lead, silver, and arsenic, can also be transported to nearby communities, water bodies, stock, and crop fields. Rainfall, mainly associated with air pollution (acid rain), can leach unwanted elements from the tailings, causing water pollution and endangering aquatic life downstream. Although the problem of dust particles can be minimised by adding water to the tailings deposits to form slurries or sludges in tailing ponds, it also has problems, such as water wastage and seepage.

2.8.4 Source of vanadium-containing ore and tailings

Both titaniferous magnetite and tailings produced from vanadium processing plants were used in this study. A brief discussion on the processing of vanadium ore and tailings is included to provide insight and direction on their processing in this study.

The samples were obtained from mines (Rhovan and Vametco near Rustenburg and Suncity, respectively) in the Bushveld Complex, located in the Northwest Province of South Africa. The processing of the titaniferous magnetite involves crushing, grinding, and magnetic separation to concentrate the titaniferous magnetite to generate a magnetic concentrate. The concentrate is then roasted in a kiln, producing water-soluble sodium vanadate, which is subsequently leached with ammonia to yield a pregnant V_2O_5 solution rich in silica. The undissolved portion of the processed mineral ore is discarded as waste and transported to the tailing sites (Ratshomo, 2013).

The pregnant solution containing V_2O_5 and silica content is then introduced to a desilication process, which removes the silica and improves the vanadium concentration in the pregnant solution. The desilication process involves precipitating vanadium from the solution using ammonia to form ammonium vanadate (NH_4VO_3), which is then filtered and deammonized. The V_2O_5 produced after this step is a powder unsuitable for customer transportation. The pentoxide powder is melted in a fusion furnace to produce vanadium pentoxide flakes, which are denser and less prone to airborne dispersion. FeV is produced by first reducing the V_2O_5 to vanadium trioxide (V_2O_3), then reacting it with iron and aluminium to produce ferrovanadium, a valuable and sought-after commodity (Mosiane, 2008). When the vanadium-containing part has been chemically processed, the remaining parts are rich in titanium, and hence, the samples studied are produced. These tailings still contain some vanadium, as well as substantial amounts of Ti, which are the tailing samples that are part of this investigation.

2.9 Ti market overview

The titanium market is primarily divided into metal and pigment segments. According to the United States Geological Survey, TiO_2 production accounted for 94 % of titanium mineral usage in 2021 (U.S. Geological Survey, 2022). The remainder was utilised in the manufacturing of titanium metal by various industries: aerospace (56 %), Industrial (26 %), military (7 %), and medical (4 %), among others (7 %) (el Khalloufi *et al.*, 2021). The development of the titanium value chain, encompassing the production of titanium pigment, metal, and downstream fabrication, is a key growth area for South Africa. Titanium alloys are the most sought-after forms of titanium metal products in the industry due to their characteristics (Table 2.9).

Table 2.8: The categories and properties of common Ti alloys (Ivasyshyn and Aleksandrov, 2008)

Categories	Typical alloys	Characteristics
α	Ti-5Al-2.5Sn Ti-6Al-2Sn-4Zr-2Mo	Good welding performance due to overall strength and durability. Strong antioxidant with increased creep strength. Less commonly utilised in the production of golf mastheads.
$\alpha + \beta$	Ti-6Al-4V Ti-6Al-2Sn-4Zr-6Mo	The heat treatment's strength and toughness may be outstanding, and it exhibits excellent weld fatigue performance, making it suitable for multiple applications, such as iron casting mastheads and fairways.
β	Ti-13V-11Cr-3Al Sp700 Ti-15Ta-3Cr-3Al-3Ni	High strength, heat treatment, malleability, and cold-forming performance, suitable for a wide range of welding techniques.
Ti _x Al	Ti3Al (a 2) & TiAl	Desire to reach 900 °C, but inadequate toughness and plasticity at room temperature.

The price of titanium has gradually increased since 1973, with a sharp increase between 2003 and 2006 (**Figure 2.20**). In 2023, the global titanium market was valued at approximately 30.66 billion U.S. dollars, with projections indicating it will grow to nearly 52 billion US dollars by 2030 (Ijaz, 2023). The United States remains the largest consumer of titanium metal worldwide. The country imported more than 90 % of the 1.4 million metric tonnes of titanium produced in 2019 (Lasley, 2020). Currently, the costs of refining, processing, and producing titanium remain high. Titanium production costs are five times greater than aluminium, from melting to refining. The production of titanium into ingots and finished products increases the production costs by orders of magnitude compared to that of aluminium (Femenia *et al.*, 2023; Fang *et al.*, 2018). Wood (2021) notes that the global titanium market is expected to increase from USD 24.7 billion to USD 33.5 billion at a CAGR (compound annual growth rate) of 6.3% from 2021 to 2026, driven by raw material derivatives such as ilmenite and rutile. The global COVID-19 pandemic, on the other hand, decreased demand and activity in the titanium mining and processing industries (Wood, 2021).

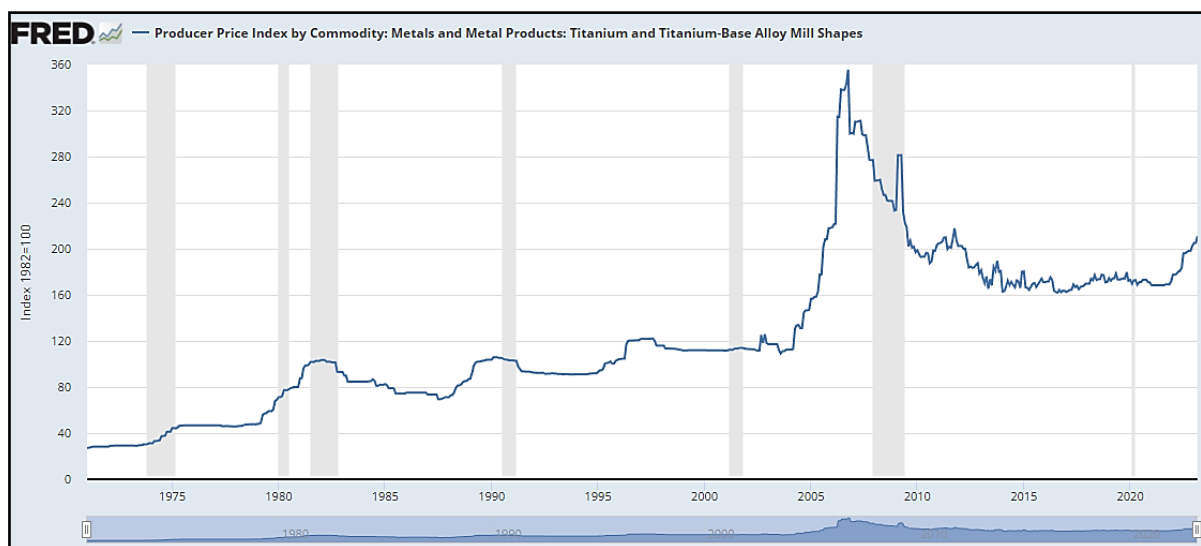


Figure 2.20: U.S Producer Price Index (PPI) for finished rolled titanium from 1971 to 2023 (FRED, 2023)

The titanium dioxide global market reached 5.5 million tonnes in 2022 and is expected to grow at a compound annual growth rate of 4.92 % during the 2024-2035 forecast period. The growing demand for paints and coatings is expected to be the primary driver of growth in the titanium dioxide market. These two industries consumed 40% of the global titanium dioxide in 2022 and are expected to increase further to approximately 80 million tonnes by 2035 (Swain, 2023). A characteristic of titanium dioxide is its price volatility, which is a challenge in the titanium dioxide market.

Worldwide TiO₂ manufacturing countries include the United States, the United Kingdom, China, Japan, Canada, and Slovenia (Sampath *et al.*, 2023). Companies involved in TiO₂ production include the

Chemours Company (US), Tronox Holding PLC (US), Lomon Billions Group (China), Venator Materials PLC (UK) Kronos Worldwide Inc (US), INEOS(UK), CINKARNA Celje d.d (Slovenia), Evonik Industries AG (Germany), TAYCA Corporation (Japan), ILUKA Resources (Australia), and ISHIHARA SANGYO KAISHA Ltd (Japan). The largest companies in the world that produce TiO_2 are shown in **Figure 2.21** (Maldybayev *et al.*, 2024). In South Africa, Nyanza Light Metals and Avertana are involved in a new titanium dioxide plant project, known as the Nyanza Light Metals project, located at the Richards Bay industrial development zone. The project was expected to be fully operational by 2024. A production capacity of 80 000 tonnes per year is anticipated (Nyanza, 2023). While the initial phase has been completed, the central production facility is still under development. It is anticipated to be operational soon, but specific timelines for full operation have not been confirmed. Titanium pigment has been selected as one of the commodities under the five value chains by the Department of Minerals and Energy of South Africa, as part of its beneficiation strategy. They were selected based on their potential for development to the last stages of downstream beneficiation. These are a) energy (coal and uranium), b) steel/stainless steel (Fe, Cr, Mn, V, and Ni), c) pigment production (titanium), d) auto-catalyst and diesel particulate (PGM) and e) diamond processing and Jewellery (gold, diamond and PGM). These locally manufactured products will reduce government expenditures on product imports. Surplus products will be exported, thus increasing the country's Gross Domestic Product (GDP). This makes the low-cost beneficiation of its resources important (Department of Minerals and Energy, 2011).

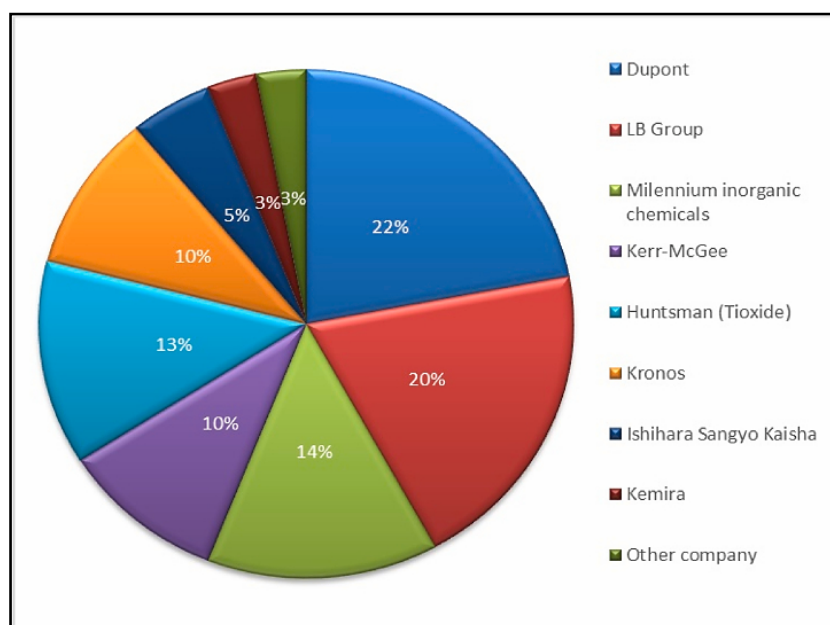


Figure 2.21: TiO_2 production by the largest companies in the world (Maldybayev *et al.*, 2024)

Titanium prices vary due to the wide range of titanium products available on the market. For example, in 2022, the Australian price of bulk rutile with a minimum titanium dioxide content of 95 % was USD 1 500 per metric tonne, whereas the average unit value price of one metric tonne of ilmenite imported to the U.S. was USD 290 (Garside, 2023).

In 2017, the Chinese titanium dioxide market generated the highest profit since Chinese manufacturers targeted the international market and revised their marketing strategy (Figure 2.22).

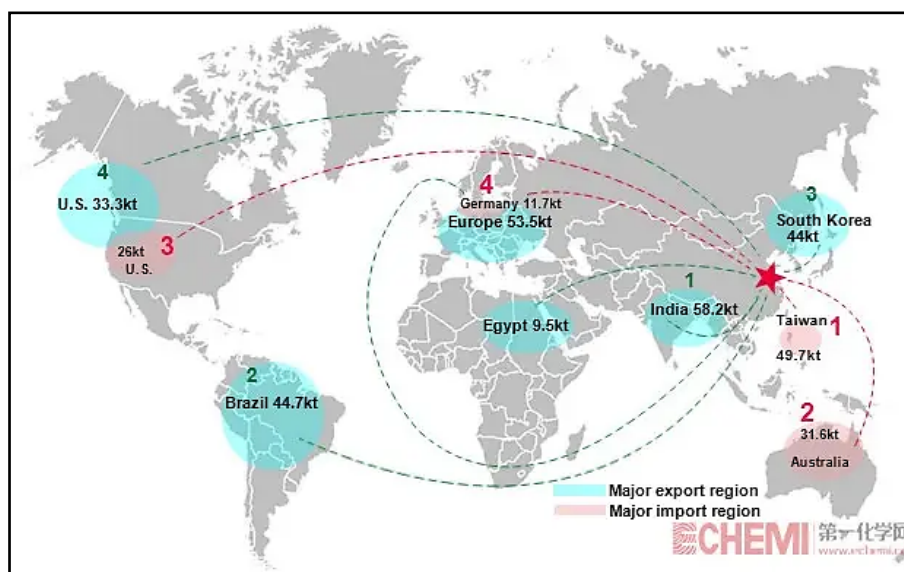


Figure 2.22: Global import and export data (excluding China) of titanium dioxide in 2017 (ECHEMI, 2018)

2.10 Conclusion

Titanium's main characteristics include high strength, corrosion resistance, and lightweight properties, among others. These characteristics make it useful in the aerospace, medical, and automotive industries. Its oxide form is also prevalent in the chemical industry, where it is used as a white pigment due to its high reflection index in the paint, cosmetic, and food industries. Titanium's demands continue to rise and will soon surpass its production rate. Rutile supplies are also depleting. As a result, processing secondary sources of titanium, such as vanadium ores and tailings, may help mitigate the supply issues we are facing. Currently, Australia leads the titanium mining industry, followed by China and then South Africa. South Africa mines large quantities of titanium primary material, but exports most of it due to a lack of local industries that process the raw titanium into finished products. Current methods used to obtain titanium, such as the chloride and sulphate, are expensive and not eco-friendly. This issue could be addressed through further investigations to enhance the efficiency of current processes, as well as the development of novel, eco-friendly, and more cost-effective technologies.

Chapter 3: Literature review - Beneficiation and extraction of titanium from ore and tailings

3.1 Introduction

Titanium-rich ores and tailings can be commercially beneficiated by combining chemical and physical methods. Hydrometallurgical processes can be used for the dissolution/leaching and separation of titanium from the solid mineral matrix. Different dissolution and separation methods can be used to isolate titanium depending on the mineralogical and geochemical characteristics of the resources. However, many techniques are costly due to their high energy requirements, time-consuming processes, and labour intensity (Zhang *et al.*, 2011). The developed and well-known beneficiation methods are often ineffective in successfully processing low-grade ores. Additionally, various chemical methods can be employed to reduce impurities in the final product, thereby enhancing its value. Physical methods, such as magnetic and gravity separation, can concentrate titanium in titanium-bearing minerals into one fraction before sample dissolution. The extraction of titanium from vanadium-bearing titanomagnetite, tailings, and ilmenite, among others, using microwave acid-assisted digestion, flux fusion, and acid digestion is reviewed in this chapter.

3.2 Physical separation of titanium from minerals

Physical methods can be instrumental in beneficiating minerals and ores before chemical or hydrometallurgical beneficiation. The methods, which include magnetic and density separation, concentrate minerals that contain the target element.

3.2.1 Magnetic Separation

Magnetic separation is used to separate magnetic minerals from non-magnetic minerals. Many iron-titanium minerals are magnetic due to the presence of magnetite. High-intensity electromagnetic separators are commonly used for this purpose.

Chen and Chu (2014) proposed a novel method of metallising reduction, magnetic separation, and electro-heat melting separation to recover large quantities of titanium, vanadium, and iron from vanadium titanomagnetite. Their study examined the impact of various experimental factors, including magnetic intensification, reduction temperature, reduction time, carbon ratio, and coal particle size (reducing agents), on the efficiency of the reduction magnetic separation process. A 135 g sample of the magnetic concentrate was dried for 3 hours at 105 °C, then mixed with 0.9 g of coal, placed in a high-purity graphite crucible, and heated in a high-temperature resistance furnace at 1 550 °C for 120 minutes to separate a metallic iron phase and a vanadium slag. They used SEM-EDS analysis

to understand the reaction mechanisms better and subsequently direct the processes. According to their study, recoveries of up to 80 % were reported for Ti, 95.1 % for Fe, and 71.6 % for V.

In another investigation, Zhao *et al.* (2014) suggested a direct reduction-magnetic separation technique for different magnetically susceptible particles. In this study, the titanomagnetite was reduced with pulverisation. The newly formed powdered iron (94.6 %) was separated from the titanium tailings by magnetic separation, which still contained vanadium. This partial reduction step ensured that the vanadium and chromium were predominantly concentrated in the titanium-bearing tailing. Hydrochloric acid was then used to leach the vanadium from the tailings, yielding a titanium-bearing residue and a vanadium-bearing lixivium. The HCl leach residue, predominantly composed of TiO_2 , was further processed to remove silicon, and ultimately produced a titanium-rich slag suitable for chlorination. This was achieved by washing the residue with water, followed by acid leaching. Although the proposed beneficiation improved the recovery of titanium, iron, and vanadium, it generated a significant amount of acid waste.

The process of reduction roasting, followed by two-stage low-intensity magnetic separation (LIMS), proposed by Jena *et al.* (2015), resulted in the production of a magnetic concentrate containing 65.74 % Fe with a yield of 61.2 % and a recovery rate of 78.1 % Fe. A secondary product with a high TiO_2 content was also generated, containing 28.8 % TiO_2 , a yield of 20.1 %, and a recovery rate of 36.8 %. He suggested that the magnetite-rich concentrate can be used as heavy media in coal washeries, while the middling fraction can be utilised for titanium recovery.

One study (Gougazeh, 2022) reported the successful separation of iron and titanium from feldspar present in a Medina syenite ore using a combination of magnetic separation and flotation. The results indicate that the most effective method for separating iron and titanium contents was achieved using a dry magnetic separator operating at a magnetic field strength of 16 000 gauss. The magnetic separation process resulted in a feldspar concentrate containing 0.5 % Fe_2O_3 , with a recovery rate of 87 % for Fe_2O_3 , and 0.6 % TiO_2 , with a recovery of 16 %. Finally, feldspar concentrates with grades of 0.07 % Fe_2O_3 and 0.06 % TiO_2 and recoveries of 89 % for Fe_2O_3 and 86 % for TiO_2 were achieved.

Xu *et al.* (2017) investigated the use of magnetic separation to concentrate low-grade vanadium-titanium magnetite ore. Results obtained from the study indicated that 73.5 % of the feed ore was immediately rejected in the magnetic separation step, which substantially decreased the ore content that had to be processed in subsequent steps. The low-grade vanadium-titanium magnetite ore yielded a vanadium-titanium magnetite concentrate with 1.1 % V_2O_5 , 22.2 % TiO_2 , and 42.5 % Fe. Additionally, a rough concentrate of ilmenite with 16.1 % TiO_2 and 20.8 % Fe was obtained. The original

ore had 0.05 % V_2O_5 , 1.7 % TiO_2 , and 8.5 % Fe, indicating a substantial increase in target element content.

Furthermore, results obtained by Geng *et al.* (2015) showed that direct coal-based reduction, followed by magnetic separation, effectively separates titanium and iron from Indonesian beach titanomagnetite (TTM). First-stage grinding was performed for 15 min, while second-stage grinding was performed for 20 min. An XCGS-73 magnetic tube with a magnetic field intensity of 151 kA/m was used to recover metallic iron. The magnetic and non-magnetic products were designated DRI powder and titanium concentrate, respectively. Na_2SO_4 significantly impacts the results of roasting and magnetic separation. The best result was obtained when the Na_2SO_4 dosage was 4 %. The direct reduction iron powder (DRI powder) had an iron grade of 94.5 %, an iron recovery of 85.2 %, and a TiO_2 content of 0.4 %. The titanium concentrate assay yielded 40.4 % TiO_2 , containing the main titanium minerals of ilmenite and ferrous pseudobrookite.

Liu *et al.* (2022) emphasised the importance of grinding and magnetic separation as essential operational steps for recovering valuable elemental components from vanadiferous titanomagnetite. This underscored the role of magnetic separation in the extraction process. They used magnetic separation to separate the ground products. Then they evaluated the impact of grinding settings on the quality and efficiency of extracting Fe and TiO_2 from the low-grade samples. Their results indicated that titanomagnetite, ilmenite, and titanite remained the primary phases in all magnetic separation products after 20 minutes of grinding. However, the intensity or concentration of these three minerals differed among the separation products. A magnetic field intensity of 232 kA/m exhibited greater separation efficiency than a magnetic field intensity of 134 kA/m.

Guo (2021) used a magnetic separation tube (XCGS- Φ 50, China) with a maximum magnetic induction intensity of 250 kA/m to separate the powder samples (previously alkali leached) into an iron concentrate and titanium tailings by applying an electric current of 1.25 A **Figure 3.1** indicates their process as a flow chart to obtain the titanium tailings.

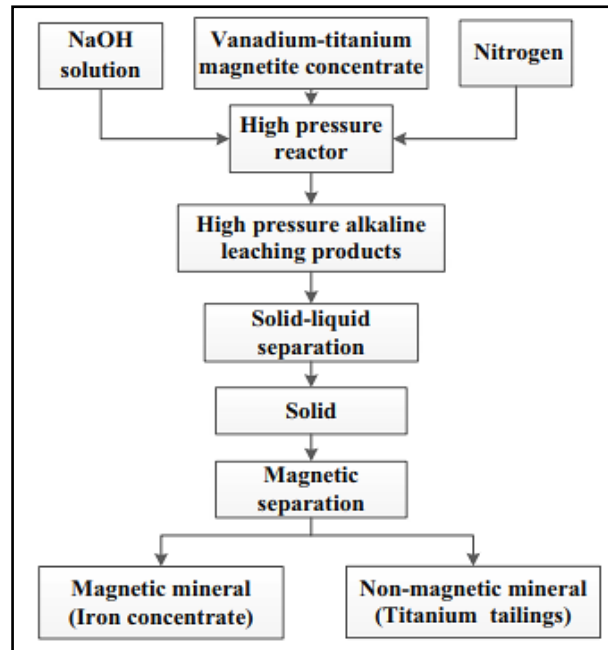


Figure 3.1: Illustration of the process of high-pressure alkali leaching followed by magnetic separation (Guo *et al.*, 2021)

In summary, the literature provides substantial evidence supporting the use of magnetic separation as a crucial technique in the processing of titanomagnetite ore for the isolation of titanium. These studies collectively show the relevance and effectiveness of magnetic separation in extracting and recovering titanium from various ore sources.

3.2.2 Gravity separation

Gravity separation is also beneficial for separating heavy particles from lighter portions and, in some cases, concentrating the target elements in one of these portions. Titanium-containing minerals, such as ilmenite and rutile, are typically denser than gangue minerals, and collecting the heavier particles will increase the quantity of Ti and Fe in the materials being processed. Spiral concentrators and shaking tables are two examples of gravity separation devices used in titanium ore processing environments.

Olifant *et al.* (2022) focused on characterising iron ore coarse particles and predicting particle distribution in gravity separation processing. The ore was screened into various size fractions, three of which were further explored here: -25+19 mm, -19+8 mm, and -8+3.35 mm. Two-kilogram aliquots of each size fraction were subsequently subjected to lab-scale sink-float test work using 6 density cut-points (4.9, 4.7, 4.5, 4.0, 3.5, and 3.0 g/cm³) via a mixture of tetra-bromo-ethane (TBE) and ferrosilicon (>2.96 g/cm³) for density cut-points below 3.8 g/cm³. Their initial findings indicated that large hematite particles could be successfully separated at high-density cut points using a sink-float

separation process. However, banded/laminated hematite-gangue particles will be lost to the floating material at various density cut points. The specific density class at which this occurs depends on the ratio of hematite to gangue in the particles. The comprehensive quantitative assessment of the mineral's composition (bulk mineralogy) results in **Figure 3.2** show that, for all three size fractions, the abundance of hematite decreases with decreasing density class, whereas the opposite is true for gangue abundance.

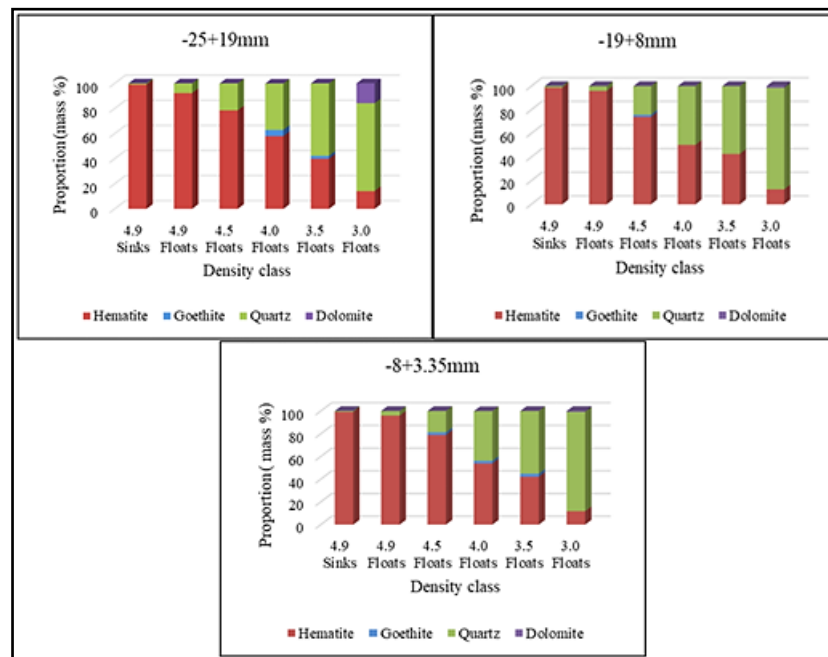


Figure 3.2: Bulk mineralogy as a function of fraction size and density class, for three size fractions of the ore (Olifant *et al.*, 2022)

Ibrahim *et al.* (2014) investigated different gravity separation equipment, including centrifugal force using a Falcon concentrator model SB40-VFD to separate an economically valuable portion of pyritic sulphur from Egyptian coal. The results indicated that the maximum separation efficiency achieved was 70.6 %, with a decrease in the total sulphur and pyritic sulphur levels to 1.7 % and 0.5 %, respectively, from their initial values of 2.9 % and 1.6 %. The highest separation efficiency level was achieved at a rotation frequency of 78.38 Hz (equivalent to a rotor speed of 2 282 rpm) with a backwater pressure of 3.9 psi.

Mishra *et al.* (2013) reported the use of gravity separation as a physical beneficiation technique for upgrading low-grade siliceous manganese ore. The results revealed that in the case of low-grade siliceous crystalline type Mn-ore, a feed having 26 % Mn could be upgraded to more than 45 % Mn by dry magnetic separation with 69 % recovery at 1 Tesla magnetic intensity. Bhandary *et al.* (2022) emphasised the use of gravity separation techniques, such as the Wilfley table, spiral gravity

separator, heavy-liquid separation, and jigging, for mineralogical studies, as well as the optimisation of tabling parameters for low-grade chromite ore.

Kumar *et al.* (2009) discussed the characterisation and pre-concentration of chromite values from plant tailings using a floatex density separation, highlighting the application of density separation in the processing of chromite ores. A maximum recovery of 83 % of chromite was achieved with a 22-23 % Cr₂O₃ content, and thus, the obtained FDS underflow is suitable for the flotation circuit. Sandag-Ochir *et al.* (2021) mentioned the use of multi-gravity separation methods, such as sink-float, jigging, and tabling, for the beneficiation and sulphuric acid leaching of manganese ore, demonstrating the effectiveness of gravity separation in ore enrichment compared to other methods used.

While the primary focus of the references varies from manganese and chromite to iron and other ores, the principles and methodologies discussed are all relevant to the processing of titanium-containing ores. This highlights the versatility and applicability of gravity separation methods in the extraction and recovery of titanium from various ore sources.

3.3 Dissolution of titanium from its minerals and tailings

According to the literature, some of the methods mentioned in this section (microwave digestion, flux fusion, and direct leaching) have been successfully used for the dissolution of various titanium-rich minerals such as ilmenite and vanadium titanomagnetite. It is important to note that the choice of dissolution method depends on factors such as the mineral composition, impurity profile, and economic considerations. The conditions (temperature, pressure, concentration, pulp density) used during the dissolution process are crucial for efficiency and selectivity. Detailed studies and optimisation are often performed to develop effective and economical processes for extracting titanium from different mineral sources. Researchers continually explore new methods and improvements to existing processes, aiming to enhance the overall efficiency of titanium extraction.

3.3.1 Leaching of titanium

Leaching refers to the selective extraction or solubilisation of a target element (and some impurities) from the solid sample, without the complete dissolution of the solid sample. The advantage of this process is the confinement of the amount and type of impurities associated with the target element in solution, hence simplifying the subsequent separation and isolation of the element in question. Leaching usually involves the use of mineral acids, bases, in some cases, reducing or oxidising agents, depending on the oxidation state of the target element in the solid sample. Common leaching reagents include H₂SO₄, HCl, NH₄Cl, oxalic acid, mixed chloride solutions (NaCl, MgCl₂), as well as reducing and

oxidising agents such as NaHSO_3 and peroxide, and alkaline lixiviants like sodium or potassium hydroxide.

Lately, microwave digestion, in combination with some of the above-mentioned reagents, has proven to be very effective as a leaching technique due to its robust experimental conditions, which involve higher temperatures and pressures. However, microwave digestion is not mainly used on an industrial scale. It is very effective for sample prep for analysis.

3.3.1.1 Acid leaching

Jabit (2017) summarised the experimental conditions, associated reagents, and yields of several acid extraction studies for titanium/ilmenite (**Table 3.1**). Research indicates that acid leaching is the most commonly used leaching method in titanium beneficiation. Under normal circumstances, titanium-containing minerals like ilmenite are somewhat resistant to many mineral acid extractions. Elevated temperatures, combined with prolonged reaction times, are often employed to enhance the leaching efficiency of these acids. The most common leaching processes appear to be the sulphate and the chloride processes, which use sulphuric acid and hydrochloric acid, respectively, at elevated temperatures to solubilise titanium. Several studies have investigated the dissolution efficiency of titanium from various ores using HCl and H_2SO_4 varying i) acid concentrations, ii) temperature, iii) particle size, iv) mechanical activation, v) stirring speed, vi) ore-to-acid ratio, and the addition of reducing/oxidizing agents, on the rate and degree of titanium extraction from its minerals.

Ebadi and Pourghahramani (2019) investigated the impact of mechanical activation (both dry and wet milling) on the reactivity of ilmenite. They reported that leaching efficiency was enhanced by 93 % in dry mode compared with 70 % in wet mode after 150 minutes of milling using 50 wt. % sulphuric acid. In a thermodynamics and kinetic study of rutile leaching by 85 wt. % sulphuric acid reactions, Dubenko *et al.* (2020) found that the upper-temperature value used in standard Gibbs energy calculations was 237 °C, the boiling point of sulphuric acid. In addition, they suggested that temperatures above 500 K (227 °C) should not be used in the sulphuric acid leaching of ilmenites. The general opinion that titanium dioxide can dissolve in concentrated sulphuric acid and generate tetravalent titanium salts was supported by the results of thermodynamic studies on the interaction between rutile and sulphuric acid in this study. Some of these studies also investigated modifying some leaching procedures to reduce iron dissolution compared to titanium dissolution (Liu *et al.*, 2006).

Studies reporting the effect of concentration and temperature on acid leaching are briefly summarised below. Most of them compare different acids to report the most efficient at leaching titanium or the impurities associated with the mineral, allowing for easier isolation. Lastly, various additives, including reducing and oxidising agents, are discussed in the following subsections.

Table 3.1: Titanium and iron extraction from ilmenite using a variety of lixiviants (Jabit, 2017).

	Lixiviant	Concentration (M)	Other reagents	Extraction (%)		References
				Ti	Fe	
Sand Ore	H ₂ SO ₄	0.03-1	-	NR	NR	Imahashi and Takamatsu, 1976
Mechanically activated Ilmenite	H ₂ SO ₄	9.2	-	65	90	Sasikumar <i>et al.</i> , 2007
Sand Ore	H ₂ SO ₄	4-6	Ti(III)(4g/L SO ₂)	NR	NR	Zhang and Nicol, 2010
Sand Ore	HCl	11.3-11.6	-	85	NR	Tsuchida <i>et al.</i> , 1982
Ilmenite	HCl	7.2-9.6	-	80	NR	Olanipekun, 1999
Ilmenite	HCl	7	Fe(0.075g /g ore)	90	0.8 ^b	Mahmoud <i>et al.</i> , 2004
Sand Ore	HCl	2-5	Fe (5g - 20g)	89	97	Lasheen, 2005
Oxidation/Reduction	HCl	2-5	-	NR	49	Sarker <i>et al.</i> , 2006
Sand Ore	HCl		Fe (0.1g/g ore)	98	81	El-Hazek <i>et al.</i> , 2007
Mechanical activation	HCl	3.4-8.6	-	92 ^a	2.1 ^b	Li <i>et al.</i> , 2008
Oxidation/Reduction, Mechanical activation	HCl	7	-	90.5 ^a	1.37 ^b	Zhang <i>et al.</i> , 2011b
Sand Ore	HCl	7	MgCl ₂ (300g/L)	96.9	84.8	Lakshamanan <i>et al.</i> , 2008
Reduction	HCl	10-30%	Gypsum	NR	95	Gireesh <i>et al.</i> , 2015
Sand Ore	HCl	32%		90	90	Haverkamp <i>et al.</i> , 2016
Rutile	NH ₄ Cl, methanol	1.5%(w/w) 0.5%(v/v)	Acetic acid	93	4.8	Jha <i>et al.</i> , 2008
Sand Ore	HCl, CaCl ₂	5-7.5 (500 g/L Cl ⁻)	-	96	97	Das <i>et al.</i> , 2013

^a Calculated as TiO₂ in residue sample, ^b Calculated as total iron in residue sample, NR: No report

a) H₂SO₄ leaching

The ore is typically roasted or pre-treated with an alkali such as sodium hydroxide to convert iron and titanium oxides into water-soluble titanium sulphate complexes before leaching. Optimisation reactions are necessary to identify the conditions that are most effective in titanium leaching. Generally, increasing temperature increases the rate of the reaction, but this is not necessarily the case with some titanium kinetics studies. Leaching is usually done at near-boiling temperatures;

however, in some circumstances, enhanced pressure is employed to allow for higher leaching temperatures.

Generally, the rate of ilmenite dissolution increases with increasing acid concentration. Han *et al.* (1987) discovered that a 14 M H_2SO_4 solution dissolved the highest percentage of iron in ilmenite. The maximum recovery at 14 M H_2SO_4 can be partially explained by the H^+ ion concentration peaks at about this concentration. They concluded that TiOSO_4 and FeSO_4 tend to cover the product's surface in concentrated solutions, preventing further reaction at higher acid concentrations. The researchers subsequently transferred the product to dilute acid solutions to expose the surface, thereby affording additional dissolution. However, this change in the reaction procedure did not increase the titanium dissolution. Their results also indicate that the titanium in solution decreased in a 20 % solution of H_2SO_4 .

Li *et al.* (2006) examined the dissolution of a Panzhihua ilmenite sample using a 50 % sulphuric acid solution that was mill-stirred. The stirred milling of the sample greatly enhanced the dissolution of ilmenite, resulting in a high leaching conversion of 80 % utilising industrial conditions such as an ore/acid ratio of 1:1.5 at 120 °C over 2 hours (Figure 3.3).

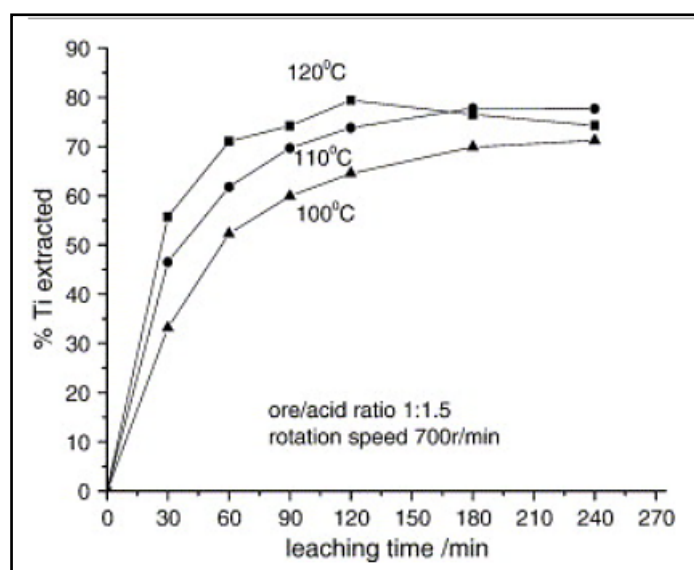
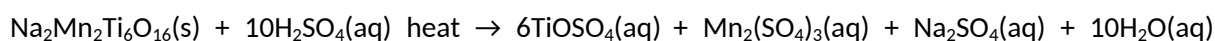


Figure 3.3: Effect of leaching time on Ti extraction at different temperatures (Li *et al.*, 2006)

In another study by Jonglertjunya *et al.* (2013), the researchers examined the dissolution kinetics of ilmenite in both sulphuric acid and oxalic solutions. Their results indicated that both acid types and their concentrations significantly affected the dissolution rate of titanium. Their results indicated that approximately 86.4 % of the titanium was leached in 10 hours at a 4 M oxalic acid concentration, a 1:10 solid-to-liquid ratio, a temperature of 90 °C, and with particle sizes smaller than 45 μm . Under identical experimental conditions except for the use of H_2SO_4 , the titanium dissolution efficiency was

16.1 %, 48.2 %, and 52.0 % using 4, 8, and 12 M sulphuric acid concentrations, respectively Ju *et al.* (2022a) established a method for the recovery of vanadium, titanium, iron, and magnesium. Using 30 % H₂SO₄, 70 °C leaching temperature, and a leaching time of 90 minutes, leaching efficiencies of 99.42 %, 99.4 %, 99.9 %, and 99.9 % for V, Ti, Fe, and Mg, respectively, were obtained. 99.5 % V and 99.9 % Ti were extracted in leachate by two-stage countercurrent extraction with 25 % P507 at an equilibrium pH of 1.6.

A kinetic study (Ismael *et al.*, 2020) to determine the mechanism of titanium dissolution from rutile ores and concentrates revealed that increased reaction temperatures, pulp density (liquid-to-solid ratio), and stirring speed enhanced Ti dissolution. It is not surprising that increased particle size decreased Ti dissolution. The researchers concluded that the chemical reaction at the rutile particle surface regulates the dissolution process. The Ti dissolving process in sulphuric acid from the water leach residue involved the reaction described in **Equation 3.1**. **Figure 3.4** shows the effects of leaching temperature (30, 40, and 50 °C) on leaching times (10, 20, and 30 minutes) as Ti dissolution increases. Further increasing the leaching temperature and time above 50 °C and 30 minutes, respectively, causes Ti hydrolysis and reprecipitation in the sulphate leaching solution.



Equation 3.1

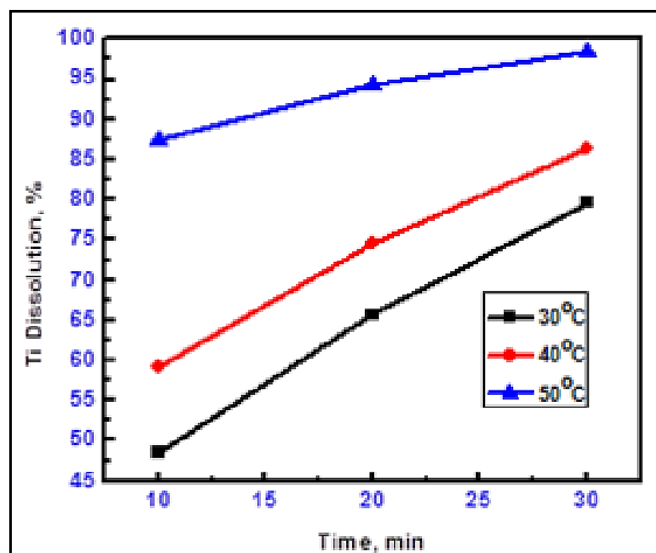


Figure 3.4: Effect of 30, 40, and 50 °C leaching temperatures on Ti dissolution at 10-, 20-, and 30-minute leaching times (Ismael *et al.*, 2020)

Temperature is a crucial experimental variable that can impact dissolution efficiency. Generally, increasing temperature increases the rate of a dissolution reaction. However, some studies showed the opposite effect. Li *et al.* (2007) reported that iron leaching increased with temperature using 20 % H₂SO₄, while titanium decreased due to the instability of titanium in the solution at high temperatures.

Nie *et al.* (2020) found that the extraction of Ti was primarily influenced by the reaction temperature, with the acid-to-solid ratio, H_2SO_4 concentration, and particle size following as secondary factors. The results in **Figure 3.5** show that, in general, the leaching rate increases as temperature rises below 513.15 K, particularly in the early stages of the reaction, but decreases as temperature rises above 513.15 K in the latter stages. Since this temperature harmed the Ti leaching rate, it was chosen as the reaction temperature for subsequent experiments. The leaching rate of Ti achieved a maximum of 89 % by employing an average particle size of 31.5 μm , an acid/solid ratio of 2:1, and an initial acid concentration of 88 %, a reaction temperature of 240 °C (513.15 K), and a water leaching temperature of 60 °C for 120 minutes.

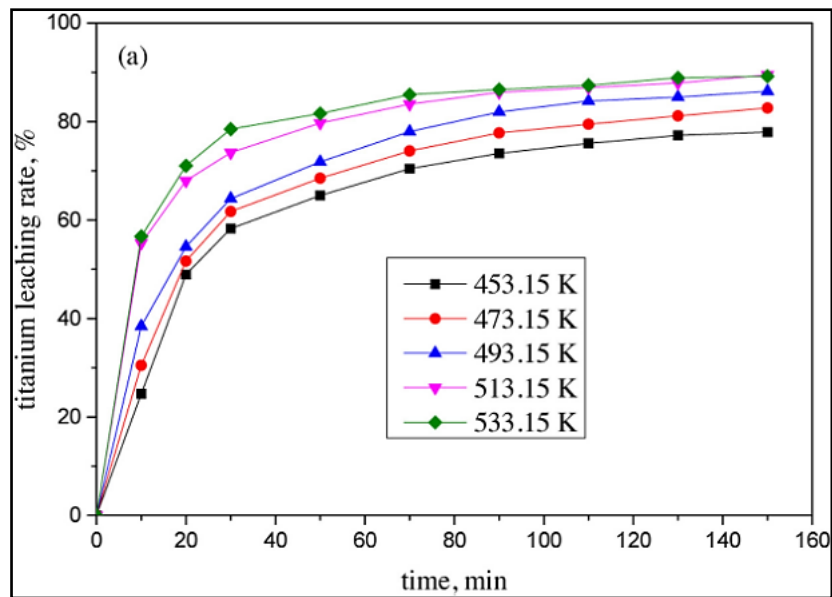


Figure 3.5: Effects of temperature on titanium leaching rate (Nie *et al.*, 2020)

Zhang *et al.* (2018) investigated the simultaneous extraction of vanadium and titanium from vanadium slag. Their method involved roasting the vanadium slag with recyclable $(\text{NH}_4)_2\text{SO}_4$ at relatively high temperatures, followed by leaching with dilute H_2SO_4 . They activated the vanadium slag by subjecting the sample to high-temperature water quenching, which improved the extraction process. The results obtained from this process revealed that the activation of the slag impacted the extraction process, resulting in a 16 % increase in vanadium extraction and a 12 % increase in titanium, compared to the two elements from the raw vanadium slag. The final vanadium and titanium extraction efficiencies were 91 % and 77 %, respectively, after the roasting step at a mass ratio of 4:1 of ammonium sulphate-to-vanadium slag and a temperature of 370 °C followed by a leaching step using 6 % H_2SO_4 .

Ju *et al.* (2022b) developed a method to remove titanium, iron, magnesium, and aluminium from a low titanium-bearing blast furnace (LTBBF) slag sample using acidic wastewater. The Ti, Mg, and Al in LTBBF slag were leached by acidic wastewater at standard pressure. This resulted in a leach solution

rich in titanium, aluminium, and magnesium, with the remaining solid slag phase containing calcium and silicon. At a leaching temperature of 80 °C, for a leaching period of 50 minutes, and a liquid-solid ratio of 9:1, it was possible to extract 99.3 % Ti, 99.5 % Mg, and 99.5 % Al from LTBBF slag using acidic wastewater.

Dubenko *et al.* (2021) investigated the influence of a fluoride activator on sulphuric acid leaching efficiency on an altered ilmenite sample. This method employed sulphuric acid as the reaction medium, with fluoride ions serving as activators to dissolve the rutile part of the raw material. The study involved optimizing the process by varying the Ti:F molar ratio, temperature, and sulphuric acid concentration. The experimental results revealed a decrease in titanium extraction efficiency at temperatures exceeding 100 °C, a molar ratio of Ti:F greater than 1:2, and sulphuric acid solutions higher than 85 wt. %. They proposed the splitting of the chemical dissolution of ilmenite into two separate stages, namely i) Sulphuric acid leaching of the altered ilmenite concentrate, and ii) Sulphate-fluoride leaching of the sludge (raw materials that did not dissolve in the previous stage). This technique facilitated the leaching of up to 95.9 % of titanium, which is 1.6-1.9 times greater than the conventional leaching of altered ilmenite.

b) HCl leaching

Hydrochloric acid is another mineral acid commonly used for leaching titanium from ores, producing soluble titanium chloride complexes. Kurniawan *et al.* (2022) examined the production of synthetic rutile from the byproduct of the tin ore beneficiation process. The mineral cassiterite (SnO_2), the primary source of tin metal, is often associated with ilmenite (FeTiO_3) in nature. Hence, cassiterite processing often yields a by-product with high ilmenite content, which is the primary source of titanium dioxide (TiO_2) and titanium metal. Their process involved the pre-oxidation and reductive leaching of the Fe in a hydrochloric acid medium to maximize iron dissolution while minimizing the titanium dissolution. The most favourable reaction conditions for achieving the highest possible amount of iron dissolution, while reducing the amount of titanium dissolution, were found to be a temperature of 80 °C, a hydrochloric acid concentration of 6 M, a solid-to-liquid ratio of 1:20 g/mL, an ore particle size distribution of 44-77 μm (-200 + 325 mesh), and a leaching period of 6 hours. The leaching experiment conducted under these conditions yielded a 98.07 % extraction of iron, along with a co-extraction of 11.35 % titanium. The residual material from the leaching process consisted of 92.6 % rutile, 2.9 % hematite, and 2.5 % cassiterite, a composition that can be categorized as synthetic-grade rutile. The sample initially contained about 46 % of TiO_2 .

Mahmoud *et al.* (2004) synthesized 90 % TiO_2 after leaching an ilmenite sample (41% TiO_2) at 110 °C for 5 hours with 20 % HCl. The concentrate also contained 0.8 % Fe_2O_3 and silicon dioxide, which were

not removed during the leaching process. Zhao *et al.* (2014) proposed a process for extracting Fe, V, and Ti from titanium magnetite concentrates. They emphasized the importance of reducing the concentrate size by employing magnetic separation to separate the magnetic and non-magnetic portions of the sample and treating the titanium-containing tailings slag with hydrochloric acid. Several steps were involved, including the previously mentioned partial reduction of the concentrates, magnetic separation, hydrochloric acid leaching of the titanium-bearing tailings, and alkaline desilication of the HCl leach residue. Acid treatment resulted in a 90.8 % leaching of vanadium and a 93.4 % leaching of chromium, whereas titanium losses were below 0.3 %. Alkaline desilication successfully removed 96.3 % of the silicon, resulting in the production of titanium-rich slag with a purity level of 93.39 %. The overall yields of Fe, Ti, V, and Cr under the given experimental conditions were 88.3 %, 93.7 %, 81.7 %, and 84.4 %, respectively (**Figure 3.6**). The leaching of the titanium-bearing tailing was greatly influenced by the initial acid concentration, which varied from 0-350 g/L. The leaching efficiencies of iron, vanadium, and chromium showed a rapid increase as the initial acid concentration reached 219.4 g/L.

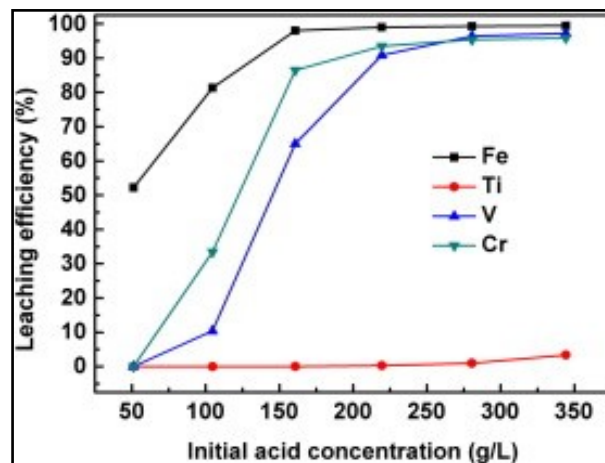


Figure 3.6: Relationship between the initial acid concentration and the leaching efficiencies of metals (Zhao *et al.*, 2014)

El-Hazek *et al.* (2007) reported that a maximum reaction temperature of 80 °C yielded the highest leaching efficiency of 98 % Ti and proposed that this temperature be deemed the optimum for the normal leaching process. According to their results, the optimal conditions for Ti extraction were achieved by employing a concentration of 12 M HCl, a solid-to-liquid ratio of 1:20, operating at a temperature of 80 °C for 2.5 hours, and using an ore ground to a particle size of -200 mesh. Reductive hydrochloric acid leaching of ilmenite using iron powder proved quite successful, resulting in almost complete dissolution of both titanium and iron. When 0.1 kg of metallic iron powder was used per kg of ilmenite, there was a significant decrease in the ideal ratio of solid to liquid to 1:8 and in the time required for leaching to 1.5 hours.

It is interesting to note that HCl is not always successful in leaching titanium from some titanium-rich samples. A thermodynamic analysis by Zhang *et al.* (2013) indicated that direct acid leaching is unlikely to significantly upgrade titanium slag due to the inertness of impurities to inorganic acid under standard experimental conditions. This was later corroborated in a study performed by Anisonyan *et al.* (2023). They indicated that a solution of 20 % HCl was unable to extract any significant amounts of Ti from rutile tailings made from a silicon-titanium ore from the Pizhetskoe deposit. Their study examined the chemical and mineral compositions of the grey and red slimes formed during the breakdown of silicon-titanium ores from the Pizhetskoe deposit. They investigated the leaching at temperatures ranging from 40 to 200 °C. Increased leaching temperatures enhanced accessibility to the slimes, which were associated with the breakdown of several mineral phases. Siderite and goethite underwent thermal decomposition within the 40-100 °C. The clay minerals underwent breakdown at temperatures exceeding 90 °C, and the formation of a gelatinous SiO₂ substance accompanied the process. During the leaching process at higher pressures, pseudorutile, monazite, and xenotime underwent simultaneous decomposition, resulting in the dissolution of cerium, neodymium, and yttrium into solution. The minerals containing rare-earth elements underwent complete disintegration at 180 °C. The non-decomposable solid residue consisted of rutile, quartz, amorphous SiO₂, and zircon, indicating the ineffectiveness of leaching Ti from these samples.

c) HF Leaching

Some Ti dissolution processes utilise fluoride-based compounds, including hydrofluoric acid, which is highly effective in dissolving mineral matrices containing silicates, phosphates, or refractory oxides. Biswas and Mondal (1987) discovered that HF was a very effective dissolution agent for titanium and iron from ilmenite sand (< 130 µm particles). Their results indicated that at a 1:20 solid:liquid ratio, an optimal HF concentration of 6.4 M at its boiling point, and a 5-hour reaction time, leached 81 % Ti and 26 % Fe from the ilmenite sample. Another study (Hansen and Traut, 1989) done on a New York rock ilmenite sample reported that the leaching rate of Ti was linearly related to HF concentration and that Ti leached more quickly than Fe, regardless of stirring speed. Their results showed that 99 % of the titanium and 100 % of the iron were leached in 40 minutes using 19.33 M HF at 45 °C. The results fit a shrinking core model with the chemical reaction step controlling the reaction rate.

Sachkov *et al.* (2017) investigated the hydrometallurgical processing of titanomagnetite ores, achieving a 63.7 % extraction of Ti using hydrofluoric acid. Initially, they used ammonium fluoride, and the results showed that the optimum NH₄F concentration of 0.42 M was needed to leach the titanium from the ore. Under these conditions, the iron and titanium content remaining in the solid was approximately 62.8 wt. % Fe and 3.5 wt. % Ti. The solution's acidity was adjusted using hydrofluoric

acid with varying concentrations (from 0.86 M to 4.07 M) to an ammonium fluoride solution with a fixed concentration of 0.42 M. The highest degree of titanium extraction was obtained using a hydrofluoric acid solution with a concentration of 4.07 M. In this case, the addition of acid made it possible to increase the Fe/Ti ratio by 3.4 times compared to the original ore. It was concluded that solution acidity and the concentration of ammonium fluoride solution significantly influence the selectivity of the hydrometallurgical process.

d) HNO_3 leaching

Nitric acid has been used recently to dissolve titanium-containing samples, but it was not very effective as a Ti extraction method. Yessengazyev *et al.* (2019) investigated the leaching of titanium and calcium from industrial waste using HNO_3 . The leaching reactions were performed at 20 °C, with a solid-to-liquid ratio of 1:10, a leaching time of 30 minutes in a dilute 0.2 % flocculant Alclar 600 solution at a dosage of 1.3-2 mL per litre of pulp, along with 15 % nitric acid. The extraction yield of titanium in the solution was 5.0 %, while that of calcium was 96 %.

e) Comparative studies on different acids and reaction conditions

H_3PO_4 and aqua regia were also used in comparative studies of different acids to identify the most effective acid for leaching titanium from various titanium-bearing ores. Pepper *et al.* (2016) investigated the effect of HNO_3 , HCl , H_2SO_4 , and H_3PO_4 on the leaching of Ti, as well as other elements (Fe, Al, Si) present in red mud (RM). Results obtained from this study indicated that H_3PO_4 and HCl performed the best, leaching 76-78 % Fe and 23-24 % Ti, respectively (**Figure 3.7**). Additionally, the use of H_3PO_4 resulted in the highest leaching for Si (49 %) and Al (50 %). H_2SO_4 had the highest Ti recovery at various RM:acid ratio, time, and temperature variations. Generally, Ti recovery increased with an increase in acid concentration, time, and temperature.

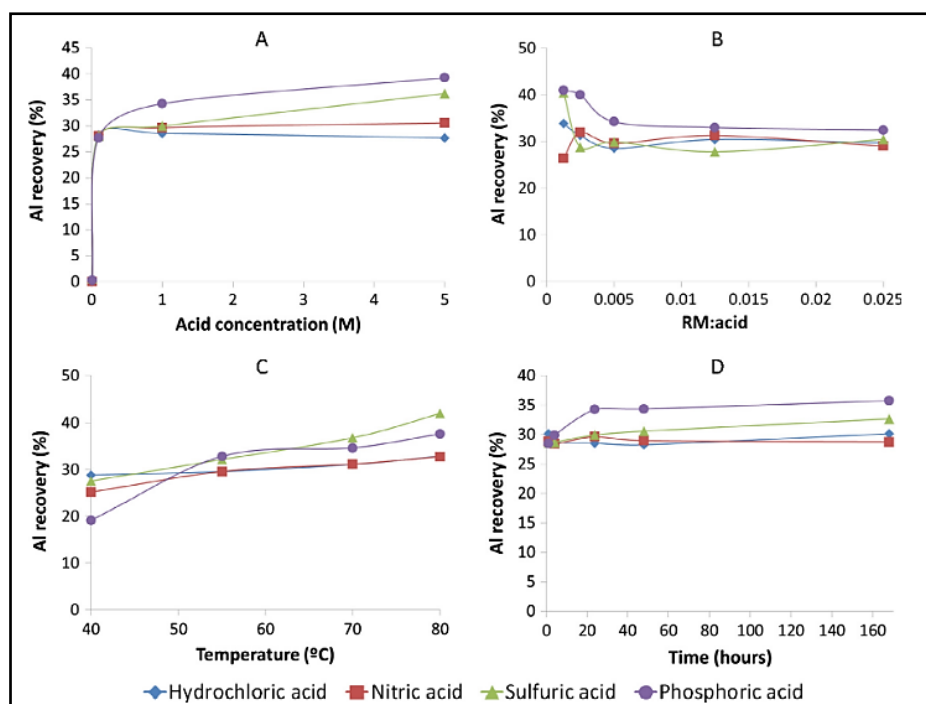


Figure 3.7: Effect of acid concentration (a), RM:acid ratio (b), temperature (c), and time on Ti recovery (d) (Pepper et al., 2016)

Snäll and Liljefors (2000) investigated the leaching of major elements using strong acids. Several typical silicate and oxide minerals, including K-feldspar, plagioclase, biotite, muscovite, chlorite, hornblende, epidote, sphene, rutile, anatase, and ilmenite, were analyzed in this study using aqua regia, nitric acid, and hydrochloric acid at varying concentrations. The Ti leachability from biotite, sphene, ilmenite, rutile, and anatase under various conditions is shown in **Table 3.2**.

Table 3.2 Leachability of titanium from biotite, sphene, ilmenite, rutile, and anatase (Snäll and Liljefors, 2000)

Mineral	Ti Fraction	Total (wt%)	Leachability (% of total wt%) in					
			1M HCl, 2h	4M HCl, 0.5h	1M HNO ₃	7M HNO ₃	SS 028150	Aqua regia
Biotite	0.5–2mm	1.7	113	110	26	55	60	91
	Powder	1.7	105	108	91	96	105	96
	<2mm	22.8				3.3	3	2.7
Sphene(titanite)	<63µm	22.8				33	36	42
	Powder	22.8				55	63	58
	Powder	35.3				15	n.d	63
Ilmenite	Powder	59.2				0.7	1	1.2
Rutile	Powder	59.1				0.2	0.4	0.4
Anatase								

Rodriguez *et al.* (2020) investigated the extraction of titanium from low-grade ore using various leaching agents, including HF and H₂SO₄, as well as combinations of these acids. The study examined the operating parameters and the concentration of leaching agents, providing practical insights into the comparative effectiveness of these acids in the leaching process. The results obtained from the study demonstrated the significant impact of concentration, temperature, and duration of contact on the leaching effectiveness of acid mixtures on titanium from low-grade ore samples. The most favourable parameters for achieving an 89 % Ti extraction were obtained at 123 °C, a stirring speed of 330 rpm, a reaction time of 80 minutes, and a concentration of 1.8 % w/v using a mixture consisting of 15 % HF (v/v) and 10 % H₂SO₄ (v/v) (Figure 3.8).

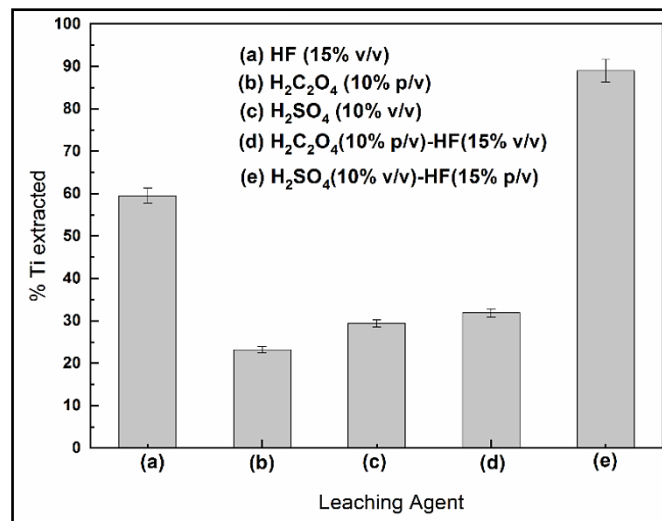


Figure 3.8: Effect of the leaching agent on Ti extraction (Rodriguez *et al.*, 2020)

In another study, Nayl *et al.* (2009) investigated the kinetics of acid leaching of ilmenite after it was reacted with KOH and then leached using oxalic acid, hydrochloric acid, and sulphuric acid. The ilmenite paste obtained after alkaline treatment was leached with sulphuric acid, hydrochloric acid, or oxalic acid to determine the leaching efficiency of iron, titanium, chromium, and vanadium from the ilmenite. The study examined the notable impact of variables, including reaction time, acid concentration, acid-to-ilmenite mass ratios, and reaction temperature, on the leaching process for each acid. Approximately 93 %, 92 %, and 89 % of Ti was extracted from the alkaline-treated ilmenite paste using oxalic acid, hydrochloric acid, and sulphuric acid, respectively.

Rashid *et al.* (2022) investigated the leaching efficiency of an Iraqi bauxite ore sample containing 4.1 % Ti using HNO₃, H₂SO₄, and H₃PO₄ as lixiviants. During this study, the researchers investigated the influence of acid concentration, solid: liquid ratio, stirring speed, contact time, and temperature on leaching efficiency. The reaction conditions for titanium recovery were varied: pulp densities ranged between 1:100 and 1:8, temperatures ranged between 25-50 °C, reaction times ranged from 30-120

minutes, and stirring speeds ranged from 400-1200 rpm. The optimal conditions were determined to be a 1:100 pulp density, at 50 °C, 4 M HNO₃, and a stirring speed of 900 rpm. From these results, as indicated in **Figure 3.9a**, it is clear that nitric acid was the most effective in leaching Ti, and therefore, it was used as the main acid in subsequent evaluations, as shown in **Figures 3.9b** and **3.10**.

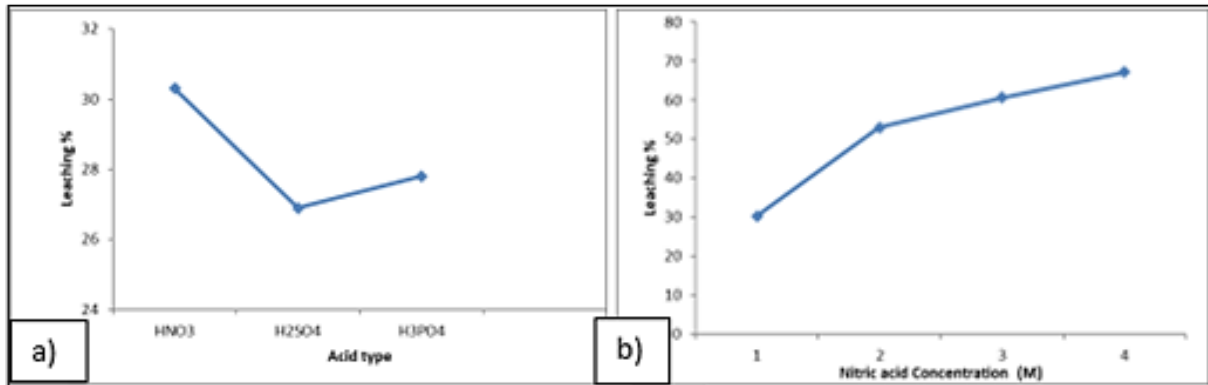


Figure 3.9: Effect of acid type (a) and nitric acid concentrations (b) on the leaching of titanium (Rashid *et al.*, 2022)

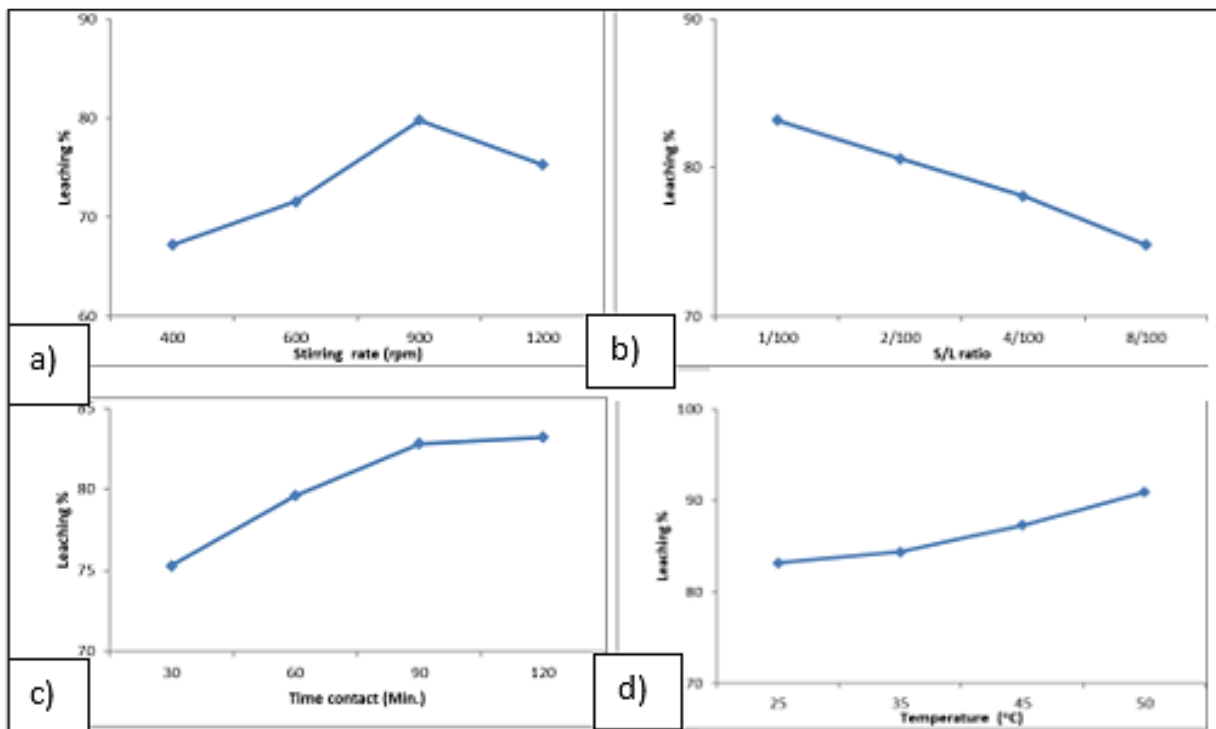


Figure 3.10: Effect of stirring rate (a), solid-to-liquid ratio (b), time contact (c), and temperature (d) on the leaching of titanium (Rashid *et al.*, 2022)

f) Addition of other reagents

The leaching of Ti was also studied in the presence of other reagents (not only acids), such as reducing agents by El-Hazek *et al.* (2007), Lasheen (2005) and Mahmoud *et al.* (2004). All of them added metallic iron as a reducing agent to the hydrochloric acid/ilmenite mixture. The results obtained from those studies indicated a significant increase in the reactivity of ilmenite. Both (Mahmoud *et al.*, 2004; El-

Hazek *et al.*, 2007) obtained comparable findings. During their studies, they added 0.1 kg of iron powder to 1 kg of ilmenite ore, significantly increasing the leaching efficiency of iron and titanium extracted during the process. In addition, Lasheen (2005) conducted a study on a leaching procedure for Ti to enhance the quality of Rosetta ilmenite concentrate (40-47 % TiO_2) by converting it into synthetic rutile without requiring a thermo-treatment phase. They demonstrated that using a high concentration of acid (specifically, a high ilmenite/acid molar ratio in the presence of metallic iron) as a reductant, the iron can be effectively removed from the structural lattice of the mineral while preventing the dissolution of titanium. In the absence of a reductant, the effectiveness of iron leaching did not exceed 55% when concentrated HCl (12 M) was used with a solid-to-liquid ratio of 1:5 at 90 °C for an 8-hour reaction period, despite achieving nearly complete dissolution of titanium. The data indicated that the addition of 6% iron powder as a reductant progressively accelerates iron removal through the reduction of ferric iron, as evidenced by an increased TiO_2 percentage in the residue. This increased the recovery rate to 89 % for synthetic rutile (TiO_2) and 6.7 % for Fe_2O_3 .

Another study that used metallic Fe as well as MgSO_4 as additives was performed by Daba *et al.* (2022) in ilmenite ore. They investigated the direct leaching of Fe from ilmenite ore in hydrochloric acid, which encourages Fe dissolution, as the high iron content in ilmenite ore poses a significant challenge, particularly in the synthesis of titanium-containing products. The parameters included in this study were the influence of additives and the addition of metallic iron powder. They concluded that the larger ilmenite particles, with a size distribution of +150 μm , resulted in higher Fe leaching throughout the process. This was observed when a hydrochloric acid concentration of 7.5 M and a solid-to-acid ratio of 1:10 were used at a temperature of 90 °C and a stirring speed of 450 rpm. Under these conditions, 92.3 % of Fe was leached. However, a loss of 2.4 % of Ti was observed, including metallic Fe and MgSO_4 as additives that significantly improved iron solubility and reduced titanium recovery in the solution. The results indicated that 1.4 % of Fe as impurity remained in the solid residue, while 98.6 % of Fe was successfully leached from the solid. The leached residue contained 91.4 % TiO_2 in the rutile phase but still contained substantial impurities, including 4.4 % of ilmenite FeTiO_3 and 2.2 % of SiO_2 . The levels of the other impurities, such as Al_2O_3 , MgO , MnO_2 , CaO , V_2O_5 , MnO_2 , and Cr_2O_3 , were all below 0.1 %.

Zhang and Nicol (2010) investigated the rate at which titanium and iron dissolve from an ilmenite sample in moderately concentrated sulphuric acid solutions, both in the absence and presence of reducing agents, such as Ti^{3+} ions and sulphur dioxide. Their findings indicated that the titanium dissolution or leaching rate is minimally influenced by particle size and sulphuric acid concentration, but that temperature had a substantial impact under the examined experimental conditions. They

concluded that a gradual chemical reaction on the mineral's surface regulates the rate at which ilmenite is dissolved in acidic solutions. However, the presence of a small quantity of Ti^{3+} ions in the solution helped reduce Fe^{3+} to Fe^{2+} in ilmenite minerals, speeding up its dissolution. The amount of titanium leached increased significantly from roughly 20 % after 6 hours without Ti^{3+} present, to about 70 % after just 5 hours when 3.5 g/L of Ti^{3+} was added. This was profitable since very little amount of Ti produced a significant difference in Ti yield. They also observed that the solubility of titanium increased with SO_2 as a reductant but only when ferrous ions were present in the solution. They postulated that both Ti^{3+} ions and SO_2 reduce Fe^{3+} to Fe^{2+} during the leaching component at the surface of the ilmenite, thus increasing the leaching of the elements.

3.3.1.2 Alkali leaching

Using alkalis as a potential for Ti dissolution was also extensively investigated. Typically, alkalis (e.g., sodium hydroxide) are used to roast ores before leaching. This roasting step is believed to convert the titanium-containing minerals into more water-soluble solids. These reactions can be complex, most probably involving the formation of alkali titanates.

Guo *et al.* (2021) investigated the leaching of a titaniferous magnetite concentrate (12.7 % TiO_2 and 54 % Fe) using a highly concentrated alkaline aqueous solution at high temperatures and pressures. The operational procedure involved a heated autoclave at 300 to 400 °C purged with nitrogen gas and stirring the mixture at 600 rpm. After the reaction, the mixture was cooled to room temperature and subjected to filtration, washing, and drying. After this step and magnetic separation, the concentrate/filtrate was obtained with a Fe purity of 66 % and an Fe recovery of 82.5 %. The tailings or residue contained 32.1 % TiO_2 purity with a TiO_2 recovery of 80.8 %.

In another study, Chen *et al.* (2013) proposed a novel process for recovering iron, titanium, and vanadium from titanomagnetite concentrates using NaOH molten salt roasting and water leaching. Their proposed method highlighted the potential for multi-metal recovery through innovative leaching methods. MgTi_2O_5 was converted to the NaCl-type structure of Na_2TiO_3 , and $(\text{Ti, Mg, Fe})_3\text{O}_5$ was converted to the α - NaFeO_2 -type structure of $\text{Na}(\text{Ti, Mg, Fe})\text{O}_2$, respectively. The conversion of titanium in the titanium-vanadium slag during NaOH molten salt roasting was significantly influenced by the roasting temperature and the NaOH-to-slag mass ratio. The titanium conversion rate reached 96.3 % after roasting at a temperature of 500 °C for 60 minutes and using a NaOH-slag mass ratio of 1:1. Another study investigated the ilmenite/KOH decomposition under atmospheric pressure, indicating that 80-85 of the titanium was leached from the ilmenite (Liu *et al.*, 2006).

A relevant study by Han *et al.* (2019) evaluated the feasibility of the alkali leaching-dilute acid washing method for preparing high-quality acid-soluble titanium slag from titanium middling ore. The study

directly addressed the impact of alkali concentration on the leaching process, but not on dilute acid washing. The titanium slag was leached using an alkali leaching process with NaOH and washed with dilute HCl. The results indicated that increased temperature benefits the alkali leaching process. A high-quality acid-soluble titanium slag (HQUESTS) with TiO_2 and Fe_2O_3 content of 75.4 wt. % and 0.96 wt. % was obtained with low iron content. The method leached the iron, which ultimately involved titanium slag processing, utilizing a “direct reduction-magnetic separation-alkali leaching-dilute acid washing process.” The source of the titanium middling ore was the Panzhihua Iron and Steel Research Institute located in Sichuan Province, China. The iron component in the titanium middling ore was extracted through the pretreatment of direct reduction and magnetic separation, generating low-grade titanium slag. The study also indicated that the alkali leaching should be done above a pH of 13.50, whereas the pH of the dilute acid washing should be below 1.00. As previously mentioned, increased temperature promoted alkali leaching, while the trend is reversed for dilute acid washing. Therefore, the recommended temperatures for the alkali leaching and dilute acid washing were indicated as 100 °C and 25 °C, respectively. These parameters have significant economic implications, as they can substantially reduce the concentration of NaOH in the alkali leaching process and the concentration of HCl in the dilute acid washing process, resulting in substantial savings on acid and alkali. The most favourable conditions for alkali leaching were achieved with a NaOH concentration at 2.8 M (pH 14.44), a liquid-to-solid ratio (L:S) of 4:1, a temperature of 95 °C, and a reaction time of 60 minutes (Figure 3.11).

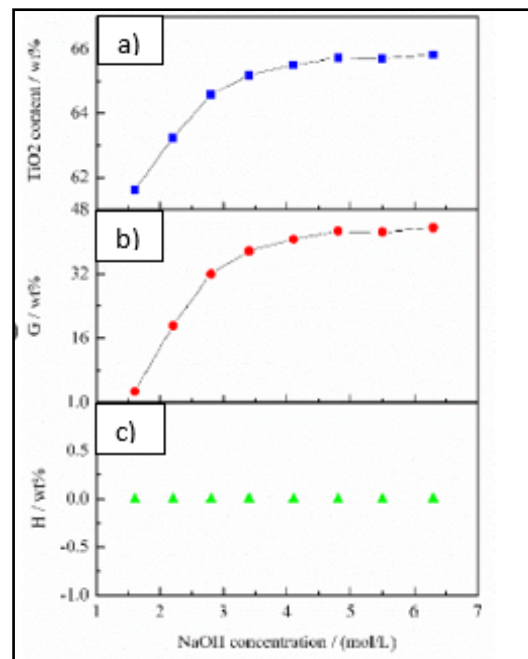


Figure 3.11: Effects of NaOH concentration on a) TiO_2 content, b) SiO_2 extraction ratio (G) and Al_2O_3 extraction ratio (H) (Han et al., 2019)

Parirenyatwa *et al.* (2016) reported a comparative study of alkali roasting and leaching performed on chromite ores and titaniferous minerals. This study investigated the use of alkali to roast ilmenite mineral concentrates, providing insights into the effect of alkali concentration on the dissolution and leaching process. The study used sodium and potassium hydroxide as alkalis to roast the chromite ores and ilmenite minerals. The roasted ilmenite samples underwent additional processing to extract partially purified titanium dioxide from titanium-containing minerals. They were first water-leached, followed by organic acid leaching (a mixture of 0.25 M oxalic and 0.01 M ascorbic acid) for 2 hours to obtain a TiO_2 -rich residue. The purity of the TiO_2 achieved through roasting at 400 °C with NaOH and subsequent double leaching was 49.2 wt. %, but the purity that was achieved with KOH was 54.5 wt. %. After subjecting the material to a roasting process at a temperature of 1 000 °C for 2 hours and subsequently treating it with both water and organic acids (oxalic and ascorbic), the resulting titanium dioxide purity reached a maximum of 84 wt. %.

Liu *et al.* (2012) investigated the extraction behaviour of titanium and other elements during the decomposition process of ilmenite using a highly concentrated KOH solution. Ilmenite was reacted with an 80 wt. % KOH solution in an alkali-to-ore mass ratio of 7:1 at 260 °C for 60 minutes with the ilmenite crushed to 58-75 μm . During this process, almost all the titanium (98.2 %) was extracted with an extraction rate efficiency of 78 % for aluminium. The extraction efficiencies for the other elements were less than 22 %. Furthermore, the purification procedure yielded a high-purity (98.2 wt.%) TiO_2 with the anatase structure.

Zhang *et al.* (2018) also reported using water to leach either titanium into solution or to leach the other metal impurities, leaving titanium in the residue. Their two-step proposed method involved i) a low-temperature roasting step for the vanadium-bearing titanomagnetite and ii) the water leaching of roasted slag. Different reductants were used in this work, including bitumite, anthracite, lignite, and graphite. They concluded that the iron oxides were reduced to metallic iron during the roasting step, using bitumite or anthracite, after which a smelting step separated the iron from the slag. They deduced that the vanadium oxides were oxidized using a sodium salt (Na_2CO_3) to produce water-soluble sodium vanadate, and according to them, all these steps co-occurred. The following optimum roasting conditions were used: 42.5 mm mixture thickness, molar ratio of 1.7, at 1 200 °C, for 2 hours, using anthracite reductant and a sodium carbonate addition of 70 wt. % to the vanadium-bearing titanomagnetite. They obtained 93.7 % iron (iron nuggets) with a 95.4 % iron purity. They also isolated 85.6 % vanadium after water leaching and finally reported total recoveries of 99.7 % Ti, 93.7 % Fe, and 72.7 % vanadium.

3.3.2 Complete dissolution of titanium ores

El-Hazek *et al.* (2007) achieved the complete dissolution of a Rosetta ilmenite using HCl by increasing the solid:liquid ratio from 1:20 to 1:8, and the addition of iron powder resulted in the complete dissolution of both iron and titanium in 1.5 hours. This contrasts with the 2.5 hours required under comparable leaching circumstances without adding iron powder. Other conditions used were 12 M HCl at 80°C using ore ground to a – 200 mesh size.

Teimori *et al.* (2022) employed a kinetics study to investigate the effect of nitric acid concentration on pyrite dissolution, thereby shedding light on the potential impact of acid variants on the dissolution of titanium-containing minerals. During a 120-minute leaching process in a 3 M HNO₃ solution, the pyrite dissolved from 72 to 95 % when exposed to temperatures exceeding 45 °C, with a maximum temperature of 85 °C. Nitric acid exhibited a potent ability to oxidize, with concentrations between 2.5 M and 4 M resulting in a significant dissolution of pyrite ranging from 74 % to 95 %. The efficiency of iron extraction significantly improved from 75 % to around 92 % when the particle size of pyrite was decreased from +150-212 µm to +53-75 µm. The extraction efficiency of Fe rose from 80 % to 98 % when the stirring speed was raised from 1 000 rpm to 4 000 rpm. Since most ores that contain iron also contain titanium, these reactions can be used on titanium ores.

Purcell *et al.* (2020) investigated the acid and flux fusion digestion techniques for ilmenite complete dissolution. The Na₂HPO₄/NaH₂PO₄·H₂O, Na₂B₄O₇, and LiBO₂ flux fusion procedures were the most effective for completely dissolving the ilmenite mineral, as the acids did not completely dissolve the sample. The H₂SO₄, H₃PO₄, HNO₃, HCl, and aqua regia acid digestion experiments were performed at a constant pulp density of 10 g/L and a stirring speed of 500 rpm for 3 hours, at temperatures ranging from 60 to 200 °C, depending on the boiling point of the acid. H₂SO₄ and H₃PO₄ dissolved/leached approximately 70.6 and 77.9 % Ti and 35.7 and 83.0 % Fe from the ilmenite, respectively. This indicated that H₃PO₄ had the potential to completely dissolve ilmenite, as the majority of Ti and Fe were dissolved from the ilmenite after 3 hours at 200 °C. Complete dissolution of the mineral was accomplished from the melt obtained after the fusion of ilmenite using Na₂B₄O₇, LiBO₂ and a mixture of NaH₂PO₄ and Na₂HPO₄ fluxes with Fe concentration averaging at 38.1 % (54.1-54.6% Fe₂O₃) and the Ti concentration with an average of 28.3% (46.4-49.3% TiO₂).

3.3.3 Microwave acid-assisted digestion

Microwave acid-assisted digestion has also proved to be a very effective dissolution/leaching method. It utilises high pressure and temperature, offering advantages such as shorter reaction times and improved leaching efficiencies.

Premaratne and Rowson (2014) investigated the use of microwave digestion on a Sri Lankan ilmenite sample. In this study, 0.2 g of ilmenite was reacted in 25 mL of 12.2 M H_2SO_4 at 600 W and 120 °C for 2 hours, resulting in the leaching of 74.2 % of titanium from the mineral. In another study by Tripathi and Chattopadhyay (2007), they digested a titanium-containing mineral in an acid mixture of HNO_3 : HCl : HF (2:2:1) for 17 minutes at 600 W. The results indicated that they leached over 99 % of Ti under harsh acidic conditions. On the other hand, McDonald and Amarin (2015) investigated a National Institute of Standards and Technology (NIST) soil sample. It was digested in the presence of a combination of HNO_3 , HCl , and HF (1:3:1), which gave of recovery of 95 % Ti compared to 74 % recovery when only H_2SO_4 was used.

Microwave acid digestion was also used by Agrawal and Dhawan (2021a) to evaluate the recovery of titanium and scandium from red mud. The microwave power was the determining factor in metal ion leaching. At 600 W, with an irradiation time of 6 minutes, a 1 mL/g H_2SO_4 : red mud ratio, 73.3 % of the titanium and 88.4 % of the scandium present in the sample were dissolved. They concluded that the difference in microwave power improved the leaching efficiency. The remaining leach residue primarily consisted of unreacted hematite, anatase, and quartz phases. In a previous study using the same sample, they leached 28 % titanium using sulphuric acid irradiated at 600 W for 3 minutes. Their results also indicated that the procedure dissolved a maximum amount of iron and aluminium at 300 W (Agrawal, 2021b)

Another study by Ma *et al.* (2021) employed acid-assisted microwave digestion to investigate the recovery of Ti and Al from coal fly ash samples. In this process, they used a combination of H_2SO_4 + NH_4HSO_4 as a solvent. Compared to conventional acidic extraction procedures, their approach enhanced Al and Ti extraction efficiencies while reducing energy consumption and gas emissions. Employing the optimized reaction parameters of 280 °C, 1.2x the theoretical quantity of reagents, 100 W, and 60 minutes irradiation time, as well as leaching conditions of 60 °C, L:S ratio of 5 g water:1 g roasted ash, and 30 minutes reaction time. They extracted 82.4 % Al and 55.6 % Ti from the fly ash sample.

3.3.4 Flux fusion digestion and dissolution

Flux fusion for sample dissolution usually involves the total destruction or dissolution of the samples. The advantage of this process is that all target elements are in solution and available for separation and isolation, allowing also for the complete and accurate chemical characterization of the sample. The disadvantages of this dissolution procedure are that all impurities are also now in solution, which often complicates the separation of the different elements present in the mineral matrix. Additionally, the large amounts of salts used as fluxes add to the complexity of the matrix and the separation and

isolation steps. This method typically uses a salt to lower the melting point of the ore and facilitate its dissolution.

Flux fusion has been used in studies of ilmenite and other titanium sources. Felman (1983) completely dissolved an ilmenite sample by fusing it with lithium borate ($\text{Li}_2\text{B}_4\text{O}_7$) at 950 °C for 20 minutes. 3 % nitric acid and 2.5 % tartaric acid were used to dissolve the melt. In another study by Premaratne and Rowson (2014), an ilmenite sample was fused with KHSO_4 at 800 °C, resulting in complete dissolution. A 20 % H_2SO_4 solution was used to dissolve the melt completely. Radhamani *et al.* (2010) used phosphate fusion on rutile (>90 % TiO_2) and synthetic ilmenite (48.6 % TiO_2 ; 47.9 % FeO) samples. A 1:1 ratio of sodium dihydrogen phosphate (NaH_2PO_4) and disodium hydrogen phosphate (Na_2HPO_4) was used to fuse the samples at 700-850 °C. Water was used to dissolve the resulting melt, and 102 % rutile and 92 % ilmenite were recovered. Flux fusion completely dissolved most samples, with lithium metaborate being the best flux salt. It also saves time and is easily scalable to industrial size, as large samples can be dissolved in one go.

A unique flux was employed in a study by Radhamani *et al.* (2007) utilizing a rapid decomposition and dissolution approach with a combination of sodium di-hydrogen orthophosphate and di-sodium hydrogen orthophosphate. The minerals were combined with a 1:1 ratio of the salts, and the resulting mixture was dissolved in distilled water. Nevertheless, the fusion process required the use of Pt-Au crucibles that failed to adhere to the substances being fused, and the melting process took longer to achieve complete dissolution. In the fusion described above, the process involved dissolving the melt in a solution of weak sulphuric acid to prevent the hydrolysis of titanium. They indicated that sodium di-hydrogen orthophosphate does not decompose titanium dioxide, but it does efficiently break down ferric oxide. They further observed that adding a small amount of di-sodium salt enables complete decomposition of TiO_2 , resulting in a clear, water-soluble melt. They reported that increasing the proportion of di-sodium salt boosts the flux's effectiveness, likely due to greater alkalinity and a higher melting point. It was also noted that fusing di-sodium hydrogen phosphate at regular burner temperatures is difficult.

3.3.5 Sequential extraction

This popular analytical technique is used to detect components associated with solid phases in environmental media based on their reactivity with solutions. It has been widely used to analyse soil samples in agriculture and some on mining waste for sample characterization purposes (Gómez-Arias *et al.*, 2022; 2021). Most studies focused on extracting Zn, Cd, Pb, Cu, As, and Hg. Most research compared various BCR protocols to perfect the method for higher reproducibility. Several protocols can be followed for the extraction of diverse geochemical phases from sediments, and the Tessier and

Community Bureau of Reference (BCR) sequential extraction protocols (SEPs) have been widely used. BCR protocol is the most common, of which there are the original and the modified ones (Caraballo *et al.*, 2018)

Liu *et al.* (2018) carried out a study to partition Ti, Fe, Ca, Mn, and Al using both the Tessier and the BCR methods. The individual minerals used to test efficiency and selectivity were carbonate minerals (calcite, dolomite, rhodochrosite, and siderite), Fe-Mn oxides (pyrolusite, hematite, magnetite, amorphous Fe(OH)₃), and clay minerals (kaolinite). **Table 3.3** shows the conditions used for each SEP.

Table 3.3: BCR and Tessier SEP conditions (Liu *et al.*, 2018)

Fraction	BCR SEPs	Fraction	Tessier SEPs
I) Carbonate	0.11 M HAc	I) Exchangeable	1 M MgCl ₂
II) Fe-Mn oxides	0.5 M NH ₂ OH-HCl	II) Carbonate	1 M NaAc-HAc
III) Sulphides and organic matter	30 % H ₂ O ₂	III) Fe-Mn oxides	0.04 M NH ₂ OH-HCl
IV) Residual	HNO ₃ , HF, HClO ₄	IV) Sulphides and organic matter	30 % H ₂ O ₂
		V) Residual fraction	HNO ₃ , HF, HClO ₄

The results obtained in this study (**Figure 3.12**) show that both BCR and Tessier SEP extracted 95 % and 98 % Ti in the residual fraction, respectively. Both SEPs had good dissolution efficiency and selectivity for the targeted geochemical phases.

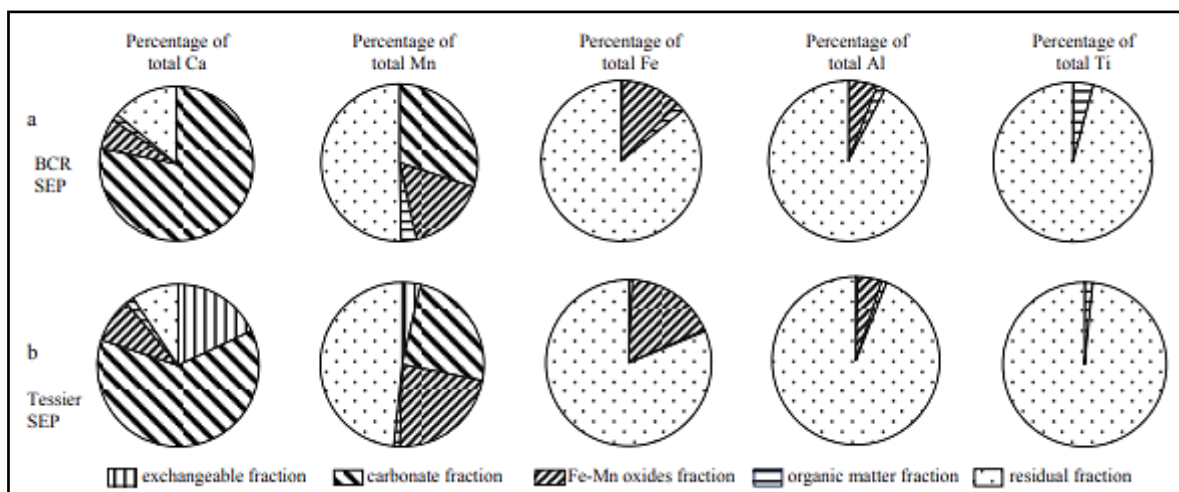


Figure 3.12: The distributions of Ca, Fe, Mn, Al, and Ti in GSD-9 were analysed using the BCR (a) and Tessier (b) sequential extraction procedures (SEPs) (Liu *et al.*, 2018)

3.4 Conclusion

The literature review has underscored the complexity and significance of titanium extraction and processing from various mineral sources. The discussions revealed that titanium beneficiation relies on a combination of physical and chemical methods, each presenting unique challenges and opportunities. Physical separation techniques such as magnetic and gravity separation have proven instrumental in pre-concentrating titanium-bearing minerals, thereby improving the efficiency and purity of subsequent chemical processes. Chemical methods, including acid and alkali leaching, flux fusion, and microwave-assisted digestion, have highlighted the balance between economic feasibility, environmental sustainability, and technical efficiency required for effective titanium extraction. While acids such as sulphuric, hydrochloric, and nitric acids remain prominent, innovative approaches like alkali roasting and sequential extraction demonstrate promising avenues for optimizing recovery rates and minimizing waste generation. Furthermore, the exploration of microwave-assisted and flux fusion techniques suggests advancements in reducing energy consumption and enhancing dissolution efficiencies. The review highlights the importance of eco-friendly and cost-effective methodologies to ensure sustainable titanium production. Additionally, the development of novel technologies and the utilization of secondary sources, including tailings and vanadium ores, present viable solutions to address future supply constraints. In conclusion, the reviewed studies provide a strong foundation for advancing titanium extraction techniques. Through innovative research and interdisciplinary approaches, the industry can achieve greater sustainability and efficiency, paving the way for broader applications in aerospace, medicine, automotive, and other industries that rely on this versatile metal.

Chapter 4: Analytical Instrumentation

4.1 Introduction

Hydrometallurgy uses aqueous solutions to extract and separate economically viable elements from ores (Hocking, 2005) and recycled or waste material. This is usually done in four main steps, which are i) sample selection and homogenization, ii) accurate chemical and mineralogical characterization, iii) total or partial sample dissolution, and iv) the separation and isolation of the target components from the other constituents of the sample. Different analytical instruments were used to characterize and quantify the samples, as well as to guide and select the processes or steps to achieve the goal set out for this study. The main goal of this study is the separation of Ti from both the ore and tailings samples to produce a titanium-enriched product with as few impurities as possible. Physical separation techniques, such as magnetic and density separation, were evaluated as preliminary steps to concentrate the target element and reduce sample sizes for the following hydrometallurgical process. The initial sample characterization is crucial to elucidate the chemical and mineralogical state of the target element (Ti), as well as to estimate the content of Ti in both the ore and tailing samples. This aids with element mass balancing and guides the separation chemistry that can be applied to the matrix to better extract the Ti. Techniques such as Scanning Electron Microscope- Energy Dispersive X-ray Spectroscopy (SEM/EDS), X-Ray Diffraction (XRD), and X-Ray Fluorescence (XRF) were employed to characterize the samples prior to dissolving them for total elemental quantification and subsequent separation steps.

Chapter 3 demonstrates that samples can be dissolved using flux fusion, microwave digestion, acid/base leaching. Sequential extraction is used to identify elements in different mineral phases and can be utilised to determine the composition of mineral samples. Then, an Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES) instrument was used to characterize the subsequent samples from the sequential extraction, as well as the aliquots produced by each experiment. This chapter provides a brief overview of the theoretical framework underlying the instruments and techniques employed in this study. **Figure 4.1** summarizes the stages of a geochemical analysis, along with some of the methods used in this study.

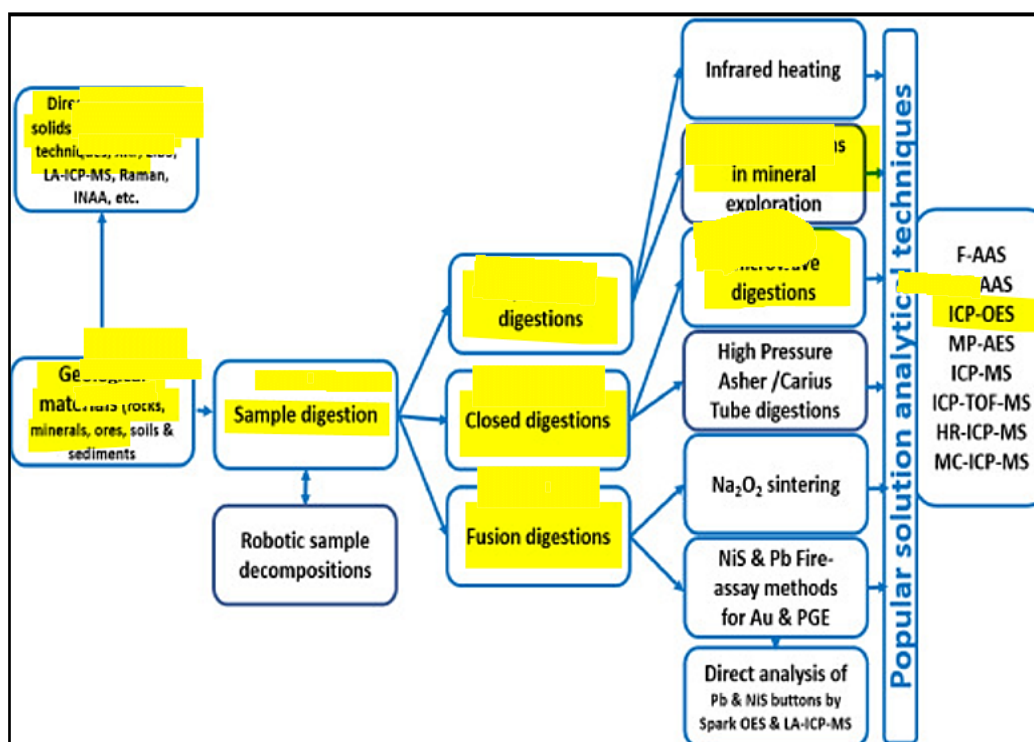


Figure 4.1: Diagram depicting several types of sample preparations and trends in geochemical analysis (Balaram and Subramanyam, 2022). Those marked in yellow were used in this study

4.2 Sampling and sample homogenization

Sampling is the removal of a piece of a given amount of material that is typical of the total, yet manageable size, for analysis. It is done either by hand or by machine (Gruner and Lorig, 1999). It should have comparable proportions of all original component elements found in mineral ore populations.

Homogenization is a step in the sample preparation process that comprises sample mixing and blending, particle size reduction, and mass reduction. Homogenization ensures consistency in sample quality and helps accurately analyze ore properties (Lacorte and Bono-Blay, 2012). It aids in reducing sampling errors and obtaining reliable results in mineral processing, hence consistency in method validation calculations, such as accuracy and precision. A combination of crushers, millers, pulverisers, and mixers is used to homogenize the samples. The samples were ground at the Geology department using a ball mill in this study. Samples can be submitted for analysis without thorough information on homogenization. However, they can still be homogenized in the laboratory using instruments such as the sample splitter used in this study (Figure 4.2).



Figure 4.2: Sample splitter (Geology Superstore, 2023)

4.3 Physical beneficiation

Physical separation or enrichment is vital in mineral processing to extract valuable minerals from ore. These methods help increase the concentration of the target elements, reduce waste and chemicals used in the processing step, and improve overall efficiency in mineral extraction processes. Magnetic separation and density/gravity separation methods were used in this study.

4.3.1 Magnetic separation

Magnetic separation is a beneficiation process that utilises the magnetic properties of minerals to separate magnetic from non-magnetic materials to concentrate and separate materials containing the target minerals from gangue for further processing. This technique is effective in separating minerals based on their magnetic susceptibility differences (**Table 4.1**). This technique can effectively separate minerals such as magnetite and ilmenite from nonmagnetic materials such as quartz, feldspar, and mica. It can be accomplished either wet or dry, depending on the specific requirements of the separation process.

Table 4.1: Magnetic susceptibilities of common minerals (Das and Roy, 2007)

Mineral	Specific susceptibility (10^{-8} m ³ /kg)	Mineral	Specific susceptibility (10^{-8} m ³ /kg)
Calcite	-0.3 to -1.4	Pyrrhotite	10 to 30 000
Quartz, Feldspar, Magnetite	-0.5 to -0.6	Hematite	10 to 760
Kaolinite	-2	Ilmenite	46 to 80 000
Halite, Gypsum, Anhydride	-0.5 to -2.0	Magnetite	20 000 to 110 000
Serpentine	120 to 2 900	Dolomite	-1 to -41
Illite, Montmorillonite	5 to 13	Sandstones, Shales, Limestone	0 to 1 200
Biotite	5 to 52	Serpentine	110 to 630
Geothite	26 to 280	Clay	10 to 15
Chalcopyrite	0.6 to 10	Coal	1.9
Pyrite	1 to 100		

In the magnetic separator, material is passed through the field of a nonhomogeneous electromagnet which causes the retention or retardation of the magnetic constituent. This process leads to preferential retention or deflection of the magnetizable particles (Richardson *et al.*, 2002). Separating one material from another or removing magnetizable particles from streams depends upon their motion in response to the magnetic force and other competing external forces, namely gravitational, inertial, hydrodynamic, and centrifugal forces (Svoboda, 2005). **Figure 4.3** shows how the interparticle forces of electromagnetic and electrostatic origin contribute to the overall scenario.

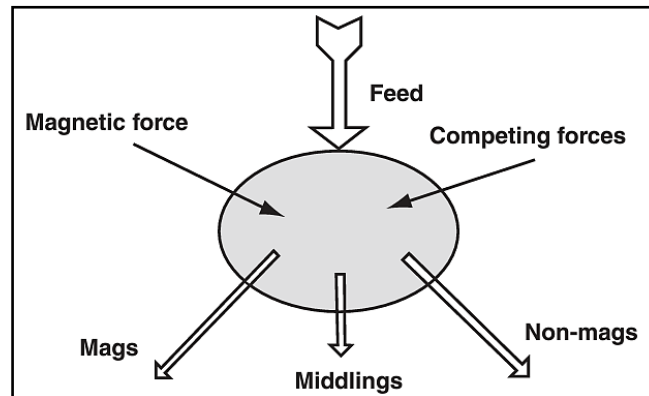


Figure 4.3: Schematic representation of the magnetic separation process (Svoboda, 2004)

The force acting between two magnetic poles (attractive or repulsive) can be accounted for by **Equation 4.1**.

$$P = \frac{km_1m_2}{r^2} \quad \text{Equation 4.1}$$

where m_1 and m_2 denote the pole strength, r represents the distance between the two poles, and k is the constant of proportionality. k can be expressed as $\mu = 1/k$, where μ is the medium's permeability (Das and Roy 2007). The University of the Free State Electronics Department provided a custom-made power supply to separate the samples into magnetic and non-magnetic portions in this study.

4.3.2 Density separation

Density separation involves separating or concentrating minerals based on their density differences to concentrate valuable portions of minerals and discarding unwanted gangue material. It helps improve the efficiency of mineral extraction processes by reducing the amount of material that needs further processing and the amount of chemicals needed for the dissolution and separation of the elements in question. There are several techniques of separation based on density properties that can be used when the density of the target minerals differs from the gangue.

Density medium separation is a common method for ore pre-concentration, rejecting waste material of coarse particle sizes. It involves immersing the ore in a dense medium, where minerals with higher

density sink and are trapped, while lighter minerals float. Gravity separation is another technique in which the ore is subjected to gravitational forces to separate minerals based on their density differences. It is effective in separating minerals with significant density contrasts.

Gravity concentration on inclined planes is carried out on shaking tables (Wilfley or Gemini), which can be smoothed or grooved, and which are vibrated back and forth at right angles to the flow of water. As the pulp flows down the incline, the ground material is stratified into heavy and light layers in the water; in addition, under the influence of the vibration, the particles are separated in the impact direction. Shaking tables are often used to concentrate finely grained tin, tungsten, niobium, and tantalum (Pryor, 2012). This is the technique that was used in this investigation to test the efficiency of density separation in both the mineral ore and the tailing samples.

Shaking tables are tables that have a rectangular shape and are equipped with ribbed decks. These decks have a moving water film on them. The feed sample is slurred by the water running parallel to the long axis of the table. Low-density particles are carried by the rapidly flowing film, resulting in the deposition of fine, high-density particles in the beds located downstream. Due to the swift backward movement of the table, the particles acquire a forward motion because of momentum, causing each structure to be separated from the others. The separation efficiency on shaking tables is directly correlated with the distribution of particle sizes and densities. Therefore, the narrower the material's grain size, the better the separation performance. Wilfley and Gemini-type shaking tables appear with different models in the recovery of precious metals, in gold mines, and in electronic waste recycling processes (RecyclingInside, 2022). An example of such a shaking table is shown in **Figure 4.4**.

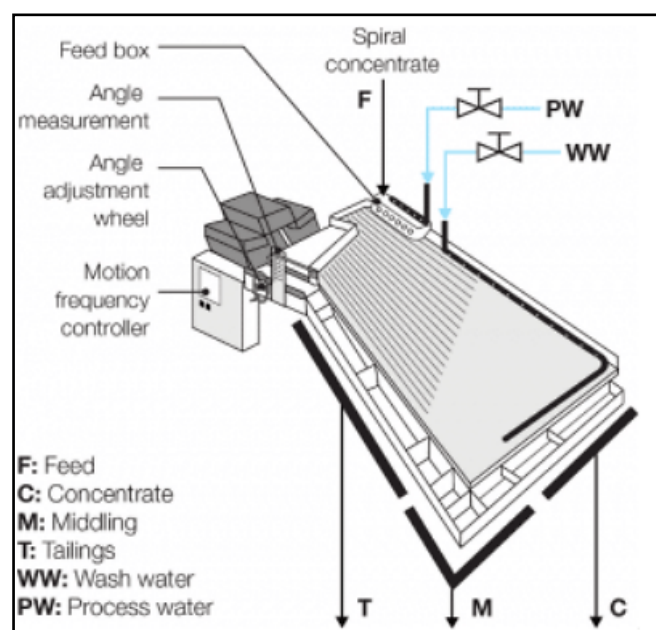


Figure 4.4: Schematic diagram of a Wilfley table (RecyclingInside, 2022)

Spiral concentrators are gravity-based devices used for the efficient concentration of low-grade ores and industrial mineral slurries. Utilizing differences in particle density and hydrodynamic behavior, these systems can process granular materials ranging from 1 mm to 0.0757 μm . Their multi-spiral design enhances throughput, making them particularly effective in the separation of heavy minerals such as zircon, monazite, and rutile from sand deposits. Cyclone separators employ centrifugal forces to achieve the classification or separation of particles based on size and density. Through the induction of a swirling flow, these devices efficiently segregate heavier particulates from lighter ones or from carrier fluids, thereby enhancing material separation **Figure 4.5** shows the spiral and cyclone separators.

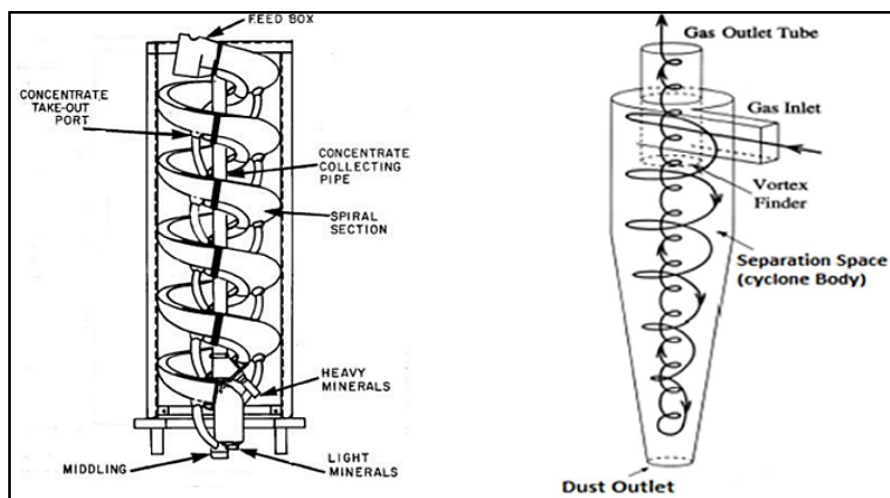


Figure 4.5: Schematic diagrams of a spiral (Humphrey) and a cyclone separator (Ketut, 2017; Mahran, 2015)

4.4 Solid-state sample characterisation

After a sample has been homogenised, as well as when it has been physically separated, it is important to perform geochemical and mineralogical characterisation to ascertain its composition. This can be done to help determine the starting point, which can be used as a reference point for all the following analyses in the study. This information is also critical because it gives insight into how to subsequently leach, dissolve, and isolate the mineral containing the target element. XRD, SEM/EDS, and XRF are examples of techniques that can be used. These techniques can also be used to semi-quantify the elements present before dissolution and even after physical beneficiation methods.

4.4.1 X-Ray Diffraction (XRD)

The X-ray diffraction method offers precise information on crystalline substances' atomic and molecular structure (Harris and White, 2015). Not only may the mineral species be identified, but the mineral substance can also be determined semi-quantitatively. The material's atoms scatter a

monochromatic X-ray beam travelling through a mineral grain. The scattered X-rays are in phase at specified angles of incidence, resulting in an amplified secondary beam. This is referred to as diffraction. W. L. Bragg discovered that diffraction could be represented as a reflection of X-ray beams by planes of atoms. Diffraction occurs when the distance travelled by one scattered beam differs from that travelled by another beam dispersed by an adjacent plane of atoms by a length equal to the X-ray wavelength. A first-order reflection is the name given to this diffracted beam. When the difference in distance travelled by X-rays dispersed from two adjacent layers of atoms equals two wavelengths, diffraction occurs. The resulting beam is referred to as a second-order reflection. Higher-order reflections occur when the path difference is a whole-number multiple of the wavelength (Epp, 2016). The Bragg equation expresses the general relationship in **Equation 4.2**, and **Figure 4.6** shows the pictorial representation of the law.

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

Equation 4.2

where n = a whole number, λ = the X-ray wavelength, d = the distance between planes of atoms, and θ = the angle of incidence. Powder diffractometry is the most often used method for studying sedimentary materials. It determines the particle size of a material, the degree of texture, and the unit cell dimensions. The diffractometer is used after the material has been pulverised into a fine powder (1-50 μm). As the sample spins along an axis normal to the primary beam, the direction of the primary X-ray beam stays constant. Diffracted beams arriving at the detection tube connected to a goniometer are recorded as peaks on a strip chart (Lindholm, 1987). **Figure 4.7** shows an example of a spectrogram of an ilmenite sample. In this study, the Panalytical Empyrean X-ray Diffractometer instrument was used. Analytical parameters are described in Chapter 5 (Section 5.4.2).

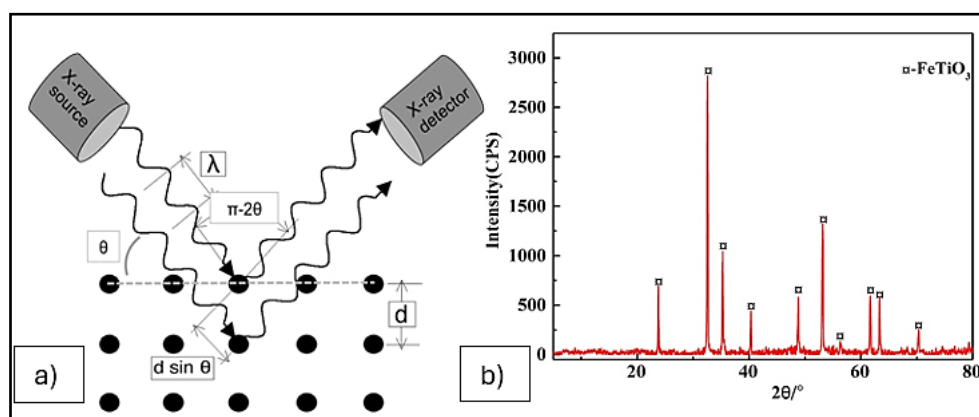


Figure 4.6a: Bragg's Law (JoVE, 2023), b: Spectrogram of an ilmenite sample (Cai et al., 2020)

4.4.2 Scanning Electron Microscope- Energy Dispersive X-ray Spectroscopy (SEM/EDS)

This non-destructive solid-state surface technique is used to analyze solid materials and chemical elements. During sample preparation, sputter coating of non-conducting materials using an electro-conductive thin film such as carbon, gold, graphite, iridium, or platinum is carried out (Balazsy and Eastop, 2011). During SEM analysis, the backscattered electrons provide information about the elemental composition, which is based on the atomic numbers and distribution of different elements within the sample, as well as a pictogram or image of the small particles. Energy Dispersive Spectroscopy (EDS) enables the identification of the elements and their relative concentrations.

SEM analysis involves a highly energetic and focused primary electron beam that scans the sample in a quick scan pattern, producing diverse effects (secondary electrons, back-scattered electrons, X-rays, photons, Auger electrons) due to the interaction between the electrons in the sample and the electrons from the beam as shown in **Figure 4.7**. The secondary and backscattered electrons are used for imaging, while the X-rays give characteristic chemical information of the emitting atoms. The targeted section of the sample will excite and remove electrons in the inner shell or core orbitals of the various elements in the sample. This causes an electron hole in the element's core orbitals, but the holes are filled by a cascade of electrons from the high or outer energy shells. During the cascading of the electrons from the higher and lower shells, energy is released in the form of X-rays, which are unique for all the elements of the periodic table (Ezzahmouly *et al.*, 2019).

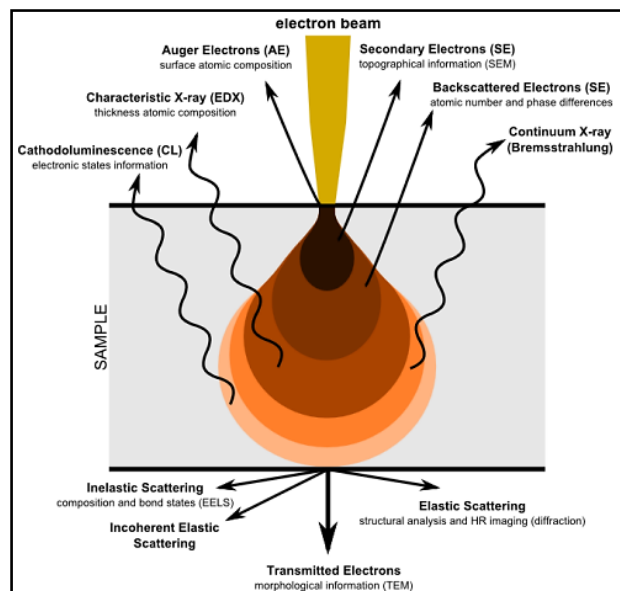


Figure 4.7: Electron beam and sample interaction (Ezzahmouly, 2019)

SEM-EDS provides qualitative and semi-quantitative information about the analyzed sample, but exceptions occur with samples containing lighter elements, such as H, He, and Li. (Skoog *et al.*, 2016). An EDS system comprises three parts: an X-ray detector, a pulse processor, and a computer system.

The X-rays are produced when the sample is excited, generating a small current that is then translated into a voltage pulse. This pulse is proportional to the energy of the entering X-rays and is amplified to reflect the measured X-ray energy. This enables the computer system to translate the voltage pulses into signals, allowing it to generate qualitative data from the elements in the sample. This study used a Jeol JSM 6610 Scanning Electron Microscope instrument. The machine is equipped for secondary electron imaging and backscatter electron analysis with Wavelength dispersive spectroscopy (WDS) (Thermofisher MagnaRay) and EDS (JED-2300 EDS) detectors. Analytical parameters are described in **Chapter 5 (Section 5.4.3)**.

4.4.3 X-ray fluorescence (XRF)

This is a non-destructive analytical technique used to determine a mineral's elemental composition, qualitatively and quantitatively, at room temperature. When excited, most elements on the periodic table produce a unique set of fluorescent X-rays; therefore, XRF utilises this concept by analyzing and quantifying the fluorescent X-rays emitted upon excitation by a primary X-ray source. The sample is raster-scanned with a monochromatic X-ray beam, which impacts electrons and emits secondary (fluorescent) X-rays. One or more electrons are ejected, and tightly held electrons from the inner orbitals of atoms are expelled, resulting in an unstable electronic structure that is stabilized by the falling of electrons from higher orbitals, thereby releasing energy (lower than the initial energy) as a photon. The detector collects the X-ray fluorescence emission spectrum (high energy absorbed results in lower energy emission) (JoVE, 2023). The collision of X-rays with atoms can result in the removal of electrons from various shells, leaving vacant positions behind. These vacancies are subsequently filled by electrons from higher energy shells, and the excess energy of these electrons is emitted as secondary X-ray fluorescence radiation, as shown in **Figure 4.8**. In this study, a Rigaku Primus IV WD XRF instrument was used. Analytical parameters and reference materials are described in **Chapter 5 (Section 5.4.4)**.

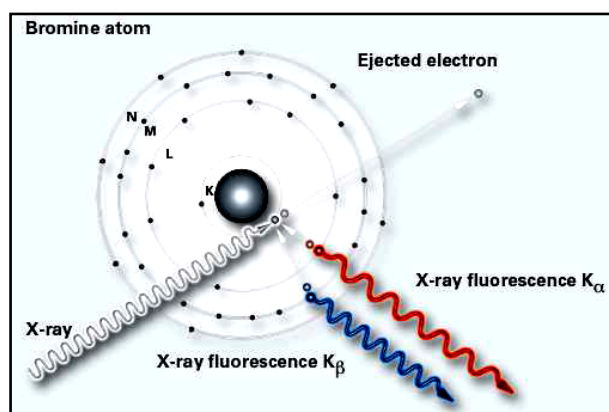


Figure 4.8: XRF interaction (Theremino, 2023)

4.4.4 Non-destructive techniques pros and cons

These nondestructive analytical techniques each have several pros and cons, which are listed in **Table 4.2**. In research, it is common to combine multiple techniques to gain a comprehensive understanding of mineral samples, using the complementary nature of these techniques to characterize the minerals thoroughly.

Table 4.2: Advantages and disadvantages of non-destructive analytical techniques (Ali *et al.*, 2023; Brocchieri *et al.*, 2023; Hamdan *et al.*, 2020).

Technique	Advantages	Disadvantages
XRD	Provides detailed information on mineral crystal structure and composition A non-destructive technique that can analyze powdered samples without altering their chemical composition Can identify minerals present in a sample based on their diffraction patterns Quantitative analysis of mineral phases in a mixture is possible Provides detailed information on mineral crystal structure and composition	Requires finely ground samples for analysis, which may not always be practical Limited to crystalline materials, so amorphous phases may not be detected Cannot provide information on elemental composition or spatial distribution within a sample Relatively time-consuming compared to some other techniques May require expertise to interpret complex diffraction patterns accurately
SEM/EDS	Provides high-resolution images of mineral surfaces and microstructures Allows elemental analysis using Energy-Dispersive X-ray Spectroscopy (EDS) within the same instrument. Can visualize features at the micron to nanometre scale Helpful in studying textures, grain boundaries, and mineral associations	Requires sample preparation, including coating with a conductive material in some cases Imaging depth is limited, so it may not reveal information about the internal structure of a sample Qualitative elemental analysis with EDS may have limitations in accuracy compared to other techniques SEM is primarily a surface-sensitive technique and may not provide information on subsurface structures
XRF	Rapid elemental analysis of major and trace elements in a sample A non-destructive technique suitable for analyzing solid, liquid, and powdered samples. Can quantify a wide range of elements simultaneously	Limited to elemental analysis and does not provide mineralogical information May require calibration using standards for accurate quantification. Detection limits for certain elements may be higher compared to other techniques like ICP-MS

High sensitivity for elements from sodium (Na) to uranium (U)

Used for geochemical analysis, mining exploration, and quality control in mineral processing

XRF analysis is surface-sensitive and may not represent the bulk composition of a sample accurately

XRF instruments can be expensive and require regular maintenance

4.5 Geochemical Analysis

4.5.1 Sequential extraction

This destructive method sequentially extracts metals from a sample, typically soil, sediment, or solid waste, based on their chemical forms and associations with different mineral phases. It is used to identify the composition of valuable elements by adding different solvents to different sample fractions. Each fraction is related to a distinct mineral phase or form (Silveira *et al.*, 2006). Different extracting agents are used in each extraction step to target specific metal species bound to different phases in the sample. These extractants are chosen based on their ability to selectively dissolve certain metal forms while leaving others intact. These extractants and conditions are fully described in **Chapter 5**. Sequential extraction schemes, although generally time-consuming, give detailed information about the origin, mode of occurrence, mobility, and biological and physicochemical availability of the trace elements in solid samples. They have been proven to be a convenient method for identifying the trace elements associated with primary accumulation phases in soils and sediments (Du Laing, 2010).

The sample undergoes a series of extraction steps, each targeting a specific metal fraction. These steps are usually designed to extract metals associated with exchangeable ions, carbonates, oxides, organic matter, sulphides, and residual phases in a sequential manner. The pH, reagent concentrations, extraction times, and temperatures are carefully controlled in each extraction step to ensure optimal dissolution of the targeted metal forms. Adjusting these chemical conditions can influence the selectivity and efficiency of metal extraction. The choice of the type of extractant is strictly correlated with i) the nature of the metal, ii) the chemical form of the metal, iii) the matrix from which the compounds are to be extracted, and iv) the analytical techniques available in the laboratory for the final determination. The extracted fractions are analyzed for metal content using analytical techniques such as atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectroscopy (ICP-OES) and/or inductively coupled plasma mass spectrometry (ICP-MS). These analyses help quantify the distribution of metals among different fractions. Sequential extraction results are interpreted to understand the speciation and mobility of metals in the sample. Information

obtained from sequential extraction is used to optimize mineral processing strategies, specifically to determine which acids to use for dissolving the minerals.

Several schemes can be employed in sequential extractions, differing slightly in the conditions used. These are Tessier, BCR, and Modified BCR, among others. Modified BCR was chosen to dissolve both the mineral ore and the tailing samples in this study. In all schemes, extractants are applied in order of increasing reactivity so that the successive fractions obtained correspond to metal association forms with lesser mobility, as shown in **Figure 4.9**. The extractants more commonly used in sequential extraction schemes generally fall within the following groups: unbuffered salts, weak acids, reducing agents, oxidizing agents, and strong acids (Filgueiras *et al.*, 2022).

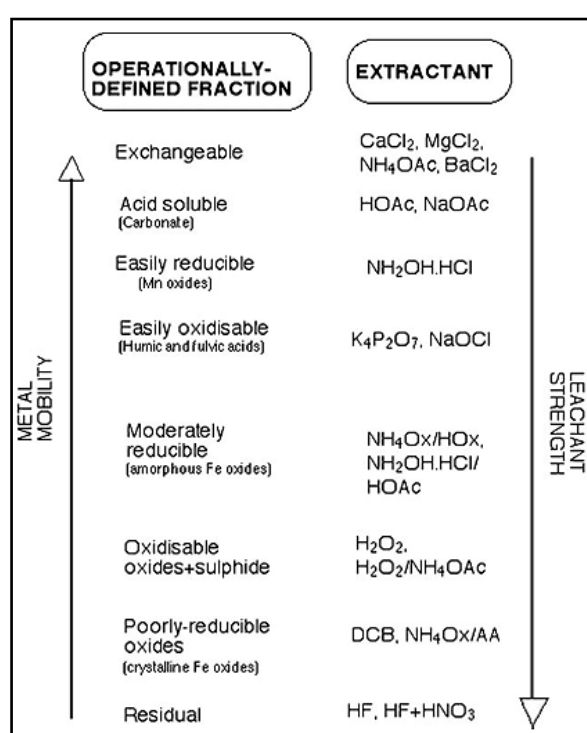


Figure 4.9: Relationship between metal mobility in the different operationally defined phases and leachant strength of common chemical reagents used for sequential extraction (Filgueiras, 2022)

The exchangeable fraction includes weakly adsorbed elements retained on the solid surface by relatively weak electrostatic interactions, elements released by ion-exchange processes, and elements co-precipitated with carbonates. The acid-soluble fraction primarily aims to contain trace elements associated with carbonates, rather than those associated with Fe/Mn oxides and organic matter. Acetic acid (buffered to pH 3-3.5 or 5) and Na_2EDTA (pH 4.6) are often used. Metals occurring in the oxidizable fraction are assumed to be bound mainly to organic matter and easily released under oxidizing conditions. As an oxidation process is usually applied to leach them, metals precipitated as sulphides or bound to sulphides are also part of this fraction. H_2O_2 in an acidic medium, NaOCl at pH

9.5, $\text{Na}_4\text{P}_2\text{O}_7$ at pH 9.5, and $\text{K}_4\text{P}_2\text{O}_7$, and a hydrogen peroxide/ammonium acetate ($\text{H}_2\text{O}_2/\text{NH}_4\text{OAc}$) mixture are the most used oxidants. The residual fraction mainly contains silicate/crystalline-bound trace elements. It is most dissolved with concentrated acids to leach all remaining trace elements, which can be assumed to be unavailable under normal environmental conditions. Strong acids such as HF or aqua regia (a mixture of HCl and HNO_3) are commonly used (Du Laing, 2010).

4.6 Sample dissolution

Samples are digested after physical characterization. This can be done using flux fusion, microwave digestion, and acid/bases to convert the solid ore or tailings into a solution that can be analysed using analytical techniques such as ICP-OES/MS. Complete dissolution is crucial to ensure that the elements in the samples are accurately quantified and to track the elements during separation steps, as well as to determine the percentage recovery of the target element after isolation. Sample preparation is a critical step in geochemical analysis, and complete sample dissolution is a prerequisite for obtaining accurate and precise data for geological materials in most studies. The sample matrix, analytes of interest to be analyzed, separated, or isolated, the analytical technique, and the intended purpose of the dissolved sample (in subsequent steps) all play a significant role in selecting the optimum sample preparation. It is also worth noting that different dissolution techniques have advantages and disadvantages. Therefore, the chosen method should have pros that outweigh its cons.

Acid/base dissolution is not always as effective in completely dissolving the samples. However, it can selectively leach elements into solution by dissolving certain minerals containing the element of interest or removing large amounts of impurities to leave the target elements in the solid sample, which can be dissolved using another technique. Reducing or oxidizing agents can be added to improve the process. **Table 4.3** shows the most common reducing and oxidizing reagents used in sample dissolution and their properties. These are vital in enhancing the efficiency of mineral extraction processes, enabling the recovery of metals and other valuable resources from ores.

Table 4.3: Common reducing and oxidizing reagents used in sample dissolution

Reducing and oxidizing reagents	Common uses
Hydrogen peroxide	Oxidizes sulphides, enhancing metal leaching
Nitric acid	Oxidative dissolution of metals from ores
Sodium metabisulphite	Reducing metal ions, leaching precious metals
Hydroxylamine NH_2OH	Reducing Fe^{3+}

Acid digestion is more popular for decomposing geological materials because it is a straightforward and reasonably practical methodology. Most of the wet digestion methods used in geochemical

analysis use acids such as HCl, HNO₃, HClO₄, H₂SO₄, and HF, or a combination of them. **Table 4.4** shows the acids and bases used and their properties and effectiveness towards different minerals. HF becomes inevitable in samples containing silica decompositions due to its unique ability to dissolve silica and other silicates. An advantage of using acids to digest samples is that it does not add extra inorganic salts (especially alkali and earth alkali salts), which can complicate subsequent chemical analysis due to line overlaps, etc. Aqua regia also has its limitations in dissolving specific natural samples or minerals such as barite, chromite, gahnite, cassiterite, ilmenite, rutile, sphene, monazite, zircon, and garnet and it is always necessary to prepare aqua regia fresh just before its use to realize its full potential (Balaram and Subramanyam, 2022).

Table 4.4: Acids typically used in sample digestion (MARLAP, 2004; Kenkel, 2002)

Acid/Base	Typical uses
H ₂ SO ₄	Dissolves oxides, hydroxides, carbonates, and various sulphide ores; hot concentrated acid will oxidize most organic compounds
H ₃ PO ₄	Dissolves Al ₂ O ₃ , chrome ores, iron oxide ores, and slag
HNO ₃	Oxidizes many metals and alloys to soluble nitrates; organic material oxidizes slowly
HClO ₄	Extremely strong oxidizer; reacts violently or explosively to oxidize organic compounds; attacks nearly all metals
HF	Removal of silicon and destruction of silicates; dissolves oxides of Nb, Ta, Ti, and Zr, Nb, and Ta ores
HCl	Dissolves many carbonates, oxides, hydroxides, phosphates, borates, and sulphides; dissolves cement
HBr	Distillation of bromides (e.g., As, Sb, Sn, Se)
HI	Effective reducing agent; dissolves Sn ⁴⁺ oxide and Hg ²⁺ sulphide

Flux fusion digestion melts the mineral at elevated temperatures in a furnace in the presence of an inorganic salt at a temperature higher than the melting point of the salt. A combination of salts can also be used. High-temperature-resistant crucibles are crucial for reducing the interaction of the crucible particles with the reactants. The high temperatures help dissolve the salt and the sample, allowing them to interact. In contrast, small portions of the pulverized sample will significantly increase the surface area, thereby accelerating the reaction. A predetermined sample-to-flux salt ratio is another important factor to consider; typically, a 1:10 ratio is used. Reaction times are usually in the range from 20 minutes to 2 hours, after which the melt is cooled, dissolved in water or a dilute acid, and analyzed using ICP-MS/OES. The solution should be prepared according to the instrument's

analysis conditions. Lithium metaborate was chosen for this study because it is recommended for use with titanium dioxide. **Table 4.5** shows common flux conditions that can be used.

Table 4.5: Fusion fluxes commonly employed in geochemical analysis during sample preparation (Balaram and Subramanyam, 2022)

Flux (mp, °C)	Fusion temperature, °C	Types of crucibles	Types of samples decomposed
Na ₂ S ₂ O ₇ (403) or K ₂ S ₂ O ₇ (419)	Up to red heat	Pt, quartz, porcelain	For insoluble oxides and oxide-containing samples, particularly those of Al, Be, Ta, Ti, Zr, and the REE
NaOH (321) or KOH (404)	450-600	Ni, Ag, glassy carbon	For silicates, oxides, phosphates, and fluorides Na ₂ CO ₃ (853 °C) or K ₂ CO ₃ (903 °C) 900-1000 °C Ni, Pt for short periods (use a lid) For silicates and silica-containing samples (clays, minerals, rocks, glasses), refractory oxides, quartz, and insoluble phosphates and sulphates
Na ₂ O ₂	600	Ni, Ag, Au, Zr, Pt (<500°)	For sulphides, acid-insoluble alloys of Fe, Ni, Cr, Mo, W, and Li; Pt alloys; Cr, Sn, and Zn minerals
H ₃ BO ₃	250	Pt	H ₃ BO ₃ 250 °C Pt For analysis of sand, aluminium silicates, titanite, natural aluminium oxide (corundum), and enamels
Na ₂ B ₄ O ₇	(878) 1000-1200	Pt	For Al ₂ O ₃ , ZrO ₂ , and zirconium ores, minerals of REE, Ti, Nb, and Ta, aluminium-containing materials, iron ores and slags
Li ₂ B ₄ O ₇ (920) or LiBO ₂ (845)	1000-1100	Pt, graphite	For almost anything except metals and sulphides. The tetra borate salt is especially good for basic oxides such as silica and TiO ₂ and nearly all minerals
NH ₄ HF ₂ (125), NaF (992) or KHF ₂ (239)	900°	Pt	For the removal of silicon, the destruction of silicates and REE minerals, and the analysis of oxides of Nb, Ta, Ti, and Zr

Microwave digestion is also an important digestion method. Geological materials often contain refractory minerals resistant to acid treatment at standard temperature (20 °C) and pressure (1 atm). As a result, open acid digestions are often unable to deliver 100 % efficient digestions and take long hours to complete. Microwave energy has been used as a heat source for sample decomposition in chemical laboratories for over 30 years. Microwaves are a form of electromagnetic radiation with wavelengths ranging from one meter to one millimetre, with frequencies between 300 MHz (100 cm) and 300 GHz (0.1 cm). Microwave digestion utilises electromagnetic radiation with a frequency of 2.45 GHz to generate heat, thereby enhancing the chemical reaction and facilitating the complete decomposition of the sample. Microwaves promote the rotation of specific molecules in a reaction

mixture. This rotation results in increased molecular collisions and the generation of heat. The polar reaction mixtures (mixture of acids) have the physical capability to interact with microwaves. They generate heat as liquids rapidly absorb microwave energy and microwaves couple with reaction mixture molecules. The pressurized dissolution technique in PTFE-lined vessels is the most promising procedure (Tan *et al.*, 2021). Microwave-assisted pressure digestions at elevated temperatures offered significant advances in geochemical analysis (Srogi, 2007). An Anton Paar microwave reaction system model, Multiwave Pro, was used in this study. The conditions set up for the dissolution of the samples are detailed in **Chapter 5 (Section 5.5.2)**.

4.7 Elemental quantification

The next step in the hydrometallurgical process is quantifying the target element and impurities in the dissolved samples. These results, along with those obtained through solid-state analysis, serve as the baseline for the target element present in the sample before separation and isolation are performed. Inductively Coupled Plasma Optical Emission Spectrophotometry is commonly used to quantify the different elements in the sample matrix accurately, and it was extensively used in this study.

4.7.1 Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES)

The theory behind the use of spectroscopy for chemical or elemental analysis is based on activating the valence electrons in elements to higher empty orbitals and the subsequent release of the absorbed energy in the form of a photon. The effectiveness of this approach stems from the fact that the valence orbital energy levels of each element differ significantly from one another, as well as the subsequently generated photons that are emitted, creating a “fingerprint profile” for each element. This enables the quick identification of most elements in the mineral matrix and their simultaneous quantification when the appropriate calibration standards are utilised.

An ICP consists of an autosampler, responsible for the aqueous sample's uptake, and a peristaltic pump, which transports the sample to the nebulizer and then the spray chamber. The sample is then transported to a torch and delivered to the plasma at temperatures between 5 500 and 10 000 °C. During this process, argon fulfills the roles of carrier and plasma gas. Once the aqueous solution reaches plasma, which is an electron-rich, high-temperature region, the metal ions are converted to gaseous metal atoms. The electrons in the valence orbitals are momentarily excited from their ground state to vacant, higher-energy levels at these high temperatures. The excited electrons return very quickly to their ground state, and the absorbed energy is released as a set of unique photons, which are used for identification and quantification (Whiteman, 2023). Elemental quantitative analysis is possible since the number of excited photons produced at a given wavelength is directly proportional

to the concentrations of all the elements in the sample solution. **Figure 4.10** represents the sample introduction to the acquired data response of the ICP-OES.

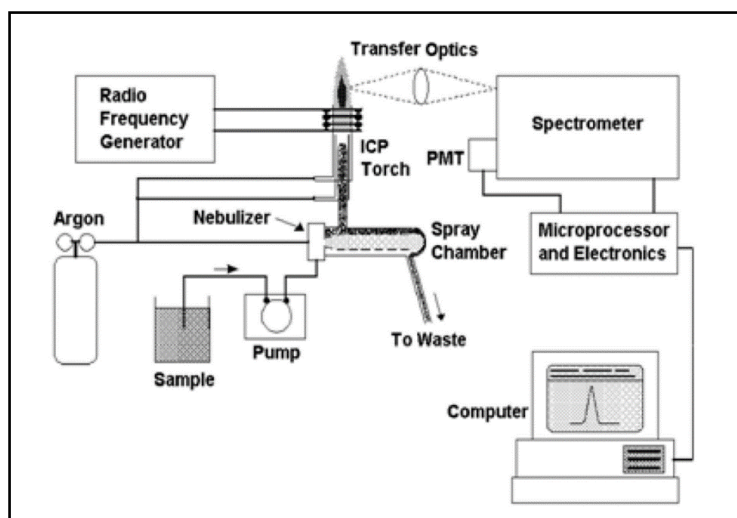


Figure 4.10: Schematic illustration of the ICP-OES sample introduction to results obtained (Oettmeier, 2007).

These techniques were selected based on the detection limits that the different spectrophotometric techniques allow. A Prodigy 7 ICP-OES was used in multi-element investigations, as well as those that had small elemental concentrations. The analytical parameters and standards preparation are described in detail in **Chapter 5 (Section 5.5)**.

4.8 Conclusion

SEM/EDS, XRF, and XRD are non-destructive analytical techniques that can be used to characterize different kinds of solid samples. These were all used in this study to characterize the mineral and tailing samples investigated. Complete dissolution with flux fusion using fluxes such as lithium metaborate produces aqueous samples that allow for the total chemical characterization of the samples in question. ICP quantification allows for the total and accurate quantification of major to trace elements in samples. The studies reviewed in **Chapter 3** mainly used ICP-OES for elemental quantification of titanium as well as other elements, which are considered impurities in this study. Density and magnetic separation are also used to concentrate the element of interest based on differences in density and magnetic susceptibility.

Chapter 5: Results and discussion - Characterisation of the samples

5.1 Introduction

Mineral processing requires accurate characterization and determination of the mineral and elemental composition of the natural or anthropogenic material that will be processed. This includes the elemental composition, the possible oxidation states of the element of interest and other impurities, minerals hosting the element/s of interest, and the gangue minerals that may interfere in the beneficiation process. The information obtained in the characterization processes will be used as a baseline for subsequent decision-making to assist in selecting the separation and isolation methods of the beneficiation process. Qualitative and quantitative analytical techniques described in Chapter 4 are used to obtain the necessary information about the investigated samples at this stage of the investigation. XRD, SEM-EDS, XRF, and ICP-OES/MS are the techniques employed to provide information on the mineral and elemental composition of the samples.

Chemical characterization using ICP instruments is an important step, as it precisely quantifies the elements present. It is used throughout the beneficiation processes to determine not only the initial concentration of the elements but also the amount present after any beneficiation step that was investigated, indicating the yield or efficiency of the concentration or isolation of the target element. It either requires the complete dissolution of the sample, the selective leaching of the target element, or the removal of major amounts of impurities to render a purified sample containing the target element. This is done using flux fusion, microwave, and acid digestion (**Chapter 4**). Flux fusion was chosen as the best method to use in this study, as it proved to be highly successful in dissolving the samples and producing less harmful waste products.

This chapter aligns with the study's objective of performing physical and chemical characterization of mineral ore and the mine tailings. SEM-EDS, XRD, and XRF characterized the mineralogy and geochemistry of the samples, while total digestion and sequential extraction were the wet /destructive chemical techniques used during this investigation. As described in this chapter, the elemental quantification of total digestion and sequential extractions was performed with ICP-OES instruments.

5.2 Reagents and equipment

The chemicals and reagents used in this study are listed in **Table 5.1**, indicating their purity and the supplier. An electronic balance was used to weigh all samples to 0.1 mg accurately at room temperature. All the sample solutions prepared in this study were quantitatively transferred to analytical equipment using a Brand Transferettes type (1.00 mL and 10.0 mL) or Lasec micro-pipettes

(100 µL-1000 µL). Schott Duran grade A beakers and volumetric flasks (100.0, 200.0, 250.0, and 500.0 mL) were used during sample preparation and quantification. All the glassware that was used in this study was cleaned by soaking it in 10 % HNO₃ (10.0 mL) for 24 hours, followed by thorough rinsing with ultra-pure water (zero total dissolved solids, TDS) before use. The ultra-pure water was produced using a custom-made water purification system made by the Electronics Department of the University of the Free State. Samples were appropriately diluted for ICP-OES analyses to avoid clogging the instrument and to remain within the standard range. This was done by transferring 1.0 mL of the filtered reaction solution into 50.0 mL or 100.0 mL volumetric flasks and diluting to the mark using ultra-pure water.

Table 5.1: Chemicals used to conduct experiments

Chemical	Formula	Purity	Supplier
Nitric acid	HNO ₃	65 %	Merck
Hydrochloric acid	HCl	32 %	Merck
Sulphuric acid	H ₂ SO ₄	98 %	Sigma-Aldrich
Acetic acid	CH ₃ COOH	96 %	Merck
Hydroxylamine hydrochloride	NH ₂ OH.HCl	99 %	Sigma-Aldrich
Hydrogen peroxide	H ₂ O ₂	100 v/v	Sigma Aldrich
Ammonium acetate	NH ₄ C ₂ H ₃ O ₂	> 97 %	Merck
Titanium standard	Ti	2 % HNO ₃ /HF	Merck
Vanadium standard	NH ₄ VO ₃	5 % HNO ₃	Ultraspec
Silicon standard	Si	HNO ₃ /HF	Merck
Multi-element standard	Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl and Zn	HNO ₃	Merck
Lithium metaborate	LiBO ₂	> 98 %	Sigma -Aldrich
Ammonium sulphate	(NH ₄) ₂ SO ₄	99 %	Merck
Sodium sulphate	Na ₂ SO ₄	99 %	Riedel-de Haën

5.3 Sample information

Two different types of samples were investigated: vanadium-bearing titanomagnetite (VBT) ore and a vanadium tailing sample. The samples were obtained from Bushveld Minerals' Rhovan and Vametco operations. The Rhovan operations are approximately 35 km northeast of Rustenburg, while the Vametco mine is located about 7 km northeast of Madibeng (formerly called Brits).

The original ore (the VBT samples) was processed through crushing, grinding, and magnetic separation to obtain a magnetic concentrate, which was then roasted with NaOH in a kiln to produce water-

soluble sodium vanadate. This sodium vanadate was subsequently leached with ammonia to produce a V and Si rich solution. The solution was further processed for vanadium beneficiation, while the undissolved portion of the processed mineral was discarded as waste to the tailing dumps that are part of the investigation (Bushveld Minerals, 2024). Initially, as described in **Chapter 1, Section 1.4**, this study aimed to use these tailings to obtain the remaining valuable Ti still present in the tailings using simple hydrometallurgy techniques. The VBT ore was also included in the study because it contained significant amounts of Ti, which was not of interest to Rhovan and Vametco. Well-sought-after Ti sources such as rutile are slowly being depleted, and therefore, alternative sources of Ti are needed, as discussed in **Chapter 2**. This newly developed hydrometallurgical method may also be an alternative for processing lower titanium grade samples, since the industrial processes available are mainly for high-grade titanium ores such as rutile.

The reprocessing of tailings contributes to sustainable mining practices, which minimize the need for new ore extraction and lower the demand for land, water, and energy. It also assists in maximizing resource recovery, minimizing environmental impact, and improving waste management. Utilizing tailings as a secondary resource can reduce costs associated with mining new materials, as the infrastructure and land are already in place. These efforts contribute to more sustainable mining practices and the responsible use of natural resources, benefiting the industry and society.

The VBT ore samples received for this study consisted of particles of about 3 cm in diameter, which were subsequently ground into particles of <53-500 μm (**Section 5.4.3**). The tailing samples were used as received, but they were dried in the oven for 24 hours at 100 °C before any analysis. Manual homogenization was performed on the samples using a sample splitter as shown in **Chapter 4, Section 4.2**. Particle size distribution was also performed on both samples.

5.3.1 VBT ore

VBT ore consisted of rock fragments, as shown in **Figure 5.1a**, and was milled down to a grey abrasive mixture of medium to very fine sand (**Figure 5.1b**). Most of the particles in the sample used in the study were in the 500-106 μm particle size range, as reported in **Section 5.9.3**. A chemical analysis (certificate composition) was done by Tennant Metals and is given in **Table 5.2**. The density of the VBT ore was measured in the lab and was found to be 3.2-3.5 g/cm^3 . The VBT ore contained less Ti than the tailings because the vanadium extraction process preferentially removed the vanadium minerals present, thereby increasing the relative abundance of Ti in the tailings.

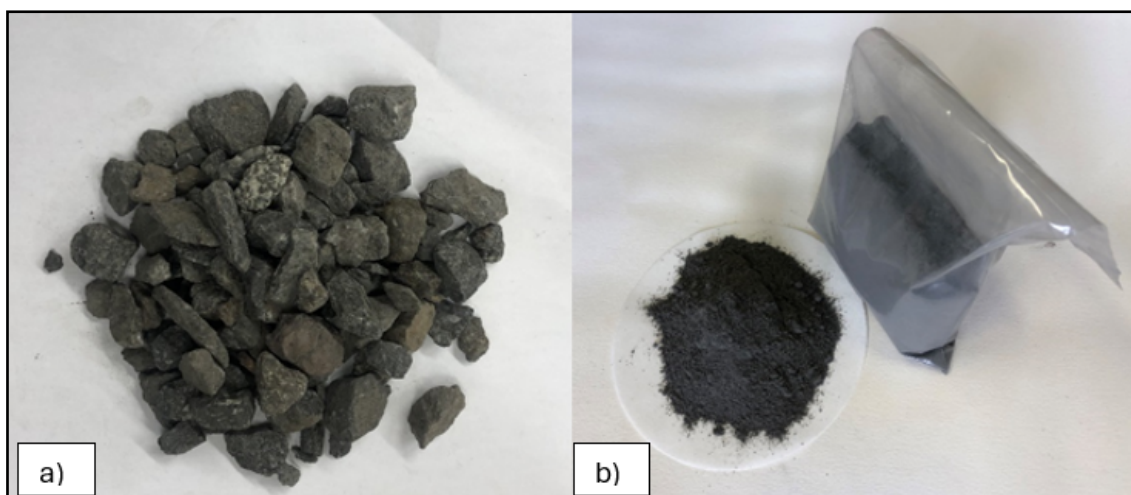


Figure 5.1: VBT ore sample raw (a) and milled (b)

Table 5.2: VBT ore certificate elemental composition (Tennant Metals, 2021)

Element/Compound	Average % composition	Element/Compound	Average % composition
TiO ₂	0.81	MgO	1.07
V ₂ O ₅	1.72	Na ₂ O	0.18
Fe	49.04	P	0.054
SiO ₂	4.12	BaO	0.022
Al ₂ O ₃	1.78	K ₂ O	0.126
Mn	0.31	S	0.092
Mn ₃ O ₄	0.434	LOI	16.05
ZnO	1.28	C	14.6
CaO	2.29		

5.3.2 Tailings

The tailings samples shown in **Figure 5.2** appear as a black mixture of fine sand and clay, and it was used in this investigation as is. According to the certificate and measurements done in the lab, the dried sample had a moisture content of 8-12 %, and its bulk density was 2.2-2.4 g/cm³. Most of the particles in the sample used in the study were in the <53-250 µm particle size range, as reported in **Section 5.10.3**.

A comparison between the two types of samples indicates that the tailings appear darker than the ground VBT ore, while the samples also differ in size. Bushveld Vametco Alloys did the elemental analysis, soluble content, and particle size of the tailings sample that came with the sample (certificate composition), which are given in **Tables 5.3-5.5**.



Figure 5.2: Tailings sample

Table 5.3: Tailings certificate elemental composition (Bushveld Vametco Alloys, 2017)

Element	Range (%)	Typical
Ti	6.5-8.5	7.5
V	0.2-0.5	0.35
Fe (total)	47-52	48.5
Fe (metallic)	<1.5	
Si	1.2-2.0	1.6
Al	2.0-2.5	2.25
Ca	0.3-0.7	0.5
Mg	0.5-1.5	1.0
Cr	0-0.3	0.2
S	-	0.5
O	balance	
pH	8-10	

Table 5.4: Certified tailings soluble content (Bushveld Vametco Alloys, 2017)

	Range (%)	Estimated average
Total Na	0.02-0.60	0.3
NaVO ₃	0.05-0.70	0.35
NaCrO ₄	0-0.03	0.015
Na ₂ SO ₄	0.03-1.4	0.7

Table 5.5: Certified tailings particle size distribution (Bushveld Vametco Alloys, 2017)

Size (μ)	Range (%)	Typical (%)
>1 000	0-1	0
>250	0-10	5
150-250	8-15	12
75-150	20-40	30
45-75	10-20	15
<45	25-40	40

5.4 Experimental procedures for geochemical and mineralogical characterization of VBT ore and tailings

5.4.1 Particle size distribution

Three sets of sieves with 500 μ m, 250 μ m, 106 μ m, 53 μ m, and <53 μ m mesh sizes were stacked onto a mechanical shaker in descending order with the largest mesh on top and the smallest at the bottom. After homogenizing the sample with a sample splitter, 5 g of a representative subsamples of the VBT ore were accurately weighed and evenly distributed into the top sieves. The sieve stacks were secured onto the mechanical shaker and shaken for 5 minutes, after which the amount of material retained in each sieve was accurately weighed. The same procedure was repeated for the tailings.

5.4.2 X-ray diffraction (XRD)

Both types of samples and their magnetic and non-magnetic portions after physical separation (**Chapter 6**) were analysed using the Panalytical Empyrean X-ray Diffractometer. The diffractometer is equipped with a copper side window tube, an anode consisting of Cu, a W cathode (filament), and an X-Celerator detector. The X-ray tube produces a $\text{CuK}_{\alpha 1}$ X-ray beam with a Bragg-Brentano geometry focus position and a theta-theta goniometer configuration. Samples were scanned between 3.5 ° and 70 ° 2 θ at tube settings of 45 kV and 40 mA. A v. 3.0c Data collector was used for data collection, and Highscore v. 3.0e software equipped with the ICDD PDF-2 database was used to evaluate the diffractograms. The analysis of the samples was performed at the Geology Department of the University of the Free State.

5.4.3 Scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS)

A Jeol JSM 6610 Scanning Electron Microscope was used in this study. The spectrometer is also equipped for secondary electron imaging and to analyze backscatter electrons using both WDS (ThermoFisher MagnaRay) and EDS (JED-2300 EDS) detectors. The accelerating voltage of the filament ranged between 0.3 and 30 kV (depending on the specific results required), but it was generally run

at 20 kV. The detection limit for the EDS capabilities is ± 100 ppm. The samples were transferred to epoxy resins, polished before analysis, and then carbon-coated. The SEM main menu program was used to run the machine, and the NSS program was used for product analysis and characterization. The analysis was done at the Geology Department at the University of the Free State.

5.4.4 X-Ray Fluorescence (XRF)

The elemental composition was characterised using the general scan function of a Rigaku Primus IV WDXRF spectrometer. The reference materials used for all calibrations were: BHVO-1, DR-N, GSP-1, JB-1, JB-2, JB-3, JG-1, JG-1A, JG-2, JG-3, JGB-1, NIM-D, NIM-G, SARM48, SARM50. Fusion discs used for major element quantification were prepared using the following method. 10 g of sample was heated to 110 °C to dehydrate and devolatilize the sample and then to 1 050 °C to produce information on the total loss on ignition (LOI) or the total gain on ignition (GOI). GOI is the result of the oxidation of all of the sample's non-oxide components during the fusion process. In contrast, after fusion, LOI results from losing all volatile components such as carbon and water (Watanabe, 2013). A flux comprising any one of the following flux salts, 0.2445 g of La_2O_3 , 0.705 g of $\text{Li}_2\text{B}_4\text{O}_7$, 0.5505 g of Li_2CO_3 , or 0.02 g of NaNO_3 , was added to 0.28 g of the sample. The mixture was heated to 950 °C for approximately 5 minutes, forming a consistent fluid within a Pt crucible. The fluid was then poured into a mould and pressed to form the disc. The Geology Department of the University of the Free State analyzed the samples.

For major elements such as SiO_2 and Al_2O_3 , the measuring conditions included the use of a pentaerythritol (PETH) crystals and proportional counter (PC) detectors, while those for the quantification of TiO_2 , Fe_2O_3 , and MnO , required a lithium fluoride ($\text{LiF}(200)$) crystal and a scintillation counter (SC) detector. CaO and K_2O quantification required a $\text{LiF}(200)$ crystal and a PC detector, MgO required an RX25 crystal and a PC detector, and P_2O_5 quantification required a GeH crystal and a PC detector. They all used a voltage of 50 kV and a tube current of 60 mA.

Na and trace element analysis were performed using pressed pellets. These pellets were prepared using 8 g of the sample, which was added to 3 g of Hoechst wax ($\text{C}_6\text{H}_8\text{O}_3\text{N}_2$) and mixed for 20 minutes in a Turbula mixer. The mixture was then compressed to above 395 N/m. The measuring conditions for Sc, V, and Ni were a PC detector, while Cr, Co, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba, Pb, Th, and U used an SC detector. They all used $\text{LiF}(200)$ crystal, 50 kV, and 60 mA. The measuring conditions for Na as a major element in a pressed pellet were RX25 crystal, PC detector, 50 kV voltage, and 60 mA tube current.

The next step in the characterization of the two samples involved more destructive techniques. These included sequential elemental extraction and total dissolution of the samples using different solvents.

5.4.5 Sequential Extraction

The extractants commonly used in BCR sequential extraction schemes generally fall within the following groups: acetic acid, reducing agents, oxidizing agents, and aqua regia. The extraction process was performed in triplicate using 0.1, 0.5, and 1 g sample sizes to avoid over-saturation. A sample splitter (riffle splitter, **Chapter 4.2, Figure 4.2**) was used to collect each subsample to ensure representative, homogeneous subsamples. The stepwise or sequential extraction process was performed as follows:

Step 1 (carbonates): 0.1, 0.5, and 1 g of dry sample were placed in a 50 mL polypropylene centrifuge tube, and 40 mL of 0.11 mol/L acetic acid solution was added. The tubes were then shaken at room temperature in a disk rotator at 40 rpm for 16 hours. The solid or undissolved residue was subsequently separated by centrifugation at 5 000 rpm for 20 minutes, and the supernatant was decanted. The solid was washed with 20 mL of distilled water at 40 rpm for 15 minutes in the rotator, and the supernatant of the washings was combined with the previous supernatant and transferred to polyethylene tubes. About 3 mL of HNO₃ was added, and the solution, **Fraction 1 (F1)**, was stored at 4 °C for further analysis.

Step 2 (Fe/Mn oxides): In the next step, the residue isolated after **Step 1** was digested in 40 mL of 0.1 mol/l hydroxylamine hydrochloride (adjusted pH ≈ 2 using HNO₃) for 16 hours. The solid or undissolved residue was subsequently separated and washed as described in step 1. The solution obtained was labelled as **Fraction 2 (F2)** and stored at 4 °C for further analysis.

Step 3 (Sulphides): The residue collected after **Step 2** was digested using 10 mL of 8.8 mol/L H₂O₂ (pH 2.0-3.0) and carefully transferred to 50 mL polypropylene centrifuge tubes. The tubes were covered, and the reaction proceeded for 1 hour at room temperature. The polypropylene centrifuge tubes containing approximately 10 mL of hydrogen peroxide were then opened and heated at 85 °C in a water bath to reduce the volume to approximately 2-3 mL. This step was performed twice, where 10 mL of hydrogen was added to the remaining solution and heated in the water bath until 1-2 mL of solution remained. After cooling the solution to room temperature, 50 mL of 1 mol/L ammonium acetate (adjusted to pH 2 by adding HNO₃) was added and shaken in a disk rotator at 40 rpm for 16 hours. The solid or undissolved residue was subsequently separated and washed as described in Step 1. The solution was labelled as **Fraction 3 (F3)** and stored at 4 °C for further analysis.

Step 4 (residual fraction including partial silicates and Al-silicates): In the final step of the sequential extraction process, 10 mL of aqua regia was added to the residue from **Step 3** in polypropylene centrifuge tubes and digested for 24 hours inside a fume hood. The mixture was transferred to a water bath on a hot plate and allowed to boil for 1 hour. Alternatively, this step was performed using

microwave digestion for 15 minutes at 160-200 °C, heating and maintaining these conditions for 10 minutes. Alternatively, the microwave conditions were changed to a ramped process, which involved heating at 100 bar pressure for 10 minutes to 90 °C, then for 10 minutes to 150 °C, followed by 15 minutes to 280 °C, and finally maintaining 280 °C for 210 minutes. The chemical content of all the different fractions was then analyzed using ICP-OES for elemental analysis. **Table 5.6** summarizes the reagents used for each fraction.

Table 5.6: Sequential extraction reagents summary

Step	Fraction	Reagent
F1	Exchangeable and acid-soluble fraction: salts-carbonates (easily soluble)	0.11 M CH ₃ COOH
F2	Reducible-oxides Fe-Mn	0.5 M NH ₂ OH.HCl (pH 2)
F3	Oxidizable (sulphides and organic matter)	8.8 M H ₂ O ₂ 1 M NH ₄ C ₂ H ₃ O ₂ (pH 2)
F4	Residual (non-extractible metals in the crystal)	Aqua regia 3:1 (12 M HCl: 15.8 M HNO ₃)

5.5 Total dissolution of the VBT ore and the tailings

For samples to be completely quantified, they must be completely dissolved, making the elements in the minerals available in solution for analysis using ICP-OES. This study used different methods and conditions before choosing the best ones. Flux fusion using different flux salts and microwave digestion using different acids were investigated for both the VBT and tailings.

5.5.1 Flux Fusion digestion

Different flux salts were used to identify both samples' best and most effective dissolution process. Lithium metaborate, sodium sulphate, and ammonium sulphate were used. 0.1 g of the sample was thoroughly mixed with 0.8-1.0 g of lithium metaborate flux in a platinum crucible. The mixtures were heated to 1 000 °C for 2 hours. The crucibles containing the yellowish melt (for both the VBT ore and the tailings) or product (in case of incomplete dissolution) were added to different beakers with about 25.0 mL of ultra-pure water and 4 mL of concentrated nitric acid. The solutions were stirred at 50 °C until complete dissolution of the melts was obtained. These solutions were quantitatively transferred to 100.0 mL volumetric flasks and filled to the mark with ultra-pure water. These solutions were then analyzed for elemental content using ICP-OES. The same procedure was repeated with sodium sulphate and ammonium sulphate flux, except that ammonium sulphate was only heated to 225 °C to prevent its decomposition, while sodium sulphate was also heated to 1 000 °C (decomposes at 1 000 °C). The same procedure was performed on the VBT ore and tailings' magnetic, non-magnetic, heavy,

and light portions obtained from the magnetic and gravity separation procedures as described in **Chapter 6**.

5.5.2 Microwave digestion

0.1 g samples of the tailings were added to the microwave vessels, and 10 mL portions of aqua regia were added. The samples were then irradiated at 180 °C, a pressure of 80 bar, and a power of 750 W for 25 minutes. The process was repeated using 10 mL of H₂SO₄ and irradiated at 240 °C, at 600 W for 45 minutes. 3. The resulting solutions were filtered and quantitatively transferred to 100.0 mL volumetric flasks and filled to the mark. Sample replicates were analysed for each acid and sample.

5.6 Chemical analysis using ICP-OES

A Prodigy 7 ICP-OES, which uses Salsa software for operation and data interpretation, was used to analyse each fraction of the sequential extractions, as well as the total dissolutions and the liquor obtained from the different experiments performed to extract Ti from both the ore and the tailing samples.

Table 5.7: Selected wavelengths for elements analyzed

Element	Wavelength (nm)
Ti	336.122
	334.941
V	292.401
	310.230
Fe	239.563
	259.940
Si	251.611
	288.157
Al	308.215
	396.152
Mn	257.610
	259.372
Ni	231.604
	341.476
Co	228.615
	236.379
Cu	213.698
	327.396
Zn	206.200
	213.856

Calibration standards were prepared by accurately adding appropriate volumes of a 1000 ppm multi-element standard solution containing Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl and Zn to 100 mL volumetric flasks. Additionally, V, Si, and Ti standard solutions were prepared from 1000 mg/L stock solutions in 100.0 mL volumetric flasks. All these standard calibration solutions had final concentrations of 0.5, 1, 3, 5, 7, and 10 ppm, and they were used to construct calibration curves for analysis. 4.0 mL of concentrated nitric acid was added to each volumetric flask, and ultra-pure water was added to the mark.

The wavelengths selected for different elements are reported in **Table 5.7**. Titanium was the element of interest, but other elements (impurities) were also analyzed. This was important because impurities can interfere with the detection and quantification of the target element in ICP analysis. Understanding the complete chemical composition allows for necessary adjustments during analysis. Knowledge of impurities also aids in managing waste products and ensuring their safe disposal. Impurities can also influence the processing behaviour, affecting separation efficiency and recovery rates. All analyses were done in triplicate, with the reported significant figures based on the standard deviation of three different analyses.

5.7 Results and discussion of the VBT ore characterization

This section extensively discusses the XED, SEM-EDS, and XRF results for the VBT ore, sequential extraction fractions, and complete dissolution ICP-OES results. Once all this physical and chemical characterization data was gathered, it gave an insight into the best way to leach, separate, and concentrate titanium as reported in **Chapters 6**. These results were compared with the reference certificate values, which showed that the VBT ore typically contained 0.81 % TiO₂, 49.04 % Fe, 1.72% V₂O₅, and 4.12 % SiO₂ as well as small percentages of other elements.

5.7.1 Particle size distribution results

The particle size distribution of the VBT ore was mostly coarse sand size. The 500 µm mesh sieve had the largest weight percentage, followed by the 250 µm mesh sieve (**Figure 5.3**). Significant quantities of the remaining particle sizes (106 µm, 53 µm, and <53 µm) were also present. The VBT ore had a wide particle size distribution in the range of <53-500 µm. Minimal sample loss occurred during the experiment (0.27 %).

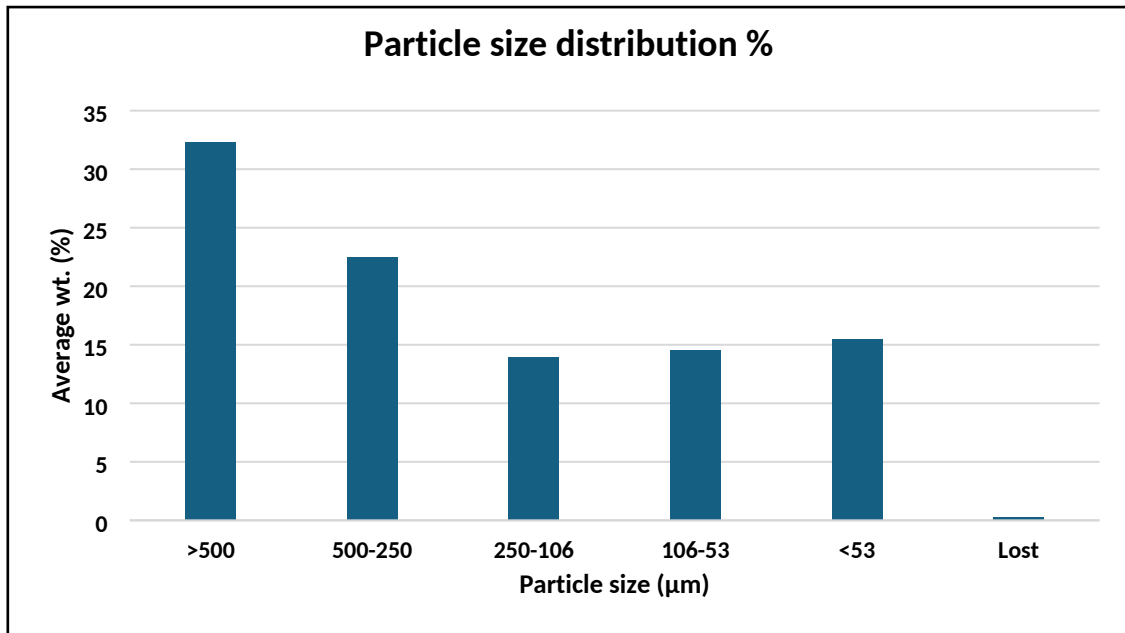


Figure 5.3: VBT ore particle size distribution

5.7.2 XRD results

XRD is used to determine the crystallographic structure, and phase identification provides critical information about the arrangement of atoms within the ore's crystal lattice. The XRD spectrum for the VBT ore is reported in **Figure 5.4**, and it clearly shows that the VBT ore sample is rich in albite, chamosite, and clinopyroxene (silicates) as well as ilmenite and magnetite (oxides) mineral phases.

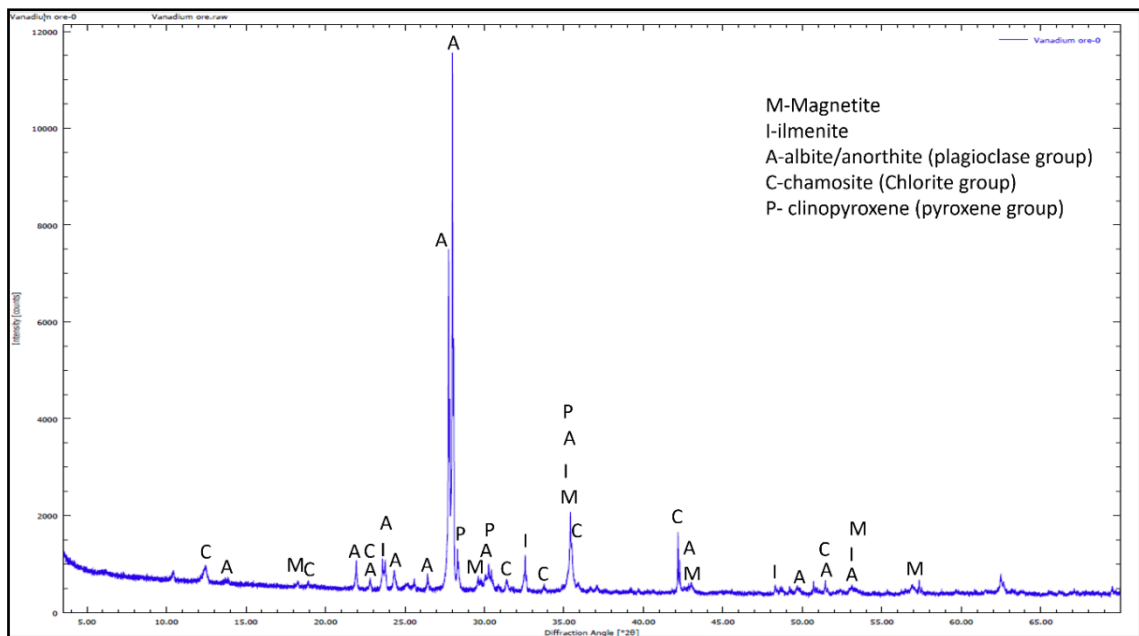


Figure 5.4: XRD analysis of VBT ore indicating the presence of magnetite (M), ilmenite (I), albite/anorthite (A), chamosite (C), pyroxene (clinopyroxene)(P)

The VBT ore is mainly made up of albite (silicate), followed by magnetite and chamosite. Significant quantities of ilmenite and clinopyroxene were also observed. The total mineral phase composition and the chemical formula of these minerals are listed in **Table 5.8**. With this analysis, it could only be assumed that the Ti was in the ilmenite and, perhaps, the magnetite. This is where XRF gives a more comprehensive insight into the sample's elemental composition of these major elements as discussed in **Section 5.7.4**.

VBT ore is mainly made up of silicates and other oxides, which are iron-rich minerals. The sample is expected to be magnetic when exposed to an electromagnet due to the presence of magnetite, which has a very high magnetic susceptibility, and ilmenite, which is also relatively magnetic. This was confirmed by magnetic mass results reported in **Chapter 6**.

Table 5.8: Mineral composition of the VBT ore

Mineral Phase	Mineral	Formula	Average % composition
Silicates	Albite (plagioclase group)	$\text{NaAlSi}_3\text{O}_8$	61.3
	Chamosite (chlorite group)	$(\text{Fe,Mg})_5\text{Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_8$	
	Clinopyroxene (pyroxene group)	$(\text{Ca,Mg,Fe})_2\text{Si}_2\text{O}_6$	
Other	Magnetite	Fe_3O_4	37.6
oxides	Ilmenite	FeTiO_3	

5.7.3 SEM-EDS results

SEM-EDS is a versatile and powerful technique for investigating materials' surface morphology and elemental composition at a microstructural level. The SEM image of the received ore is presented in **Figure 5.5**. It shows VBT ore to have a rough and irregular surface texture. Microstructural features such as grain boundaries and inclusions were observed. The grains display various shapes (anhedral) and sizes ranging from several micrometres of coarse grains (up to 100 μm) to fine grains (<10 μm).

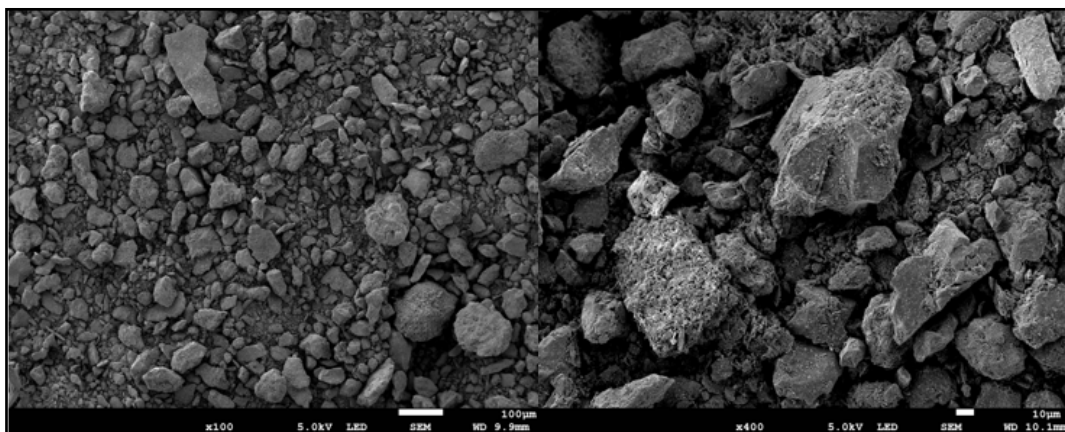


Figure 5.5: VBT ore unpolished samples

The sample was polished for SEM analysis to achieve a smooth and flat surface for precise imaging, enhance image quality, and facilitate accurate elemental analysis through uniform exposure. Different points were analysed and shown in **Figure 5.6a**, and the minerals present were labelled in **Figure 5b**. The results in **Table 5.9** show the composition of the elements present. Analysing the spectra obtained from different ore regions helps identify the key elements and their respective concentrations, essential for understanding the ore's metallurgical properties and potential beneficiation processes.

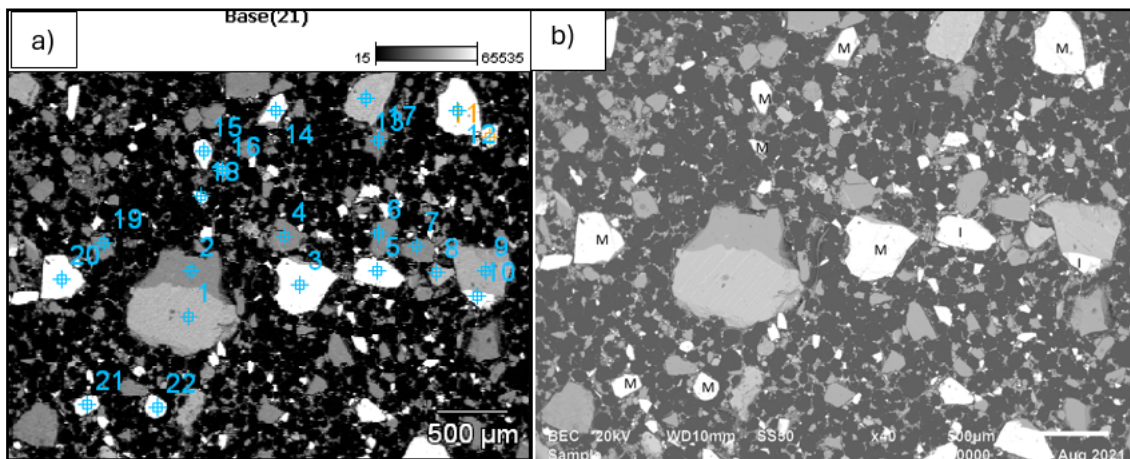


Figure 5.6a: VBT ore SEM-EDS analysis showing the different points analysed and b) the identified minerals indicating Ilmenite (I) and magnetite (M)

Table 5.9 indicates that the VBT ore sample is very rich in titanium, iron, aluminium, silicon, and calcium. These were identified in almost all the points analysed. It also contains significant quantities of sodium and magnesium. All these metal cations are found as oxides, hence the large quantities of oxygen. Trace quantities of vanadium, manganese, potassium, and chloride ions were also found at some points. The mineral composition of the different particles stands out in the table, which helps identify the minerals present. An example is the particle in point 3, which was found to be magnetite, contained large quantities of Fe, double the amount of O, and significant quantities of Ti and Al; therefore, it is helpful in this study. Particles like the points labelled 1 and 2 comprise silicates, as was also suggested by previous XRD results.

The high average concentrations of oxygen, silicon, and aluminium indicate a predominance of silicate and alumina minerals. However, the presence of iron, calcium, and potassium indicates the possibility of other mineral types, such as the oxides reported by XRD results. Titanium, vanadium, and manganese are trace elements that may contribute to specific mineral properties but are less significant in overall composition.

These results showed that the VBT ore is associated with Fe and O, meaning the Ti was predominantly found in the oxides, just as the XRD results showed. Most of the points with Fe and Ti did not have Si,

showing that Ti was not associated with silicates. Some target points in **Figure 5.6** also showed that Al is associated with Ti. This may be due to the presence of Al impurity in the ilmenite and/or magnetite minerals.

Table 5.9: SEM-EDS elemental results of different VBT ore points

Atom %	Ti	V	Fe	Si	Al	Mn	Na	Mg	Cl	K	Ca	O
Base(21)_pt1			9.74	18.43	0.44			7.93			1.70	61.76
Base(21)_pt2				18.39	11.49		3.22				5.63	61.26
Base(21)_pt3	4.59		33.92		0.57							60.92
Base(21)_pt4				18.63	11.20		3.28				5.59	61.29
Base(21)_pt5	19.04		16.52					0.79				63.65
Base(21)_pt6				18.33	11.54		3.29			0.19	5.46	61.18
Base(21)_pt7				18.86	11.28		3.12				5.28	61.47
Base(21)_pt8			9.45	18.75	0.31			8.98			0.69	61.82
Base(21)_pt9			4.57	18.33	0.98		0.14	5.89			9.57	60.52
Base(21)_pt10	18.90		16.89			0.54						63.67
Base(21)_pt11	1.48	0.89	36.34		0.64							60.65
Base(21)_pt12	3.27	1.04	33.18		1.45							61.07
Base(21)_pt13		0.18	7.16	15.16	6.17		0.81	0.93	0.44	0.33	8.27	60.55
Base(21)_pt14	6.06		32.35		0.37							61.21
Base(21)_pt15	4.45		32.81		1.86							60.89
Base(21)_pt16			6.83	18.90	0.48			8.02			4.48	61.28
Base(21)_pt17				17.93	11.84		2.68				6.30	61.25
Base(21)_pt18	5.59		31.81		0.92			0.59	0.21			60.87
Base(21)_pt19				18.89	11.24		3.25				5.17	61.45
Base(21)_pt20	6.27		30.67	0.37	0.94			0.52				61.22
Base(21)_pt21	6.43		28.85	0.33	2.59			0.56				61.24
Base(21)_pt22	5.53		27.45	2.80	1.88			0.85				61.50

Ti quantities range from 1 to 19 %, with a typical value around 6 %. This variation is expected in mineral samples, confirming the need for proper sample homogenization and the analysis of the whole mineral during all stages of mineral processing. It is due to point analysis at a specific point on the sample's surface and non-homogeneous distribution of elements in a natural material, while a usual XRF analysis gives the average composition of the sample analysed. Quartz, a common gangue mineral, is a silicon and oxygen mineral; its presence is therefore evident in this sample. However, its presence may affect the overall processing efficiency due to its inert nature during the beneficiation processes, thus requiring strong acids to completely dissolve samples if required.

A textual analysis of the SEM-EDS shows that the VBT ore was made up of natural idiomorphic minerals. The VBT ore is expected to be magnetic due to significant amounts of highly magnetic magnetite. The magnetite in this portion is also attached to other minerals, like mica, that may require separation from the titanium-rich mineral (magnetite) that is valuable to the study. This makes the magnetic separation of the target minerals from the gangue difficult.

The typical elemental content of Ti was way higher in these EDS results than in the reference certificate (0.81 %). This could have been due to a lack of sample homogeneity. The Fe composition (typically 33 %) was fairly close to the one in the certificate (49.04 %). Another possibility is that Bushveld Vametco Alloys analyzed a different sample. This could be because two different techniques are being compared which will show a range of different values since their resolution and accuracy are different. Generally, all the elements observed in this SEM-EDS analysis were also present in the certificate values, except for Cl, which is also not found in a lot of points in these results.

Ilmenite and magnetite are the minerals that contain the element of interest in this study, and hence, they were associated with significant amounts of Ti, with ilmenite containing up to 30 wt.% Ti and magnetite with 2-10 wt.% Ti and 1 wt. % V. The exact concentration of the elements present would give more insight into how much Ti is available for extraction.

5.7.4 XRF results

The results obtained from XRF analysis provide invaluable insights into the concentration of elements within a sample, which is important in the next stage of beneficiation. The XRF results for the major element oxides present in the sample and their percentage composition are reported in **Table 5.10**, showing that VBT ore has significant quantities of the element of interest, Ti, as well as Fe, Si, Al, and Ca impurities. It contains 3.80 % Ti and almost 30 % Si. This corroborates the XRD results, which showed that the VBT ore is made up of a large percentage of silicates (61.3 %).

Table 5.10: XRF elemental composition of major elements in VBT ore

Major element oxides	Average composition (%)
TiO ₂	3.80
Fe ₂ O ₃	37.76
SiO ₂	29.74
Al ₂ O ₃	15.69
MnO	0.14
MgO	1.87
CaO	7.90
Na ₂ O	1.82
K ₂ O	0.16
P ₂ O ₅	0.04
LOI	0.11
Total	99.02

Ti, Fe, and Al concentrations were very similar to those observed in the SEM-EDS analysis, even though they do not agree with those reported by the received certificate. This supports the idea of performing internal characterisation while not relying on the certificate, since better sample homogenization was performed, or different samples were analysed. The XRF results reported a very high percentage of Si.

This agrees with the XRD results showing that most of the minerals in the VBT ore are silicates. **Table 5.11** shows the composition of trace elements, showing that significant amounts of V are present in the VBT ore with trace amounts of Cr, Cu, and Sr, which also confirms the primary V beneficiation of these mineral deposits.

Table 5.11: Elemental composition of trace elements in VBT ore

Trace elements	Concentration (ppm)
V	2891
Sc	24
Cr	993
Co	109
Ni	92
Cu	230
Zn	102
As	32
Rb	4
Sr	270
Y	10
Zr	10
Nb	2
Ba	116
Pb	<2
Th	16
U	<3

Although these concentrations are very low, they are significant. 0.2 % V was observed in the XRF analysis. This agrees with the SEM-EDS results, which show that V is not very abundant in the ore, with a 0.18-1.04 % concentration compared to the 1.72 % V reported by Bushveld Vametco Alloys (2017).

Comparing the current elemental content with that previously reported is also important. One study analysed VBT samples obtained from the Pan Steel Company in the Sichuan province of China. The samples had a particle size of -0.074 mm. The chemical composition analysed using multiphase XRF showed that the VBT sample contained 1.43 % V_2O_5 , 9.86 % TiO_2 , and 54.7 % total iron (TFe), respectively (Bian *et al.*, 2021). A vanadium magnetite concentrate was characterised using XRF in one study, and the following composition was obtained: 12.68 % TiO_2 , 72.55 % Fe_2O_3 , 4.66 % Al_2O_3 , 3.82 % SiO_2 , 3.26 % MgO , 0.75 % V_2O_5 , and 0.64 % MnO (Zheng *et al.*, 2019). Certified concentrations of a reference material, AMS0501 (vanadium-bearing titanomagnetite), were reported for the Eastern Bushveld Limb, Mapochs Mine. The certified composition of the sample was reported as 13.1 % TiO_2 , 76.4 % Fe_2O_3 , 4.19 % Al_2O_3 , 1.87 % SiO_2 , 1.75 % MgO , 1.7 % V_2O_5 , and 0.24 % MnO (AMIS, 2017). These results show a similar trend in Ti, Fe, and V concentrations as in this study.

5.7.5 Sequential extraction results

The ICP-OES results reported in **Table 5.12** show that titanium was exclusively found in the residual fraction (7694 ppm), indicating it is strongly bound within the mineral matrix and not available in exchangeable forms.

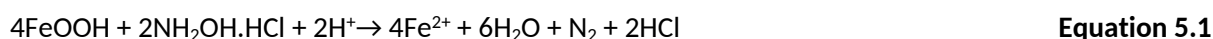
Table 5.12: Elemental composition of different sequential extraction fractions of the VBT ore

Element	F1 (ppm)	F2 (ppm)	F3 (ppm)	F4 (ppm)	Total (ppm)
Ti	bdl	bdl	bdl	7694	7694
V	8	44	14	3643	3710
Fe	1922	2988	bdl	65367	70278
Si	149	270	273	236	929
Al	641	680	bdl	23135	24457
Mn	106	22	1	807	937
Ni	6	5	18	94	124
Co	9	6	13	505	534
Cu	13	10	22	30	78
Zn	4	5	0.8	332	3710
Ca	1044	110	413	12983	14551
Sn	2	bdl	9	48	60
K	3	1122	bdl	203	1330
In	2	21	3	4	31
Pb	bdl	bdl	168	1411	1580
Li	bdl	12	0.5	3	16
Cr	3	4	bdl	393	401

Titanium was exclusively found in the residual fraction (7 694 ppm), confirming its inertness and the strong bonds between the Si in its high oxidation state and oxygen ions. SEM-EDS showed polymineral particles of target minerals (ilmenite and magnetite) with silicates, which could explain the absence of Ti from the initial steps of the sequential extraction. Silicates are generally stable and highly resistant to chemical reactions and dissolution under standard extraction conditions used in **Steps 1-3**. In addition, the strong ionic bonds in titanium oxide structures make them resistant to acidic or basic dissolution. However, aqua regia can effectively dissolve these chemical compounds if needed.

The residual fraction **F4** also had relatively large quantities of Fe, Al, Ca, V, and Ti. This is because the minerals that contained portions of these elements were not easily dissolved by **Step 1-3** solvents

such as hydrogen peroxide but may require strong acids such as aqua regia used in **Step 4** for complete dissolution. The results clearly indicate that iron compounds in the sample are relatively inert and not readily available for dissolution. Typically, **Fraction 1** includes iron associated with more reactive soluble anions such as carbonates, which weak acids may dissolve, while **Fraction 2** may include iron that is bound to organic matter or stable minerals that can be oxidized, such as Fe-sulphides (i.e. pyrite). The residual fraction contains the bulk of iron, mainly with Fe in a stable, less reactive form, like hematite, and silicate minerals such as chlorite contain iron, making it less available for extraction. The high concentration of Fe in the residual fraction suggests that most iron exists in oxidation states present in compounds that are not readily available for biological uptake or leaching. Interestingly, the data in this table shows that very low percentages of Fe were found in **Fraction 2**, which was used $\text{NH}_2\text{OH}.\text{HCl}$ as a reducing agent, suggesting that it reduced some Fe^{3+} to the more soluble Fe^{2+} . However, most of the iron remained unreacted, even though the mineral ore contains Fe-rich minerals such as ilmenite. This may be attributed to the fact that this reagent is more effective at dissolving amorphous and crystalline Fe oxyhydroxides typically found in the Fe/Mn oxide fractions, but not so for the stable ilmenite and hematite present in the sample. The specific reactions can vary depending on the exact composition of the oxides present, but a typical example is the reduction of goethite (FeOOH) to ferrous iron (Fe^{2+}) according to **Equation 5.1**.



The fact that the total concentrations of the elements largely differ in the sample (for example, total the Fe was 70 278 ppm compared to the total Li concentration of 16 ppm), two different graphs were used to indicate the concentration levels of the major and trace elements as shown in **Figure 5.7** and **Figure 5.8**.

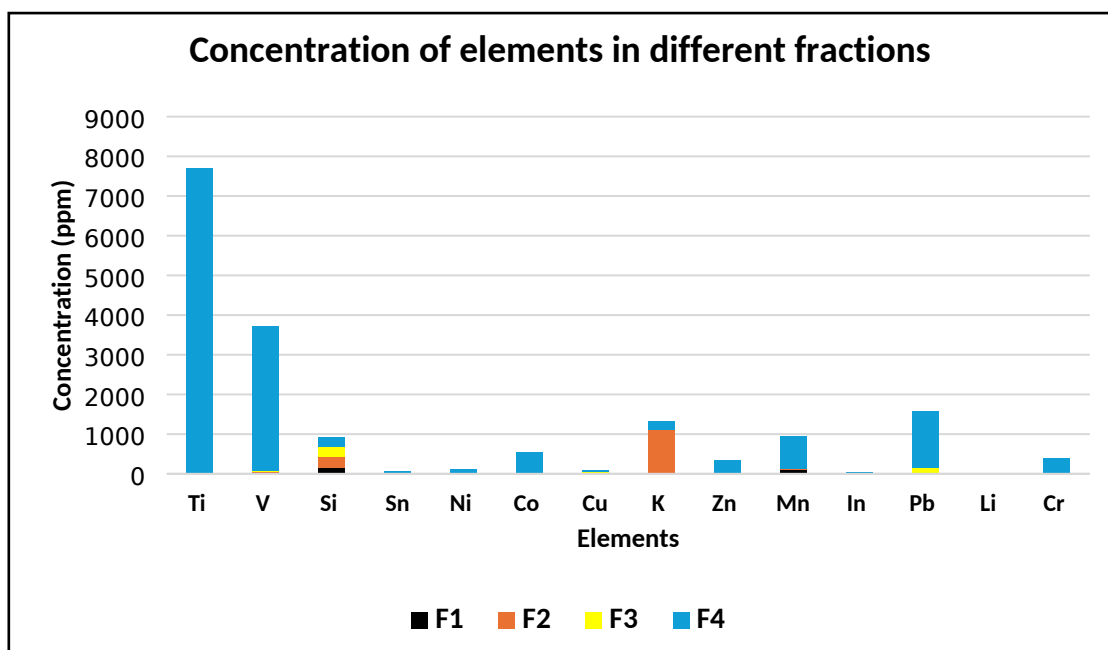


Figure 5.7: Plot of minor concentration of the elements found in the different fractions of the VBT Ore sample

In contrast, elements such as Al and V showed significant concentrations in the more mobile fractions, indicating potential bioavailability or ease of extraction. In total 7 695 ppm Ti was extracted with aqua regia.

Vanadium was present in all fractions, indicating some degree of mobility, which may be attributed to the large variety of oxidation states of V and its potential oxidation-reduction reactions and soluble complexes with organic molecules or ligands, and has the highest concentration in the residual fraction (3 643 ppm). Vanadium can exist in several oxidation states, with V^{3+} , V^{4+} , and V^{5+} being the most common in natural environments. It can potentially form the stable vanadate anion (VO_4^{3-}), while other vanadium oxides (such as V_2O_5 , which is amphoteric) are relatively inert at specific pH levels and insoluble in water. The residual fraction contained most of the vanadium, indicating it was predominantly bound in stable oxides or present in the silicate mineral matrices.

Silicon was evenly distributed among all the fractions, with a total concentration of 929 ppm. It primarily exists in silicate minerals, such as quartz (SiO_2), feldspars, and clay minerals. It can also exist as soluble silicates, particularly in alkaline or acidic environments. The presence of silicon in all fractions indicates its diverse chemical behaviour as it can be found in acidic soluble forms, such as silicate ions (SiO_4^{4-}) and amorphous silica, which can dissolve in acidic conditions. High percentages of Si (34 %) were reported in XRF in contrast with the sequential extraction results (< 1 %), showing that the silicates were not properly dissolved to correctly quantify them, which it was expected since the best acid known to dissolve silicates at room temperature is hydrofluoric acid and not aqua regia.

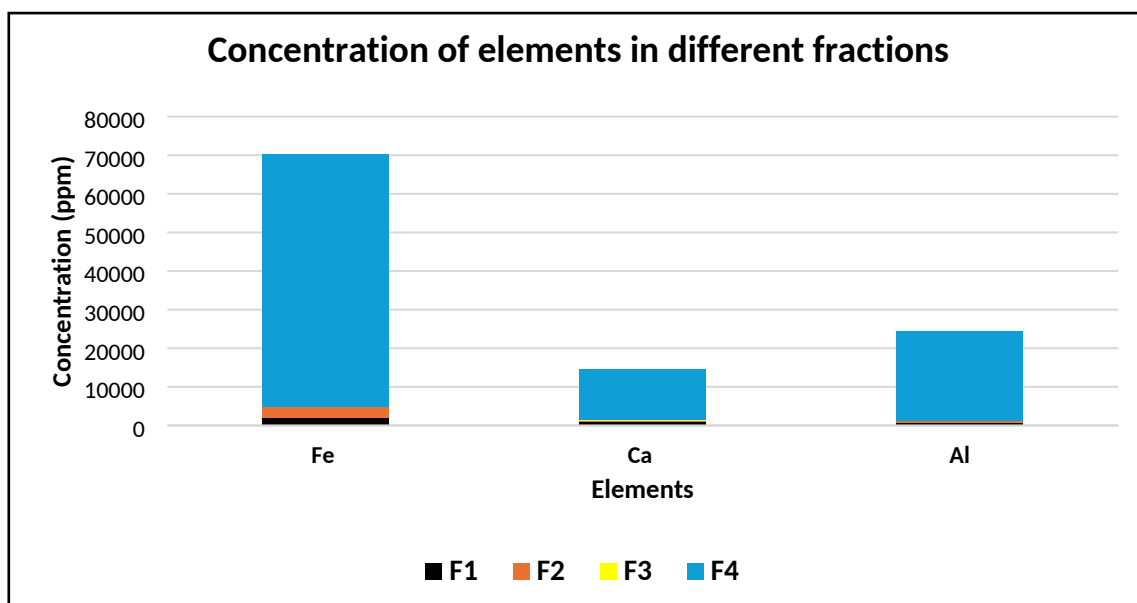


Figure 5.8: Plot of the major concentrations of the elements found in the different fractions of the VBT Ore sample

Sequential extraction is commonly used in soil samples and not mineral ores because the mineralogy of ores is often more complex than that of soils. This makes it more challenging to develop a sequential extraction procedure that can accurately separate the different mineral phases in ores. Additionally, this research focused on mineral ores on the recovery of valuable metals, rather than what happens to the elements present in the mineral when they are in contact with the environment, as is usually studied in sequential extraction studies. It was adopted into this study to give more insight into the mineral characteristics, but its results are not necessarily an accurate reflection of the actual composition of the samples but is, however, useful as an informative technique. Other methods for complete dissolution were investigated.

5.7.6 Flux fusion results

The dissolution efficiency of the three different flux salts was evaluated to identify the most appropriate for this mineral sample. These included lithium metaborate, sodium sulphate and ammonium sulphate. The reactions were performed in triplicate, and the results were used to calculate the standard deviations and reported in brackets.

5.7.6.1 LiBO₂ flux fusion

The VBT mineral ore was treated according to the procedure in **Section 5.5.1** and the ICP results for the elements detected in solution are reported in **Table 5.13**. Sample dissolution using lithium metaborate was deemed very successful with visual inspection indicating no residue present after the final dissolution step of the melt obtained.

Table 5.13: Elemental composition of VBT mineral ore after LiBO₂ flux fusion

Element	Average % Composition
Ti	3.0(1)
V	0.612(1)
Fe	24.6(3)
Si	1.10(8)
Al	10.3(4)
Mn	0.322(5)
Ni	0.194(6)
Co	0.261(4)
Cu	0.114(3)
Zn	0.066(5)

The results indicate that the main elements are Fe and Al with Ti and Si as the minor elements and V, Mn, Ni, Co, Zn impurities. 3.0 % Ti, which is quite significant, was used as the baseline to calculate the recovery of all the reactions performed in this study, such as leaching, separations, and isolation processes, as shown in **Chapter 6**. The dissolution gave 24.6 % Fe, which was less than half of that in the certificate results (49.04 %) and lower Si (1.10 %) than the certificate (4.12 %). This may be due to different samples being analyzed. Different batches of VBT ore may exhibit variability in composition, which can affect the extraction process and the analytical results.

The results obtained by flux fusion were lower than those obtained by XRF (7.27 %). However, the flux fusion ICP-OES results were used since complete dissolution of the samples was achieved, and ICP-OES is more accurate and cheaper to use at all stages of analysis.

5.7.6.2 (NH₄)₂SO₄ flux fusion

The VBT ore was not dissolved by ammonium sulphate. Visual inspection of the crucible did not show a glass bead (yellowish melt) that is expected after flux fusion. ICP results confirmed the incomplete dissolution as shown in **Table 5.14**, with low elemental recoveries of all the elements of interest.

Table 5.14: Elemental composition of the VBT mineral ore after (NH₄)₂SO₄ flux fusion

Element	Average % Composition
Ti	0.107(1)
V	bdl
Fe	1.40(5)
Si	1.09(2)
Al	0.97(1)
Mn	0.002(2)
Ni	0.16(1)
Co	bdl
Cu	0.13(1)
Zn	bdl

bdl - below detection limit

The composition of the VBT ore during this dissolution step indicated very low percentage of Ti recoveries of only 0.1 %. Compared to the LiBO₂, these were even lower than the certificate value (0.81 % Ti). Elements such as V were below detection limit which was understandable due to its low concentration in the starting material.

5.7.6.3 Na₂SO₄ flux fusion

The sodium sulphate digestion was also unsuccessful as most of the VBT ore remained undissolved in the crucible and hence the salt was not further investigated as a possible flux reagent. The results reported in **Table 5.15** show that only 0.14 % Ti was dissolved from the VBT ore which is way less than that were originally in the mineral sample.

Table 5.15: Elemental composition of the VBT ore after Na₂SO₄ flux fusion

Element	Average % Composition
Ti	0.14(1)
V	bdl
Fe	5.2(7)
Si	0.77(3)
Al	15.5(1)
Mn	0.134(2)
Ni	0.071(2)
Co	bdl
Cu	0.19(3)
Zn	bdl

bdl - below detection limit

Lithium metaborate was the only flux reagent that was able to completely dissolve the sample enabling the accurate quantification of all relevant elements. Ammonium sulphate and sodium sulphate were not able to successfully break down the ilmenite and magnetite minerals (as shown to be present by XRD results), which contained the Ti, and hence gave very low percentages in

comparison to lithium metaborate as well as other methods that were used to quantify Ti in the VBT ore.

5.7.7 Microwave digestion results

Two different acids were evaluated as potential media to successfully dissolve the VBT ore sample using microwave digestion, which were aqua regia and sulphuric acid. The analyses were also performed in triplicate, and the results were used to calculate the standard deviations and reported in brackets.

5.7.7.1 Microwave digestion using aqua regia as solvent

VBT mineral ore was treated according to the procedure in **Section 5.5.2**, and the ICP results for the elements detected in solution are reported in **Table 5.16**. Microwave sample digestion using aqua regia was very successful, with visual inspection indicating no residue present after the reaction.

Table 5.16: VBT ore elemental composition after microwave digestion using aqua regia

Element	Average (%) composition
Ti	2.74(2)
V	1.01(1)
Fe	55(1)
Si	0.447(2)
Al	9.383(4)
Mn	0.37(1)
Ni	0.04(3)
Co	0.047(3)
Cu	0.54(2)
Zn	0.031(1)

The composition of VBT ore showed very significant quantities of Ti, highlighting the effectiveness of microwave digestion using aqua regia to completely dissolve the VBT ore. The VBT ore was shown to be rich in Ti with large quantities of Fe, Al, and V impurities. 2.74 % Ti, which was almost equal to the LiBO₂ digestion results (3 %), giving credibility to this method of digestion. 55.70 % Fe and 1 % V were reported, and these were close to the certificate values. Aqua regia is a very strong acid that can completely dissolve minerals such as titanium-bearing minerals, ilmenite, and magnetite, which were shown to be present in the VBT ore. The high pressure and temperature of the microwave added to the dissolution effectiveness.

5.7.7.2 Microwave digestion using sulphuric acid as solvent

The microwave digestion using sulphuric acid was unsuccessful in completely dissolving the VBT ore sample. The microwave vessels had undissolved solids present, and this is also confirmed by the ICP

results reported in **Table 5.17** which show very low percentages of Ti, Al, Si and Fe. The rest of the elements were not even present in the solution.

Table 5.17: VBT ore elemental composition after microwave digestion using sulphuric acid

Element	Average % composition
Ti	0.191(2)
V	bdl
Fe	0.48(1)
Si	0.363(3)
Al	3.70(2)
Mn	bdl
Ni	bdl
Co	bdl
Cu	bdl
Zn	bdl

*bdl – below detection limit

The complete dissolution of the VBT ore using sulphuric acid as a solvent was unsuccessful, regardless of the harsh experimental conditions of the microwave. This suggests that the solvent plays a very important role in microwave digestion, and the stronger the acid, the more complete the dissolution and the better the dissolution results.

5.7.8 Comparison of the chemical characterization results of the VBT ore with different characterization techniques

The comparison of chemical content across different analytical methods reveals significant variability in elemental compositions, as each method has its strengths and may yield different insights into the chemical composition of the VBT ore. Understanding these differences is crucial for selecting the appropriate analytical methods for leaching and separation (**Chapter 6**). The results from the different methods used were tabulated in **Table 5.18**. The ability of non-destructive methods to provide reliable quantitative analysis results for the mineral constituents was evaluated by comparing them with those obtained using ICP-OES analysis after different dissolution techniques. It is important to note that only the ICP-OES results in which the sample was completely dissolved were used for comparison with the SEM-EDS and XRF results.

Table 5.18: Comparison of the chemical content of the VBT using different analytical methods

Element	Certificate (%)	LiBO ₂ Flux fusion (%)	Aqua regia microwave digestion (%)	Sequential Extraction (%)	XRF (%)	SEM-EDS (%)
Ti	0.81	3.0(1)	2.74(2)	0.77	3.80	1.48-19.0
V	1.72	0.612(1)	1.01(1)	0.37	0.29	0.18-1.04
Fe	49.04	24.6(3)	55(1)	7.03	22.37	4.57-36.3
Si	4.12	1.10(8)	0.447(2)	0.09	29.74	0.33-18.8
Al	1.78	10.3(4)	9.383(4)	2.45	15.69	0.44-11.8
Mn	0.31	0.322(5)	0.37(1)	0.09	0.14	0.54
Ni	-	0.194(6)	0.047(3)	0.012	0.01	-
Co	-	0.261(4)	0.54(2)	0.053	0.01	-
Cu	-	0.114(3)	0.031(1)	0.01	0.02	-
Zn	1.28	0.066(5)	0.04(3)	0.03	0.01	-

Certificate results provided by the company showed a lower Ti concentration (0.81 %) than the concentrations obtained in this study, except for the sequential extraction. However, the certified values were constantly referred to since all the elements that were analyzed were present in the techniques used in this study, just in different concentration ranges.

Lithium metaborate flux fusion proved to be more reliable and effective than other salts, as complete digestion was obtained, and ICP-OES results showed similar quantities to those achieved by microwave digestion as well as XRF, especially for Ti, Fe, and Al. It was used as the baseline for all the reactions that were done and used to calculate the recovery when other leaching and separation processes were done (**Chapter 6**).

Microwave digestion using aqua regia as a solvent was effective in dissolving the VBT ore sample, producing a Ti composition of 2.74 %, which is close to the lithium metaborate flux fusion result obtained. However, microwave digestion is neither large-scale friendly nor a general commercial dissolution method, and it also uses a lot of electricity and hence, flux fusion was opted for as the main dissolution method. The same complete dissolution was also observed in leaching reactions using aqua regia in **Chapter 6**, where aqua regia reactions yielded high titanium recoveries. This shows that aqua regia is strong enough to digest ilmenite and magnetite, which were shown to be present in the VBT by the XRD results. A fairly high percentage of Fe was obtained (55 %), which was close to the certificate value (49 %).

The sequential extraction method generally indicated lower concentrations for most elements. Suggesting it may be less effective for accurate quantification. The aqua regia digestion (**Step 4**) dissolved most residual solids. However, aqua regia combined with microwave digestion achieved complete dissolution of the mineral ore sample, unlike the sulphuric microwave digestion, in which all the samples were only partially dissolved. Low quantities (0.093 %) of SiO_2 were found in the sequential extraction process, which was unexpected because, according to XRF, the VBT ore contained about 16 % silica, while XRD showed that the VBT ore was made up of 61 % silicate minerals. Therefore, a larger percentage of Si was expected. However, the presence of silicate minerals in XRD does not necessarily correlate with the amount of free silica, as some silicates may not release SiO_2 during extraction.

SEM-EDS gave large differences in elemental composition at different points analyzed for the sample that was investigated. The Ti concentration ranged from 1-19 % with other points with no Ti detected. These results confirm the deficiencies of these analytical methods in their ability to perform surface analysis and not total elemental composition. An extensive analysis of various portions of the sample would be required for accurate identification. These results did not provide as much depth as XRF when it came to the bulk material composition, and hence, they were only used to determine where the Ti was situated in the sample and to identify possible acids for dissolution purposes.

XRF proved to be a better analytical method compared to SEM-EDS for elemental quantification. The results obtained from this method were compatible with those using the destructive methods, especially the lithium metaborate flux fusion results. The different experimental conditions used in all these techniques have contributed to the clear picture of the mineral sample investigated. The employment of a variety of analytical methods allowed for a comparison of the nature and composition of the ore, thereby enhancing the reliability and comprehensiveness of the analysis. It allows for a thorough comprehension of the ore's mineralogy, facilitates accurate resource evaluation, and aids in optimizing extraction and beneficiation methods. Integrating different techniques ultimately leads to better decision-making on the isolation methods. All these methods gave different sides of the same coin. The selection of a specific method depends not only on the type of information that is required, but also on its effectiveness, availability, ease of use, applicability in industry, and many other factors.

5.8 Results and discussion of the tailings characterization

The tailings were obtained from a mine that focused on extracting vanadium from a vanadium-bearing titanomagnetite ore. The mineral process entails the isolation of the magnetic portion of the ore, which contains the vanadium-rich concentrate, which is further processed while the Ti-rich tailings are

discarded as waste (Bushveld Minerals, 2024). The same physical and chemical characterization techniques that were used for the VBT ore were applied to the tailings to have an exact comparison of both sample types. The results obtained were compared with the reference certificate values, which showed that the tailings contained 7.5 % Ti, 48.5 % Fe, 0.35 % V, 2.25 % Al, and 1.6 % Si as well as small percentages of other elements.

5.8.1 Particle size distribution results

Particle size distribution evaluation of the tailings was conducted according to the procedure in **Section 5.4.1**, and the results are shown in the graph in **Figure 5.9**. The 53 μm mesh sieve had the largest weight percentage of approximately 35 % followed by 31 % for particles < 53 μm and 27 % for particles of 106 μm .

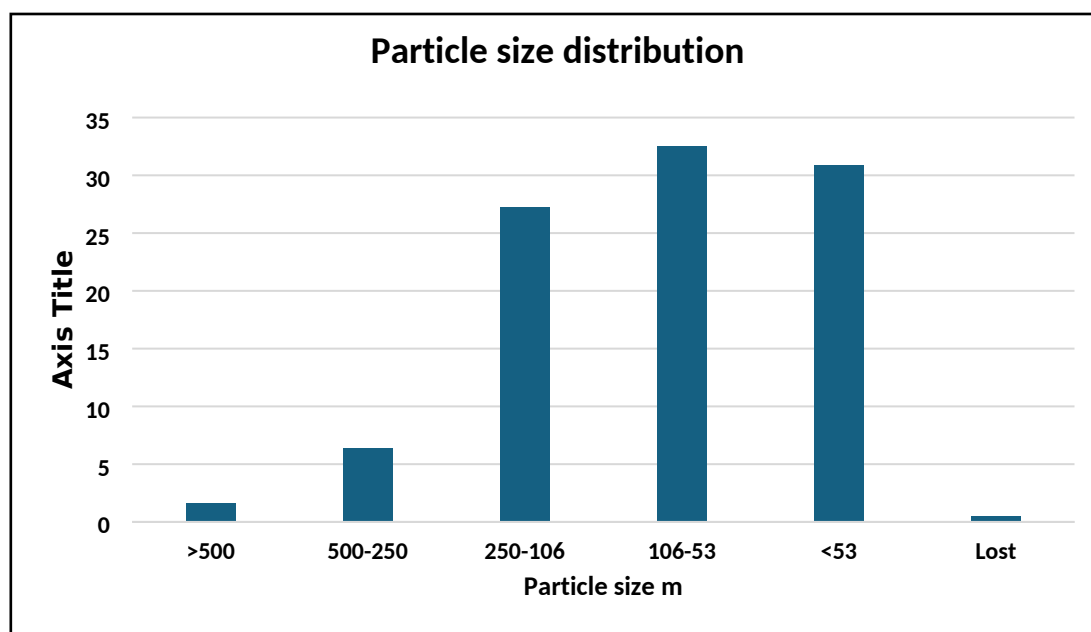


Figure 5.9: Tailings particle size distribution

These results indicate that most of the sample (88.5 %) was <106 μm and that very little sample was lost during the experiment (0.48 %), indicating that tailings were much finer than the original VBT ore particles.

5.8.2 XRD results

The XRD spectrum for the tailings (**Figure 5.10**) clearly shows that it predominantly consisted of hematite (Fe_2O_3), ilmenite (TiFeO_3), and pseudobrookite (Fe_2TiO_5), all of which are in the oxide mineral phase as reported in **Table 5.19**. Titanium primarily occurs in ilmenite and pseudobrookite and may be present in hematite as an impurity.

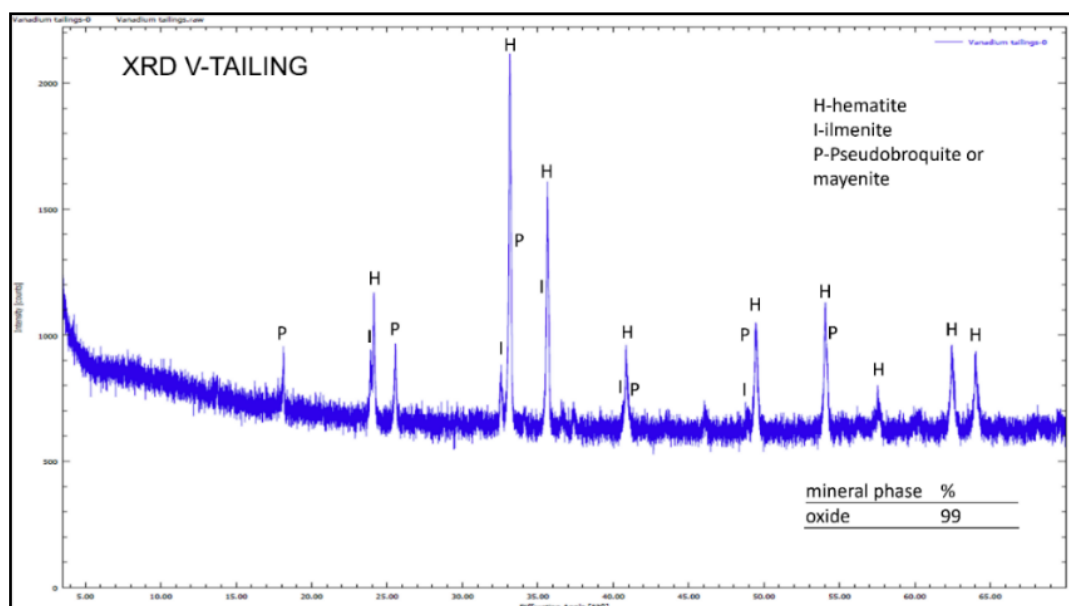


Figure 5.10: XRD analysis of the tailings

These peaks show that the most abundant ore is hematite, followed by pseudobrookite and ilmenite. Traces of Ti may be present in hematite, which can substitute for Fe in the crystal lattice of hematite. This process is known as solid solution formation. Therefore, it is a possible source of titanium.

Table 5.19: Mineral composition of the tailings

Mineral phase	Minerals present	Average % composition
Oxides	Hematite	99
	Ilmenite	
	Pseudobrookite	

The presence of these minerals in the sample suggests the absence of any magnetic compounds such as magnetite. Ilmenite has very low magnetic susceptibility ($46-80\,000 \times 10^{-8} \text{ m}^3/\text{kg}$), and the low percentages of ilmenite in the sample, as indicated by the weak XRD peaks in Figure 5.11, indicate that the sample will be weakly susceptible to any magnetic separation. This was supported by the magnetic separation results reported in **Chapter 6**.

5.8.3 SEM-EDS results

The SEM-EDS characterization of the tailings was analyzed according to the procedure described in **Section 5.4.3**. The SEM-EDS results obtained from this study reveal interesting results regarding the texture and the presence of trace elements within the sample matrix. Clustered particles of hematite and ilmenite cemented by silicates or siliceous compounds were present in the tailings (**Figure 5.11**), which is per the XRD results.

The SEM-EDS images show that the tailings consisted of several different minerals, which were small and irregular in size and clustered around each other in a melted flowy pattern, unlike the VBT ore, which was bigger and regular with just two minerals (at most) joined together and clearly defined. This could be attributed to the chemical alteration that occurred during the ore processing stages, for example, the roasting step.

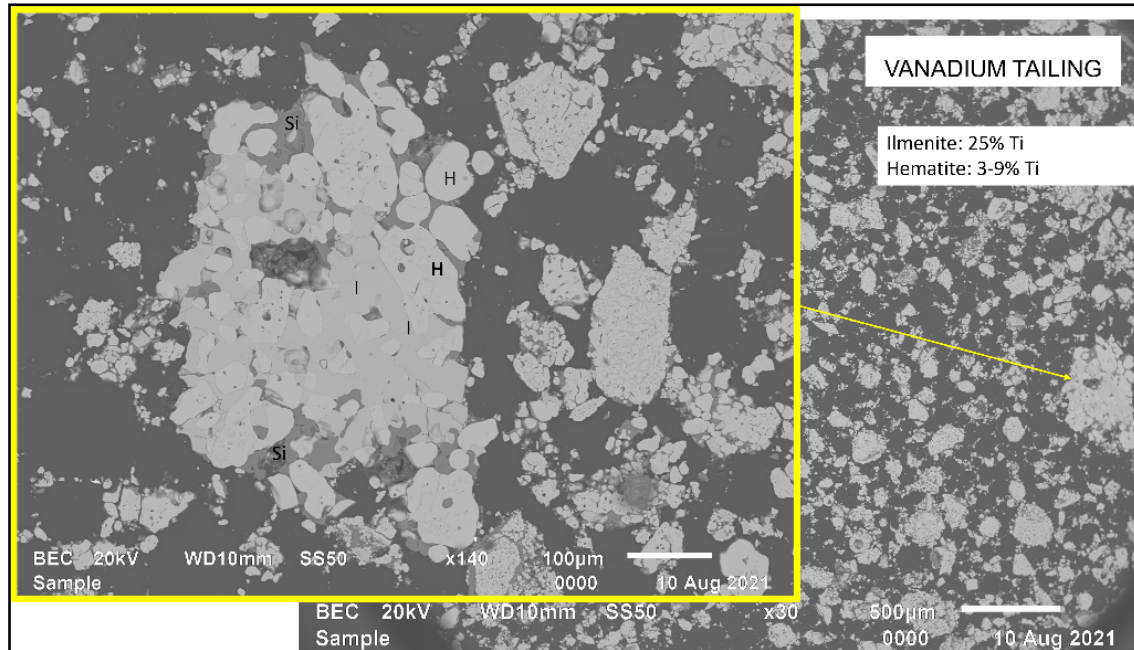


Figure 5.11: Tailings SEM analysis showing the composition of one particle, indicating ilmenite (I) and hematite (H)

EDS analyses indicate that the ilmenite particles contained 25 % Ti and hematite contained approximately 3-9 % Ti. Due to the high Fe and Ti content, this particle might possibly be ilmenite and hematite. It is also important to note that silica was also closely packed with these minerals, as shown in **Figure 5.11**. Mineral associations of hematite and silicate were observed. This phenomenon can influence the dissolution and isolation behaviour of the sample. **Figure 5.12** clearly shows that silicates and hematite remained intact after the beneficiation process of the VBT ore, indicating that they were resistant to the harsh conditions (high temperatures) applied during the beneficiation process.

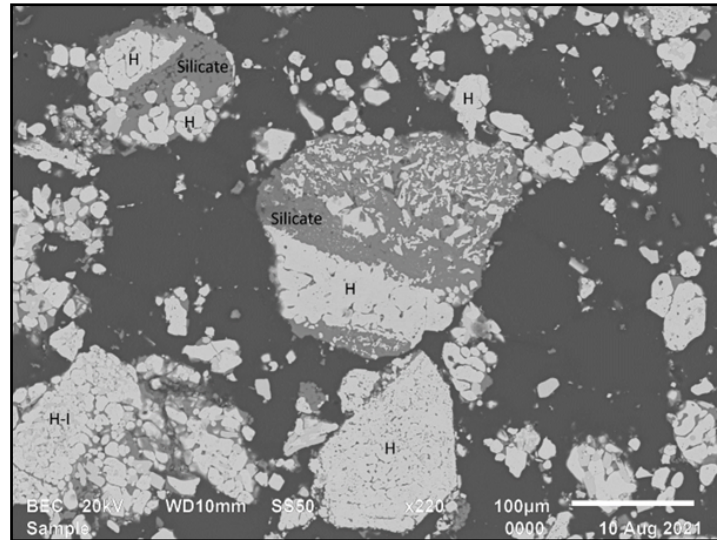


Figure 5.12: Tailings SEM analysis showing hematite

The EDS analysis (points labelled **1** and **2** in **Figure 5.13a**) detected a titanium-enriched albite mineral (**Table 5.28** and **Figure 5.13b**). This mineral was embedded in a substance enriched in 14.5 % V, 7.6 % Fe, and 5.2 % Ti (indicated by the red arrow in **Figure 5.13b**). Therefore, the vanadium beneficiation processes at the mine seem to produce a new product (tailings) rich in titanium

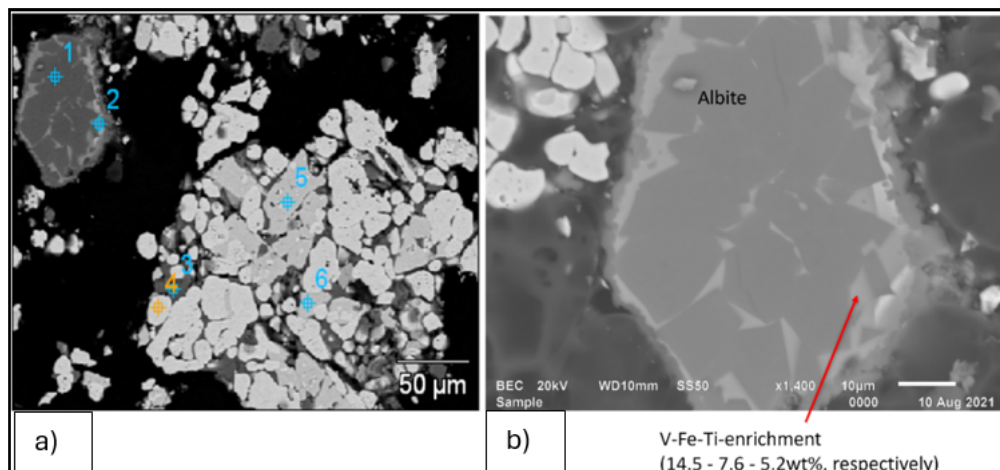


Figure 5.13a: VBT tailings SEM showing a titanium-enriched albite mineral labelled 1 and 2, and b) the enriched particle showing V-Fe-Ti enrichment

The elemental compositions of the albite, ilmenite, and hematite minerals are reported in **Table 5.20**. All particles exhibited a high oxygen content (around 57-63 %), suggesting a significant presence of oxides in the ore. The points analyzed showed that the tailings contained Ti, Fe, Al, and O, amongst other elements. The table highlights significant variations in the elemental composition between different particles. This indicates that the tailings were heterogeneous, containing a mixture of different minerals such as silicates (10.70-15.09 % Si) and iron/-titanium oxides (20.94-33.21 % Fe,

14.12-14.64 % Ti). This, in fact, supports the XRD results that showed that the tailings are predominantly a mixture of metal oxides (up to 99 % oxides).

Table 5.20: SEM-EDS elemental composition of different vanadium tailing particles

Atom %	Ti	V	Fe	Si	Al	Na	Mg	K	Ca	Cr	O
Base(29)_pt1	0.23		1.41	15.09	11.91	13.23		0.13	0.34		57.65
Base(29)_pt2	2.54	6.64	3.17	12.29	2.06	9.41		0.18	2.41		61.30
Base(29)_pt3	0.36		1.35	10.70	10.55	13.55			1.41		58.60
Base(29)_pt4	4.02		33.21		1.13		0.59			0.37	60.69
Base(29)_pt5	14.64		20.94		1.13		0.46				62.84
Base(29)_pt6	14.12		21.73		1.32						62.82

These SEM/EDS findings highlight the mineral's behaviour during processing and infer possible strategies for recovery methods of the elements present in the tailings (**Chapter 6**) after further analysis to determine the actual concentrations of the elements present.

5.8.4 XRF results

The XRF characterization of the tailings was performed according to the procedure described in **Section 5.4.4**. The XRF results for the major element oxides present in the sample and their percentage composition are reported in **Table 5.21** showing that the tailings were rich in the element of interest, Ti, as well as Fe, Si and Al in significant quantities, while the results in **Table 5.22** shows the composition of trace elements present in the tailing sample. The XRF results agree with the SEM-EDS point analysis, which showed significant quantities of these major elements. Higher percentages (11.89%) of Ti were obtained compared to the certificate values (7.50%). These results corroborate the findings of SEM-EDS, which showed a maximum of 14.64 % Ti in some particles.

Table 5.21: Elemental composition of major elements in the tailings

Major elements	Average composition (%)
TiO ₂	11.89
Fe ₂ O ₃	79.28
SiO ₂	2.72
Al ₂ O ₃	2.05
MnO	0.15
MgO	0.15
CaO	0.37
Na ₂ O	1.52
K ₂ O	0.02
P ₂ O ₅	0.04
LOI	0.38
Total	98.55

The results also showed that the tailings have a low percentage of silica (2.72 %). This finding seems to differ from the results reported by the SEM-EDS data, where abundant silica was observed. However, the XRF value was very close to the certified range, which was 1.2-2.0 %. This shows that XRF results are quite credible for the quantification of the tailings. Very interesting is the large amounts of Ti that are now present in the sample, which motivated this study to try and isolate the significant quantities of Ti that are present in the tailings after the initial removal of V from the VBT ore. The same trend is also reported for iron with a Fe_2O_3 concentration of 79 % compared to the 38 % of the VBT ore, which is easily explained by the close association of iron and titanium in the same ores, such as ilmenite.

The concentration of the trace elements reported in **Table 5.22** shows the presence of relatively high concentrations of vanadium and chromium and lower quantities of Co, Cu, Zn, and As. Considered as a minor element in the tailings, vanadium was still found in significant quantities, indicating that the vanadium-extraction process was not completely efficient. The relatively high vanadium concentrations are still high enough to develop a process to recover and isolate the vanadium from these tailings. The high Cr concentrations require careful consideration of the environmental management of the tailings during the beneficiation process and the final discard products.

Table 5.22: Elemental composition of trace elements in the tailings

Trace elements	Concentration (ppm)
V	2378
Sc	26
Cr	5815
Co	346
Ni	79
Cu	254
Zn	314
As	254
Rb	<1
Sr	22
Y	64
Zr	9
Nb	3
Ba	<17
Pb	<2
Th	105
U	<3

The calcine roasting-acid leaching (CRAL) process used in another study on the tailings obtained from an iron and steel plant located in Panzhihua, China, was analyzed, and the elemental composition was

determined as 9.27 % Ti, 37.93 % Fe, 15.00 % Mn, 1.87 % Al, 7.33 % Si, 11.54 % Cr, 9.36 % Ca, and 0.84 % V (Li *et al.*, 2023). These results show a similar trend in the concentrations of Ti, Fe, and V as in the current study.

5.8.5 Sequential extraction results

The tailings were treated according to the procedure in **Section 5.4.5**, and the provided sequential extraction results are reported in **Table 5.23**, which indicates the dissolution of various elements across different fractions and the total concentration for each element. The results indicate that titanium was found in all fractions with increasing concentrations towards the residual fraction (3 721 ppm), indicating the resistance of Ti-containing material to chemical manipulation.

Table 5.23: Elemental composition of different sequential extraction fractions of the tailings (ppm)

Element	F1	F2	F3	F4	Total
Ti	31	63	179	3721	3996
V	632	996	25	119	1774
Fe	877	1222	bdl	64724	66824
Si	4419	223	63	555	5261
Al	9656	401	0.17	615	10673
Mn	1	15	bdl	233	251
Ni	0.33	0.29	0.7	52	54
Co	2	1	0.51	178	182
Cu	149	0.79	0.31	20	170
Zn	0.77	0.25	6.65	97	105
Ca	1989	93	146	1050	3279
Sn	5	0.091	7	30	43
K	47	96	bdl	bdl	143
In	1	2	1	0.11	5
Pb	bdl	bdl	613	2260	2874
Li	bdl	2	4	bdl	6
Cr	4	0.41	bdl	271	27

Fraction 1 represents titanium that was easily extractable, possibly from soluble titanium-bearing minerals, while **Fraction 2** showed additional titanium associated with reducible iron oxides. More titanium was dissolved from reducible phases, while most of the titanium was found in residual **Fraction 4**. Fe showed a significant concentration in the residual fraction as well (64 724 ppm). This suggests that iron was predominantly bound and not easily available for extraction. Si was distributed

across all fractions, with a total concentration of 5 261 ppm. This suggests that it is present in both soluble and recalcitrant forms.

The total concentrations of the elements varied significantly from major to trace elements. Therefore, the results are plotted in two graphs to give a clear indication of their relative concentrations. Fe and Al with very high concentrations were plotted on their graph (**Figure 5.14**) while the rest were plotted together in **Figure 5.15**.

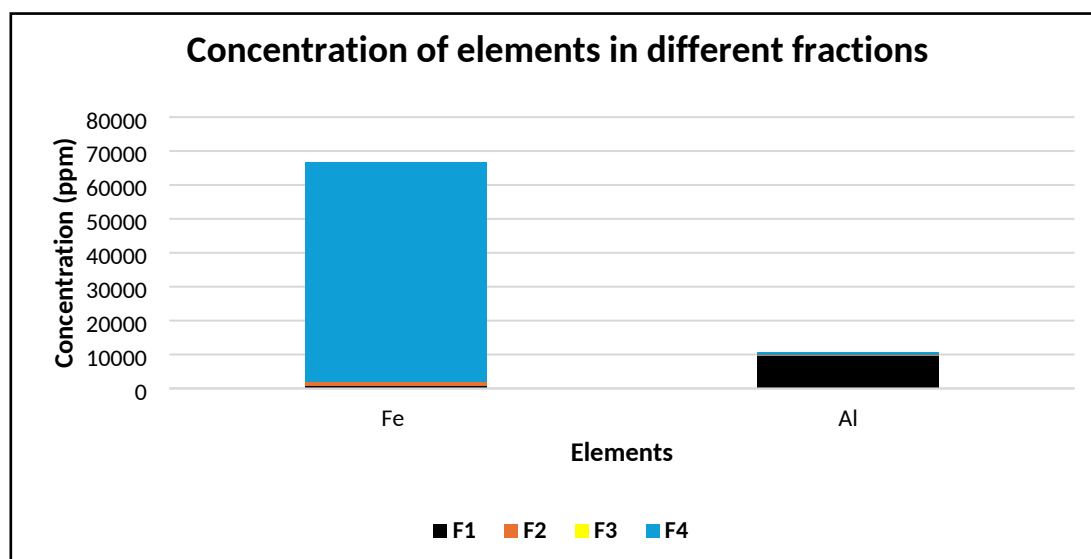


Figure 5.14: Plot of minor concentration of the elements found in the different fractions of the tailings sample

The sequential extraction results clearly indicate the partial dissolution of elements in the different fractions, while Fe and Ti were primarily found in the residual fraction, suggesting they are inert towards reactions at the milder conditions. This information indicates that the use of stronger acids for their complete dissolution is necessary. Conversely, elements like Al and V exhibited significant concentrations in the more mobile fractions, indicating potential bioavailability or ease of extraction. The presence of a high concentration of silica in **Fraction 1** is also supported by the SEM-EDS results, which showed that the tailings contained some newly formed siliceous compound (as a mineral intergrowth with hematite). The XRF results also showed a high percentage of Si (13.5 %).

Sequential extraction is not entirely a dissolution method for the tailings; therefore, complete dissolution of the tailings was required for easier comparison of the results from these non-destructive and semi-destructive techniques with the ICP results obtained after complete dissolution of the tailings, and later on, with the extraction experiments described in **Chapter 6**.

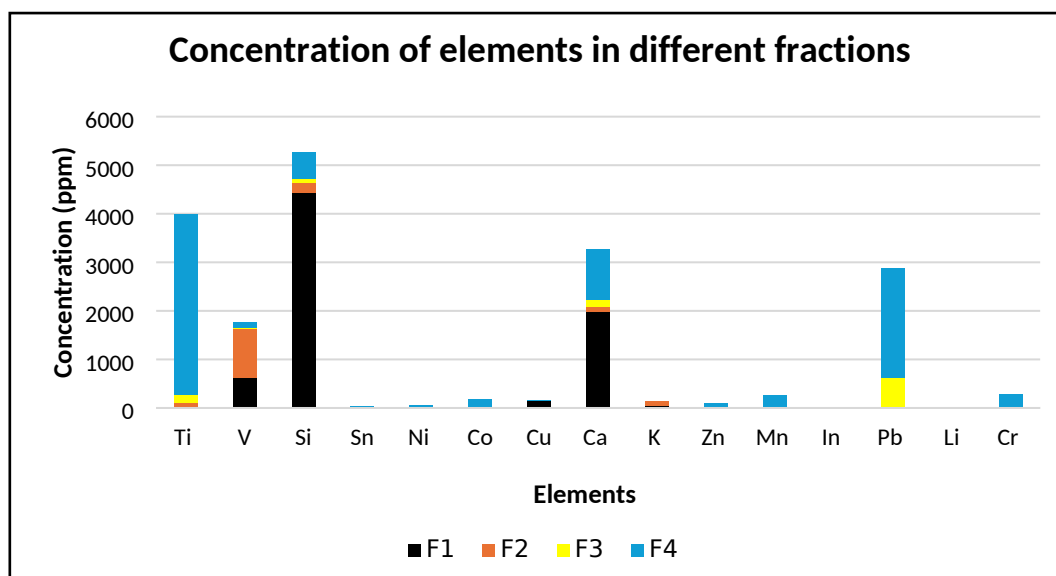


Figure 5.15: Plot of the major elemental concentration of the elements found in the different fractions of the tailings sample

5.8.6 Flux fusion results

The dissolution efficiencies of lithium metaborate, sodium sulphate, and ammonium sulphate were also evaluated to identify the most suitable salt for the total dissolution of the tailings. Once again, the reactions were performed in triplicate, and the results were used to calculate the standard deviations, which are reported in brackets.

5.8.6.1 LiBO₂ flux fusion

The tailings were treated according to the procedure in **Section 5.5.1**, and the ICP results for the elements detected in solution are reported in **Table 5.24**. Sample dissolution using lithium metaborate was deemed very successful, with visual inspection indicating no residue present after the final dissolution step of the melt obtained.

Table 5.24: Elemental composition of the tailings after LiBO₂ flux fusion

Element	Average % Composition
Ti	5.2(2)
V	0.425(7)
Fe	53(2)
Si	0.06(1)
Al	2.42(9)
Mn	0.396(9)
Ni	0.119(8)
Co	0.43(1)
Cu	0.104(8)
Zn	0.073(1)

LiBO₂ flux fusion successfully digested the tailings, and these ICP-OES results show significant quantities of Ti, Fe, and Al, with very little to no silica (0.06 %). These results were also used as the baseline to calculate the recovery of all reactions performed in this study, including leaching, separations, and isolation processes, as shown in **Chapter 6**, since the important element Ti results correlated with those from other techniques used. A comparison of the Ti, Fe, and V results obtained in this section (5.2, 53, and 0.425 % respectively) compares well with those reported on the certificate (7.5, 48.5, and 0.35 %). Notably, the very low percentage of Si is likely due to the presence of other elements in the tailings, which may have affected the absorption and emission of X-rays, potentially leading to an overestimation of the silicon content. Silicon may have existed in various mineral forms within the tailings; therefore, some silicates may not fully dissolve in the LiBO₂ flux, resulting in lower silicon recovery in the dissolution analysis.

5.8.6.2 (NH₄)₂SO₄ flux fusion

The tailings were treated according to the procedure in **Section 5.5.1**, and the ICP-OES results for the elements detected in solution are reported in **Table 5.25**. The tailings sample was barely dissolved by ammonium sulphate. Visual inspection of the contents in the crucible did not show the expected yellowish melt that is obtained when complete dissolution occurs. However, residues of the salt and the tailings were observed. The ICP results of the solution obtained confirm that the ammonium sulphate indeed could not dissolve the tailings, as was evident by the low elemental composition present in the melt. Only 0.246 % of Ti was dissolved.

Table 5.25: Elemental composition of the tailings after (NH₄)₂SO₄ flux fusion

Element	Average % Composition
Ti	0.246(2)
V	bdl
Fe	0.502(7)
Si	bdl
Al	2.821(2)
Mn	0
Ni	0.35(3)
Co	bdl
Cu	0.098(1)
Zn	bdl

bdl - below detection limit

5.8.6.3 Na₂SO₄ flux fusion

The tailings were treated according to the procedure in **Section 5.5.1**, and the ICP results for the elements detected in solution are reported in **Table 5.26**. Their composition results show that only 0.07 % Ti was dissolved from the tailings, which was significantly less than the initial amount present,

as no complete digestion was observed. The sodium sulphate digestion was thus ineffective in dissolving Ti, as most of the tailing's particles remained undissolved in the crucible; hence, the salt was discredited as a flux salt.

Table 5.26: Elemental composition of the tailings after Na₂SO₄ flux fusion

Element	Average % Composition
Ti	0.07(4)
V	bdl
Fe	0.27(9)
Si	bdl
Al	3.79(6)
Mn	0.003(4)
Ni	0.06(9)
Co	bdl
Cu	0.16(8)
Zn	bdl

bdl – below detection limit

In conclusion, the sulphates did not dissolve both the tailings and the VBT ore samples completely, possibly because the required lower temperatures to melt the salts were not high enough, or the salts were not acidic enough to facilitate the complete dissolution of the samples. Ammonium sulphate has a melting point of 235 °C and decomposes at 250 °C, while lithium metaborate, which successfully dissolved both samples, has a melting point of 1 000 °C and is regarded as an acidic flux medium.

5.8.7 Microwave digestion results

Dissolution efficiencies of two different acids, namely aqua regia and sulphuric acid, were evaluated to identify the most appropriate for the tailings sample. The reactions were also performed in triplicate, and the results were used to calculate the standard deviations and reported in brackets.

5.8.7.1 Microwave digestion using aqua regia as solvent

Tailings were treated according to the procedure in **Section 5.5.2**, and the ICP results for the elements detected in solution are reported in **Table 5.27**. Microwave sample digestion using aqua regia was very successful, with visual inspection as no residue was present at the end of the reaction.

A significant amount of Ti (1.41 %) was reported, and the high percentage of Fe (78.69 %) was possibly due to the loss of silica particles, which artificially increased the iron percentage relative to the percentages reported by other techniques. However, the Ti levels were not high enough for the method to be considered competitive with the LiBO₂ digestion or certificate results as a baseline for subsequent analysis, such as the VBT ore.

Table 5.27: Elemental composition of the tailings after microwave digestion using aqua regia

Element	Average % Composition
Ti	1.41(3)
V	0.331(1)
Fe	78.69(3)
Si	0.483(1)
Al	3.592(1)
Mn	0.49(6)
Ni	0.053(2)
Co	0.78(1)
Cu	0.01(2)
Zn	0.07(5)

5.8.7.2 Microwave digestion using sulphuric acid as solvent

Tailings were treated according to the procedure outlined in **Section 5.5.2**, and the ICP-OES results for the elements detected in solution are reported in **Table 5.28**. These results indicate that the microwave digestion using sulphuric acid as the medium was unsuccessful in dissolving significant amounts of the tailings sample. Undissolved solids were visually observed in the microwave vessels, indicating incomplete digestion, as evidenced by the very low Ti, V, and Fe percentages.

Table 5.28: Elemental composition of the tailings after microwave digestion using sulphuric acid.

Element	Average % Composition
Ti	0.38(1)
V	0.30(2)
Fe	0.393(1)
Si	3.491(1)
Al	24.6(5)
Mn	bdl
Ni	0.044(2)
Co	0.02(3)
Cu	0.053(2)
Zn	0.05(2)

bdl - below detection limit

The combination of high pressure and temperature may have enhanced the solubility of silica and Al in the sample, leading to a more effective dissolution of the silicates compared to the conditions used in LiBO₂ digestion, although complete dissolution of the tailings using sulphuric acid as a solvent was not achieved for the tailings.

5.8.8 Comparison of all the results of the tailings with different characterization techniques

Using multiple analytical methods to assess the composition of the tailings was crucial for obtaining a comprehensive and accurate understanding of the tailings' mineralogy and chemistry. Different analytical techniques can detect and quantify a range of elements, including major and trace elements. Some methods may be better suited for specific elements or compounds, ensuring a more complete analysis. Comparing results from different methods helps validate the findings, ensuring that the data collected is reliable, reproducible, and that accurate decisions and interpretations can be made. If one method yields unusual results, another method can help identify potential errors or anomalies, thereby reducing the likelihood of errors. Various techniques have different sensitivity levels, allowing for the detection of elements at varying concentrations. A compositional comparison of the different characterization methods was tabulated in **Table 5.29**.

The certified analysis reported only five elements, which were 7.5 % Ti, 0.35 % V, 48.50 % Fe, 2.25 % Al, and 1.60 % Si. These values are very close to those obtained in this study after lithium metaborate flux fusion and ICP-OES quantification. The highest concentration of Ti was reported in the certificate (7.50 %) and XRF (11.89 %) in this study, while the LiBO₂ flux fusion showed a slightly lower Ti value of 5.2 %.

Table 5.29: Comparison of the chemical content of the tailings using different analytical methods

Element	Certificate (%)	LiBO ₂ Flux fusion (%)	Aqua regia microwave digestion (%)	Sequential Extraction (%)	XRF (%)	SEM-EDS (%)
Ti	7.50	5.2(2)	1.41	0.40	11.89	0.23-14.64
V	0.35	0.425(7)	0.33	0.177	0.238	6.64
Fe	48.50	53(2)	78.69	6.682	79.28	1.35-33.21
Si	1.60	0.06(1)	0.48	0.526	2.72	10.70-15.09
Al	2.25	2.42(9)	3.59	1.067	2.05	1.13-11.91
Mn	-	0.396(9)	0.49	0.025	0.15	-
Ni	-	0.119(8)	0.05	0.005	0.007	-
Co	-	0.43(1)	0.78	0.018	0.03	-
Cu	-	0.104(8)	0.01	0.017	0.03	-
Zn	-	0.073(1)	0.07	0.011	0.01	-

Complete dissolution of the tailings was achieved using lithium metaborate salt, and this method was adopted for dissolution and ICP quantification in the remainder of this study due to the more realistic elemental analysis obtained, as well as the visually effective and completely digested samples, which motivated this decision.

The XRF results also correlated well with the lithium metaborate results. The small disparities in quantification between LiBO_2 flux fusion and XRF data may be due to the differing particle compositions of the mineral samples analyzed while using the two procedures.

Microwave digestion results were less reliable. The use of microwave digestion on industrial samples is possible, but it is not a widely used method on a large scale. The method was not only ineffective in dissolving the impurities present in the sample, but it might have produced false positive Fe quantities.

Sequential extraction gave 0.4 % titanium in the vanadium tailing sample, which was lower than the other methods used. SEM-EDS results showed that up to 25 % Ti can be extracted from the Ilmenite mineral and 3-9 % from hematite (in which it is contained as an impurity within the hematite structure) and up to 5 % from the silicates. Microwave digestion using aqua regia (78.69 %), followed closely by sequential extraction (66.82 %), gave high Fe percentages.

SEM-EDS results provided detailed microstructural information about the samples and semiquantitative composition of the particles, corroborated by the XRD results.

In conclusion, various techniques were employed to characterize the tailings. Lithium metaborate flux fusion emerged as the most reliable method for determining the bulk composition. This method provided results consistent with XRF analysis, indicating complete sample digestion and accurate representation of the overall elemental composition. SEM-EDS provided valuable microstructural insights. The discrepancies observed between different techniques underscore the importance of selecting methods that are tailored to the specific objectives of the analysis and considering the potential limitations inherent in each technique.

5.9 Comparison of chemical content in the VBT ore and the tailings

Finally, a comparison between the vanadium-bearing titanomagnetite ore and the tailings reveals significant differences in elemental composition, mineral phases, and overall physical properties. The results summarized in **Table 5.30** are the average of 3 replicates of lithium metaborate digestion. These results show that the VBT ore contains 3 % Ti, 0.6 % V, and 24.6 % Fe, while the tailings contain 5.2 % Ti, 0.43 % V, and 53 % Fe. These were used as the starting point for the study, providing a basis for comparison with all the VBT ore and tailings reactions that were performed (**Chapter 6**).

The certified values of the tailings compared well with the values obtained in this study, whereas the elemental analysis of the VBT ore differed more significantly. Sequential extraction revealed that Ti was present in all four fractions of the tailings, with the quantities increasing exponentially in each fraction. In contrast, the VBT ore contained Ti only in **Fraction 4**, and it had almost double the amount of Ti compared to its tailings. This means that the strong bonds of the original mineral phases were

broken down and produced Ti-rich compounds that were easier to dissolve. The results also showed that the residual fraction of the tailings contained a large quantity of iron. This was different for the VBT ore. **Fractions 2 and 3** were shown to contain mainly V as well as significant quantities of Ti. The significant amount of vanadium in the tailings, rather than the VBT ore, could be due to the vanadium extraction removing a large quantity of vanadium from the material.

Table 5.30: Comparison of the chemical content of the VBT ore and tailings

Element	VBT ore Certificate (%)	VBT ore LiBO ₂ flux fusion (%)	Tailings Certificate (%)	LiBO ₂ Flux fusion (%)
Ti	0.81	3.0(1)	7.50	5.2(2)
V	1.72	0.612(1)	0.35	0.425(7)
Fe	49.04	24.6(3)	48.50	53(2)
Si	4.12	1.10(8)	1.60	0.06(1)
Al	1.78	10.3(4)	2.25	2.42(9)
Mn	0.31	0.322(5)	-	0.396(9)
Ni	-	0.194(6)	-	0.119(8)
Co	-	0.261(4)	-	0.43(1)
Cu	-	0.114(3)	-	0.104(8)
Zn	1.28	0.066(5)	-	0.073(1)

Table 5.31: Comparison of the most significant differences and similarities between the VBT ore and its tailings

Property	VBT ore	Tailings
Colour	Grey	Black
Texture	Abrasive granular powder	Abrasive fine powder
Magnetism	Very magnetic	Generally non-magnetic
Bulk density	Heavier	Lighter
Mineral content	Silicates and oxides	Predominantly oxides
Main elements	Fe, Al, Ti and Si	Fe, Ti, Al, and V
Ti source	Ilmenite, magnetite, and clinopyroxene	Ilmenite, hematite and pseudobrookite

XRF revealed different elemental composition between the VBT ore and the tailings. The VBT ore contains almost half of the Ti and Fe found in the tailings. The difference in Ti and Fe is confirmed by SEM-EDS analysis, which shows that the tailings were enriched with Ti and Fe content during the beneficiation process. The decrease in the Si percentage also shows that the VBT ore was processed and removed Si, as the VBT ore contains 29.74 % while the tailings contain 2.72 %. The higher Fe

concentration is likely due to hematite (the non-magnetic portion) remaining in the waste after the beneficiation process, thereby forming a more substantial part of the tailings content.

The analysis techniques revealed distinct properties of the VBT ore and the tailings. A summary of these differences between the two samples is reported in **Table 5.31**.

5.10 Conclusion

Comparative analysis of vanadium-bearing titanomagnetite (VBT) ore and the tailings reveals critical insights into their physical and chemical properties, as well as their potential for titanium recovery. Both samples show significant amounts of Ti, Fe, V, and Si, albeit in differing proportions due to the beneficiation process. According to the complete dissolution results, the ore contains 3.0 % Ti, 0.612 % V, 24.6 % Fe, and 1.10 % Si, while the tailings contain 5.2 % Ti, 0.425 % V, 53 % Fe, and 0.06 % Si. XRF, XRD, and SEM-EDS allowed for the physical characterization and semi-quantification of the elements present in the sample. This will enable decisions to be made regarding the next steps in the beneficiation process. The results clearly showed that the tailings came from the VBT ore after the removal of vanadium from the magnetic portion of the VBT ore. The similarities in the composition and properties of both samples are thus valuable for their dissolution as they behave similarly in the same acids; hence, this is utilised in leaching the samples as reported in **Chapter 6**.

Chapter 6: Leaching and separation - Results and discussion

6.1 Introduction

After the samples were analysed qualitatively and quantitatively, it was important to attempt to selectively isolate the titanium by concentrating the Ti-bearing minerals into one portion using magnetic and gravity separation techniques. These techniques help provide more information on the nature of the different portions of the samples. If one portion contains all or most of the titanium minerals, then the other one can be discarded to improve the beneficiation process by reducing costs, as discussed in **Chapter 2**.

The next step in the beneficiation process is the leaching process, which requires the addition of different solvents to selectively leach as much titanium into solution as possible with minimum impurities. Information on the minerals present was provided using different dissolution and characterization techniques as discussed in **Chapter 5**, and it was used to decide how best to attempt leaching in this chapter and to concentrate the element of interest, titanium. The VBT ore and the tailings showed similar dissolution behaviour, hence similar leaching trends were expected in the methods used. Both samples contain significant amounts of Ti, as well as high levels of Fe impurity, and small amounts of V.

This chapter focuses on the separation of Ti using magnetic and gravity separation, leaching using various acids, alkalis, oxidizing and reducing agents, and roasting salts, as well as optimizing the best conditions, economically (using relatively less energy and chemicals) and environmentally friendly. Results from **Chapter 5** show that Ti, V, and Fe are significantly high in both samples; hence, the methods used are expected to selectively minimize the V and Fe impurities. This aligns with the study's objective to dissolve the sample, investigate, and evaluate different dissolution and leaching methods for Ti/V separation.

6.2 Reagents and equipment

The equipment, chemicals, and reagents described in **Chapter 5** and **Table 5.1**, in addition to those listed in **Table 6.1**, were used in the leaching and separation procedures described in this chapter.

Table 6.1: Chemicals used to conduct the experiments

Chemical	Formula	Purity	Supplier
Sodium hydrogen carbonate	NaHCO ₃	>97 %	
Sodium hydroxide	NaOH	97 %	Sigma Aldrich
Ammonium hydroxide	NH ₄ OH	33 %	Sigma Aldrich
Titanium trichloride	TiCl ₃	15 %	
Titanium dioxide	TiO ₂	99 %	Sigma Aldrich

6.3 Experimental procedures for magnetic and gravity separation of VBT ore and tailings

6.3.1 Magnetic Separation

A sample splitter was used to homogenize the sample by thoroughly mixing 100 g of the VBT ore sample. From the resulting sample, 20.00 g of the VBT ore sample was weighed and evenly spread on a smooth glass surface. A variable electromagnet was passed over the sample for 10 minutes, separating it into magnetic and non-magnetic portions. The electromagnet was thoroughly cleaned after removing all magnetic particles. The mass of each portion was determined and reported. These steps were performed in triplicate to obtain an average and reduce error. The same procedure was done for the tailings. The obtained portions were characterized using XRD and XRF, and then completely dissolved using LiBO₂. Afterward, they were analyzed using ICP-OES.

6.3.2 Gravity separation

A 100 g portion of the VBT ore sample was weighed and put on a Wilfley shaking table, and it was connected to the water supply. The inclination of the table was set to 5°, and the weighed sample was gradually and evenly fed onto the shaking table. A steady water flow was started to create a fluidized bed that aids in the separation process. The table mechanism was started for 5 minutes. The resulting two portions (heavy and light) were dried and weighed. The same procedure was performed on the tailings. The portions obtained were characterized using XRD and XRF, completely dissolved using LiBO₂, and analyzed using ICP-OES.

6.4 Experimental procedures for the leaching reactions of the VBT ore

6.4.1 Preliminary reactions

The preliminary leaching reactions of the samples were essential for determining the most effective acid or base for leaching Ti. This investigative step systematically evaluated different leaching agents, such as sulphuric acid, hydrochloric acid, nitric acid, aqua regia, sodium hydroxide, and ammonium

hydroxide, to assess their efficiency in dissolving target minerals and releasing the valuable element Ti. By conducting a series of controlled experiments, it was possible to identify optimal leaching conditions, including concentration, temperature, and reaction time, that maximize recovery while minimizing the dissolution of undesired components. These preliminary reactions were performed on the VBT ore only, with the assumption that both the ore and the process tailings behave similarly when different solvents are used (inferred from **Chapter 5** data) to conserve resources. The VBT ore was manually homogenized in preparation for the leaching reactions.

1.000 g samples of the VBT ore were quantitatively transferred to round-bottomed flasks containing 10 mL of 1 M solutions of each of the following acids and bases, HCl, H₂SO₄, HNO₃, aqua regia, NaOH, and NH₄OH at a reaction temperature of 90 °C, 600 rpm stirring speed and 3 hours reaction time. After the reactions were completed, the mixtures were filtered, and the leach liquor was diluted tenfold and analyzed with ICP-OES. Each acid or base reaction was performed in triplicate.

6.4.2 Optimization of leaching conditions

After establishing that sulphuric acid, hydrochloric acid, and aqua regia leached the most Ti into solution, the optimization of leaching reactions was a fundamental aspect of the Ti extraction processes that aimed to enhance the efficiency and effectiveness of Ti recovery from the VBT ores and tailings. This optimization involved systematically investigating acid concentration, reaction time, and temperature to determine the ideal conditions for maximizing the leaching of Ti. The most favourable conditions not only increased the yield of the Ti but also minimized the environmental impact and costs associated with the leaching process, resulting in improved resource utilization and the development of a more efficient and sustainable Ti leaching procedure, in line with the objectives of this study.

6.4.2.1 Temperature variation

0.200 g samples of the VBT ore were quantitatively transferred to round-bottomed flasks containing 20 mL of 0.1 M and 1 M solutions of each of HCl, H₂SO₄, and NaOH at room temperature, 90 °C, and 120 °C while stirring at 600 rpm for 3 hours. After the reactions were completed, the mixtures were filtered, and the leach liquor was diluted tenfold and analyzed with ICP-OES to determine Ti, Fe, and V. Each reaction was performed in triplicate, and the same procedure was followed for the tailings.

6.4.2.2 Concentration variation

1.000 g samples of the VBT ore were quantitatively transferred to round-bottomed flasks containing 10 mL of 0.5 M, 1 M, 3 M, 5 M, 7 M, and 10 M sulphuric acid at 90 °C and 600 rpm for 3 hours. After the reactions were completed, the mixtures were filtered, and the leach liquor was diluted (10 x) and

analyzed with ICP-OES to determine Ti, Fe, and V. Each reaction was performed in triplicate and the same was done for the tailings.

6.4.2.3 Time variation

5.000 g samples of the VBT ore were quantitatively transferred to round-bottomed flasks containing 50 mL, 1 M sulphuric acid at 90 °C and 600 rpm. 1.000 mL aliquots of the solution were taken after 5 minutes, 15 minutes, 45 minutes, 1 hour, 3 hours, 5 hours, 6 hours, 8 hours, 12 hours and 24 hours from the reaction mixture and analyzed with ICP-OES to determine Ti, Fe and V. Each reaction was performed in triplicate. The same was done for the process tailings.

6.4.2.4 Optimum reaction conditions

From the various optimization reactions, the optimal conditions were combined into a single reaction to monitor Ti recovery. 1.000 g samples of the VBT ore were quantitatively transferred to round-bottomed flasks containing 10 mL of 7 M sulphuric acid at 90 °C and 600 rpm for 5 hours. After the reactions were completed, the mixtures were filtered, and the leach liquor was diluted tenfold and analyzed with ICP-OES to determine Ti, Fe, and V. Each reaction was performed in triplicate. The same procedure was followed for the tailings.

6.4.2.5 Upscaling reactions

The applicability of the optimum leaching reaction in the industry was mimicked by using large-scale reactions. 5 g, 10 g, 50 g, 100 g and 250 g samples of the VBT ore were quantitatively transferred to round-bottomed flasks containing 50, 100, and 500 mL, respectively, of 7 M sulphuric acid at 90 °C and 600 rpm for 5 hours. After the reactions were completed, the mixtures were filtered, and the leach liquor was diluted (10x) and analyzed with ICP-OES. The residue was washed, dried, and flux fusion using LiBO_2 was performed. Each reaction was performed in triplicate, and the same was done for the process tailings.

6.4.3 Roasting reactions

Roasting is a crucial step in the leaching of metals. It involves heating the ore in the presence of air or other gases to transform the metal into a more soluble form. This process is often used to convert metal sulphides into oxides, which are more easily leached. In this case, it was used to attempt to improve the leaching of Ti.

0.0500 g of VBT ore was accurately weighed and placed in a platinum crucible with 1.000 g of sodium hydrogen carbonate. The mixture was thoroughly mixed and roasted in a furnace at 500 °C for 1 hour. The crucible was cooled to room temperature, and the product was washed with 100.0 mL distilled water and dried in an oven. Subsequently, flux fusion was performed on the roasted product.

0.0400 g of sample was accurately weighed and thoroughly mixed with 0.40 g of lithium metaborate in a platinum crucible and heated in a furnace at 1 000 °C for 1 hour. After the reaction, the crucible was cooled to room temperature, 25 mL of ultrapure water and 4 mL of concentrated nitric acid were added, and the mixture was stirred at 60 °C until the melt had completely dissolved. The solution was transferred to a 100.0 mL volumetric flask and diluted to the mark with ultra-pure water. The residue was washed, dried, and flux fusion using LiBO_2 was performed. The solutions were then analyzed using ICP-OES.

For sodium hydroxide roasting 0.100 g of the VBT ore was accurately weighed and thoroughly mixed with 0.3800 g of NaOH in a Pt crucible and heated in a furnace at 700 °C for 1 hour. After the reaction, the crucible was cooled to room temperature, 25 mL of ultrapure water and 4 mL of concentrated nitric acid were added, and the mixture was stirred at 60 °C until the melt had completely dissolved. The solution was transferred to a 100.0 mL volumetric flask and diluted to the mark with ultra-pure water. The residue was washed, dried, and flux fusion using LiBO_2 was performed (0.05 g of the residue was accurately weighed and mixed with 0.500 g of LiBO_2). The solutions were then analyzed using ICP-OES. The same procedure was applied to the vanadium process tailings.

6.4.4 Oxidation and reduction reactions

Incorporating oxidizing agents into leaching processes significantly advances the optimization of metal extraction from ores and mineral samples. Oxidizing agents, such as hydrogen peroxide or ferric ions, can enhance the dissolution of metals by facilitating the oxidation of metal ions and promoting the breakdown of complex minerals. This enhancement can lead to increased leaching rates and improved recovery efficiencies, particularly for metals that may be less soluble under standard conditions. By evaluating the effects of various oxidizing agents on leaching reactions, it is possible to identify optimal concentrations and conditions that not only improve Ti extraction but also mitigate the formation of undesirable by-products. Hydrogen peroxide (oxidizing agent) was added to the sulphuric acid leaching reactions to attempt to increase the amount of titanium leached into the solution.

The enhancement of leaching reactions can significantly improve the efficiency and yield of metal recovery by adding reducing agents, by altering the oxidation states of specific metal ions, facilitating their solubility and subsequent extraction. By employing reducing agents, such as sodium bisulphite sulphur dioxide, and hydrogen sulphide, the leaching process becomes more effective, particularly for minerals that are otherwise difficult to dissolve.

6.4.4.1 Addition of hydrogen peroxide to H_2SO_4 leaching

5.000 g samples of the VBT ore were quantitatively transferred to round-bottomed flasks containing 50 mL of 1 M sulphuric acid and different ratios of hydrogen peroxide at 90 °C and 600 rpm. Reactions

with hydrogen peroxide were carried out at five different ratios of sample: hydrogen peroxide, 1:1, 1:1.2, 1:1.4, 1:1.6 and 1:2 ratios. After the reactions were completed, the mixtures were filtered, and the leach liquor was diluted (10 x) and analyzed with ICP-OES to determine Ti, Fe, and V. Lower temperatures were also used in the 1:2 sample for the hydrogen peroxide reaction. A 5g sample of the VBT ore reacted with 50 mL of 1 M sulphuric acid at 50 °C and 600 rpm at a ratio of 1:2 of sample: hydrogen peroxide.

6.4.4.2 Sodium bisulphite in H₂SO₄ leaching

0.5000 g of the tailings were weighed and mixed with 0.5000 g of sodium bisulphite reducing agent in 50 mL of 1 M sulphuric acid. The reaction was conducted at 90 °C for 3 hours at 600 rpm. ICP-OES was used to analyze the sample.

6.4.4.3 Sodium bisulphite in H₂SO₄ leaching of pure titanium dioxide

0.5000 g of the pure titanium dioxide was weighed and mixed with 0.5000 g of sodium bisulphite reducing agent in 50 mL of 1 M sulphuric acid. The reaction was conducted at 90 °C for 3 hours at 600 rpm. ICP-OES was used to analyze the sample. This was done with the TiO₂ salt to see if any titanium is released into the solution when a reducing agent is present.

6.5 Results and discussion of VBT ore results

The next step in the investigation was to examine several approaches that could provide information on the chemical reactivity of the different elements in the samples. To successfully achieve this, firstly, magnetic and gravity separation were performed to attempt to concentrate the Ti-bearing minerals into one portion. The obtained portions were characterized using XRD and XRF, and these results were compared with those of raw VBT ore to assess the effectiveness of the two techniques. Secondly, preliminary acid and alkali reaction conditions were used to identify the best acid or alkali that leaches the highest concentration of Ti while being economically feasible. The insights gained from the preliminary analysis not only guided the selection of leaching agents but also contributed to the development of a more sustainable and economically viable extraction process for the low-grade Ti mineral ore. The solvent was then used in the third step to optimize all reaction conditions, including temperature, concentration, and time. These optimum conditions were combined into a single procedure to leach as much titanium as possible. Since this study is industrially applicable, large-scale reactions were performed to see if the Ti leaching efficiency increases with increasing quantities. Other factors, such as using a roasting salt, oxidizing, and reducing agents, were investigated to determine their effect on leaching efficiency.

6.5.1 Magnetic separation

The magnetic separation procedure was performed according to the description in **Section 6.3.1**. The masses of the different portions obtained from the magnetic separation, as well as the XRD, XRF, and ICP-OES results, were evaluated and compared with the original sample to note any significant differences that would warrant the effectiveness of the magnetic separation step.

6.5.1.1 Mass results

The mass results reported in the pie chart in **Figure 6.1** show the proportion of different categories of the magnetic separation that 79.55 % of the VBT ore is magnetic. Due to the nature of the sample, 5.2 % of the sample was lost due to adhesion to the electromagnet surfaces or unexplained losses.

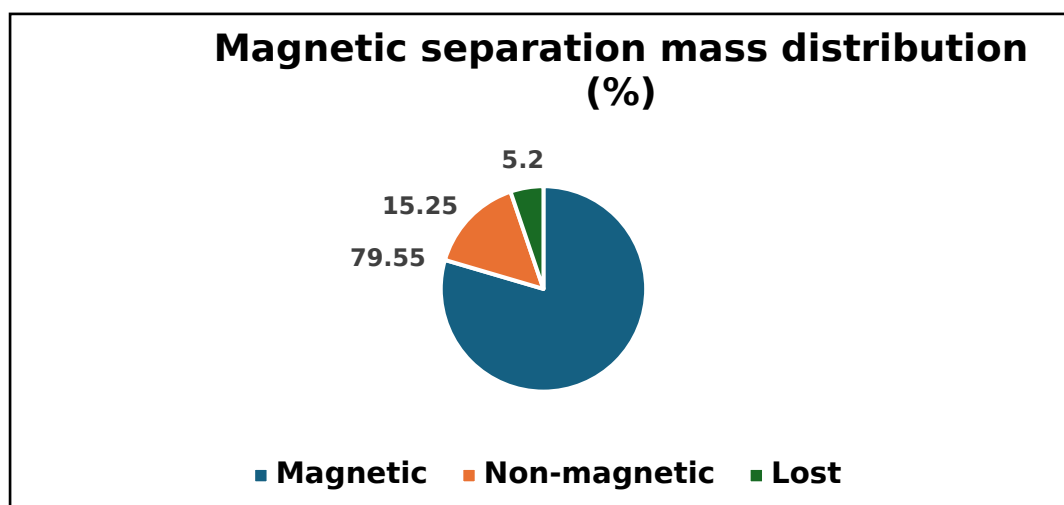


Figure 6.1: VBT ore mass distribution percentages of magnetic separation portions

The mass results led to the investigation using XRD to identify the minerals present and to estimate their approximate quantities.

6.5.1.2 XRD results

XRD analysis was employed to investigate the mineral composition and structural changes in the samples before and after magnetic separation. This provides valuable insights into the effectiveness of the separation process in enriching specific mineral phases, while also revealing any potential alterations in the crystal structures of the minerals.

The magnetic susceptibility and XRD analysis of the VBT ore were analysed according to the procedures described in **Section 6.3.1** and **Chapter 5, Section 5.4.2**, respectively. The mineral composition results obtained are compared in **Table 6.2**. It shows that the compositions of the VBT ore's magnetic and non-magnetic portions are similar to those of the raw VBT ore, which comprises plagioclase, magnetite, ilmenite, chlorite, and clinopyroxene.

Table 6.2: XRD mineral composition of the VBT ore magnetic and non-magnetic portions (wt. %)

Portion	Plagioclase	Chlorite	Amphibole	Clinopyroxene	Magnetite	Ilmenite
Magnetic	62	18	8		7	5
Non-magnetic	64	18	8	4	2	4

These results also align with the earlier XRD observations, which revealed that the VBT ore contains magnetite, a highly magnetic mineral, with a higher percentage found in the magnetic portion. This was supported by the mass results, which reported that the VBT ore was very magnetic.

The magnetic and non-magnetic portions contained equal or almost equal percentages of all the minerals present in the VBT ore sample, except magnetite, which is more than triple in the magnetic portion than in the non-magnetic portion. The percentage of magnetite in the non-magnetic portion (2 %) is likely due to multimineral particles whose portion of magnetite was not enough to carry the weight of the entire non-magnetic particle. It could also be because the magnetite was bound to non-magnetic minerals (polymineral particles) that forced it to remain in the non-magnetic portion if the magnetite was not enough to carry the weight of the entire, and mostly non-magnetic, particle. This shows that magnetic separation was not entirely successful in separating the VBT ore.

Comparison of raw VBT ore and VBT ore magnetic portion

A comparison of the raw VBT ore and the magnetic portions spectra is illustrated in **Figure 6.2**. The main peak of plagioclase (silicate) is much smaller in the magnetic fraction of the VBT ore than in the raw ore sample. This means that some silicates have been removed during the magnetic separation process. The same also occurs with the peaks of other silicates detected, such as clinopyroxenes and chlorites, as well as the peaks of some oxide minerals, including ilmenite. As expected, the magnetic fraction exhibits magnetite peaks that are higher than those of the raw VBT ore.

Magnetic separation was not entirely effective. Although there is an increase of magnetic material in the magnetic fraction, the overall concentration of non-magnetic minerals in the magnetic portion is still unacceptably high to regard this method as a successful separation method.

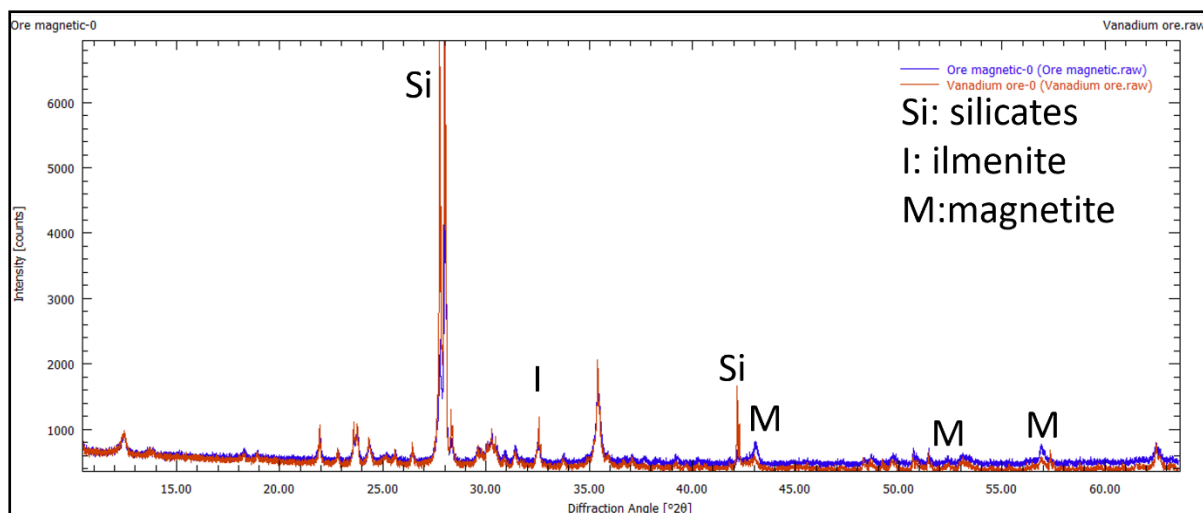


Figure 6.2: XRD comparison of raw VBT ore and VBT ore magnetic portion

Comparison of raw VBT ore and VBT ore non-magnetic portions

The diffractogram in **Figure 6.3** shows the pictorial comparison of the raw VBT and its non-magnetic portion. The main peak of plagioclase (silicate) is longer in the non-magnetic fraction of the VBT ore than in the raw ore sample. This shows that the silicates have been concentrated in the non-magnetic fraction. The same happens with the peaks of other silicates detected, such as clinopyroxenes and chlorites. The peaks for magnetite are lower in the non-magnetic fraction. Although magnetic separation was not entirely effective, reduction of magnetic minerals in the non-magnetic fraction is evident and congruent with the increase of magnetite in the magnetic fraction previously described.

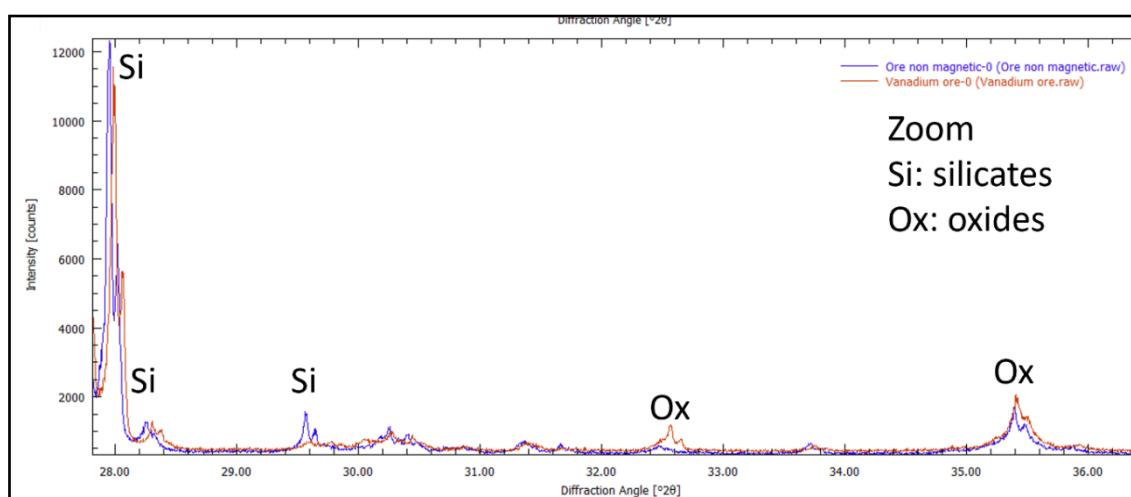


Figure 6.3: XRD comparison of raw VBT and VBT ore non-magnetic portion

6.5.1.3 XRF results

The XRF of the magnetic separation results of the major elements are reported in **Table 6.3**, and the trace elements in **Table 6.4**. The magnetic portion was shown to contain 7.90 % Ti while the non-

magnetic portion contained 2.17 %. The method was not entirely successful because the Ti levels in the non-magnetic portion are still too high to consider the method practical, since the Ti concentration in the VBT ore was originally low.

Table 6.3: Major elemental composition of the VBT ore, magnetic and non-magnetic portions

Major elements	Magnetic portion concentration (%)	Non-magnetic portion concentration (%)
TiO ₂	7.90	2.17
Fe ₂ O ₃	43.19	16.08
SiO ₂	24.87	43.17
Al ₂ O ₃	14.20	20.99
MnO	0.14	0.11
MgO	1.70	2.59
CaO	6.47	10.74
Na ₂ O	1.58	2.61
K ₂ O	0.13	0.22
P ₂ O ₅	0.04	0.04
LOI	-0.29	0.72
Total	99.93	99.43

Table 6.4: Trace elemental composition of the VBT ore, magnetic and non-magnetic portions

Trace elements	Magnetic portion concentration (ppm)	Non-magnetic portion concentration (ppm)
Sc	25	17
V	3493	662
Cr	3607	99
Co	220	66
Ni	98	72
Cu	307	187
Zn	194	77
As	85	2
Rb	3	4
Sr	152	352
Y	23	2
Zr	10	9
Nb	2	3
Ba	60	127
Pb	<2	<2
Th	34	<3
U	<3	<3

The magnetic portion also contained V and Cr and significant quantities of Co, Cu, and Zn (**Table 6.4**). The non-magnetic portion contained Si, Al, Fe, and Ca (**Table 6.3**). This implies that magnetic

separation was able to maintain the silicates, most probably Al-silicates, in the non-magnetic fraction, although some Si was detected in the magnetic fraction (24.9 %), probably due to the presence of polymineralic particles.

The magnetic portion (trace elements) of the VBT ore contains significant amounts of V, which is why the ore is used in the mine as a source of V. The substantial difference in V concentration between the two portions highlights the potential for vanadium recovery from the magnetic component of the VBT ore, as it is present in a much more concentrated form. The data also suggests that magnetic separation techniques could be highly effective for concentrating vanadium and chromium from the VBT ore, as these elements are primarily located in the magnetic fraction.

6.5.1.4 ICP analysis of magnetic separation portions after LiBO₂ flux fusion

The results obtained from the analysis are shown in **Table 6.5**. A visual inspection of the crucible revealed total dissolution in both portions, as indicated by the yellowish melt that completely dissolved in water.

Table 6.5: Elemental composition of the VBT mineral ore after LiBO₂ flux fusion on the magnetic and non-magnetic portions

Element	Magnetic portion average % composition	Non-magnetic portion average % composition
Ti	2.76(2)	3.9(1)
V	2.15(3)	bdl
Fe	72.1(4)	27.1(6)
Si	2.82(1)	9.01(5)
Al	3.3(5)	53.9(1)
Mn	1.14(9)	0.42(1)
Ni	0.03(1)	0.076(3)
Co	0.84(9)	0.049(4)
Cu	0.34(6)	0.274(4)
Zn	0.02(2)	bdl

bdl - below detection limit

A significant percentage of Ti was found in the magnetic portion of the VBT ore (2.76 %). This indicates that magnetic separation is reasonably practical for concentrating the titanium into a single portion of the material. However, this was almost half of the total Ti present in the tailings therefore the magnetic separation step was deemed unnecessary. The non-magnetic portion contained significant amounts of Ti (3.9 %).

Magnetic separation mass results showed that almost 80 % of the VBT ore sample was magnetic. However, XRD analysis of the magnetic separation showed that percentages of both magnetic and non-magnetic elements present in the VBT ore magnetic portion compared to the non-magnetic

portion exhibited a significant difference, indicating that this method might be inadequate for concentrating certain elements in any of the fractions. Plagioclase, chlorite, and amphibole are non-magnetic and were not expected to be present in the magnetic portion of the ore. However, as expected, more magnetite was found in the magnetic portion than in the non-magnetic portion. This implies the possible partial isolation of the titanium-bearing mineral into one portion, and with further dissolution of these portions, could give a better picture of the sample and hence more reliable elemental values. LiBO_2 digestion of this portion yielded high titanium recoveries, but not sufficiently high to justify the extra step, as the non-magnetic portion still contained significant amounts of Ti. The Ti in the sample portion may occur as an impurity in the magnetite, possibly replacing an Fe atom in the structure. For magnetic separation to be improved, it is recommended to grind the particles into finer particles of less than 10 μm to reduce the amount of polymineral particles and prevent non-magnetic minerals from being “attracted” to the magnetic field. The magnetic separation and subsequent LiBO_2 dissolution results demonstrated the feasibility of utilizing magnetic separation to enhance the purity of the sample and to concentrate the elemental-rich phases obtained before the flux fusion process. This has the potential to produce a more efficient and environmentally friendly approach to elemental recovery. However, since the Ti percentages in the VBT ore are already low (3 %), it is not strategically and practically sound to discard the non-magnetic portion, as it contains significant amounts of titanium. Therefore, further grinding the ore may improve the process and yield better separation.

6.5.2 Gravity separation

This is a cost-effective, environmentally friendly, and efficient method for enhancing the recovery of valuable minerals in ore beneficiation when there is a sufficient difference in specific gravity between valuable minerals and gangue. The gravity separation procedure was performed according to the description in **Section 6.3.2**. The different fractions obtained were weighed, dissolved using LiBO_2 , and analysed by XRD, XRF, and ICP-OES.

6.5.2.1 Mass results

The gravity separation of the ore resulted in 81.55 % of the ore in the heavy fraction, while 15.1 % was in the light fraction (**Figure 6.4**). The density of the sample was previously reported as 3.2-3.5 g/cm^3 , showing that it was a relatively heavy sample. Only 3.35 % of the sample was lost during the procedure. The Ti minerals are expected to accumulate preferentially in the heavy fraction, while silicate minerals should appear in the light fraction. To assess the effectiveness of the gravity separation, both heavy and light fractions were analysed.

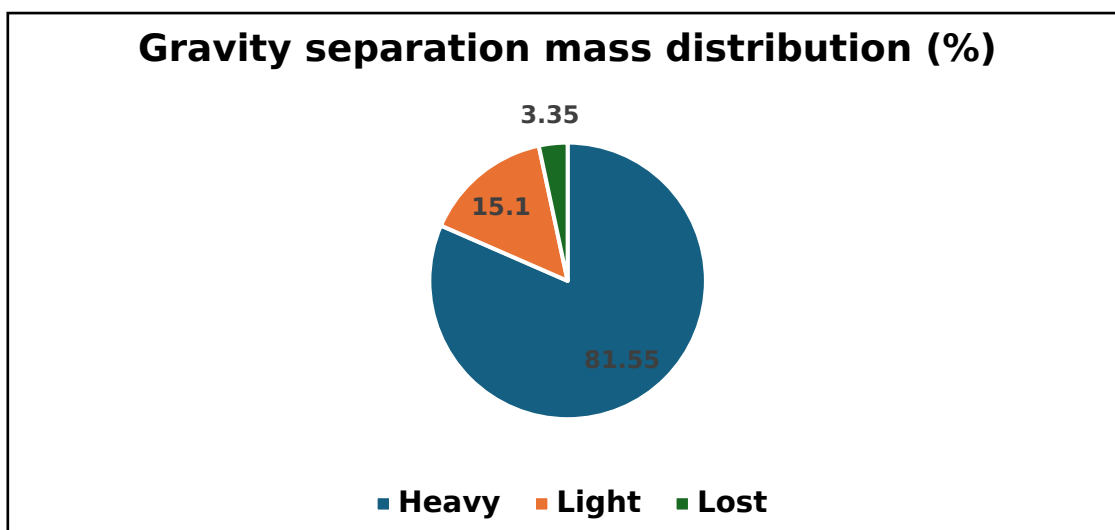


Figure 6.4: VBT ore mass distribution percentages of gravity separation portions

6.5.2.2 XRD results

The XRD mineral composition results obtained from the preliminary analysis of the gravity separation portions are reported in **Table 6.6**. The heavy portion of the VBT sample shows a significant presence of plagioclase (35 wt. %) and magnetite (24 wt. %), with specific gravities of 2.67 and 5.17 g/cm³, respectively. The dominance of plagioclase in this fraction gives the first insight into the inefficiency of the gravity separation for VBT ore. The light portion contained a higher percentage of plagioclase (40 wt. %) and magnetite (38 wt. %) (specific gravity of 4.7 g/cm³). The presence of heavy minerals in the light fraction corroborates the inefficiency of this separation process. Clinopyroxene was present in both portions, but it was more abundant in the light portion (22 wt. %) compared to the heavy portion (15 wt. %). Kaolinite and amphibole were primarily found in the heavy portion (6 and 8 wt. %, respectively).

Table 6.6: XRD mineral composition of VBT ore heavy and light portions (wt. %)

Portion	Plagioclase	Clinopyroxene	Kaolinite	Amphibole	Magnetite	Ilmenite
Heavy	35	15	6	8	24	12
Light	40	22			38	

Gravity separation did not successfully separate the Ti-oxide minerals because similar percentages of the plagioclase, clinopyroxene and magnetite minerals were found in both portions. The light portion contained only 38 wt. % magnetite with no ilmenite present, while the heavy portion contained 24 wt. % and 12 wt. % which is a total of 36 wt. % (almost equal to 38 wt. %). Kaolinite was not observed in the VBT ore sample XRD, possibly because the sample was not representative enough (homogeneity) to show the mineral, or the quantities were too low. Instrument limitations (sensitivity,

resolution, calibration) could be the reason, as the XRD instrument may not have been sensitive enough to detect low-abundance minerals. Its lower resolution may have struggled to differentiate between closely spaced peaks, leading to the omission of certain minerals. However, it was concentrated in the heavy portion together with amphibole or it may be amorphous.

6.5.2.3 XRF results

Table 6.7: Major elemental composition of the VBT ore, heavy and light portions

Major element	Heavy portion concentration (%)	Light portion concentration (%)
TiO ₂	4.84	1.15
Fe ₂ O ₃	43.70	18.71
SiO ₂	27.10	42.83
Al ₂ O ₃	12.09	21.01
MnO	0.16	0.09
MgO	1.99	1.77
CaO	7.38	9.65
Na ₂ O	1.59	2.60
K ₂ O	0.13	0.21
P ₂ O ₅	0.04	0.04
LOI	-0.34	1.60
Total	98.68	99.66

Table 6.8: Trace elemental composition of the heavy portion of VBT ore

Trace element	Heavy portion concentration (ppm)	Light portion concentration (ppm)
Sc	33	11
V	5273	701
Cr	4035	87
Co	200	71
Ni	107	82
Cu	178	178
Zn	194	75
As	74	3
Rb	3	3
Sr	177	377
Y	23	3
Zr	11	10
Nb	2	1
Ba	42	117
Pb	<2	<2
Th	35	<2
U	4	<2

The XRF major elements results of the heavy and light portions are reported in **Table 6.7**, and the trace elements in **Table 6.8**. 4.84 % Ti was found in the magnetic portion and 1.15 % in the non-magnetic portion. This difference was insufficient to consider the method effective, as the Ti percentages are already low. A lower percentage in the non-magnetic portion would be desirable.

The high concentration of vanadium in the heavy portion (5 273 ppm) versus the light portion (701 ppm) shows that gravity separation effectively concentrated the vanadium into one portion better compared to the magnetic separation (3 493 ppm).

6.5.2.4 ICP analysis of the gravity separation portions after LiBO₂ flux fusion

Complete dissolution of the ore was performed using LiBO₂ flux fusion digestion on each fraction obtained from the gravity separation procedure to assess if it could effectively separate heavier minerals from lighter ones and if any of the portions contained more titanium than the other. The VBT mineral ore was treated according to the procedure in **Chapter 5, Section 6.3.2**, and the ICP results for the elements detected in solution after LiBO₂ flux fusion digestion are reported in **Table 6.9**.

Table 6.9: Elemental composition of the VBT mineral ore after LiBO₂ flux fusion on the heavy and light portion composition

Element	Heavy portion average % composition	Light portion average % composition
Ti	8.9(2)	0.0476(3)
V	bdl	bdl
Fe	43.1(5)	0.277(3)
Al	41.3(6)	3.7(4)
Mn	0.52(6)	0.003(4)
Ni	0.03(1)	0.065(1)
Co	0.14(5)	bdl
Cu	0.21(1)	0.16(1)
Zn	bdl	bdl
Si	5.9(1)	bdl
bdl - below detection limit		

The increase of Ti in the heavy fraction from the initial 5.2 % (concentration of Ti in the raw VBT ore sample) to 8.9 %, together with the low Ti concentration in the light fraction (0.05 %), suggests that the gravity separation effectively accumulated the Ti-bearing minerals and Ti-mineral in the heavy fraction. However, the results obtained here differ from the XRF analysis (4.8 % Ti in heavy fraction). This might be due to the heterogeneity of the sample or the inefficiency of the analytical methods due to interferences, background noise, or sensitivity of the instruments.

6.5.3 Preliminary acid and alkali leaching

Preliminary acid leaching, often employing sulphuric acid, is commonly used for ores containing oxides, sulphides, or carbonates. In contrast, alkali leaching, which utilises solutions such as sodium hydroxide, is particularly effective for ores rich in aluminium or other amphoteric metals. The effectiveness of these techniques depends on factors such as ore composition, particle size, and solution concentration. Carefully controlling the leaching parameters helps maximize the dissolution of desired minerals while minimizing the dissolution of unwanted components, leading to a more efficient and environmentally friendly extraction process.

6.5.3.1 Acid leaching

The leaching of the VBT ore was performed according to the procedure described in **Section 6.4.1**, and analyzed using ICP-OES as described in **Chapter 4, Section 4.7**. The results reported in **Table 6.10** show that all the acids generally leach very high Ti percentages into solution, accompanied by smaller impurity concentrations.

Table 6.10: Elemental recovery from the VBT ore after leaching with different acids (%)

Element	HCl	HNO ₃	H ₂ SO ₄	Aqua regia
Ti	70.71(2)	90.32(1)	97.77	108.29(1)
V	21.44(1)	37.85(2)	37.79(2)	10.60(1)
Fe	25.87(2)	47.14(1)	21.21(1)	11.20(1)
Al	11.61(1)	45.41(2)	24.27(3)	44.96(4)
Mn	11.59(1)	44.97(2)	26.49(1)	53.87(2)
Ni	4.67(3)	13.19(1)	10.18(3)	19.82(4)
Co	16.70(1)	34.91(2)	14.29(1)	93.96(1)
Cu	17.28(1)	51.05(3)	15.66(4)	39.37(1)
Zn	9.77(2)	17.99(1)	20.55(1)	35.86(2)
Si	12.49(2)	23.24(2)	bdl	bdl

HCl, HNO₃, H₂SO₄, and Aqua regia removed substantial amounts of titanium. These are strong acids that can remove titanium from the mineral in which it is encapsulated. The highest concentration of Ti was found after leaching with aqua regia, followed by H₂SO₄, HNO₃, and HCl. This information was pivotal in deciding the acid suitable for the leaching of Ti. H₂SO₄ was chosen because, although aqua regia leached more titanium, it is less eco-friendly and economical than H₂SO₄, which yielded a reasonable high percentage of Ti. The difference between the two acids is not that significant. This data was also supported by the characterization data in **Chapter 5**, which showed that aqua regia leaching of the residual fraction gave high percentages of Ti, as well as other undesirable elements. Reactions that removed high percentages of titanium also leached Fe. It is important to separate the

two. Aqua regia leached high amounts of titanium into the solution. However, it exhibited high co-leaching of impurities, making it difficult to use this acid for optimization purposes.

In one study, ammonium chloride pressurized pyrolysis and low-concentration acid leaching were performed on VBT ore. Extraction of vanadium, titanium, and iron reached 95.1, 1.2, and 92.5 %, respectively, after leaching in 61.7 M HCl solution at 90 °C for 3.5 hours (Bian *et al.*, 2021). High concentrations of hydrochloric acid can enhance the extraction efficiency of metals, particularly in complex ores like VBT. However, such high concentrations may also require careful handling and consideration of the environmental impact. In this study, only 70.7 % of Ti was leached, but the HCl used for it was diluted to 1 M. The difference in yield is not as big as the difference in acid concentration, which means that using HCl more concentrated (above 1 M, but still below 61.7 M) in the VBT ore could achieve a similar yield.

6.5.3.2 Alkali leaching

The leaching of the VBT ore was performed according to the procedure described in **Section 6.4.1** and analyzed using ICP-OES as described in **Chapter 4, Section 4.7**. The results reported in **Table 6.11** show that the bases were not efficient in leaching Ti into solution, as shown by the low Ti levels in both NaOH and NH₄OH.

Table 6.11: Elemental recovery of the VBT ore after leaching with different bases

Element	NH ₄ OH (%)	NaOH (%)
Ti	0.44(2)	1.45(3)
V	0.14(1)	2.47(4)
Fe	0.02(1)	0.19(2)
Al	0.02(5)	10.09(2)
Mn	0.40(1)	0.57(4)
Ni	1.11(5)	1.12(2)
Co	0.22(8)	0.31(9)
Cu	1.40(8)	3.67(3)
Zn	bdl	2.79(1)
Si	2.17(1)	86.56(2)

NaOH and NH₄OH leached only 0.44 % and 1.45 %, respectively, of the titanium from the VBT ore. This indicates that they are not very effective at dissolving titanium. Hence, they were not chosen as the primary solvent for Ti leaching from the VBT ore. Interesting to note is the high Si content (86.56 %) leached by NaOH compared to NH₄OH (2.17 %). This significant difference is because NaOH reacts with silica to form soluble silicate compounds, allowing for the dissolution of silicon from the ore (Rao *et al.*, 2022). Ammonium hydroxide, being a weaker base, is less effective at reacting with silica. Therefore, alkali leaching is not suitable to extract Ti from oxide minerals but could be used as a

separation step to remove the silicates, leaving the Ti in the solid (undissolved) fraction, although the loss of Ti needs to be taken into account (0.44 % and 1.45 % for NaOH and NH₄OH experiments, respectively).

6.5.4 Optimisation of leaching conditions

Optimising leaching conditions is essential for enhancing the efficiency and effectiveness of ore processing. This process involves adjusting various parameters to maximise the recovery of valuable metals while minimising costs and environmental impact.

6.5.4.1 Temperature variation

The optimisation process was performed according to **Section 6.4.2**, and the results are presented in **Figure 6.5**. Increasing the temperature generally enhances the reaction rates, leading to higher leaching efficiencies. However, it is essential to strike a balance between temperature, energy costs, and the stability of the leaching agent. **Table 6.12** shows the recovery of the elements in dilute HCl and NaOH (**Table 6.13**) and how temperature affects the recovery.

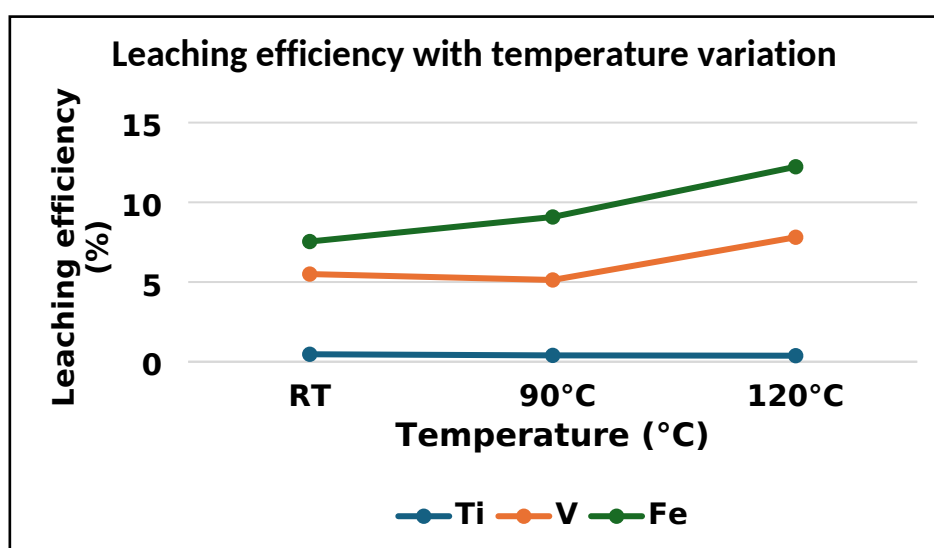


Figure 6.5: Recovery of elements in 1 M sulphuric acid at room temperature, 90 °C and 120 °C

Generally, increasing the reaction temperature from room temperature to 90 °C increases the amount of titanium, as well as other impurities, that are leached into the solution. This is because the rate of reaction increases significantly with an increase in temperature. It would be expected that further increasing the temperature to 120 °C would increase the amount of titanium in the solution even more.

Table 6.12: Recovery of elements in 0.1 M Hydrochloric acid at different temperatures

Element	0.1M HCl r.t (%)	0.1M HCl 90°C (%)	0.1 HCl 120°C (%)
Ti	0.41(2)	0.34(2)	0.34(3)
V	5.98(2)	6.01(5)	6.90(2)
Fe	1.45(4)	2.17(3)	2.53(5)
Al	0.96(6)	1.20(1)	1.35(1)
Mn	9.41(2)	11.59(1)	11.02(2)
Ni	35.64(2)	39.28(2)	38.71(7)
Co	18.19(2)	19.78(2)	18.94(2)
Cu	58.02(3)	55.83(3)	53.78(2)
Zn	1.79(3)	10.18(2)	2.83(3)
Si	3.10(2)	3.07(4)	3.04(8)

Table 6.13: Recovery of elements in 0.1 M Sodium hydroxide at different temperatures.

Element	0.1M NaOH r.t	0.1M NaOH 90°C	0.1M NaOH 120°C
Ti	0.35(1)	0.39(4)	0.39(2)
V	4.88(2)	4.98(3)	5.50(3)
Fe	0.16(5)	0.02(1)	0.02(1)
Al	0.51(1)	0.45(2)	0.64(2)
Mn	5.43(9)	4.44(2)	4.36(6)
Ni	35.95(1)	33.84(6)	34.10(1)
Co	16.74(1)	64.57(1)	15.10(3)
Cu	50.45(2)	45.36(2)	45.46(2)
Zn	bdl	bdl	bdl
Si	3.30(2)	3.18(1)	2.78(1)

6.5.4.2 Sulphuric acid concentration variation

The concentration of the acid or alkali used can significantly affect the leaching rate. Higher concentrations may increase the dissolution of target minerals but can also lead to increased costs and potential environmental issues. Using the right concentration of acid or alkali ensures that the target minerals dissolve effectively without excessive costs or environmental impact. **Figure 6.6** shows the leaching efficiency of Ti, Fe and V as the sulphuric acid concentration increases.

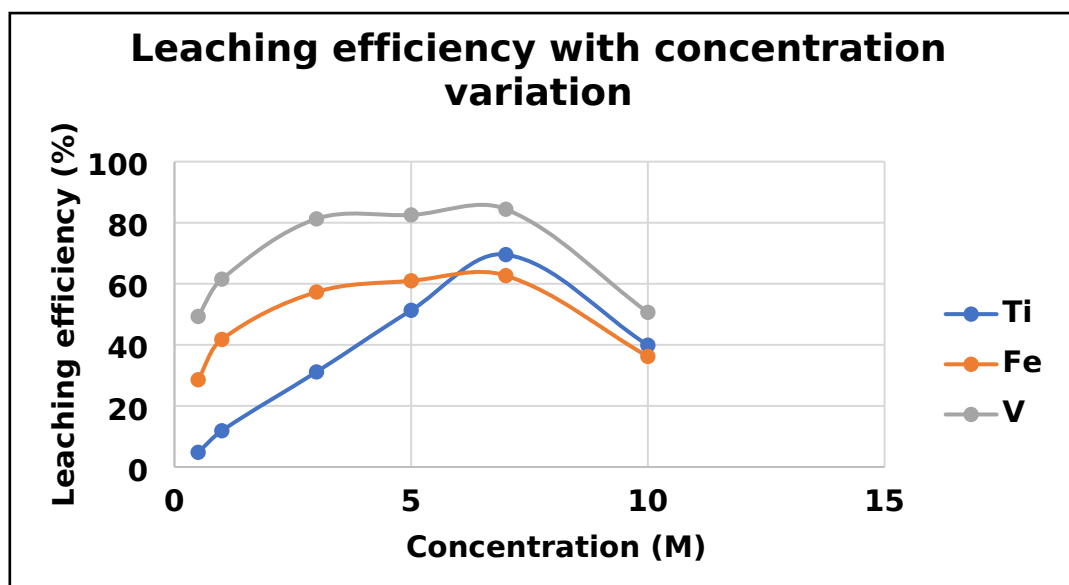


Figure 6.6: Effect of sulphuric acid concentration on the leaching efficiency of Ti, V and Fe

Increasing the concentration of sulphuric acid increases the recovery of titanium in solution, because the more acid molecules present, the more collisions occur with the titanium ore, thereby increasing the rate of reaction. However, this only happens up to a concentration of 7 M; after that, the yield decreases. This indicates that the optimum concentration for the reaction is 7 M. The same happens for the impurities below, V and Fe, hence there is no selective dissolution of titanium. However, it is worth noticing that the efficiency of sulphuric acid to dissolve Fe is higher than Ti and it increases directly proportional to the concentration of the acid until 5 M. Thereafter, the efficiency remains constant, around 60 %. It is at 7M that the yield for Ti (69.55 %) surpasses the yield for Fe for the first time. In conclusion, it can be said that the optimum concentration for obtaining maximum Ti recovery was 7 M.

6.5.4.3 Time Variation Results

The duration of the leaching process is crucial. Longer reaction times can improve recovery rates, but they may also lead to the dissolution of unwanted minerals. Finding the optimal time is key. **Figure 6.7** shows the leaching efficiency of Ti, Fe and V as the reaction time increases.

The results showed that the maximum recovery time to obtain the best reasonable concentration of Ti was 300 minutes. Increasing the time further than that did not significantly increase the recovery of Ti, but increased the leachate of Fe and V. The leaching or dissolution of Ti can be expressed as a pseudo-first-order reaction. The initial reaction rate is dependent on both reactants, and as the reaction proceeds, the concentrations of both reactants change, thereby affecting the rate. If the concentration of one reactant were made very large in comparison to the other, it would eliminate the concentration dependence of one of the reactants (Ismael *et al.*, 2022). In this investigation, a

substantial excess of acid was utilised to dissolve titanium, allowing the reaction to be considered pseudo-first order with respect to titanium since the acid concentration remained largely unchanged. The optimum reaction time was combined with other optimal conditions to achieve maximum leaching efficiency.

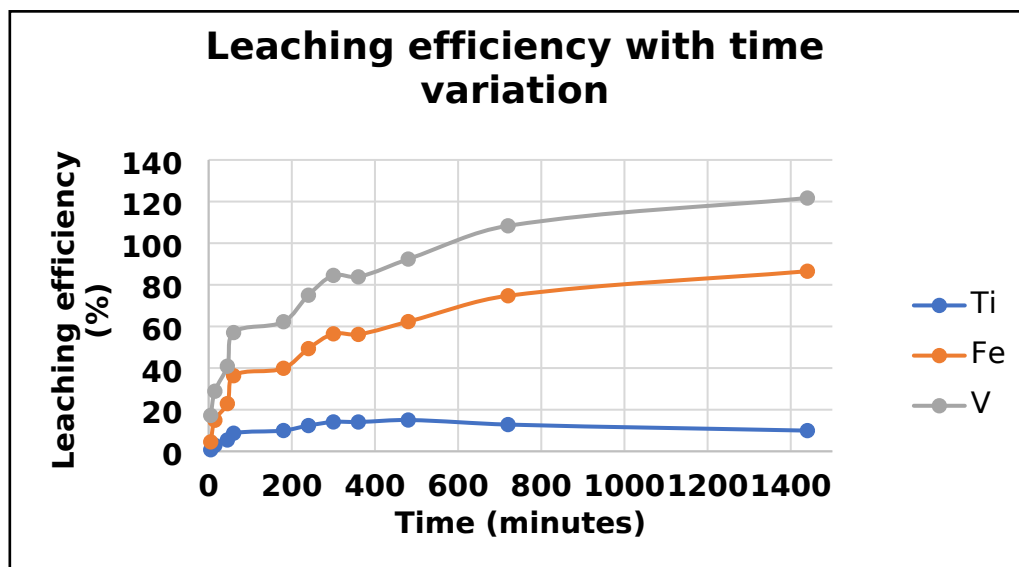


Figure 6.7: Leaching efficiency of Ti and Fe, and V impurities with reaction time variation

6.5.4.4 Optimum conditions results

Integrating optimal conditions significantly enhances the leaching process, resulting in improved recovery rates and a reduced environmental impact. When these conditions are combined, they create a synergistic effect that enhances the overall leaching performance. The reactions were done according to the process described in **Section 6.4.2.4**, and the results are reported in **Figure 6.8**.

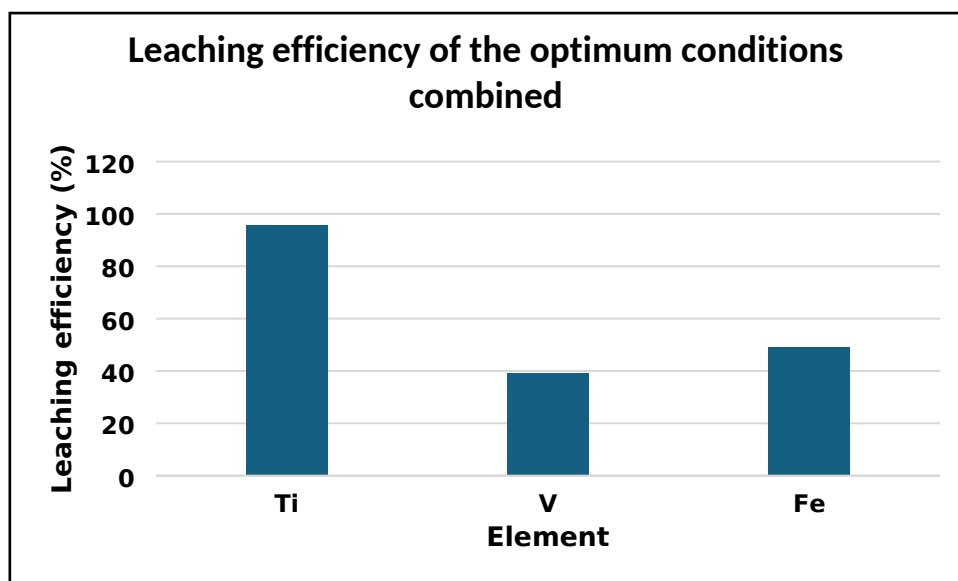


Figure 6.8: The effect of the combined optimum conditions on leaching efficiency at 7 M H₂SO₄, 90°C, 600 rpm, 5 hours

Ti was leached in higher quantities than the impurities in the sample. This showed that 7 M H₂SO₄, at 90°C and 600 rpm for 5 hours, yielded the best leaching of Ti (98 %), resulting in a Ti-enriched solution. Upscaling the reaction is required to measure the feasibility of the leaching method optimized and proposed based on the results of this study.

6.5.4.5 Upscaling results

This method is being developed for industrial applications. Hence, it is essential to imitate industrial processing by increasing the reactants used and see if the performance is sustained. The reactions were done according to the process described in **Section 6.4.2.5**, and the results are reported in **Figure 6.9**.

Upscaling the reaction size showed a steady slight decrease in the leaching efficiency of Ti elements from 98.38 % at 5 g to 95.% at 10 g. This may cause a challenge in lab reactions, pilot, and industrial scale. This could be solved by performing smaller reactions in parallel reactors. However, taking into account that efficiency only decreased 2.88 % during the upscale from 5 g to 250 g, the decrease could be considered negligible.

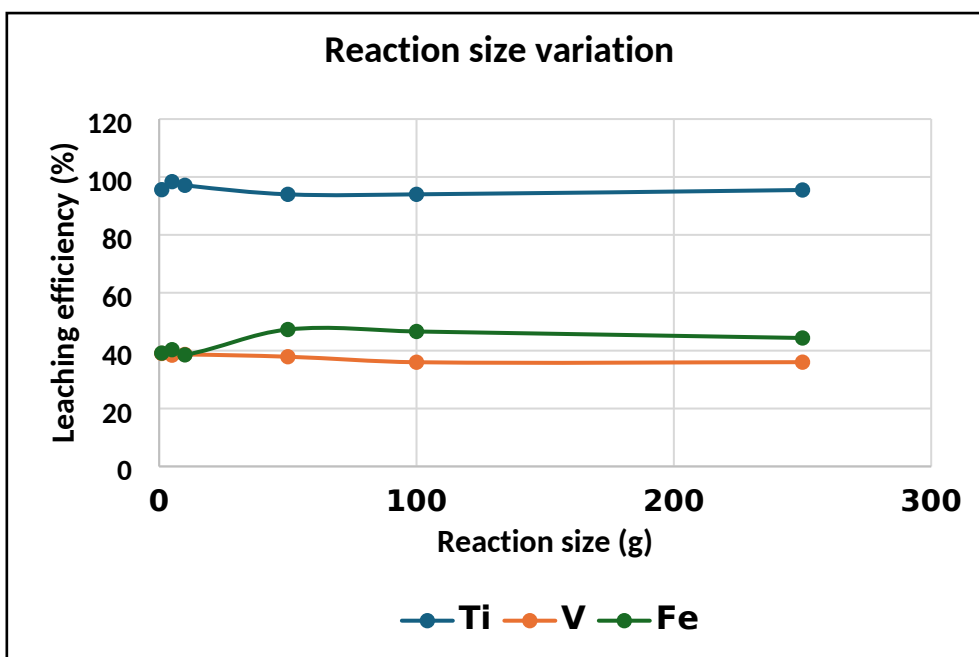


Figure 6.9: Leaching efficiency with an increase in reaction size

6.5.5 Oxidation and reduction results

Reducing agents can also accelerate the leaching process by promoting the faster dissolution of metals, particularly when the metal is present in an oxidised form that is less soluble, such as Ti^{4+} . Oxidising agents, on the other hand, are used to convert metals from a lower oxidation state to a higher one, thereby increasing their solubility in the leaching solution. By controlling the oxidation state of the metals, oxidising agents can help selectively dissolve specific metals while leaving others in the solid phase. This selectivity is crucial for efficient metal recovery.

6.5.5.1 Addition of H_2O_2 to the sulphuric acid leaching

The VBT ore was treated according to the process described in **Section 6.4.4.1**, and the results are shown in **Figure 6.10**. H_2O_2 can react with some ions, such as Fe^{2+} and V^{4+} , under acidic conditions to form strong oxidizing free radicals (Liu *et al.*, 2021). Generally, the recovery of Ti increases with an increase in the ratio of sample to hydrogen peroxide. Lower Fe recoveries were present in the 1:1 ratio, showing some level of selectivity of the oxidizing agent. However, the recovery of Ti was very low, despite an incipient increase being observed. This means that very high amounts of hydrogen peroxide would be required to increase the recoveries of Ti, which could be uneconomical.

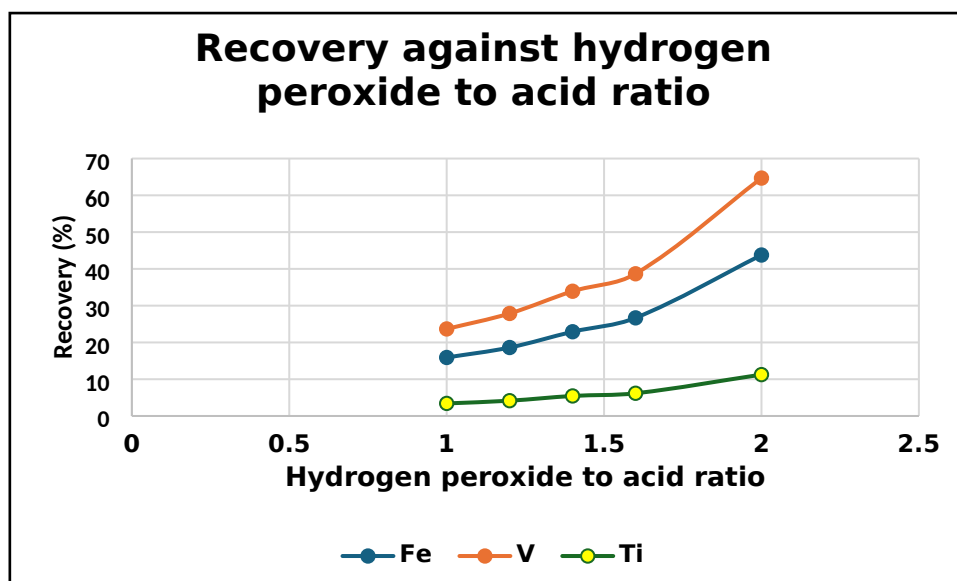


Figure 6.10: Effect of increasing hydrogen peroxide on recovery of Ti, V and Fe per ratio of sample: hydrogen peroxide

Lower temperatures might increase the recovery of titanium, but it is not high enough to rely on the method to selectively dissolve the titanium into solution before its removal. Oxidation transforms titanium compounds into forms that dissolve more easily, such as titanium peroxo sulphate, improving both the speed and effectiveness of leaching. It also reduces issues with unwanted byproducts like iron sulphate and silica gel. Increasing the ratio of ore to hydrogen peroxide increases the recovery of titanium; however, lowering the temperature could help if a temperature just below the decomposition temperature of hydrogen peroxide is used. In one study 97% leaching efficiency was achieved of both Ti and Li at a sulphuric acid solution of 4 M, H_2O_2 of 20 vol.%, leaching temperature of 80 °C, and leaching time of 4 hours (Tang *et al.*, 2014).

6.5.5.2 Hydrogen peroxide as an oxidizing agent in sulphuric acid at a lower temperature

The VBT ore was treated according to the process described in **Section 6.4.4.1**, and the results are shown in **Table 6.14**. Increasing the ratio and decreasing the temperature at which the reaction occurs had little effect on the recovery of Ti in solution. This is because Ti is already in the +4 oxidation state, so not many +3 ions were present that needed to be oxidized into the +4 state. Ti^{4+} is the highest oxidation state for titanium. Reducing the temperature reduces the Ti recovery because the temperature of 50 °C is too low for the ore to dissolve, even though it is low enough for the hydrogen peroxide to work without decomposing.

Table 6.14: Recoveries of elements per ratio of sample: hydrogen peroxide

Element	1:2 ratio (%)
Ti	4.27
V	24.86
Fe	17.51
Si	5.30
Al	6.85
Mn	21.20
Ni	37.04
Co	82.20
Cu	61.98
Zn	22.32

6.5.6 Roasting results

The roasting and sample digestion were performed in triplicate with the same manually homogenized portions. **Table 6.15** displays the results regarding roasting effectiveness, along with the standard deviation for NaOH, while Table 6.16 presents the results for NaHCO₃.

Table 6.15: Elemental compositions before and after NaOH roasting

Element	NaOH roasting product composition (%)	LiBO ₂ flux fusion product composition (%)
Ti	0.20(1)	2.85(2)
V	3.81(3)	0.01(1)
Fe	0.47(1)	7.87(3)

NaOH did not show any effectiveness in increasing the leaching efficiency of Ti. Its composition in the product after roasting and flux fusion (2.85 %) was similar to the initial composition (3 %). This indicates that this extra step is unnecessary. However, it was effective in selective leaching by significantly reducing the amount of Fe leached (from the expected 24.6 % to 7.87 %).

As reported in **Table 6.16**, NaHCO₃ also did not show any effectiveness in leaching all elements, as the roasting product had all the elements below the detection limit. When this product was subjected to lithium metaborate flux fusion, the composition of Ti was even lower (1.90 %) than using NaOH roasting.

Table 6.16: Compositions before and after NaHCO₃ roasting

Element	NaHCO ₃ roasting product (%)	LiBO ₂ flux fusion product (%)
Ti	bdl	1.90(1)
V	bdl	0.22(2)
Fe	bdl	12.89(1)

* bdl - below detection limit

Another constraint on conducting this experimental study was the reaction size. The crucible's volume limits the size of the reaction, and larger furnaces and crucibles will be needed for further investigations with industrial applications in mind. Secondly, attempting to increase the leaching of Ti from the ore would need to increase the ratio of NaHCO_3 :ore, which would significantly raise operating expenses.

6.6 Results and discussion of the tailings results

The same methods that were applied to the VBT ore were applied to the tailings. This is essential for optimizing titanium extraction and facilitating its comparison.

6.6.1 Magnetic separation

The investigation into separating Ti-bearing minerals from tailings using the magnetic separation method was also conducted following the procedure described in **Section 6.3.1**. It was designed to target the removal of iron-rich gangue minerals and demonstrated varying degrees of effectiveness in separating these components, just like the ore. The mass of the different portions obtained, XRD, and XRF results were also evaluated and compared with the original sample to note any significant differences.

6.6.1.1 Mass results

Mass results reported in the pie chart shown in **Figure 6.11** indicate that 82.5 % of the tailings are non-magnetic. A large percentage of the sample, 14.45 %, was lost due to its adhesion to the surfaces of the electromagnet and workbench or unexplained loss. In general, it was more challenging to work with finely divided tailings. Only 3.05 % of the tailings were found to be magnetic.

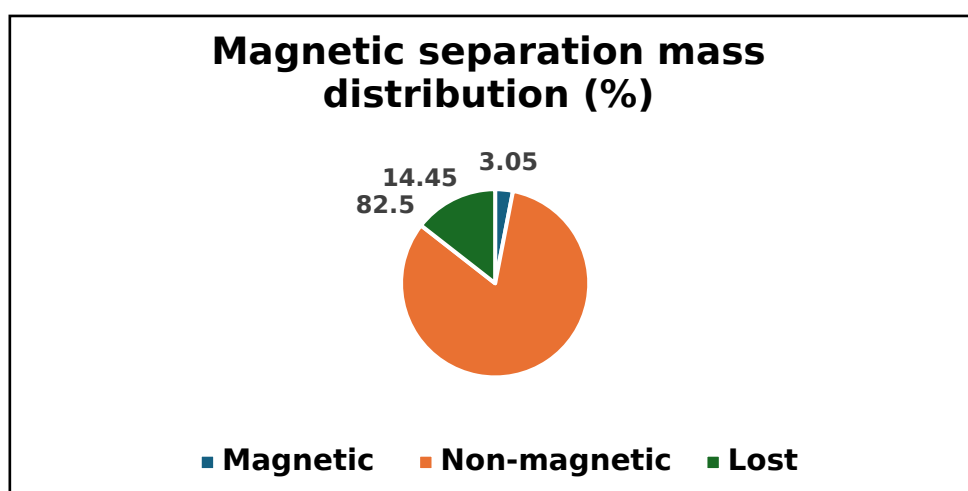


Figure 6.11: Tailings mass distribution percentages of magnetic separation portions

The tailings were generally not magnetic. This may be attributed to the processing of their source (VBT ore), which removed the magnetic portion, leaving behind a non-magnetic waste (tailings). XRF and SEM-EDS analyses were performed on the different portions.

6.6.1.2 XRD results

The magnetic separation of the tailings was analyzed according to the procedure described in **Section 4.4.1**. The results show that the magnetic portion of the tailings contained hematite, pseudobrookite, and sodalite ($\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$), and the average percentage compositions are reported in **Table 6.17**. The analysis revealed the presence of sodalite, not ilmenite, as observed in the raw tailings. The dominant mineral in both fractions was found to be hematite, with 77 % present in the magnetic fraction and 73 % in the non-magnetic fraction. Pseudobrookite was present at 19 % in the magnetic fraction and 13 % in the non-magnetic fraction. This mineral, which contains both iron and titanium, appears to be more concentrated in the magnetic fraction, suggesting that it may be more readily separable via magnetic separation techniques. Its presence in both fractions indicates that while it has magnetic properties, it might also be found in polyminerale particles associated with non-magnetic minerals. Sodalite shows a contrasting distribution, with only 4 % in the magnetic fraction but a higher percentage of 14 % in the non-magnetic fraction. This suggests that sodalite is primarily non-magnetic and may be more associated with the gangue materials and other silicate phases in the ore.

Table 6.17: XRD mineral composition of the tailings magnetic and non-magnetic portions

Portion	Hematite (%)	Pseudobrookite (%)	Sodalite (%)
Magnetic	77	19	4
Non-magnetic	73	13	14

This magnetic separation was not very effective, as it included non-magnetic minerals (pseudobrookite and sodalite) in both the magnetic and non-magnetic fractions. It is possible that all the magnetic portion of the tailings was removed at the plant during processing of the VBT ore, hence the absence of magnetite. The magnetic portion contained their element of interest (vanadium), hence they removed it, leaving non-magnetic tailings. The mine usually has tailings only for magnetite, which are sold as a byproduct.

Comparison of raw tailings and the magnetic portion

The main peaks of hematite are of the same height in the raw tailings sample as in the magnetic fraction, as illustrated in **Figure 6.12**. The peaks of the magnetic fraction are slightly higher than those of the raw tailings.

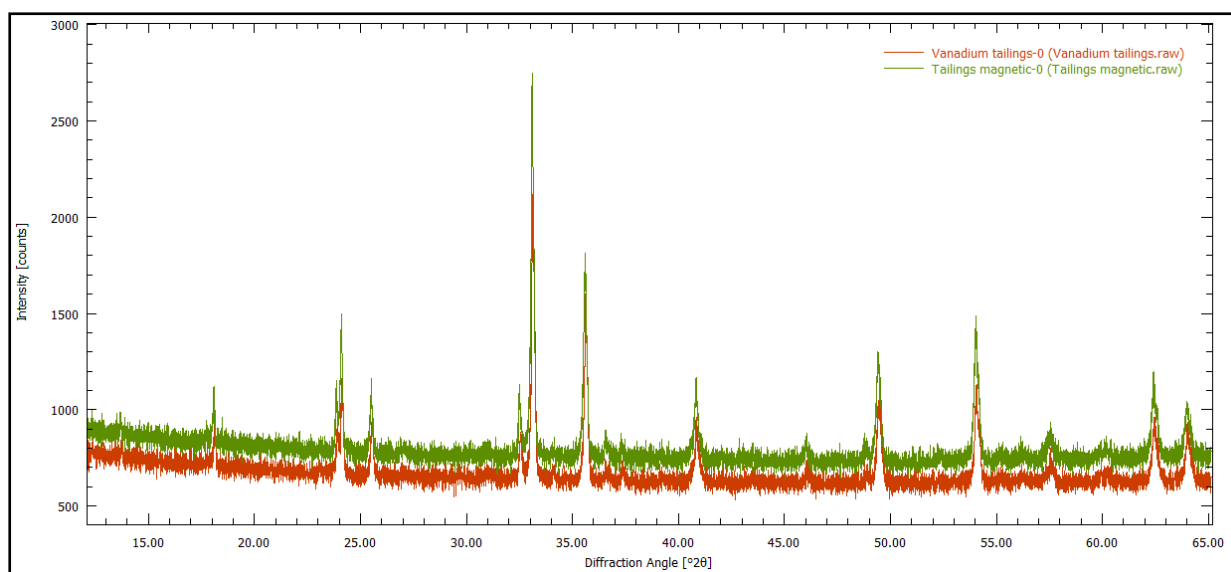


Figure 6.12: XRD pattern of raw tailings (green) and the magnetic fraction (red)

There was no significant difference between the raw tailing samples and the magnetic fraction. This indicates that the magnetic separation was not very effective in separating the sample, likely due to the technique's poor performance or the presence of a high percentage of non-magnetic particles.

Comparison of raw tailings and the non-magnetic portion

The main peaks in the raw tailings sample are almost identical to those of the non-magnetic fraction, as illustrated in **Figure 6.13**.

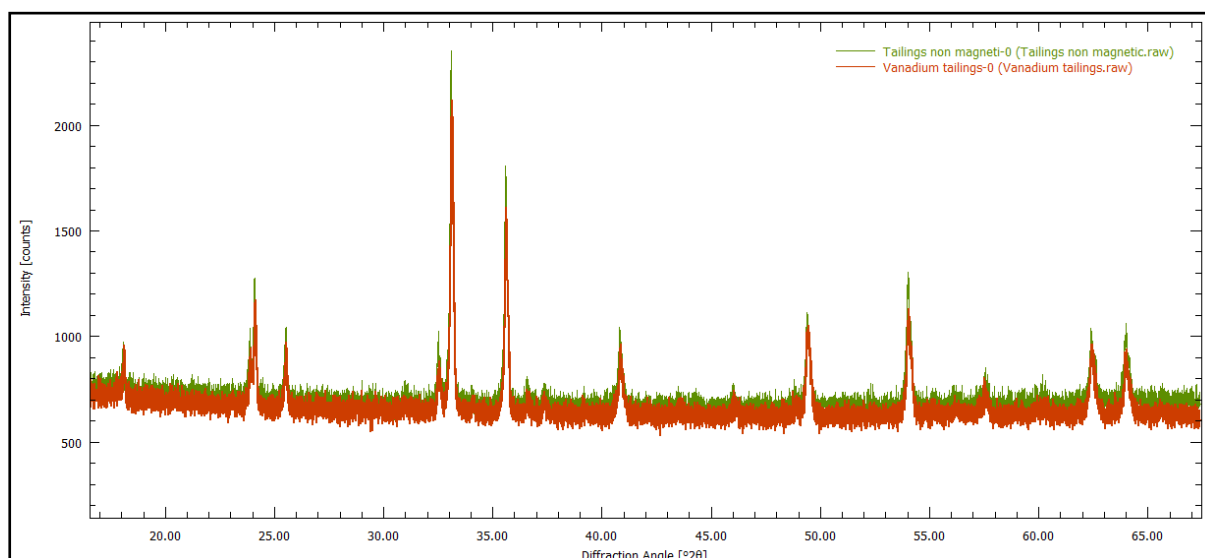


Figure 6.13: XRD pattern of raw tailings (red) and the non-magnetic fraction (green)

This characterization reveals that the tailings are more similar to the non-magnetic portion than to the magnetic portion in terms of mineral composition, confirming the ineffectiveness of the method in isolating the Ti-rich minerals.

6.6.1.3 XRF results

An XRF analysis was also performed on the two different portions obtained after the magnetic separation. The results that are reported in **Table 6.18** indicate the concentration of various trace elements in both the magnetic and non-magnetic portions. The magnetic portion contained 10.99 % Ti while the non-magnetic portion contained 12.77 %. These values were very similar to those obtained for the raw tailings, indicating the ineffectiveness of magnetic separation in concentrating Ti into a single portion. This could be explained by the fact that the tailings were very non-magnetic, as previously reported. The concentrations of the remaining elements also exhibited the same trend.

Table 6.19 shows that the magnetic portion was rich in V and Cr, with significant quantities of Co, Cu, and Zn also present. The non-magnetic portion was rich in V and Sr as well as significant quantities of Cu, Cr, Zn, and Ni. The presence of trace elements, particularly arsenic, and the concentrations of heavy metals highlight potential environmental risks associated with tailings disposal.

The concentrations of all the elements were similar in both portions. This clearly shows the ineffectiveness of magnetic separation as a possible beneficiation step. The higher concentration of vanadium in the magnetic portion is supported by information from the mine, which indicates that the beneficiation process concentrates vanadium-containing minerals in this portion, as the mineral is rich in vanadium (Bushveld Minerals, 2024). Significant trace amounts are therefore found in the magnetic portion of the tailings.

Table 6.18: Major elemental composition of the magnetic and non-magnetic portions of the tailings

Major elements	Magnetic portion concentration (%)	Non-magnetic portion concentration (%)
TiO ₂	10.99	12.77
Fe ₂ O ₃	79.45	76.42
SiO ₂	2.55	3.96
Al ₂ O ₃	2.61	3.60
MnO	0.18	0.18
MgO	0.40	0.43
CaO	0.35	0.40
Na ₂ O	1.34	1.95
K ₂ O	0.00	0.01
P ₂ O ₅	0.04	0.04
LOI	0.14	-0.94
Total	98.05	98.82

Table 6.19: Trace elemental composition of the magnetic and non-magnetic portions of the tailings

Trace element	Magnetic portion concentration (ppm)	Non-magnetic portion concentration (ppm)
Sc	24	19
V	1936	1630
Cr	6417	4968
Co	433	388
Ni	89	83
Cu	318	263
Zn	342	317
As	204	193
Rb	2	1
Sr	23	22
Y	51	50
Zr	12	14
Nb	3	4
Ba	<7	<7
Pb	<2	<2
Th	90	84
U	<3	<3

6.6.1.4 ICP analysis of the magnetic separation portions after LiBO₂ flux fusion

The tailings were treated according to the procedure in **Section 6.3.1**. The results obtained from the ICP-OES analysis are shown in **Table 6.20**. Complete dissolution of the tailings was achieved, as evidenced by a visual inspection of the crucible, which showed total dissolution in both portions.

Similar percentages of Ti were found in both the magnetic (3.57 %) and non-magnetic (3.72 %) portions as in the ore (5.2 %). The remaining impurities were also present in similar quantities in both portions. This method was not successful in concentrating titanium into one of the portions. This was likely due to the magnetic field strength being too weak to capture the ilmenite. This was supported by LiBO₂ flux fusion, XRD, mass, and XRF data. They were composed of non-magnetic oxides, and magnetite, the primary magnetic mineral, was not present. Only about 3 % was magnetic, possibly due to the ilmenite, which has a low magnetic susceptibility.

Table 6.20: Elemental composition of the tailings after LiBO₂ flux fusion on the magnetic and non-magnetic portions

Element	Magnetic portion average % composition	Non-magnetic portion average % composition
Ti	3.57(6)	3.72(2)
V	0.628(1)	0.212(5)
Fe	87.1(3)	90.7(5)
Si	0.056(1)	bdl
Al	15.56(4)	9.8(6)
Mn	1.325(1)	1.22(3)
Ni	0.184(1)	bdl
Co	0.109(4)	1.95(2)
Cu	0.322(3)	0.18(8)
Zn	0.041(5)	0.062(8)

*bdl below detection limit

6.6.2 Gravity separation

The same gravity separation applied to the VBT ore was also applied to the tailings. By testing both the ore and tailings, the recovery rates of titanium were compared. This helps in assessing the efficiency of the extraction process.

6.6.2.1 Mass results

The gravity separation analysis of the tailings was conducted according to the procedure in **Section 6.3.2**, and the results are shown in the graph shown in **Figure 6.14**. 75.31 % of the ore was found to be heavy while 25.44 % was light. The density of the sample was previously reported as 2.2-2.4 g/cm³, showing that it was relatively lighter than the VBT ore sample. Only 0.75% of the sample was lost, as it was not as dusty as the VBT ore.

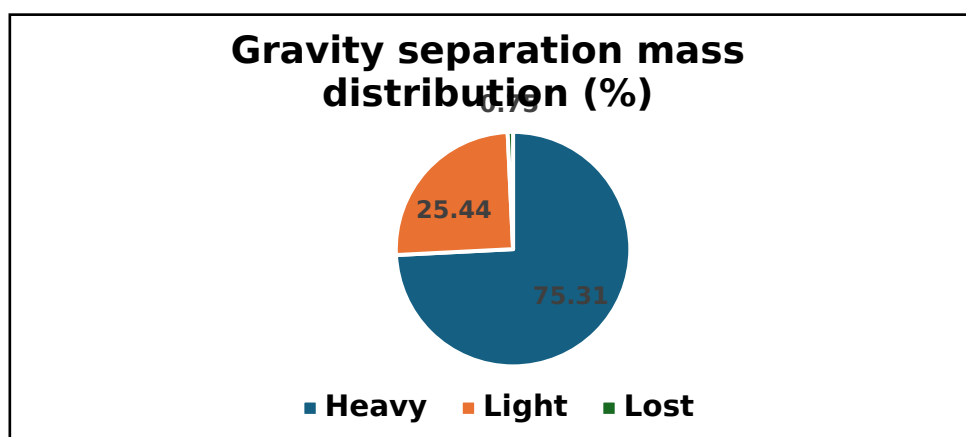


Figure 6.14: Tailings mass distribution percentages of the gravity separation portions

6.6.2.2 XRD Results

The XRD analysis of the gravity separation portions of the tailings was performed according to the procedure described in **Section 5.4.2**. The XRD results indicate the presence of a large amount of hematite (84 wt. %) in the heavier portion of the tailings as the dominant mineral in this fraction, and only (16 wt. %) pseudobrookite. The light portion contained a similarly high percentage of hematite (83 wt. %) and low percentages of pseudobrookite and K-feldspar. The results are reported in **Table 6.21**.

Table 6.21: XRD mineral composition of tailings' heavy and light portions

Portion	Hematite (wt. %)	Pseudobrookite (wt. %)	K-feldspar (wt. %)
Heavy	84	16	
Light	83	12	5

The gravity separation was not successful in separating the abundant Ti-rich minerals, as seen by the high percentages of both hematite and pseudobrookite minerals in both portions, as they both contain the required Ti. However, it seems to effectively remove the silicates (K-feldspar) to the light portion.

6.6.2.3 XRF results

An XRF analysis was also performed on the two different portions obtained after the gravity separation process previously discussed in **Section 5.6.2**. The results are reported in **Table 6.22** and **Table 6.23**. The heavy portion contained 12.65 % Ti while the light portion contained 11.63 %. There is no effective concentration of Ti into one portion; therefore, gravity separation was not effective. The rest of the impurities also had similar percentages in both portions.

The vanadium concentration was slightly higher but very similar, in the light portion (2 178 ppm) compared to its concentration in the heavier portion (2 046 ppm). The same trend was observed for all other elements present in the almost-equal distribution between the two portions.

Table 6.22: Major elemental composition of the heavy and light portions of the tailings

Major elements	Heavy portion concentration (%)	Light portion concentration (%)
TiO ₂	12.65	11.63
Fe ₂ O ₃	78.06	82.52
SiO ₂	2.58	2.47
Al ₂ O ₃	3.25	2.42
MnO	0.18	0.15
MgO	0.41	0.21
CaO	0.34	0.26
Na ₂ O	1.74	0.92
K ₂ O	0.00	0.01
P ₂ O ₅	0.04	0.04
LOI	0.28	0.26
Total	99.52	100.87

Table 6.23: Trace elemental composition of the heavy and light portions of the tailings

Trace elements	Heavy portion concentration (ppm)	Light portion concentration (ppm)
Sc	255	27
V	2046	2178
Cr	4921	5708
Co	420	421
Ni	73	73
Cu	293	316
Zn	336	358
As	324	326
Rb	1	2
Sr	22	21
Y	81	82
Zr	6	6
Nb	2	1
Ba	<7	<7

6.6.2.4 ICP analysis of the gravity separation portions after LiBO₂ flux fusion

After gravity separation, the tailings were digested using LiBO₂ as described in **Section 5.5.1**. The ICP results for the elements detected in solution after LiBO₂ flux fusion digestion are reported in **Table 6.24**. The heavy portion contained 3.49 % Ti while the light portion contained 1.64 % Ti.

Table 6.24: Elemental composition of the tailings after LiBO₂ flux fusion on the heavy and light portions

Element	Heavy portion average % composition	Light portion average % Composition
Ti	3.4903(5)	1.64(1)
V	bdl	bdl
Fe	56.2(2)	12.5(1)
Si	bdl	bdl
Al	8.1(1)	3.63(3)
Mn	0.66(1)	0.42(1)
Ni	bdl	bdl
Co	0.05(1)	0.4(4)
Cu	0.19(1)	0.08(3)
Zn	0.11(2)	0.02(1)

*bdl - below detection limit

These results indicate that both the heavy and light portions contained significant percentages of Ti. Once again, this demonstrated that gravity separation did not effectively concentrate the titanium-containing minerals into a single portion.

6.6.3 Optimisation of leaching conditions

This optimal conditions reaction was also done on the tailings as it was done on the ore to determine the maximum leaching of Ti in the tailings, with the assumption that the preliminary and optimisation reactions, which were performed on the ore, were similar to the ones obtained on the tailings.

6.6.3.1 Optimum conditions results

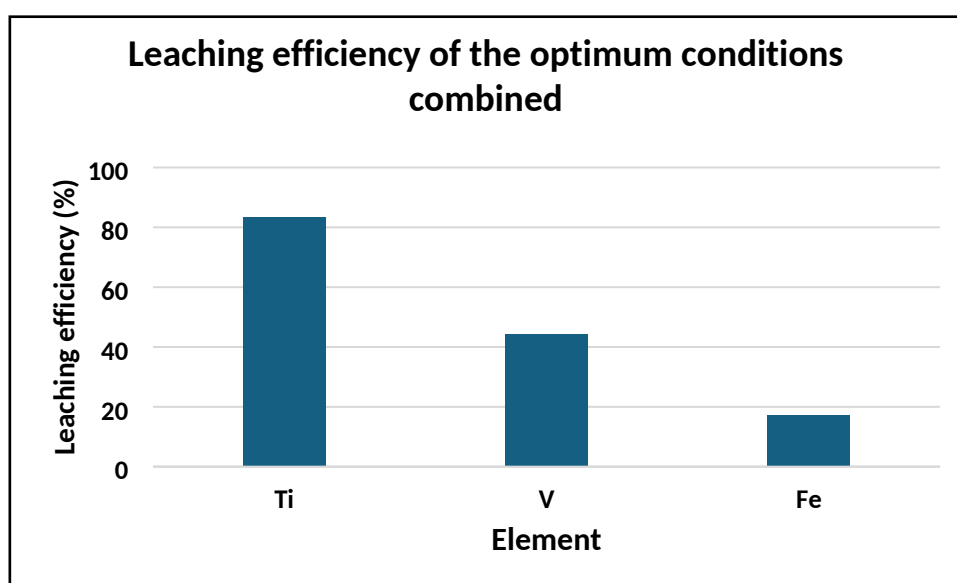


Figure 6.15: The effect of the combined optimum conditions on leaching efficiency at 7 M H₂SO₄, 90°C, 600 rpm, 5 hours

The reactions were done using 7 M H_2SO_4 at 90°C, 600 rpm for 5 hours, according to the process described in **Section 6.4.2.4**, and the results are reported in **Figure 6.15**. The reaction proved successful as a high Ti recovery was obtained (83.55 %). V is already very low, so a co-extraction of 44.16 % could be acceptable.

6.6.3.2 Upscaling results

This method is being developed for application in industry. Hence, it is essential to imitate industrial processing by increasing the reactants used and see if the performance also increases. The reactions were done according to the process described in **Section 6.4.2.5**, and the results are reported in **Figure 6.16**. Upscaling the reaction size shows a slight increase in the leaching efficiency of Ti from 85.43 % at 5 g to 87.2 % at 10 g. Thereafter, the efficiency decreased between the 10 g reaction to the 100 g reaction and stabilised (leaching efficiency of 100 and 250 g reactions were 78 % for both). However, taking into account that efficiency only decreased 7.48 % during the upscale from 5 g to 250 g, the decrease could be considered negligible.

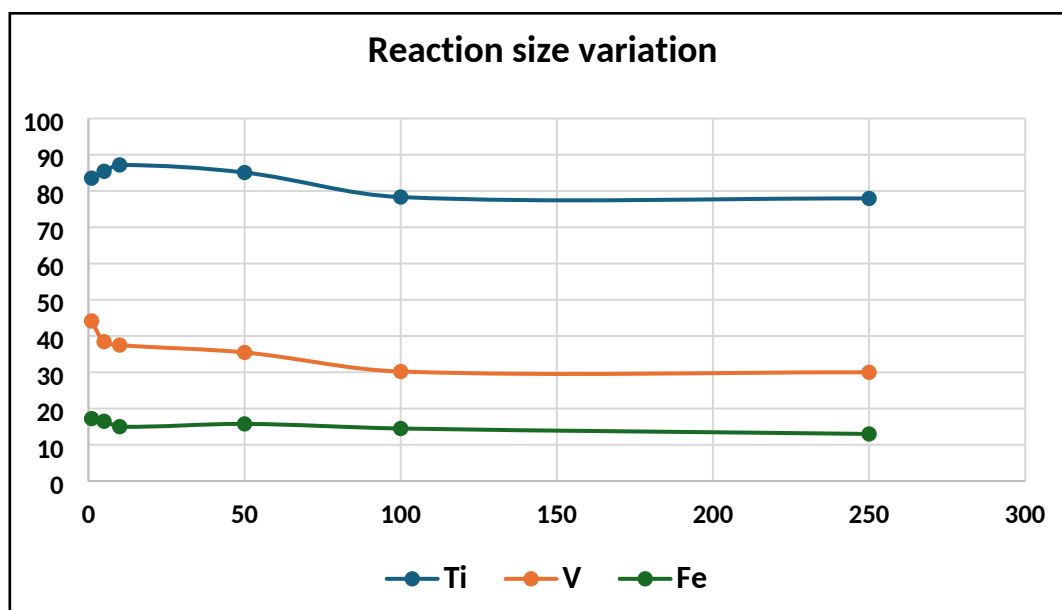


Figure 6.16: Leaching efficiency with an increase in reaction size

6.6.4 Reduction

The leaching of titanium from its ores often necessitates the use of oxidising and reducing agents to enhance the dissolution process. The choice of oxidising or reducing agent, and its concentration, depends critically on the specific ore mineralogy and the desired outcome of the leaching process, influencing both the efficiency of titanium extraction and the overall purity of the resulting product. For the tailing samples, sodium bisulphite was selected as a reduction reagent and added to the

sulphuric acid leaching reaction. The leaching reactions were performed according to the procedure described in **Section 6.4.4**, and the results are shown in **Table 6.25**. The addition of sodium bisulphite did not show any increase in the leaching efficiency of Ti in solutions of both tailings and pure TiO₂ powder.

Table 6.25: Titanium recovery percentage

Sample	Ti (%)
Process tailings	1.23
TiO ₂ powder	1.10

This extra step proved unnecessary, as it did not increase the leaching efficiency of Ti into the solution. Other procedures were also attempted.

6.6.5 Roasting reactions

The roasting and sample digestion were performed according to **Section 6.4.3**, and **Table 6.26** shows the roasting effectiveness with the standard deviation.

Table 6.26: Elemental compositions before and after NaOH roasting

Element	NaOH roasting product (%)	LiBO ₂ flux fusion product (%)
Ti	bdl	4.74(1)
V	bdl	0.03(1)
Fe	bdl	44.68(2)

*bdl – below detection limit

NaOH did not improve the leaching efficiency of Ti. Its composition in the product after roasting and flux fusion (4.74 %) was similar to the initial composition (5.2 %). However, it was effective in selective leaching by reducing the amount of Fe leached (from the expected 53 % to 44.68 %). **Table 6.27** shows that the elemental compositions of Ti, Fe, and V were below the detection limit.

Table 6.27: Elemental compositions before and after NaHCO₃ roasting

Element	NaHCO ₃ roasting product (%)	LiBO ₂ flux fusion product (%)
Ti	bdl	0.02(1)
V	bdl	0.00(1)
Fe	bdl	0.11(1)

*bdl – below detection limit

NaHCO₃ also did not improve the leaching of all elements, as the roasting product had all the elements below the detection limit. When this product was subjected to lithium metaborate flux fusion, the composition of Ti was close to insignificant as well.

6.7 Conclusion

Lithium metaborate flux fusion was the best method for sample dissolution with 3 % Ti for the ore and 5.2 % for the tailings. Using flux salts with sodium sulphate and ammonium sulphate was ineffective, as seen by the lower percentages of 0.07 % and 0.246 % of titanium dissolved from tailings, while only 0.14 % and 0.107 % for ore. Aqua regia digestion was almost as good as lithium metaborate in dissolving the samples. Reaction pressure was important, as seen by low levels of Ti in microwave digestion in an oven with no pressure. Magnetic separation mass results agree with XRD results, which showed that the process tailings contain non-magnetic minerals, and the ore is very magnetic due to high quantities of magnetite. NaOH and NaHCO₃ roasting did not improve the leaching efficiency of titanium; therefore, the extra step was not beneficial to the process. After all experiments were performed, optimum conditions to leach the titanium, while minimizing the amount of impurities, were 7 M H₂SO₄, at 90 °C, 600 rpm for 5 hours. Selective leaching efficiency was 95.61 % for Ti and as low as 39.02 % V and 49.16 % Fe for the ore, and 83.55 % Ti, 44.16 % V, and 17.22 % Fe for the tailings. The final leach liquor of the ore contained 2.86 % Ti compared to the initial 3.0 % while the tailings leach liquor contained 4.34 % Ti compared to the initial 5.2 %. This showed that the method was successful at leaching the maximum Ti with the least expensive conditions from both the ore and the tailings.

Chapter 7: Critical Evaluation and Future Investigations

7.1 Introduction

Recovery of Ti presents the opportunity for possible development of an industrial process that could utilise acid leaching to selectively extract Ti from ore and tailings using large-scale acid leaching reactions. An evaluation of this study follows here, namely by comparing obtained results to the objectives defined in **Chapter 1, Section 1.4**. It also identifies potential future research studies to address research questions arising from this study, which can aid in the development of a financially viable industrial process.

7.2 Critical Evaluation

The aim of this research study, as stated in **Chapter 1, Section 1.4**, was to recover titanium from Ti-bearing minerals in ore deposits and mine tailings by applying appropriate chemical leaching methods that can be scaled to an industrial level.

The results of this study successfully achieved most of the objectives. The literature study presented in **Chapter 3** identified current methods utilised for Ti dissolution and isolation were predominantly acid and alkali leaching. This also provides data that indicates that Ti in minerals react with chemicals such as H_2SO_4 , HCl , HNO_3 , HF , NaOH , and NH_4OH .

Characterization and compositional determination were successfully achieved through XRF, XRD, SEM-EDS, Sequential extraction, and ICP-OES analyses. XRF data positively identified the composition of all samples. These results highlighted problems associated with homogenizing mineral samples across different samples. XRD and SEM-EDS provided further mineralogical characterization of the samples, with XRD indicating the presence of Ti-oxide minerals as well as Ti-bearing minerals, predominantly ilmenite and magnetite in the VBT ore and hematite, ilmenite, and pseudobrookite in the tailings.

The analytical techniques selected for Ti beneficiation in this study were magnetic separation, gravity separation, oxidation, reduction, alkali roasting, and leaching. Gravity separation showed magnetite, hematite, and pseudobrookite were uniformly distributed through light and heavy portions of VBT ore and tailings. Magnetic separation showed that most of the VBT ore particles were magnetic (80 %), while only 14 % of tailing particles were magnetic. Alkali roasting performed with sodium hydrogen carbonate and sodium hydroxide showed no increase in Ti recovery or decrease in dissolved impurity quantities. Increasing the reagent-to-ore ratios and using larger crucibles could help to improve the roasting efficiency.

Preliminary leaching reactions were investigated using mineral acids such as HCl, H₂SO₄, HNO₃, and H₃PO₄, as well as aqua regia, and alkali mediums containing NaOH, KOH, and NH₄OH. Results from these reactions indicated the need for further investigation with H₂SO₄. Leaching reactions were highly successful at elevated temperatures and concentrations.

The selected sulphuric acid was further investigated for Ti recovery through systematic variations in experimental conditions, including concentration, temperature, time, and the addition of reducing and oxidizing agents. Optimal conditions for both VBT ore and tailing were 7 M H₂SO₄, at 90°C, 600 rpm for 5 hours. The selective leaching efficiency of Ti was 95.61 % for the ore and 83.55 % for the tailing. Acid leaching reactions with H₂SO₄ improved impurity removal; however, oxidizing and reducing agents were not efficient towards this end. Alkali leaching reactions with NaOH and KOH were the least effective for Ti recovery. Consequently, the use of alkalis as leachants was discarded.

7.3 Future Investigations

This study was able to successfully leach 96 % and 84 % of Ti from VBT ore and tailing, respectively. Future research should focus on isolating Ti from liquor using 7 M H₂SO₄, at 90 °C, 600 rpm for 5 hours. Techniques such as solvent extraction, selective precipitation, or metal-organic framework (MOF) membranes could be an option to develop the full industrial process to obtain a purified titanium product. In addition, future research could optimize the conditions for large-scale acid leaching processes, addressing financial and industrial scalability, and exploring alternative approaches to impurity removal. This study paves the way for developing a viable process for titanium extraction from ores and tailings. Future studies that may enhance understanding of the leaching process, as well as improve the identified process, include:

- in-depth study on isolation of Ti from samples
- in-depth study on isolation of Ti from samples by decreasing Fe and V impurities
- evaluate chemical properties of pure Ti solutions regarding Ti isolation
- use solvent extraction, ion exchange, and other isolation methods to give purer solutions of Ti
- study to optimize scaling reaction conditions, from lab to pilot scale

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