ALTERATION OF ILMENITE IN THE INANI HEAVY MINERAL DEPOSIT

by

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DECLERATION

It is hereby declared that this thesis or any part of it has not been submitted elsewhere of any degree or diploma.

Signature of the student

Shamsun Nahar

Name of the student

DEDICATION

To my father,
who would be very happy to see my thesis paper

and

to my mother,
who gave me encouragement to complete my paper.

The thesis titled "**ALTERATION OF ILMENITE IN THE INANI HEAVY MINERAL DEPOSIT**" submitted by Shamsun Nahar, Roll no:040511104F, Session: April 2005, has been accepted as satisfactory in partial fulfillment of the requirement for the degree of Master of Philosophy in Materials Science on 16 June,2009.

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Abstract

In this dissertation, the natural alteration of Inani ilmenite has been investigated. The separation of ilmenite from the heavy minerals were effected through conventional ore dressing techniques i.e., techniques based on the difference in physical properties like density, electrical and magnetic properties.

The sample of ilmenite was separated into different size and magnetic fractions and each fraction was analyzed chemically by standard methods of wet chemical analysis. X-ray diffraction analysis was performed to identify the phases present in the various fractions Thermo-gravimetric analysis of the magnetic fractions was carried out to detect the presence of water in the sample. The effect of oxidation (2 hour at 950°C) on the extent of reduction and also on subsequent leaching of iron in ilmenite has also been investigated. Chemical analysis results have shown that oxidation converts all but 0.43 percent FeO.

Ilmenite sample under investigation contained 25.48% FeO, 34.22% Fe_20_3 and 39.90% $Ti0_2$. From the sieve analysis it was found that more than 98.28% of the ilmenite belongs to the US Sieve No. 100, 140 and 200. The sphericity of ilmenite of all size fractions was found to lie in a narrow range of 0.822-0.843. The finer size fractions were found to have a slightly higher sphericity than the coarser one. Magnetic fractionation showed that about 90.08% of Inani ilmenite belongs to the fractions separated by a current of 0 10 - 0.30 amperes.

X-ray diffraction patterns of different magnetic fractions of as received ilmenite showed the presence of pseudorutile phase. Thermogravimetric analysis indicated the presence of bound water. Optical polar microscopy, magnetic susceptibly balance , Cyclic voltammetry was used to see the alteration process. In Cycilc voltammetry method the presence of ferric iron was observed. Magnetic susceptibility value shows that Inai ilmenite is the in the process of alteration. These investigations led to the conclusion that Inani ilmenite is in a partially altered state

The samples of ilmenite were reduced by charcoal at 1050°C for 4 hr with a ilmenite-coke ratio of 1:1. The maximum extent of reduction was found to be 88 00%.

Finer size fractions and lower current fractions of Inani ilmenite contain higher percentage of iron oxide But finer fractions and fractions separated at lower currents are reduced to a higher extent. This indicates that separate reduction for the different size or magnetic fractions is not required.

Reduction with charcoal under optimum condition showed that the maximum metallic iron content of the sample reduced after oxidation were higher (39.75%) than in the samples reduced (39.31%) in the as received condition. Oxidation prior to reduction of Inani ilmenite was found to increase the rate of leaching.

Chapter 1

INTRODUCTION

1.1 Introduction-

Chemical formula of ilmenite is $FeO.TiO_2$.

Physical properties of ilmenite are

Color:	Iron black, Black.
Density:	4.72 g/cc
Diaphaniety:	Opaque
Fracture:	Conchoidal - Fractures developed in brittle materials characterized by smoothly curving surfaces, (e.g. quartz).
Habit:	Massive - Lamellar - Distinctly foliated fine-grained forms.
Habit:	Tabular - Form dimensions are thin in one direction.
Hardness:	5-5.5 - Apatite-Knife Blade
Luminescence:	None.
Luster:	Sub Metallic
Magnetism:	Naturally weak
Streak:	Brownish black

Chemical properties of ilmenite are

Chemical Formula:	$FeO.TiO_2$			
Composition.	Molecular Weight = 151.73			
	Titanium	31.56 %	Ti	52.65 % TiO_2
	Iron	36.81 %	Fe	47.35 % FeO
	Oxygen	31.63 %	O	
		100.00 %		100.00 % = TOTAL OXIDE
Empirical Formula:	$FeO.TiO_2$			

Environment: Common accessory mineral in igneous and metamorphic rocks Commonly concentrated in placers as "black sand" deposits

Locality: Ilmen Mountains, southern Urals, Russia
Name Origin: Named after its locality.

Crystallographic properties of ilmenite are

Ilmenite Crystallography
Crystal System: Trigonal - Rhombohedral
Axial Ratios: a:c = 1:2.76065
X Ray Diffraction. By Intensity(I/I_o): 2.754(1), 2.544(0.7), 1.7261(0.55)
Cell Dimensions: a = 5.093 A^o, c = 14.06 A^o,
Z = 6 A^o;
V = 315.84 A^{o3}
Density(Calculated)= 4.79 g/cc

Ilmenite most often contains appreciable quantities of magnesium and manganese and the full chemical formula can be expressed as $(Fe,Mg,Mn,Ti)O_3$. Ilmenite forms a solid solution with geikielite ($MgTiO_3$) and pyrophanite ($MnTiO_3$) which are magnesian and manganiferous end-members of the solid solution series. Although there appears evidence of the complete range of mineral chemistry in the $(Fe,Mg,Mn,Ti)O_3$ system naturally occurring on earth, the vast bulk of ilmenites are restricted to close to the ideal $FeTiO_3$ composition[1]. Titanium dioxide occurrences in nature are never pure; it is found with contaminant metals such as iron. Psudorutile and leucoxene are the altered products of ilmenite. These products contain higher titanium and are usually limited in beach sands. When ilmenite grains are highly altered then it consists almost of leucoxene. Leucoxene is a typical component of altered ilmenite [2].

Most ilmenite is recovered from heavy mineral sands ore deposits. Ilmenite can also be recovered from layered intrusive sources colloquially known as "hard rock titanium" ore source

Ilmenite forms as a primary mineral in mafic igneous rocks and also concentrated into layers by a process called "*magmatic segregation*". It crystallizes out of magma relatively early before most of the other minerals. As a result, the heavier crystals of ilmenite fall to the bottom of the magma chamber and collect in layers. These layers constitute a rich ore body for titanium miners [3].

1.2 Uses and Economic Importance

Ilmenite is a source of titanium-di-oxide. Ilmenite is used in paints, fabrics, plastics, paper, sunscreen, food and cosmetics industries [4]. Titanium alloys have found many applications in high tech airplanes, missiles, space vehicles and even in surgical implants.

Rutile is also a rich source of titanium dioxide. Titanium dioxide is the most widely used white pigment because of its brightness and very high refractive index. Titanium dioxide is also an opaque substance. When TiO_2 deposited as a thin film, its refractive index and color make it an excellent reflective optical coating for dielectric mirrors and some gemstones. TiO_2 is also an effective opacifier in powder form, where it is employed as a pigment to provide whiteness and opacity to products such as paints, coatings, plastics, papers, inks, foods, medicines (i.e. pills and tablets) as well as most toothpastes. In cosmetic and skin care products, titanium dioxide is used both as a pigment and a thickener. This pigment is used extensively in plastics and other applications for its UV resistant properties where it acts as a UV absorber, efficiently transforming destructive UV light energy into heat. Titanium dioxide is also used in sunscreen because of its ability to reflect UV light [5].

Titanium dioxide TiO_2, is a white pigment that is used more and more in paints as lead paint is discontinued due to health considerations. In fact, the largest percentage (up to 95%) of world wide use for titanium is for the production of this white pigment. The pigment has great luster, good endurance, high opacity (it hides whatever is under it, important for paint) and a pure white color. Titanium and titanium compounds have found uses in desalination plants, electrical components, glass products, artificial gemstones, jewelry and even as smoke screens.

Titanium oxide is also used as a semiconductor. Titanium dioxide, particularly in the anatase form, is used as a photocatalyst. It has potential for use in energy production: as a photocatalyst, it can

(i) carry out hydrolysis; i.e., break water into hydrogen and oxygen. The efficiency of this process can be greatly improved by doping the oxide with carbon.

(ii) produce electricity when in nanoparticle form.

TiO_2 powder is chemically inert, and is very opaque: this allows it to impart a pure and brilliant white color to the brown or gray chemicals that form the majority of household plastics [1].

Due to their high tensile strength to density ratio, [6] high corrosion resistance [1] and ability to withstand moderately high temperatures without creeping, titanium alloys are used in aircraft, armor plating, naval ships, spacecraft and missiles[8,1].

TiO_2 is biocompatible (non-toxic),for that it is used in a gamut of medical applications including surgical implements and implants, such as hip balls and sockets (joint replacement) that can stay in place for up to 20 years. Titanium has the inherent property to osseointegrate, enabling use in dental implants that can remain in place for over 30 years. This property is also useful for orthopedic implant applications [9,10]

TiO_2 offers great potential for detoxification or remediation of wastewater due to several factors.

1. The process occurs under ambient conditions very slowly, direct UV light exposure increases the rate of reaction.
2. The formation of photocyclized intermediate products, unlike direct photolysis techniques, is avoided.
3. Oxidation of the substrates to CO_2 is complete.
4. The photocatalyst is inexpensive and has a high turnover.
5. TiO_2 can be supported on suitable reactor substrates [11].

1.3 Prospect of ilmenite in Bangladesh

Heavy minerals found in the beach sands of Bangladesh are one of the most important deposits that have, so far, been identified in Bangladesh. Ilmenite is most abundant minerals in the deposits and contributes about 25 percent of all the heavy minerals [12].

In 1977, a pilot plant was set up at Cox's Bazar by the Bangladesh Atomic Energy Commission to separate the individual heavy minerals from these deposits. Unfortunately, however the ilmenite produced at Cox's Bazar pilot plant contains about 40 percent TiO_2 together with a large amount of iron in the form of oxide, silica, magnesium and other trace elements such as manganese, chromium etc. Different constituents of Bangladesh ilmenite are shown in the Table 1.1 .This table shows the minimum and maximum percentage of the constituents [13-14].

Ilmenite containing less than 52 percent titanium-di-oxide is not considered suitable for industrial use. As a result this valuable mineral which is separated from the beach sands of Bangladesh could not find a market in Bangladesh or elsewhere

Table 1.1 Constituents of Bangladesh ilmenite.

Constituents	Constituents
TiO_2	39.00-45.37
Fe_2O_3	25.62-33.00
FeO	24.01-29.75
SiO_2	1.20
MnO	1.17-1.30
Cr_2O_3	0.02-0.57
P_2O_3	0.03

In view of rapid depletion of known reserves of natural rutile (TiO_2) efforts are being made throughout the world to transform ilmenite to rutile through thermo chemical treatments. As a result of these investigations, a number of commercial processes for the production of rutile from ilmenite have been developed. This rutile is known as synthetic rutile It is believed that the successful conversion of Bangladesh Ilmenite to synthetic rutile will make these valuable minerals useful at home and abroad

1.4 Scope of present work

Ilmenite sample collected from the beach sands of Inani was separated into different size and magnetic fractions. The amount of TiO_2, Fe^{2+}, $Fe^{3+}$and total iron in all the fractions were determined. Samples of ilmenite was subjected to optical and scanning electron microscopic investigations. Thermogravimmetric analysis was done to detect the presence of bound water in the sample Bound water is the main reason for alteration of ilmenite to rutile [15]. Water can oxidize and reduce the iron to leach iron from ilmenite. Scanning Electron Microscopy was used to see the surface of ilmenite grain. To determine the transformation of ferrous iron to ferric iron magnetic susceptibility was measured. In magnetic size fractionated sample the amount of ferric iron will indicate the alteration process is continuing. Oxidation of ferrous iron to ferric iron enhances the alteration process. The opacity of ilmenite grains was investigated by optical polar microscope Reduction was done to see if synthetic rutile could be made from Bangladesh ilmenite.

Chapter 2

Literature review

2.1 Introduction

Ilmenite and rutile dominate their titanium-minerals assemblages. Rutile is common in pelitic lithologies. Erosion of terranes release about 0.1 to1.0 percent ilmenite and rutile to the transport system The other terranes that contribute valuable assemblages of titanium minerals are small - for example alkali stocks and hydrothermal systems Locally intermediate sedimentary hosts are the most important source rocks [16]. If the source terranes do not supply the right materials, an economic titanium mineral placer cannot form. There are several other minerals that contain appreciable quantities of titanium. Ilmenite, arizonite, titanoferrous magnetite are commercially important. Table. 2.1 show the composition specific gravity and titanium percent of chief titanium minerals [17].

Table 2.1. Chief Titanium Minerals

Mineral	Composition	Specific Gravity	Titanium percent
Rutile	TiO_2	4.25	59.95
Ilmenite	$FeTiO_3$	4.5-5.0	31.6
Arizonite	$Fe_2O_3.3TiO_3$	... ...	36.6
Titaniferous Magnetite	Fe_2O_4 with Ti	5.0-5.5	up to 20
Sphene	$CaTiSiO_3$	3.54	24.5
Pervoskite	$CaTiO_3$	4.0	35.3

Ilmenite ($FeTiO_3$)

Ilmenite is the most common mineral of titanium. The composition is close to the theoretical formula ($FeO.TiO_2$). Usually the TiO_2 content varies between 48 - 53 percent. It occurs in metamorphic and igneous rock (particularly in basic ores) and in some schistose rocks Ilmenite is slightly magnetic, able to withstand extreme temperatures. Ilmenite is the main source of titanium-di-oxide which is used in paint industry, fabrics industry etc. It is black in color with a sub-metallic luster having specific gravity 4.6-5.

Titaniferrous Magnetite

It is as common as ilmenite. Many magnetite of magmatic origin contain a certain amount of ilmenite which originally must have been in solid solution in the magnetite structure but separated out later as lamellae along the octahedral planes. The percentage of titanium is usually low, but it may rise occasionally from 15 to 20 percent.

Arizonite ($Fe_2O_3.3TiO_3$)

Arizonite is a material found in very small quantity in Arizona. It has the formula $Fe_2O_3.3TiO_3$ which gives 60 percent of TiO_2. As it is similar in appearance to ilmenite, it is thought to be present in the beach sands giving a higher titanium content than ilmenite [18].

Sphene ($CaTiSiO_3$)

Sphene ($CaTiSiO_3$) is also called titanite. It has yellow brown color and specific gravity 3.54. It occurs as an accessory mineral in various types of igneous rocks, particularly in granite, syenite and diorite and also in certain amphoiboles-schists, chloride-schists, epediotes etc. It contains 24.5 percent titanium. Sphene is often associated with rare earth and may carry quantities of yttrium earths, columbium, tantalum, cerium etc.

Perovskite ($CaTiO_3$)

Pervoskite is a yellow to orange or grey mineral with a specific gravity of 4. It is found generally in alkaline rocks (especially in those of a basic character like melilite basalts) and also sometimes in metamorphic rocks. The mineral does not occur in large enough quantities to be used commercially It contains 35.3 percent titanium.

Ilmenite and titaniferrous magnetite

Ilmenite and titaniferrous magnetite are frequently associated with an alteration product called leucoxene, an opaque brown or grey substance Leucoxene increases the percentage of titanium, as it appears to be largely composed of titanium dioxide. There are few titanium silicates (some of them carrying rare earths) and titanates, but none of these merits consideration as a commercial source of titanium.

Rutile and ilmenite are the most abundant minerals containing titanium. Titanium content of rutile is higher but it is relatively scarce. Even though the supply of rutile has increased in the recent years the deposits are fast depleting and the demand outstrips supplies. The shortage of natural rutile has forced the technologist to develop process for the production of titanium rich materials to be used as a substitute of the scarce natural rutile.

2.2 Alteration Process in Nature

Ilmenite grains are rounded to subhedral, and commonly contain hematite exsolution blebs. Dissolution pits are observed along the boundaries of the exsolution blebs, with rutile occurring as an alteration product [19]. The liberation of iron during the progressive alteration of ilmenite to leucoxene (possibly including the intermediate alteration product pseudo-rutile) has been reported [20-21] Iron-containing mineral, Ilmenite, is weathering and releasing iron into the water [22] i.e the oxidation of all the ferrous iron and the leaching of one third of the ferric iron from the ilmenite lattice by electrochemical corrosion and is considered to occur in a mildly acidic groundwater situation. Alteration of ilmenite may also occur by a process where both the iron and titanium are dissolved but the iron is leached while the titanium is redeposited.

In sand deposits ilmenite exhibits various degree of alteration as a result of oxidation and preferential leaching of iron. The extent of alteration may from 48% TiO_2 to 70% TiO_2. This alteration of ilmenite to progressively higher grade products appears to take place mainly above water level. Appreciable amounts of still higher TiO_2 material, consisting almost entirely of leucoxene, can be concentrated from highly altered ilmenite by high-intensity magnetic separation. Massive deposit of ilmenite is found in a mafic igneous complex in Arakansas.

2.3 Alteration products of ilmenite

Ilmenite undergoes remarkable transformation in the weathering environment; it is moderately stable there, but iron is progressively leached from it. The result of extreme leaching can be tan-colored grains having specific gravity of about 3.0. Variation occurs in microstructure, chemistry, crystallography and magnetism of ilmenite.

Ilmenite from unweathered parent rock as supplied to the weathering environment generally contains less TiO_2 than stoichiomatric ilmenite because of intergrowths of hematite, magnetite, other oxides and silicates. The trace element content of ilmenite also varies with the intensity of weathering alteration. Based on rather fragmentary evidence, it appears that MgO content decreases as alteration proceeds while MnO content increases in the first stages of alteration (to low-TiO_2 altered ilmenite) but decrease at higher TiO_2 value. This has been supported by S Mitra [23]. This alteration process may be

Ilmenite→Hydrated ilmenite→ Pseudoilmenite → Pseudorutile → Leached Pseudorutile → Leucoxene.

Chemical Formula

$(Fe^{2+}_{1.87}\ Mn_{0.06}\ Mg_{0.04}\ Fe^{3+}_{0.10})Ti_{1.93}O_6 \rightarrow (Fe^{2+}_{0.77}\ Mn_{0.05}\ Mg_{0.03}\ Fe^{3+}_{0.84})Ti_{1.93}O_6 \rightarrow (Fe^{2+}_{0.88}\ Mn_{0.05}\ Mg_{0.04}\ Fe^{3+}_{0.44})Ti_{1.93}O_6 \rightarrow (Fe^{2+}_{0.27}\ Mn_{0.03}\ Mg_{0.03}Fe^{3+}_{1.07})Ti_{2.02}O_6 \rightarrow (Fe^{2+}_{0.13}\ Mn_{0.06}\ Mg_{0.02}\ Fe^{3+}_{1.17})Ti_{2.02}O_6 \rightarrow TiO_2$

Oxidation and humic acid leaching facilitate the weathering alteration of ilmenite. Initial alteration oxidized iron to Fe_2O_3 and later alteration leaches iron Teufer and temple showed that Pseudorutile (about 60% TiO_2 or $Fe_2Ti_3O_9$) is commonly an intermediate product of ilmenite alteration. Fine pseudorutile is a pseudomorph of ilmenite that retains some optical properties of ilmenite grains [24].

Unaltered ilmenite is the dominant mineral. When altered, ilmenite changes directly or through the intermediate products to leucoxene Unaltered ilmenite grains with a composition close to the theoretical formula ($FeTiO_3$) and a TiO_2 content ranging from 48-53 percent. No distinction is made between ferrian-ilmenite and ilmenite. Although varying in intensity and pattern from grain to grain. the most common alteration is along grain boundaries and crystallographic direction. The minerals represent a distinct intermediate in the chemical composition. Weathering in the ilmenite, having a pseudorutile structure but a leucoxene like composition A common ilmenite alteration mechanism can be explained as follows:

$$Fe^{2+}TiO_3 \rightarrow Fe_2^{3+}Ti_3O_9 \rightarrow Fe_2O_3 + TiO_2$$

Hydrated ilmenite

This is also known as leached ilmenite, which is not completely altered to pseudorutile. This commonly replaces ilmenite along crystallographic directions, leading to the formation of micro-cracks. Areas of alteration within the ilmenite grains exhibit TiO_2 contents between 53 – 60 percent. These areas are distinguished microscopically from the ilmenite by their gray-blue colour and weaker anisotropism.

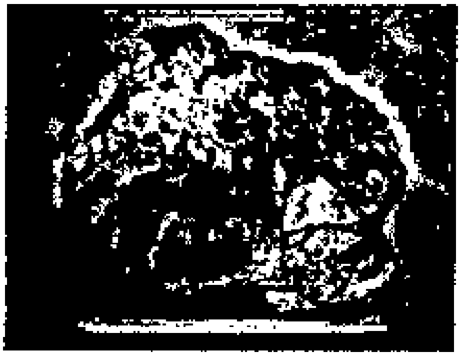


Fig.- 2.1 Typical photograph of hydrated ilmenite [25].

Pseudorutile

A heavy Ilmenite mineral concentration with dark brown hydroxyian grain is called pseudorutile Chemical Formula $Fe^{+++}2Ti_3O_9$, Molecular Weight 399.33 gm It contains 60.01 % TiO_2 39.99 % Fe_2O_3. Crystal system is trigonal, its density 3.8gm/cm^3, axial ratio a:c = 1:0 32104 and luster is sub metallic Pseudoilmenite is a deformed oxyhydroxide close to $Fe_2Ti_3O_9$ or $Fe_{1.5}Ti_9O_{7.5}(OH)_{1.5}$ with an extended range of homogeneity due to hydrogen exchange for iron during hydration. Characteristically it shows rough and porous texture. Compared to ilmenite it appears brighter in contrast to typical grayish color. Under reflected light isotopic pseudorutile is blue-grey color with a slightly higher reflectance than ilmenite [26]. Psedorutile developed along crystallographic orientations, in order or disorder patterns, along boundaries and fracture sand is characterized by the development of microstructure. The mineral is difficult to identify positively as those optical properties are often indistinct and its major XRD peaks exhibits d-spacing similar to those of ilmenite, rutile and hematite [27]

Fig.- 2.2 Typical photograph of natural pseudorutile [28]

Leached Pseudorutile

Leached Pseudorutile is hydrated Fe titanate mineral in the form of orange to red colored translucent grains. The grains are weakly magnetic and have a low density <$3.03 g/cm^3$ due to microporosity, which enable it to be easily concentrated in a pure state. Analysis report of these minerals are 67-69% TiO_2, 8-9% Fe_2O_3, 2-3%FeO, 11-12% H_2O and 8-9% intra-pore impurities mainly SiO_2 and Al_2O_3. Electron microprobe and SEM studies provided evidence for formation of the mineral by replacement reaction acting on Mg-rich ferrian ilmenite grains. The minerals represent a distinct intermediate in the chemical weathering of ilmenite, having a pseudorutile like structure but a leucoxene like composition, undergone any [29].

Leucoxene

Leucoxene, a mineraloid , is an alteration product of ilmente in which a portion of the iron has been leached from the crystal structure. Chemical composition is $(Fe^{3+}_{0.01}\ Al_{0.02}\ Mg_{0.03}\ Ti_{0.93})O_2$, Chemical formula TiO_2. Production historically has come from three types of deposits

(1) Beach and stream placer

(2) Massive deposits of titanoferrous ore and

(3) Igneous complexes in which rutile occurs in association with anorthosite and similar mafic crystalline rocks[30].

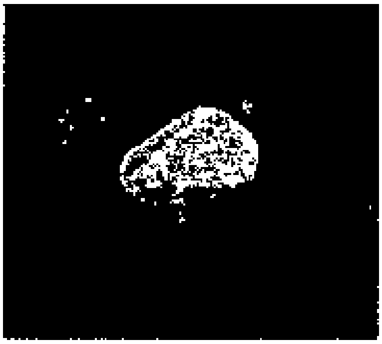


Fig.- 2.3 Typical photograph of natural Leucoxene[25].

Primary Rutile

Primary rutile can easily be distinguished from secondary rutile. Primary rutile exhibits idiomorphic, non-corroded crystal faces and is characterized by a bright grey color, high reflectivity and characteristic twinning.

Fig.- 2.4 Typical photograph of primary rutile[28].

2.4 Alteration of ilmenite

Ore-microscopic examinations and microprobe analysis showed that the alteration of ilmenite by leaching is a continuous process, proceeding from "leached ilmenite" through pseudorutile to leucoxene. In this process that takes place at near the surface and requires the presence of water, a temperature of 50°C is not exceeded Therefore, diffusion processes are of no importance

There are continuous phase transitions between ilmenite and its successive products. pseudorutile, with its iron-poor members (="leached pseudorutile") in particular, is unstable and decomposes into leucoxene As a result of this and also of leucoxene changes brought about by recrystallization, there are sharp grain boundaries towards other alteration products, simulating discontinuous leaching processes.

Ilmenite, leucoxene and their intermediate products are well distinguishable from each other by ore-microscopic and also by X-ray method [31].

Water is the main agent in the leaching process which keeps going on as long as there is iron present that is able to migrate.

The continuous alteration of ilmenite can be expressed in terms of reaction:

$Fe_2^{3+}Ti_3O_9 \rightarrow Fe_{2-y}^{3+}Ti_3O_{9-3y}(OH)_{3y}$.

In this equation y=0–2; y=0 corresponds to pseudorutile, y=2 to leucoxene. The range of y from 0.8–1.4 is identical with "leached pseudorutile". Reaction can be explained by hydroxilization and leaching of iron.

It comprises all phases with iron occurring in its trivalent state and the O: (OH) ratio increasing as the Fe^{3+} content is decreasing.

The study based on microscopic and microprobe techniques reveals that ilmenite of Manavalakurichi deposit has generally reached the alteration phase of 'leached ilmenite' in some modern beach and deposits, mainly in the belt between 30°S and 30°N, ilmenite occurs in a highly altered state. This altered ilmenite has been subjected to a process whereby iron has leached from the crystal structure and mineral grains [32].

Most ilmenite grains in sandstones completely altered to pseudorutile, leucoxene and rutile. Ilmenite grains [Ti/(Ti+Fe) ≈0.48] alter patchily to pseudorutile [Ti/(Ti+Fe) ≈0.5–0.7] with volume loss, forming a porous structure and this process continues with the development of leucoxene [Ti/(Ti+Fe) ≈0.7–0.9] [33].

This has been proved that textural, chemical and mineralogical changes takes place in alteration It was identified by using electron microprobe analyses, backscattered electron images, and elemental maps. Weathering exerts a powerful influence on the relative composition of titanium oxide bearing rock, its weathering mantle, and erosion debris. The weathering and erosion of titanium oxide material is the bridge between "primary" (igneous metamorphic) and "secondary" (sedimentary) titanium deposits. As a result the enrichment is less than 50 percent to 100 percent have been reported even in noncalcarious rocks. In extreme weathering TiO_2 may be mobilized within the rock to form concentration. Titanium oxide minerals are mostly resistant to weathering but they may be residually enriched in TiO_2.

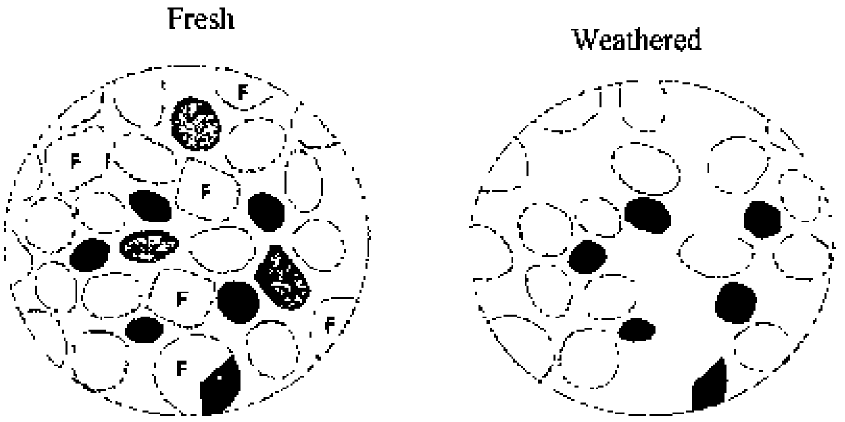


Fig . 2.5 Diagram contrasting fresh and weathered rock consisting Titanium oxide Minerals F-Feldsper , Shaded- Pyroxenes and amphiboles, Black-Titanium oxide reminder Quartz[17].

Weathering beneficiates titanium minerals deposits in the following steps

(1) Reduction in the mass of the parent's rock by leaching at approximately constant volume. Normally this reduction is less than 50 percent, locally to lesser volume are possible. Titanium oxide materials are thus residually enriched.

(2) The corollary destruction of such minerals as garnet amphiboles and pyroxenes which have no economic value but are difficult to separate from titanium oxide minerals.

(3) Disaggregation of the rock into monomineralic grains.

(4) The chemical enrichment of TiO_2 in several titanium oxide minerals, from which iron is leached in weathering [17].

2.5 Mechanism of Alteration of Ilmenite

Different mechanism of alteration of ilmenite have been proposed by different investigations [34-35]. This mechanism can be classified follows

Type I: Gradual weathering of ilmenite to leucoxene via hydrated ilmenite and pseudorutile in ground water environment.

Type II : The direct weathering of ilmenite to leucoxene in sediments above the water level.

Type III: The alteration of ilmenite to hematite plus rutile or anatase in source rocks; followed by the preferred dissolution of hematite to form ilmenite grains containing a porous network of TiO_2 microcrystals.

Type IV: Rutile reducing reaction in porphyry system.

Type I Alteration:

Many authors [34-35] described this mechanism in their own way. According to this mechanism alteration begins as irregular patches of hydrated ilmenite along grain boundaries and weakness within the grain or as oriented stringers along the basal cleavage planes of ilmenite. The second stage of alteration is marked by the development of leucoxene, which forms as irregular patches along grain boundaries, or stuctural weakness The development of leucoxene along grain boundaries is less common than expected for the in situ alteration of ilmenite [36].

In a number of grains, the boundaries between leucoxene and the phases it is replacing, are truncated by the grain surface, showing the alteration occurred in a large grain Fig 2.2a. This type of alteration may be explained by the two stage model proposed by [37]. The first stage involves the oxidation of all the ferrous iron and the leaching of the ferric iron from the ilmenite lattice by electrochemical corrosion. The reaction is

$$3Fe^{2+}TiO_3 + 2H^+ + \frac{1}{2} O_2 \rightarrow Fe_2^{3+}Ti_3O_9 + Fe^{2+} + H_2O \quad \ldots\ldots\ldots(1)$$

The reaction is considered to operate a mildly acidic groundwater situation. The second stage of alteration beyond pseudorutile occurs via a dissolution-reprecipitation process whereby both iron and titanium are dissolved, but the titanium is redeposited whilst the iron is leached from the grain. This leads to the formation of rutile in sand beach and anatase in lattice soils and can be described by the reaction.

$Fe_2Ti_3O_9 + 4H^+ \rightarrow TiO_2 + Fe^{2+} + \frac{1}{2} O_2 + H_2O$ ....(2)

Pseudorutile Rutile Dissolved iron

The second stage of alteration is thought to occur in the near-surface regions of the deposit in an environment, which is rich in organic acids and inorganic acids derived from the upper soil layer and condensation, creating mildly reducing and acidic solutions

Type II Alteration:

In this type of alteration ilmenite or slightly altered ilmenite, is observed altering directly to the leucoxene, this alteration occurs at grain boundaries or along weaknesses, such as fractures within the grains In some cases leucoxene may grow as replacement fronts across the grain [Fig. 2 2(c)].

Studies on iron–titanium oxides has shown that ilmenite may alter directly to leucoxene or optically identifiable anatase [38-39]. Frost et al noted relatively unaltered ilmenite cores surrounded by leucoxene in a concentration and concluded that these assemblages represent a single step dissolution reprecipitation process without the formation of pseudorutile[49]. The style of alteration of ilmenite leucoxene, rutile or anatase may be expressed by the equation

$FeTiO_3 + 2H^+ \rightarrow TiO_2 + Fe^{2+} + H_2O$ ....(3)

Significantly altered ilmenite (leucoxene) is shown in Fig 2 2(d)

Type III Alteration:

In this type of alteration two distinct intergrowths are noted. This type of intergrowth is characterized by the replacement of ilmenite by prismatic TiO_2 microcrystal According to this mechanism the alteration does not occur along the grain boundaries, but rather as patches within grains The second type of intergrowth is characterized by the development of anhedral, often-vermiform, rutile microcrystal patches within the ilmenite grains In a few instances microcrystal of hematite are found in rutile intergrowth of some ilmenite deposit [36]. Subsequent dissolution of hematite results in grains consisting of only ilmenite and microcrystalline rutile.

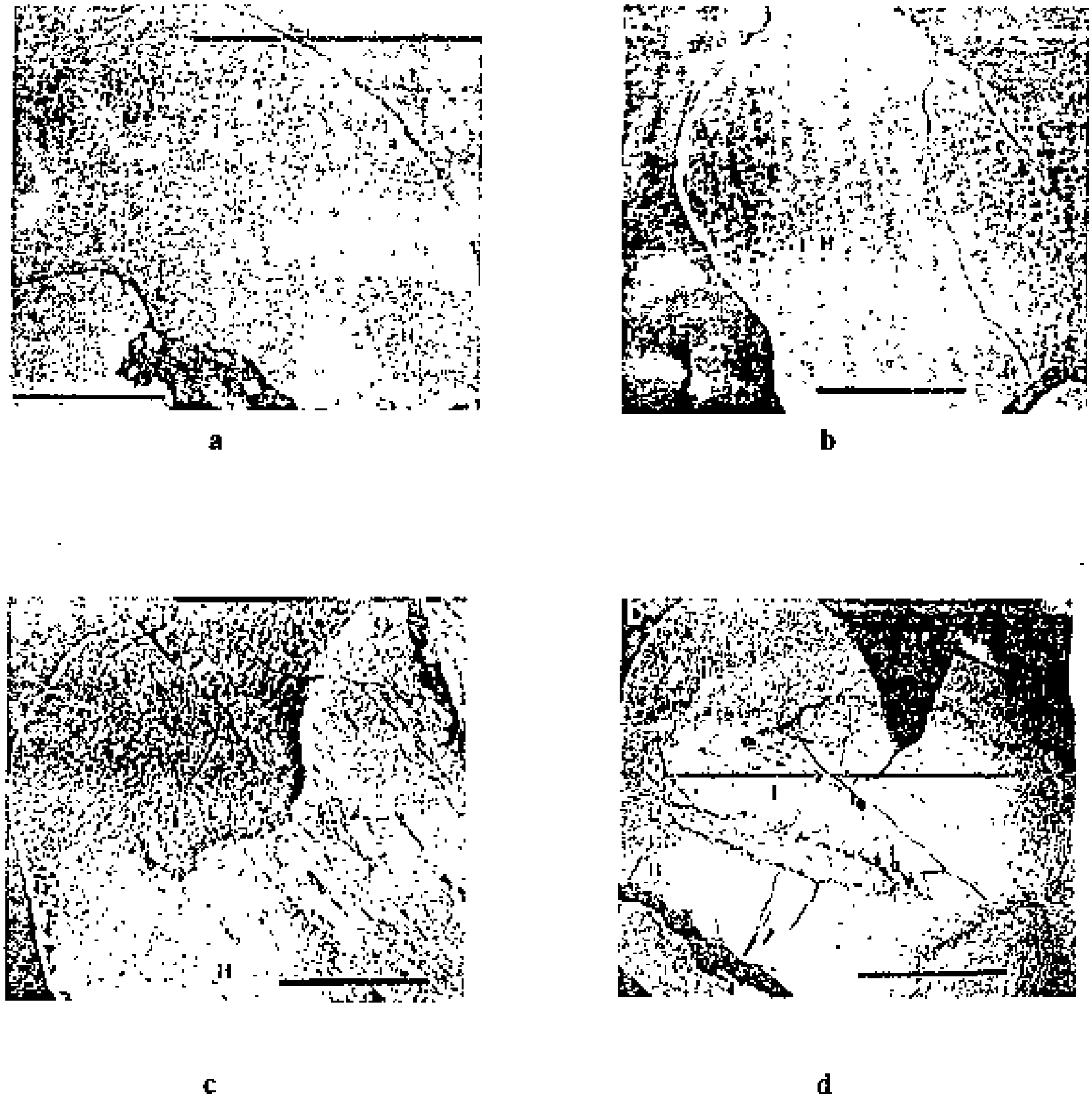


Fig 2.6 Scanning electron micrographs of partially altered and highly altered ilmenite grains [36]
(a) Patchy alteration of ilmenite to hydrated ilmenite
(b) Co-existence of unaltered and altered ilmenite
(c) Hydrated ilmenite grain altering to leucoxene
(d) Highly altered ilmenite grain showing a porous surface [36]

Type IV Alteration:

None of the altered material is stable in the alterated environment. Ilmenite disappears by alteration. Apparent mineral reaction is largely driven by the introduction of S and CO_2

$FeTiO_3$ +S_2 →FeS_2+ TiO_2..................(4)
Ilmenite +Sulphur →Pyrite + Rutile

A considerable literature exists on variations of heavy-mineral assemblages with the elevation of quaternary marine terraces. The higher terraces are known to be older and each represents an interglacial high stand of sea level. The higher terraces contain the more matured or weathered heavy minerals. The TiO_2 contents of altered ilmenite from the same marine terraces deposits show that within a given sea ilmenite is more enriched in TiO_2 on the higher terraces and that within a terrace the higher values are at lower latitude Fig. 2 7

Composition of ilmenite is a function of latitude. At high latitude, the composition of detrital ilmenite is the composition supplied by the source rocks. At lower latitude, TiO_2 content of ilmenite is extremely variables as function of weathering duration and deposit type but shows a maximum at low latitude beyond which leucoxene loses coherence and density. Ilmenites having TiO_2 contents greater than about 50% are mostly between 35^0N to 50^0N latitude

Minerals show great variation in degree of postdepositional weathering from terrace to terrace. The array in Fig.2 8 is quite orderly at any given latitude, weathering is greater in the older, higher latitude, where as at any given terrace elevation, there is an equally striking increase in weathering toward lower latitudes

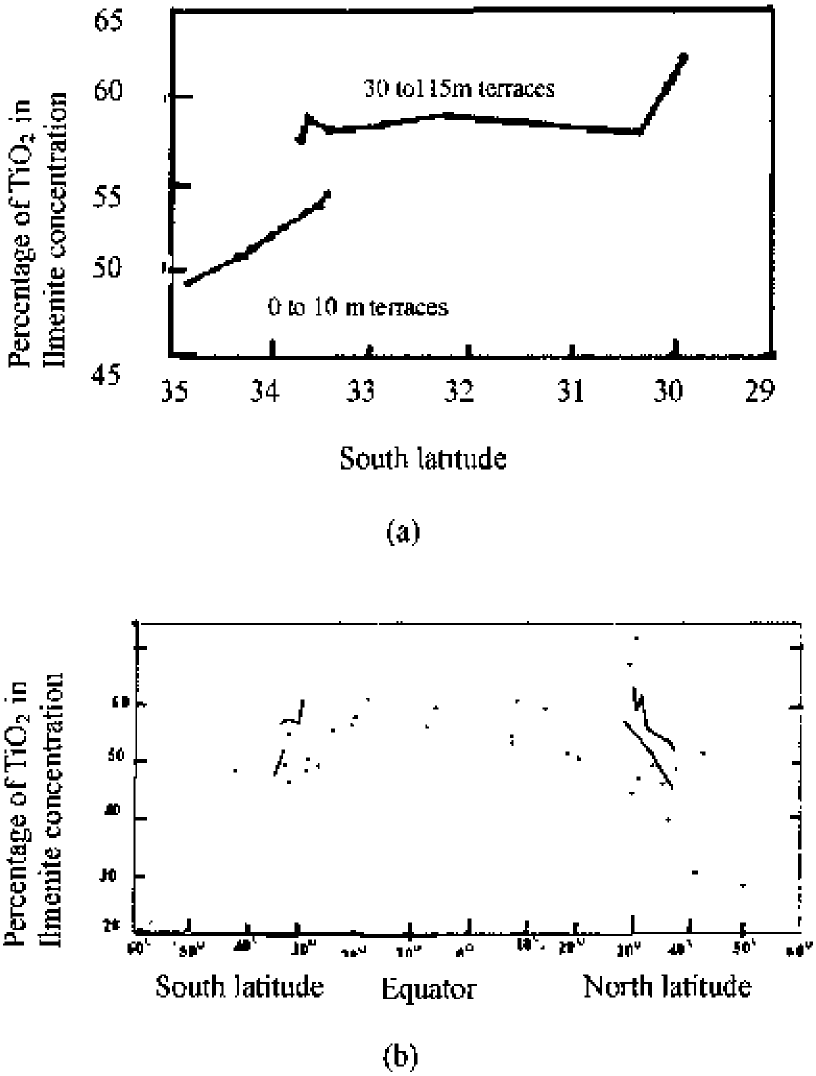


Fig. 2.7 (a) Plot of TiO_2 content of ilmenite concentration (Upper)
(b) Plot of TiO_2 content of ilmenite concentration as a function of latitude, in quaternary shoreline deposits of world (lower) [17]

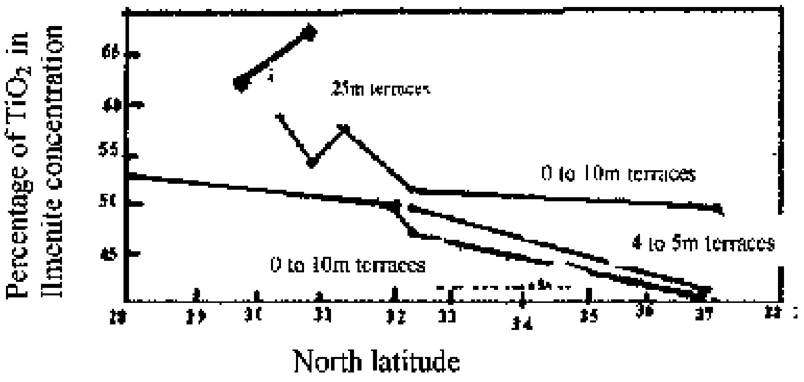


Fig 2 8 Plot of TiO_2 content of ilmenite concentration [17]

2.6 Climate change and weathering

Climate zones on continents are basically latitude parallel with an overprinted difference between east and west coasts. Climate change can be visualized as relative motion between a given continent and the climate belts crossing it. This motion may be of two general types

(1) Latitude-parallel belts or isothermal may move away from or toward the equator by the climate change, this is potentially the more rapid motion.

(2) Tectonic motion of a continent may carry it through climate zones with fixed positions. This factor is important in the Cenozoic for Australia and Indian subcontinent.

Two example of resultant climate change that affects weathering rates are

(1) A cool moist area becomes a worm moist area, accelerating the weathering rate.

(2) A hot dry area becomes hot moist area, also accelerating the weathering rate.

Each geologic time period is characterized by certain climate regimes and consequently by different aerial distributions of intense weathering. These temporal variations in weathering are recorded in the detrital mineral assemblage of sedimentary rock deposited through these time periods. The mineralogy of some of these rocks records weathering more severe than at present. Where these rocks function as intermediate sedimentary hosts for younger deposits of titanium oxide minerals, they release grains to the modern environment that are weathered beyond the power of present climatic conditions. The cretaceous is a good example of a time period when climate and weathering were much different than today Temperate climate extended to high latitudes perhaps to 80^0C, and CO_2 and O_2 in the atmosphere were higher Ilmenite-bearing placer deposits that formed during cretaceous time commonly have mature mineral suites, including ilmenite having high TiO_2 contents.

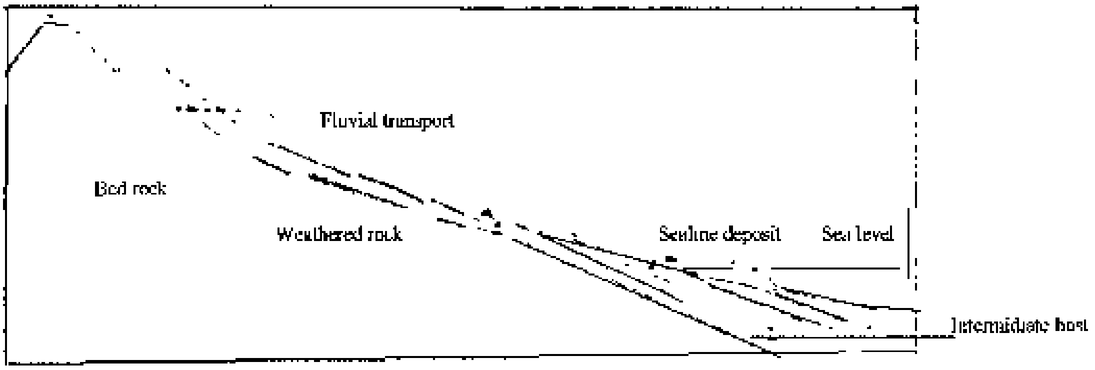


Fig. 2.9 Diagram showing sites of weathering beneficiation of TiO_2 mineral grains [17].

Variation with Quaternary sea levels:

During the quaternary, climate variation have been tied more or less mechanically to variation in ice volume and thus to sea levels. During peak glacial periods, sea level was about 85m lower than today's sea surface temperature average about 4^0C cooler and the CO_2 content of the atmosphere was about 30 percent less. Two factors interact to determine the subaerial weathering history of shoreline deposits:

(1) The duration of subaerial exposure, that is, the age of the deposits minus duration of the submergence.

(2) The weight average of weathering rate while exposed, which is a function of paleoclimate. Total weathering should be a product of the function of these two factors, both of which in turn are functions of the present depth of the submergence

$$W = Ra = f_1(D)f_2(D)$$

Where W = Total post depositional weathering
R = Weathering rate
a = Function of climate
t = Time intervals of subaerial exposure
D = Present depth of submergence.

If temperature variation were representative of all climate variation, the favorable zone for the formation of ilmenite placer deposits would shrink during a glacial period to latitudes lower than about 32^0.

The other factor in weathering, duration of subaerial exposure $[t = f_2(D)]$ acts as a permissive condition. When a previously formed shoreline deposit is submerged below sea level, it can not weather in the conventional sense; there is no evidence of submarine leaching of titanium oxide minerals. Thus subaerial expose is necessary for weathering of mineral suite of interest. A shoreline deposit that formed at sea level but is now 60m depth on the floor would seldom have been exposed as sea level cycled though the range of glacially controlled stands.

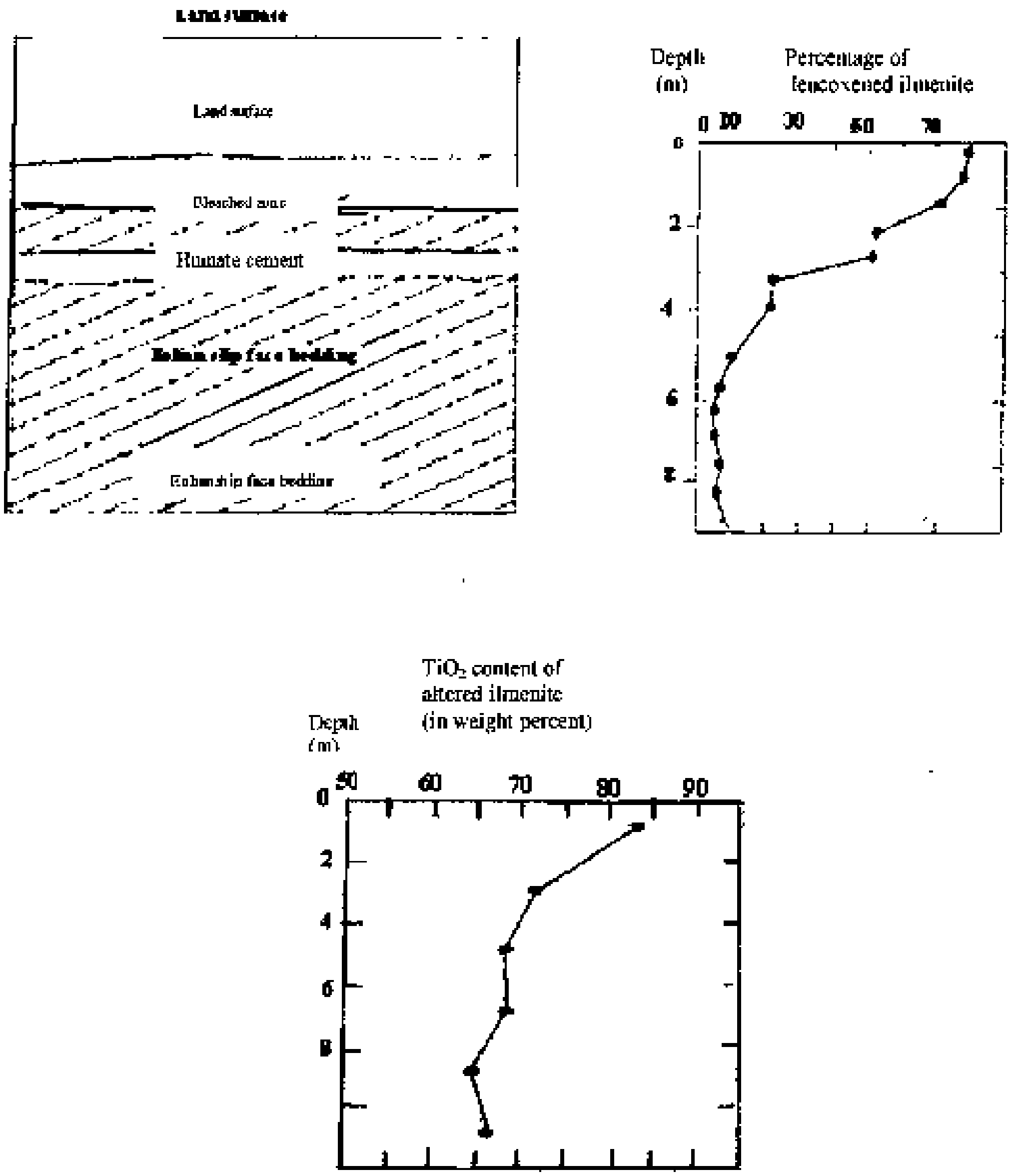


Fig. 2.10 Vertical profile of ilmenite alteration in surfacial sand [17]

2.7 The effect of alteration on ilmenite quality

It has been shown that magnetic susceptibility of ilmenite decreases with increasing alteration. Hugo [41] estimated the magnetic behavior of ilmenite and alter ilmenite in the Richards Bay deposits by determination their mass proportion in different magnetic fraction by heavy mineral concentration.

These results show that

a. Ilmenite –hydrated Ilmenite –Pseudorutile grains are slightly less magnetic than unaltered grains, but most of the grains will report to the ilmenite concentrate.

b. Altered ilmenite grains containing leucoxene have a large range of magnetic susceptibility such grains may report to ilmenite concentrate or magnetic middling fraction and

c. Leucoxene grains too have large grains of magnetic susceptibility extending from that of ilmenite to that of non-magnetic rutile, and that most leucoxene will report to magnetic or rutile concentrate.

It is Clear that the type of alteration will effect the recoverability of altered ilmenite grains [36].

It has shown that there is a marked increase in the SiO_2 and Al_2O_3 contents of ilmenite alteration phase containing more than 60 percent TiO_2 in western Australian deposits. The increase in these impurities has been ascribe to the co precipitation with, or adsorption on to, alteration products [42] or the formation of clay minerals within pore space between alteration phases. It is, therefore evidence that ilmenite grains containing leucoxene and leucoxene grains themselves, are undesirable as they are often no recoverable and they contribute to impurity levels in concentrates.

Weathering process have upgraded large number of titanium oxide minerals deposits and have made some of the economic. In a number of deposits, the most valuable material is a saprolite developed on the primary deposits. All detraital deposits can be regarded as upgraded by prepositional, weathering. Superimposed in situ (post depositional) weathering of detraital deposits is also of great importance in some deposits.

2.8 The Importance of Study of Extent of Alteration

Altered ilmenite constitutes more than one third of the world production of titanium minerals. By virtue of its being a product of varying composition, altered ilmenite has in the past presented problems both with ore dressing and in the sulphuric acid digestion method of pigment manufacture. a process that consumes more than 90 percent of ilmenite and altered ilmenite produced. More recently, a better understanding of the natural alteration of ilmenite has become important in view of work directing at upgrading and altered ilmenite concentrates to products much higher in TiO_2.

There has been appreciable work on the alteration of ilmenite.

Hugo and Cornell studied alteration of ilmenites in Halocene dunes from Zululand. They observed two types of altered ilmenite:

1) Two stage alteration in which ilmenite alters to leucoxene via pseudorutile

11) Single stage alteration of ilmenite directly to rutile. In addition ilmenite altered by high temperature oxidation and hydrothermal process [36].

Suresh Babu D S et al [42] studied alteration of ilmenite of the Manavalakurichi deposist, India. Magnetic fractionation, chemical and structural analysis proves that alteration of ilmenite from Manavalakurichi deposit extends up to the formation of pseudorutile and traces of rutile. The data indicate that ferrous to ferric iron transformation, ferric oxide formation and iron removal contribute to the alteration sequence. They also stated that beach placer ilmenite concentration of world show significant variation in the degree of alteration. Manavalakurichi deposits minerals have been identified as weathering products of ilmenite .

Azith and Suresh Babu [43]studied differential alteration of ilmenite in a tropical beach placer in Southern India. This study based on microscopic and electron probe techniques reveals that ilmenite of Manavalakurichi deposit has generally reached the alteration phase of 'leached ilmenite'. The XRD and bulk chemical analysis confirm the limited alteration undergone by ilmenite grains. The prevalence of reducing environment at present in the deposit indicates that the oxidation of ferrous iron leading to pseudorutile formation would have occurred during transportation of sediments.

Teufer and Temple worked on "Pseudorutile a new mineral intermediate between ilmenite and rutile in the alteration of ilmenite" [35]. They observed that alteration of mineral ilmenite FeO TiO_2 in nature involves the processes of oxidation and leaching whereby iron is progressively removed to give a residual product, essentially TiO_2. Several investigations have been reported on the alteration products of ilmenite, but apart from composites of known oxides of iron and titanium, no distinct intermediate phase has been discovered As a result of an investigation of several altered ilmenite concentrates by x-ray techniques hitherto not applied to this problem, a new crystalline phase has been identified as a major constituent of altered ilmenite. The new phase crystallizes in a disordered structure of hexagonal symmetry and has the theoretical composition $Fe_2O_3 \cdot 3TiO_2$. They propose the name 'pseudorutile' for this new mineral.

Pe-piper et al [33] concluded that detrital ilmenite grains in sandstones of the Chaswood Formation are completely altered to pseudorutile, leucoxene and rutile. The textural, chemical and mineralogical changes involved in alteration were tracked using electron microprobe analyses, backscattered electron images, and elemental maps. Ilmenite grains (Ti/(Ti+Fe) ≈ 0.48) alter patchily to pseudorutile [Ti/(Ti+Fe) 0.5–0.7] with volume loss, forming a porous structure and this process continues with the development of leucoxene (Ti/(Ti+Fe) 0.7–0.9). Within the pseudorutile and leucoxene, stubby prismatic rutile crystals have been precipitated. Si and Al presence was observed in the altered ilmenite. With increasing amounts of leaching in different types of paleosols, there was increasing alteration of pseudorutile to leucoxene. In light gray mudstones and interbedded sandstones with diagenetic kaolinite that formed beneath the water table from percolating meteoric water, most leucoxene was converted to rutile. Burial diagenesis (to vitrinite reflectance values >0.4%) also promoted the change from leucoxene to rutile. The alteration of ilmenite is an important source of Fe for diagenetic minerals in the Chaswood Formation and correlative offshore deltaic and marine facies of the

Gray and Li [29] worked on hydroxylian pseudorutile derived from picroilmenite in Murry Basin, Southern Australia. They found that ilmenite concentrates obtained from heavy mineral deposits in the Murray Basin, south-eastern Australia contain appreciable quantities (up to 10 wt.%) of an unusual hydrated Fe-titanate mineral in the form of orange to red colored translucent grains. The grains are weakly magnetic and have a low apparent density (<3.3 g cm^{-3}) due to microprosity, which enables them to be easily concentrated in a pure state.

Stefen Bernstein et al [44]worked on leaching of Ilmenite and its alteration products form important sources for titanium production. They found that this altered ilmenite has been subjected to a process whereby iron has been leached from the crystal structure and the mineral grains, known as leucoxene, have elevated TiO_2 contents with values up to 80 wt.% The study is based on CCSEM and microprobe analyses of heavy mineral separates of the sand coupled with whole-rock XRF analyses.

Karkhanawala and Momin [24] studied that the alteration products of ilmenite due to oxidation at 850^0C in air was found to be mixture of hematite, pseudobrookite and rutile in an approximate molar ratio of 1:5:7. This product is almost identical with naturally occurring "brown leucoxene". At lower temperatures (650^0C) a mixture of hematite probably some rutile and as yet unidentified phases was obtained. From color change as well as the thermo gravimetric analysis it was observered that slow oxidation could take place at a temperature of even 100^0C to 200^0C The oxidation periods the susceptibilities decrease with increasing the temperature of oxidation.

Antoine F. Mulaba-Bafubianda et al [44] worked on alterartion of ilmenite . Their work sheds light on alternative routes for the extraction of the ilmenite. It moreover points out the usefulness of the Mössbauer spectroscopy in the mineral processing product monitoring. The beach sands were used in their study after the economic industrial minerals zirconia, ilmenite and rutile had been extracted in previous mining operations About 61% natural ilmenite recovery was observed in the flotation concentrate of a Humphrey Spiral concentrate while a 62% recovery of hematite was found in the flotation tailings. The combination of screening, spiral concentration and magnetic separation, and flotation yielded a product with the highest ilmenite and hematite concentration being 71% and 19%, respectively. A natural ilmenite mineral, containing 87% ilmenite and 13% hematite, could be produced and extracted from the tailings of the flotation process, collected subsequently to the spiral concentration and the initial screening.

A. Mücke and J.N. Bhadra Chaudhuri [31] studied on ore-microscopic examinations and microprobe analyses show the alteration of ilmenite by leaching to be a continuous process, proceeding from "leached ilmenite" through pseudorutile to leucoxene. In this process which takes place near the surface and requires the presence of water, a temperature of 50°C is not exceeded. Therefore, diffusion processes are of no importance

Chapter 3

MATERIALS AND EXPERIMENTAL METHODS

In this chapter the properties of the raw materials and the experimental procedure /works used for this investigation have been briefly described.

3.1 Materials

Ilmenite: Raw sand containing the heavy materials was collected from the back dune surface layers of the heavy minerals deposits at Inani sea beach area from points located 2-3 km away from the water line and 5-6 meters above mean sea level. The area selected for the study falls between the latitude $21^0 18'7''$ to $21^0 18'16''$N and longitude $92^0 05'10''$ to $92^0 06'04''$E at Inani. This placer deposit forms one of the most important heavy minerals concentrations of Bangladesh. The heavy minerals concentration were determined to be 89-92% by point counting grains using both reflected and transmitted light microscope The Inani beach placer deposit, consists of ilmenite, rutile, zircon and quartz mixed ilmenite. Ilmenite consisfitutes around twenty seven percent of heavy minerals tonnage.

The sample was dried and screened (~8 mesh) to remove shell and other trash. Factory grade ilmenite was produced by the flow sheet developed at the Beach Sand Minerals Exploitation Center, Cox's Bazar and the details can be found elsewhere [13]. The technique of separations is based on the difference on physical properties like density, electrical and magnetic properties The ilmenite separated from Inani beach sand is black shiny mineral powder having particles of different size. The major constituents of ilmenite are oxides of iron and titanium. The results of wet chemical analysis of the as-received Inani ilmenite contain a substantial amount of iron in the form of ferrous and ferric oxide. The result of chemical analysis is given in Table 3.1 .

Table 3 1: Chemical analysis of as received Inani Ilmenite

Component	% in ilmenite
FeO	25.48
Fe_2O_3	34.22
$Fe_{(tot)}$	43.55
TiO_2	39.90

Charcoal: The reducing agent used for this study was charcoal. The charcoal was collected from local market. The charcoal was dried and ground. The ground Charcoal was sieved and only +30 mesh size charcoal powder was selected as reductant. It was then dried at 110^0C for 4-6 hours, cooled and stored for use in the experiments

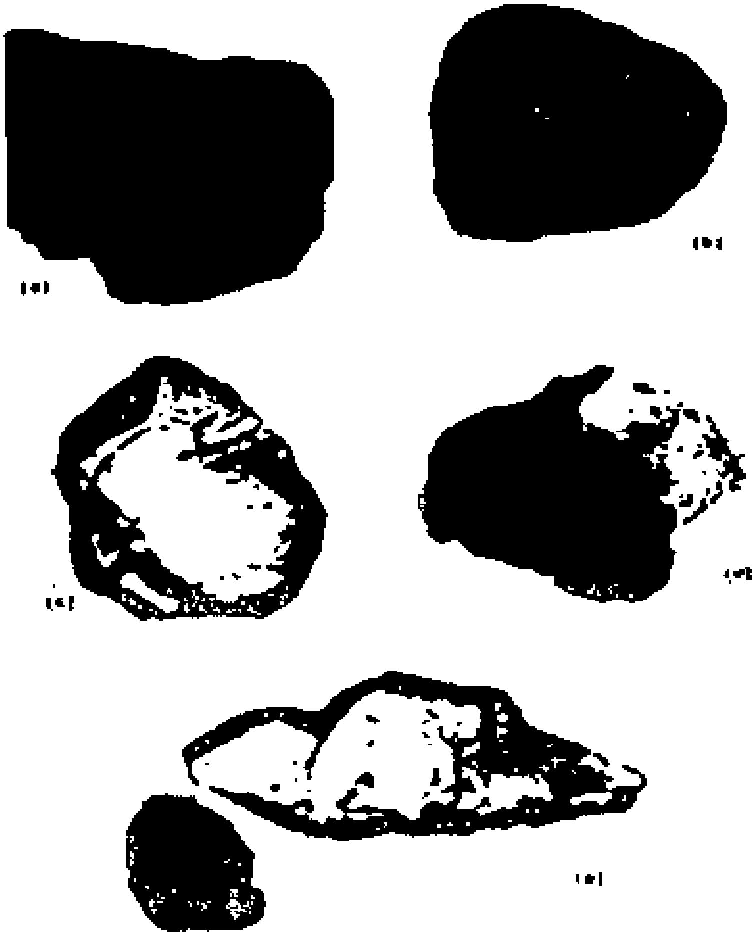


Fig 3.1 Mineralogy of as received heavy mineral sample(a)Ilmenite, (b) Rutile,(c) Zircon, (d) Quartz mixed Ilmenite, (e) Garnet.

The chemical analysis of charcoal is given

Table 3.2 Specification of charcoal used as reductant

Component	%
Fixed carbon	59.35
Ash content	6.80
Volatile matter	26.20
Phosperous	0.30
Moisture	6.46

3.2 Experimental methods

The following investigations were carried out

01. Chemical analysis
02. X-ray diffractometry
03. Magnetic fractionation
04. Sieve analysis
05 Measurement of specific gravity
06 Measurement of sphericity
07. Oxidation result analysis
08. Reduction result analysis
09. Leaching result analysis
10. Thermogravimmetric analysis
11 Optical microscopy
12. Scanning electron microscopy
13. Electrochemical voltammogramme analysis (Cylic voltammetry)
14. Magnetic susceptibility measurement
15. Optical polarized microscopic result analysis

3.2.1Chemical analysis

Chemical analysis was done by the standard wet chemical methods namely aluminum reduction methods for TiO_2, dichromate titration for iron . The detailed procedure for chemical analysis has been given in Appendices (A.-F). The prime interest was to determine percentage of ferrous oxide (FeO), ferric oxide (Fe_2O_3), and titanium di oxide (TiO_2) in the ilmenite sample used in these investigations. Reagent grade chemicals and acids were used for analysis.

Chemical analysis was also carried out in the different stages as mentioned below.
(a) For all fractions (both size and magnetic fractions) to determined the concentration of ferrous oxide (FeO), ferric oxide (Fe_2O_3), and titanium di oxide (TiO_2) to investigate the difference, if any, after separation into different size fractions and magnetic fractions.
(b) Oxidized ilmenite sample to determine ferrous oxide (FeO) and the extent of oxidation
(c)After reduction to determine the content of metallic iron (Fe_M), total iron (Fe_T) and Titanium oxide (TiO_2) and thus to determine the extent of reduction.

(d) Leached sample of ilmenite to determine the extent of removal of metallic iron and final TiO_2 content.

3.2.2 X-ray diffraction pattern analysis

X-ray diffraction analysis was conducted to identify the different phases present in ilmenite. The X-ray diffraction pattern were recorded by a Jeol DX-GE-2P X-ray diffractometer. Before recording the patterns, the samples were finely ground in an agate mortar.

The pattern was recorded with the following setting of the X-ray diffractometer

Target :	Mo(Zr)
Current:	20 mA
Voltage.	30kV
Angle of Diffraction:	8-38°
Scanning Speed:	½° per min
Chart Speed:	0.5 mm per min
Full scale Intensity:	2×10^{-4} cps

Some X-ray diffraction patterns were recorded by a two-circle (2θ- θ)X-ray diffractometer, X'Pert PRO PW 3040 with high temperature attachment upto 1600^0C.

The pattern was recorded with the following setting of the X-ray diffractometer

Target :	Cu(Ni)
Current:	30 mA
Voltage:	40kV
Angle of Diffraction.	20-70°
Step	0.20^0
Time for each step	0.6 sec
Data collection	

X-ray diffraction patterns of the different size and magnetic fractions were also recorded to identify the different phases present in the different fractions.

3.2.3. Magnetic fractination of as-received Ilmenite:

Frantz isodynamic separator was used to separate the different magnetic fractions present in the ilmenite sample. Frantz isodynamic magnetic separator is an effective tool for the separation of different minerals which have low but different specific magnetic susceptibilities. The Frantz isodynamic separator used in this study consisted of a vibrating chute mounted centrally between the pole pieces of an electromagnet as shown in Fig 3.2

Mineral separations are normally made by arbitrary adjustment of the current. At any such adjustment the separator divides a sample into two fractions. The more magnetic fraction consist of particles each having a specific susceptibility above a value determined by the settings. The less magnetic fraction consists of particles of susceptibility below this value. The sample of ilmenite was separated into five different magnetic fractions (at a current of

0.10-0.30 Amp) with a chute angle of 15° and feed rate about 50g/hr. The magnetic fractions were recycled through the separator to ensure a clean separation.

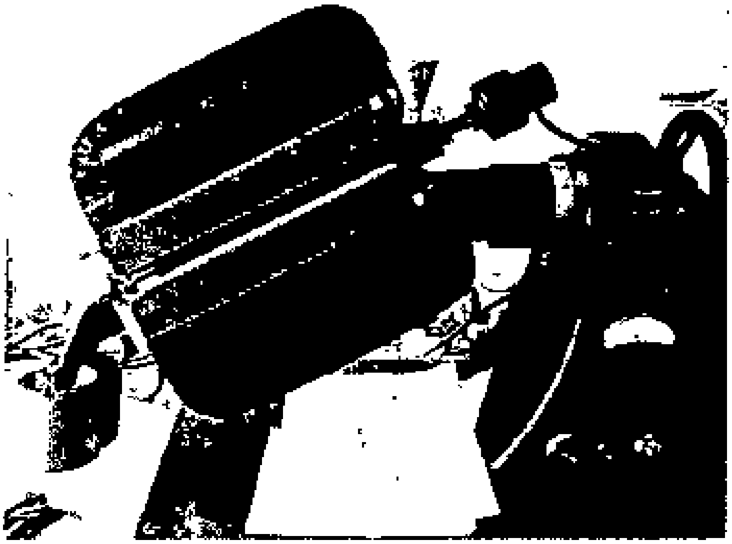


Fig 3.2 The frantz isodynamic magnetic separator

3.2.4. Sieve Analysis:

Sieve analysis of the received sample was performed in a standard US Sieve shaker At first the sieves of different mesh sizes were arranged in such a way that the sieve no 60 remained at the top most position while the pan remained at the bottom. The other sieves were placed from top to bottom according to their increasing sieve number Then 50g of as-received ilmenite was placed in the top most sieve and the power was turned on for a shaking period of 15 minutes. The samples retained on different sieves were collected and weighed .

3.2.5. Specific gravity measurement

Specific gravity of different fractionated ilmenite was determined using 50ml size specific gravity measurement bottle and water as a medium. Specific gravity were measured by using the following formula

$$\delta - \frac{Wt\ of\ sample}{Vol\ of\ sample} = \frac{W_2 - W_1}{50-(W_3 - W_2)}$$

Where,

W_1 = Wt. of empty bottle
W_2 = Wt. of sample and bottle
W_3 = Wt. of sample, bottle and water
$W_2 - W_1$ = Wt of sample
$W_3 - W_2$ = Wt. of water

50 = Vol. of the sp.gr. measuring bottle
$50-(W_3- W_2)$ = Vol. of sample

3.2.6 Measurement of Sphericity

In the present study, the shape characteristics of ilmenite particles have been expressed in the term of sphericity. Sphericity means the particle has the shape of sphere and hence the lowest surface area to volume ratio. Particles with lowest sphericity will be elongated in shape and hence have larger surface area The sphericity of different size fraction of Inani ilmenite was calculated by using formula given by Grade and Razu [37] and is explained below

Sphericity = d_a/a

d_a = Nominal diameter of the particle

The nominal diameter of the particle is calculated as $d_a = (a+b+c)/3$

Where a=Length of its major axis

b= Length at 90°C to length of its major axis. a and

c= Length at 45°C to length of its major axis, a

For measuring sphericity ilmenite sample of different size fractions were photographed under a microscope.

3.2.7 Oxidation of as-received sample:

Oxidation of ilmenite samples were carried out in temperature controlled furnace 20 gm of dry as-received ilmenite was spread on porcelin lid as a thin layer and was placed inside a electric muffle furnace. The temperature of the furnace was 950^0C and controlled by an on-off controlled to ± 5^0 C. The sample was placed for 2 hrs. After oxidation, the sample was taken out from the furnace and cooled to room temperature.

3.2.8 Reduction of as-received and pre-oxidized ilmenite:

Reduction was carried out in small stainless steel crucibles 25 mm in diameter and 125 mm in length. In each case 9 gm of ilmenite and equal amount of charcoal was taken Ilmenite and charcoal were placed in the crucible layer by layer. A layer of charcoal was placed at bottom of the crucible then a layer of ilmenite was placed on the charcoal. The top most layer was charcoal to resist oxidation. A metallic lid made of same material of that of the crucible covered the crucible. This arrangement is shown in the Fig. 3.3. A number of such crucibles were placed in an electric muffle furnace and set at the desired temperature

The temperature of the furnace was controlled to ± 5^0C by an off-on controller. After reduction crucibles were taken out one by one at different time intervals and allowed to cool at room temperature After cooling the reduced mass was separated from charcoal Separation was carried out in two stages. At first the bigger particle were separated by sieving. In the second stage particle of reduced ilmenite were separated from the fine particle of charcoal by small hand magnet. The samples both in the oxidized and in the as received condition were reduced with charcoal in the temperature range of $900\text{-}1050^{0}C$ for treatment time up to 4 hours. The magnetic and size fractions were reduced under otherwise identical conditions. The extent of reduction was followed by wet chemical analysis and X-ray diffraction analysis.

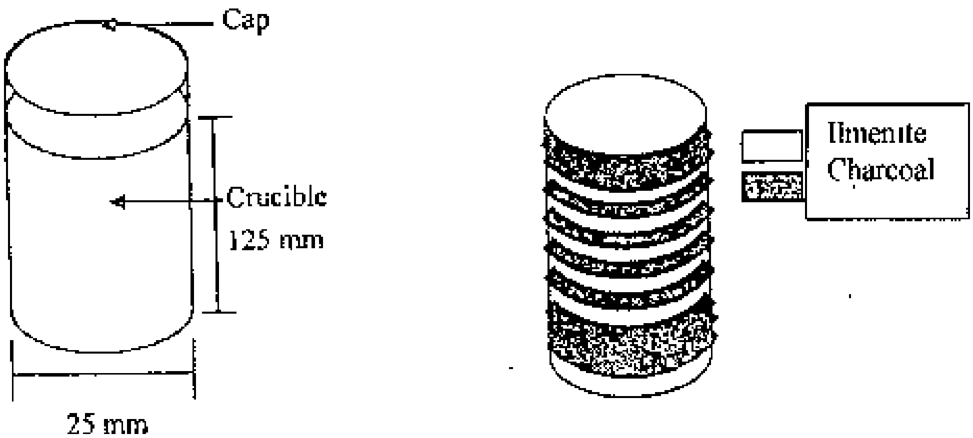


Fig. 3.3 Arrangement of reduction

The extent of reduction was followed by the chemical analysis of the reduced mass for the content of metallic iron. From the experimental results, the degree of reduction was calculated by using the formula [46]

$$\% \text{ of reduction} = \frac{\% \text{ of metallic iron in the sample}}{\% \text{ of total iron in the sample}}$$

3.2.9 Leaching of the reduced ilmenite

Ilmenite sample reduced both in the as received and in the pre-oxidized condition and were used to study the effects of prior oxidation on the extent of subsequent leaching of the reduced mass For leaching process a three necked round bottom flask with a reflux condenser was used (Fig.3.4). Three neck flask was used because one neck was for thermometer to measure the temperature, one neck to collect leached solution after specific time intervals and the other for the reflux condenser. Leaching was performed at $75^{0}C$ for 2hrs. in acid solution containing 20% HCl. During leaching 2gm of sample were taken in 200 ml HCl solution. The leaching solution was stirred by a magnetic stirrer. Care was taken to maintain similar stirring speed in all cases.

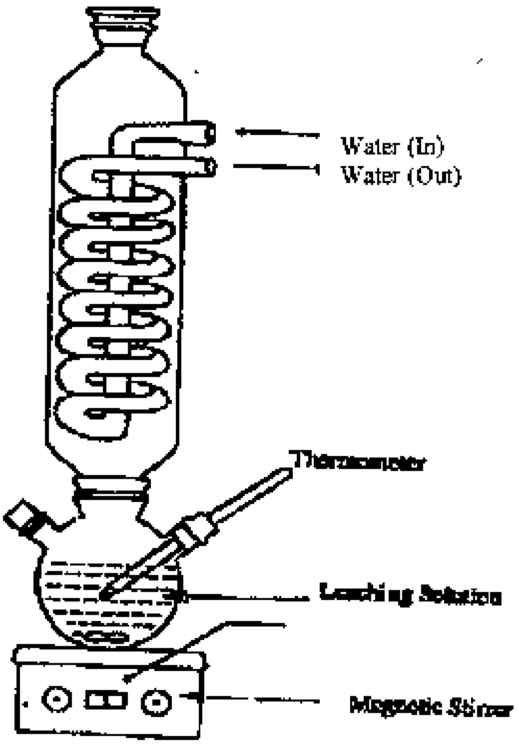


Fig. 3.4 Experimental setup for leaching

Temperature of the leaching solution was controlled to the specified value and was continuously monitored by a thermometer. During leaching 5 ml of solution was taken after 2 hrs and was analyzed to determined iron content of the solution. This was used to determine the amount of iron removed from the experimental samples. The amount of iron in leaching solution was determined by wet chemical analysis. The effect of oxidation on the quality of the synthetic rutile produced was identified by comparison of the contents of iron and TiO_2 of the samples reduced in the as received and in the oxidized conditions.

3.2.10 Thermogravimetric analysis for the different magnetic fractions

Thermogravimetry is "A method of measuring the mass of a substance as a function of temperature or time by varying the temperature of the substance according to a controlled program, usually performed by measuring the mass of the test piece as a function temperature" (JIS). The change of mass indicates thermal decomposition, dehydration combustion, oxidation, reduction, sublimation, evaporation and so on. The change of the mass of a sample is measured by the use of the thermobalance. The thermobalance is a device, which continuously weighs a sample when it is being heated or cooled.

Thermogravimetric analysis was performed in a SHIMADZU TGA-50 machine [Fig 3.5 and Fig 3.6]. It has a TGA chamber, the main heating, a control unit that is used to set different parameters, an inert gas set-up, and some electrical wiring.

A TGA chamber is a small induction furnace, made up of steel body with proper high temperature insulation in the inner surface It contains a small platinum crucible hang by a tungsten wire to contain charge or sample, and a small thermo-couple to measure temperature. There is a small inlet in the chamber to introduce the inert gas.

The platinum crucible was cleaned properly and then sample was placed on it

(a) Initial weight was taken.

(b)The crucible was inserted in the TGA chamber slowly and when completely in the TGA chamber it was closed

(c) Inert gas was introduced in the chamber to provide inert atmosphere.

(d) The heating rate was set at a value of 20^0 /min and the heater were turned on.

(e) When temperature rose up to 1000^0C the machine was turned off and the chamber was allowed to cool

(f) The machine produced the report as a graph.

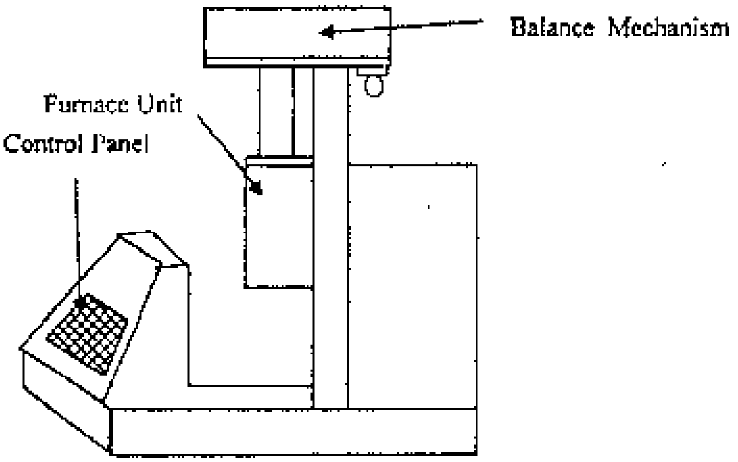


Fig 3.5 External view of TGA machine.

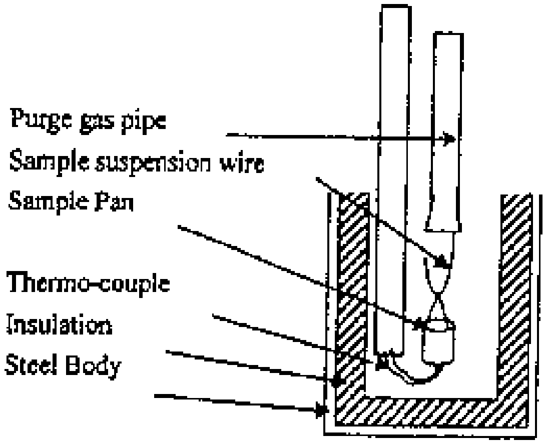


Fig 3 6 The cross-sectional view of the furnace unit of the TGA machine.

3.2.11 Optical Microscopy

Microstructure of samples was examined under an optical microscope before and after reduction. Particles of sample were mounted in a cold setting resin and prepared for the observation by using standard technique. Photographs of the significant areas of the sample were also recorded.

3.2.12 Scanning electron microscopy (SEM)

The SEM images vividly display the three dimensional, characteristic of the object surface, under examination and the high resolution images are usually produced by the secondary electron. In order to observe specimen surface, as it actually exist, special care must be taken. Ion spattering device was used for specimen preparation. The metal used to coat the specimen is placed on the cathode plate. Ion generated by the glow discharge. It hits the plate and eject the metal atom from it. These ejected metal atoms deposit on the surface of the specimen, which has been placed on anode plate.

Characteristics x-rays are emitted from a specimen when an electron beam irradiates it. By detecting and analyzing the characteristic x-ray the elements contained in the specimen can be determine. Electron beams are very finely focused. Therefore, by using the spot mode an elemental analysis of very small area on a specimen surface can be determined.

3.2.13Electro-Chemical analysis

A block diagram of instrument is shown in Fig.3.7. It consists of a data acquisition and controll board inside a personal computer (IBM committable). The data acquisition board is used to control the custom potentiostate (ModelHQ-2030/2040 by advance analytics, USA) and integrated computer controlled magnetic stirrer. The potentiostate has light emitting diods (LED) in the front panel and the connector plugs at the back. A diagram of the back panel of the potentiostate and the description of connector is shown. The electrochemical cell normally consists of three electrodes with a working electrode, an appropriate reference electrode and a platinum counter electrode. Cyclic voltammetry (CV) is a very versatile electroanalytical technique, used for the study and analysis of electro active species. A redox reaction is often represented in the generic form of reaction (1), but can be of many different types examples are given in reaction (2):

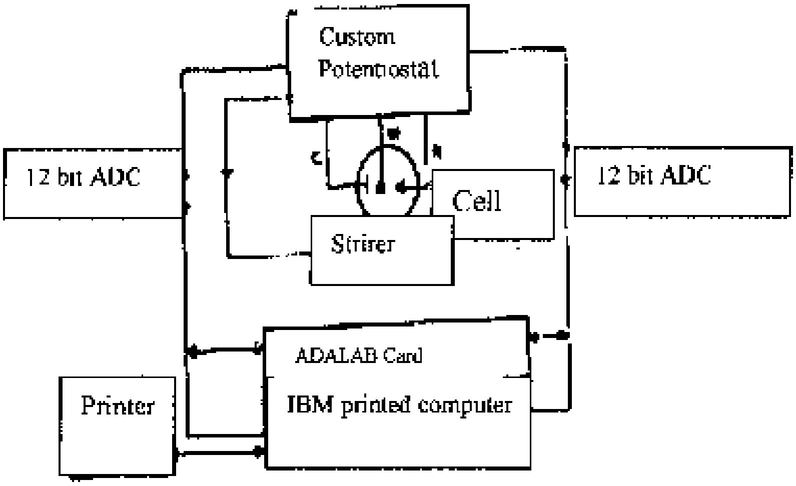
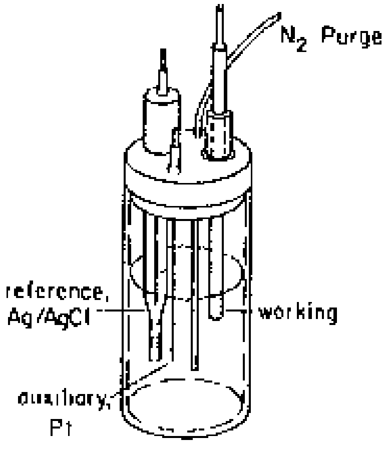


Fig 3.7 Block diagram of the computerized electroanalytical system.



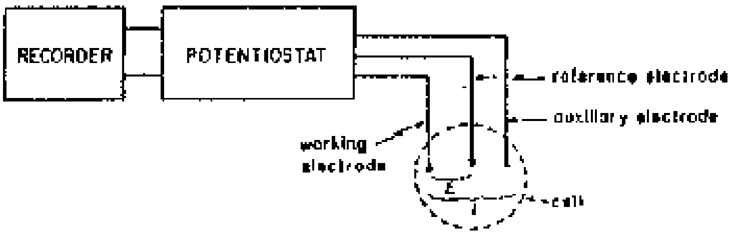


Fig 3 8 Electroanalytical cell for voltammetry.

Fig 3.9 Instrumentation for voltammetry.

$Ox + ne \rightarrow R$ (1)

$Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)$ (2)

Cyclic voltammograme of as received ilmenite sample were analyzed. Iron in the ilmenite sample was in ferrous and ferric state. In nature alteration begins with the transformation ferrous iron to the ferric iron Differently treated samples, such as oxidized, reduced. preoxidised and reduced samples, were analyzed by cyclic voltammetry Weathering effect in ilmenite creating alteration was also tried to understand

3.2.14Magnetic susceptibility Balance

The Sherwood scientific Magnetic Susceptibility Balance (M.S.B) is a method to measure the intensity of magnetism. In this balance a magnet exerts force on the sample, the equal and opposite force which the sample exerts on a suspended permanent magnet is observed.

The M.S.B works on the basis of a stationary sample and moving magnets. The pairs of magnets are placed at opposites ends of a beam so placing the system in balance. Introduction of the samples between the poles of one pair of magnets produces a deflection of the beam that is registered by the means of phototransistors. A current is made to pass through a coil mounted between poles of the other pair of magnets, producing a force restoring the system to balance. At the position of equilibrium, the current through the coil is proportional to the force exerted by the sample, and can be measured as a voltage drop.

The following general expression for mass susceptibility, χ_g, in $cm^3.g^{-1}$. Units may be derived in the same manner as for the traditional Gouy method

$$\chi_g = \frac{C \times l \times (R - R_o) \times 10}{10^9 \times m}$$

Where. χ_g =the volume susceptibility of the displaced air

C= a constant of proportionality

R= the reading obtained for tube plus sample

R_0= The empty tube reading (normally a negative value)

l = the sample length (in cm)

m= the sample mass (in g)

Operation of the balance

1 Range knob was turned to the x1 scale and 10 minute warm-up period was allowed before use.

2. Zero knob was adjusted until the display reads 000 The zero was adjusted on each scale used.
3. Empty sample tube of known weight was placed into the tube guide and the reading, R_0 was taken.
4. Sample was packed and the sample mass m in grams and the samples length l in cm was noted
5. Packed sample tube was placed into tube guide and take reading. R.

N.B. A negative reading indicates that the tube plus samples have net diamagnetisms.

3.2.15Optical polarized microscope

The samples were examined under an optical polar microscope before and after oxidation, reduction and leaching. The particle were sprayed on a layer of Canada Balsom on a slide This Canada Balsom attached the sample particle to the slide.

Chapter 4

RESULTS AND DISCUSSION

4.1 INTRODUCTION

The object was to study "Alteration of ilmenite in the Inani heavy mineral deposit." The results of these investigations are presented and discussed in the following subheadings:

(a) Characterization of as received ilmenite
(b) Oxidation of as received ilmenite
(c) Reduction of as received and oxidized ilmenite
(d) Optical polar microscopy study
(e) Optical microscopy study
(f) Micro probe analysis
(g) Study of voltammogram of different conditioned sample
(h) Measurement of magnetic susceptibility for the alteration

4.2 Characteristic of as- received ilmenite

As received ilmenite was analyzed by standard methods of wet chemical analysis. Sieve analysis of the as received ilmenite was performed in a standard sieve shaker. The sphericity of different sieved fractioned was also measured. Frantz isodynamic separator was used to separate the different magnetic fractions present in the ilmenite sample. The phases present were identified by X-ray diffraction analysis. Few samples were observed under optical microscope.

4.2.1 Chemical analysis of as-received sample

The result of wet chemical analysis of the as received ilmenite is shown in the Table 3.1 It can be inferred from the chemical analysis of the as received sample, that Inani ilmenite contains a substantial amount of iron in the form of ferrous oxide and ferric oxide. The ferrous iron content is 25.48%, ferric iron content is 34.22% and the amount of rutile (TiO_2) is 39.90%

A comparison of the chemical composition of as received ilmenite collected from Inani deposit with those commercially available from other sources as compiled from the data found in different references [20] is given in the Table 4.1. Inani ilmenite contains only about 39 08% TiO_2 while commercial grades of ilmenite contains a minimum of 55% TiO_2.

Table:4.1 Comparison of the chemical composition of ilmenites of different origin.

Constituent	USA	Canada	Brazil	Srilanka	Norway	Australia	Kerala	Cox'ba-zar	Inani
TiO_2	44.30	42.50	40.30	53.61	43.90	54.20	55.89	39.12-42.85	39.90
FeO	35.90	31.10	32.40	20.67	36.00	24.00	0.33	29.83-32.02	25.48
Fe_2O_3	13.8	20 70	16 60	20.95	1.11	18 00	40 37	40 37	32.89

4.2.2 X-ray diffraction analysis of as-received sample

X-ray diffraction pattern of as received Inani ilmenite is shown in Fig.4.1. Analysis of the pattern shows that ilmenite is the main phase while diffraction lines belonging to hematite, ferrous oxide, rutile and psedorutile could also be detected The nature is some what same as that of Cox'bazar Sarker and Kurny [46] detected hematite (Fe_2O_3) along with ilmenite in Cox's Bazar. The pattern analysis was strictly confined to qualitative analysis. Slight shifts in the locations of the diffraction lines were also noted. This can be attributed to the fact that placer deposits are not the chemically standard substance; the impurities present may also affect the lattice parameter values.

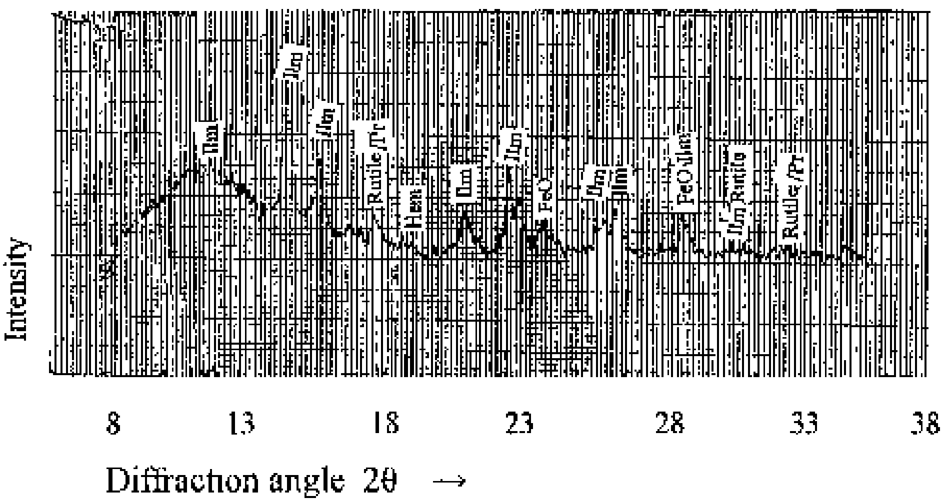


Fig 4.1 X-ray diffraction pattern of as received ilmenite

4.2.3 SEM Analysis

Scanning electron micrographs revealed that surface of ilmenite grain was not uniform (Fig.4.2)

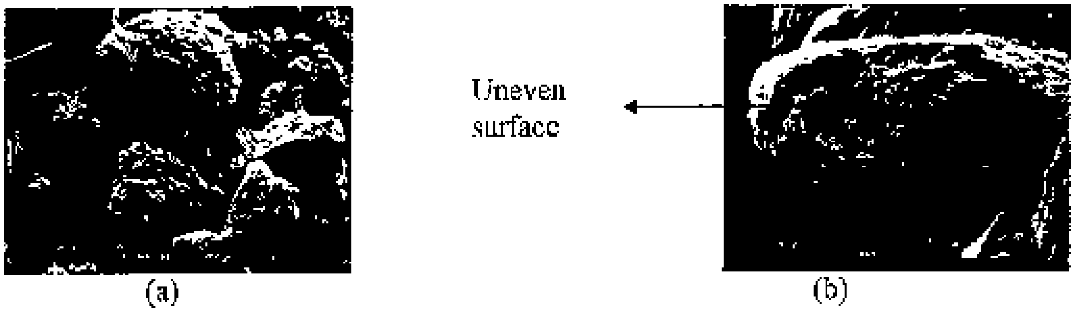


Fig 4.2 SEM of as received sample (natural ilmenite)
(a) 200 Magnification
(b) 500 Magnification

4.2.4 Optical polar microscopic analysis

The as received sample was observed under a polarized microscope Ilmenite is an opaque mineral. So light should not be transmitted through it. But in cross polar light microscope, it seemed that light is emitting from the outer surface of the grain. It seemed that light is scattering from outer surface of every grain. Photographs of standard ilmenite and Inani ilmenite were recorded and shown in Fig. 4.3. The differences are shown in the pictures. Some grains of Inani sample are in the process of alteration. Because some portion of the grains is translucent and color is milky white. Some grains are fully altered to leucoxene. Some typical pictures are given below.

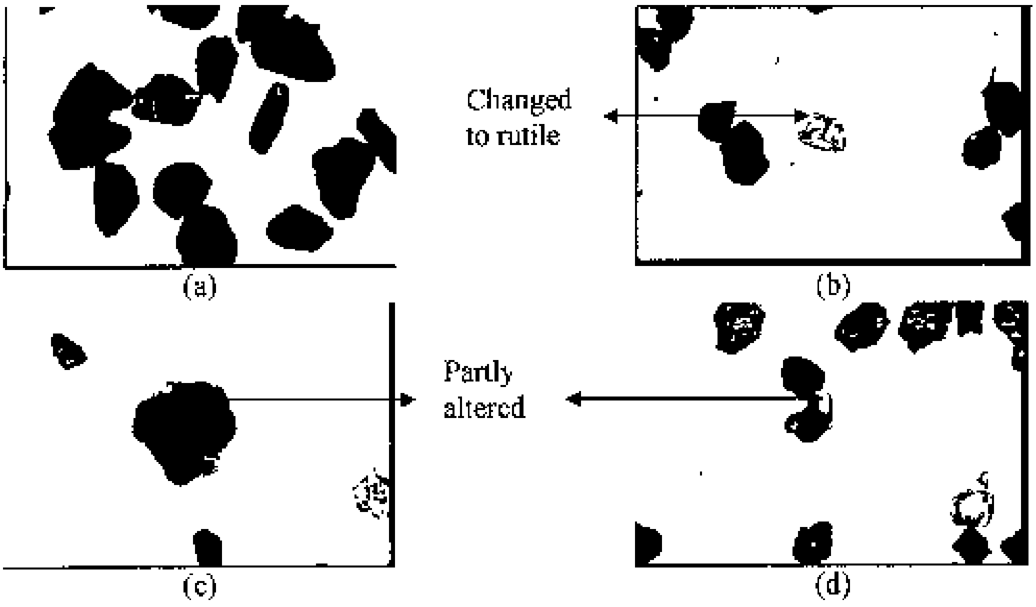


Fig. 4.3 Optical polar microscopic picture of as received sample
(a) Picture of standard ilmenite sample (b) Picture of standard ilmenite sample
(c) Ilmenite sample has slightly changed to rutile (Transparent portion)
(d) Weathered ilmenite which is shining

4.2.5 Sieve analysis

Size fraction of as received sample was performed with a standard Taylor sieve shaker 50g sample was placed on the top most sieves and power was turned on for 15 minutes. The sample on the different sieve was weighed and the results are presented in the Table 4.2. It was found that almost 90% of the sample was retained on three sieves; US sieve Nos 100, 140, 200, the individual amount belonging to each of the sieve being 18.26%, 30.92% and 40.90% respectively Only 8.2% was retained on the other sieves, which were not sufficient for further investigations. Investigations were therefore, conducted only on these three main size fractions.

Table 4.2 Sieve analysis of as received ilmenite

US Sieve no	Mesh opening µm	%Size fraction Inani	%Size fraction Teknaf
70	210	1.30%	0.05
100	149	18.26%	5.09
140	105	30.92%	47.05
200	74	40.90%	44.51
>200	53	6.90%	2.99

4.2.5.1 Chemical analysis of different size (Sieve) fractions

Samples of the major size fractions were analyzed chemically by standard techniques to find out the amounts of titanium oxide, ferric oxide and total iron and the results are presented in Fig.4.4. It can be seen that the finer fractions contain the lower percentages of TiO_2, higher percentage of total iron and lower percentage of ferrous oxide. Similar variation in the composition of finer and coarse size fractions of ilmenite has also been reported by Ahmed et al [13[

Although finer fractions of Inani ilmenite contain a higher percentage of total iron, the percentage of ferrous oxide was actually found to be slightly lower in finer fractions. This also is in good agreement with the findings of the earlier studies [13]. Percentage concentration of different composition in the Inani ilmenite is shown in the Fig 4.4 as a function of different size fraction. The ferric oxide content of in the finer fraction is obviously higher.

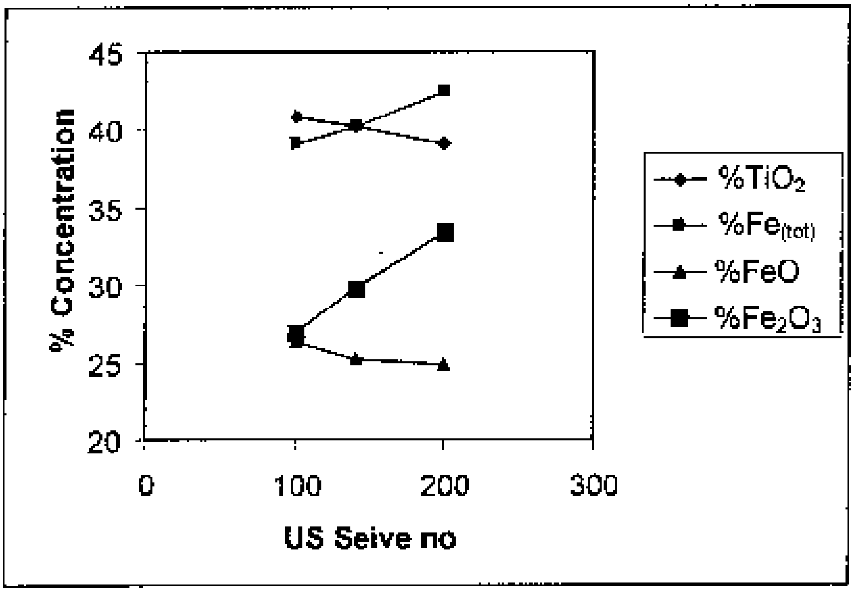


Fig. 4.4 Percentage concentration of different composition in the ilmenite as a function of different size fraction (Before reduction)

4.2.5.2 Sphericity of different size (sieve) fractions

In the present study, the shape characteristics of ilmenite particles have been expressed in the term of sphericity. Sphericity means that the particle has the shape of sphere and hence the lowest surface area to volume ratio. Particles with lowest sphericity will be elongated in shape and hence have larger surface area.

Sphericity of at least forty grams of each size fractions was measured and the average value was taken as the sphericity of that particular fraction and the data are tabulated in the Table4.3

Table 4.3 Sphericity of different particle ilmenite of different size fraction

US Sieve No	Sphericity of Inani
100	0.858
140	0.861
200	0.871

The sphericity of three fractions in the Inani sample is found to be in a narrow range, 0.858-0.871. Sphericity of Mohaskhali ilmenite[46] lies in narrow range 0.773-0.845, Teknaf ilmenite [48] lies in 0 822-0 843 Inani sample lies in 0.858-0.71. From the sphericity value it was found that finer size fractions are found to have a higher sphericity while the coarser one has the lower value of sphericity. This is possibly linked with the finer fractions may have longer history of weathering, erosion etc.

4.2.5.3 X-ray diffraction analysis of different size reaction

X-ray diffraction of different size fractions of ilmenite are shown in the Fig. 4.5. A large number of diffraction lines were observed in the samples of different size fractionated ilmenite. Moreover some of the more intense diffraction lines of the different phases expected to be present may overlap. From the figure it is evident that ilmenite is the main phase in all the size fractions. Diffraction lines characteristic of few other compounds including rutile, pseudorutile and hematite also been reported [13]. The presence of hematite in ilmenite-hematite solid solution can shift the ilmenite peak to the right and the observation of such a shift in relation to the diffraction data in present case suggest that some hematite also exist in solution in ilmenite.

4.2.4 Magnetic fraction of as received ilmenite

Magnetic fractionation was carried out using an isodynamic separator. Table 4.4 shows the relative amounts (wt percent) of the different magnetic fractions It can be seen that about 90% of Inani ilmenite belong the fraction separated by a current of 0.10-0.30 amperes The amount in the other fractions was not of sufficient quantity for further investigations. Further investigations were therefore confined to the major magnetic fractions only. Specific gravity of different magnetic fraction of ilmenite was determined using specific gravity measurement bottle and water as a media. It shows that bulk of this has specific gravity range 4.78-4 13

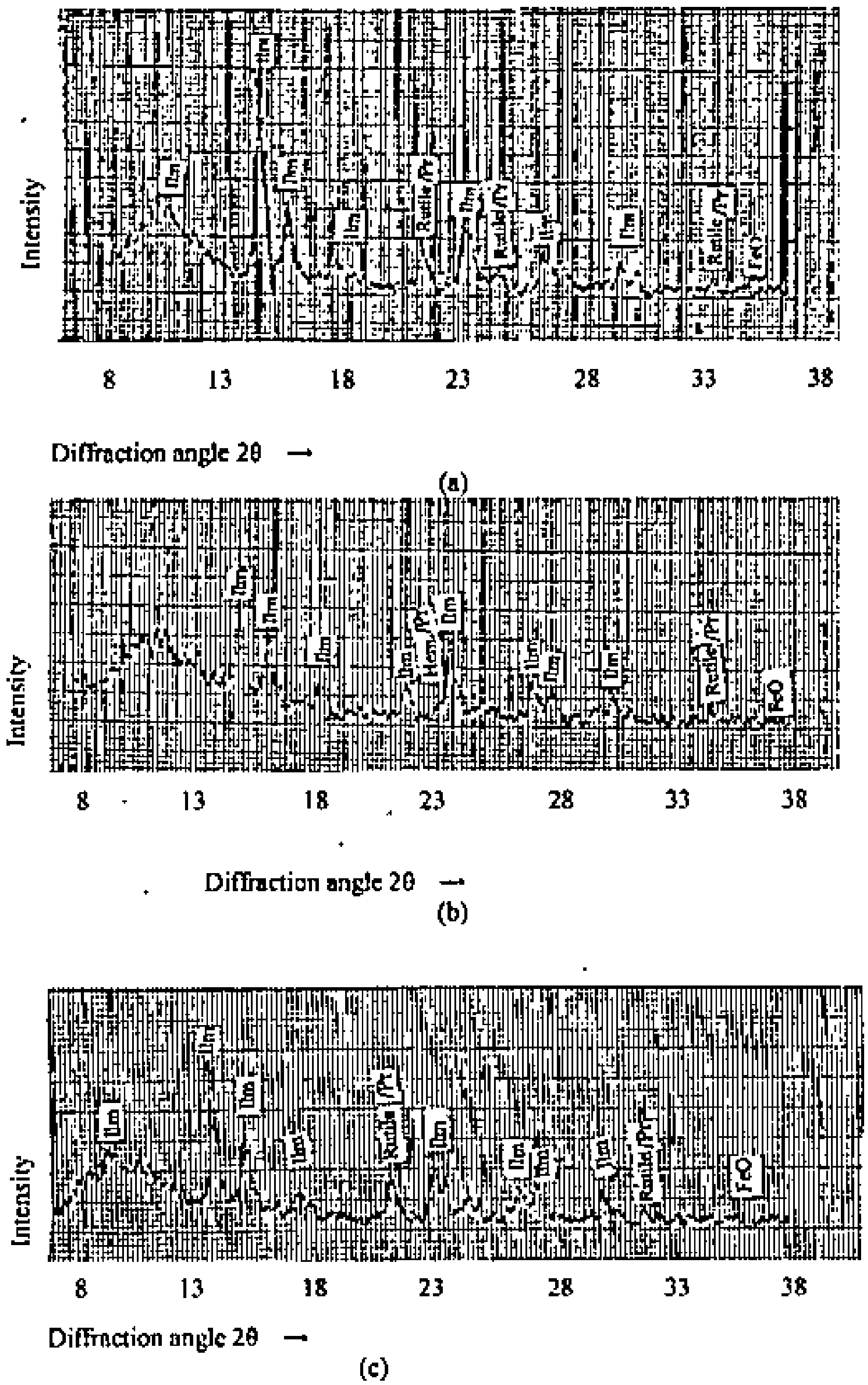


Fig 4.5 X-ray diffraction patterns of different size fractionated ilmenite

(a) Fraction retained on US sieve No.100

(b) Fraction retained on US sieve No.140

(c) Fraction retained on US sieve No. 200

Table 4.4 Specific gravity of different magnetic fractionated Ilmenite

Current of fraction (Amp)	Percentage (Inani)	Specific Gravity (Inani)
0 10	10.70	4.78
0 15	22.24	4.58
0.20	34 70	4.50
0.25	16 22	4.43
0.30	6 12	4.13

4.2.4.1 Chemical analysis of the different magnetic fractions

The magnetic fractions separated at different currents were analyzed chemically Fig 4.5 shows the composition of different magnetic fractions. It is evident from the analysis that with increasing current of separation the content of Fe_2O_3 and FeO decreases. It also shows that Inani ilmenite contain higher amount of ferrous oxide than ferric oxide. TiO_2 content was also found to decrease with increasing current of separation.

4.2.4.2 X-ray diffraction analysis of the magnetic fractions

The X-ray diffraction patterns of different magnetic fractions is shown in Fig 4.5 .There are many diffraction lines in the pattern, the most prominent being those of ilmenite. Diffraction lines characteristics of a few other compounds including rutile, pseudorutile, ferrous oxide and hematite can also be detected. The pattern analysis was strictly confined to qualitative analysis Slight shifts of the diffraction lines were also noted This may be explained as the placer deposits are not the chemically standard substance, it is a heterogeneous compound, as well as some impurities are present, which may affect the lattice parameter value.

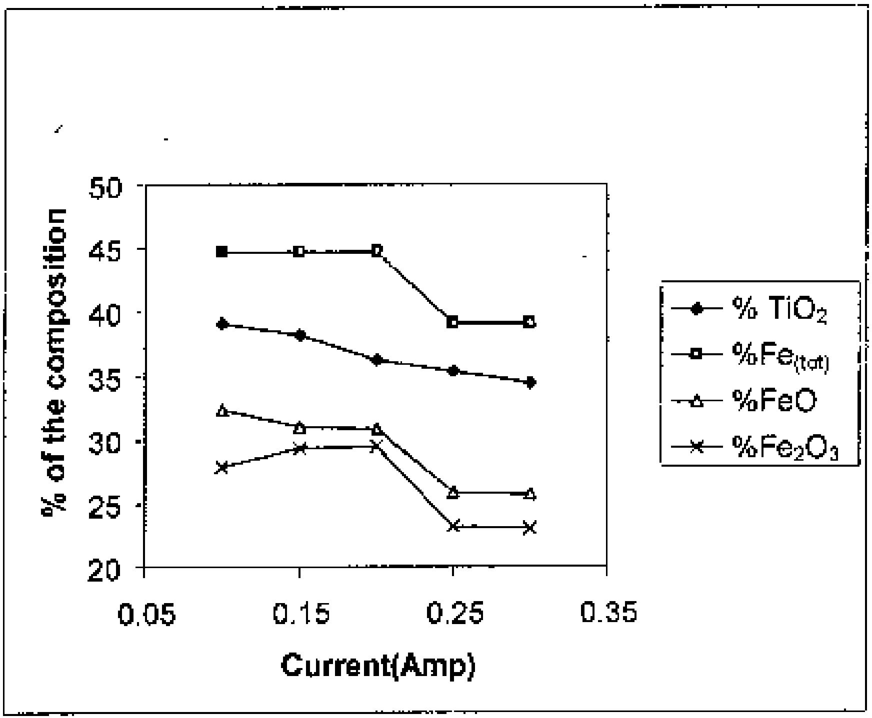


Fig 4.6 Distribution of composition of different magnetic fractioned ilmenite

4.2.4.3 Thermo gravimetric analysis of the different magnetic fractions

Thermogravimetric analysis experiment has been carried out for different magnetic fractions (0 10-0.30 amp) to observe any changes in weight. During heating inert atmosphere was maintained by the supply of nitrogen TGA thermograme in the Fig.4.8 -4.13 showed that the weight loss occurs for all the fractions after certain temperature. The weight lose was due to the presence of bound water.

Under investigations the five magnetic fractionate samples are 0.10, 0.15, 0.20, 0 25 and 0.30 amp. Having FeO content of 32.36, 31.07, 30.89, 25 83, 25.71% respectively. Fig.4.8 to Fig 4.10 shows that, initially wt loss occurs but after certain temperature an effective wt gains have been noticed.

This could be due to the oxidation of substantial amount of FeO present in those samples. The change in weight gain/loss in different magnetic fractions is shown in Table 4.5

A number of researchers [48-49] studied the alteration of Indian ilmenite of Chavara, Orissa deposits. During their study, they identified the weight loss at a temperature around 600^0C. This decrease in weight indicates the presence of bound water. Naturally bound water(H_3O^+)increase as the degree of alteration increases on the other hand pseudorutile structure actually contain hydroxyl ions ($FeOOH-TiO_2$). Ramakrishnan et al [49] found that

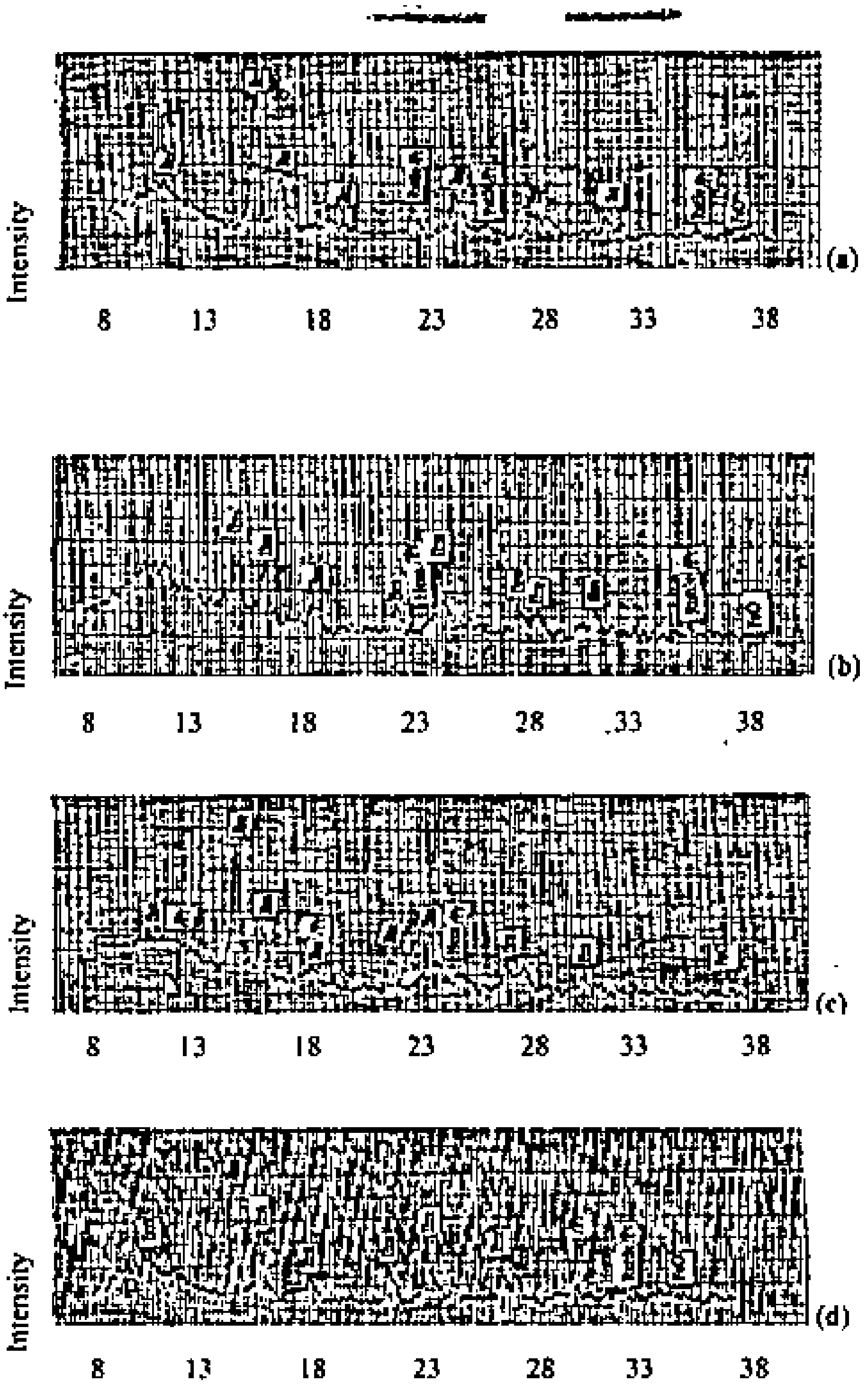


Fig 4.7 X-ray diffraction patterns of different magnetic fractionated ilmenite
(a) Fraction retain at 0.10 Amp (b) Fraction retain at 0.15 Amp
(c) Fraction retain at 0.20 Amp (d) Fraction retain at 0.25 Amp

the release of hygroscopic free water (50^{0}C) and structurally bound water (300^{0}C) cause loss in weight. They also found that an effective wt gain has been noticed in two samples (1.08% and 1.49%) due to the presence of substantial amount of FeO, which could oxidized at high temperature more than 800^{0}C It is generally recognized that in natural deposits ilmenite undergoes alteration due to weathering. The alteration is a complex process, but it can be summarized by two major, sequential reactions [50].

Stage (1) · $3Fe^{2+}TiO_3 + 2H^+ + 1/2\ O_2 \rightarrow Fe^{3+}Ti_3O_9 + 2\ Fe^{2+} + H_2O$ (1)

Stage (2) . $Fe^{3+}Ti_3O_9 + 2H^- \rightarrow 3TiO_2 + Fe^{2+} + 2\ H_2O + 1/2\ O_2$ (2)

In stage (1) ilmenite is converted into pseudorutile by the loss of one third of the total iron and oxidation of the remaining iron to the ferric state. In stage (2) removal of the remaining iron and loss of some oxygen take place to yield rutile. The extent of alteration of ilmenite depends on the world is quite varied - those of Zululand (South Africa), Orissa (India) and Brazil being altered relatively little but , those of Australia and Florida (USA) showing extensive alteration.[36]. A partial altered deposit shows the coexistence of different phase's i.e ilmenite, hematite, rutile and pseudiorutile. But complete alteration will lead to predomionantly rutile phase. X-ray diffraction pattern of Inani ilmenite showed the co-existence of different phases and the thermogravimetric analysis of this present study showed weight loss. It is concluded that the Inani ilmenite is in a partial altered state but not hydrated enough.

On the other hand weight gain implies that the presence of substantial amounts of Fe^{2+}which may be due to some extent of oxidation of FeO during TGA. So it is assumed that TGA atmosphere was not 100% inert Thus any possible compensation of the loss in weight due t o the removal of any combined water by the weight gain due to oxidation can be ruled out. This implies that significant quantity of bound water (H_2O) was not present in the gains of Ilmenite.

Table · 4.5 TGA reports for magnetic fractions at different current

points	0.10 Amp		0.15 Amp		0 20 Amp		0.25 Amp		0.30 Amp	
	^{0}C	Wt%	^{0}C	Wt%	^{0}C	Wt%	^{0}C	Wt%	^{0}C	Wt%
1	39	100	44	100	44	100	43	99.9	44	100
2	496	100.4	100	100	487	98.7	556	98.1	219	100.1
3	781	100.9	642	99.4	799	98.9	782	99.8	650	102.4
4	1001	95.1	833	99.8	1019	79.9	986	84.0	987	102.5

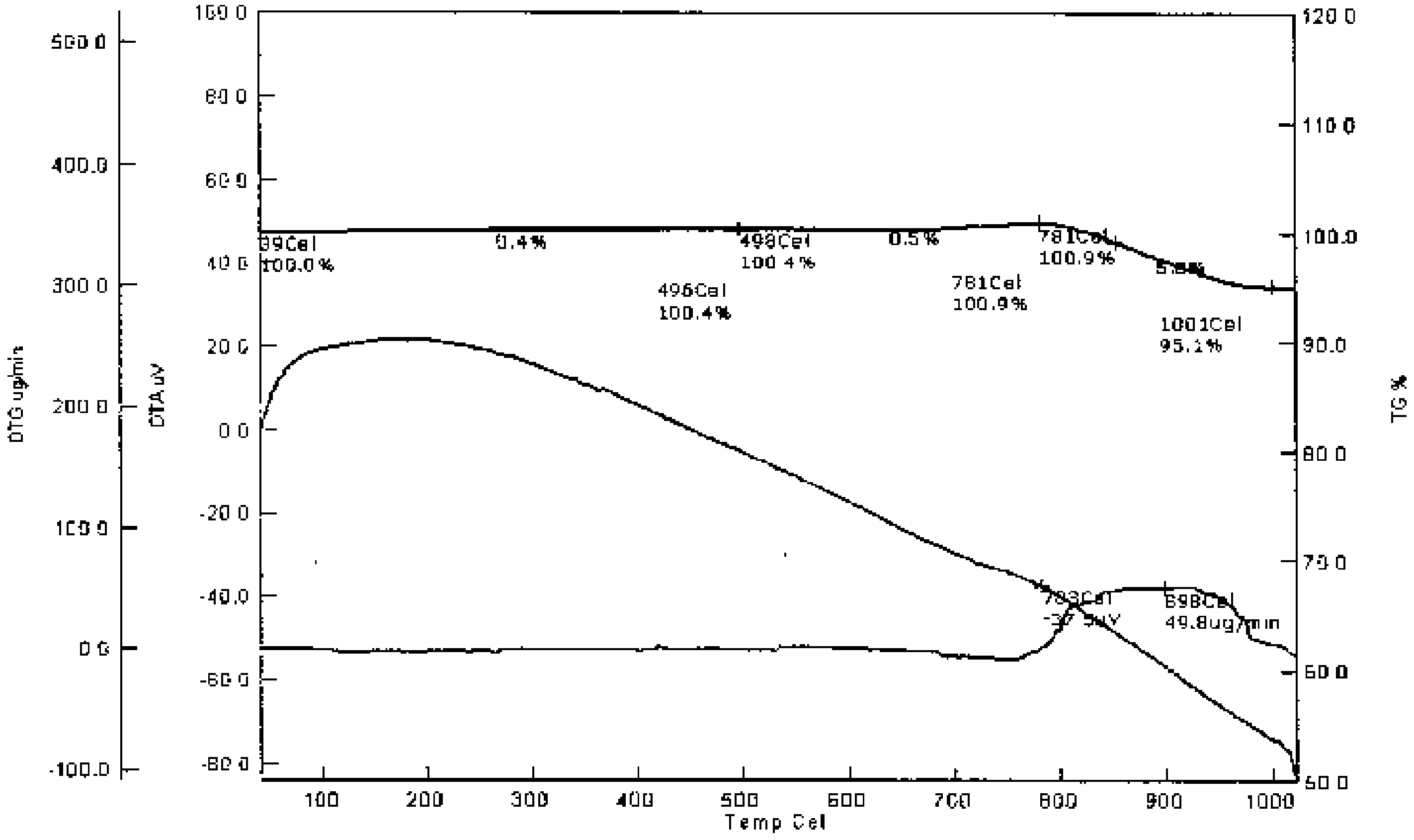


Fig 4.8 TGA graph of as received ilmenite sample

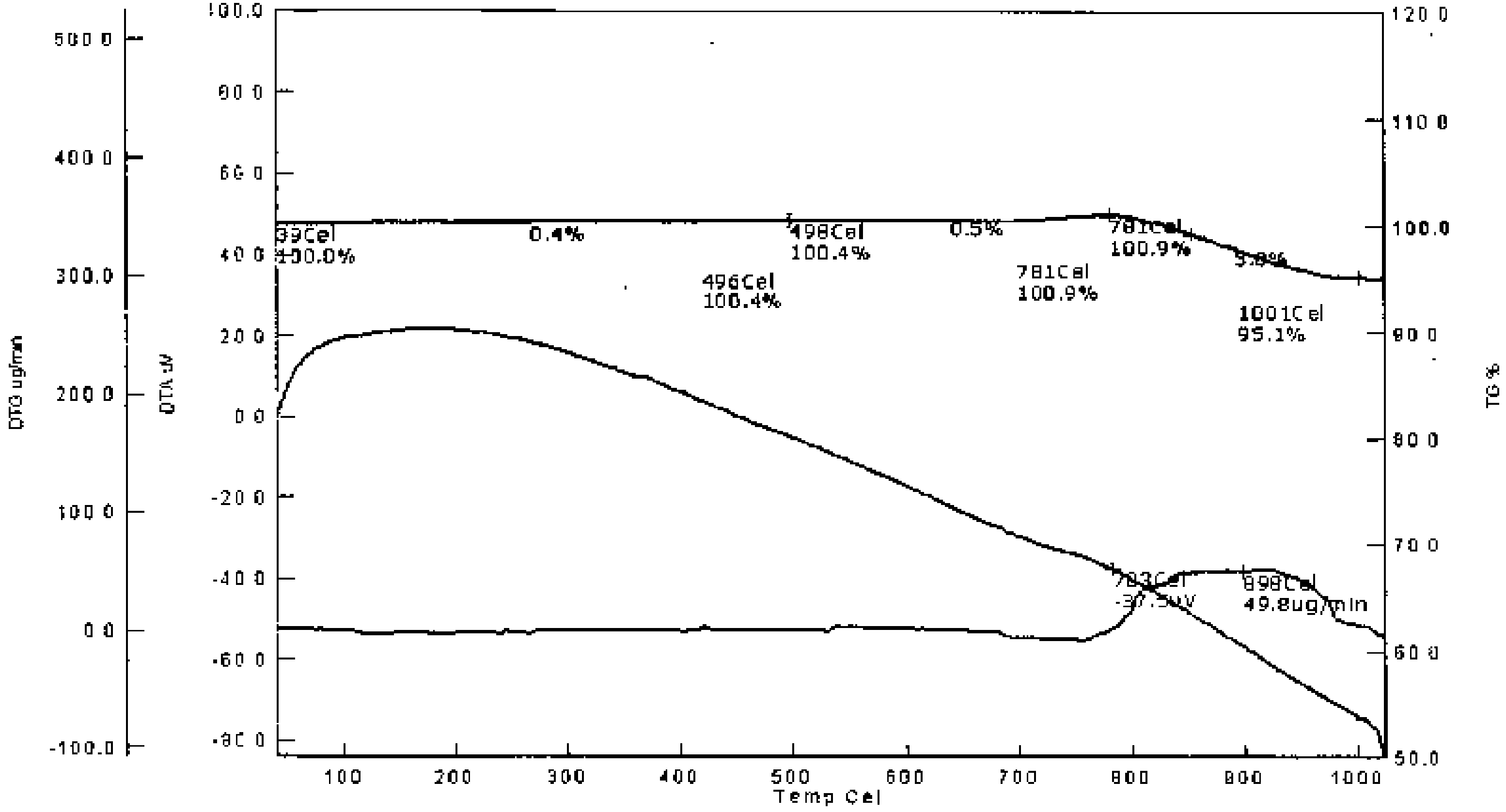


Fig 4.9 TGA graph of ilmenite sample fractionated at 0 10Amp

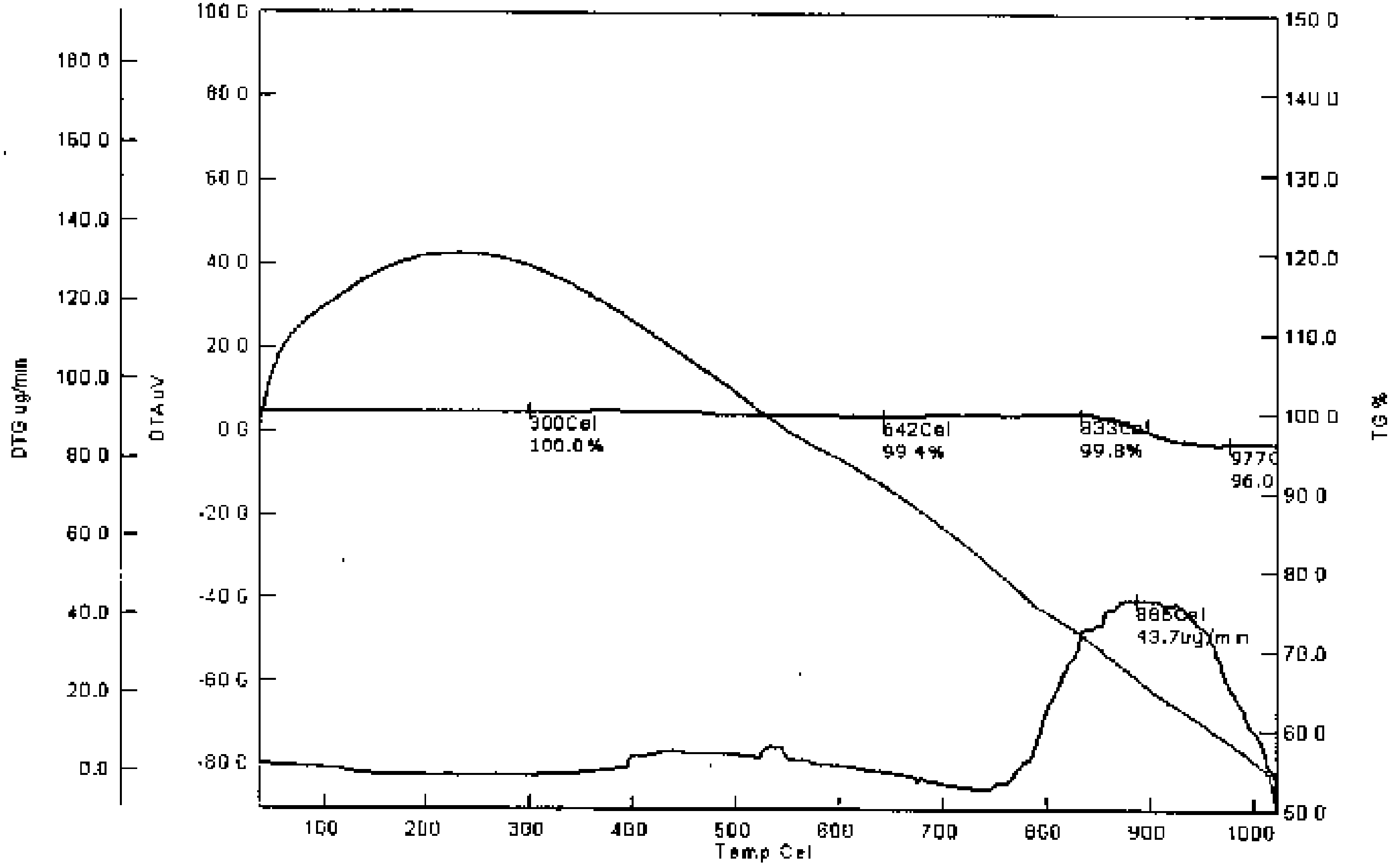


Fig 4.10 TGA graph of ilmenite sample fractionated at 0.15Amp

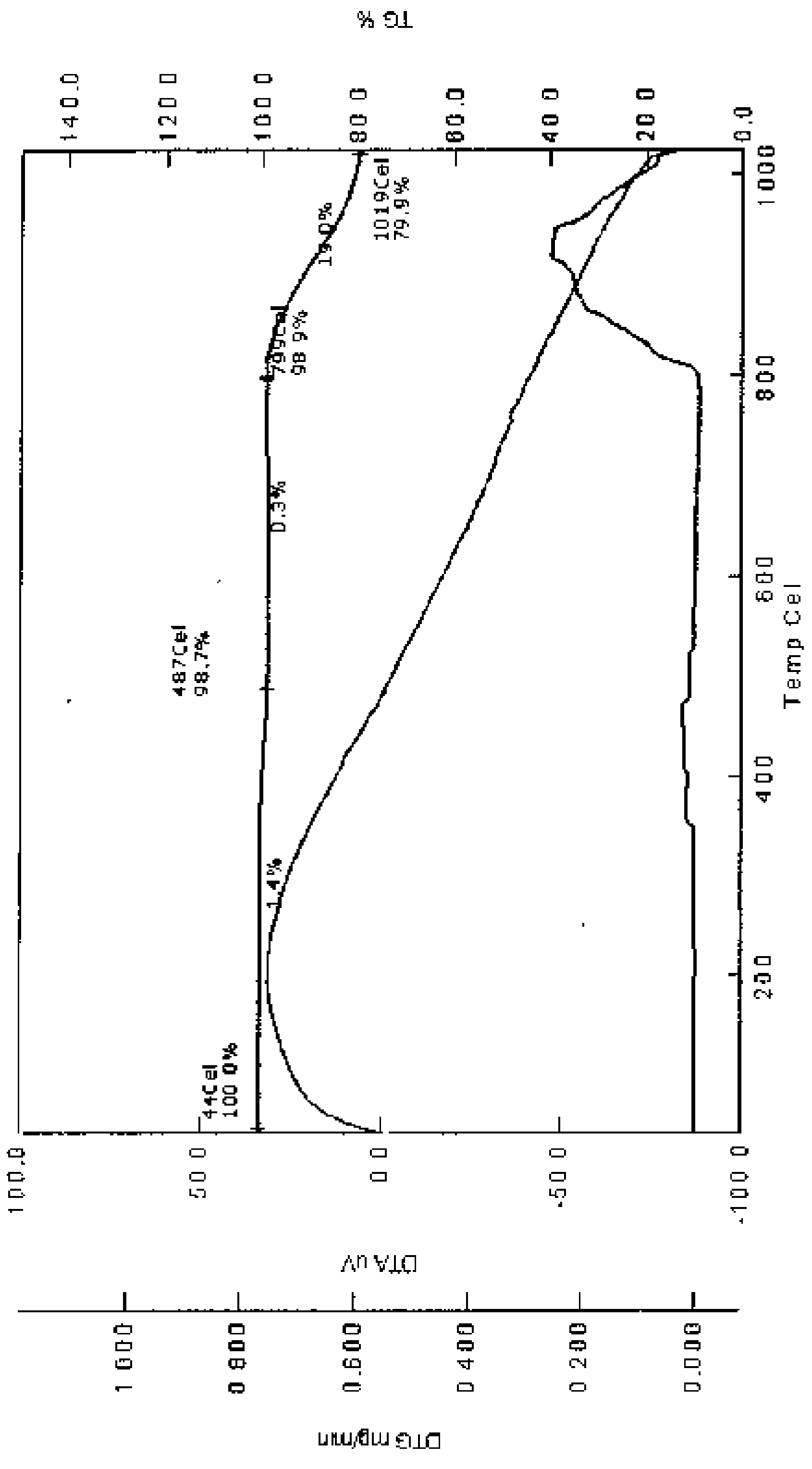


Fig 4.11 TGA graph ilmenite sample fractionated at 0.20 Amp

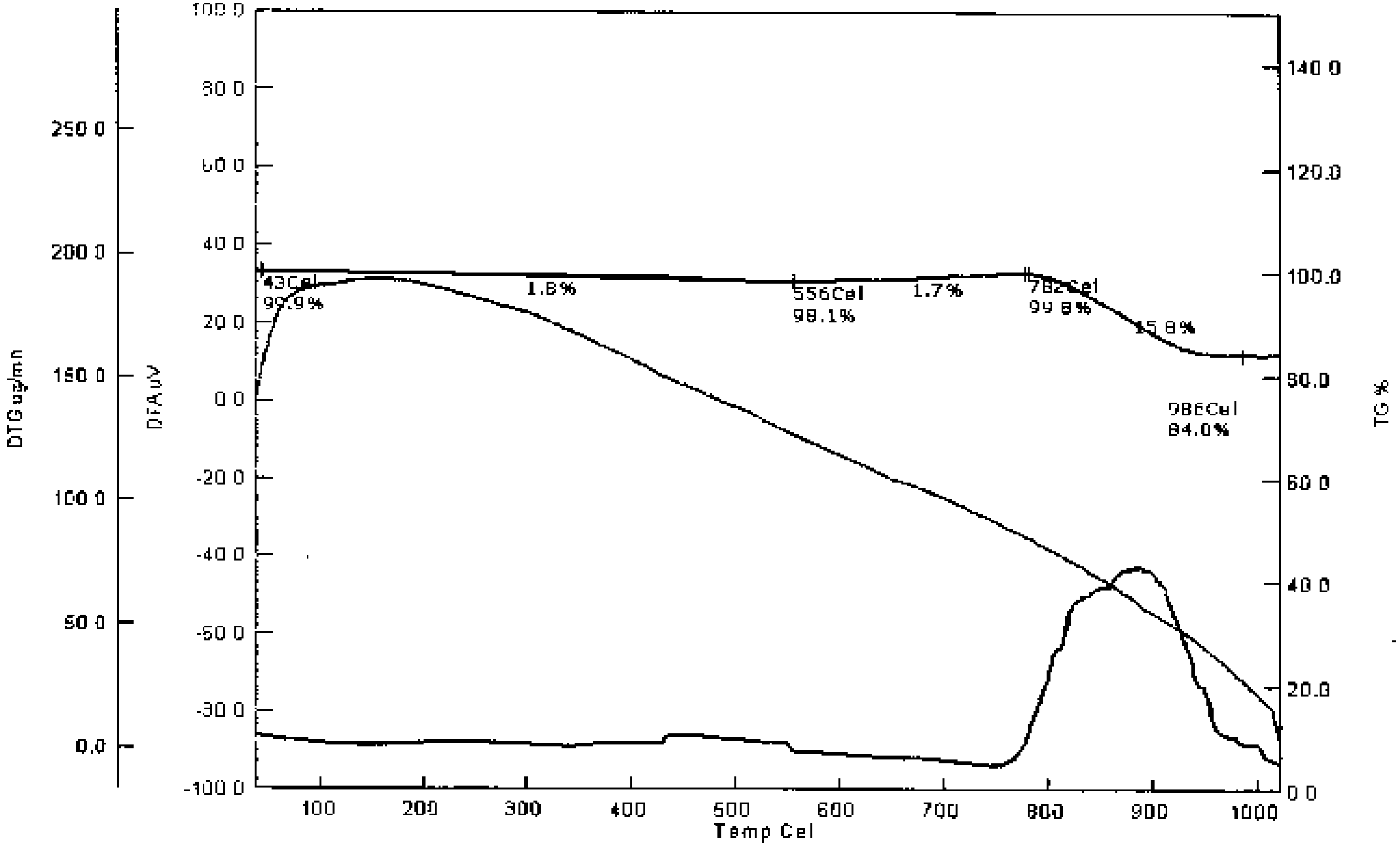


Fig 4.12 TGA graph of ilmenite sample fractionated at 0.25Amp

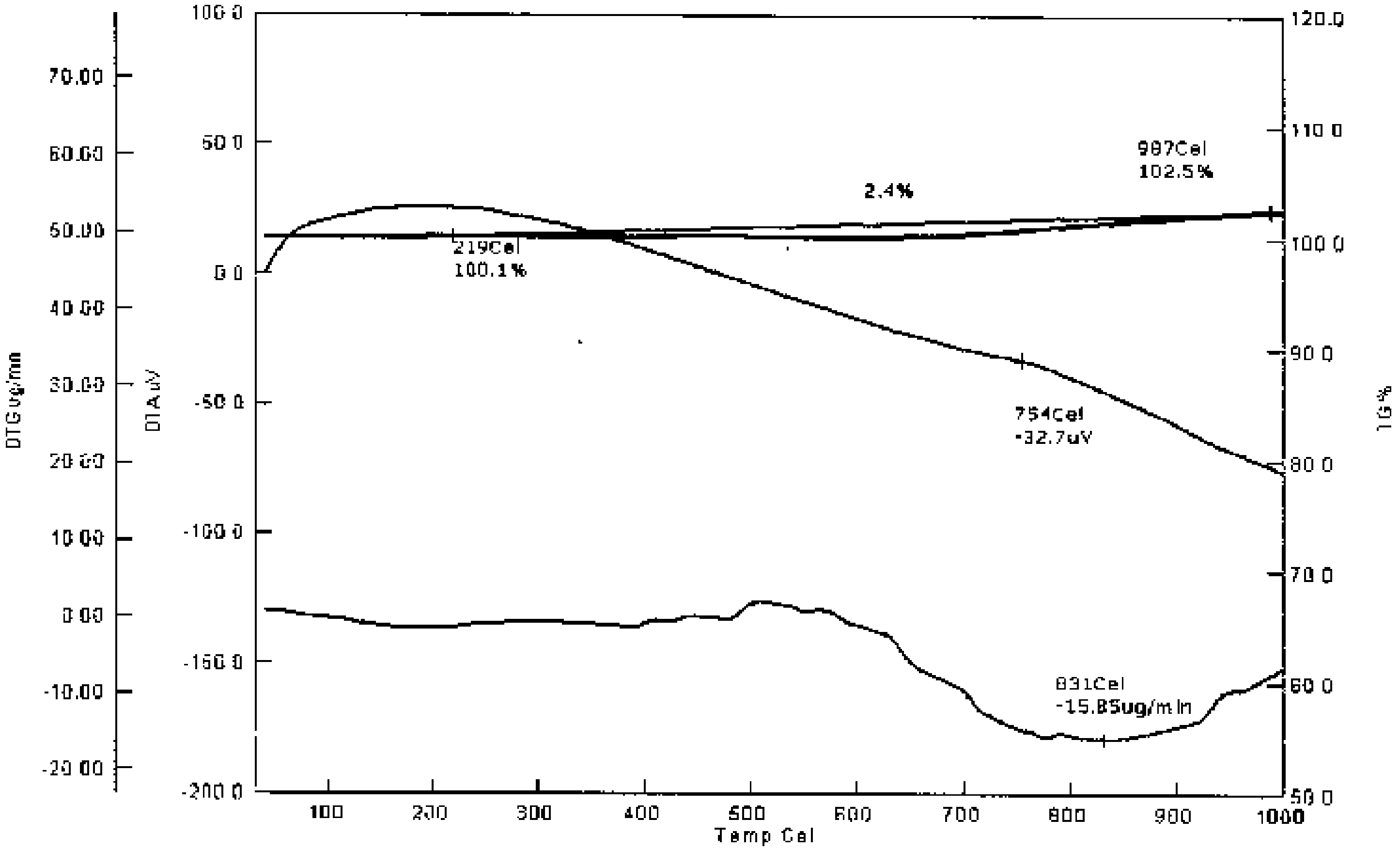


Fig 4.13 TGA graph of ilmenite sample fractionated at 0.30Amp

4.2.4.4 Optical polar microscopic analysis

In optical polar microscope, different magnetic fraction samples were observed. Photograph of different magnetic fractionation ilmenite were recorded. There was difference in pictures. In Inani sample, some grains were observed and seemed that it is in the process of alteration. Some grains were fully altered to Leucoxene. With increasing the separating current the amount of alteration was decreasing. Lower magnetic fractionation ilmenite was emitting light more than higher fractionation grains Some typical picture are given below.

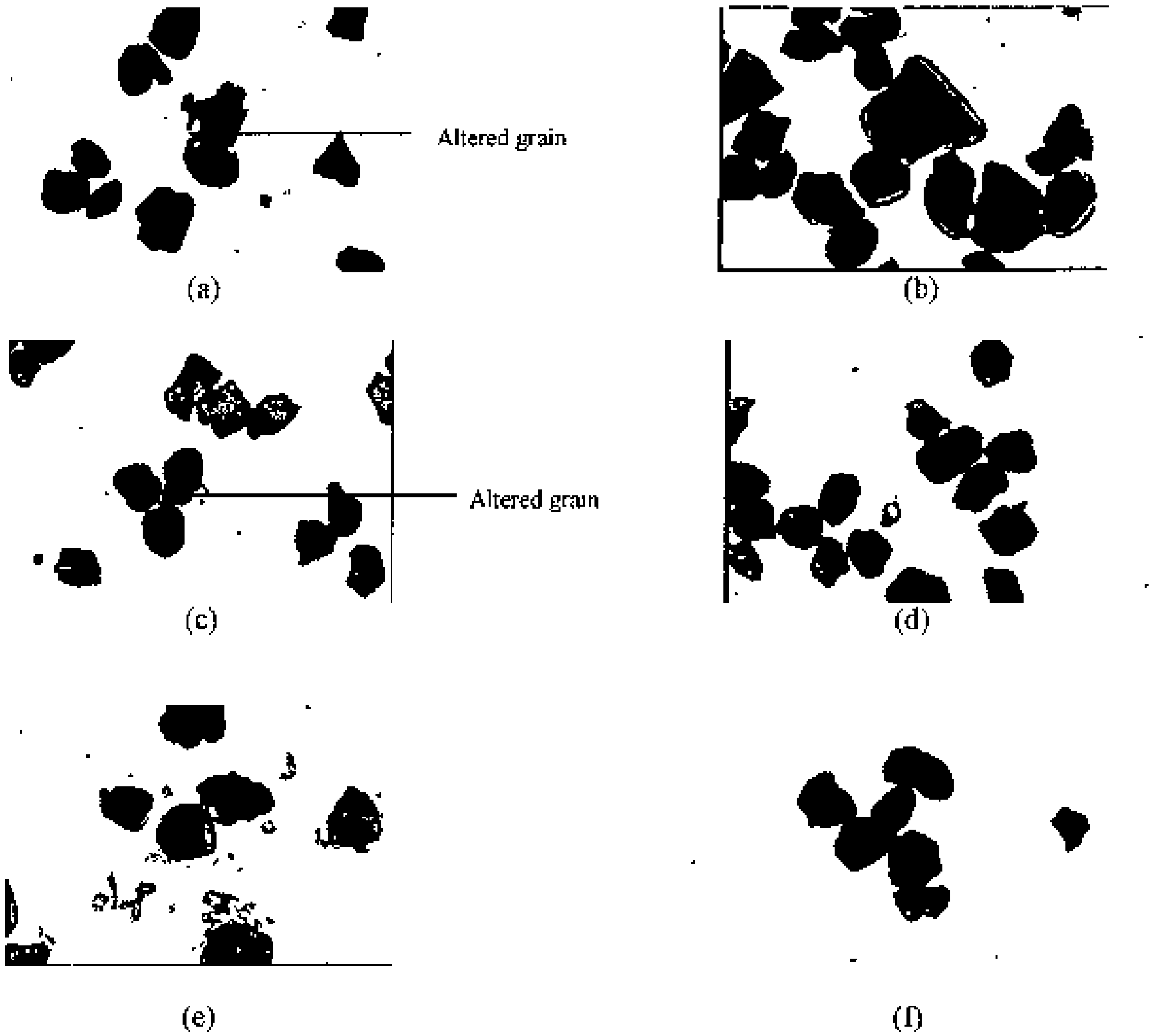


Fig 4.14 Optical polar microscopic picture for different magnetic fractions of ilmenite
(a)(b) Fractionation at 0.10 Amp
(c) Fractionation at 0 15 Amp (d) Fractionation at 0.20 Amp
(e) Fractionation at 0.25 Amp (f) Fractionation at 0.30 Amp

Fractionated ilmenite samples were observed under optical polar microscope and found that grains are altered. In magnetic fraction 0.10 Amp some of the grains are altered into rutile The amount of leucoxene was observed more in 0.15 Amp magnetic fraction grains

Leucoxene was also observed in all other magnetic fractions. From magnetic fractions it can be concluded that alteration process is continuing but not completed

Table 4.6 Percentage of alteration of different magnetic fraction

Inani ilmenite	% of altered grains
0.10 Amp Magnetic fraction	4.1%
0.15 Amp Magnetic fraction	5.7%
0.20 Amp Magnetic fraction	5.0%
0.25 Amp Magnetic fraction	4.9%
0.30 Amp Magnetic fraction	4.1%

4.3 Oxidation of as received sample

4.3.1 Optimization of oxidation parameter

Oxidation of ilmenite was performed at 950^{0}C for 2 hrs. This was established by Momin [47]. The conversion of ferrous iron to ferric iron was determined by chemical analysis of oxidized samples.

Chemical analysis

The result of chemical analysis (Table 4.7) also showed that during oxidation, under the conditions investigated, all the ferrous iron present in the sample was not oxidized to ferric state. i.e. some ferrous iron was present in the oxidized sample (e.g. at 950^{0}C for 2 hrs ferrous iron was 0.335%).

Table. 4.7 Chemical analysis of ilmenite oxidized at 950^{0}C for 2 hrs

Materials	% of the materials present in the Inani ilmenite
Fe^{++} Iron	0.335
FeO	0.430
Fe^{+++} Iron	39.865
Fe_2O_3	56.995
Total Iron	40.200

A typical photograph of the oxidized sample is shown in Fig 4.15. It can be seen that the products covers the surface of solid ilmenite in the form of dense film.

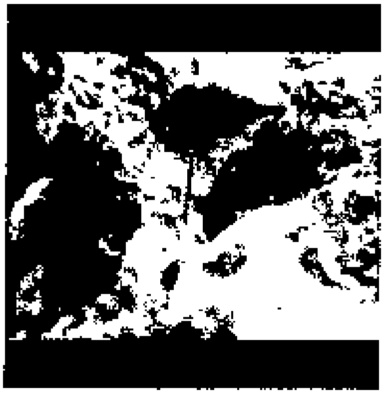
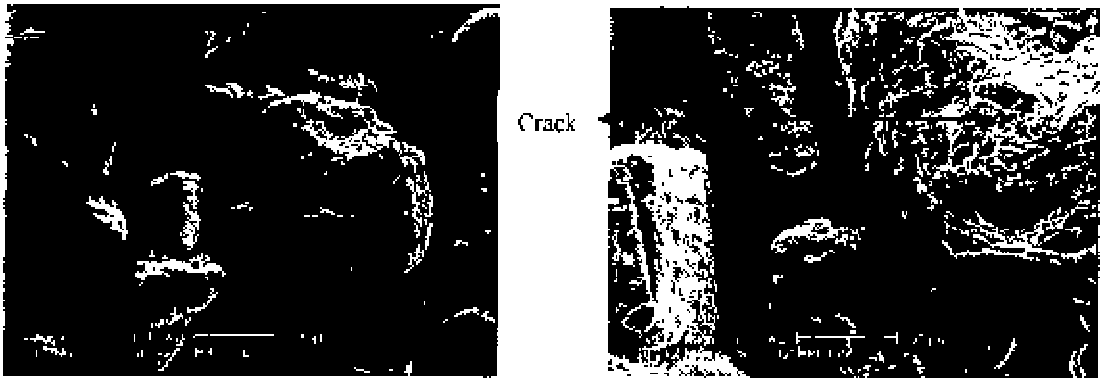


Fig. 4 15 Typical photography of Psuedobrokite [71].

4.3.2 SEM Analysis

Scanning electron micrographs were taken for oxidized sample in both 200 magnifications and 500 magnifications. The surface of the grain was not uniform. Some cracks were observed in the grain. This is may be due to the formation of different crystal structure. SEM photograph of oxidized sample shown in Fig 4.16.



(a) (b)

Fig. 4.16 (a) SEM of oxidized sample 200 magnification
(b) SEM of oxidized sample 500 magnification

4.3.3Optical Polar microscopic analysis

The sample of ilmenite was oxidized for two hour at 950^{0}C and was observed under optical polarized microscope. Oxidized particles were scattered on a slide with Canada balsom solution and was covered with another slide. Fig 4 17 shows that the structure of ilmenite oxidized at 950^{0}C, the grain size appears to be large. Reddish and transparent appearance was observed. In optical polar microscope, it was observed that the surface of grains have become transparent and light was transmitting through grain surface. Middle part of the grain has become brown and the surroundings were black. As a part of optical property of pseudobrookite, it should be optically biaxial positive. Inani oxidized sample was found to be optically biaxial positive. The color of pseudobrookite (Pb) is dark brownish to brown black color. Oxidized sample was also found to be dark brownish to brown black color. Light was passing through it.

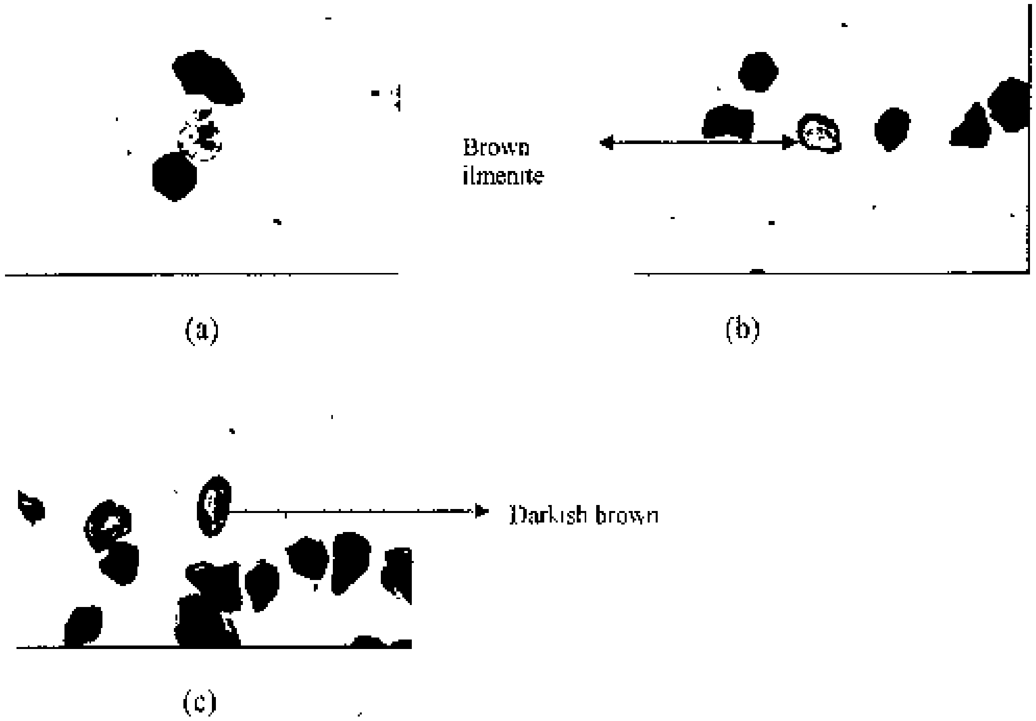


Fig. 4.17 (a)Optical photograph of Oxidized ilmenite
(b) Brown ilmenite (c) Darkish brown ilmenite

4.3.4 Optical Metallography Study

The microstructure of as received ilmenite and oxidized ilmenite was studied under an optical microscope. Particles of oxidized ilmenite were mounted in cold-setting resin and the samples were prepared by using standard techniques. Microstructure of oxidized ilmenite is shown in Fig 4.18.

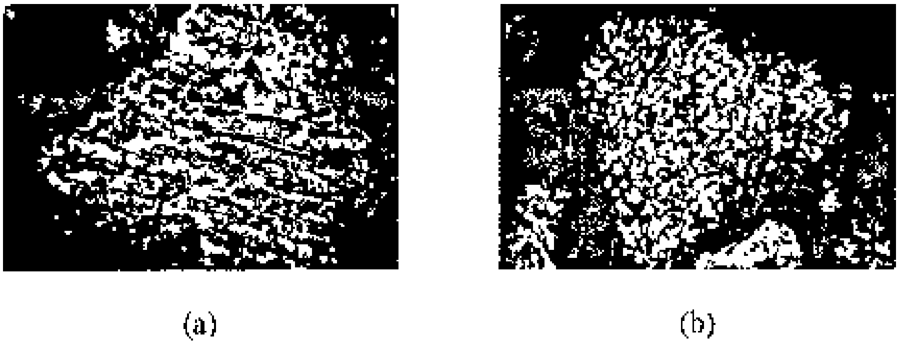


Fig. 4.18 (a) and (b) Optical Micrograph of oxidized sample

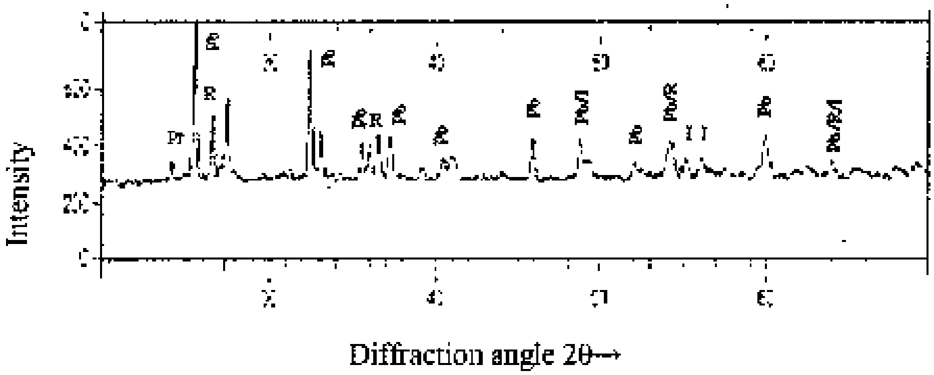
4.3.5 X-ray diffraction Study

X-ray diffraction pattern of oxidized Inani ilmenite is given in the Fig 4.19 Fig 4 19 shows that the FeO phases have been diminishes and a new phase of pseudobrookite (Pb) have been appeared. Oxidation converts particles of ilmenite to pseudobrookite with disseminated particles of rutile. Diffraction lines of ilmenite coincide with the diffraction lines of the new phases at 25.64, 32.59, 37.42, 41.21. 46.01,48.88 angle [50].The formation of pseudobrookite can be expressed by the reaction .

$$3FeTiO_3 + 3/2O_2 \longrightarrow Fe_2Ti_3O_9 + \tfrac{1}{2} Fe_2O_3$$

By heating pseudorutile above 850^0C pseudobrookite is formed

$$Fe_2Ti_3O_9 \longrightarrow Fe_2TiO_5 + 2TiO_2$$



Pb = Pseudobrookite

Fig 4 19 X-ray diffraction pattern of Inani ilmenite oxidized at 950^0C

4.4 Reduction of as received sample

Reduction of iron oxide in ilmenite to metallic iron was carried out by using charcoal as a reductant. From the Ellingham diagram it is apparent that the stability of titanium-di-oxide is much higher than that of oxide of iron and cannot be reduced by carbon at a temp range of 950^0C-1100^0C. Thus when ilmenite is heated by mixing with charcoal at a temperature range of 950^0C to 1100^0C. iron oxide is reduced to metallic state and the titanium oxide remain unchanged. Thus iron oxide is reduced to metallic form without changing the titanium oxide. Since the both oxides of iron and titanium are more stable than metallic iron, so metallic iron can easily be dissolved into hydrochloric acid and therefore, the titanium content of the ilmenite can be increased.

To examine the feasibility of reduction of Inani ilmenite, reduction conditions were selected with a maximum temperature of 1050^{0}C for 4 hours in presence of excess charcoal (reductant). It was found from literature this condition is sufficient for the reduction of ilmenite.

Optimization of various parameters that affects and controls the reduction reaction of ilmenite was determined [47] Ilmenite to coke ratio was established 1:1

4.4.1 Optimization of time and temperature

For optimization of temperature reduction experiments were carried out for time period of 0.5-4 hrs in the temperature interval 900-1050^{0}C. Ilmenite and charcoal 1:1 (w/w) ratio was heated 900^{0}C for each of the time period 0.5 hr,1.hr, 2hr, 3hr, 4 hrs. The reduced mass was cooled and then analyzed. Another experiment with fresh charcoal and ilmenite was carried out at 950^{0}C for the above time periods. Each experiment was carried out with fresh raw materials and was not a continuation from the previous one.

Fig. 4 20 and Fig 4.21. give a plot of percentage of metallic iron and percentage of reduction as a function of time It is clear from the figures that for any specified of time, the percentage of reduction and percentage of metallic iron increased with an increase in temperature. During reduction between 900-1050^{0}C temperatures, metallic iron content was less for 3 hours than after reduction for 4 hours. Up to the about 1050^{0}C extent of reduction increases sharply. After that no considerable effect of temperature on reduction was observed, experimented by Momin. At about 1050^{0}C the reduction got stabilized, after that the increase in metallic iron content is nominal. At 1100^{0}C the extent of reduction curve merges with the curve of at 1050^{0}C. the reduction got stabilized, after that the increase in metallic iron content is nominal. Merk and Pickles [51] investigated reduction of ilmenite with CO and noted that above 1000^{0}C, the degree of reduction remains essentially constant due to the formation of metallic shell of iron that segregate to ilmenite grain boundaries and retards CO diffusion.

The figures show that optimum temperatures require for the reduction of ilmenite was around 1050^{0}C, after that the percentage of reduction increases with time is nominal. It also showed that after any specified time the % of reduction was more or less same.

For reduction 9gm of ilmenite and 9gm of charcoal of mesh size +30 was taken. A bed of charcoal was first charged in vertical stainless steel tube. Small amount of ilmenite and charcoal were then charged as alternate layer. The top layer was made of charcoal The tube had a lid to minimize entrance of air in it. After increasing the temperature, required time, the tube was cooled to room temperature: the reduced ilmenite was separated by using hand a magnet. The results of chemical analysis are given in Table 4 8

Table 4.8 Chemical analysis of as received reduced Ilmenite (reduction at 1050^{0}C)

components	% in Inani ilmenite
TiO_2	42.05
Fe_{tot}	44.67
Fe_{Met}	39.31
%Degree of reduction	88.00

Ilmenite, the starting material, contains no metallic iron, while ferrous and ferric iron were 25.48% and 32.89% respectively. The Table no 4.6 shows that ilmenite had undergone reduction during heating with the formation 39.31% metallic iron and the degree of reduction is 88%. The extent or degree of reduction of an oxide can be defined as the function of oxygen removed during the reduction processes and is given by

$$DOR= \frac{O_2^{i} - O_2^{r}}{O_2^{i}} \times 100$$

Where, DOR =degree of reduction ,O_2^{i}= Initial oxygen content of the sample
O_2^{r}= Oxygen content of the reduced sample

Degree of reduction is based on different forms on reduction This equation has been used for iron ores [54] In the case of ilmenite, oxides of both iron and titanium are present. Although TiO_2 is more stable than oxides of iron, it possible that some TiO_2 is reduced to lower oxides However earlier study [55] on Bangladesh ilmenite has shown that for 4 hrs reduction at 1050^0C, TiO_2 is not reduced. In the present case it can thus be assumed that loss of oxygen of ilmenite sample during reduction was due to the reduction of iron oxide only. Using this argument the degree of reduction of iron oxide in the ilmenite sample can now be defined as

$$DOR_{Fe} = \frac{O_2^{i}Fe - O_2^{r}Fe}{O_2^{i}Fe} \times 100$$

Where DOR_{Fe} =degree of reduction

O_2^{i} Fe= Oxygen content of iron oxides in as received ilmenite

O_2^{r} Fe = Oxygen content of iron oxides in reduced ilmenite

While calculating O_2 Fe it was assumed that iron. other than in metallic form, is present in the reduced ilmenite as FeO only. This valid assumption supported by earlier study on Bangladesh ilmenite [56] A study on iron ore [57] has also shown that if the degree of reduction is more than 40%(which is true in the present case as will be seen earlier) , then no FeO is present before all higher oxides are reduced to metallic iron.

Ferric and ferrous oxide present in the ilmenite was reduced to metallic iron. The reduction reaction is $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$

It can be concluded that it was possible to reduce the ferrous and ferric iron present in ilmenite to metallic iron by using charcoal as a reducing agent.

The main overall reaction taking place in the reduction may be written as

$Fe_2O_3.TiO_2 + 3C \rightarrow 2Fe + TiO_2 + 3\ CO$ and,

$Fe_2O_3\ TiO_2 + 3CO \rightarrow 2Fe + TiO_2 + 3\ CO_2$

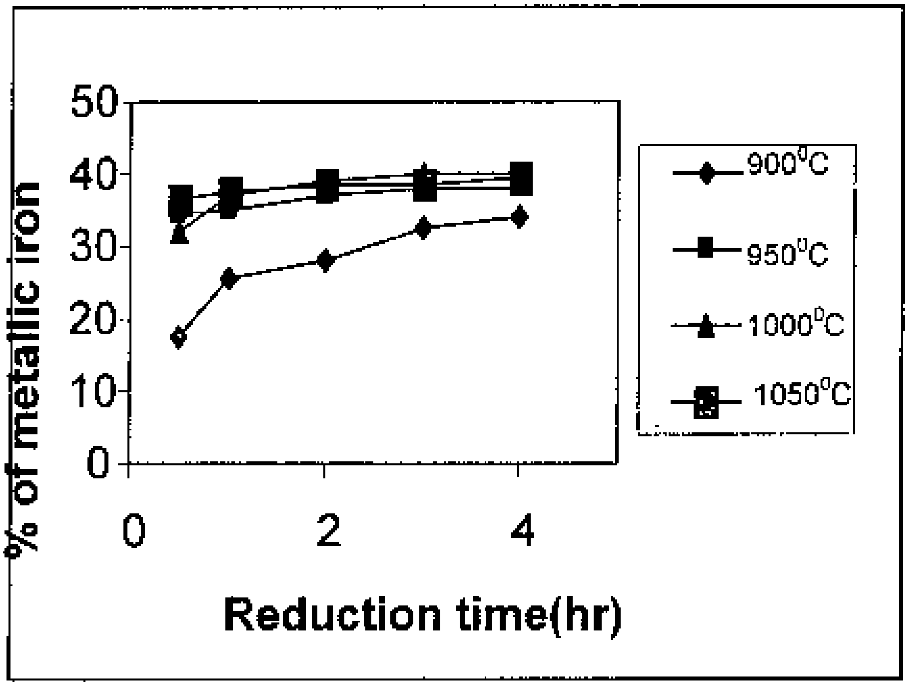


Fig. 4.20 Effects of time and temperature on the extent of reduction (% metallic iron) in the as received ilmenite

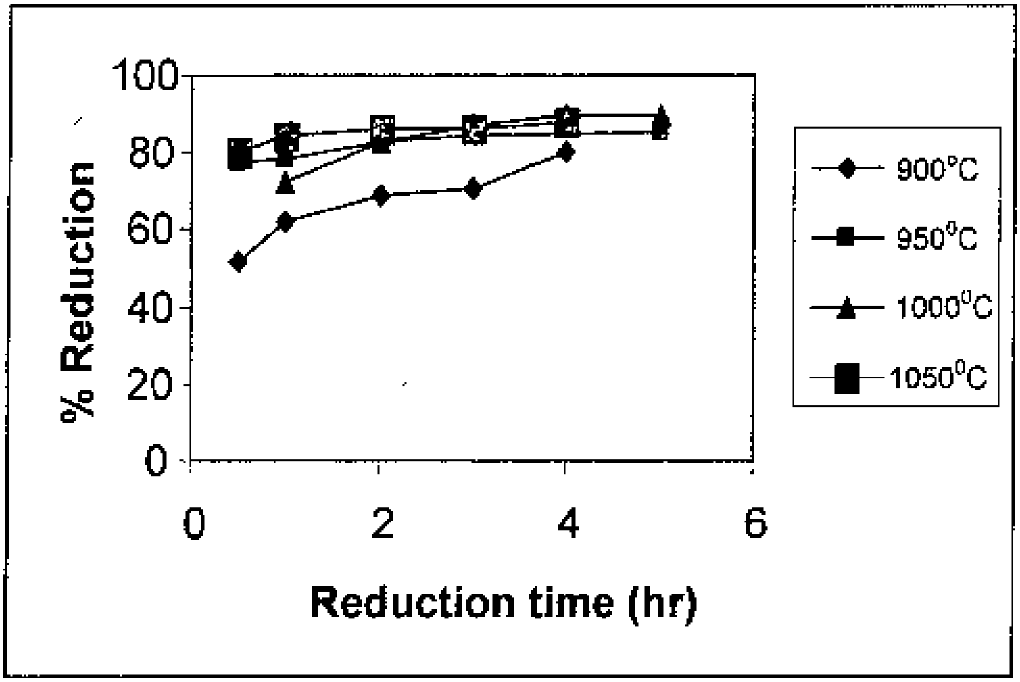
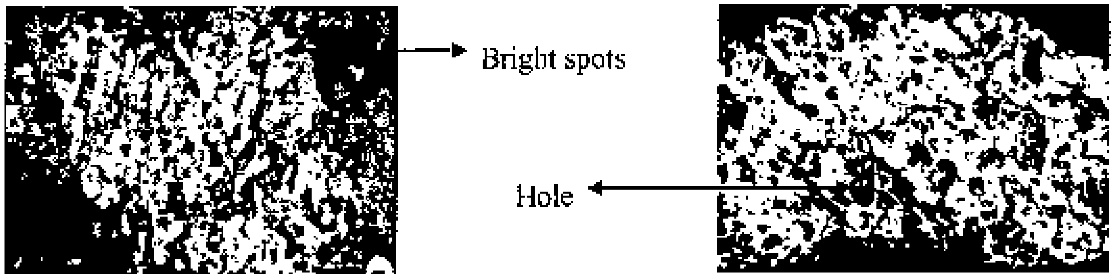


Fig. 4.21 Effects of time and temperature on the extent of reduction (% reduction) in the as received ilmenite

4.4.2Optical Metallography

The reduced ilmenite was observed under an optical microscope. The microstructures of the unreduced and reduced ilmenite are shown in the Fig 4 22. In Fig. 4.22 the internal structure of the polished particles are shown. The progress of the reduction can be observed in the microstructure. Dark grey and black area was seen in the particle. Small bright spots due to metallic iron were observed. The pores were found due to the removal of oxygen from the ferric oxide during reduction. Metallic iron spots were seen only few particles. In some of the reduced ilmenite grains, these globules started diffusion from the interior to the periphery and got concentrated there The particles have being more voids and pores due to reduction

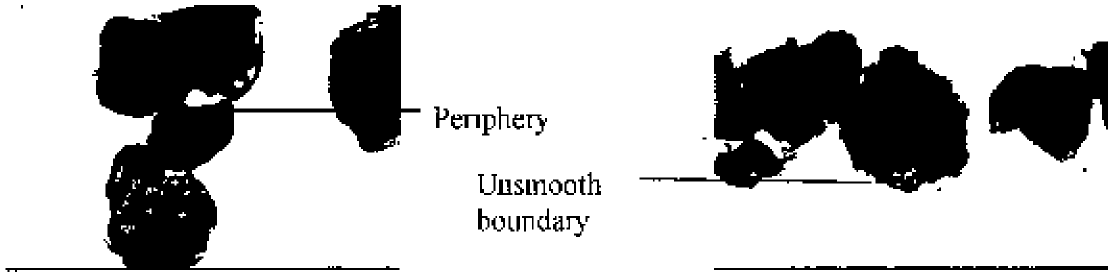


(a) (b)

Fig. 4.22 Microstructure of reduced ilmenite sample
(a)Reduced at 1050°C for 4hr (b) Reduced at 1050°C for 4hr

4.4.3Optical Polar Microscopic study

Reduced Inani ilmenite particle was observed under optical polar microscope. The optical polar micrograph of reduced ilmenite is shown in the Fig. 4.23 Grain surface of reduced ilmenite have become porous Porous surface was developed in the reduced ilmenite grain. Fracture of ilmenite is convecture shape. But shape of reduced ilmenite grain boundaries was not uniform. Due to reduction grains shapes have changed and it was not smooth. In the grain boundaries of reduced mass ilmenite grain tunnel was observed. It seemed that light was scattering from it. Periphery was observed in the reduced ilmeite.

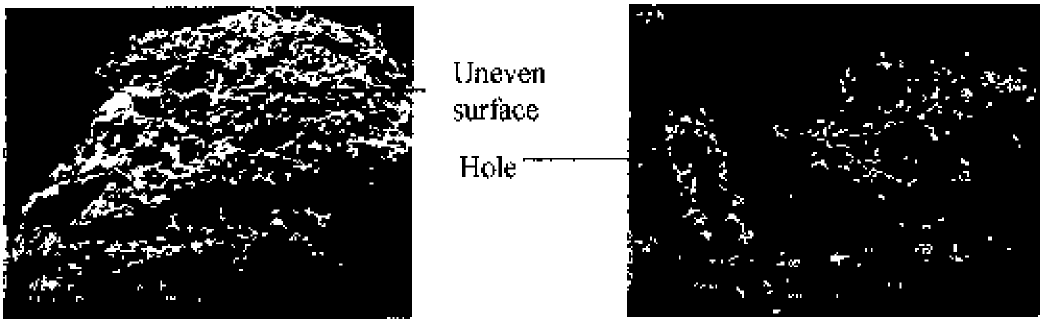


(a) (b)

Fig 4.23 Optical microscopic studies of reduced sample
(a) Reduced at 1050°C for 4h (Periphery was observed)
(b) Reduced at 1050°C for 4h (Surface boundary was not smooth)

4.4.4 Scanning Electron Microscopy (SEM) studies

The unreduced and the reduced sample were studied under SEM. This was done to observe the changes taking place on the surface of the particle during the reduction Results are shown in the Fig. 4.24 the unreduced ilmenite has no porous or microporous surface. After reduction ilmenite grains showed the formation of uneven surface. Large pores of few micron size with interconnection were observed in the reduced grain The pores were formed due to the removal of the ferric oxide during reduction.



(a) (b)

Fig 4.24 SEM studies of unreduced and reduced sample
(a)Reduced at 1050°C for 4h (Uneven surface was observed)
(b) Reduced at 1050°C for 4hr (Porosity was observed)

4.4.5 X-ray diffraction studies

X-ray diffraction analysis of reduced ilmenite was carried out. Typical x-ray diffraction pattern of ilmenite reduced at 1050°C is given in Fig, 4.25. Ilmenite was reduced with charcoal for that the proportion of the phase's changes and a new phase, metallic iron, appears. This change can be determined by x-ray diffraction pattern Ilmenite reduced at 1050°C showing that the ilmenite has changed to metallic iron. Ilmenite phases diminished with the increase of temperature Chemical analysis also showed the presence of maximum metallic iron present at this temperature.

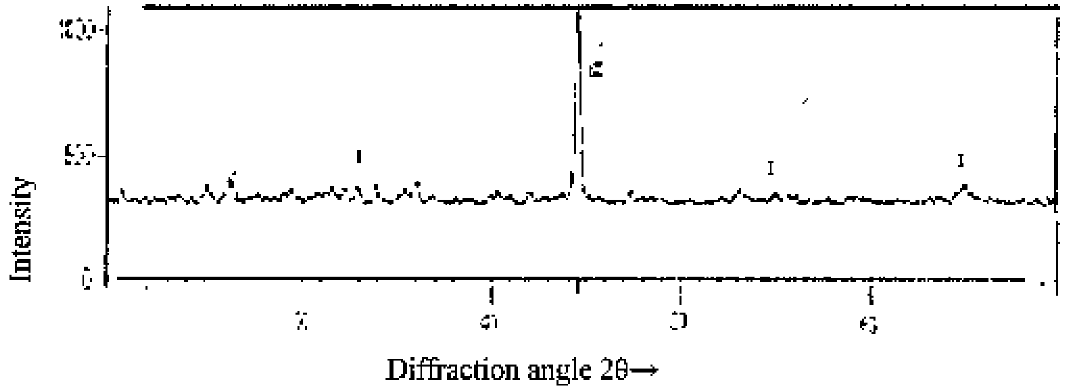


Fig. 4.25 X-ray diffraction pattern of Inani ilmenite reduced at 1050^0C

4.5 Reduction behavior study

Inani ilmenite was reduced to study the

(a) Effect of time and temperature on the extent of reduction of as received ilmenite.

(b) Effect of particle size on the extent of reduction

(c) Reduction behavior of different magnetic fractions

(d) Effect of prior oxidation on the extent of reduction behavior

4.5.1 Effect of time and temperature on the extent of reduction of as received ilmenite

The effect of time and temperature on the extent of reduction of ilmenite in the as received condition was studied. In all cases the ratio of ilmenite and charcoal was kept constant at 1:1. The result of isothermal reduction experiment is presented in the form of percent metallic iron and percent of reduction of ilmenite The chemical analysis (Fig. 4.20) indicates the extent of reduction for specific period of time increases. The amount of metallic iron increases with the increase of the reduction temperature and also with an increase in time for a specified temperature.

Hasseb et al. [14] investigated reduction of ilmenite with charcoal and suggested that at lower temperature ($900\text{-}1000^0C$) the reduction of ilmenite proceed via the solid-state reaction between carbon present in the charcoal and ilmenite They identified this model of reaction to be responsible for the slower rate of reduction at lower temperatures, at temperature higher than 1000^{0}C, the reduction mechanism changes and is caused by CO in accordance with the boudouard reaction (equation 1) proceeds, at a significant rate at temperatures higher than 1000^{0}C.

$$CO_2+C \Rightarrow 2CO \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

4.5.2 Effect of particle size on the extent of reduction

Degree of reduction and percentage of Fe_{met} in different size fractions of as received reduced ilmenite is shown in Fig. 4.26. In Table- 4 9 variation of total iron in as received and reduced size fractioned ilmenite is shown. The reduction was done at 1050 °C for 4 hrs.

Table-4.9 Initial and final iron content of ilmenite sample in different size fraction..

US Sieve no	%of total iron in as received ilmenite	%of total iron in reduced ilmenite
100	39.08	44.67
140	40.20	45.07
200	42.44	49.14

Fig. 4.26 shows that the percentage of total iron in the reduced sample is higher as compared with the corresponding value in the raw samples. This is due to the removal of oxygen during reduction. After reduction the finer fractions are found to contain higher percentage of total iron as before. From Fig 4.26 it is evident that the content of metallic iron increases with the increases of fineness of particles. It is clear from the table that although finer ilmenite contain a higher amount of oxygen associated with iron, this fractions actually contain a lower amount of oxygen in the reduced mass.

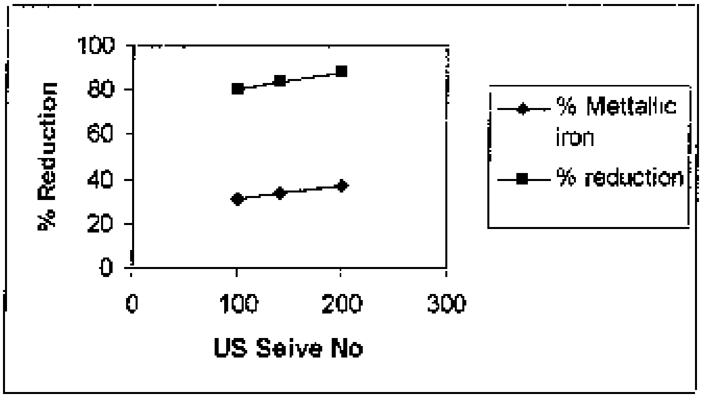


Fig 4.26 Extent of reduction of as received ilmenite as function of size fraction

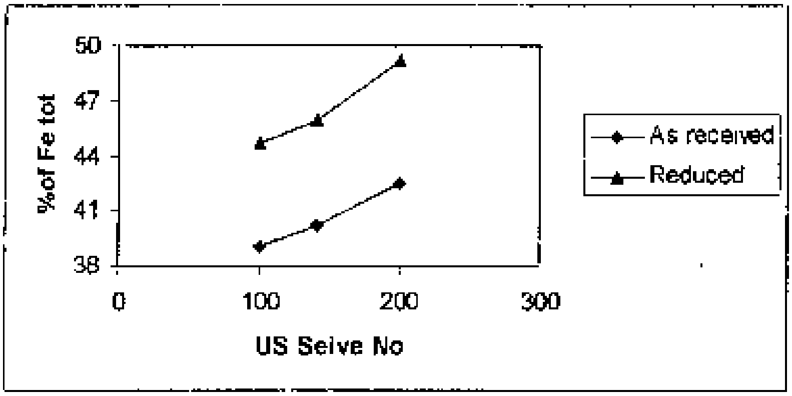


Fig 4 27 Variation of total iron of as received ilmenite as function of size fraction ilmenite

4.5.3 Reduction behavior of different magnetic fractions

The extent of reduction and content of metallic iron were determined by the chemical analysis of the reduced mass. Chemical analysis results of the different reduced magnetic fractionated samples are plotted in the Fig 4 28. It shows that contents of metallic iron as well as Fe_{tot} decreases with an increase in the separation current.

The calculated percentage reduction is plotted in the Fig 4 28

ig and the degree of reduction was calculated by using the formula

$$\%\text{of reduction} = \frac{\%\text{ of metallic iron in the reduced sample}}{\%\text{ of total iron in the reduced sample}}$$

It is evident that magnetic fraction separated at lower current (0.10-0.30 amp) are reduced to a higher extent than those separated at higher currents It may be due to higher ferrous oxide contents in those fractions which are separated at higher currents. So it is beneficial to reduction for the five fractions. But these major fractions contain about 89.98% of the ilmenite sample

Table-4.10 Chemical analysis of fractionated reduced sample (reduction 1050 °C for 4)

Fractionated Amp	TiO_2 %	$\%Fe_{Tot}$	Fe_{Met}	% of reduction
0.1	43.96	44.67	38.76	86.79
0.15	43.01	44.67	31.95	84.97
0.2	42.01	42.93	31.93	76.03
0.25	39.19	40.2	26.24	65.29
0.3	38.23	33.5	19.53	58.3

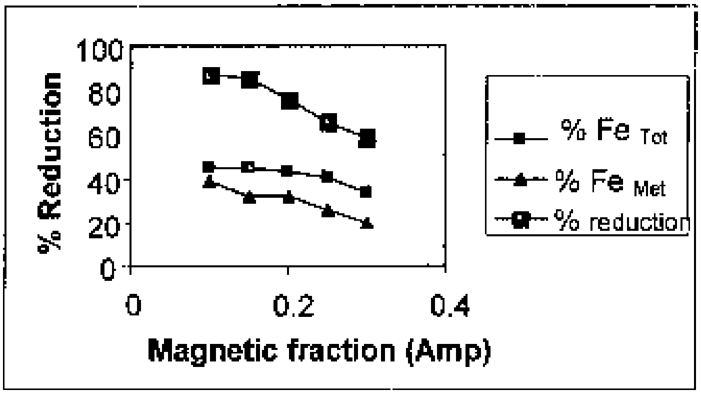


Fig 4.28 Chemical analysis of fractionated reduced sample (reduction 1050 °C for 4 hrs)

4.5.4 Effects of Prior Oxidation on the Extent of Reduction

A comparison of the extents of reduction of as received and pre-oxidized ilmenite reduces at 1050°C is shown in Fig.4.29 and Fig. 4.30. It can be seen that at any time the extent of reduction is higher in the case of pre-oxidized samples than in the case of as received ilmenite.

As oxidation of Inani ilmenite converts almost all the ferrous iron content in ilmenite to ferric iron, this alters the reduction mechanism. Moreover the generation of cracks in the oxidized sample prevents sintering, increases the surface area of the oxidized particles and hence enhances the rate of subsequent reductions.

The possible reduction of Inani ilmenite in the oxidized condition proceeds in two stages. The first stage is the reformation of ilmenite according to the either or both of the following reactions:

$$Fe_2TiO_5 + TiO_2 + CO \rightarrow 2FeTiO_3 + CO_2$$

$$Fe_2O_3 + 2TiO_2 + CO \rightarrow 2FeTiO_3 + CO_2$$

The second stage is progressive reduction of ilmenite to metallic iron and rutile according to following reaction.

$$Fe_2TiO_3 + CO \rightarrow Fe + TiO_2 + CO_2$$

Thus the mechanism of reduction of naturally weathered and pre-oxidized sample of Inani ilmenite appear to be slightly different. The first step in the reduction of oxidized ilmenite is the rapid formation of pseudobrookite, rutile and carbon monoxide or hematite, rutile and carbon monoxide or both these reductions. The second stage is the reduction of reformed ilmenite to metallic iron and rutile Reduction of as received Inani ilmenite by charcoal, on the other hand, involves 1 conversion of pseudorutile into rutile and ilmenite and 2.change of ilmenite iron and rutile [54].

Fig.4.28 shows a comparison of the extent of reduction in as received and pre-oxidized magnetically fractions. It can be seen that the extent of reduction for all the magnetic fractions is higher in the case of pre-oxidized reduction than in the case of as received ilmenite.

Oxidation converts monocrystalline particles of ilmenite to polycrystalline ones of pseudobrookite with disseminated particles of rutile During gas reduction of preoxidized material at 1000°C, the fragments of the particles are reduced topochemically, each in its own zone of liquid enrichment. and metallic iron is concentrated at the boundaries of the fragments. The total amount of ilmenite isolated under the influence of the liquid enrichment zone is reduced, and the sintering tendency of the particles is minimized [58].

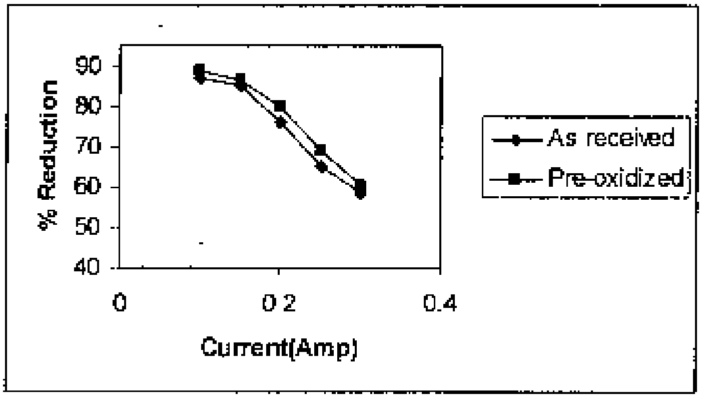


Fig. 4.29 Extent of reduction of as received and preoxidised fractionated ilmenite.

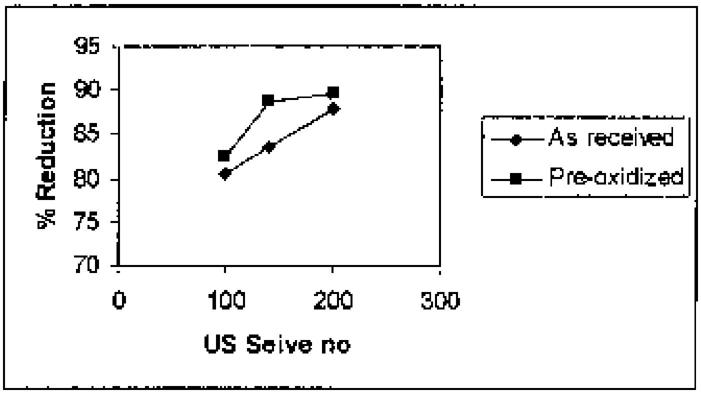


Fig. 4.30 Extent of reduction of as received and preoxidised reduced ilmenite of different size fractions.

On oxidation single crystal ilmenite converts to polycrystalline array of pseudobrookite and rutile. The presence of cracks in the oxidized ilmenite increases the rate and extent of reduction of ilmenite.

4.5.5 Optical Metallographic studies

The microstructure (Fig 4 31) of preoxidized reduced ilmenite showed the internal structure of the polished particles. The progress of the pre-oxidize reduction was observed in the microstructure. Dark grey and black area was seen in the cross section of the particle Small bright spots due to metallic iron were observed From figure it is evident that the volume fraction of the metallic iron formed (from x-ray diffraction) on reduction and in the case of oxidized sample is much more compared to that of as received condition. The pores were found due to the removal of oxygen from the ferric oxide during reduction Metallic iron spots were seen only few particles In some of the reduced ilmenite grains, these globules started diffusion from the interior to the periphery and got concentrated there. In the pre-oxidized reduced grain crack was observed. It seemed that grains became large on oxidation and reduction Porosity was developed in the pre-oxidized reduced sample.

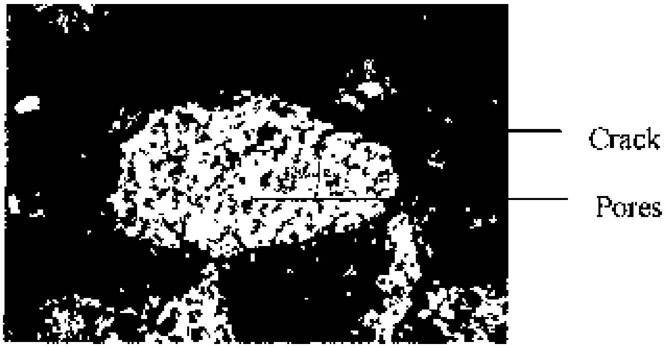
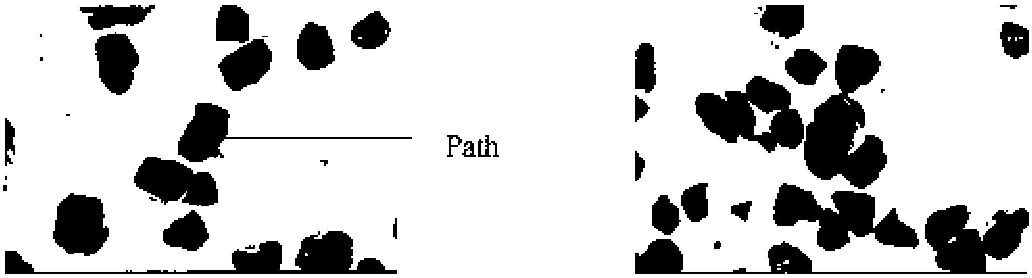


Fig.4.31 Microstructure of pre-oxidized reduced ilmenite sample

4.5.6 Optical Polar Microscopic study

Sample of Inani ilmenite reduced in the oxidized condition was observed under optical polar microscope Grain boundaries of pre-oxidized reduced particles have become transparent Periphery was developed in pre-oxidized reduced particle. The shape of grain boundaries of pre-oxidized reduced particle was uniform. It seemed that light was scattering from it It is also observed that the grains of pre-oxidized reduced particles have became pseudorutile, leucoxene and brookite.

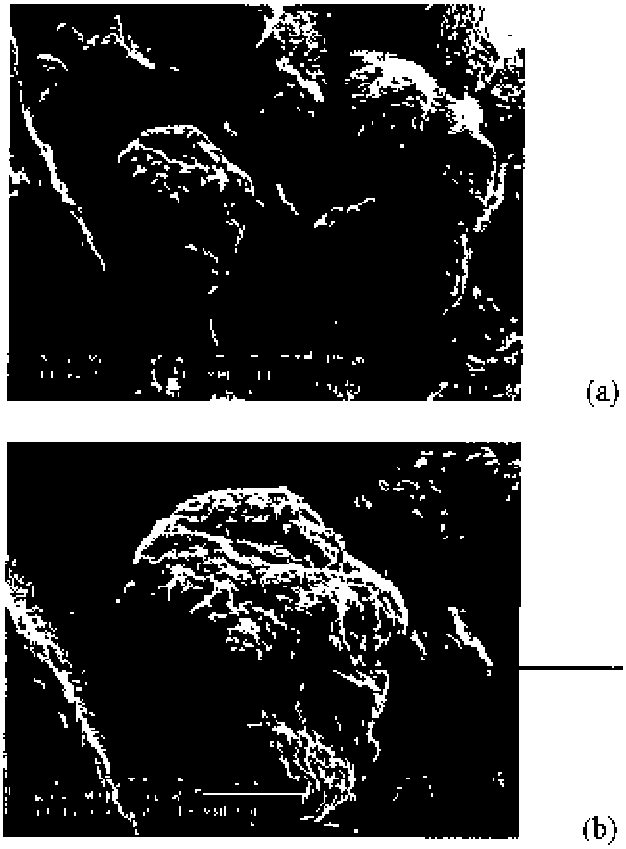


(a) (b)

Fig. 4.32 Optical microscopic studies of preoxidized reduced sample
(a) Pre-oxidized reduced at 1050°C for 4hr (Path was observed)
(b) Pre- oxidized reduced at 1050°C for 4h

4.5.7 Scanning Electron Microscopy(SEM) studies

The microstructures of pre-oxidized reduced sample were observed in SEM. This was done to observe the changes taking place on the surface of the particle during the reaction. Micrographs are shown in the Fig 4 33. The SEM pictures showed the rough surface, which is in contrast to the smooth plane surface of the unreduced sample. The unreduced ilmenite particle has a smooth plane surface having either no porous or no microporous. After reduction particle showed the formation of uneven surface. Large pores of few micron sizes with interconnection were observed. The pores were formed due to the removal of the ferric oxide during reduction The surface of the oxidized and then reduced sample becomes completely uneven and more porous than the sample reduced in the as received condition.



Pores with uneven surface

Fig 4 33 SEM studies of (a) Pre oxidized reduced at 1050°C for 4hr ×200
(b) Pre oxidized reduced at 1050°C for 4hr ×500

4.5.8 X-ray diffraction studies

X-ray diffraction analysis of ilmenite was carried out Typical x-ray diffraction pattern of ilmenite pre-oxidized and then reduced at 1050°C is given in Fig: 4 34 Ilmenite reduced at 1050°C showed the complete decomposition of ilmenite to TiO_2 and metallic iron. Ilmenite phases diminished with the increase of temperature. Chemical analysis also showed the presence of maximum iron present at this temperature.

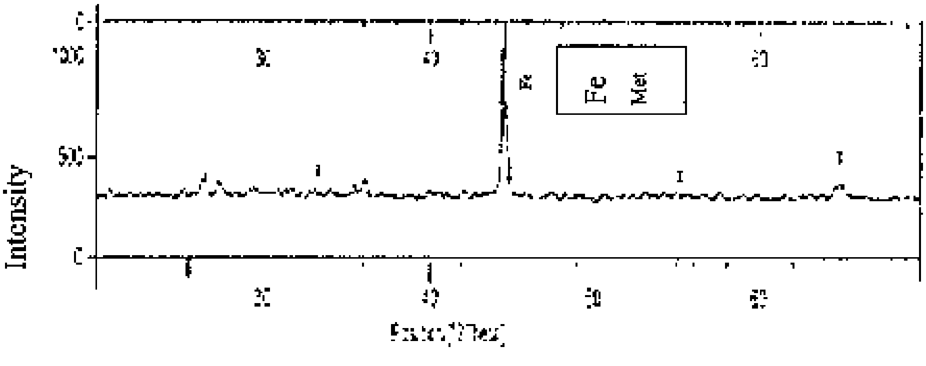


Fig. 4.34 X-ray diffraction patterns of pre-oxidized reduced ilmenite

4.6 Leaching

4.6.1 Introduction

Sample reduced in the as received condition containing about 39.31 percent metallic iron (44.67% total iron) and the reduced after oxidation containing 39.86 percent metallic iron (45.23% total iron) were used for the experiments.

4.6.2 Leaching of Reduced ilmenite

Leaching was performed at 75°C for 2 hrs in an acid solution containing 20% HCl. A three necked flask equipped with a reflask condenser, a thermometer and a magnetic stirrer was used as the reaction vessel for leaching The arrangement for leaching is shown in Fig. 3.4 After leaching for two hours the solution was cooled and filtered. The leached ilmenite was washed several times with water, dried in an oven at 110°C for 2 hrs and analyzed. After leaching the product was found to contain 2.51% iron and percentage of iron removed 97.49%. The main reactions taking place during the leaching are

$$Fe+2HCl=FeCl_2+H_2$$

$$FeO+2HCl= FeCl_2+H_2O$$

i.e iron present in the reduced ilmenite as metallic and ferrous iron will dissolve in the acid with formation of chloride.

4.6.3 Optical Metallographic Studies

The Microstructures of pre-oxidized reduced leached showed the internal structure of the polished particles in the Fig.4.35. From figure it is evident that the iron has leached from preoxidized reduced particle. Preoxidized reduced Particles have become shining with reddish color. Grains of preoxidized reduced particles become large. Much more hole was observed in preoxidized reduced particle.

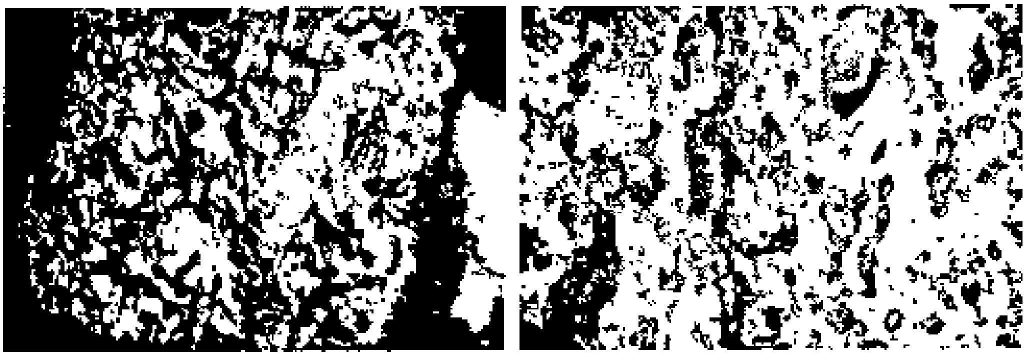

(a) (b)

Fig 4.35 .Microstructure of pre-oxidized, reduced and leached sample
(a) Pre-oxidized reduced leached sample (Radish shining spots)
(b) Pre-oxidized reduced leached sample (Grain with large hole like honeycomb)

4.6.4 Scanning Electron Microscopy (SEM) studies

The SEM studies showed that unreduced ilmenite has got a smooth plane surface with no pores on the surface either no porous or no micro porous surface. After reduction the surface became uneven. Large pores with interconnection were observed on the pre-oxidized reduced particle. But in pre-oxidized reduced particle has porous surface. This was formed due to the removal of the ferric oxide during reduction. In pre-oxidized reduced leached particle large holes was observed This was due to the removal metallic iron. The particle is completely porous through out the body with the appearance of beehive. The globular structures seen on the surface of the reduced ilmenite had disappeared during leaching Iron is the only soluble material and all particle is containing iron ,so only iron will be leached. Absence of iron on the surface of the ilmenite particle observed in SEM spot analysis. In the reduced particle high concentration of iron was observed on the surface But after leaching all the iron on the surface was dissolved.

4.6.5 X-ray diffraction studies

Typical x-ray diffraction pattern of ilmenite pre-oxidized reduced and then leached is given in Fig: 4.38. Ilmenite reduced at 1050^0C showing the complete decomposition of ilmenite to Ritile. Ilmenite phases diminished at that temperature. Chemical analysis also showed the presence of rutile present at this temperature.

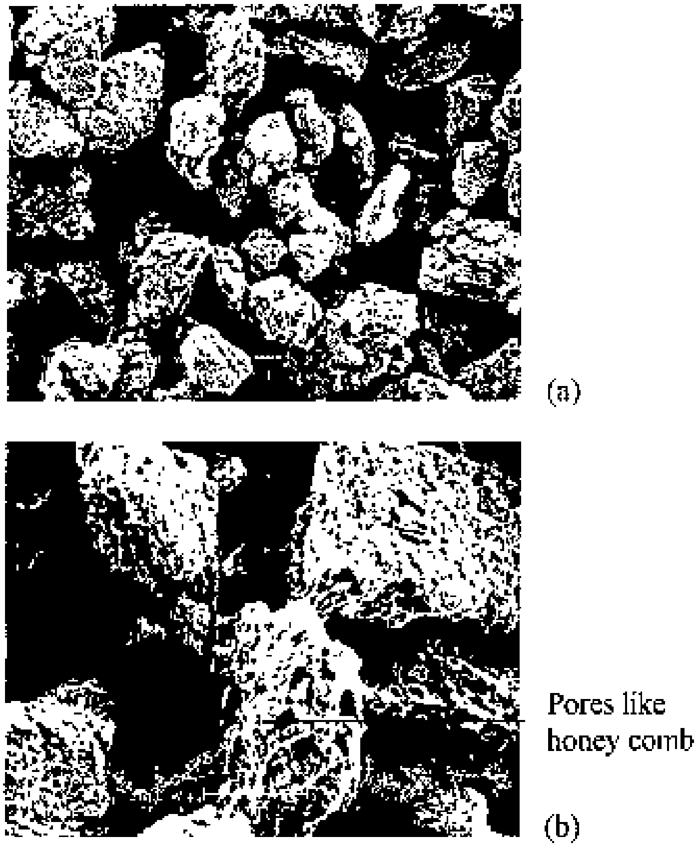


Fig. 4.36 SEM studies of preoxidized, reduced and leashed ilmenite sample
(a) Pre oxidized reduced leached sample ×200 (Porosity and uneven was Observed)
(b) Pre oxidized reduced leached sample ×500 (Porosity and uneven like honeycomb was Observed)

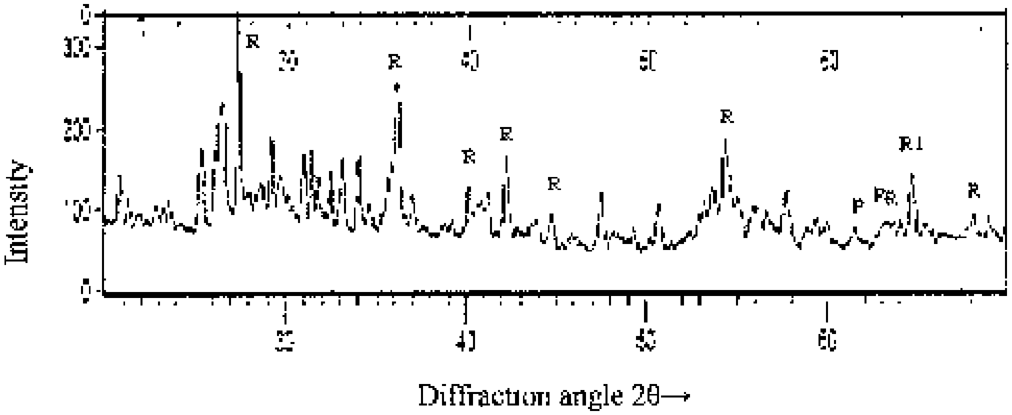


Fig. 4.37 X-ray diffraction patterns of pre-oxidized reduced leached ilmenite
R= Rutile

4.7 Comparison of the leached products

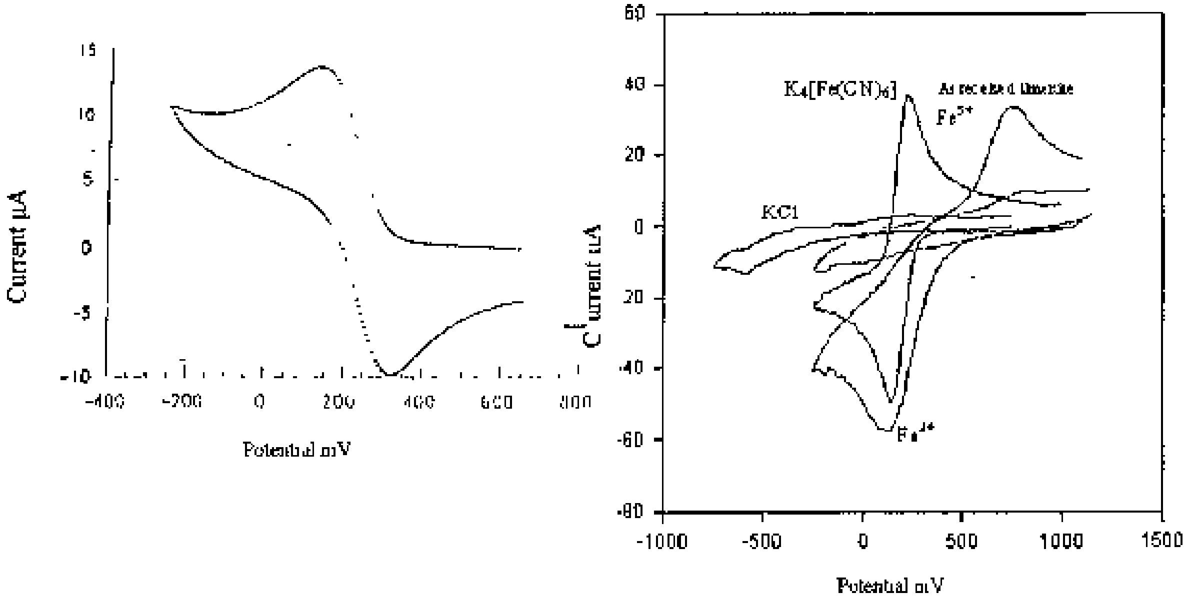
Iron content was found 2.51% for as received and 0.374% for oxidized reduced sample and titanium oxide content 89.51% for as received reduced leached and 90.50% for oxidized reduced leached sample. In general, it can be stated that Inani leached products prepared by this oxidation-reduction-leach route is equally good if not better than the commercially available synthetic rutile sample

Table 4.11 Comparison of the reduced leached product

Component	Reduction temperature	Without oxidized		Pre- oxidized	
		Inani	Teknaf	Inani	Teknaf
Fe%	1050^0C	2.51	2.57	1.76	2.18
TiO_2%	1050^0C	89.59	90.45	90.50	91.50

4.8 Electrochemical analyzer result

From electroanalytical measurement of cyclic voltammetry it was found that in voltammograme lower peak is for ferrous ion (Fe^{2+}) and the upper peak is for ferric ion (Fe^{3+}). It is a qualitative test. In this procedure the amount of iron was 0.0022 gm To test this procedure same amount of iron ion containing potassium ferricyanide solution was tested. Voltammogrames are shown in the Fig. 4.39. It seems that amount



(a)

(b)

Fig 4.38 (a) Standard voltammogram of iron

(b) Voltammograme of different condition sample and standard voltammograme of iron of ferrous iron is higher. In different magnetic fraction (0 10-0.30) it was found that a different behavior. In optical polar microscope 0.15 amp magnetic fraction is containing more altered ilmenite In this sensitive method in 0.0022 gram iron solution was taken for to observe the deviation All other magnetic fraction was regular but only the 0.15 amp fractionated magnetic size was not uniform. All other magnetic size fraction showed the regular decrease of ferric and ferrous iron content and that is shown in the Fig.4.40.

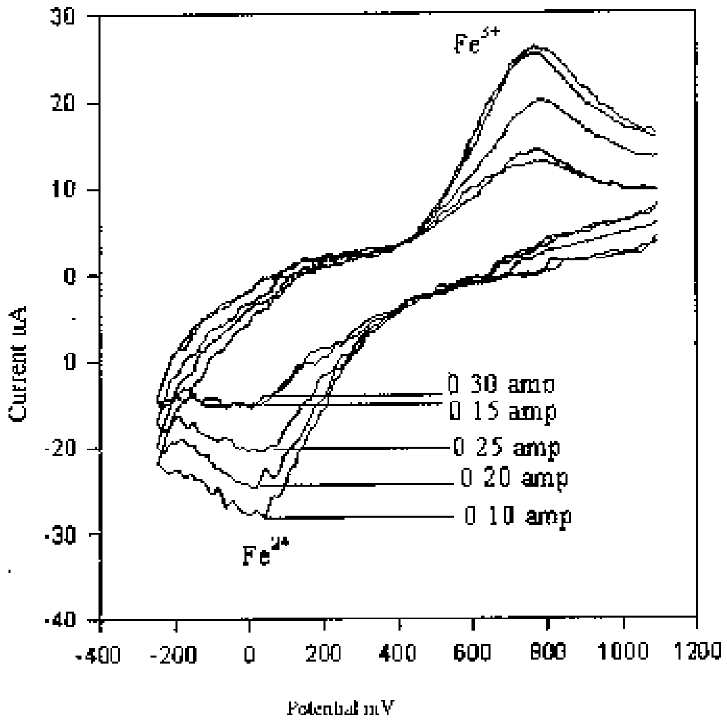


Fig 4.39 Voltammograme of different fractionations sample

In different period time of reduction the amount of ferrous iron was reducing. In voltammogramme it was also shown Fig.4.42.

The standard voltamogramme of potassium ferricyanide and Inani sample it was observed. The peak potential has shifted Fig.4.39 It was due to the presence of impurities like Mg, Mn, Si and sulfuric acid.

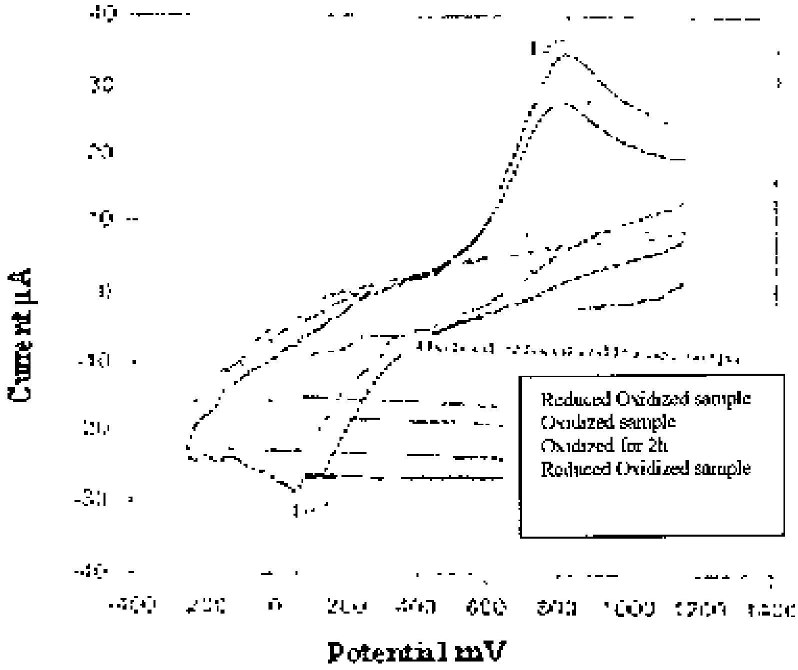


Fig 4.40 Voltammograme of different condition sample

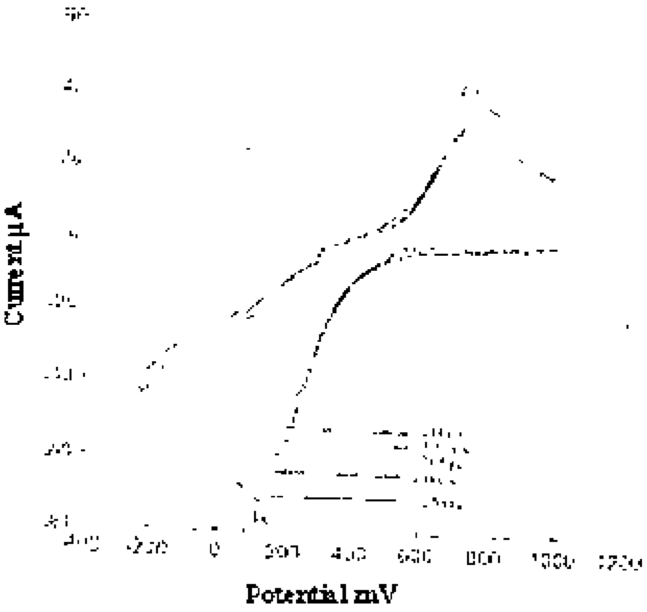
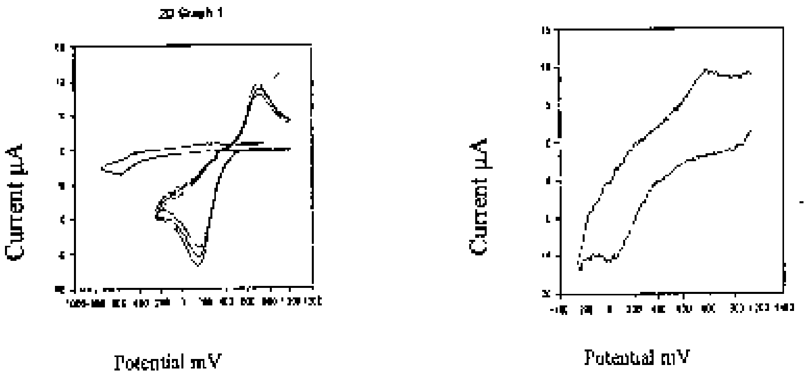
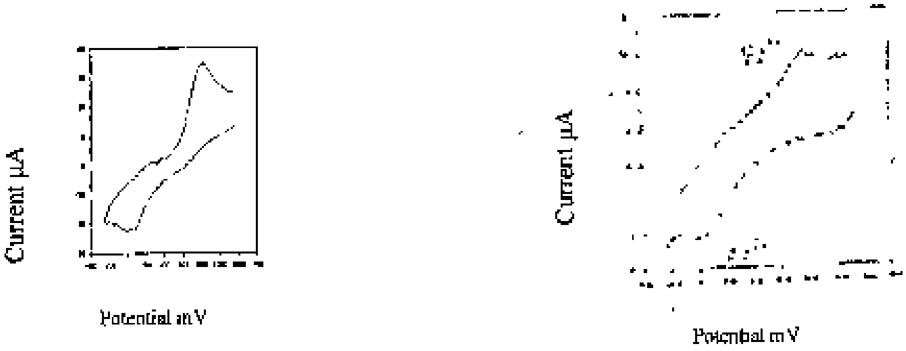


Fig 4.41 Voltammograme of different condition (time) sample



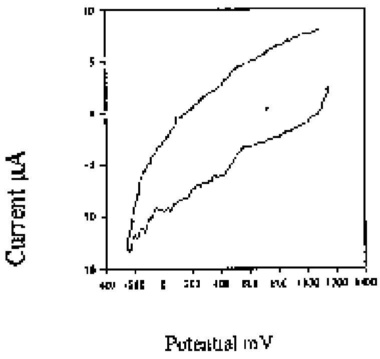
As received sample

Reduced for 1050^0C,4hrs



Oxidized for 2 hrs

Preoxidized reduced sample



Oxidized, reduced and leached sample

Fig 4 42 Voltammograme of different conditions of sample

The voltammograme of electrolyte KCl and solution sulfuric acid was also taken. Their voltamograme was not in iron ion potential range.

Sample of Inani was followed different chemical treatment In cyclic voltammetry method the voltamograme shows the agreement with the chemical treatment in Fig. 4.41 and 4.43..In the as received sample peak for ferrous and ferric iron was observed. In the reduced sample peak for ferrous and ferric iron were reduced. In the oxidized sample peak for ferrous iron was not observed In the oxidized reduced sample only ferric iron peak was observed. Because in oxidation maximum iron was converted to ferric form and in reduction all ferric iron converted to metallic iron. In the pre-oxidized reduced leached sample no peak for ferrous or ferric iron was observed It is also a good agreement with chemical analysis, x-ray analysis SEM analysis.

4.9 Magnetic Susceptibility

Magnetic susceptibility of Inani ilmenite was measured .Inaini ilmenite is weakly magnetic. In the reduced sample no magnetic value was observed. It was assumed that on reduction metallic iron surrounded the grain Inani ilmenite is in the process of alteration. If not in the alteration process then It will not show any magnetism. But due to the presence of ferric iron Inani ilmenite is showing very weak magnetism On oxidation the value the magnetism was increased. Because all most all iron ion was converted to ferric iron. After leaching a very weak magnetism was noted.

Table 4 11 Magnetic susceptibility in fractionated as received ilmenite sample

Size fraction	Magnetic susceptibility($cm^3\ g^{-1}$)
as received	1.26×10^{-5}
0.10	1.26×10^{-5}
0.15	1.19×10^{-5}
0.20	9.41×10^{-6}
0.25	8.73×10^{-6}
0.30	7.73×10^{-6}
0.35	7.50×10^{-6}

Table 4 12 Magnetic susceptibility in fractionated as received ilmenite, oxidized and preoxized reduced leached sample

Size fraction	Magnetic susceptibility(cm^3 g^{-1}) of as received sample	Magnetic susceptibility(cm^3 g^{-1})of oxidized sample	Magnetic susceptibility ($cm^3.g^{-1}$) of ox+red+leached sample
as received	1.26×10^{-5}	2.05×10^{-5}	5.41×10^{-7}
0.10	1.26×10^{-5}	2.01×10^{-5}	5.61×10^{-7}
0.15	1.19×10^{-5}	1.95×10^{-5}	5.31×10^{-7}
0.20	9.41×10^{-6}	1.82×10^{-5}	0.54×10^{-7}
0.25	8.73×10^{-6}	0.26×10^{-5}	0.35×10^{-7}
0.30	7.73×10^{-6}	0.198×10^{-6}	0.11×10^{-7}

Magnetic susceptibility (C.G.S) of oxidized sample is higher than the as received ilmenite When the sample is oxidizes then ferrous iron is converted to ferric iron. The number of unpaired electron increases As a result the magnetic susceptibility increases. But when the ilmenite is pre-oxidized, reduced and leached then again ferric iron converted to metallic iron and this iron is leached to hydrochloric acid. As a result magnetism falls.TiO_2 is a non magnetic substance Very weak magnetic susceptibility was observed

Chapter 5

SUMMARY

5.1 Introduction

Investigations were carried out on the alteration of Inani ilmenite. The process of its up gradation into synthetic rutile was also examined. Bangladesh ilmenite at Inani contains about 40 percent TiO_2 together with a large amount of iron in the form of oxides. Weathering processes have upgraded a large number of titanium oxide mineral deposits and have made some of them economic.

Weathering in nature i.e. oxidation of ferrous iron to ferric iron making promotes alteration. Textural intergrowths of iron oxide phase intensify the alteration of ilmenite.

Oxidation-reduction leach route was selected for the up gradation of low grade ilmenite.

5.2 Characterization of as-received ilmenite

Chemical analysis of Inani ilmenite revealed that the content of ferrous iron is 25.48%, ferric iron is 32.90% and TiO_2 is 39.90%. X-ray diffraction pattern analysis shows that ilmenite is the main phase; other phases rutile, pseudorutile, ferrous oxide and hematite were also detected. SEM of as received sample surface was more or less uniform in appearance. More than 90% of Inani ilmenite was retained on US sieve no 100, 140, 200 individual amounts belong to each sieve being 25.48%, 34 22% and 40.90% respectively.

Finer fractions of ilmenite were found to contain lower percentage of TiO_2 and higher percentage of total iron From the sphericity value, finer size fraction was found to have higher sphericity. X-Ray diffraction analysis of all the size fractions showed that the ilmenite was the main phase and together with rutile, psedorutile and hematite.

The bulk (more than 91%) of the Inani ilmenite belongs to the magnetic fractions separated at different current of 0.10-0 30 amperes. The content of ferrous and ferric oxide was found to decrease with increasing current of separation. With increasing current of separation titanium oxide content was found to decrease From the material charcoal becomes the main reducing agent while at lower temperature solid carbon act as the main reducing agent. Haseeb et al [14] investigated the reduction of Bangladesh ilmenite with charcoal and suggested that at lower temperatures 950^0-1000^0C the reduction of ilmenite proceed via the solid-state reaction between the carbon present in the charcoal and ilmenite. They identified this model of reaction to be responsible for the slower rates of reduction at lower temperatures. At temperature higher that 1000^0C, the reduction mechanism changes and is caused by CO in accordance with Boudoured reaction. This change in mechanism increases the extent of reduction.

5.6 Leaching

20% Hydrochloric acid was used for leaching out iron from the sample. The sample after leaching in the oxidized condition contained less residual iron. While TiO_2 contains in the leached product was found to increase. The leaching of ilmenite was enhanced by the presence of cracks from during oxidation .On the other hand leaching of ilmenite reduced with prior oxidation was found to slower

A comparison of the chemical constituents of synthetic rutile prepared in these studies from Inani ilmenite with that of a commercially available synthetic rutile sample [59] is given in the Table-5.1 In general it can be stated that synthetic rutile prepared from Inani ilmenite by this oxidation-reduction leach route is equally good as those prepared from ilmenite of other origin.

Table-5.1 Comparison of chemical constituents of synthetic rutile samples

Constituents	Commercially available synthetic rutile			
	Australia	Kerala	Teknaf	Inani
TiO_2	92 80	93.50	91 50	90 50
Residual iron	2.10	1.30	2.51	1 74

6. Conclusions

1) Oxidation prior to reduction of Inani ilmenite enhances the rate of subsequent reduction.

2) The metallic iron content of the reduced ilmenite is higher in the case of sample reduced in the oxidized condition.

3) Synthetic rutile obtained in these studies contains 90.50 percent TiO_2, which is very much comparable in chemical constituents with those from ilmenite of other origins.

4) Inani ilmenite is in the process of alteration but the process is yet to the completed.

REFERENCES

1. American Welding Society . AWS G2.4/G2.4M:2007 Guide for the Fusion Welding of Titanium and Titanium alloys Miami: (2006).American Welding Society Abstract
2. Flower, Harvey M. (2000). "Materials Science: A moving oxygen story". Nature (2000). pp -407: 305.
3. Hampel, Clifford A. The Encyclopedia of the Chemical Elements Van Nostrand Reinhold, (1968). p 738 ISBN 0442155980.
4. Cyr M.; Carles-Gibergues A.; Tagnit-Hamou A.1,Titanium fume and ilmenite fines characterization for their use in cement-based materials,Ingenta connect Cement and Concrete Research, Volume 30, Number 7, July 2000 , pp. 1097-1104(8)Air & Waste Management Association 91st Annual Meeting & Exibition,San Diago
5 Stevens, Lisa; Lanning, John A.; Anderson, Larry G.; Jacoby, William A.; Chornet, Nicholas "Photocatalytic Oxidation of Organic Pollutants Associated with Indoor Air Quality". Air & Waste Management Association 91st Annual Meeting & Exibition,San Diago. Retrieved on 2006-12-26. (June 14 – 18, 1998)
6. "Titanium". Columbia Encyclopedia (6th edition). (2000 – 2006). New York: Columbia University Press. ISBN 0787650153 Columbia Encyclopedia
7 Titanium. Los Alamos National Laboratory (2004). Retrieved on 2006-12-29. Natures Building Blocks: An A-Z Guide to the Elements
8. Emsley, John (2001). Natures Building Blocks: An A-Z Guide to the Elements.Oxford: Oxford University Press, pp. 451 – 53. ISBN 0-19-850341-5.
9 Chen, George Zheng; Fray, Derek J.; Farthing, Tom W. (2000). "Direct electrochemical reduction of titanium dioxide to titanium in molten calcium chloride". Nature 407: p-361 – 64.
10. Flower, Harvey M. (2000). "Materials Science. A moving oxygen story". Nature 407: 305.
11. Paul A. Schroeder, John J. Le Golvan and Michael F. Roden,Weathering of ilmenite from granite and chlorite schist in the Georgia Piedmont, American Mineralogist; November 2002; v. 87; no. 11-12; pp- 1616-1625

12. Report on the seminar on beach sand minerals in economic development, Bangdesh Atomic Energy Commission. Cox's Bazar, Nov 1983

13 Ahmed.S.T.Pal and Mitra, S., " Ilmenite from Cox's' Bazar Beach sand Bangladesh their intergrowth", J. Geol, Soc India, 44,(1992),pp29-32

14. Information Booklet; Beach sand Explotation Centre, Bangladesh Atomic Energy Commission. Cox's bazar, June,1994.

15. Haseeb A.S.M.A and Kurny, A.S.W., Trans., Instn. Min. Metall., Sec.C,106(1997),p.c39

16. Krishnan, and Roy.B.C. Geological Survey of India, vol. LXXVI,1942,no-5.pp-3

17. Force r. Eric , Geolgy of Titanium Mineral Deposit , Amazon.com pp-51

18. Gilson,J.L. "Titanium in industrial Minreals and Rock" A.I.M.E, Newyork, (1949),pp-1042-1072.

19. http://wwwmidal.org/gallery.php/min-3296html

20. Anand,R.R and Gilkis, R.J. "Weathering of ilmenite in a Lateritic Pallid Zone, Clays and Clays Minerals", 32,(1984), pp-363-374

21 Morad, S. and Aladahan, A.A.. "Authigensis of Titanium Minerals in two proterzoic Sedimentary Rocks from Southern and Central Sweden." J. Sediment. Patrol. 52(4),(1982),pp.1295-1305

22 Joseph W. Troester, Ground-water chemistry in the valley de Yabucoa alluvial aquifer, southeaster Puerto Rico Third International Symposium on Tropical Hydrology *San Juan, Puerto Rico, July 12-16, 1998*

23. Sachinath Mitra.S.S. Ahmed and Moon,Hi-Soo "Mineralogy and Chemistry of the opaques of Cox's Bazar (Bangladesh)beach sands and oxygen fugacity of their provence, Sedimentary Geology,77(1992), pp-235-247.

24 Karkhanawala,M.D and Momin, A.C "The alteration of ilmenite" Economic Geology, 54, (1959), pp1302-1308

25. http://wwwmidal.org/min-6176html

26. Langtry E. Lynd , Alteration of ilmenite Economic Geology; August 1960; v. 55; no. 5; p. 1064-1068

27. Grey* I E and Li, C. Hydroxylian pseudorutile derived from picroilmenite in the Murray Basin, southeastern Australia, Mineralogical Magazine, August 2003; v. 67; no.4;p.733-747.
28. http://wwwmidal.org/min-6176html photo ID13440
29. Grey I E , Reid A F , The structure of pseudorutile and its role in the natural alteration of ilmenite, American Mineralogist , 60(1975) pp-898-906,
30 U.S Geological Survey, Retrieved on2006-03-07
31. Mucku,A.A and Chandhuri, J N B. "The continuous Alteration of ilmenite through Pseudorutile to leucoxene",Ore Geology, Reviews.,6, (1991), pp.25-44
32 Stefan Bernstein, Dirk Frei, Christian Knudsen, Henrik Stendal, with Roger McLimans, Leaching of ilmenite in sediments, APPLIED MINERALOGY
33. Pe-Piper, Georgia; Piper, David J W ; Dolansky, Lila Clays and Clay Minerals, Volume 53, Number 5, October 2005 , pp. 490-510(21)
34. Grey, I.E. and Watts, J A "Hydrothermal Synthesis of Geothite-Rutile Intergrowth Structures and their Relationship to Pseudorutile", Amer. Mineral, vol-68, (1983), pp.981-988.
35. TEUFER. G. & TEMPLE A K,, Pseudorutile—a New Mineral Intermediate between Ilmenite and Rutile in the N Alteration of Ilmenite, Nature 211 , 179 - 181 (09 July 1966).
36. Hugo,V.E and Cornell,D.H, Altered ilmenites in HoLocene Dunes from Zululand,South Petrographic evidence for Multistage altration"S Afr ,J.,Geol., 94(5/6), (1991), pp-365-378
37. Grade and Ranga, "Mechanics of Sediments transport and Alluvial stream problem, wiley Estern limited, New Delhi, 2nd Edition.1985,p17
38. Frost, M.T. Grey,I.E Harrowfield, I.R and Mason, K., " Alteration Profile and impurity element distribution in magnetic fractions of weathered ilmenite", American Mineral, 71 (1986), pp.167-175
39. Hartman, J.A., "The Titanium Minerology of Certain Bauxites and their parents Minerals", Economic Geology ,54, (1983), pp.1380-1405

40. Frost, M.T. Grey,I.E. Harrowfield, I.R and Mason, K., "The Dependence of Alumina and Silica Contents on the Extent of Weathered ilmenite from Western Australia", Mineral. Mag, vol-47, (1983), pp.201-208.

41. Hugo,V.E, "A mineralogocal and chemical study of Titanium loses at Richards Bay Minerals" M.Sc Thesis (unpublished) University of Natal,Durban,(1988),812pp

42. Babu,D.S.S thomas, Thomas,K.A. Mohan Das,P.N. and Domodaran, A.D.," Alterration of ilmenite in Manavalkurichi Deposits, India, Beach Sand Minaral Reasearch unit, Regional Research Laboratory (CISR), Trivandrum 695019, India.

43. Nair Azith G, Babu, D.S.S, Differential Alteration of Ilmenite in a Tropical Beach Placer, Southern India: Microscopic and Electron Probe Evidences, Resource Geol Economic Geology; August 1960, v. 55; no. 5, pp- 1064-1068

44. H.G. Dill, F. Melcher, M.Füßl and B.Weber Accessory minerals in cassiterite A tool for provenance and environmental analyses of colluvial–fluvial placer deposits16 September 2005, revised15March2006; accepted22March2006.

45 Shams ,N N."Characterization of ilmenite of Moheskhali heavy mineral deposit."M Sc Engg, Thesis, Dept. of MME, BUET, 2001. pp. 42-45.

46. Sarker, M.K and Kurny,A.S.W. "Effect of prior oxidationon the reduction and leaching of Bangladesh ilmenite",Recent advances in materials and mineral resources,Penang parkroyal resort, Malaysia, 3rd -5th May1999, pp-712-722.

47. Momin, M A., "Characterization of Bangladesh Ilmenite in the process of its upgradation into synthetic Rutile", Ph.D Thesis. Dept. of MME,BUET, 2006,pp.165

48. Babu,D S.S. Mohan Das,P N. and Domodaran, A.D.," Alterration of ilmenite in Manavalakurichi Deposits, India, Beach Sand Minaral Reasearch unit, Regional Research Laboratory (CISR), Trivandrum 695 019, India.

49. Ramakrishanan, C. Mani, R. and Babu,S.," Ilmenite fronm the Chavara deposist, India, A Critical evalution", Mineralogical Magazine, 61,(1997), pp- 233-242

50 Jones, D.G., "Reaction sequences in the reduction of ilmenite: 2- Gasious reduction by carbon mono-oxide" Trans. Inst Metall. (U K.) 83 sec.C, (1974), pp. 186-192.

51. Merk.R., and Pickles, C.A. "Reduction of ilmenite by Carbon mono-oxide"Canadian Metallurgical Quaterly,27(3).(1988),p. 179

52. Haque,R. Ray, H.S. and Mukherjee, " Estimation of the progress of direct reduction of iron ores on the basis of total iron analysis of the reduced mass." Trans Indian Inst. Met., 44 (5), (1991), pp. 403-407.

53. Huq, M.Z and Kurny, A.S W, "Upgradation of Cox's Bazar beach sand ilmenite. Paper presented at international conference on recent advances of materials and mineral resources", University Sains Malaysia,May, 1994

54 Huq, M.Z , Haseeb,A.S M A.and Kurny, A.S.W,,Proc. 1st Ann Paper meet, Mech. Engg. Div., The Inst. of Engrs Bangladesh, 16-29 oct (1994),pp. 396-404.

55. Dam Gongles, D.G. and Jeffes, J H , "Iron making and steelmaking" 14(5),(1987),p.217.

56. Bracanin, B.F. clmates, RJ and Davey,J.M Proc.Australia.Int.Min, Metall.,275(1980) pp.32-42.

Estimation of ferrous iron

Keep all the solutions ready before analysis

- Take 0.5gm of finally ground sample in a 500ml flask
- Add
    - a) 40ml of distilled water
    - b)25ml conc. H_2SO_4
- Heat gently to boiling, boil for one minute
- Add 10ml of HF, boil for 10 mintues
- Remove from hot plate and immediately add
    - a) 100 ml of 4% boric(4gm boric acid in 100cc water)
    - b)15 ml of distilled H_3PO_4-H_2SO_4 mixture
    - c) 100 ml of ditilled water
    - d) Cool in running water
- Add 1ml of Barium diphenyl amine sulphonate indicator

Titrate with 0 1N potassium dichromate solution to a violet-blue end point

Calculation

$$\%Fe^{++} = \frac{\text{ml of } K_2Cr_2O_7 \times N \times 0.5584 \times 100}{\text{wt of the sample}}$$

Appendix-B

Estimation of metallic iron:

- Add 4-6 gm of $HgCl_2$ to 100-150cc of distilled water
- Add 0.5 gm of Finely Ground sample
- Boil for 20 minutes
- Filter and wash(6 times) with hot water

Test the residue for iron content

a) Add one drop of potassium ferricyanide solution.
b) Green color will indicate presence of iron
c) Boil ppt with 100cc distilled water and filter
d) Test again for Fe content
e) Repeat, if necessary.

Add

a)10 ml H_3PO_4-H_2SO_4 mixture
b)10 ml of Zimmerman solution
c)5 drops of Barium diphenylamine sulphonate indicator

- Titrate with 0.1N potassium dichromate solution
- Appearance of violet color is the end point

$$\% \text{ Metallic iron} = \frac{\text{Vol of } K_2Cr_2O_7 \times \text{Factor of } K_2Cr_2O_7 \times 10 \times 100}{\text{Weight of sample}}$$

Appendix-C

Estimation of Total iron:

- Melt 10-15 gm of potassium-hydrogen sulphate (in a silica crucible) to get clear solution
- Allow the melt to solidify
- Weigh about 0.5 gm of finely ground sample
- Spread the weighed sample evenly over solidify potassium bi-sulphate
- Heat gently to melt
- Swirl the contents of the crucible carefully
- Increase the temperature to the maximum (900^0C)
- Heat (at $900^0C$for 30 minutes)
- Allow to solidify
- Place the crucible(and the lid) inside a beaker contain 20 % H_2SO_4
- Heat till dissolution is complete
- Make upto 250ml

Use this solution for the determination of TiO_2-also

- Pipette out 25 ml of the solution in a conical flask
- Add 5ml concentrated HCl, Heat to 80^0C
- Reduce the iron solution by adding drop wise freshly prepared SnCl2 solution (Add till the color disappears, add one-drop excess)
- Cool immediately in ice(To 20^0C)
- Dilute to about 100 ml
- Add 10 ml of Saturated Hg_2Cl_2 solution (rapidly, at a time)
- Silky white precipitate will be obtained allow to stand for 5 minutes
- Add 5 ml of conc. H_2SO_4 and 10 drops of n-phenylanthralinic acid indicator
- Titrate with standard Potassium dichromate solution to pink color. This color change is not very prominent, has to be noticed carefully

Calculation

$$\% \text{ Total iron} = \frac{\text{Vol of } K_2Cr_2O_7 \times \text{Factor of } K_2Cr_2O_7 \times 10 \times 100}{\text{Weight of sample}}$$

$$\text{Factor } K_2Cr_2O_7 = \frac{55.84 \times \text{Normality of } K_2Cr_2O_7}{1000}$$

Ferric ion can be estimated from the difference between total iron and ferrous iron

$\%Fe^{+++} = \%$ Total iron- $\%$ Fe^{++}

Appendix-D

Determination of Total iron from Leached Solution

- Take 5 ml of solution
- Dilute to50 ml
- Add conc. HCl (5ml)
- Heat to 60^0-80^0C (just to boiling)
- Immediately reduce with $SnCl_2$ (keep cool in ice)
- Excess $SnCl_2$ to be neutralized (to cold solution)(Should not be too excess)
- Shake well to get a silky white ppt. of Hg_2Cl_2
- Add

  10 ml Zimmerman

  10 ml of acid mixture

  5 drops of Sodium/ Barium diphenyle amine indicator

  Titrate with Std. Potassium dichromate go got the amount of total iron

Calculation

% Total iron is calculate from the following relationship

1 Litre 1N $K_2Cr_2O_7$ = 55.84 gm of iron

Determination of TiO_2

Tile apparatus consist of a 500 ml Erylmeyer flask with a 2-tube rubber stopper. A pointed glass rod nearly touching the stopper and the short end of the delivery tube is placed into a 400 beaker containing saturated sodium-bi- carbonate solution. The Aluminum foil is attached to the glass rod fixed with stopper.

- Take 25 ml of solution (prepared for estimation of total iron) in a 500ml Erlemneyer Flask.
- Add 30 ml of HCl (conc.)
- Boil the solution.
- Attach 2 gm of high purity aluminum foil to the end of the glass rod of the redactor, Remove the flask from the heating mantle.
- Immediately insert the rubber stopper carrying the glass rod with aluminum and delivery tube to the flask.
- Place the other end of the delivery tube below the level of the saturated sodium-bi-carbonate solution taken in the 400 ml beaker.
- The reaction between the aluminum foil and the solution is rapid
- Towards the end of the reaction swirl the flask to ensure complete mixing and reduction .
- When all the aluminum appears to be dissolve gently boil the solution for 3-5 minutes keeping the delivery tube still immersed in the sodium-bi-carbonate solution.
- Ensure that the rubber stopper is rightly fitted.
- Cool the flask (in ice)
- To less than 60°C
- As the sample (in the Erylmeyer flask) cools, the sodium-bi-carbonate solution is drawn into the Eryenmeyer flask and carbon Dioxide evolved gives necessary protective atmosphere.
- When the solution is cool remove the stopper and rinse the glass rod and the delivery tube with distilled water
- Add 2ml of 24 percent ammonium thicoyante indicators.
- Titrate with standard ferric ammonium sulphate

Calculation

$$\% \ TiO_2 = \frac{\text{ml of titrant} \times \text{factor} \times 1000}{\text{Wt(in gm)of the sample}}$$

$$\text{Factor} = \frac{\text{wt of Std. } TiO_2 \times \% \text{ in Std } TiO_2}{\text{ml of titrant} \times 1000}$$

Appendix- F

Preparation of Solution

1. Ammonium Thiocyanate indicator

Dissolve 24 5 of ammonium thiocyanate in 80 ml of hot distilled water. Filter through two Whatman 42 filter paper using vacuum. Cool, dilute to 100 ml and store in a dark colored bottle .

2. Standardization of Ferric Alum

Dissolve 30.16 gm of ferric ammonium Sulphate in 800 ml distilled water and 15 ml Conc. H_2SO_4 add H_2O_2 to ensure complete oxidation of the iron. Boil the solution to remove excess H_2O_2 and dilute to 1 liter Standardize the solution against standard TiO_2 reduced in the same way as describe for the sample.

3. Preparation of $SnCl_2$

Conc. Solution of $SnCl_2$ is prepared by dissolving 12 gm of pure tin or 30 gms of AR crystalline $SnCl_2$ ($SnCl_2.2H_2O$) in 100ml of conc HCl and dilute to 200ml with distilled

4. Phosphoric acid Sulphuric acid Mixture

150 ml of conc H_2SO_4 and 150 ml of H_3PO_4 in 700 ml distilled water Total volume will be 750ml.

5. Zimmerman Solution

50 gms $MnSO_4$ in 250ml H_2O + 100ml conc. H_2SO_4 + 300 ml distilled water + 100 ml H_3PO_4. Total volume will be 750 ml.

6 Diphynyl amine sulphonate Indicator

Dissolve 1 gm of the diphenylamine salt in 100 ml of conc. H_2SO_4

7. Barium diphenylamine sulphonate Indicator

0.2 gm of barium diphenyle salt in 100 ml distilled water

8. N-phenanthralic acid indicator

0.1 gm phenanthralic acid in 100 of 0.005 molar solution of NaOH

9.20% HCl solution

Conc HCl contains 35% HCl take 100cc HCl

10 $K_2Cr_2O_7$ Solution

4.9033 gm 1 litre (0.1N Solution)

11. 0.005 molar NaOH

0.02 gm NaOH crystal in 100 ml H_2O

12. 4% Boric acid

4 gm Boric acid in 100 ml H_2O

13. Potassium ferricyanide solution

0.02gm Potassium ferricyanide in 100 ml water.

14. 20% H_2SO_4

80ml H_2O and 20 ml H_2SO_4.

Chemical Analysis of Inani ilmenite

Table 1: Chemical analysis of different size fractions of as received Inani Ilmenite before reduction(4.2.3)

US seive No	%TiO_2	%Fe(tot)	%FeO	%Fe_2O_3
100	40.80	39.08	26.35	26.87
140	40.20	40.20	25.15	29.79
200	39.00	42.44	24.86	33.31

Table 2: Chemical analysis of magnetically fractioned as received Inani Ilmenite (4.2.4.1)

Fractionated Amp	TiO_2	%Fe_{Tot}	Fe^{2+}	FeO	Fe_2O_3	Fe^{3+}	Specific Gravity	%Total
0.10	39.18	44.67	25.15	32.36	19.52	27.91	4.78	99.45
0.15	39.23	44.67	24.12	31.07	20.55	29.38	4.58	98.68
0.20	36.23	44.67	24.01	30.89	20.66	29.53	4.50	96.65
0.25	35.36	39.08	22.89	25.83	16.19	23.14	4.43	84.33
0.30	34.40	39.08	19.99	25.71	19.09	27.29	4.13	87.40

Table-3 Variation of metallic iron in the as received sample as function of temp and time(4.5.1)

% Metallic iron				
Time hr /Temp	900°C	950 °C	1000 °C	1050 °C
0.5	17.42	34.75	32.16	36.74
1.0	25.87	34.98	36.85	37.74
2.0	27.92	36.96	39.08	38.41
3.0	32.49	37.89	40.09	38.75
4.0	34.17	37.96	40.20	39.31

Table-4 Extent of reduction of ilmenite as function of temp and time(4.5.1)

% Reduction				
time hr /Temp	900°C	950 °C	1000 °C	1050 °C
0.5	52.00	77.79	71.99	80.25
1.0	67.34	78.30	82.49	84.49
2.0	60.81	82.74	87.48	85.98
3.0	67.58	84.82	89.74	82.62
4.0	87.21	84.97	89.99	88.00

Table- 5 Extent of reduction of ilmenite(4.5.1)

Time hr	Temp	$Fe_{(met)}$	Reduction
0.5	1050 °C	36.74	80.25
1.0	1050 °C	37 74	84.48
2.0	1050 °C	38.41	85 98
3.0	1050 °C	38.75	82.62
4 0	1050 °C	39.31	88.00

Table-6 Extent of reduction of as received ilmenite as a function of size fraction(reduction 1050 °C for 4 hrs)(4.5.2)

US Sieve No	Total iron	$Fe_{(met)}$	Degree of Reduction
100	39.08	31.45	80.50
140	40.20	33.56	83.50
200	44 67	37.30	87.91

Table- 7 Variation of total iron of as received and reduced size fractioned ilmenite (reduction 1050 °C for 4 hrs)(4.5.2)

US Sieve No	%of total iron in as received ilmenite	%of total iron in reduced ilmenite
100	39.08	44.67
140	40.20	45.07
200	42 44	49.14

Table-8 Chemical analysis of fractionated reduced sample (reduction 1050 °C for 4 hrs)(4.5.2)

Fractionated Amp	TiO_2 %	%Fe_{Tot}	Fe_{Met}	% of reduction
0 10	43.96	45.78	40 65	86.79
0.15	43 01	45.01	38 56	84.67
0.20	42.01	44 67	32 89	76.03
0.25	39 19	40.20	26 25	63.29
0.30	38 23	33 50	21 54	58.32

Table-9 Extent of reduction (% of reduction) of as received and pre-oxidized reduction of different size fractionated ilmenite (reduction 1050 °C for 4 hrs)(4.5)

US Sieve No	% of reduction (as received)	% of reduction (Pre- oxidized)
100	80.50	82.50
140	83.50	88.69
200	87.91	89.60

Table-10 Extent of reduction (% of reduction) of pre-oxidized) and as received fractionated ilmenite (reduction 1050 °C for 4 hrs)(4.5.4)

Fractionated Amp	% of reduction (as received)	% of reduction (Pre- oxidized)
0.10	86.79	89.00
0.15	85.67	86.44
0.20	78.03	79.90
0.25	63.29	67.00
0.30	58.32	60.49

Table-11 Chemical analysis of reduced ilmenite (reduction 1050 °C for 0.5,1.0,2.0,3.0,4.0 hrs)(4.5.4)

Temp ° C	Time hrs	%Fe_{Tot}	Fe_{Met}	% of reduction
1050	0.5	45.78	36.74	80.25
1050	1.0	44.67	37.74	84.45
1050	2.0	44.67	38.41	85.98
1050	3.0	46.90	38.75	82.62
1050	4.0	44.67	39.31	88.00

Table 12 Chemical analysis of pre-oxidized reduced ilmenite as a function of time and temp(4.5.4)

Temp ° C	Time hrs	%Fe_{Tot}	Fe_{Met}	% of reduction
1050	0.5	45.78	36.74	80.25
1050	1.0	44.67	37.74	84.45
1050	2.0	44.67	38.41	85.98

Table 13 Chemical analysis of reduced ilmenite as a function of time and temp(4.5.3)

Temp °C	Time hrs	%Fe_{Tot}	Fe_{Met}	% of reduction
900	0.5	33.50	17.42	52.00
900	1.0	37.97	25.57	67.00
900	2.0	45.91	27.92	66.81
900	3.0	48.07	32.49	67.59
900	4.0	45.84	34.17	74.54
950	0.5	44.67	34.75	77.79
950	1.0	44.67	34.98	78.30
950	2.0	44.67	36.96	82.78
950	3.0	44.67	37.89	84.82
950	4.0	44.67	37.96	84.97
1000	0.5	44.67	32.16	71.99
1000	1.0	44.67	36.85	82.49
1000	2.0	44.67	39.08	87.48
1000	3.0	44.67	40.09	89.74
1000	4.0	44.67	40.20	89.99
1050	0.5	45.78	36.74	82.24
1050	1.0	44.67	37.74	84.48
1050	2.0	44.67	38.41	85.98
1050	3.0	46.90	38.75	86.74
1050	4.0	44.67	39.31	88.00

Table-14 Chemical analysis of pre-oxidized reduced ilmenite as a function of time and temp(4.5)

Temp °C	Time hrs	%Fe_{Tot}	Fe_{Met}	% of reduction
1050	4.0	44.67	39.31	89.00

Table-15 Chemical analysis of pre-oxidized fractionated reduced sample (reduction 1050 °C for 4 hrs)(4.5)

Fractionated Amp	TiO_2 %	%Fe_{Tot}	Fe_{Met}	% of reduction
0.10	45.87	45.78	40.74	89.00
0.15	43.96	44.67	38.61	89.44
0.20	43.00	44.67	35.69	79.90
0.25	41.09	44.67	29.02	67.00
0.30	38.23	44.67	27.02	60.49

Table-16 Chemical analysis of pre-oxidized fractionated reduced sample (reduction 1050 °C for 4 hrs) after leaching

Fractionated Amp	%FeO	%Fe_M	%Fe_{tot}	%Removal
as received	1.23	Nill	2.51	97.49
0.10	1.23	Nill	1.70	98.30
0.15	1.22	Nill	1.55	98.45
0.20	1.11	Nill	1.11	98.89
0.25	0.90	Nill	0.90	99.10
0.30	0.25	Nill	0.25	99.75

Table-17 Chemical analysis of pre-oxidized size fraction reduced sample (reduction 1050 °C for 4 hrs) after leaching

US Sieve No	%FeO	%Fe_M	%Fe_{TOT}	%Removal
as received	1.23	Nill	2.51	97.49
100	2.23	Nill	14.29	85.71
140	1.56	Nill	13.90	86.10
200	1.22	Nill	13.10	86.90

LEACHING

Table- 18 Percentage removal of iron vs. reduction time of ilmenite sample(Sample reduced at 1050°C,4h leaching time 1h at20% HCl at 75°C)(4 6)

Reduction time hr	Fe_{tot}% In the reduced sample	Fe_{met} in the Leached sol^n	% of iron removal
2	44.67	43.55	97.49