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# **Beneficiation Study of Titanium Ore from a selected site in Mongolia**

**Bachelor Thesis**

by

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Beneficiation Study of Titanium Ore from a selected site in Mongolia

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## **Abstract**

Within the scope of this bachelor's thesis, the possibilities of enriching titanium minerals from recently discovered Mongolian titanium deposits are investigated. The deposit is estimated 500 million tons, and it has the potential to become 1 billion tons; therefore, it is considered a strategical deposit of Mongolia (from the project report). For this purpose, from the outcrops at the site representative, drilling core samples were delivered to our university. These samples have subjected to mineralogical and chemical analyzes after size reduction, classification, and enriching processes.

Mineralogical results were defined by an ore mineral that contains magnetite of 16%, chalcopyrite of 0.2%, and leucoxene of 15%. Ore mineral development sequence is leucoxene–magnetite-chalcopyrite. In the study of enrichment, there was a method high field intensity magnetic separation, gravity separation (shaking table), and flotation experiments were carried out.

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# 1. Introduction

## 1.1 Background

Titanium is a hard, silvery-white, bright element. Although titanium is known as a rare element, it is the sixth most abundant element in the earth's crust. The ore concentration is sparse, and titanium is relatively difficult to obtain from the ore, making it a precious metal. The essential titanium minerals are; rutile, ilmenite, and anatase. Titanium minerals are indispensable raw materials of the pigment industry, titanium metal industry, and welding electrodes coating industry. Titanium minerals have broad usage areas in paint, paper production, ceramic and glass industry, space and aviation industry, military industry, and medicine, and the demand for these products is increasing day by day.

Concerning titanium beneficiation techniques, flotation, gravity separation, magnetic separation, and electrostatic separation strategies are utilized. Titanium dioxide is a dark-colored mineral which, with further processing, becomes a white, opaque powder. To perform that, sulfate and chloride techniques have used. The old sulfate method produces a lot of environmental pollution. However, the chloride method requires very high graded ores. Around 90% of titanium dioxide widely is utilized as a color in the production of paint, plastic, paper, and fiber, where, notwithstanding being a non-poisonous whitener, it additionally gives UV and chemical resistance(1). The board range of end applications for pigment includes house and car paints, laminates, ceramic glaze, welding rod construction, plastic pipes and packaging, inks, clothing, leather and cloth dyeing, sunscreen, toothpaste, and make-up.

Titanium minerals are either used to produce titanium metal, which has the highest strength to weight ratio of all metals. It is utilized over a different scope of uses, including aeronautics, clinical implants, resistance, outdoor supplies, and componentry in the seaward mining and petrochemical industries. Welding is a further key market of high-level titanium feedstocks, utilized in the production of welding flux wire string, as used in the steel development and shipbuilding industries. Titanium minerals are favored for their strength and corrosion resistance.

Besides, the use of titanium can be expanded when alloyed with different components. An alloy is a substance made out of at least two parts (metals or nonmetals) that are intimately mixed by combination. On this basis, titanium composites are made by adding components such as aluminum, vanadium, molybdenum, niobium, zirconium, and numerous others to produce compounds such as Ti-6Al-4V and Ti-24Nb-4Zr-8Sn and a few others. These alloys have unique properties, as shown below(2). Contingent upon their impact on the pleasant warmth temperature and the alloying components, the combinations of titanium can be arranged into the accompanying three types:

1. The alpha alloys (is most often alloyed with aluminum and tin, is ductile, with high notch toughness, good mechanical properties at cryogenic temperatures, and has the highest corrosion resistance.)
2. Alpha-Beta titanium alloys (has medium to high strength and is both heat treatable and weldable. Alpha Beta is used to fabricate aircrafts, prosthetic devices, and marine hardware.)
3. Beta titanium alloys (the toughest of the group, is fully heat treatable and weldable. Very dense, it displays a high formability that makes it ideal for fabrication of aircraft parts that need to maintain their shape and structure, even under the most extreme pressure.)

Moreover, a little, however a quickly developing part of titanium demand is in the nanomaterials area where numerous interesting properties of titanium are used in such applications as ye-sensitized solar cells, water sanitization, tumor treatment, and noise absorption.

## **1.2 Objectives of the study**

### **1.2.1 General objective**

The industrialization of a country needs local available raw materials. This will, thusly, lead to the manufacture of local products and the export of finished products accordingly boosting foreign trade. This, thusly, will prompt the financial strengthening of our nation along these lines encouraging the accomplishment of Mongolia.

The main of this study is to explore the overview of selected titanium deposit and its market situations, investigate the beneficiation techniques, and develop the processing flowsheet of the selected titanium ore. Before any mineral processing, the fundamental methodology in the treatment of titanium metals is focused on ordinary mineral beneficiation strategies. The ore is crushed and milled. The iron substance (magnetite) is removed by magnetic separation. Humphrey spiral, shaking table, filtering, drying, and so on are one of the gravity separation methods, and for flotation, it's used to separate silica, silicate, and aluminates from the ore.

According to the objective, there were the following questions through hypotheses. Low-grade titanium dioxide contains plenty of undesirable materials. Beneficiation is the way toward expelling undesirable components in ore (alluded to as gangue) to build its financial worth (for this situation, increment the level of titanium dioxide by more than 10-20 percent). Beneficiation of low-grade titanium dioxide minerals will altogether lessen gangue. This research aimed at improving the percentage levels of titanium to obtain better value for titanium ores.

In this thesis, the proposed technique of beneficiating titanium ores uses physical separations such as magnetic separation, gravity separation, and froth flotation.

Additionally, to fulfill the general objective, the specific objective determined as follows:

### **1.2.2 Specific objectives**

- To determine chemical composition of Titanium ore from selected area in Mongolia, using X-Ray Fluorescence analyzer (XRF).
- Gravity separation tests using vibrating table would be conducted.
- To concentrate the Titanium ore by wet and dry magnetic separation
- Suggestions of further tests will be given for upgrade possibility of the titanium content etc.

### **1.3 Hypothesis**

Titanium resources will concentrate using froth flotation, gravity and magnetic separation methods; however, deposit composition contain magnetite mineral about 20% according to ALS Laboratory and titanium is heavy element therefore mentioned methods will beneficiate the titanium. It would increase percentage of titanium significantly from low grade (4.5% TiO<sub>2</sub> to approximately 10-20% of TiO<sub>2</sub>) ores.

### **1.4 Expected outcomes**

The study will develop the percentage levels of titanium so as to obtain better value for titanium ores. Following the aim of this thesis one of the consequential expected outcome is to identify appropriate beneficiation process of titanium ore. In which way of beneficiation process that ore is enrich in highest value. However, the research is based on a laboratory set up thus will consider certain challenges. Planned ore beneficiation experiment in laboratory scale-would it work effectively in real industry?

## 2. Literature review

### 2.1 General facts about titanium

Titanium is playing an essential role in the history of the world from the mid-20th century up until today. It discovered during the 1700s, produced in little amounts until the late 1800s. Finally, it went into commercial production once the Kroll process devised, and the militaries of different countries started to understand its importance(3).

History:

Titanium mineral was first found in England by William Gregor in 1791. The Reverend was analyzing some black magnetic sand from Cornwall when he came across a residue he couldn't identify(4). He believed it was a new metal, and that was confirmed a couple of years later (1793) by the German chemist Martin Heinrich Klaproth. When M.H. Klaproth identified the oxide, he also named it titanium, after Titans of Ancient Greek mythology. In spite of the discoveries, and the information that this metal would almost certainly be outrageous (thus being named after mythological beings that embodied physical strength), it wasn't until 120 years after the fact in 1910 when pure titanium would at long last produce(4).

Titanium timeline:

- 1791- Discovery of the metal by William Gregor
- 1793- Confirmation and naming of the discovery by M. H. Klaproth
- 1910- Matthew A. Hunter builds up a strategy for extricating the metal from the ore
- 1938- William Kroll develops his method for extracting titanium
- 1947- Two tons of titanium produced
- 1948- The U.S. Government begins giving motivating forces to create titanium manufacturing
- 1953- Annual production reaches thousand tons
- 1965- Per-Ingvar Brånemark places the first titanium dental implant
- 2010- More than 6 million tons being produced annually

In the periodic table, titanium is marked with the symbol Ti and an atomic number of 22. Titanium is the most known whitening agent. It used as a pigment and pasteurizer in the paint industry. Titanium minerals also find use in the paper industry to facilitate filler and printing. One of the most common applications is the plastic industry, as it increases the resistance to ultraviolet rays. It also used in the ceramic and glass industry, floor covering, printing ink, wall coverings, roofing, and organic titanium compositions as a catalyst in polymerization processes(5).

Over 70 titanium minerals known in mineral science, the economically valuable titanium minerals are limited. Among the fundamental titanium minerals, which have the most widely recognized use, are rutile (titanium dioxide) and ilmenite (iron titanium oxide). The essential primary deposits of titanium minerals are in basic rocks, and secondary deposits located in coastal sands.

## 2.2 Titanium minerals and ores

### 2.2.1 Titanium mineral occurrence

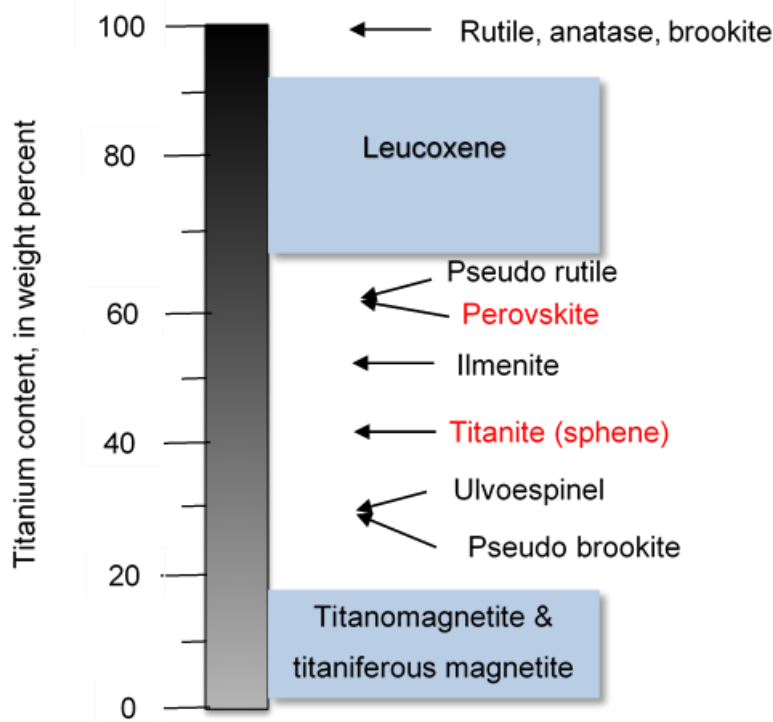
Titanium happens predominantly in two structures, ilmenite, and rutile. Those are the two commercial minerals. Titanium is also found in several other minerals, and a summary of naturally occurring titanium-bearing minerals is given in **Table 1**.

**Table 1:** Non-commercial natural occurring titanium minerals(6).

Minerals	Formula	TiO <sub>2</sub> , [%]	Geological occurrence
Ilmenite	FeTiO <sub>3</sub>	45-53	Common accessory mineral in most igneous and metamorphic rocks. Common detrital mineral.
Rutile	TiO <sub>2</sub>	95-100	Common accessory mineral in medium to high grade metamorphic and igneous rocks. Common detrital mineral and alteration products of ilmenite and other titanium minerals.
Anatase	TiO <sub>2</sub>	95-100	Low-temperature polymorph of rutile. Usually secondary, formed by the alteration of the other titanium minerals.
Brookite	TiO <sub>2</sub>	95-100	Metastable polymorph of rutile and anatase. Found in cavities, fissures, and veins. Weathering product of other titanium minerals. Relatively rare.
Pseudo rutile	Fe <sub>2</sub> Ti <sub>3</sub> O <sub>9</sub>	60-65	Alteration product of ilmenite in sediments. Common phase in altered ilmenite concentrates.
Altered Ilmenite	FeTiO <sub>3</sub> - Fe <sub>2</sub> TiO <sub>9</sub>	53-70	Term of the alteration products of ilmenite consisting of mixtures of ilmenite, pseudo rutile, and leucoxene. Common in heavy mineral sands.
Leucoxene	High TiO <sub>2</sub>	70-100	Term for high TiO <sub>2</sub> alteration products of ilmenite and occasionally sphene, usually consisting of

Minerals	Formula	TiO <sub>2</sub> , [%]	Geological occurrence
			microcrystalline rutile, or anatase, with minor pseudo rutile, ilmenite, hematite, or goethite.
Titanite (sphene)	CaTiSiO <sub>5</sub>	40	Widely distributed accessory mineral in intrusive igneous, low-grade metamorphic rocks and as a detrital mineral.
Perovskite	CaTiO <sub>3</sub>	58	Accessory mineral in metamorphic and igneous rock.
Pseudo brookite	Fe <sub>2</sub> TiO <sub>5</sub>	33	Accessory mineral in igneous rocks. Forms as an oxidation product of ilmenite and titanomagnetite
Ulvoespinel	FeTiO <sub>4</sub>	36	Accessory mineral in basic igneous rocks, usually found as exsolution lamellae in magnetite.
Titanomagnetite	(Fe, Ti) <sub>3</sub> O <sub>4</sub>	0-34	Term for optically homogeneous Fe-Ti spinel containing magnetite and ulvoespinel in solid solution. Common accessory in basic igneous rocks.
Titanohematite	(Fe, Ti) <sub>2</sub> O <sub>3</sub>	0-30	Term for optically homogeneous hematite-ilmenite. Common accessory in acid intrusive and anorthosite suites.

The silicate minerals - biotite, augite, melanite garnet, calcic amphiboles which contain little amounts of titanium are excluded from **Table 1**.



**Figure 1:** The figure shows that common titanium-bearing oxide and silicate minerals (black text) and (red text) respectively with their approximate titanium content (in weight percent). The blue shaded boxes represent the range of titanium content for the mineral species in the boxes.(7)

There is also a set of minor titanium naturally occurring minerals listed in **Table 2**(8). These minerals are not of economic importance.

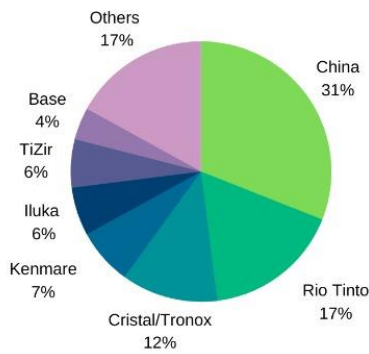
**Table 2:** Minor titanium bearing naturally occurring minerals (8)

Mineral	Formula	Mineral	Formula
Anosovite	Ti <sub>3</sub> O <sub>5</sub>	Hydroturile	TiO <sub>2</sub> .xH <sub>2</sub> O
Chrictonite	(Ca,Ln,Ac) <sub>2</sub> - x(Ti,Mg,Al,Fe,Tr) <sub>21</sub> O <sub>38</sub>	Kalkowskyn	Fe <sub>2</sub> Ti <sub>3</sub> O <sub>9</sub>
Knopite	(Ca,Ti,Ce <sub>2</sub> )O <sub>3</sub>	Doetlerite	TiO <sub>2</sub>
Pyrophanite	MnTiO <sub>3</sub>	Fulvite	TiO
Mananilmenite	(Fe,Mn)TiO <sub>5</sub>	Geikielite	MgTiO <sub>3</sub>
Picroilmenite	(Mg,Ge)TiO <sub>5</sub>	Tielite	AlTiO <sub>3</sub>
Yttrocraosite	YTh <sub>2</sub> Ti <sub>4</sub> O <sub>11</sub>		

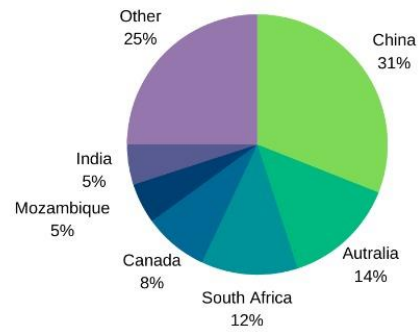
## 2.2.2 World Titanium Feedstock Resources

Globally titanium producing countries and producer's information shown by the pie chart below **Figure 2**. In 2018 total production of titanium feedstock by county and producers was approx. 7.4 Mt.

**Global Titanium Feedstock By Major Producer**

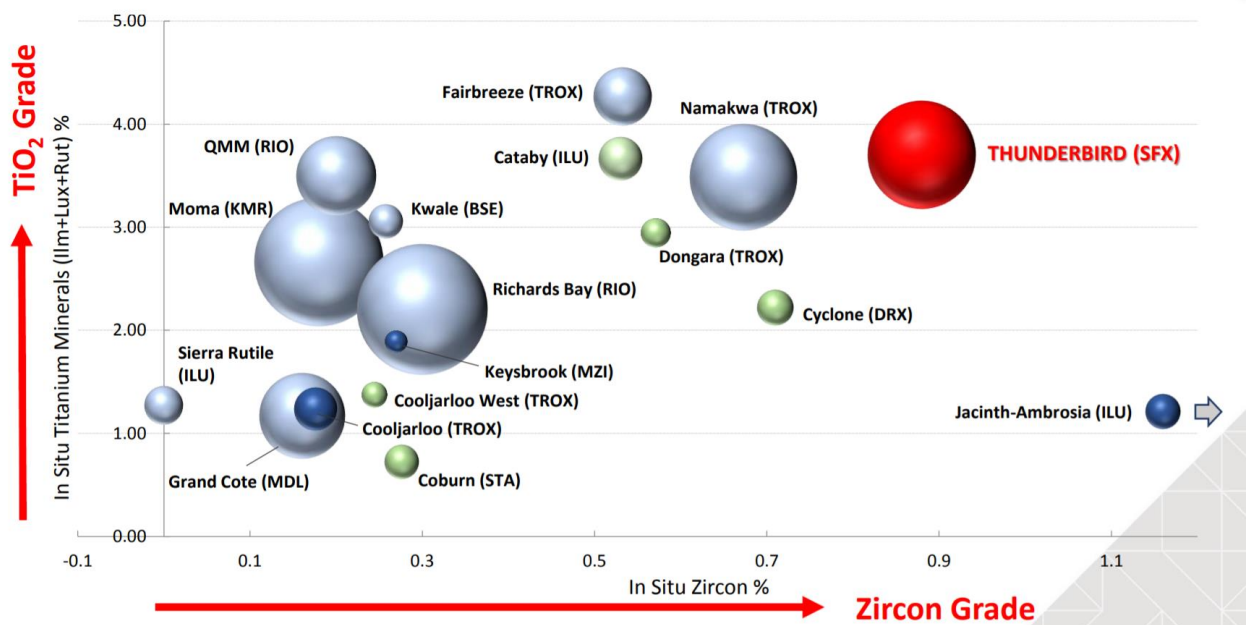


**Global Titanium Feedstock By Country**



**Figure 2: Global titanium feedstock by country and producer(9)**

From the figures, China is the leading titanium feedstock producer and also country, around 31% (out of 100%) produced in China. According to USGS, China is the world's largest titanium reserves, with a total of 200 million tons identified to date, which makes up 31% of the world's total. Around 108 minefields across 21 territories, self-ruling districts, and regions have discovered titanium assets, with Panxi in Sichuan, Chengdu in Hebe, alongside others in Yunnan, Hainan, Guangxi, and Guangdong the most prominent. Panxi and Chengde have most of the world's total principal reserves. Titanium placer deposits are also distributed in Hainan, Yunnan, Guangdong, and Guangxi provinces. Henan, Hubei, and Shanxi provinces have limited rutile reserves.



**Figure 3: World class, high grade ore reserve**

Blue bubbles are illustrating the operating mines, green bubbles are indicating ore reserves however operating is not started yet. Light blue bubbles show the operating African mines' deposit reserves. Bubble size is relative to tons of contained valuable heavy mineral (VHM). Only deposit

reserves >1.2Mt contained VHM illustrated. Data compiled by Sheffield from public sources. This investigation doesn't show the difference in product value between rutile, leucoxene, and ilmenite.

## 2.3 Titanium minerals occurrence

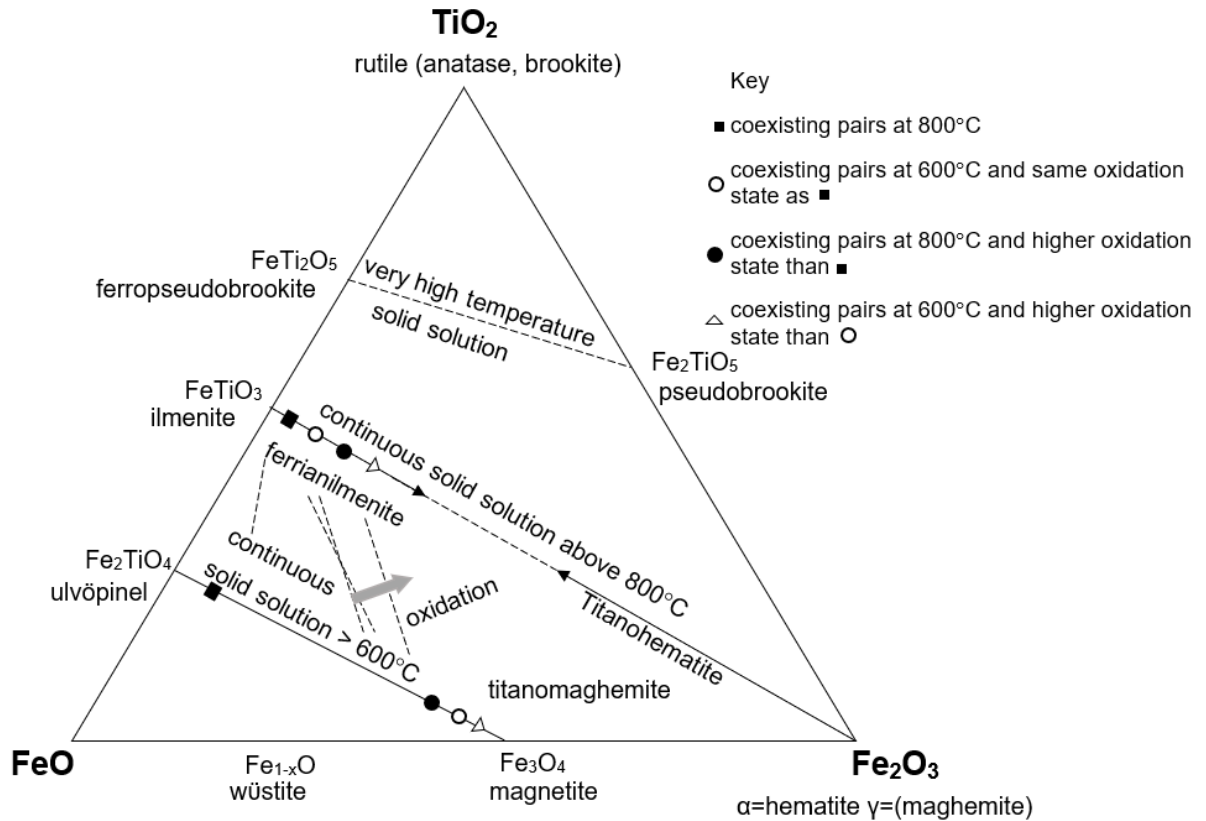
### 2.3.1 Mineralogical occurrence

Titanium is relatively widely distributed and abundant. With an approximated average concentration in the world's crust of 0.6 %, it is ninth arranged by wealth after oxygen, silicon, aluminum, iron, magnesium, calcium, sodium, and potassium (10). Its concentration is approx. 1/20 that of aluminum, and 1/10 that of iron. It is 5 – 10 times as abundant as chlorine, sulfur, or phosphorus, and more abundant than the rest of the metals put together. Thus, for example, it is 60 times as abundant as copper or nickel and 300 times as abundant as molybdenum (10).

Basic and alkalic rocks tend to have the highest  $\text{TiO}_2$  contents of igneous rocks. Few igneous, sedimentary, or metamorphic rock types have an average  $\text{TiO}_2$  content as much as an order of magnitude different from the crustal average. In many rocks, common silicate minerals rather than oxides contain most of the  $\text{TiO}_2$  in the rock. Titanium happens in the crust in two chief minerals: ilmenite and rutile. Ilmenite is a common accessory mineral in many igneous and metamorphic rocks. The ore can contain up to 6%  $\text{Fe}_2\text{O}_3$  and structures an extensive solid solution with hematite at temperatures above  $600^\circ\text{C}$ . Magnesium and manganese may substitute for ferrous iron in ilmenite, giving rise to the rare end-members geikeilite ( $\text{MgTiO}_3$ ) and pyrophanite ( $\text{MnTiO}_3$ )(3).

The titanium, as mentioned earlier, is present in rocks as oxide and silicate minerals. Thus, oxide minerals in the system  $\text{FeO} - \text{Fe}_2\text{O}_3 - \text{TiO}_2$  are shown in **Figure 4**. The world's primary raw materials of Ti are rutile and ilmenite. Force (10) classified Ti deposits into five significant classes: igneous, metamorphic, hydrothermal, sedimentary, and weathered. Currently, the igneous, sedimentary, and weathered types are of most economic interest. In the world, about 80% of the total mine production of Ti mineral sources are in Australia, South Africa, and Canada, while Norway is producing approx. 5 %, as ilmenite. The world resources of Ti minerals are huge, in spite of the fact that the known resources of excellent ilmenite and rutile are most likely

constrained.



**Figure 4:** Composition of oxide minerals in the system FeO-Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>. The dashed line among ilmenite and magnetite shows regular geological conjunction at moderately low temperatures, in which magnetite usually contains ilmenite lamellae. Such intergrowths are formed by the oxidation of magnetite-ulvöspinel followed by oxidation-exsolution of ilmenite(10).

The 1996 classification scheme of Buddington for describing the minerals of the TiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub>-FeO system has been adopted(11). The mineral nomenclature follows:

- Rutile is an optically homogeneous, essentially pure, common form of TiO<sub>2</sub>. It forms tetragonal crystals.
- Anatase is polymorph of rutile forming a blue or black tetragonal phase at low temperature.
- Brookite is a rare metastable form of rutile and anatase, formed by alteration of other titanium minerals, with an orthorhombic crystal structure.
- Ilmenite is a homogeneous, hexagonal phase consisting of FeO•TiO<sub>2</sub>, with less than 6% Fe<sub>2</sub>O<sub>3</sub> in solid solution.
- Ferrian-ilmenite is a homogeneous, hexagonal phase consisting of FeO•TiO<sub>2</sub>, with 6% to 13% Fe<sub>2</sub>O<sub>3</sub> in solid solution.
- Magnetite is an optically homogeneous, spinel phase with a formula close to Fe<sub>2</sub>O<sub>3</sub>, containing less than 5% TiO<sub>2</sub>.
- Titanomagnetite is a single-phase, homogeneous, cubic mineral, with Fe<sub>2</sub>O<sub>3</sub> as the dominant phase, but contain more than 5% TiO<sub>2</sub>.

- Hematite is a hexagonal-trigonal phase with a formula approaching  $\text{Fe}_2\text{O}_3$ , containing less than 5%  $\text{TiO}_2$ .
- Titanohematite is hematite with greater than 5%  $\text{TiO}_2$ , usually as  $\text{FeO} \cdot \text{TiO}_2$  in solid solution, with little excess  $\text{TiO}_2$ .
- Pseudo rutile is a hexagonal mineral, originally referred to as arizonite, formed by the alteration of ilmenite, with a composition approximating  $\text{Fe}_2\text{Ti}_3\text{O}_9$  or  $\text{Fe}_2\text{O}_3 \cdot 3\text{TiO}_2$ .
- Altered ilmenite is a general term used to describe the alteration products of ilmenite, having a chemical composition between ilmenite and pseudo rutile. Altered ilmenite need not be optically homogeneous and is essentially amorphous, although submicroscopic intergrowths of ilmenite and pseudo rutile may be present.
- Leucoxene is a general term for the high  $\text{TiO}_2$  alteration products of all titanium-bearing minerals. Leucoxenes are distinguished optically from rutile by their characteristic internal reflections, although they may consist almost entirely of cryptocrystalline rutile or anatase in the final stage of the alteration.

Ilmenite is a typical detrital mineral in sediments. In close surface environments, it regularly experiences alteration by a process in which the iron is oxidized and leached from the ilmenite grain, bringing about the enhancement of titanium until it comprises of  $\text{TiO}_2$ , either as rutile or anatase. Rutile is steady over a wide scope of geological conditions and thusly is a boundless widespread accessory mineral in metamorphic gneisses and schists and some igneous rocks, for example, pegmatites. Its stability and hardness bring about rutile being a typical detrital mineral(12).

Other significant titanium-bearing minerals incorporate anatase and brookite (the low-temperature polymorphs of rutile), perovskite ( $\text{CaTiO}_3$ ), titanite ( $\text{CaTiSiO}_5$ ), titanomagnetite and titanohematite. Anatase is normally formed by the alteration of other titanium minerals, is a minor constituent of some igneous and metamorphic rocks, and is generally found in rock pegmatites and hydrothermal veins, or as an authigenic mineral in sediments(12).

### 2.3.2 Petrography, and Chemistry of the Ilmenite and Leucoxene

Pure **ilmenite** has following properties:

Formula	$\text{FeTiO}_3$
Chemistry	52.66% by mass $\text{TiO}_2$ , 47.43% by mass $\text{Fe}_2\text{O}_3$
Density	$4.72\text{g/cm}^3$
Mohs hardness	5 to 5.5
Color	Black to black brown

Magnetic property	Intensely paramagnetic
Electrostatic property	Conducting

Ilmenite, occasionally known as titanite, was named in 1827 after a locality in the Ilmen Mountains, Southern Urals, Russia. It is an essential dispersed accessory mineral in almost all intrusive and extrusive rocks. It has overriding significance as a titanium mineral in norites, gabbro's, and anorthosites. There is consistent miscibility at high temperatures (>600 °C) among ilmenite and hematite (Fe<sub>2</sub>O<sub>3</sub>). In the mixed crystals, though, part of the Fe can be replaced by Mg, Mn, and Al, as well as part of the Ti by Mg. As the temperature drops, hematite and ilmenite become segregated forming titanite-hematite: here, thicker or more slender lamellae of hematite in fluctuating sums are intercalated with ilmenite(12).

Another crucial mineral is titanium magnetite. The two spinel's magnetite (Fe<sup>2+</sup> Fe<sub>2</sub><sup>3+</sup>O<sub>4</sub>) and ulvite (iron titanium oxide mineral) (Fe<sub>2</sub>TiO<sub>4</sub>) are seamlessly miscible at high temperatures. Further, the Fe<sup>2+</sup> part can be replaced isomorphous by Ti, Mg, Mn, and other elements, and part of the Fe<sup>3+</sup> can be replaced by Ti, Al, V and Cr in the magnetite. As the temperature diminishes, there is segregation into magnetite, ilmenite, and ulvite. Complete segregation into pure magnetite and ulvite doesn't occur. Besides, ilmenite is precipitated in the form of fine lamellae on the octahedral faces of the magnetite. The slower the cooling, the coarser the segregation structure.

After the ilmenite is discharged from solid rocks, it is liable to weathering (12). Prominently under humid tropical conditions, iron progressively dissolves and titanium becomes relatively enriched. The final component in the weathering process is the mineral mixture **leucoxene**, principally consisting of Ti oxides and, to a far lesser degree, Fe oxides(12). The process of weathering is the so-called leucoxenization. Leucoxenization only arises above the groundwater level. Content of the TiO<sub>2</sub> in the ilmenite is remarkably crucial for the economic-geological and processing context thus, the process of leucoxenization has been thoroughly investigated. Starting at the grain and structural boundaries, the disintegration of the ilmenite structure and development of an amorphous iron/titanium oxide blend happens. FeO is progressively oxidized to Fe<sub>2</sub>O<sub>3</sub>, Fe oxides disintegrate. The amorphous TiO<sub>2</sub> recrystallizes as finely crystalline rutile, all the more once in a while anatase or brookite(12). This finely crystalline mineral mixture consisting mostly of TiO<sub>2</sub> is called leucoxene. The disintegration of the iron oxides instigates the relative increase in TiO<sub>2</sub> and the decrease of magnetic susceptibility. The inherent color of "leucoxene" directly depends on its TiO<sub>2</sub> content **Table 3**.

**Table 3:** Dependence of the color of leucoxenes on their TiO<sub>2</sub> content.(12)

TiO <sub>2</sub> (%)	Color
52-63	Dark gray
63-68	Reddish gray
68-75	Auburn
75-80	Yellowish-brown
80-85	Yellow orange
85-90	Yellowish-gray
90-95	Yellowish-white
95-100	White

In 1992 Elsner (12) listed further distinguishing characteristics of ilmenite, leucoxene, and rutile **Table 4**.

**Table 4:** Differentiation of ilmenite, leucoxene, and rutile in the industry.(12)

Mineral	Density	Magnetic susceptibility
Ilmenite	>4.1 g/cm <sup>3</sup>	magnetic
Leucoxene	<4.1 g/cm <sup>3</sup>	nonmagnetic
Rutile	>4.1 g/cm <sup>3</sup>	nonmagnetic

### 2.3.3 Petrography, and Chemistry of the Rutile

The name of the rutile originates from the Latin rutilis. Of the three crystal modifications of natural titanium dioxide (rutile, anatase, and brookite), rutile is the most significant from an economical point of view in **Table 5**.

**Table 5:** Crystal modification of TiO<sub>2</sub> and their properties.(12)

Mineral	Rutile	Anatase	Brookite
Formula	TiO <sub>2</sub>		
Chemistry	On average 100% TiO <sub>2</sub>		
Density [g/cm <sup>3</sup> ]	4.21	3.90	4.14
Mohr hardness	6 to 6.5	5.5 to 6	5.5 to 6

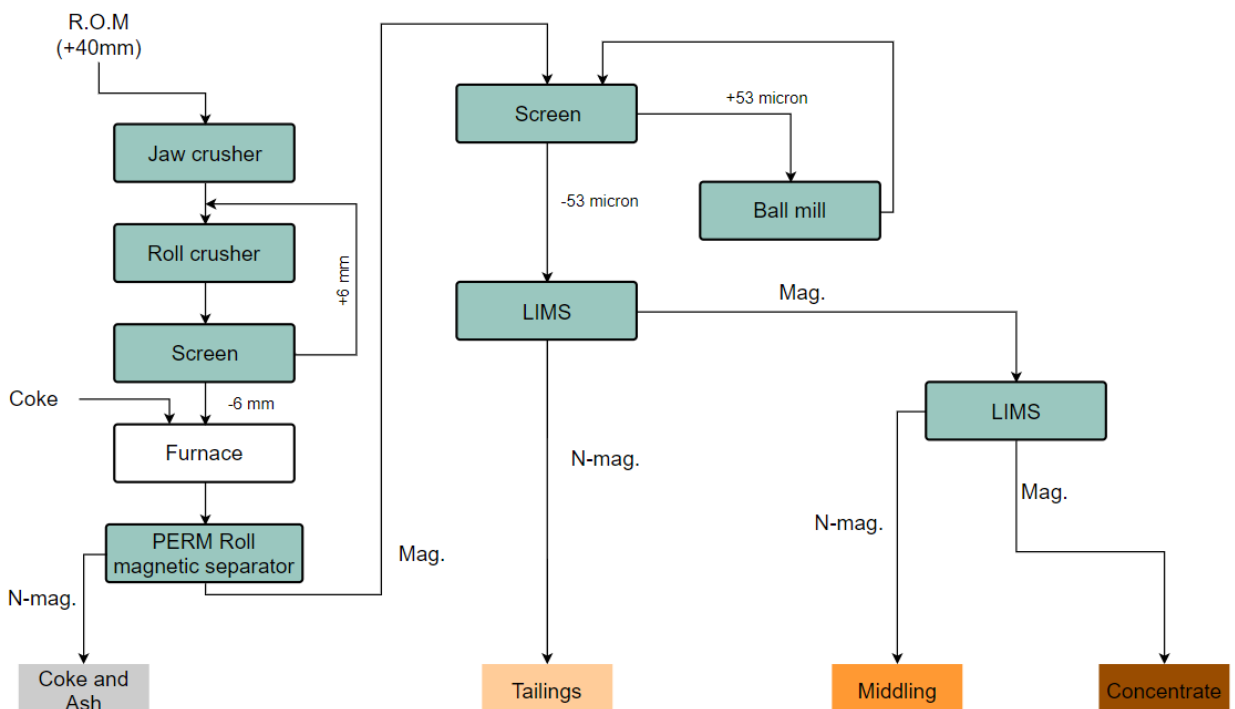
Mineral	Rutile	Anatase	Brookite
Color	Yellowish, gray, beige, bluish, violet	Black, auburn, yellowish, brown, dark blue, gray	Dark brown to green black
Magnetic properties	Nonmagnetic		
Electrostatic properties	Conductive		

**Brookite** is infrequent and of no economic importance. **Anatase** can be created through transformation of rutile in placers, but is also infrequent in these cases.

## 2.4 Beneficiation of Titanium ore

### 2.4.1 Titanium Minerals Enrichment Processes

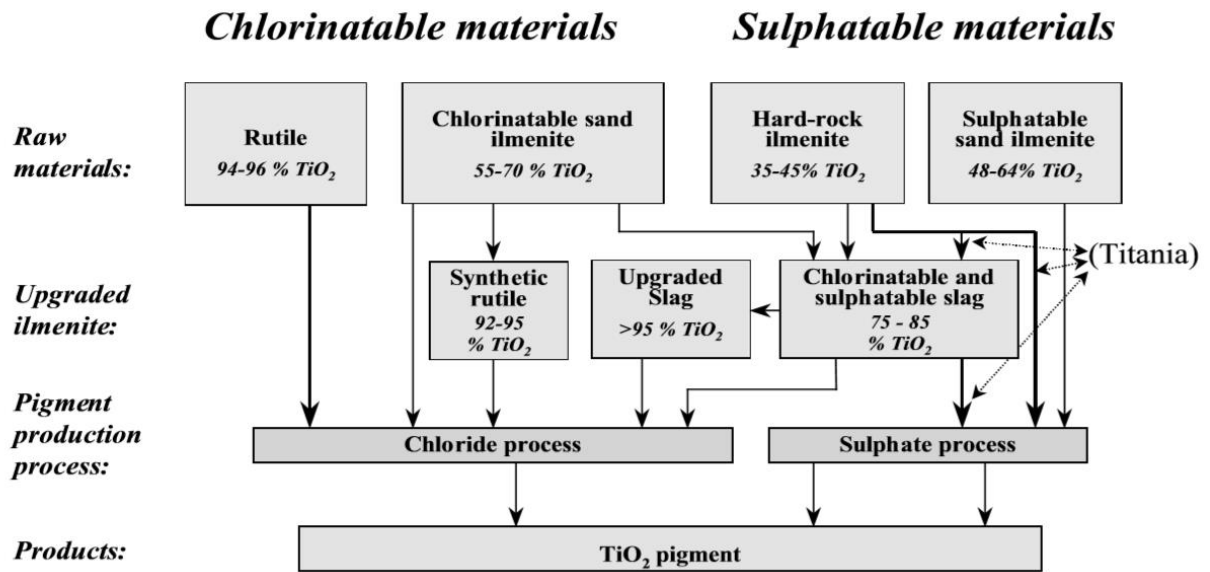
The main mineral processing methods used in enrichment and recovery of titanium minerals are gravity enrichment, electrostatic enrichment, magnetic enrichment, flotation, and chemical enrichment. The enrichment flow diagram of an exemplary titanium minerals (low-grade titano-magnetite ore) enrichment facility is given in **Figure 5**.



**Figure 5:** Process flowsheet for recovery of Fe and TiO<sub>2</sub> values from low grade titano-magnetite ore (13)

Furthermore, for the production of titanium dioxide pigment; there are two different processes, the sulfate, and chlorite processes. All high titanium slags produced through smelting

processes worldwide have used as feedstock for one of these two processes. A few connections between titanium raw materials and their products have appeared in **Figure 6**.



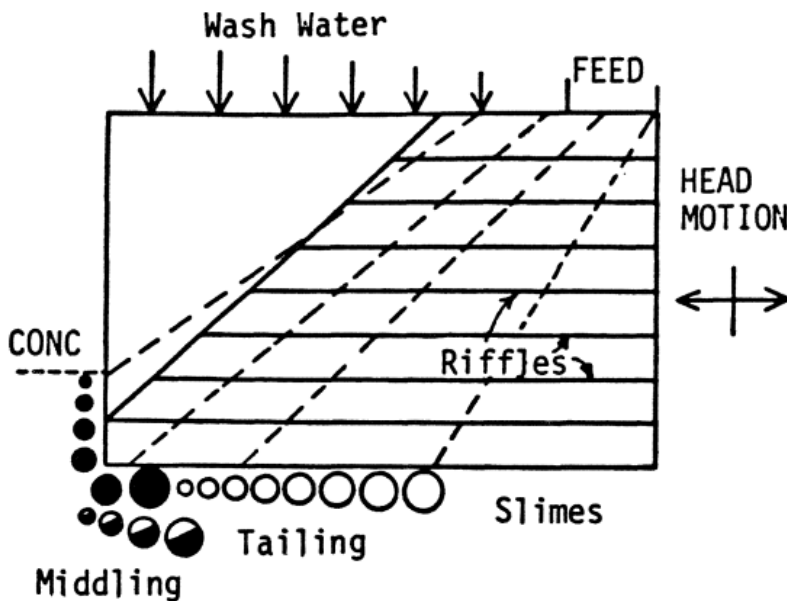
**Figure 6:** Paths from titanium raw materials to products(10).

#### 2.4.2 Gravity Separation

A gravity separation process is mostly applied in deposits like gold, tungsten, tin, manganese, mercury, titanium, lead, tantalum-niobium, galena, barite, fluorite, pyrite, limonite, hematite, antimony, chromium, and ferrous. This process is the earliest method applied in mineral processing. In its simplest definition, gravity separation is a class of methods that take advantage of the density difference among mineral particles. Therefore, particles of which densities are not quite the same as one another have their relative movement against the power of the gravity relying upon the variables, for example, a viscosity of the earth, resistance to the motion in viscous environment, weight, particle size, density, and shape(14). As expressed by the density distinction among mines and the complexity of gravity, liquid force, and mechanical power in moving medium, mines realize mineral grains detachment through density contrast, and gravity separation technique despite everything possesses a fundamental role in the contemporary mineral processing.

This part introduces developed gravity concentration equipment, particularly vibrating table, and reports detailed explanations of the material in terms of principles of design and their effects on operational parameters. Known physical phenomena of a teetered bed associates initial vibrating table, resistance to water flow, vibration, and density contrasts. The resultant effect of these associated forces can also be manipulated by integrated settings of feed rate, solid percent, plate inclination, and water rate.

### 2.4.2.1 Wilfley Shaking table



#### Particle Movement on a Shaking Table

**Figure 7:** Principal of operation of the Wilfley shaking table

The gravity (wet shaking table) separator is the oldest mineral processing (or beneficiation) technique used to demonstrate the maximum gravity recovery, and it is used to separate the samples into a light and heavy mineral fraction supplied that there is a marked difference in the density of the minerals. Because of its low limit (a few kilograms), the shaking table is regularly utilized as a cleaner for the last updating of gravity concentrate delivered from divergent concentrators, dances, and spirals. An effective separation is provided in the shaking table, which is widely used among enrichment methods in a flowing medium. The table surface, which is normally rectangular, parallel edge, V-shaped or trapezoidal, typically secured with tight and long ledges, with a few degrees of inclination with the horizontal axis, is moved to and froth along with the x-axis of the table. The mineral grains fed to the shaking table surface move diagonally in line with the motion of the fluid medium flowing in layers and the back and forth movement perpendicular to it, and the heavy minerals separate from the light minerals.

The shaking table has four decomposition zones, slime, middling, tailing, and concentrated. The light minerals that make up the residue cover the shortest distance. The heavy minerals that make up the concentrate are shifted to the longest distance on the table surface.

The thresholds on the shaking table surface are either laths that are added later, or grooves cut into the table surface. The heights of the limits are zeroed towards the concentrated zone. As the presence of the thresholds changes the flow conditions, as with the jigs, a classification of disability collapse occurs between the limits, thereby making both an effective separation and increasing the shaking table capacity.

There are a feeding box and washing water dispenser at the top of the table. The water dispenser consists of a groove with holes. The amount of water flowing is adjusted with a latch to allow the water on the table surface to flow as a layer. The shaking movement of the table is provided by an eccentric mechanism.

Parameters such as ore size, speed and amplitude, amount of wash water and slope affect shaking table performance.

**Feed Ore Size:** The size of the fed ore is between 1-0,025 mm. However, in coal enrichment, the upper size goes up to 8 cm. Since coarse-light and fine heavy mineral grains move together on the table surface, to eliminate this defect, classification should be made according to the size before feeding the table.

**Speed and Amplitude:** The shaking table for coarse ore is operated with a speed of 240-270 rpm and an amplitude of 18-25 mm. In fine ore, short amplitude and high speed are used.

**Water Consumption:** The water given to the table consists of the total of washing and feeding water. Water consumption is around 1.2-1.4 tons per ton of ore.

**Slope:** Slope between 1/48 - 1/24 for fine ores and 3/48 - 1/12 for coarse ores.

The parameters that can be controlled at the table are as follows:

- The slope of the table top
- Amplitude of the table
- Frequency of the table
- Washing water amount
- Feed amount

A laboratory scale shaking table is shown in **Figure 8**.



**Figure 8:** Wilfley lab scale shaking table

### **2.4.3 Magnetic Separation**

Magnetic separation has long used to upgrade and beneficiate a wide range of industrial minerals. Progresses in both wet and dry magnetic separators throughout the years have

expanded their use, and questions are regularly raised about which separation technique or equipment type is most appropriate for a particular operation(15).

Magnetic separation is a process usually accepted for concentrating the iron-bearing minerals from the raw ore. The most frequently used beneficiation methods for iron ores are the gravity and magnetic separation techniques, as they are simple, inexpensive, and non-destructive. Depending on the ore characteristics, magnetic separation may be preferred individually or in combination with gravity separation. The choice of a magnetic separation method relies upon numerous factors like mineral mineralogy, mineral liberation size, and magnetic susceptibility of minerals. Magnetic separation uses the differences in the magnetic properties of minerals. Based on the magnetic properties minerals generally categorized into three different groups: ferromagnetic, paramagnetic, and diamagnetic. The magnetic susceptibility of the minerals may determine the selection of high or low-intensity magnetic separators(16).

Concentration is attained by coincidentally applying to all particles in an ore a magnetic force acting on magnetic particles and a combination of forces that act in a different direction and affect magnetic and non-magnetic particles. The most commonly applied non-magnetic forces are gravitational and centrifugal. Other forces like frictional, electrostatic, Van Der Waals, and capillary usually enter in an incidental manner. When maximum field intensity is less than about 2000 gauss, it has classified as a low-intensity magnetic separator. These separators used to treat paramagnetic and ferromagnetic minerals like iron and magnetite. High-intensity magnetic separators (HIMS) generally have field strengths of 10 to 20 kilogauss. These separators have used to treat weakly magnetic minerals, such as hematite (16). Titanium-bearing minerals specific magnetic susceptibilities are shown in below. Specific susceptibility means that susceptibility per unit mass.

**Table 6:** Magnetic susceptibilities of common minerals(17)

Mineral	Specific susceptibility ( $10^{-8}$ m <sup>3</sup> /kg)	Mineral	Specific susceptibility ( $10^{-8}$ m <sup>3</sup> /kg)
Calcite	-0.3 to -1.4	Pyrrhotite	10 to 30,000
Quartz, Feldspar, Magnesite	-0.5 to -0.6	Hematite	10 to 760
Kaolinite	-2	Ilmenite	46 to 80,000
Halite, Gypsum, Anhydrite	-0.5 to -2.0	Magnetite	20,000 to 110,000
Serpentinite	120 to 2900	Dolomite	-1 to -41

Mineral	Specific susceptibility ( $10^{-8}$ m <sup>3</sup> /kg)	Mineral	Specific susceptibility ( $10^{-8}$ m <sup>3</sup> /kg)
Illite, Montmorillonite	5 to 13	Sandstones, Shales, Limestone	0 to 1200
Biotite	5 to 52	Serpentine	110 to 630
Goethite	26 to 280	Clay	10 to 15
Chalcopyrite	0.6 to 10	Coal	1.9
Pyrite	1 to 100		

#### 2.4.4 Froth Flotation

Flotation represents one of the outstanding technological achievements of the 20th century for the concentration of valuable minerals, especially in mineral, metallurgical and chemical industries. It has estimated that about two thousand million tons of approximately 100 different minerals, including 95% of all base metals and raw materials, are floated annually(18).

In mineral processing fine-sized particles ore, flotation is a significant method to use. Three phases are always present in the flotation process; these are gas, liquid, and solid phases (19). Applying flotation processes in the physical and chemical properties of the phases it is beneficial. In the flotation, the air supplied to the pulp forms the gas phase to establish the required air bubbles during the mineral grains. The liquid phase is the phase forming the pulp in which the events take place. There are also water-soluble or emulsified flotation reagents in the liquid phase, which consists mostly of water. The solid phase consists of mineral grains that have desired to be separated(20). Besides, the interfaces between these phases and their properties are also necessary. In principle, flotation is an adsorptive bubble separation technique based on the differences in the surface activity of different materials. It has characterized by the fact that only specific solid components are selectively attached to the surface of bubbles and thereby causing separation of the materials(21).

For the flotation of rutile minerals, its fundamental standard is to utilize flotation reagents with active functional groups-COOH, -AsO<sub>3</sub>H<sub>2</sub>, -PO<sub>3</sub>H<sub>2</sub>NOH, which can adsorb on the outside of rutile by compound bonds, and afterward cause flotation as the hydrophobic hydrocarbyl. The advancement of the flotation method principally relies upon the improvement of flotation reagents, including the collectors and the regulators(22).

The fundamental collectors in the flotation of rutile incorporate anionic collectors like arsenic acid, fatty acid, and collectors like chelating and styrene phosphonate, hydroximic acid.

These collectors can be utilized alone, some can be blended in with one another, which may cause the synergistic impact and improve the impact of flotation(23).

According to the literature reviews, froth flotation is an efficient method to separated rutile from the gangue minerals. Even so, there are still some difficulties still exist in rutile flotation, for instance, the lack of admirable collectors. As sodium oleate has broadly utilized in the flotation of rutile, its selectivity is weak(24). In addition, despite its efficiency, the benzyl arsenic acid (BAA) is virulent. Recently, composite collectors have gotten significantly famous in the flotation of rutile. Analysts have deliberately looked at different kinds of collectors, and have illustrated styryl phosphoric acid (SPA) to be powerful. Under the help of fatty alcohols, the flotation turns out to be immeasurably better than the state of a single SPA (24).

In 1986 Cui et al. developed a flotation reagent scheme for the rutile ore of Zaoyang Rutile Mine, China. They used sodium fluorosilicate ( $\text{Na}_2\text{SiF}_6$ ) as a gangue depressant, benzyl arsenic acid (BAA), as a rutile collector. Good results have obtained, and have used in industrial applications. However, benzyl arsenic acid is virulent, it cannot widely have used in the application, so it should have replaced by other nontoxic and effective collectors. Buiatovic S (25) considered the flotation of rutile and ilmenite minerals in igneous rocks. What's more, the outcomes indicated that the joined collector of organophosphate and amber amido acid ester was the most effective for the flotation of rutile other than the pH estimation of pulp. Using sulfuric acid to adjust pH to 4.5, they floated a rutile concentrate assaying 84.5%  $\text{TiO}_2$  from a tabling concentrate. The recovery of the flotation process was 86.4%. They found that the fatty acid type collectors were not capable(24).

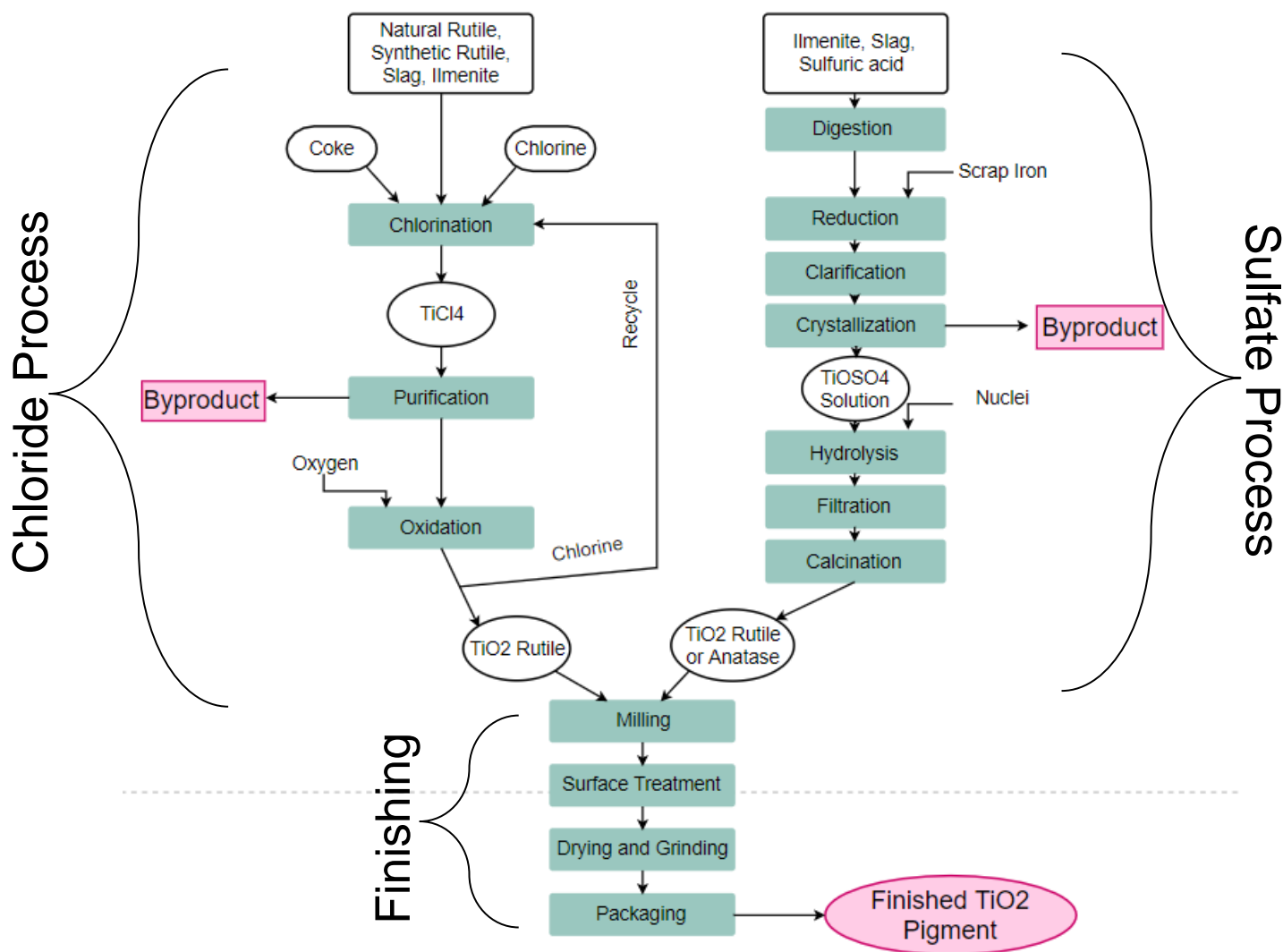
Flotation of ilmenite, rutile, and perovskite can be achieved using aliphatic acids at acid pH or sodium oleate at a pH between 6.5 and 8.0. Typically, these flotation techniques apply to ores with a gangue consisting mainly of quartz(26). Successful ilmenite and rutile flotation from siliceous gangue were achieved using a succinimide collector at a pH between 3.5 and 4.5. The procedure was effectively tried at a pilot plant scale. It has also been reported that successful ilmenite flotation from pegmatites was achieved using an arsenic acid collector in the presence of acidified silicate. Significant research work was additionally done on the flotation of titanium minerals utilizing hydroxamate as a collector(27).

#### **2.4.5 Further processing of titanium dioxide raw materials into titanium dioxide pigments**

About 90% of the titanium dioxide raw materials are used for the production of titanium dioxide pigments, also for the production of titanium and titanium sponge (approx. 5% of the annual consumption of titanium dioxide raw materials) as well as for the manufacture of welding products (another approx. 5% of the yearly use of titanium dioxide raw materials), for example as

a component of coating masses for welding electrodes, as a powder filling in cored wire and as a component of welding powders(28).

In the area of pigment production, there are two different production processes for which different types of titanium dioxide raw materials are used, namely the chloride process and the sulfate process (illustrated, the schematic diagram below **Figure 9**).



**Figure 9:** Schematic diagram for chloride and sulfate process(29)

### 2.4.5.1 Sulfate process

Dried ilmenite or slag is pulverized and mixed with concentrated sulfuric acid. Water or steam is injected to initiate the reaction **Figure 9**. The main reaction can be described by the following equation(1).

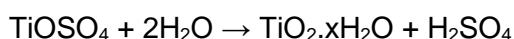


The cake is allowed to mature (1–12 h) and dissolved in water, or recycled dilute sulfuric acid. The temperature must be maintained at 85 °C to avoid premature hydrolysis. Ferric ions in

solution are reduced to the ferrous state. Still, a small proportion of titanous ions must also be reduced to the titanous state ( $Ti^{3+}$ ), preferentially, to ensure the reduction of ferric species(28).

The solution is filtered to remove solids. The filtrate is cooled under vacuum, precipitating  $FeSO_4$  as copperas (ferrous sulfate –  $FeSO_4 \cdot 7H_2O$ ). Copperas is used in sewage water treatment and as raw material for iron oxide pigment. Alternatively, the filtrate can be roasted to  $Fe_2O_3$  and  $SO_2$ , thereby recovering sulfuric acid.

The final solution is thermally hydrolyzed to  $TiO_2$ , according to the reaction below. For higher yields,  $TiO_2$  nuclei are added. Hydrous Titania is collected and washed with weak acid. The product is bleached with acid and mixed with zinc or aluminum powder. The Titania is finally dried, calcined, and processed.

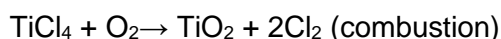
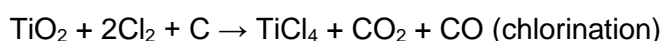


Spent acid (20–28%  $H_2SO_4$ ) is concentrated to 70–80% and reused. In another approach, the spent acid is neutralized with lime. Alternatively, the spent acid can be used in the fertilizer industry. The process is summarized in **Figure 9**.

Part of the titanium sulfate byproduct crystallized as copper is used in water treatment plants and sewerage, as well as in the production of iron oxide pigments. The remainder is disposed of (1).

#### **2.4.5.2 Chloride process**

The chloride process **Figure 9** uses mostly slag, rutile, synthetic rutile, and, rarely, ilmenite, or leucosene as raw materials. Calcined petroleum coke and chloride are used as a reducing agent. This coke has low ash content and low volatiles content. This is a continuous process and the main reactions are as given below(30):



The chlorination process is conducted at 1000 °C. Under these conditions, most of the metal chlorides are gaseous. However, the magnesium and calcium chlorides are liquid and clog the chlorination surface bed. Their content in the raw material must not exceed 1% and 0.2% respectively as oxides.  $SiO_2$  must also be kept within certain limits (1.5%) as it coats mineral grains and reduces their reactivity. All the raw materials must be dry to avoid losses of chlorine as HCl. The conversion rate in this process is high, 98–100% for chlorine, and 90–100% for  $TiO_2$ .

$TiCl_4$ , together with other gaseous metal chlorides, combustion gases, and residual  $TiO_2$ ,  $SiO_2$ , and petroleum coke, is discharged from the reactor and cooled, by adding cold  $TiCl_4$ , to a temperature just above the boiling point of  $TiCl_4$ . Most of the chlorides condense, are separated from the residual solids and are then dissolved in water. This solution is used in wastewater

treatment as a precipitation agent, provided it contains mainly FeCl<sub>2</sub>. If the solution has a different composition, it is neutralized with lime and discharged.

TiCl<sub>4</sub> is cooled and separated from the gases. The liquid TiCl<sub>4</sub> is refined by the addition of a reducing agent and distillation in order to eliminate vanadium. Vanadium, even in trace amounts, gives a yellow color to the pigment. Small amounts of AlCl<sub>3</sub> are added to the purified TiCl<sub>4</sub>, prior to oxidation, to disrupt the TiO<sub>2</sub> lattice. This prevents paints from chalking. TiCl<sub>4</sub> is then burned to TiO<sub>2</sub> in oxygen. Thereafter, the TiO<sub>2</sub> is finally processed to obtain the desired qualities.

The chloride procedure is less destructive to the environment contrasted and the sulfate procedure. Like the previous process, the chloride process emits volatile organic compounds that can cause cancer or vomiting and are also responsible for ozone production. Excess ozone causes permanent lung damage.

Chlorine itself is highly corrosive and poisonous. Special reaction vessels are therefore required. The reaction conditions are said to be less flexible and the reaction occurs at high temperature.

One of the most hampering aspects in the chloride process is the need for raw material with high Titania content. FeCl<sub>3</sub> does not have a commercial value and would result in a waste of chlorine. So, for the chloride process, there is a need to pre-treat the most abundant source, ilmenite, resulting in additional production costs.

The sulfate process utilizes a simpler method than the chloride process and can utilize lower grade, less expensive minerals. However, it generally has higher production costs and acid treatment is more expensive to build than a chloride plant. Comparisons between both two processes are shown in **Table 7**.

**Table 7:** Comparison of the two processes for manufacture of titanium dioxide

Chloride process	Sulfate process
New technology	Long established and simple technology
Needs high grade ore	Uses lower grades, cheaper ores
Continuous process	Discontinuous process
Small amount of waste formed with toxicity problems: Cl <sub>2</sub> and TiCl <sub>4</sub>	Large amount of waste materials
Recovery and recycling of chlorine possible	Pollution control expensive
Only produces rutile pigments	Produces anatase and rutile pigments

The chloride process and the sulfate process are roughly equally widespread and used in the pigment industry, but the chloride process dominates in Europe and the sulfate process in

China. According to the plausible representation in the application, it does not matter for approximately 80% of the requirements of the pigment applications whether the titanium dioxide pigments were produced using the chloride process or whether they were produced using the sulfate process. Exceptions are, for example, textile dyes for synthetic fibers or certain applications in the fields of pharmacy, cosmetics, and food, for which only titanium dioxide pigments produced by the sulfate process can or may be used. In both manufacturing processes, the production of the base body is followed by post-processing in which the pigments are adapted to the properties desired by the end-user. Among other things, the pigments are given a specific coating as part of the surface treatment.

The titanium dioxide pigments are primarily used for the production of paints and coatings (approx. 55% of the pigments), plastics (approx. 26% of the pigments), paper (approx. 8% of the pigments), ink (approx. 3% of the pigments) as well as ceramics, fibers, cosmetics, sunscreens, toothpaste, and other special products. Due to its high refractive index, titanium dioxide gives these products brightness, a high degree of whiteness, and opacity.

## 2.5 Applications

Manufactures use titanium to make parts and products for a wide variety of low and high stakes applications. Many titanium parts play an essential role in proper system functioning. Due to its superior properties, customers turn to titanium metal manufacturing for their applications. Moreover, titanium is convenient to utilize for industries, including healthcare, aerospace, and defense. For example, since titanium has a fundamentally the same as density to human bones, it's ideal for orthopedics. Plus, marine, metal completing and fabrication, aquarium, car, sport, the navy, and all purchase titanium to make their items and materials. As can be found in the accompanying pie diagram, the production of paint represents the greater part of the world's titanium dioxide utilization.

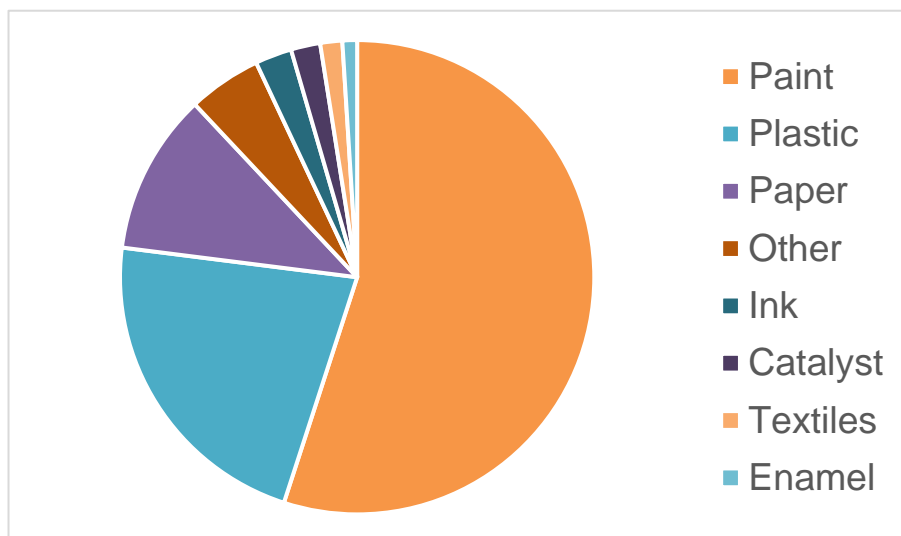


Figure 10: The world's Titanium dioxide consumption

### **2.5.1 Paint, Coatings, and Plastic**

The utilize of titanium dioxide pigment in paint and coating industries is much broad, where other dyes have substituted. Cause coatings applied in thin layers; a generally high quantity of pigment must be utilized to accomplish covering up—the measure of color in a covering is normally noticed the pigment volume concentration (PVC). Divergent sorts of paints (high gloss, flat) will have various degrees of PVC.

The industrial coatings market covers a wide range of services, including transportation equipment, metal fabric, wood product, prepainted metal, and appliances. The coating of automotive is essential in the pigment industry and it is considered as a separate business. In the automotive coating industry, automotive polishes have the most critical performance, which includes the need for photo durability, corrosion protection, and chip resistance. Characteristics of pigment are essential in automotive finishes for gloss, gloss retention, and hiding power.

Besides, titanium dioxide pigment is utilized to opacity plastic materials. Un-pigmented plastic is translucent to transparent and, in this way, not stylishly engaging. In specific applications, TiO<sub>2</sub> is used to improve photograph solidness. The necessities for TiO<sub>2</sub> in plastics are acceptable dispersibility in a polymer framework, blue suggestion, and high warmth solidness. The blue connotation is required because people see pale blue whites as cleaner than yellow ones. A couple of uses, light shades among them, call for yellow feeling color because the transmitted light is somewhat blue.

### **2.5.2 Pharmaceutical and Cosmetics Industries**

TiO<sub>2</sub> generally utilized as a pigment for coloring of various items in pharmaceuticals and beauty care manufactories. The primary target is to supply to the final product a suitable color, which will cause lovely subjective sensations in the last buyer, based on the refraction caused by the color included. The characteristics of titanium dioxide provide exciting colors and allow new properties to pharmaceuticals with tiny amounts of pigments. Numerous items contain titanium dioxide, including shampoos, balms, soaps, creams, cleansers, sunscreens, lipsticks, toothpaste, hair colors, anti-wrinkle treatment, protect baby cream, stretch imprints, and cellulite medicines, hair medicines, and so on.

### **2.5.3 Textiles**

Pigmenting of synthetic fibers has required more hydrophobic dyes and the growth of new techniques to break the structural regularity deliberately and to accept the color. The titanium dioxide pigment characterized by high whiteness, good dispersibility, good hiding power, excellent heat and light resistance, and radiation UV. Through the items where they can be applied are polyester fibers, polyethylene terephthalate (PET), acrylic, and polyamide. For this sort of utilization, anatase pigment preferred.

#### **2.5.4 Food Industry**

Due to very low toxicity, TiO<sub>2</sub> widely used in the food industry as coloring. Titanium dioxide is allowed as a food coloring (E171), in the anatase structure, by the Spanish Royal Decree 2001/1995 of 7 December.

It often used as an additive to decrease or to blend any unwanted color in the food. Normally, in extent, no upper than 1% by weight, is utilized in baked, confectionery, cheeses, icings, garnishes, and food supplements. Likewise, it used to brighten skim milk, getting more white milk with a creamy texture. Moreover, it has used to enhance the color of codfish, reaching about 1000 ppm of titanium dioxide, without changes in the taste of the cooked product.

#### **2.5.5 Titanium Dioxide Nanomaterials**

A significant examination into nanotechnology in the most recent decade has demonstrated promising new applications for titanium dioxide. As an example, titanium dioxide nanoparticles used in dye-sensitized solar cells (“DSSC”). This relatively new photovoltaic technology mimics how plants convert sunlight into energy, although in this case, the sunlight transformed into an electrical current. The potential applications are boundless and go from lightweight low-power markets to huge scope applications. Other areas of research for the use of titanium dioxide nanoparticles are: as an arsenic removal agent in water treatment facilities, in cancer treatments (ability to target and destroy cancer cells), and in cement containing TiO<sub>2</sub> with self-cleaning properties.

## 3. Titanium ore in Mongolia

### 3.1 Studies in Mongolia

The deposit is located in Dornod province which is in the territory of eastern Mongolia. Currently, the company holds an exploration license of permitted areas for conducting exploration and other geological studies. The deposit is located 750km north-east of the capital city Ulaanbaatar. It is 89 km away from Ereentsav border point with Russia to the south-west, 118km away from Khavirga border point with China to the north-west, and 58km away from Choibalsan railway station to the north.

The total depth of the drilling amounted to 2120.5 meter. The drilling intersected mineralization over 285.2 m with highlighted average grades of 4.48% TiO<sub>2</sub> and 12.09% Fe with Sulphur values less than 1%, and had potential to continue through the entire core length but drilling program stopped at 285 m. These results measured by internal measure of Niton XP.

Over 400 surface samples taken from the outcrops at the site, was delivered to SGS lab for assay analyses of different mineral grades such as iron (Fe), titanium (Ti), vanadium (V), lead (Pb), zinc (Zn), rubidium (Rb) and geochemical analysis. In 2013, total of 454 core samples from 3 drill holes were collected, and 9 core sample were carried to SGS Mongolian laboratory for TiO<sub>2</sub>, Fe, Fe<sub>2</sub>O<sub>3</sub>, and V<sub>2</sub>O<sub>5</sub> elements testing. The result is shown in below.

### 3.2 Facts of the Mineralogy and Petrography of the deposit

Deposit is estimated 500 million tons and it has potential to become 1 billion tons. The company's major interest product is Leucoxene which is titanium feedstock products containing a titanium content of 65 to 91 percent. Leucoxene is an industrial term used for the alteration products of all titanium bearing minerals. These leucoxene species will contain very fine to fine intergrowths of pseudo rutile (mineral formed by alteration of ilmenite, whose composition approximates Fe<sub>2</sub>Ti<sub>3</sub>O<sub>9</sub>) or rutile with quartz and other silicates, which could include clays (such as kaolinite, and at times possibly smectite). A whole host of minerals can be deposited in the open structure of pseudo rutile/secondary rutile.

Leucoxene prices are linked to rutile based on TiO<sub>2</sub> content-L88 typically expected to receive 80-85% of rutile price. It is considered an effective substitute of Rutile, which is titanium mineral with highest TiO<sub>2</sub> content and priced comparably higher than other titanium minerals. The commodity pricing for Leucoxene is not readily reported however according to recent presentations from MZI Resources Ltd (November 2018), the L70 Leucoxene (65-85% TiO<sub>2</sub>) and L88 Leucoxene (85-95% TiO<sub>2</sub>) price were reported to be US\$352 and US\$1166 per ton respectively(31).

From the project report, some of the ore samples had been analyzed by several laboratories with chemical methods to determine the constituents in the ore. Samples were analyzed during exploration for  $\text{Fe}_2\text{O}_3$ , Fe, and  $\text{TiO}_2$  by Act labs and Ti, V by Central Geological Laboratory. Over 400 surface samples, taken from the outcrops at the site, were delivered to SGS for lab assay analyses for different mineral grades such as Fe, Ti, V, Pb, Zn, Rb, and geochemical analysis.

The samples taken from the “as received” low grade titanium ore sample are polished and the polished sections are prepared as per the standard procedure for mineralogical study under microscope. According to that, the mineralogy result shows that an ore mineral contains magnetite of 16%, chalcopyrite of 0.2% and leucoxene of 15%. Results of Central Geological Laboratory, black-gray rocks with shale texture are fine grained **Figure 11**. Isometric magnetite grains (0.01mm-1mm) with oval, square and rectangular shapes have developed independently and distributed evenly in ore mineral. Accumulations of chalcopyrite grains (0.02mm-0.1mm) with ungeometrical and oval shapes do appear and chalcopyrite grains creates thin vein up to 0.04mm. Isometric leucoxene grains (0.02mm- 0.1mm) are seen in regular intervals in large amount. Leucoxene is formed as a result of secondary alteration of titanium containing minerals, especially epidote. Ore mineral development sequence is: leucoxene–magnetite-chalcopyrite.



**Figure 11:** Samples for Petrography (result of CGL)

Petrography result shows that rock contains quartz and micro-granoblastic and fluorite grains, and sericite scales and small grains of ore mineral **Table 8**.

**Table 8:** Mineralogical composition of rocks

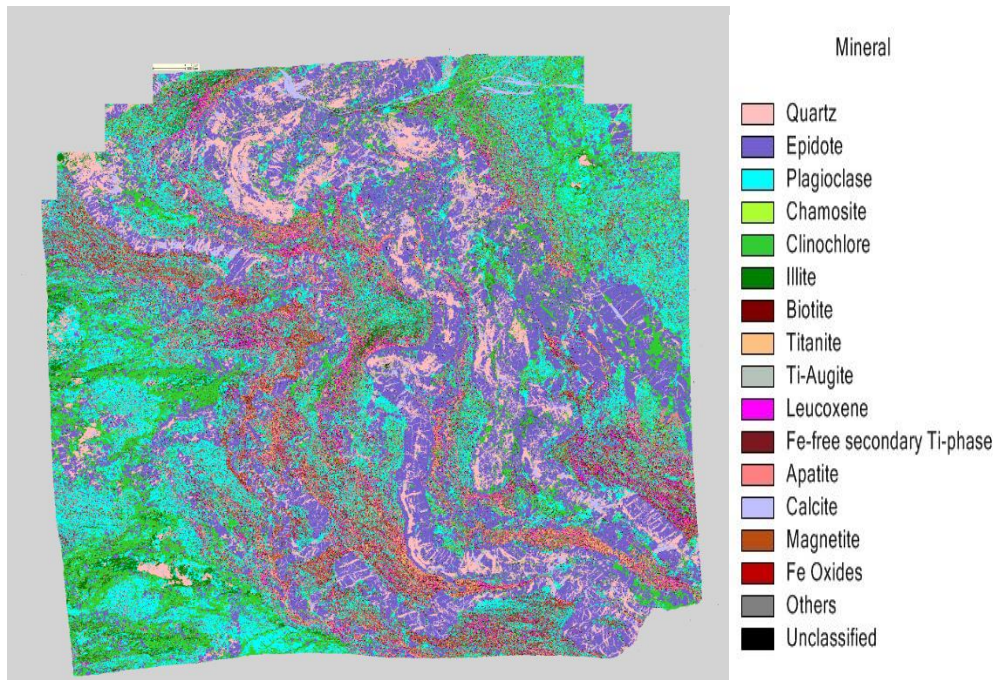
Main	%	Secondary	%	Accessory minerals
Sericite	25-30	Carbonate	10-15	Apatite - few
Fluorite	20-25	Quartz		
Ore mineral	10-15	Leucoxene		
Quartz	10-15			
Epidote	10-15			

Petrographic records: Fluorite grains are of isometric and granoblastic structure and occur in 0.02mm–0.06mm in size. Quartz in size of 0.02mm-0.04mm occurs. Sericite scales are usually colorless and rarely green in color and 0.04mm-0.1mm in size. They developed towards one direction and do create shale texture. In rocks, ore minerals grains in 0.02mm-0.06mm developed along the shale have even distribution and create thin veins. They are of isometric irregular shape. Accessory minerals of apatite of short prism structure occasionally occur in 0.04mm-0.06mm size.

### 3.3 Mineral distribution

These studies indicated that titanite, leucoxene, and magnetite were presented in the sample as valuable minerals. In contrast, the gangue minerals were silicates such as epidote, plagioclase, quartz, clinocllore, calcite, and some secondary minerals.

Mineralogical examination was first conducted to identify the main minerals present in the ore, as well as their liberation size. According Titanium bearing minerals identified in deposit area comprise mainly of titanite,  $\text{CaTiSiO}_5$ , Augite,  $(\text{Ca, Na})(\text{Mg, Fe, Al, Ti})(\text{Si, Al})_2\text{O}_6$ , and Leucoxene **Figure 12**. Titanium may be present in several other phases. Physical properties of titanium oxides and other minerals found along the deposit of Mongolia are illustrated in **Table 9** (mod=moderate).



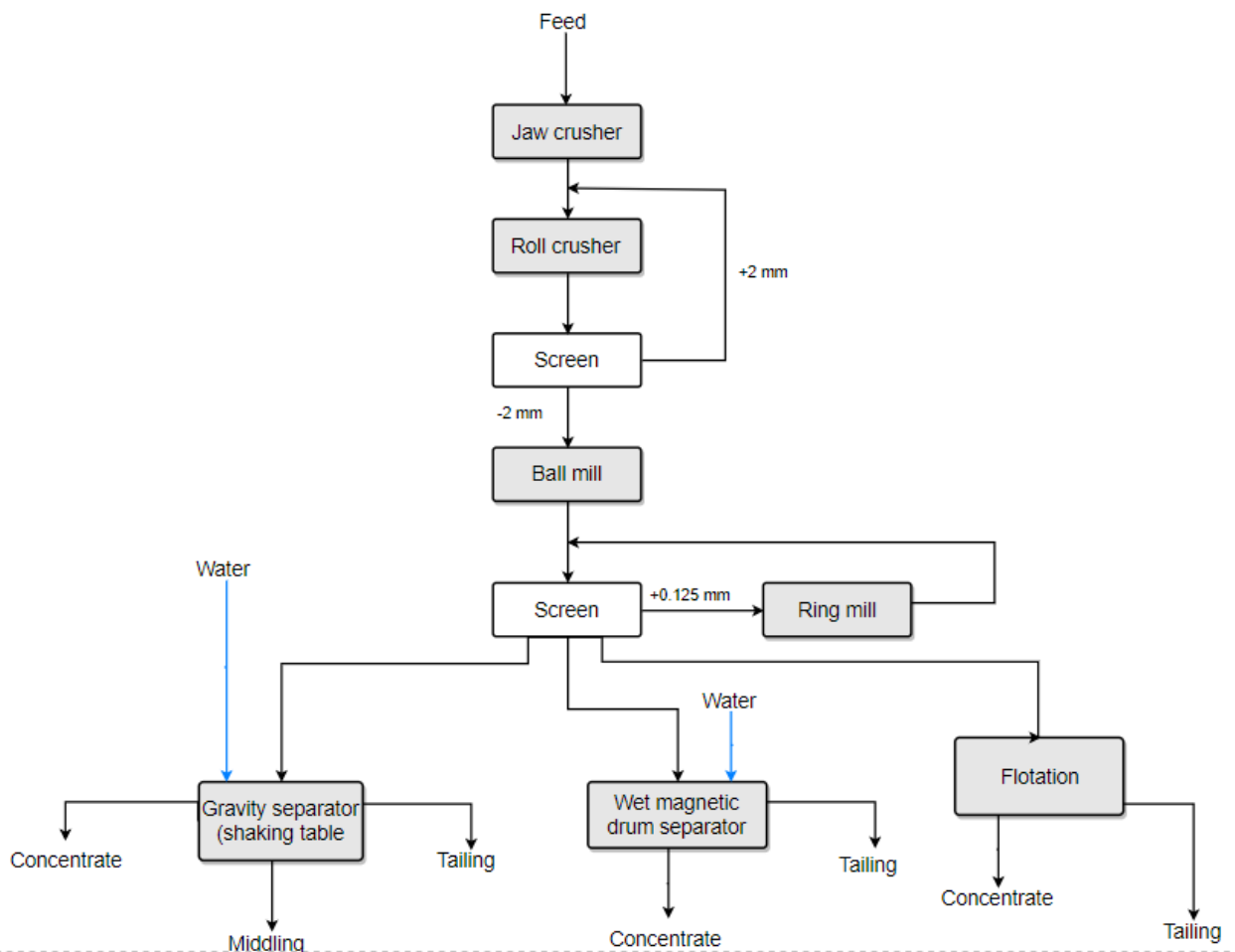
**Figure 12:** Titanium mineral distribution map of Mongolia

**Table 9:** Physical properties of titanium oxides and other minerals found along the deposit of Mongolia

Mineral	Formula	Density [g/cm <sup>3</sup> ]	Magnetic susceptibility	Electrical conductivity
Leucoxene	High TiO <sub>2</sub> phase	3.6-4.2	non-mod	mod
Magnetite	Fe <sup>2+</sup> Fe <sup>3+</sup> <sub>2</sub> O <sub>4</sub>	5.2	very high	-
Titanite (sphene)	CaTiSiO <sub>5</sub>	3.4-3.5	low	non-mod
Ti-Augite	(Fe,Mg,Ca,Ti) SiO <sub>3</sub>	3.1-3.6	low	non
Epidote	Ca <sub>2</sub> (Al,Fe) <sub>3</sub> (SiO <sub>4</sub> ) <sub>3</sub> OH	3.2-3.5	low-mod	non
Apatite	Ca <sub>5</sub> (PO <sub>4</sub> ) (F,OH,Cl)	3.2	non-low	mod
Calcite	CaCO <sub>3</sub>	2.71	low	-
Plagioclase	(Na,Ca)(Si,Al) <sub>4</sub> O <sub>8</sub>	2.61-2.76	-	-
Chamosite	(Fe <sup>2+</sup> ,Mg) <sub>5</sub> Al(AlSi <sub>3</sub> O <sub>10</sub> )(OH) <sub>8</sub>	3-3.4	-	-
Biotite	K(Mg,Fe) <sub>3</sub> (AlSi <sub>3</sub> O <sub>10</sub> )(F,OH) <sub>2</sub>	2.8-3.4	-	-

## 4. Experimental Methodology

This bachelor thesis aims to determine the most suitable ore enrichment technique to obtain titanium minerals from the samples (drilling core) taken from the main deposit area. Therefore, this section describes the materials, apparatus, and experiment procedure employed in the research. In addition, provides the source and types of samples used, magnetic separation, gravity separation, and flotation experiments and chemical analysis that were carried out. The crushed materials were firstly dry-ground in a laboratory ball mill (model HLXMQ- $\Phi$ 240 $\times$ 90) at a ratio of 1:9 solid and ball until a particle size below 125 micrometers was achieved. The ground product was referred to as separation feed and subjected to separation by a dry high-intensity magnetic separator (model DFA 50 rise). Wet high-intensity magnetic separation (WHIMS) tests were carried out with a magnetic drum (model CRIMM- $\Phi$ 400 $\times$ 300) on the ground raw sample. The products of high-intensity wet magnetic (WHIMS) separation included titanium-magnetite concentrate and weakly magnetic minerals. Experiment conducted following flow diagram **Figure 13**



**Figure 13:** Experiment flow diagram

### Titanium ore composition:

Titanium ore was subjected to enriching in this experiment. The 23.5 kg of drilling core sample was delivered from deposit area. The ore mineral contained an average amount of 15% of leucoxene, 16% of magnetite, and 0.2% of chalcopyrite, generally. Unfortunately, more detailed information on the composition of the ore was not provided. However, the head assay of titanium, iron, silica, and other composition determination analysis made in the ALS laboratory of Mongolia.

## **4.1 Sample preparation**

Main objective of sample preparation in the thesis is first to take acceptable representative sample for further successful process. About 23.5 kg of low-grade titanium ore drilling core sample is collected from deposit area of Mongolia and used for these present investigations. The whole “as received” sample is thoroughly mixed and some representative samples are drawn for characterization studies. The rest of the material is classified at 2 mm screen and the oversize material is stage crushed (by jaw crusher followed by roll crusher) to pass through the 2 mm screen. In experiment, totally all of the sample were used to enrich by magnetic separation, gravity separation and froth flotation. To enrich the sample, principal to take a good representative sample. Therefore, sampling is the one most important step in mechanical and chemical processing tests because the representative sample is taking small amount of material that accurately represents the whole mass. Three representative samples from this -2 mm size material is taken for gravity separation, froth flotation, and magnetic separation studies, respectively. For beneficiation by magnetic separation (WHIMS and DHIMS), and gravity separation the -2 mm raw ore is ground by ball mill and is passed through the 125-micron sieve.

To perform that there are several conventional laboratory methods to taking acceptable representative sample which are cone and quartering and jones riffle.

### **4.1.1 Method of Cone and Quartering**

This method is used for splitting a sample (maximum 50 kg) to obtain a sample of several kilograms. Before using that method, we need to clean a tool which needed for splitting.

The procedure of the cone and quartering:

1. Prepare the working area
2. Weighting the bulk sample (23.5 kg)
3. Spread out the sample
4. Mix the sample and shovel it into conical heap
5. Flatten the conical heap by pressing the top without further mixing
6. The top surface of the frustum marked into four quarters using shovel.
7. Discard 2 opposite quarters using shovel

8. Thoroughly mix the 2 remaining quarters, and shovel them into a conical shape again
9. Repeat step 4-8 until the sample is reduced to needed size around 2 kg.

Procedure taken around 30 minutes to take good representative sample.

#### **4.1.2 Method of Jones riffle**

This method is mechanical splitting device. Division channels perform parting and the last partition of the channel releases into two delegate parts is practiced by having each other division channel convey into a similar repository. This unit is generously developed and is the handiest, generally advantageous, and most precise example splitter yet contrived for hand operation. The hopper is set in a rigid, convenient to transport and additional equipment consists of a scoop, two sampling pans, and a cleaning brush.

Sample is going into the top of the splitter; it flows through chutes and is randomly divided into same fractions. One of the fractions could be split again and the procedure can be repeated until a sample of the desired size is obtained. This devise is the most accurate method to extracting representative samples from dry granular or grounded material.

Those representative samples were used in sieve analysis, dry and wet magnetic separation, gravity separation (shaking table), froth flotation, and chemical analysis.


## **4.2 Size reduction**

Comminution or size reduction of a mineral is normally completed in order to increase the surface area because, in many reactions including solid particles, the rate of the reaction is proportional to the zone of contact with a subsequent stage, break material into little particles so as to isolate the valuable amongst the two constituents.

### **4.2.1 Jaw crusher and Roll crusher**


About 23.5 kg of drilling core sample was taken from the deposit area and a representative sample was used in the experiment. The maximum drilling core feed size diameter was 5 centimeters with different lengths. The ore sample was crushed in two-stage crushers. First crusher serial number of jaw crusher (model 5E-JCA150\*125) used in the experiment as a primary crusher to reduce the ore sample. The second crusher was roll crusher (model LRMC). And then it was crushed in jaw crusher and roll crusher and it was sieved by 2 mm sieve. Retained part of a portion on the sieve (+2mm) crushed in roll crusher. Finally, all the grain in the ore sample was crushed until they become smaller than 2 mm in size. Crushed ore was mixed by cone and quartering method until it becomes uniform. Then 500 grams of sample were taken for chemical analysis, element definition, and titanium content definition analysis which is fusion X-ray fluorescence (XRF) by ALS laboratory.

**Table 10:** Technical data of laboratory jaw crusher

	Model	5E-JCA150*125
	Feed opening size [mm]	-100
	Output size [mm]	-6 to -38
	Capacity [kg/h]	100
	Motor power [kW]	380
	Weight [kg]	235

**Figure 14:** Jaw crusher

**Table 11:** Technical data of laboratory roll crusher

	Model	LRMC
	Feed opening size [mm]	-30
	Output size [mm]	-2
	Capacity [kg/h]	100
	Motor power [kW]	380
	Weight [kg]	480

**Figure 15:** Roll crusher


#### 4.2.2 Grinding (Ball mill)

Comminution is the largest energy-consuming part of mineral processing. Hence, efficient use greatly affects performance and cost implications. The ball mill is operating in two term which dry and wet grinding. Grinding was performed using a ball mill (dimensions: pamel 460x600, 1600x850x1000) at 10 minutes of grinding time, speed of 40 revolutions per minute (rpm), and sample charge (10kg of the crushed sample with 90kg steel ball). The grinding ratio was 1:9.

Working procedure:

1. Steel ball, at least 30% compared to shell capacity, must be put into empty shell
2. Then, put in samples into shell with ratio of 1:9
3. Check the ball mill closed properly
4. Set revolution speed and grinding time, 40rpm and 10 min respectively. Push the start bottom.
5. When the grinding finishes, switch off the mill and separate the milled sample from steel ball.

**Table 12:** Technical data of laboratory ball mill

 <p><b>Figure 16:</b> Ball mill</p>	Model	HLXMQ-Φ240×90
	Feed opening size [mm]	-2
	Output size [mm]	0.074
	Capacity [kg/h]	100
	Motor power [kW]	380
	Weight [kg]	235

## 5. Result and Discussion

This section includes discussion for results for mineralogical and chemical composition for raw and enriched tests utilizing XRF, on top of that, the studying of beneficiation utilizing flotation, magnetic, and gravity separation techniques that are utilized to upgrade levels of titanium content is additionally centered around in this section.

In enrichment experiments carried out within the scope of the study, it is aimed to obtain the titanium minerals in drilling core sample with high  $\text{TiO}_2$  concentrate grade and high  $\text{TiO}_2$  concentrate yield. For this reason, enrichment, flotation, high and low field intensity magnetic separation, and gravity separation tests were completed by the particular gravity distinction utilizing a vibrating table.

Around 23,5 kg of representative ore samples were crushed to below 2 mm size with a two-phase jaw crusher and a one-phase roll crusher. The crushed samples were then consistently blended and partitioned into 2 kg of samples for characterization and pre-concentration examines. Those representative samples were used in sieve analysis, dry and wet magnetic separation, gravity separation (shaking table), and chemical analysis.

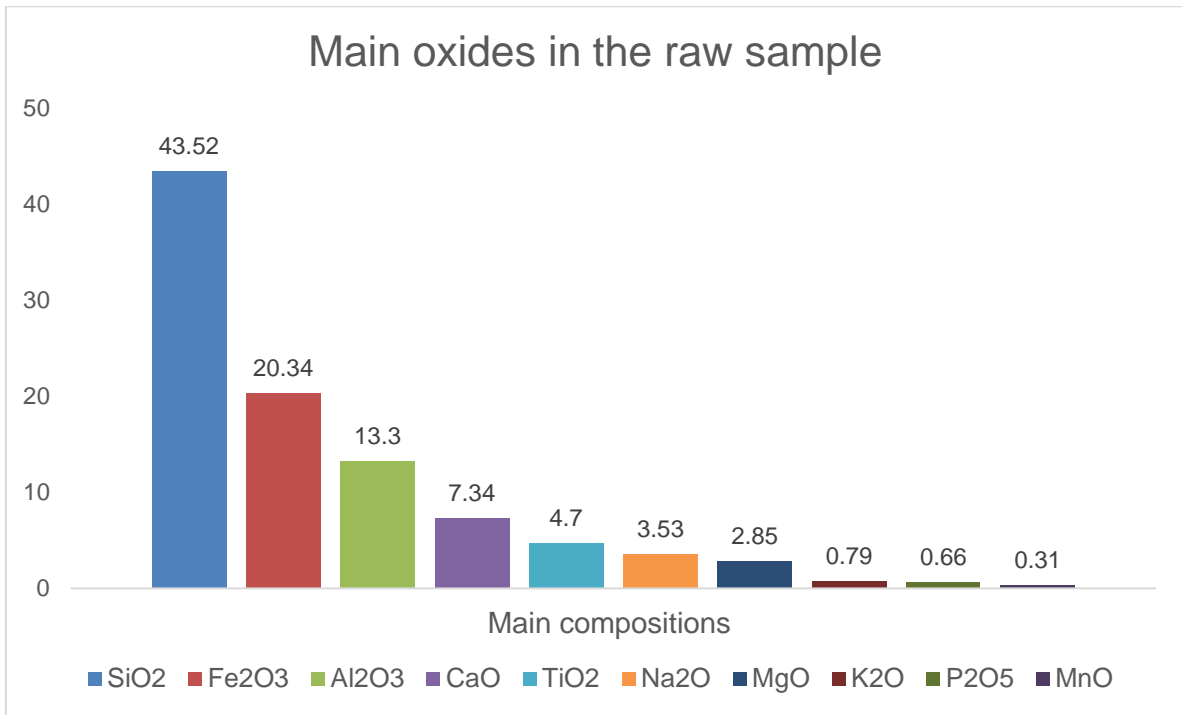
Already, a total of twenty samples were analyzed for chemical analysis using XRF (gun) analyzer of GMIT laboratory, eleven of them are analyzed by XRF (fusion) analyzer of ALS laboratory.

### 5.1 Chemical Composition Analysis

The principal chemical constituent of the raw sample is introduced in **Table 13**, which shows that the fundamental constituent of the sample is  $\text{SiO}_2$ . Not only is the content of the  $\text{TiO}_2$ , 4.70%, but there is also a  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  content of 20.34% and 13.3%, respectively. It is a typical low-grade titanium-magnetite ore.

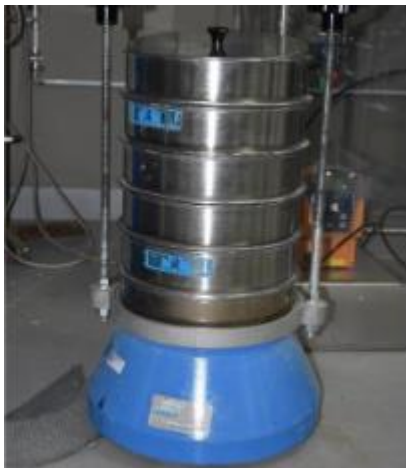
**Table 13:** Main chemical composition of raw sample by fusion XRF (wt. %).

Oxides	$\text{TiO}_2$	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	CaO	$\text{SiO}_2$	MgO	$\text{Na}_2\text{O}$	$\text{P}_2\text{O}_5$	$\text{K}_2\text{O}$	MnO
Content [%]	4.70	20.34	13.3	7.34	43.52	2.85	3.53	0.66	0.79	0.31



**Figure 17:** Main chemical composition as an oxide form in raw sample

## 5.2 Sieve Analysis



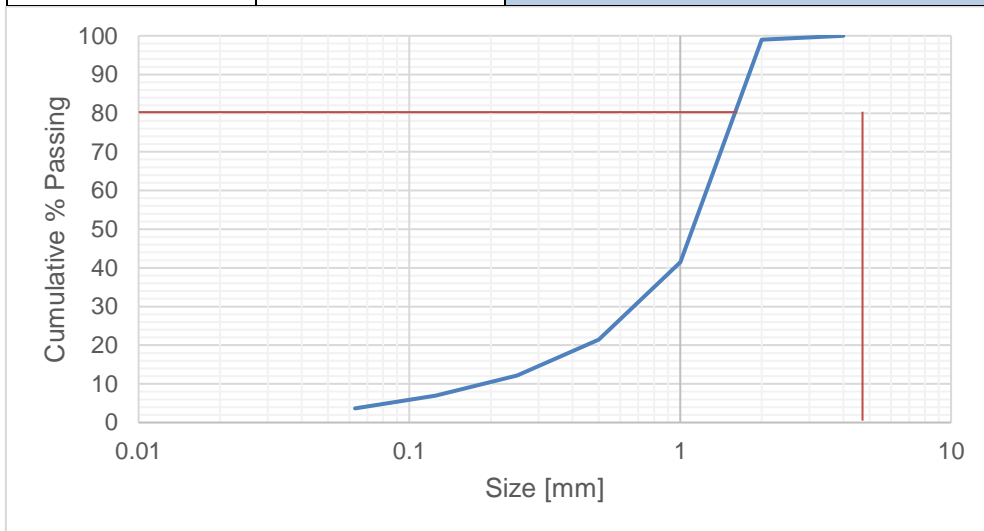
**Figure 18:** Laboratory vibrating sieve machine

The vibrating sieve machine is used for the determination of fine particles (<74  $\mu\text{m}$ ). A finer size meshes such as 2 mm, 1mm, 500 $\mu\text{m}$ , 250 $\mu\text{m}$ , 125 $\mu\text{m}$ , 63 $\mu\text{m}$  handled in the shaker. The stainless-steel shaker separation is based on vibration movement and can hold up to 10 sieves at the same time. Operating time can manage from 0 to 99 minutes, the experiment lasts 20 minutes per sieving. In this experiment, sizing analysis was conducted on the feed samples by using laboratory dry screening methods. The dry screening was done by a standard vibration sieve machine (HLSDB- $\Phi$ 200). The screening test was carried out for the intensity of 70 and the

duration was 15 minutes. Making use of that sample, operated the sieve analysis at 7 mesh, the result is shown in **Table 14**. Additionally, to determine chemical composition of Titanium ore by X-Ray Fluorescence analyzer, were milled each fraction for 8 minutes separately by ring mill. In each sample measurement were done for 5 times in XRF analyzer, minerals content estimated average of those 5 measurements. XRF analysis showed, mainly those elements such Titanium, Iron, Silicon, Calcium, Aluminum, Potassium, Manganese, Magnesium, Zinc, Zircon were present. The presence of Iron can be advantageous used to concentrate the Titanium by magnetic separation. For the following size distribution attained by laboratory sieving **Table 14**:

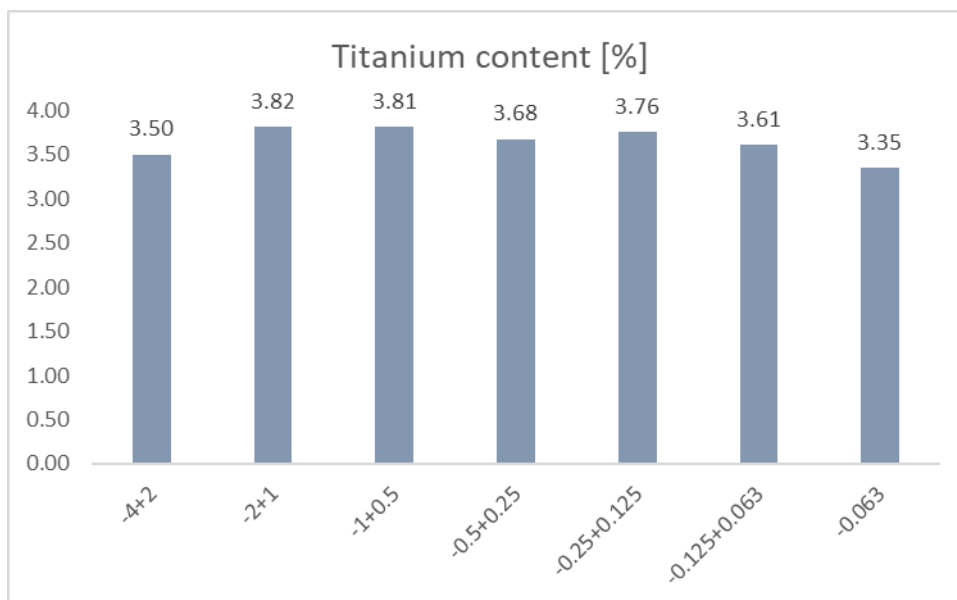
**Table 14:** Result of sieve analysis data

Weight sample: 2416 g				
Sieve size [mm]	Retained weight [g]	Percent passing [%]	Cumulative % passing	Cumulative % Retained
+4	0.0	0.0	100.0	0.0
-4+2	24.7	1.0	99.0	1.0
-2+1	1388.5	57.5	41.5	58.5
-1+0.5	482.7	20.0	21.5	78.5
-0.5+0.25	224.7	9.3	12.2	87.8
-0.25+0.125	125.5	5.2	7.0	93.0
-0.125+0.063	79.4	3.3	3.7	96.3
-0.063	88.4	3.7		100.0
Total	2413.9	P <sub>80</sub> ≈ 1.68 mm		



**Figure 19:** Example of particle size distribution curve for feed

As a result (**Figure 20**) of sieve fractions and mineralogical studies, it was determined that the titanium in the sample was same amounts in each fraction between 3.35 and 3.82 percent.



**Figure 20:** Titanium content measurement in each sieve fraction by XRF [%]

### 5.3 Wet Magnetic Separation Experiment

The WHIMS study was carried out using the laboratory scale drum type WHIMS. In the experiment, around 1.5 kg of -125-micron samples were taken for the WHIMS study. The slurry of 1.5 kg sample with 10-12 liter of water is fed to the magnetic separator. The concentrate is washed with fresh water before the disconnection of the magnetic field. The current was 4.1 ampere to create the magnetic intensities of 1400 gauss. Both magnetic and nonmagnetic fractions are collected and dried. Concentrate and tailings were weighed and analyzed for Fe and Ti content by XRF.

The result of X-ray fluorescence (XRF) analysis shown in **Table 15**.

**Table 15.** The result of wet magnetic separation of GMIT laboratory XRF test (%).

Element	Ti	Fe	Si
Feed	3.227	13.195	6.675
Concentrate	3.362	17.313	6.323
Tailing	2.796	8.852	7.784

As a result of the experiment carried out with Wet Magnetic Separator in optimum conditions, a concentration of 3.227% Ti content was obtained in the amount of 3.362%. Although enrichment was observed in terms of Ti content, it was concluded that the low content in the results was obtained thus, conduct the experiment again with changing the parameters like intensity and particle size of the feed.

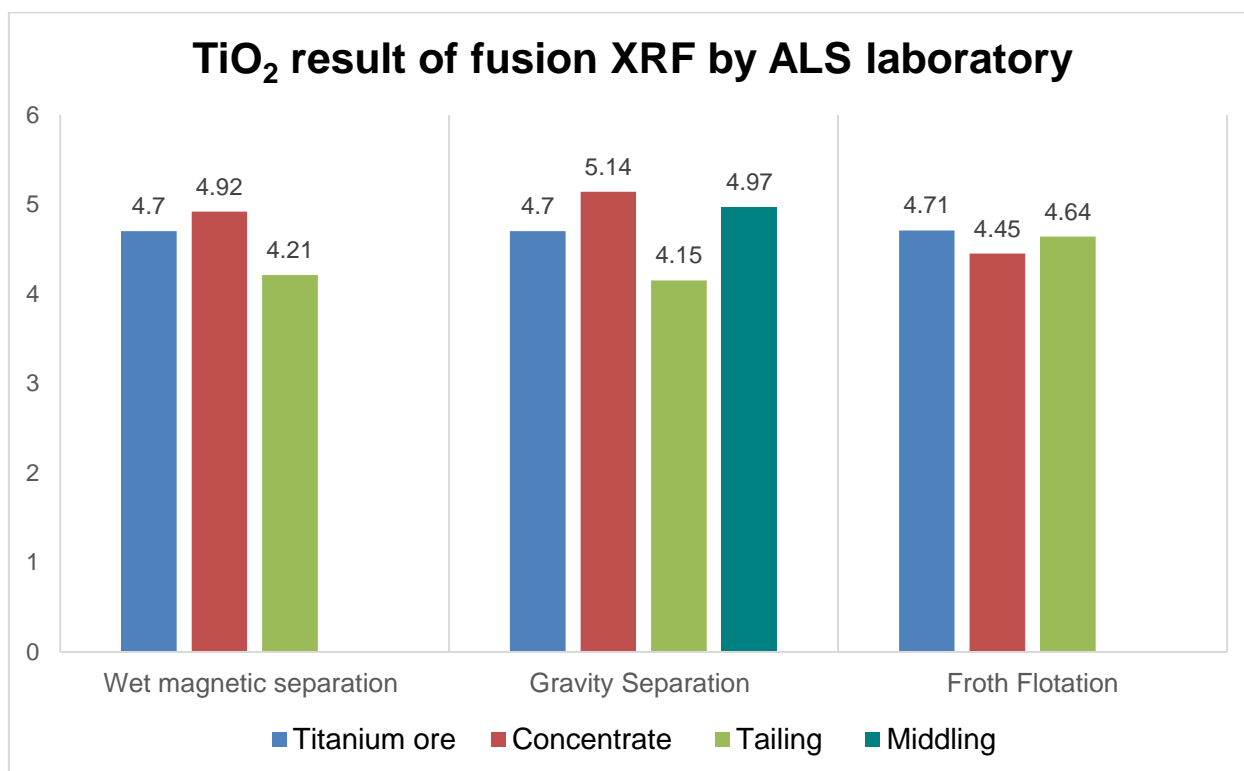
Besides, to control that **Table 15** results, samples from raw and wet magnetic separation products were sent to ALS Mongolia laboratory for TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and other elements testing. The result is shown in **Table 16**.

**Table 16.** The results of ALS laboratory fusion XRF test (wt. %).

Oxides	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	SiO <sub>2</sub>	MgO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	MnO
Raw sample	4.70	20.34	13.3	7.34	43.52	2.85	3.53	0.66	0.79	0.31
Concentrate	4.92	24.67	12.32	7.21	41.07	2.48	3.43	0.64	0.61	0.27
Tailing	4.21	13.40	14.72	7.37	46.92	3.50	3.59	0.69	1.11	0.36

Comparing those two results were almost identical, hence, there are possibility to beneficiate the ore by magnetic separation with changing the parameters.

The results for titanium dioxide percentages from gravity separation and magnetic separation using given parameters are illustrated below **Figure 21**.



**Figure 21:** Comparisons of magnetic, gravity separation and flotation results of TiO<sub>2</sub>

**Table 17:** Result of gravity and magnetic separation experiment samples for TiO<sub>2</sub>.

Gravity Separation				
	Mass [g] M	TiO <sub>2</sub> assay [%] A	Mass of TiO <sub>2</sub> M*A	Recovery [%]
Feed	500	4.7	2350.0	100
Concentrate	107.8	5.14	554.1	23.58
Middling	218.5	4.97	1085.9	-
Middling (upper)	100.6	4.54	456.7	-
Tailing	73.1	4.15	303.4	76.42
Magnetic Separation				
Feed	1434.8	4.7	6743.6	100
Concentrate	909.3	4.92	4473.8	66.34
Tailing	525.5	4.21	2212.4	33.66

#### 5.4 Gravity Separation (Shaking table)

From the mineral processing methods shaking table is one of the oldest that is used to recover the maximum recovery. When there is a marked difference in the density of the minerals, it utilized to separate the samples into the light and heavy-mineral fractions. When the mineral density is higher than quartz is considered as heavy minerals, the most common rock-forming soil mineral with a density of 2.65g/cm<sup>3</sup>. Therefore, the specific gravity of the titanium mineral, which is quite different from the side stones (rutile: 4.3 g/cm<sup>3</sup>, albite: 2.6 g/cm<sup>3</sup>, quartz: 2.65 g/cm<sup>3</sup>, microcline: 2.56 g/cm<sup>3</sup>, muscovite: 2.82 g/cm<sup>3</sup>, apatite: 3.19 g/cm<sup>3</sup> etc.).

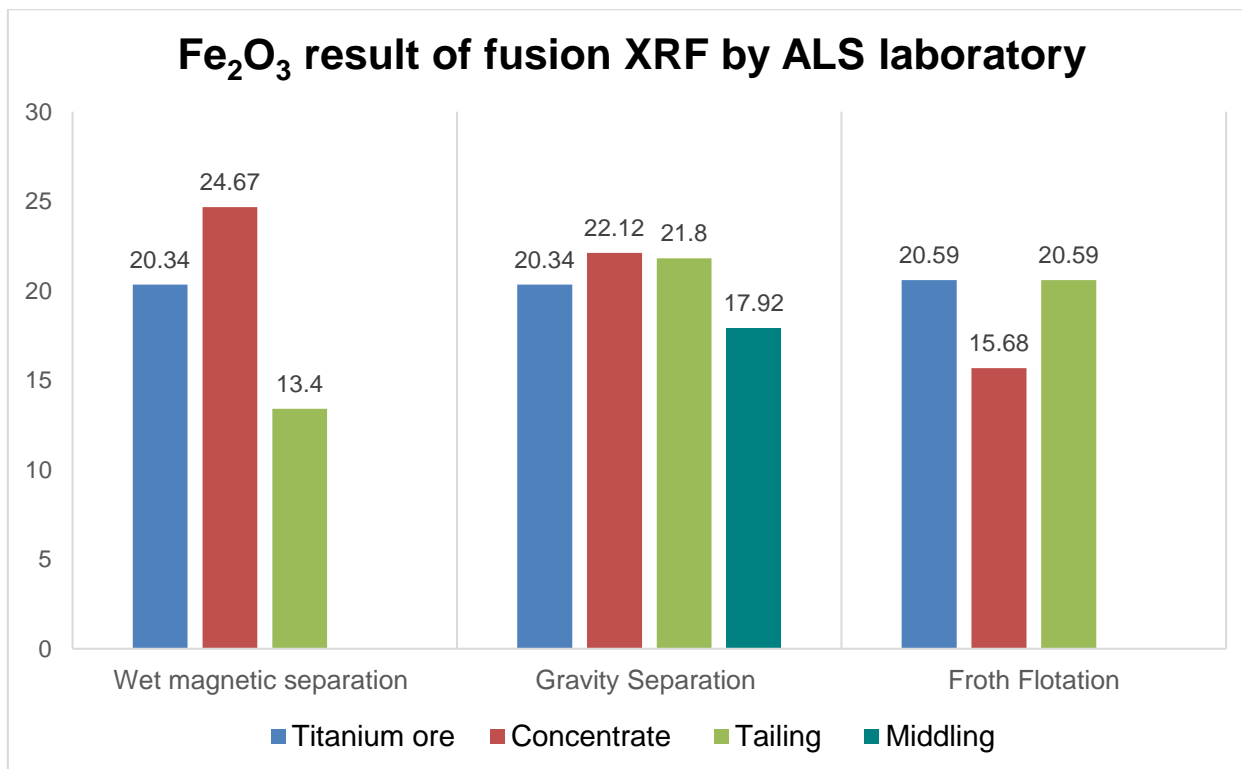
Based on this property, the experiment was carried out under a 4-degree slope and 250 rpm table speed conditions, above 32-micrometer fraction samples with average 4.70% of titanium dioxide, were used. In the literature, the size group of below 32 μm (considered as a sludge) because it would impair the flow regime of the shaking table, thus, it was not part of the experiment.

Concentrate, Middling, Middling(upper) and Tailings was obtained in the first stage in shaking table experiments. Later, these products were subjected to dry at 105 degrees Celsius in the drying oven for evaporating the water content in the product and measured the component in each sample using the XRF analyzer. The results shown in below.

**Table 18:** The results of XRF test (wt. %).

Oxides	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	SiO <sub>2</sub>	MgO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	MnO
Raw sample	4.70	20.34	13.3	7.34	43.52	2.85	3.53	0.66	0.79	0.31
Concentrate	5.14	22.12	12.74	7.74	42.52	2.48	3.71	0.71	0.56	0.28
Middling	4.97	21.80	12.78	7.55	42.30	2.56	3.51	0.65	0.66	0.28
Middling (upper)	4.54	19.50	13.52	7.19	43.92	3.07	3.51	0.63	0.87	0.32
Tailing	4.15	17.92	14.42	6.77	44.21	3.62	3.54	0.68	1.12	0.35

As a result of that experiment, grade of titanium was enriched it was 4.70% to 5.12%. It is well known that gravity separation efficiency decreases as the range of sizes in the feed increases. This is related to the compounding effect of size and density on the weight of particles and their subsequent movement in a gravity concentrator. Thus, a gravity feed is often divided into separate size intervals for treatment on separate gravity units such as jigs or shaking tables. We concluded that, the desired concentrate could not be obtained due to insufficient table slope, speed or size fraction. Therefore, next experiment is changing the parameters of the shaking table for instance, 3 and 5 degree of table slope and grinding the feed even more until the desired mineral liberation size.



**Figure 22:** Fusion XFR results of magnetic separation, gravity separation, and froth flotation

**Table 19:** Result of gravity and magnetic separation experiment samples for Fe<sub>2</sub>O<sub>3</sub>.

Gravity Separation				
	Mass [g] M	Fe <sub>2</sub> O <sub>3</sub> assay [%] A	Mass of Fe <sub>2</sub> O <sub>3</sub> M*A	Recovery [%]
Feed	500	20.34	10170.0	100
Concentrate	107.8	22.14	2386.7	23.47
Middling	218.5	21.8	4763.3	-
Middling (upper)	100.6	19.5	1961.7	-
Tailing	73.1	17.92	1310.0	76.53
Magnetic Separation				
Feed	1434.8	20.34	29183.8	100
Concentrate	909.3	24.67	22432.4	76.87
Tailing	525.5	13.4	7041.7	23.13

## 5.5 Froth Flotation

The flotation of titanium ore from a deposit site has been tested in this work. For laboratory flotation test specification as follows:

- Feed size range: 0,106 + 0,038 mm (Slime removed)
- Percent solid (P.S): 25%
- pH: 3 (adjusted by H<sub>2</sub>SO<sub>4</sub>)
- Collector: R845 (800 g/ton – 400 g/ton (I) + 400 g/ton (II))
- Frother: MIBC (350 g/ton)
- Conditioning time: 4 min (I) + 3 min (II)
- Frother taking time: 2 min (I) + 2 min (II)
- Agitation: 1000 rpm (revolution per minute)

250 g of ground sample was weighed and put in a 500 mL beaker. 250 mL distilled water was added to make 1:1 slurry. The mixture was placed in a flotation cell and agitated for 5 minutes to make the slurry. 5.0 mL of conditioning reagent was added. The mixture was stirred for 5.0 minutes after adding conditioning reagent. More water was added to the mix to make a slurry with 25% solid. The pH of the slurry adjusted to 3 using sulfuric acid. Collector and frother were added. Air was bubbled through and froth collected in plastic containers. Flotation was done for 10.0 minutes. By using the proposed procedure to treat a feed ore of 4.71% TiO<sub>2</sub>, a rougher

concentrate of grade 4.45% TiO<sub>2</sub> was achieved. The results of the chemical analysis on samples using XRF are given in **Table 20**.

**Table 20:** Flotation result of XRF (fusion) by ALS lab.

Oxides	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	SiO <sub>2</sub>	MgO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	MnO
Raw sample	4.71	20.59	13.33	7.30	42.80	2.88	3.49	0.65	0.78	0.31
Concentrate	4.45	15.68	13.80	7.12	41.90	3.71	3.58	0.71	1.06	0.36
Tailing	4.64	20.59	13.02	7.04	42.56	2.74	3.49	0.65	0.74	0.29

## 6. Conclusion and Recommendation

### 6.1 Conclusion

The thesis began with a board introduction to the study, which identified its significance and briefly indicated what was to come the first chapter reviewed the introduction of titanium minerals that include geological occurrence, properties, and significant ore minerals. The second chapter outlined literature on beneficiation unit operations such as gravity separation, magnetic separation, floatation, and further processing of titanium concentrate. The third chapter mentioned the titanium deposit in Mongolia. The experimental methodology describes what works done in this study, while the fifth and sixth chapters presented the result and conclusion of these studies.

Within the scope of the study, to obtain  $\text{TiO}_2$  contents from first discovered Mongolian titanium deposits, laboratory-scale gravity, magnetic separation, and flotation enrichment experiments were carried out. The purpose of enrichment experiments; is both the production of a high  $\text{TiO}_2$  concentrate with high metal recovery efficiency. According to the Central Geological Laboratory, mineralogical results were defined by an ore mineral that contains magnetite of 16%, chalcopyrite of 0.2%, and leucoxene of 15%. Isometric leucoxene grains (0.02mm- 0.1mm) have seen in regular intervals in large amounts. Leucoxene is formed as a result of the secondary alteration of titanium-containing minerals, especially epidote. Ore mineral development sequence is leucoxene–magnetite-chalcopyrite.

In the study, mineralogical and chemical analyzes were carried out to determine the impurities in the sample, which is the basis of the experiments. It was determined that the sample based on experiments consisted of quartz, epidote, plagioclase, illite, apatite, titanite, magnetite, leucoxene, and chamosite minerals in the raw ore. As a result of the analysis on the drilling core sample with XRF analyzer, sample contains: 43.52%  $\text{SiO}_2$ , 13.3%  $\text{Al}_2\text{O}_3$ , 20.34%  $\text{Fe}_2\text{O}_3$ , 7.34%  $\text{CaO}$ , 3.53%  $\text{Na}_2\text{O}$ , 2.85%  $\text{MgO}$ , 0.79%  $\text{K}_2\text{O}$ , 4.70%  $\text{TiO}_2$ , 0.66%  $\text{P}_2\text{O}_5$ , 0.31%  $\text{MnO}$ , and 0.02%  $\text{SrO}$ .

In enrichment experiments by using a shaking table, it is aimed to gain heavy minerals such as leucoxene in the drilling core sample as a concentrate by making use of the difference in density between them with light minerals such as silicate minerals. For this purpose, we were planning to conduct in different size groups, and also study the effects of table slope and table speed on enrichment but due to the corona crisis, only one size group experiment carried out at -125 +32  $\mu\text{m}$ . According to the literature the -32  $\mu\text{m}$  size group was disposed of as slam because it would disrupt the table regime. As a result of the experiment, 5.1% of the amount was obtained from a concentration of 4.7%  $\text{TiO}_2$  in the feed as a recovery of 23.44%. The main reason why titanium concentrate could not be obtained in the desired grade and recovery in shaking table enrichment experiments was, the experiment performed only one size group.

In magnetic separation enrichment experiments, it is aimed to acquire paramagnetic minerals such as leucoxene in the feed sample. In this context, first of all, experiments were carried out using high field intensive dry magnetic separator but positive results could not be obtained. For the high field intensity, wet low intensity magnetic separator enrichment was given us a little positive result, its upgraded little bit compared to high field dry magnetic separator. As a result of the experiment performed with low intensity wet magnetic separator in optimum conditions, a concentration of 4.7% TiO<sub>2</sub> content of 4.92% is obtained.

The flotation of titanium ore from a deposit site has been tested in this work. It consists of the sulfuric acid as the pH modifier, alkyl succinimide as the collector, and MIBC as the frother. By using the proposed procedure to treat a feed ore of 4.71% TiO<sub>2</sub>, a rougher concentrate of grade 4.45% TiO<sub>2</sub> was achieved.

Shaking table experiments carried out with a sample of -125 +32 μm (grain size) size group at 4-degree table slope and 250 rpm table speed. Result of shaking table tests feed concentrate containing 4.7% TiO<sub>2</sub> from that was enriched 5.1 % TiO<sub>2</sub> with a recovery of 23.44%. Wet high-intensity magnetic separation experiments were carried out, and the result shows that a concentrate of 4.92% with a content of 4.70% TiO<sub>2</sub> was obtained. For flotation test collector, alkyl succinimide, frother, MIBC, and pH modifier, sulfuric acid was used. By using the proposed procedure to treat a feed of 4.71% TiO<sub>2</sub>, the concentrate on grade 4.45% TiO<sub>2</sub> was achieved.

## **6.2 Recommendation for future research**

Results from this thesis work have indicated that upgrading the titanium mineral by magnetic separation, gravity separation, and froth flotation improves levels of titanium dioxide little from the raw sample. Hence, more investigations should be done for the titanium mineral processing, such as changing the parameters or testing different reagents at the aforementioned methods.

Grinding is a very essential procedure in the mineral processing sector. Therefore, identifying the liberation size of titanium mineral and this will avoid over-grinding at the same time, so the further study should be conducted, including grinding process, grinding additives, etc.

Combined processes like diverse joined procedures of gravity and magnetic separations and flotation should be studied according to the properties of essential titanium minerals.

One of the classic methods to recover the titanium mineral is flotation, however, in the experiment result used flotation reagents effect was not good enough to recover the titanium dioxide, thus for the further study to develop/test high effective flotation reagents in our sample.

## 7. References

1. Ametek. Application Note: Titanium Dioxide - Sulfate Process. Ametek, Inc. 2015;4.
2. Fajardo S, García-Galvan, R. F, Barranco V, Galvan JC, Batlle SF. We are IntechOpen , the world ' s leading publisher of Open Access books Built by scientists , for scientists TOP 1 % . Intech [Internet]. 2016;i(tourism):13. Available from: <https://www.intechopen.com/books/advanced-biometric-technologies/liveness-detection-in-biometrics>
3. Gloe CS, Holdgate GR. Geology and Resources. Sci Vic Brown Coal. 1991;1–43.
4. Gessner T. Triarylmethane and Diarylmethane Dyes. Ullmanns Encycl Ind Chem. 2012;37:425–74.
5. Of R, Market T, Methods OREP. GM-.
6. Hugo VE. A Study of Titanium-Bearing Oxides in Hea Vy Mineral Deposits Along the East Coast of South Africa. 1993;357.
7. Hayes, Timothy; Miller, Michael; Orris, Greta; Piatak N. Fluorine Chapter G of Critical Mineral Resources of the United States — Economic and Environmental Geology and Prospects for Future Supply Fluorspar Figure 1 Professional Paper 1802 – G. 2017;
8. Fischer H. 1 Introduction. Magn Prop Free Radicals. 2005;1–8.
9. Briefing I. Iluka Resources Limited Investor Briefing. 2019;(October).
10. Korneliussen A, McEnroe S, Nilsson LP, Gautneb H, Meyer GB, Schiellerup H, et al. An overview of titanium deposits in Norway. Norges Geol undersøkelse Bull. 2000;436:27–38.
11. Kogel JE. Industrial minerals and rocks : commodities, markets, and users. New York: Society for Mining, Metallurgy, and Exploration; 2006.
12. Elsner H. Assessment Manual: Heavy Minerals of Economic Importance. Bgr. 2007;222.
13. Jena MS, Tripathy HK, Mohanty JK, Mohanty JN, Das SK, Reddy PSR. Roasting Followed by Magnetic Separation: A Process for Beneficiation of Titano-Magnetite Ore. Sep Sci Technol. 2015;50(8):1221–9.
14. Yıldırım Gülsoy Ö, Gülcan E. A new method for gravity separation: Vibrating table gravity concentrator. Sep Purif Technol [Internet]. 2019;211:124–34. Available from: <https://doi.org/10.1016/j.seppur.2018.09.074>
15. Warui SK, Muthengia JW, Mutembei PK, Waithaka PN. Beneficiation of Iron in Thermal-Reduced Ilmenite by Magnetic Separation. Int J Sci Res. 2015;4(5):2118–20.
16. Shahien MG, Khedr MMH, Maurice AE, Farghali AA, Ali RAM. Synthesis of high purity rutile

- nanoparticles from medium-grade Egyptian natural ilmenite. Beni-Suef Univ J Basic Appl Sci [Internet]. 2015;4(3):207–13. Available from: <http://dx.doi.org/10.1016/j.bjbas.2015.05.013>
17. Das A, Roy S. Magnetic Separation - Principles and Application in Beneficiation of Iron Ores. 2007;89–102.
  18. Kitchener JA. The froth flotation process: past, present and future - in brief. Sci Basis Flot Proc Nato Adv Study Inst, (Cambridge, UK Jul 5-16, 1982), KJ Ives (Ed),. 1984;(75 ) (ISBN 90-247-2907-6));3–51.
  19. Liu Q, Peng Y. The development of a composite collector for the flotation of rutile. Miner Eng. 1999;12(12):1419–30.
  20. Cheng T. Surface Properties and Flotation Behaviour of Monazite and Xenotime The University of New South Wales. 1993;
  21. Bulatovic SM. Flotation of Titanium Minerals. Handb Flotat Reagents Chem Theory Pract. 2010;175–207.
  22. Sekimoto H, Yahaba S, Chiba S, Yamaguchi K. New Separation Technique of Titanium and Iron for Titanium Ore Upgrading. Proc 13th World Conf Titan. 2016;159–63.
  23. Zhai J, Chen P, Wang H, Hu Y, Sun W. Flotability improvement of ilmenite using attrition-scrubbing as a pretreatment method. Minerals. 2017;7(1):1–13.
  24. Wang J, Cheng HW, Zhao HB, Qin WQ, Qiu GZ. Flotation behavior and mechanism of rutile with nonyl hydroxamic acid. Rare Met. 2016;35(5):419–24.
  25. Zhao, Hongbo & Jun W. Review on Mineral Processing Technology of Rutile in China. 2013;(February). Available from: [https://www.researchgate.net/publication/275214804\\_Review\\_on\\_Mineral\\_Processing\\_Technology\\_of\\_Rutile\\_in\\_China](https://www.researchgate.net/publication/275214804_Review_on_Mineral_Processing_Technology_of_Rutile_in_China)
  26. Fan X, Rowson NA. Effect of Pb(NO<sub>3</sub>)<sub>2</sub> on ilmenite flotation. Miner Eng. 2000;13(2):205–15.
  27. P r o c e s s d e v e l o p m e n t f o r t r e a t m e n t. 1999;12(12):1407–17.
  28. Braun JH, Baidins A, Marganski RE. TiO<sub>2</sub> pigment technology: a review. Prog Org Coatings. 1992;20(2):105–38.
  29. Whitfield R, Brown F. The Economic Benefits of Chlorine Chemistry in Water Treatment in the United States and Canada. IHS Econ Rep. 2016;
  30. AEA group. Analysis of the Simplification of the Titanium Dioxide Directives. 2007;(3):1–107.

31. US Geological Survey. Mineral Industry Surveys: Chromium. 2020;(January):1–10.