Characterization of Ilmenite of Cox's Bazar Heavy Mineral Deposit

By

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Dedicated to my Parents

Md. Nurul Islam Bhuiyan

Mrs. Tahera Islam

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ABSTRACT

Ilmenite and rutile are natural sources of TiO_2 and titanium metal. Rutile, naturally occuring pure TiO_2 is preferred to ilmenite as a raw material. Due to rapid decrease in supply of rutile, the necessity of alternate sources of rutile cannot be overemphasized. As a result, investigations are being carried out throughout the world on the upgradation of low-grade ilmenite to rutile. Consequently, it has become necessary to identify the best possible route for the upgradation of ilmenite to what is known as synthetic rutile.

Ilmenite may contain main minerals like hematite, magnetite etc in its structure. Natural weathering of ilmenite results in the increase in the TiO_2 content of ilmenite with increasing time of weathering. So detailed investigation into the extent of weathering of ilmenite of a particular placer deposit is essential not only for the qualitative assessment of the deposit but also to improve the technique of production of synthetic rutile.

Samples of ilmenite containing 24.4 per cent FeO, 33.0 per cent Fe_2O_3 and 39.5 per cent TiO_2 were collected from the Beach Sand Exploitation Center, Kalatli, Cox's Bazar. The samples were then subjected to magnetic and size fractionation. The phases present in the different fractions (both magnetic and size) were identified by X-ray diffractions analysis. The chemical compositions of the different magnetic and size fractions were determined by wet chemical analysis. The fractions were reduced for 4 hour at 1050^{O}C by equal amounts of charcoal. The extent of reduction was followed by chemical analysis of the reduced mass for metallic iron. The results obtained were supplemented by X-ray diffraction analysis and optical microscopy.

Samples of the different magnetic fractions and size fractions were oxidized for two hour at 900^{O}C and were reduced under otherwise identical conditions. The effects of the oxidation on the extent of reduction were followed by the determination of metallic iron content of the reduced samples. The effect of addition of 10 per cent

Na_2CO_3 on the extent of reduction of the different fractions (both before and after oxidation) under otherwise identical conditions were also investigated.

From the chemical analysis, it was found that Cox's Bazar ilmenite is characteristically similar to Moheskhali ilmenite. Presence of alteration products of ilmenite, particularly pseudorutile, could not be detected in the X-ray diffraction patterns of any of the six magnetic fractions of this deposit. Attempts were also made to detect the presence of water and hence the presence of pseudorutile by thermogravimetric analysis. Thermogravimetric analysis did not show any significant change of weight near about 600^0C for any magnetic fraction. Mineralogical study has also been carried out. The results of these investigations led to the conclusion that Cox's Bazar ilmenite has not undergone alteration to any significant extent.

This study also concentrated upon the reduction behavior of the different magnetic fractions as well as upon reduction behavior of different size fractions. It has been concluded that separate reduction procedures for the different fractions (either magnetic or size) is not necessary.

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INTRODUCTION

1.1 Introduction

Titanium is the 9th most abundant element in the earth's crust and account for about 0.93 per cent of all the element found in nature. The chief mineralogical occurrences of titanium are as oxides, titanates and silicotitanates. The titanates, highest in iron and lowest in acid forming oxides yield iron titanates like ilmenite and arizonite. The most important commercial titanium bearing minerals are ilmenite and rutile. The alteration products of ilmenite, known as leucoxene and arizonite, are widely distributed in nature. Major deposits of ilmenite and rutile are located in Australia, Canada, Norway, USA, India, Malaysia, and Ceylon.

Ilmenite is a heavy mineral with a metallic luster and is usually referred to as ferrous titanate, it has a specific gravity of 4.5 to 5 and crystallizes in the rhombohedral class of the hexagonal system. The color is usually iron black. Brown and red varieties are also known. It is opaque and slightly magnetic. The composition of ilmenite theoretically corresponds to $FeO.TiO_2$ or an equivalent of 52.6 per cent TiO_2 However, in most cases the ferrous iron is partly replaced by ferric iron. The individual grains of ilmenite may contain submicroscopic inclusions of rutile, a mineral when pure consisting essentially of TiO_2 with very small quantities of iron. Others grains may also be altered, resulting in the breakdown of ilmenite structure with the partial leaching and oxidation of the iron. This can increase the alteration products of ilmenite to 60 per cent or more. Leucoxene is the name applied to the TiO_2 content of ilmenite high in titanium and is always present to some extent in beach sands. The grains that have been highly altered and consist of almost entirely of leucoxene may contain as high as 80 per cent TiO_2. Small quantities of leucoxene may contain as an acceptable substitute for rutile.

Rutile is essentially naturally occurring TiO_2 and deposits are relatively rare. Even though the supplies of rutile have increased, the deposits are fast depleting and demands outstrip supplies. This shortage of nature rutile has forced technologists

throughout the world to develop processes to enhance the titanium content of ilmenite for use as a substitute for scarce natural rutile. The enriched ilmenite is known as synthetic rutile.

1.2 Commercial Uses of Ilmenite

Ilmenite is used in the manufacture of titanium dioxide pigment. TiO_2 has unique properties of high refractive index, low specific gravity, chemical stability, high hiding power, light fastness, non-toxic nature and compatibility and has now replaced all other white pigments like zinc oxide, white lead and zinc sulfide.

Ilmenite is a source of titanium metal. Due to its extreme resistance to corrosion, high strength to weight ratio and high fatigue resistance at high temperature titanium is used as a structural metal. For example titanium is used in supersonic transports, in desalination systems, and in chemical process industries, as a material for reaction vessels, pipes, pumps, heat exchangers, etc.

Rutile, leucoxene, and ilmenite are used for coating welding rods. Natural rutile is preferred to ilmenite for this purpose but synthetic rutile is an acceptable substitute. 0Ilmenite is used in the preparation of high gloss finishes in ceramic industries. It is also used in the manufacture of electrical insulators, brilliant white pigment, in the production of white rubber, and as filler for paper.

Ilmenite is also used to produce titania rich slag, which is an ideal feed material in the existing titanium dioxide plants. The attractive feature of this process is that pig iron is also produced along with the slag. This ensures the full utilization of the valuable constituents of ilmenite. The important uses of ilmenite as well as its products are summarized as follow:

Ingredient Uses

Titanium Dioxide: Paints, plastics, printing inks, paper, leather cosmetics, vitreous enamels, synthetic gems, etc.

Titanium Tetrachloride: Water proofing paints, adhesive promoter, polymerization catalyst, titanium metal. etc.

Titanium Metal: Corrosion resistant alloys, chemical process industries, spacecraft, heat exchangers, shipbuilding, structural metal, etc.

Synthetic Rutile: Welding rods, raw material for chloride route of titanium extraction, titanium dioxide extraction, etc.

The products of commercial importance give a broad idea of the attractive avenues open for the utilization of ilmenite. There is a wide and growing gap between demand and supplies of titania rich raw materials in the world. The shortage of natural rutile has forced technologists to develop processes to produce titania-rich materials to be used in place of natural rutile.

1.3 Methods of Upgrading

Ilmenite contains titanium oxide (TiO_2) and iron oxide (FeO). It may also contain other oxides such as Fe_2O_3, SiO_2 and trace elements (Al, Mn, Cr etc). The techniques of upgradation of ilmenite involve preferential removal of iron. Some of these techniques are now being exploited on a commercial scale and a few are undergoing trial in pilot plants. Most methods are, however, still confined to the laboratory. The existing techniques of upgradation are based on the following five principles [1-4].

Smelting

A pyrometallurgical technique involves heating with metallurgical or petroleum coke and flux, at high temperature (> 1500^0C) to get molten iron and titania rich slag containing most of the gangue material. This slag layer is to give further treatment. The process can be represented as follows:

Ilmenite + Coal + Flux ⟶ Pig iron + Titania rich slag + Carbon monoxide.

Smelting a mixture of ilmenite pellets, coke and lime in an electric arc furnace also produces synthetic rutile. The slag obtained is tapped at 1600^0C and treated with O_2 and phosphate glass. The treated slag is then ground and leached with H_2SO_4 to dissolve the phosphate glass and to obtain rutile crystal.

Reduction Followed by Removal of Iron

In these processes, the iron oxide present in ilmenite, either in ferrous or in ferric form are converted to lower oxide or to metal so that they can be separated by leaching with a suitable leaching solution. Coal, hydrogen, charcoal, coconut pith etc. have been used as reducing agents. Reduction temperatures in the range of 1000^0- 1100^0C are usually employed. Iron is then removed from the reduced mass by leaching, rusting or magnetic separation[1-2].

HCl acid and $FeCl_3$ solutions are commonly used to leach out iron from reduced ilmenite Leaching is usually carried out at atmospheric pressure, higher pressures have also been used. These methods produce synthetic rutile containing 85-95 per cent TiO_2.

Direct Acid Leaching

In the direct leaching of ilmenite sulfuric acid and hydrochloric acid is commonly used. Digestion with conc. sulfuric acid is not selective and brings both the iron and titanium oxides in solution but subsequent processing of leach liquor yields pigment grade Titania. On the other hand digestion with hydrochloric acid is essentially selective and only iron oxide is brought to solution. The product obtained is synthetic rutile which requires further processing to get pigment grade titania.

Leaching of ilmenite in hydrochloric acids has also been attempted at higher pressures. It has been found that leaching at atmospheric pressure is less efficient and the product is of inferior quality. High-pressure leaching[3] under suitable conditions can produce a product containing more than 98% TiO_2.

Conversion of Iron and/or TiO_2 in Ilmenite to Leachable Product

Conversion to Titanate

Ilmenite is treated with Na_2CO_3 at elevated temperatures (900^0-1100^0C) to obtain sodium titanate according to the following reaction:

$$FeTiO_3 + Na_2CO_3 \longrightarrow Na_2TiO_3 + FeO + CO_2$$

The sodium titanate is leached out with water and subsequently with dilute acid resulting in a product containing 93% TiO_2 [1].

Conversion to Sulfate

Both iron and titanium in ilmenite can be converted to their respective sulfates by treating with $(NH_4)_2SO_4$ at 300-500^{0}C or $NaHSO_4$ at 400-800^{0}C. About 90% Fe and 95% Ti of ilmenite can be recovered by leaching with 7N H_2SO_4. Titanium oxide (TiO_2) is separated from leach liquor by controlled hydrolysis.

Conversion to Sulfide

The preferential sulphidisation of iron in ilmenite is possible in presence of some sulfur bearing material such as ZnS, Na_2SO_4+C, and sulfur vapor. Heating of a mixture of ilmenite, Na_2SO_4 and carbon at 1000^0-1300^{0}C results in the formation of FeS.

$$Fe\ TiO_3 + Na_2SO_3 + 2C \longrightarrow FeS + Na_2\ TiO_3 + 2CO_2.$$

The reaction product is treated with boiling H_2SO_4 to yield a titania rich product. Synthetic rutile is also prepared by heating the ilmenite at 500-1000^{0}C in sulfur vapor in absence of oxygen. The product is cooled in absence of oxygen and leached with water and oxygen at 20-100 psi. The product is rutile aggregate, soluble sulfur and ferric hydroxide sludge. Ilmenite can also be beneficiated by treating at 100^{0}C with any gaseous sulphidising medium like H_2S, CS_2, H_2S +CS_2 mixture for 2 to 3 hours followed by leaching with dilute HCl acid for half hour resulting in a titania rich product.

Halogenations

These processes are based on the selective conversion of iron to iron halides by treatment of ilmenite with a suitable halogenating agents such as Cl_2, HCl gas, Cl_2+HCl, Cl_2+H_2, H_2+HCl, CO+Cl_2, C+Cl, NH_4Cl, Br_2, etc. The residue left after treatment is synthetic rutile.

a) Chlorinating With Cl_2

Ilmenite is mixed with a carbonaceous reducing agent and chlorinated at 850-950^{0}C to produce iron chloride and titanium tetrachloride. Titanium dioxide is obtained from titanium tetrachloride by hydrolysis.

Selective chlorination of ilmenite has also been carried out in two steps at two different temperatures to effect the separation of both iron and titanium chloride. In this process, the ore is mixed with coal or charcoal and heated in the absence of air at 800^{0}C and then cooled in reducing atmosphere to 350^{0}C. At the same time dry chlorine gas is passed through the reducing mass. In this stage only iron is attacked and the ferric chloride vapor is condensed in a cooling chamber. The direction of flow of chlorine vapor is then reversed and temperature is maintained at 550^0-600^{0}C. In this stage titanium compounds are attacked and resulting titanium tetrachloride vapor is condensed in the cooling tower. Some investigators [51,52] have investigated preferential chlorinating of iron oxide in ilmenite. Ilmenite with charcoal (6%) and $FeCl_3$ binder and then treated with chlorine at 500^0-600^{0}C. This processes results in a product containing about 90% TiO_2. The rate of chlorinating is reported to be faster in presence of some catalysts like CuO, PbO, MnO_2, CaO, CeO and $Ca_3(Po_4)_2$. CeO is found to be the best catalyst among them. Chlorination with $CO+Cl_2$ has been carried out in fluidized bed at 900^0- 1000^{0}C and a product containing 95-98 per cent TiO_2 has been obtained[53,54].Tianium dioxide has also been prepared by the selective chlorination of ilmenite with gaseous mixture of Na and Cl_2 in a chlorinator with a certain amount of air or oxygen[54, 55].

b) Chlorinating With HCl Gas

In a laboratory scale production a product containing 97% of TiO_2 has been obtained[57] by selective chlorinating of ilmenite at 1000^{0}C for 3 hours. Preoxidized ilmenite was found to require higher temperatures for effective removal of iron. However, no solid $FeCl_2$, which causes experimental difficulties in conducting chlorinating, was found when peroxide samples were used for chlorinating. When the

percentage of H_2 in the gas mixture of HCl and H_2 is increased, the percentage of iron chlorinated is decreased and the condensate mainly consists of $FeCl_2$. In presence of air $FeCl_3$ is obtained and the total iron chloride is decreased. Partial chlorinating of ilmenite is a fluidized bed reactor by H_2 and Cl_2 mixture results in high grade TiO_2 (80-95% TiO_2) product[58].

A product containing with 90% TiO_2 and 6.6% Fe_2O_3 has been obtained[59] by selective chlorinating of ilmenite with a mixture of $TiCl_4$ and Cl_2 at a temperature of 1050^0C. Treatment of ilmenite with NH_3 and HCl at 600^0C removes about 92% of iron. At a temperature of 800^0C all the iron is removed[60,61]. A product containing about 96% TiO_2 has been obtained by treating a mixture of ilmenite and powdered coke (1%) in a kiln at 800^0-900^0C with a gas mixture of Br_2 and N_2 or Br_2, N_2 and CO_2[17]. The $FeBr_3$ formed is cooled and passed into a cyclone where $FeBr_3$ separates as powder

1.4 Ilmenite Deposits in Bangladesh

Heavy mineral deposits along the coastal belt of Bangladesh constitute a potential national asset. The exploration, exploitation, development and uses of these resources are essential for upliftment of national economy. Beach Sand Exploration Center explored 17 deposits along the entire southeastern and southern coasts of Bangladesh and the adjacent islands. Among these deposits 6 deposits are located along the Cox`s Bazar and Teknaf coasts (Badramokam, Sabrang, Teknaf, Shikhali, Inam and Cox`s Bazar), 7 deposits on Moheshkhali Island (Foreshore deposit, Kutubjum, Fakirghona, Fakirhata, Baroghoria Para, Panichara and hoanak), 1 deposit on Matarbari Island and 1 deposits on Kutubdia Island, Fig 1.1 shows the map of these areas. Only two deposits have been found in the southern coast of the country, 1 in Nijhum Dwip of Hatia and 1 in Kuakata of Patuakhali district. Most of these deposits occur as low linear ridges and dunes standing just above the clay-rich paddy fields at a distance of about 1-2 miles inland from the present shoreline. A total of 2, 04, 96, 981 tons of crude sands containing 43, 54, 501 tons of heavy minerals are available in the deposits in which ilmenite content is 10, 25, 558 tons (Table-1.1).

Table -1.1 : Summary of heavy mineral reserves in the deposits along the coastal belt of Bangladesh.

SL No	Deposit	Sand Tonnage	Heavy Mineral Tonnage	Reserve of valuable minerals (in ton)							
				Zircon	Rutile	Ilmenite	Leucoxene	Kyanite	Monazite	Magnetite	Garnet
Main Coast.											
1	Badarmokam	1,765,000	411.000	4,932	3.288	94,530	18,002	-*	4,932	10.275	-*
2	Sabrang	347,558	68,582	4,184	1,372	19.614	3.470	727	206	1 001	3,018
3	Teknaf	1.939,580	442,291	28,306	13.230	163.170	20 124	14,728	3 045	7,209	22,424
4	Silkhali	2,756,828	489,714	33,300	10.774	173,360	10,970	4,407	3,918	3.085	39,422
5	Inani	729,286	175,476	10,880	4.036	53,170	439	1,404	965	5.545	12.810
6	Cox's Bazar	5,119.000	920,000	23.000	6 440	161,000	10,488	-*	2,024	33.212	50.600
7	Kuakata	2,872,486	831,668	9.647	3.911	76,015	9,647	16.800	83.2	4,325	52.229
Moheshkhali Island											
8	Fore-shore beach	276,560	119.480	7,145	3,788	54,961	2,891	Trace	131	824	-*
9	Kutubjum	577,980	106.240	4,568	2,104	36.440	1,158	2,635	202	1,169	-*

SL	Deposit	Sand	Heavy	Reserve of valuable minerals (in ton)							
No		Tonnage	Mineral Tonnage	Zircon	Rutile	Ilmenite	Leucoxene	Kyanite	Monazite	Magnetite	Garnet
10	Fakiraghona	273,940	68,460	1,513	1,458	15,746	952	5,006	55	288	4,655
11	Fakirahata	409,120	96,750	5,515	3,970	22,157	3,677	9,579	194	97	5,998
12	Baraghoriapara	888,440	181,770	6,017	6,744	52,168	6,416	13,815	927	1,236	11,815
13	Panirchara	1,595,410	204,390	12,264	6,479	60,091	5,519	16,351	531	3,863	13,490
14	Hoanak (Nalbila)	92,780	7,120	100	153	1,400	69	110	4	127	-*
15	Materbari	69,030	15,215	794	295	4,962	374	Trace	20	575	-*
16	Nijhum Dwip	379,337	96,348	2,052	424	12,978	77	2,592	19.3	4,384	-*
17	Kutubdia Island	404,656	119,997	3,900	1,908	23,796	2,436	2,592	96	3,384	6,300
	Total:	20,496,981	4,354,501	158,117	70,274	1,025,558	96,709	90,746	17,352.5	80,599	222,751

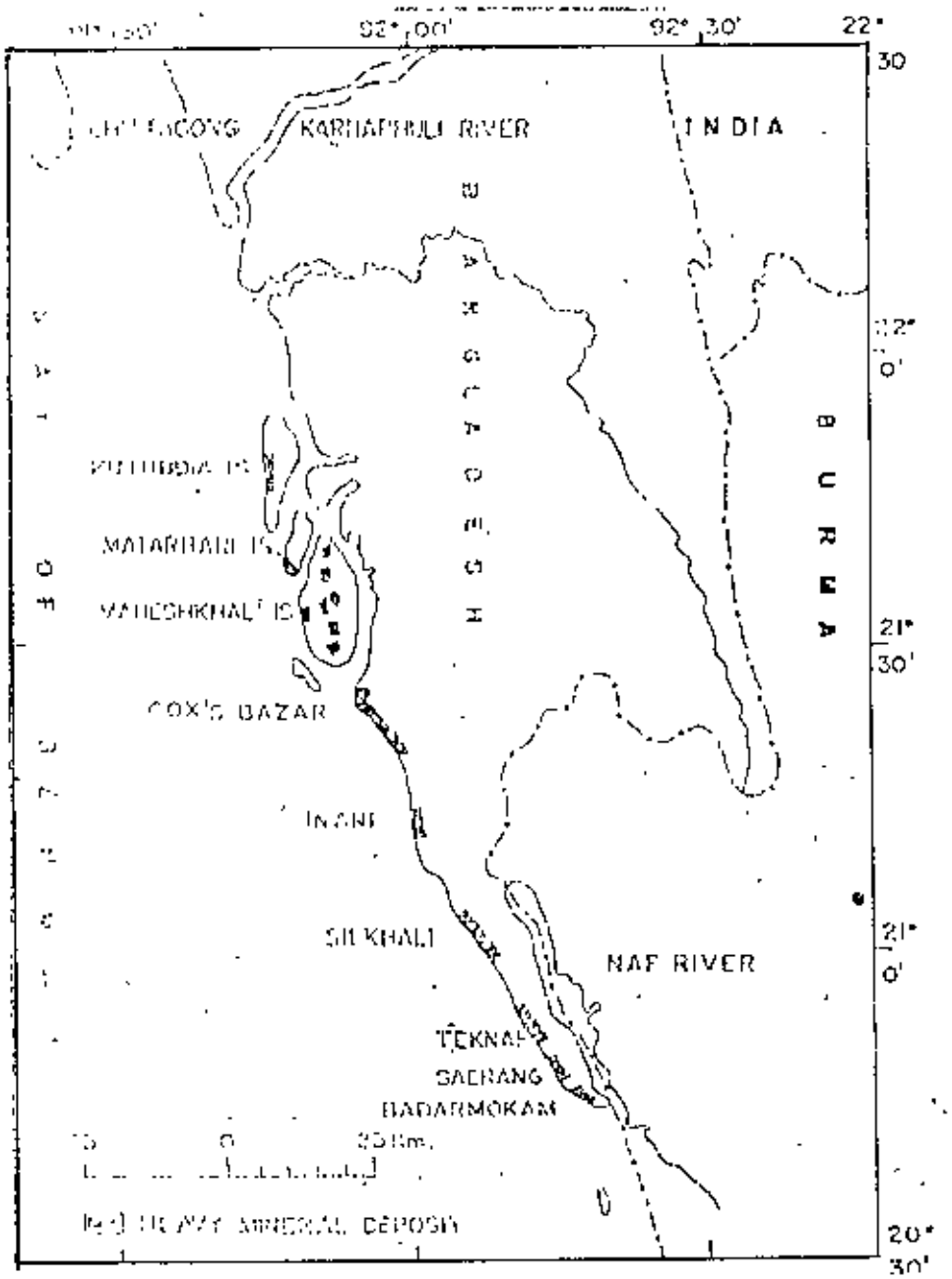


Fig: 1.1: Map Showing Location of Heavy Minerals Deposits Along the Southern Coast of Bangladesh.

1.5 Beach Sand Exploration Center

Beach sands containing valuable heavy minerals were first detected in 1961 during a geological survey for radioactive minerals in Cox's Bazar beach area. The exploration drilling began in 1968 under joint supervision of External Affairs Ministry of Australian Government and bulk sample from Cox's Bazar was sent to Mineral Deposits Limited (MDL), Australia, for testing. In 1970 initial plans for a pilot plant were drawn up on the basis of MDL flow sheets and recommendations. In 1973, Bangladesh requested the Government of Australia to build a pilot plant at Cox's Bazar. The plant came in operation in 1975. The activities of the plant remained suspended from 1987 to 1991, and the center started functioning again in 1992. The plant has successfully separated several hundred tons of ilmenite with some other heavy minerals.

Separation of Heavy Minerals in Cox's Bazar Pilot Plant

The pilot plant separates individual minerals from the heterogeneous mixture. The techniques of separation are based on the difference in physical properties like density, specific gravity, electrical and magnetic properties. Heavy minerals in original samples are plotted to show the lateral and vertical variations in heavy minerals contents and provide demarcation of the rich sands from the poor one. Cox's Bazar Pilot plant has two sections for the separation. Primary separation is done by a wet method and then a dry method is applied for the final separation. Slurry of raw coastal deposits and water is pumped into a gravity spiral to separate the heavy mineral from the light one. Separated heavy sand is then passed through dewatering cone to remove water, to attritional to clean the surface and then passed over a drum magnet to separate magnetite. These magnetite free heavy minerals are then shaken in the Wilfley Table from where the dense minerals are collected as table concentrates and sent to the dry section.

In the dry section the mineral is first fed into a high-tension electrostatic separator. It produces the conductor and nonconductor fractions. The conductor fractions are passed through cross belt magnetic separator where ilmenite and rutile are separated. The detailed flow sheet of the pilot plant is shown Fig 1.2 and Fig

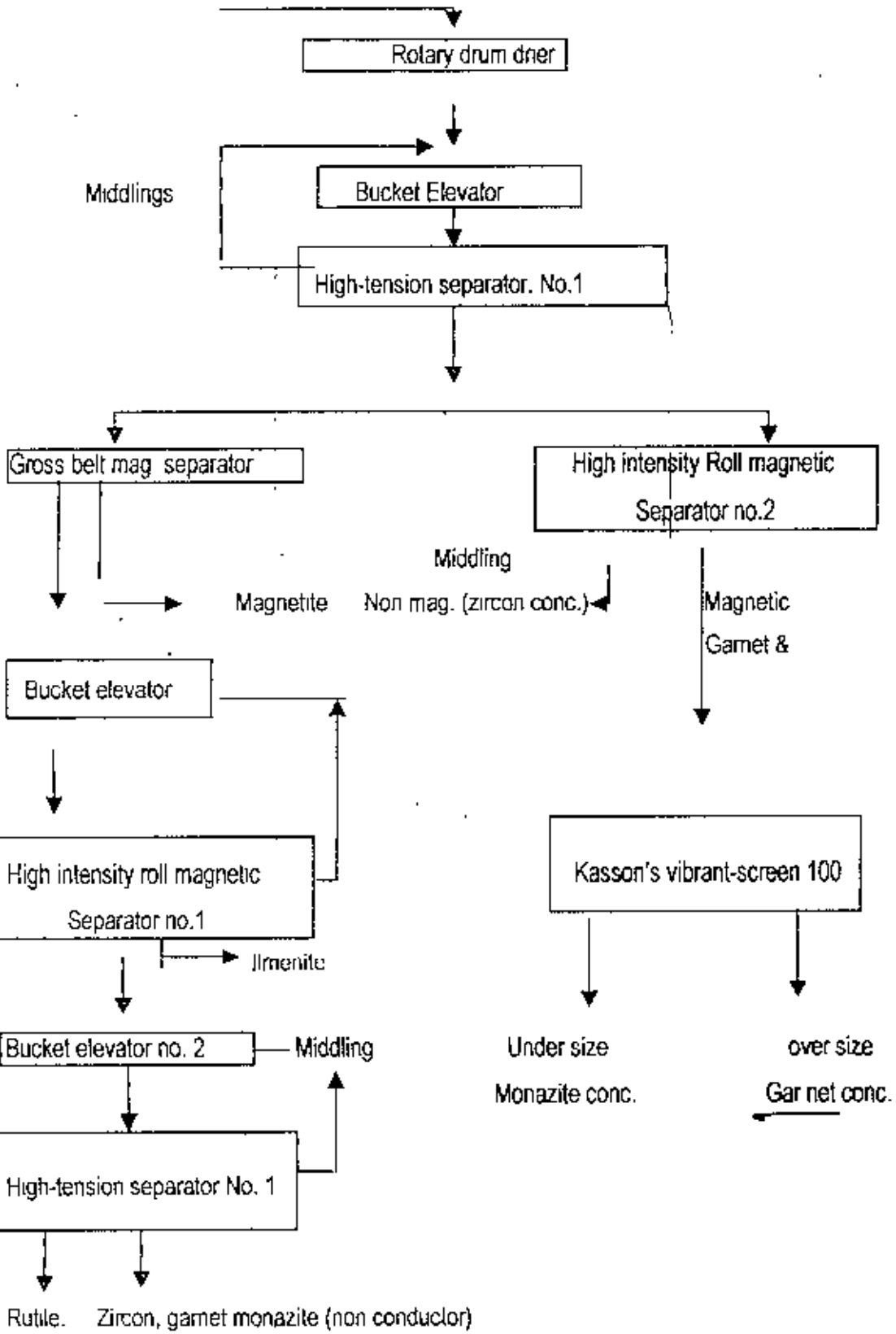


Fig 1.2 The Pilot Plant Flow Sheet (Dry Section)

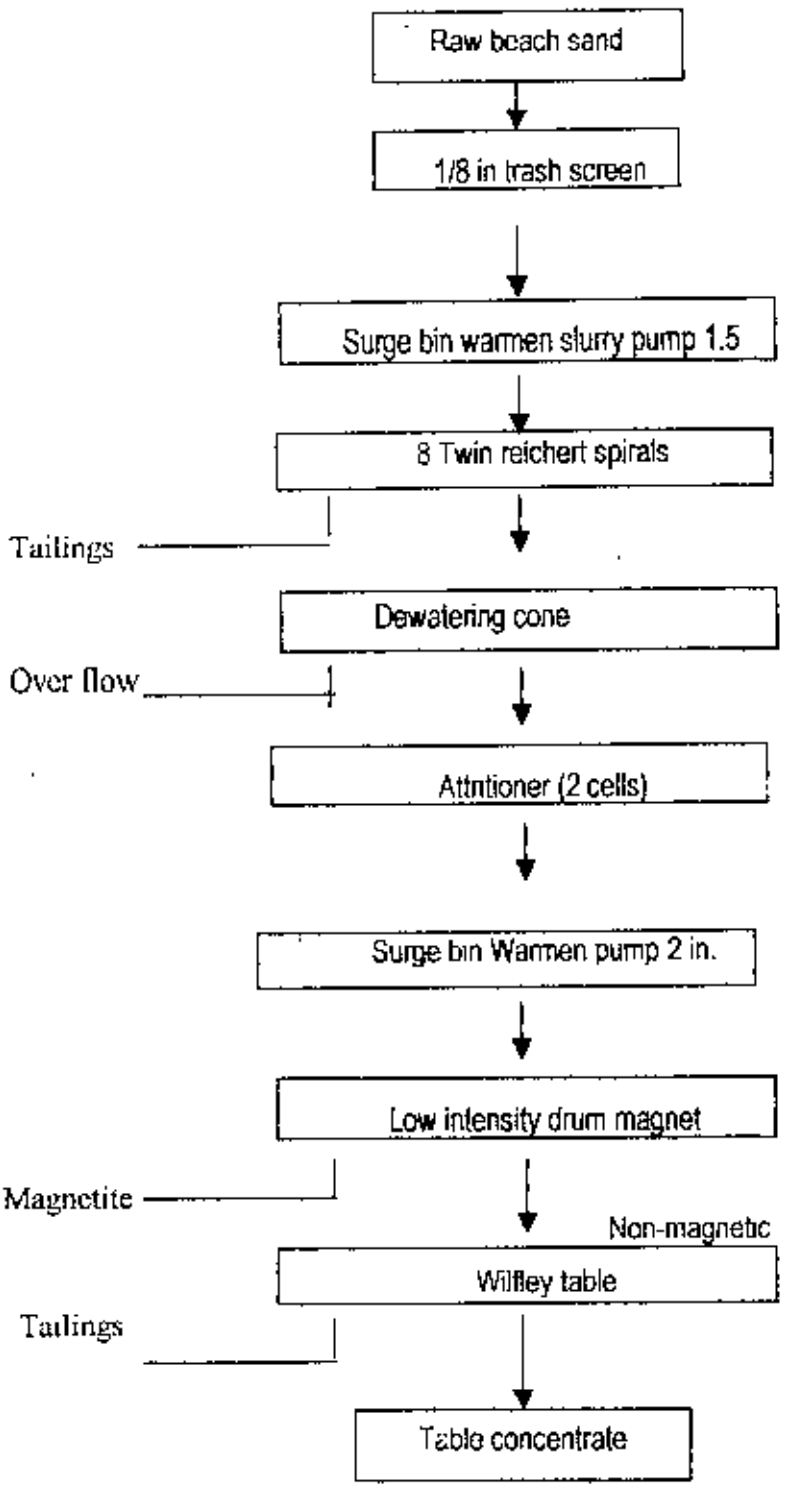


Fig 1.3 The Pilot Plant Flow Sheet (Wet Section)

1.6 Advantages and Disadvantages of the Processed Developed

The relative merits and demerits of the processes that have been developed so far are shown below:

Process	Advantages	Disadvantages
Halogenations:	1. Rutile of high purity can be obtained. 2. Selective chlorination is cheap.	1. Chlorine is highly corrosive. 2. Special reactive vessel lining is required. 3. High temperature is required. 4. Reaction conditions are not flexible and hence must be precise.
Reducing and Leaching	1. It can be exploited commercially. 2. Reductant is coal or charcoal, which are cheap and temperature required is generated by the reductant itself. 3. Reduction can be carried out on large scale using rotary kiln. 4. The process is flexible and can be made continuous. 5. Spent acid and Fe_2O_3 can be recovered. 6. Rutile with minimum Fe content can be prepared. 7. Recovery of TiO_2 is possible.	Only limitation is it is multistage process.

Process	Advantages	Disadvantages
Fusion Method	1. Ferrous material converted to pig iron as bi-product. 2. It also produces less corrosive waste material.	Not exploited on a commercial scale 1. High temperature is required for fusion. 2. Alkali used are corrosive 3. Energy input is high. 4. Fusion in large quantity is difficult. 5. High cost of chemicals 6. Recovery is not satisfactory. 7. Multistage process is involved.
Direct Leaching	1. Single stage process 2. Can be operated at low temperature. 3. Reagent costs are comparatively low.	1. Leachants are highly corrosive. 2. Special materials are required for construction of vessels. 3. Long leaching time is required. 4. In many cases extent of benefaction is low.

1.7. Prospects of Bangladesh Ilmenite

Due to lack of other mineral resources the best utilization of the heavy minerals found in the coastal belt is very important for the economy of Bangladesh. At present Bangladesh imports titania for paper mills, paint industries, and for other industries like welding electrodes, plastics, rubber, textiles, synthetic fibers, etc. Under these circumstances a process for the extraction of titanium dioxide from Bangladesh ilmenite, will go a long way to fulfil the needs of the domestic industries. The excess, if any, may find some suitable market outside the country.

1.7.1. Scope of the Present Work

At the Pilot plant at Cox's Bazar the heavy minerals are separated on the basis of their physical properties such as the specific gravity, electrical conductivity, magnetic properties, etc. These methods allow the separation of heavy minerals from the beach sands but they are not suitable for the separation of impurities, which are intimately mixed or chemically combined with the individual minerals.

Chemical analysis performed at the laboratories of the Department of Materials and Metallurgical Engineering at BUET, Dhaka and also at the Regional Research Laboratory, Trivandrum, India has shown that the ilmenite separated at the pilot plant at Cox's Bazar contains only about 40 percent titanium-di-oxide. Ilmenite containing less than 55 percent titanium-di-oxide is not considered suitable for industrial use. Thus the ilmenite separated from the beach sands of Bangladesh has to be processed further to remove the chemically combined useless minerals before it can be sold in the market. Unfortunately the pilot plant at Cox's Bazar is not equipped with such facilities.

This project is a part of the work now in progress at the Department of Materials and Metallurgical Engineering at BUET, Dhaka, which aims at the development of a technique for the upgradation of ilmenite separated from the beach sands of Bangladesh. The work done in the department so far has yielded encouraging results and the TiO_2 content of Bangladesh ilmenite could be raised to about 92 per cent. Reduction of ilmenite in the as-received condition followed by leaching was used for the production of synthetic rutile.

The present work involved the characterization of ilmenite of Cox's Bazar deposits. Detailed characterization of Cox's Bazar ilmenite concentrate has been studied. Reduction behavior at different size and magnetic fractions has also been studied.

The economic benefits expected from this project are by-fold. First, the characterization will help comparison of this ilmenite with the world-class deposits and the second, it will help to find out the optimum process parameters for the production of synthetic rutile from the deposits of ilmenite in Bangladesh.

CHAPTER-2 LITERATURE REVIEW

2. Introduction:

Ilmenite and rutile are the most abundant minerals containing titanium. Concentrated ilmenite obtains titanium rich product. Various processes for the beneficiation of ilmenite have been developed and some of the methods are now being exploited on a commercial scale. The literature, on the work that has been performed through out the world may be divided into four parts that is magnetic fractionations study, reduction study, oxidation study and the study on the alteration techniques.

2.1 Magnetic Fractionation

Mineral separations by magnetic fractionation are normally made by arbitrary adjustment of the current of the electromagnet and the transverse slope of the chute of the isodynamic separator until the most suitable splitting is obtained. At any such setting the separator divides a sample into two fractions determined by the settings. The less magnetic fraction consists of particles of susceptibility below this value. With suitable calibration Frantz Isodynamic separator will accordingly provide absolute measurements of the specific susceptibility of mineral grains.

Theory of Magnetic Separation

The inclination of the chute is measured by the transverse slope θ^0 set by the left – right axis on the separator, and the longitudinal slope I^0, which is set on the front – to – back axis and is measured in the plane of the magnet face inclined at θ^0 to the vertical as shown Fig.2.1

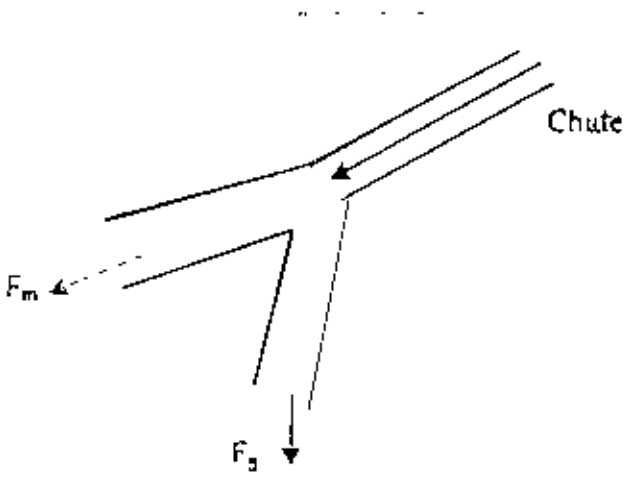


Fig: 2.1: The Forces That Act on a Particle to Move It Down the Chute of the Frantz Isodynamic Separator.

The forces in the plane of the chute, which act on a grain to move it down the chute, are shown in Fig 2.1. A force F_g down the direction of maximum slope is due to gravity, and a magnetic force F_m acts at right angles to the length of the chute.

The magnetic force F_m on particular grain sliding without change in orientation is constant for any one electromagnet current, regardless of the position of the particle on the chute. On a paramagnetic particle of mass m gram and specific susceptibility Φe.m.u. per gram in the direction across the chute the force due to the magnetic field is

$$F_m \quad \Phi\ m\ \frac{dH^2}{dx} \text{ dynes} \text{ ---------- (1)}$$

as given in standard texts[1], where H oersted is the magnetic field strength at a distance x cm across the chute. A constant value of Fm at any current for all positions across the chute requires $\frac{dH^2}{dx}$ being constant, a condition determined by

the appropriate shape of the pole pieces. Increase of $\frac{dH^2}{dx}$ with increasing current produces an increase in F_m.

The component F_g across the chute of the gravitational force is

$$F_g = m.g.\sin T \text{ dynes} \quad \text{----------} \quad (2)$$

Where g is the gravitational constant, and is of magnitude 980 cm per sec^2.

When Fg is greater than Fm the grain slides toward the lower side of the chute, and for Fg less than Fm the grain is pulled to the upper side of the chute. The critical combination at which Fg equals Fm, and the resultant force F on the particle is parallel to the length of the chute.

At this setting, by equating equations (1) and (2)

$$\frac{\sin T}{\Phi} \quad \frac{1}{g}.\frac{dH^2}{dx} \quad \text{----------} \quad (3)$$

and the grain moves directly down the chute without being pulled toward either side. The action of the separator on a single particle, by this relationship, is determined solely by the specific susceptibility of the particle in the direction of transverse slope, and is independent of both the mass and density of the particle. In actual operation, however, cleaner separations are obtained from sized products, in which the interaction between grains and their speed of movement down the chute is more uniform. The magnitude of the term $\frac{1}{g}.\frac{dH^2}{dx}$ is for any one instrument determined by the current in the electromagnet. It is readily evaluated for various values of current, as $\frac{\sin T}{\Phi}$, by determining critical combinations of transverse slope and current for materials of known susceptibility. Measurement of the magnetic field strength across the chute is not required.

The relationship of magnetic field strength to the current is predictable from the characteristics of this type of magnetic circuit. When the electromagnet is operated not too close to saturation of the core, the magnetic field strength at any position on the chute will increase with current at about the same rate. At higher currents the rate

of increase field strength will decrease relative to the rate of current increase as the core approaches saturation. Therefore $\frac{1}{g}.\frac{dH^2}{dx}$ may be empirically expressed as $k.i^n$, where n is a constant close to 2 and k has a constant value at low currents, and one or both decrease slightly at higher currents.

The relationship (3) above thus becomes

$$\frac{\sin T}{\Phi} = k.i^n \qquad \text{---------- (4)}$$

The most sensitive magnetic separation is obtained by using the highest practicable current and transverse slope, and lowest practicable longitudinal slope.

Calibration of the Machine

Three inorganic compounds, ferrous ammonium sulphate, $Fe(NH_4)_2(SO_4)_2.6H_2O$, nickel sulphate,$NiSO_4.6\text{-}7H_2O$, and cupric sulphate, $CuSO_4.5\ H_2O$, are selected for the calibration. These substances have the specific susceptibilities, which enable much of the range of the electromagnet current to be used, and they show no appreciable range of susceptibility on the separator. Magnetic susceptibility of these standard materials is given in table2.1. The value used here are recommended and supported by Dodd, Robinson, Jackson et-al.[1-2]

Table: 2.1 Magnetic Susceptibility of Standard Substances:

Substance (Chemical Formula)	Magnetic Susceptibility (X 10^{-6} e.m.u.per gm)	Temperature (°C)	Critical Current (Amp)
$Fe(NH_4)_2(SO_4)_2.6H_2O$	32.4	20	~0.45
$NiSO_4.6\text{-}7H_2O$	15.8	20	~0.66
$CuSO_4.5\ H_2O$	5.88	20	~1.09

Experimentally it was found that all materials were magnetically separated at their respective current value. So we may conclude that the calibration was correct. Then using the following condition ilmenite samples were separated out for different current value, ranging from 0.15 to 0.4 amps.

Experimental conditions are shown below.

Condition of separation:
Transverse angle = 15^{O}C
Longitudinal angle = 25^{O}C
Vibration (max) =10 unit
Feed = 100 gm

2.2 Oxidation of Ilmenite

It is generally agreed that the purpose of oxidation roasting is to i) convert iron in ilmenite from ferrous to ferric state which overcomes different ferrous to ferric iron ratio ii) Alter equilibrium condition and the rate of reduction from ferric to ferrous state and iii) introduce of defects in ilmenite grains to enhance the rate of subsequent reduction. Ramdohr [63] and Overhault et al [64] found from X-ray diffraction patterns that ilmenite when heated in air at 900^{0}C yielded pseudobrookite and rutile. D.G. Jones[8] found that oxidation product of ilmenite over 800^{0}C yielded ferric pseudobrookite and rutile and according to data given by Webstar and Bright[14] ferric pseudobrookite in commercially oxidized Western Titanium ilmenite contains approx. 4%, Fe^{2+}.

Cumow and Parry[65] studied the oxidation of ilmenite from beach sand of Australia by magnetic susceptibility and X-ray diffractometry and concluded that i) heating of ilmenite to 600^{0}C enhances magnetic susceptibility and X-ray pattern gives lines similar to ilmenite and rutile. ii) Prolonged heating at 800^{0}C results in the formation of weakly ferromagnetic material and Debye Scherrer X-ray photograph of this material gives lines due to rutile and indicate the formation of new product with tetragonal lattice symmetry.

Karkhanawala and Momin[45] studied the oxidation of ilmenite and concluded that:

- The products of oxidation of ilmenite is weakly paramagnetic and for products heated for equal periods the magnetic susceptibility decreases with increasing temperature.

- ξ The products of oxidation at around 650^0C contain mixture of hematite, rutile and an unidentified phase. At 850^0C the oxidation products contain a mixture of hematite, pseudobrookite and rutile in an approximate ratio of 1:5:7 respectively.
- ξ There are three distinct regions of oxidation: 100^0 – 450^0C, 540^0-800^0C, and 800^0-900^0C. The oxidation over first region is very slow.

Later investigations [18,20,47,66] indicated the formation of Fe_2O_3 as an alteration product when ilmenite is oxidized at temperature between 600^0C to 800^0C. Results regarding the products of oxidation of ilmenite up to 800^0C are conflicting. Various results obtained by different investigators are given below:

1. $2FeTiO_3 + ½\ O_2 = Fe_2O_3 + 2TiO_2$
2. $3FeTiO_3 + ¾\ O_2 = Fe_2Ti_3O_9 + ½\ Fe_2O_3$
3. $2FeTiO_3 + ½\ O_2 = Fe_2O_5 + 2TiO_2$
4. $12FeTiO_3 + 3O_2 = Fe_2O_3 + 5FeTiO_5 + 7TiO_2$

But reaction 4 could occur only under, metastable condition.

Rao and Rigaud[62] calculated the free energy changes for the above reactions. They found that the standard free energies over a specified temperature range is favorable for both reaction (1) and (3). Thus either or both reactions may take place up to the decomposition of Fe_2O_3 or Fe_2TiO_3 or Fe_2TiO_5. The free energy change for the formation of pseudobrookite from its oxides is also favorable and reaction (3) takes place in preference to reaction (1) and (4).

Akimoto et al[66] found that higher temperature and longer time is required for the formation of pseudobrookite from their oxides and the lower temperature limit for the formation of oxides at lower temperature is slow which might prevent the formation of pseudobrookite.

Rao and Rigaud[62] also performed thermogravimetric and differential thermal analysis of ilmenite prepared by mixing Fe_2O_3, Fe and TiO_2 in the required ratio. Their general observations of the thermogravetric analysis in both oxygen atmosphere and air are as follows:

- ξ An abrupt weight gain is observed when particle size is less than 200 meshes and it is difficult to observe a break in the thermogram. In case of very fine particle reaction is complete before temperature 800^0C is reached.
- ξ An inflection in thermogram could be noticed at around 770^0C when particles of 100 mesh size or more were used and a heating rate $10^0 min^{-1}$ was employed.
- ξ Up to 100^0C, the reaction products were identified as pseudobrookite and rutile. Any other product formed at low temperature e.g. hematite and rutile and rutile react to from pseudobrookite above 900^0C.

They summarized the differential thermal analysis results as follows:

- ξ The first stage of oxidation starts at 100^0C is exothermic and ended around 770^0C.
- ξ The stage is endothermic and ended around 890^0C. Because of the larger peak it is difficult to assess ending of reaction but definitely this step continues up to 870^0C.
- ξ A third exothermic reaction sets in at around 900^0C.

Differential thermogravimetric curves showed that weight gain is not a linear function of time and decreases with time at any given temperature. The rate of reaction of time and decreases with time at any given temperature is, to some extent, compensated by corresponding decrease due to lapse of time. As a result DTG curves slopes very little. Around 800^0C this transition may be due to a temperature gradient created as exothermic reaction changes to endothermic reaction. A change of reaction profile may also lead to such distribution.

Product Morphology

In the gas solid reaction a dense film of reaction product is usually formed on the surface of the solid and the rate is determined by the migration of ions or electrons through the product layer. One might expect that the reaction product may be uniform but recent investigations provided evidence of discontinuous formation of

product especially at early stage of reaction. Fischemeister [69] reviewed and discussed the subject; he also considered the influence of product growth of crystal. The morphology of the product of ilmenite is important and influences the subsequent leaching of the oxidized ilmenite. The mechanism of growth of whiskers is not well established. Hardy[72] suggested that screw dislocation in metals causes the oxide to grow as whiskers This concept assumes that the continuation of dislocation in the metal into the oxide layers serves as nucleation site for growth of oxides. However it has also been proved[49] that in a system in which more than one oxide is stable the whiskers grows from the lower oxides[74, 75] Nabrro-Herring mechanism suggests that the grain boundaries under stress might supply the necessary current of reactant storms required for the formation of whiskers.

This is particularly true at high temperature where chemical potential variations between different spot on the surface are small. At high temperature and at enough oxygen pressure, the product particle grows randomly. Conditions favorable for the formation volatile sub-oxides may also lead to the formation of whiskers[76,77] although thermodynamic calculation indicates is oxidized at 850^0C Fe_2O_3 segregates at grain boundaries in the shape of a columnar crystal aggregates surrounding pseudorutile phase.

The growth morphology of products can also influence significantly the kinetics of gas solid reaction. The whisker growth only affects[69]. The kinetic in the early stages and before the product reaches appreciable thickness. The kinetic data of the oxidation of ilmenite reported elsewhere[80] is also in agreement with this hypothesis. Rao and Rigaud[62] found logarithmic rate law of oxidation in initial stage and suggest that it is due to penetration of oxygen through short circuit path. Oxidation is otherwise parabolic. They found one break in Arhenius plot corresponding to reaction (1) and (3) and could not distinguish the range of reaction (2). They suggested that this may be due to short range of range of reaction (2) or due morphological effect of the reaction (2) and (3) might be controlled by the same or similar mechanism.

Mechanism of Reactions

Actual mechanism for the formation of products of different textures is not known and the data related to the diffusion rate and conductivity of reactants and the products are also not available. Wort and jones [81] studied the alteration of ilmenite and suggested that it takes place in two different stages.

Stage 1. $3FeTi^{+2}TiO_3 + 2H^+ + 1/2\ O_2 \longrightarrow Fe_2^{3+}Ti_3O_9 + Fe^{+2} + H_2O$

Stage 2. $Fe_2Ti_3O_9 + 2H^- \longrightarrow 3TiO_2 + 2F^{++} + 2H_2O + 1/2\ O_2$

Teufer and Temple [47] established a disorder structure – transition phase between rutile and ilmenite and formulated the alternation of ilmenite as chemical reaction in which number of oxygen atom in ilmenite essentially preserved in pseudorutile and rutile.

$$3FeTiO_3 \longrightarrow FeTi_3O_9 + 1/2\ Fe_2O_3$$

By heating pseudorutile above 800^0C pseudobrookite is formed.

$$Fe_2Ti_3O_9 \longrightarrow Fe\ TiO_5 + 2TiO_2.$$

Rao and Rigaud[62] upon their extensive study on the oxidation mechanism and product morphology provided some tentative upon the general reaction mechanism. During oxidation at temperatures below 770^0C Fe_2O_3 formed on the surface and when the surface of ilmenite is covered by Fe_2O_3 oxygen diffuse through the product layer [82] and further reaction takes place at $Fe_2TiO_3 - Fe_2O_3$ interface and the diffusion rate of O_2 in Fe_2O_3 and Fe_2TiO_3 is low.

They found $Fe_2Ti_3O_9$ to be stable at temperatures from 770^0 to 900^0C where iron will diffuse through it to the grain boundaries. This suggested that iron is mobile through pseudorutile. Pseudorutile has the highest titanium oxide content and there is possibility for the formation of solid solution with Fe_2O_3 leading to the formation of Fe_2TiO_5 allowing iron to diffuse. Since a showed temperature limit exists for the formation of Fe_2TiO_5, Fe_2O_3 is precipitated. At temperature greater than 900^0C, TiO_2 is formed on the surface and mobility of titanium increases. When the sample is heat treated above 950^0C the initial whiskers of Fe_2O_3 formed on surface of the samples at 750^0C is transformed to pseudobrookite. The movement of titanium is confirmed by

the fact that when ilmenite is oxidized with markers at 950^{0}C, TiO_2 was formed above markers. The markers were covered with rutile at particular locations of the crystal. This is assumed due to rapid diffusion to Ti through certain preferred orientation of ilmenite. But the orientation favorable for diffusion of ilmenite was not confirmed due to its polycrystalline nature. The mobile Ti will leave some excess O_2, which in turn could be utilized in the oxidation step or escape to the gas stream. They found a central pore in each grain as well as in the center of TiO_2 structure. They suspected that oxygen might have escaped from this portion. Their tentative mechanism of oxidation is given in Fig. 2.2.

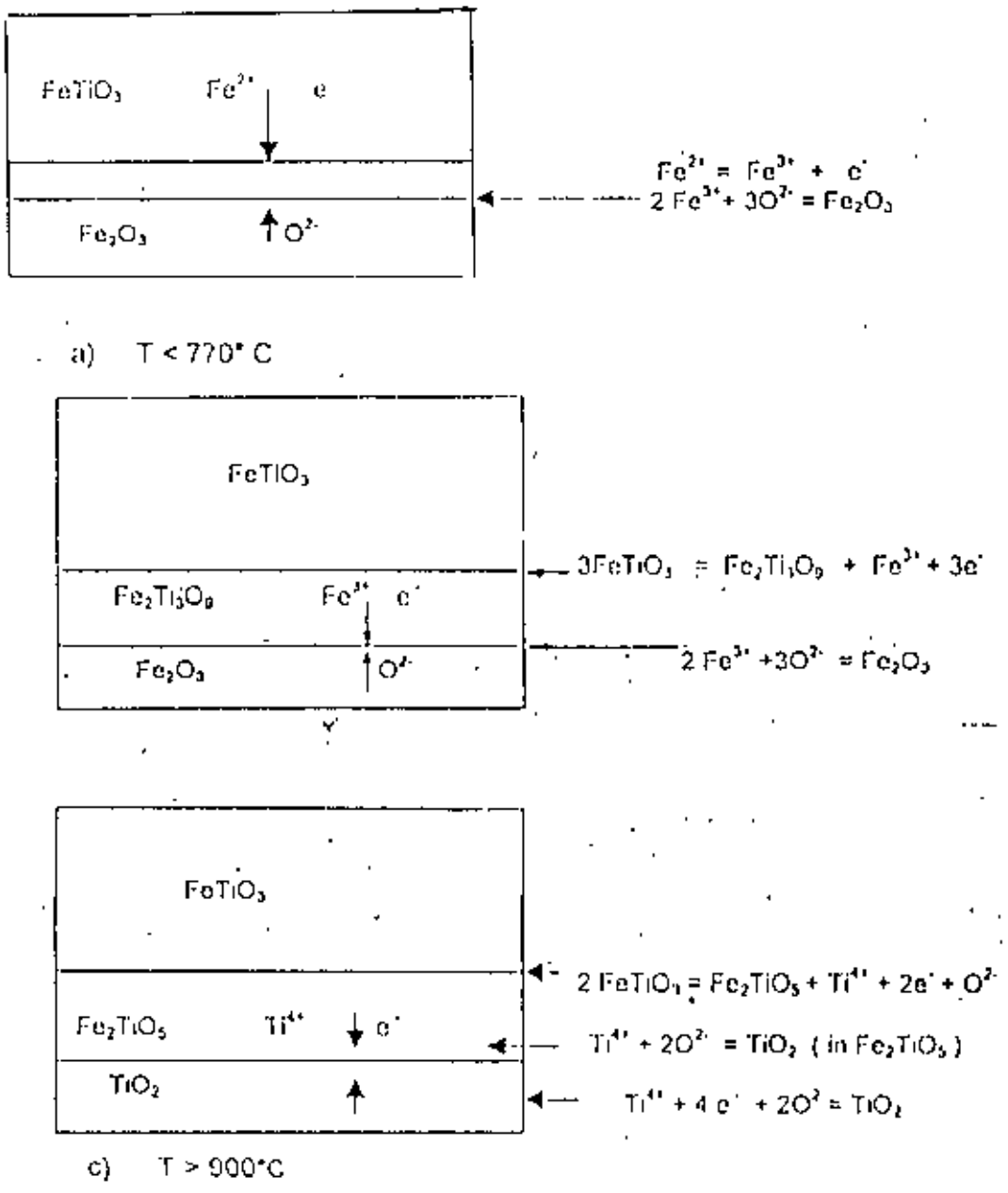


Fig 2.2 Schematic Representation of Proposed Mechanisms of Oxidation.

2.3 Reduction Behavior

Among the different methods of upgradation the solid-state reduction of oxides of iron in the ilmenite involving a suitable reducing agent and subsequent leaching in acid solid solution of iron present in the reduced mass of ilmenite is the most important. The processes consist of the following stages.

Stage-1: Reduction.

Stage-2: Removal of metallic iron.

Stage-1: Reduction

This stage involves the reduction of oxides (both ferrous and ferric) of iron to metallic iron. From the Ellingham diagram, it is apparent that the stability of titanium oxide is much higher than that of the oxides of iron and cannot be reduced by carbon at temperatures around 1100^0C. Thus when ilmenite is heated by mixing it with carbonaceous fuel (charcoal) at temperatures a 950^0C-1150^0C, iron oxide is reduced to metallic state, but the titanium oxide remains unchanged. Thus iron oxide can be theoretically reduced to metallic form without changing the titanium oxide.

Since both oxides of iron and titanium are more stable than their corresponding metals, metallic iron can easily be dissolved into hydrochloric acid and therefore the titania content can be increased.

The reduction occurs in two stages At the initial stage of reduction pseudorutile is rapidly converted to ilmenite and rutile.

$$Fe_2O_3.xTiO_2 + C/CO \longrightarrow xFeO.TiO_2 + CO/CO_2.$$

This reaction involves the conversion of ferric iron to ferrous iron. At the later stage the iron oxide is reduced to metallic iron.

$$xFeO.TiO_2 + C/CO \longrightarrow xFe.TiO_2 + CO/CO_2.$$

A number of workers[6,7] have studied the reduction of ilmenite using different reducing substances. These studies have shown that carbon or graphite is more effective as a reducing agent[6]. Reduction behavior of Cox's Bazar ilmenite studied by Haseeb, et al[7] using charcoal as reductant has also shown that solid carbonaceous

substance is the suitable reducing element. Reduction is controlled by the diffusion process and is accelerated as the temperature increases. They observed that solid state reduction initiate at temperatures near 860^0C at contact points between the reactants. The solid-state reduction is the main reaction mechanism at temperatures of up to 1020^0C. Above this temperature a rate increase has been observed and the mechanism was found to have changed to reduction by gaseous CO generated by the reaction between carbon of charcoal and oxygen. The reactions that occur during the reduction of ilmenite by charcoal summarized as follows.

Solid-State Reaction

$$C + FeTiO_3 \longrightarrow CO + Fe + TiO_2.$$

This reaction initiate at a temperature near about 850^0C at point of contact between reactants and proceeds as long as their remains contact point between the reactants.

Gaseous Reaction

$$CO + FeTiO_3 \longrightarrow CO_2 + Fe + TiO_2.$$
$$C + CO_2 \longrightarrow CO$$

The overall thing is governed by the availability of gaseous reductant, CO that is produced by the Boudouard reaction. The reactivity of the solid reactant is very important because it affects both the reduction rate as well as the operating temperature.

According to D.G. Jones[8] the reduction of naturally weathered and pre-oxidized sample proceeds in two district stages. First stage is the rapid re-formation of ilmenite Fe^{3+} compounds in the sample according to the reactions mentioned below:

$$Fe_2TiO_9 + CO \longrightarrow 2FeTiO_3 + TiO_2 + CO_2$$
$$Fe_2O_3 + 2TiO_2 + CO \longrightarrow 2FeTiO_3 + CO_2$$

In the second stage the proportion of ilmenite progressively diminishes with corresponding increase in the metallic iron and rutile

$$FeTiO_3 + CO \longrightarrow Fe + TiO_2 + CO_2$$

In case of solid carbonaceous reductant there are a number of ways to increase the reduction rate. Prior oxidation transforms ilmenite ($FeTiO_3$) to pseudobrookite ($FeTi_2O_5$), which results in substantial cracking and lattice expansion[9]. This cracking and expansion enables the subsequent reduction to proceed at both an accelerated rate and to a greater extent without much sintering. Thus, oxidation of ilmenite prior to reduction has a beneficial effect on the rate of reduction. Another effective way is to use a suitable carbonate[10]. The carbonate ensures an adequate supply of CO gas, it enhances the rate of reduction reaction. Size fractions also play an important role during reduction. It was previously found that finer size fraction of Cox's Bazar deposit contains lower percentage of TiO_2 and it showed the maximum degree of reduction[11].

Stage-2: Removal of Iron

Selective leaching of ilmenite by mineral acid removes[3,12] iron from ilmenite. In direct acid leaching both sulfuric and hydrochloric acid have been used as leachant. Digestion with conc. H_2SO_4 is not selective and brings both iron and titanium oxide to solution but subsequent processing of leach liquor yields pigment grade titania. On the other hand digestion with hydrochloric acid is selective[3,12] and only iron is brought to solution. Direct acid leaching is carried out at somewhat higher temperature. The preferential chlorinating of iron with hydrochloric acid gas is represented as

$$FeO.TiO_2 + 2HCl \longrightarrow FeCl_2 + TiO_2 + H_2O$$

The standard free energy[13] for the reaction as a function of temperature is shown below

$$\Delta F^0 = -81420 + 0.99\ T \log T + 7.4T\ (298 - 1640^0K)$$

From the thermodynamic data[13] it may be seen that the reaction is possible even when more than 99% H_2O is present in the mixture. It should be mentioned that the above reaction is complex and a side reaction of $FeCl_2$ with steam would take place in a gaseous mixture containing steam and HCl gas. It is also apparent form this thermodynamic data[13] that chlorinating of Fe_2O_3 is not possible at the normal

chlorinating temperature. Therefore the possibility of the following reaction can be ignored

$$^1/_3\ Fe_2O_3.TiO_2 + 2HCl \longrightarrow {}^2/_3\ FeCl_3 + {}^1/_3\ TiO_2 + H_2O$$

Pre reduced ilmenite reaction with HCl will lead to the formation of less volatile $FeCl_2$. Iron in reduced ilmenite is dissolved by dilute acid even at room temperature but complete removal of iron may require higher temperatures and pressures and longer time. Fe_2O_3 and FeO to metallic iron can be leached out with dilute HCl at lower temperature and in a short period[14]. The leaching reaction of ilmenite can be expressed as

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2.$$

FeO, if present, in ilmenite can be removed by following reaction.

$$FeO + HCl \longrightarrow FeCl_2 + H_2O.$$

TiO_2 present in the ilmenite may be converted to $TiCl_4$ according to following reaction

$$½\ TiO_2 + 2HCl \longrightarrow {}^1/_2\ TiCl_4 + H_2O.$$

The free energy change[14] for this reaction is represented as

$$\Delta F^0 = -7765 - 1.08\ T \log T + 18.8\ T$$

Which shows that this reaction in not possible above 523^0K

Different investigators worked on this selective leaching and got almost similar results. Mohan Das et al[13] studied leaching of the ilmenite using $FeCl_3$ solution and they found a product of 2% Fe and 92.6% TiO_2. Annie et al[15] also found leached product containing 2% Fe while in Murso process[16] reduced ilmenite, leaching with 20% HCl at 108-110^{0}C, produced 95-97% TiO_2.

2.4 Alteration of Ilmenite

Beach placer ilmenite concentrates of the world show significant variation in the degree of alteration that is independent of provenance. Differential weathering of ilmenite after its release from the country rock and natural mixing of fresh and

altered grains during migration impart complexity to the placer deposit. Various minerals have been identified as weathering products of ilmenite. Alteration of ilmenite, $FeO.TiO_2$ in nature undergoes the process of oxidation and progressive removal of iron to give a residual product that is essentially TiO_2. Alteration is initiated along grain boundaries and structural discontinuities within the grain.

Oxidation and partial removal of iron from ilmenite lattice results in an intermediate iron titanate of definite structure for which the name pseudorutile has been proposed. Another alteration product, leucoxene is found in the ilmenite deposit. The alteration product at the stage of complete oxidation of iron in ilmenite analyzes 65-70% TiO_2 as compared with the 52% TiO_2 in ilmenite[17]. Complete removal of iron from the pseudorutile lattice results in a grain composed of crystallites of the mineral rutile. Only four mineral phases[18] ilmenite, pseudorutile, leucoxene and rutile have been identified in the commercial titanium mineral concentrates studies. Natural occurrence, in sand deposits, indicates that in weathering final removal of iron from pseudorutile to give the rutile end product takes place only either above or in the zone of fluctuating water table.

2.4.1 Alteration Products of Ilmenite

Several attempts have been made to characterize the sequence, mechanism, depth and products of alteration. The important alteration indicators[19] are changes in Fe^{2+} / Fe^{3+} and Fe/Ti ratios, variations in magnetic susceptibility, density, hardness and reflectivity, structural and morphological changes, increases in impurities like Cr and V and decreases in Mn, Ni, Zn, Cu, Mg, Co and Ca[20-22]. The difference in the degree of ilmenite alteration in various heavy mineral placer deposits implies differential weathering due to age difference and / or in situ and multistage alteration of ilmenite[23]and also due to different weathering environments. In nature, progressive alteration of ilmenite results in the formation and co-existence of different phases.

Moreover positive identification of all altered phases is difficult because of indistinct and similar structural as well as physical properties. There is also considerable uncertainty in their individual respect. Lynd[24] reviewed the literature on titanium minerals and pointed out the importance of knowledge of the chemical composition

(% TiO_2, % FeO, % Fe_2O_3), and concluded that the term leucoxene should be used as a general name for alteration products containing TiO_2. On the other hand Golding[25] presented the petrography, as opposed to the commercial, viewpoint and pointed out the range of rock types where ilmenite and its alteration products occur. So analyzing these different opinions it is clear that the initial product is ilmenite and leucoxene is the end product of the alteration process. According to Mucke et. al[26]. During the transformation of ilmenite to leucoxene following products can be identified:

Ilmenite ⟶ Hydrated Ilmenite ⟶ Pseudorutile ⟶ Leached Pseudorutile ⟶ Leucoxene

From this analysis it may be concluded that three distinct phases ilmenite, pseudorutile and leucoxene may be present in the altered ilmenite. No standard nomenclature exists for the alteration products of ilmenite, but roughly following characteristics are generally found[23]

Ilmenite

Unaltered ilmenite is the dominant mineral. When altered, ilmenite has changed directly or though the intermediate products to leucoxene. Unaltered ilmenite grains with a composition close to the theoretical formula ($FeTiO_3$) and a TiO_2 content ranging between 48-53 percent. Although varying in intensity and pattern from grain to grain, the most common alteration grains boundaries and fracture, crystallographic directions.

Hydrated Ilmenite

This is also known as leached ilmenite that 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 color and weaker anisotropism. The term "hydrated ilmenite" was first used by Dyadchenko & Khatuntesva[27] and was adopted by Frost et. al[28] to indicate the mixture of ilmenite and pseudorutile which contain

crystalline water while the term "leached ilmenite" was used by Mucke et. al[26] and Chernet[29] to identify a distinct intermediate leaching product between ilmenite and pseudorutile.

Pseudorutile

A deformed[30] hexagonal, oxyhydroxide close to $Fe_2Ti_3O_9$ or $Fe_{1.5}Ti_3O_{7.5}(OH)_{1.5}$ with an extended range of homogeneity due to hydrogen exchange for iron during hydration[27]. Characteristically it shows rough and porous texture. Compared to ilmenite, it appears brighter, in contrast to its typical grayish color. Under reflected light isotropic pseudorutile is blue-gray in color with a slightly higher reflectance than ilmenite[23]. Pseudorutile is developed along crystallographic orientations, in ordered or disordered patterns, along boundaries and fractures, and is characterized by the development of micro fractures. The mineral is difficult to identify positively as these optical properties are indistinct and its major XRD peaks exhibit d spacing similar to those of ilmenite, rutile and hematite.

Leached Pseudorutile

It is another optically identifiable intermediate phase[26,29] lying between pseudorutile and leucoxene. This results from leaching of iron from pseudorutile. It is difficult to distinguish leached pseudorutile form iron poor members of pseudorutile merely by color impression and reflectance. The abundance of micro fractures led to the breakdown of the pseudorutile structure.

Leucoxene

A single grain of secondary rutile or aggregates of fine-grained rutile crystals mixed with impurities. It is an inhomogeneous cryptocrystalline, high TiO_2 product of ilmenite alteration[20]. Leucoxene displays abundant internal reflections, changes from brownish to white with the decrease in iron content. Replacement of ilmenite and the intermediate phases by secondary rutile of definite crystal structure is common. Leucoxene is distinguished optically from rutile or anatase by its characteristic sugary internal reflections although it may consist almost entirely of crypt or microcrystalline rutile and/or anatase in the last stages of reflections[23].

Primary Rutile

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

2.4.2 Main Schematic Textures of Ilmenite

The main texture of alteration (Fig 2.3) of the ilmenite through the grain is given below.

a) Alteration of ilmenite along grain boundaries and fracture lines, b) pseudorutile, with dense pattern of fine oriented leached holes, which was originally hemo-ilmenite, c) dense and oriented pattern in leached ilmenite showing the removal of iron in a regular way, d) progressive oxidation and leaching of grains resulted in the formation of oriented pseudorutile, e) development of micro cracks with the formation of pseudorutile phases, f) Intense alternation of ilmenite along grain boundaries and fractures, g) aggregates of fine rutile crystals hosted by leached ilmenite, h) ilmenite grains rimmed by leucoxene, and a leucoxene grain at the lower right corner.

2.4.3 Mechanism of Alteration of Ilmenite

Different mechanisms of alteration of ilmenite have been proposed by different investigators[16-30] These mechanisms can be classified as follows:

Type-1: Gradual weathering of ilmenite to leucoxene via hydrated ilmenite and pseudorutile in a groundwater environment.

Type- 2:The direct weathering of ilmenite to leucoxene in sediments above the water table.

Type- 3:The alteration of ilmenite to hematite plus rutile or anatase in source rocks, followed by the preferred dissolution of the hematite to form ilmenite grains containing a porous network of TiO_2 microcrystal.

Type –1 Alteration

Many authors[18-30] described this mechanism in their own way. According to this mechanism alteration begins as irregular patches of hydrated ilmenite along grain boundaries and weaknesses within the grain, or in the from of oriented stringers along the basal cleavage planes of the ilmenite. The second stage of alteration is marked by the development of leucoxene, which forms as irregular patches along grain boundaries, or structural weakness. The development of leucoxene along grain boundaries is less common than expected for the in situ alteration of ilmenite[23]. This type of alteration may be explained by the two-stage model proposed by Grey & Reid[20]. The first stage involves the oxidation of all the ferrous iron and the leaching of one third of the ferric iron from the ilmenite lattice by electrochemical corrosion. The reaction is:

$$3Fe^{2+}TiO_3 + 2H^+ \div 1/2\ O_2 \longrightarrow Fe_2^{3+}Ti_3O_9 + Fe^{2+} \div H_2O \text{ ---------- (1)}$$

Ilmenite — Pseudorutile — Dissolved Iron

This reaction is considered to operate in 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 redeposit whilst the iron is leached from the grain. This leads to the formation of rutile in beach sand and anatase in lateritic soils and can be described by the reaction:

$$Fe_2Ti_3O_9 + 4H^+ \longrightarrow TiO_2 + Fe^{2+} + {}^1/_2O_2 + H_2O \text{ ---------- (2)}$$

Pseudorutile — Rutile (or Anatase) — Dissolved Iron

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

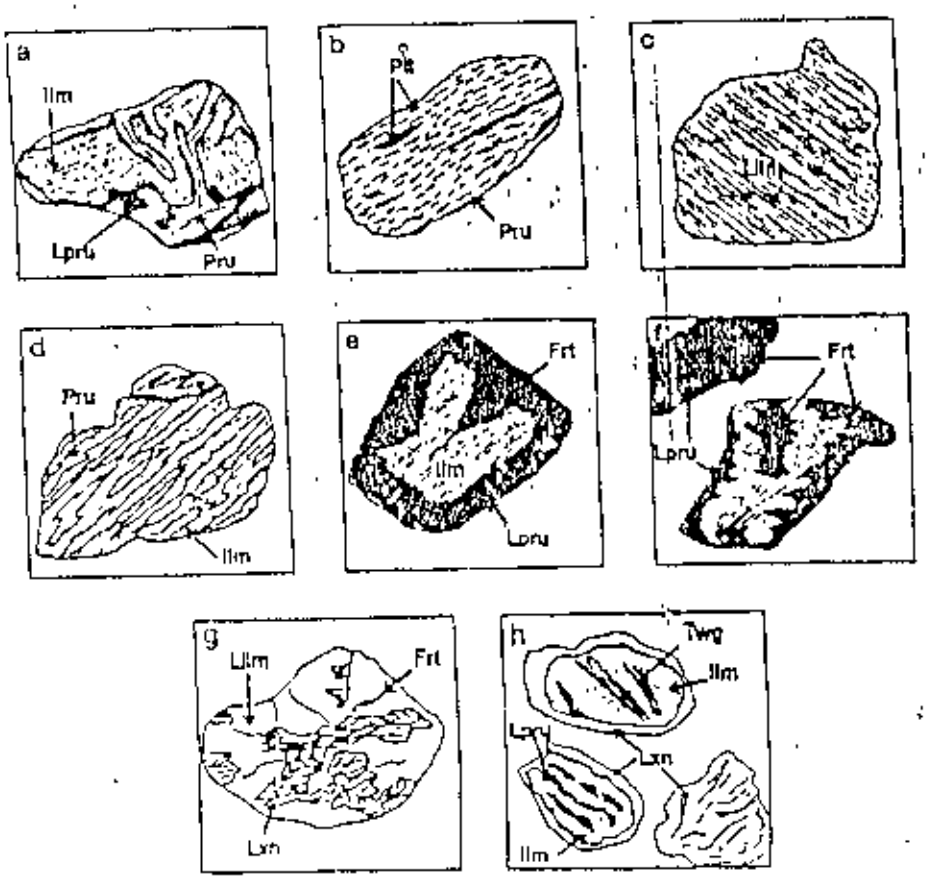


Fig. 2.3 : Alteration of Ilmenite

Type 2 Alteration

In this type of alteration, ilmenite, or slightly altered ilmenite, is observed altering directly to leucoxene. The alteration occurs form grain boundaries Fig2.3(A), or along weaknesses, such as fractures Fig 2.3(B & C) within the grains. In some instances leucoxene may grow as replacement fronts across grains Fig 2.3(D) or may mimic the original crystallographic directions of ilmenite grains Fig 2.3(E). The boundary between the ilmenite and leucoxene may consist of a porous area of cellular or microcrystalline leucoxene, indication that is volumetric replacement has occurred. SEM analyses indicate that the pores in these areas have silica and aluminum contents well in excess of 10 per cent.

Fig 2.4(A): Back Scattered Electron Image of Leucoxene Replacing Ilmenite from the Surface of the Grain. Despite the Fairly Advanced State of Alteration of the Grain, the Ilmenite Relicts are Unaltered [28,31]

Fig 2.4(B): Back Scattered Image of Leucoxene Replacing Ilmenite From the Grain Surface and Along Fracture Operating at this Surface[28,31].

Fig 2.4(C): Displaying the Replacement of Ilmenite by Leucoxene Along a Crack Within the Grain [28,31].

Fig 2.4(D): Alteration of Ilmenite to leucoxene [28,31].

Beyond this zone the leucoxene is usually less porous as shown in Figure 2B; however, significant quantities of SiO_2 and Al_2O_3 may still be present.

This style of alteration is similar to that observed by Hartman[32], Frost *et al* [28,31]. Hartman [32] studying iron-titanium oxides during bauxitization, found that ilmenite may alter directly to leucoxene or optically identifiable anatase. Frost *et al* [43]noted relatively unaltered ilmenite cores surrounded by leucoxene in a concentrate from the Capel 150 ft strand line, and concluded that these assemblages represent a single step dissolution reprecipitation process without the formation of pseudorutile. This style of alteration of ilmenite to leucoxene, rutile or anatase may be expressed by the equation:

$$FeTiO_3 + 2H^+ \longrightarrow TiO_2 + Fe^{2+} + H_2O$$

Ilmenite rutile + dissolved hematite

Type 3 Alteration

According to this mechanism the alteration does not occur along grain boundaries, but rather as patches within grains. The second type of intergrowth is characterized by the development of anhidral, often-uniform rutile micro crystals in patches within the ilmenite grains. In a few instances micro crystals of hematite are sometimes found in rutile intergrowth of some ilmenite deposit[23]. Subsequent dissolution of hematite has results in grains consisting of only ilmenite and microcrystalline rutile.

2.4.4 The Effect of Alteration on Ilmenite Quality

It has been shown[18] that the magnetic susceptibility of ilmenite decreases with increasing alteration. Hugo estimated[33] the magnetic behavior of ilmenite and altered ilmenite in the Rechards Bay deposits by determining their mass proportions in different magnetic fractions from a heavy mineral concentrate. These results show that

- Ilmenite-hydrated ilmenite-pseudorutile grains are slightly less magnetic than unaltered ilmenite grains, but most of these grains will report to ilmenite concentrate.

- Altered ilmenite grains containing leucoxene or TiO_2 pseudomorphs have a large range of magnetic susceptibility and such grains may report to ilmenite concentrate or magnetic middling fractions.
- Leucoxene grains too have a large range of magnetic susceptibility extending from that of ilmenite to that of nonmagnetic rutile, and that most leucoxene will report to magnetic middling or rutile concentrate.

It is clear from the results of Hugo[33] that the degree and type of alteration will affect the recoverability of altered ilmenite grains.

Frost et al.[28] have shown that there is a marked increase in the SiO_2 and Al_2O_3 contents of ilmenite alteration phases containing more than 60 percent TiO_2 in Western Australian deposits. The increase in these impurities has been ascribed to the co-precipitation with, or adsorption on to, alteration products[28] or the formation of clay minerals within pore spaces between alteration phases. It is therefore evident that altered ilmenite grains containing leucoxene, and leucoxene grains themselves, are undesirable as they are often non-recoverable and they contribute to impurity levels in concentrates.

2.4.5 Progressive Alteration of Ilmenite to Leucoxene

Alteration of ilmenite advances from leached ilmenite, through pseudorutile and leached pseudorutile to leucoxene. Leached ilmenite and leached pseudorutile are transitional metastable phases, and are formed during continuous leaching of ilmenite and pseudorutile, respectively. Leached pseudorutile decomposes into leucoxene consisting of aggregates of very fine-grained rutile crystals.

Hugo[33] and Muck & Chaudhuri[26] also discussed the continuous transformation of ilmenite to leucoxene. The alteration starts with the continuous removal of soluble Fe(II), and the electrostatic charge is balanced by oxidizing the remainder to Fe (III) and /or by adding H^+. Ferrous iron is totally oxidized at the formation of pseudorutile. Further removal of ferric iron is compensated for by the addition of OH^- to the mineral lattice. At later stages, the OH^- is released due to the breakdown of the pseudorutile structure into rutile and water. Many researchers[23,26,41] have described the relationship between water content and the leaching of iron, and the

effect of water on the alteration of ilmenite. As alteration advances, the water content increases until the pseudorutile phase breaks down. The breakdown of the pseudorutile structure appeared at a composition of about 77-79% TiO_2 and 9-12% Fe_2O_3. Leucoxene is a product of the incomplete breakdown of pseudorutile, and consists principally of fine-grained, usually acicular, crystalline rutile.

The transformation of ilmenite to leucoxene is associated with a decrease in volume and subsequent stress on the crystal lattice and results microcracking. Grey and Reid[41] discussed the structural relationship between ilmenite and its alteration product, pseudorutile. The frequent development of fractures and pores in the alteration products implies reduction in cell volume. Fracturing and the formation of pores generally increase with a decrease in iron content.

2.4.6 Paragenesis of Ilmenite Alteration

It is important to determine the paragenesis of the ilmenite alteration, because the site of alteration will affect the distribution and proportions of different types of altered grains in the deposits. If the alteration occurred before final deposition then a fairly random distribution of altered grains is expected. It is widely believed that ilmenite alteration occurs in situ in beach and dune deposits for the following reasons:

- Alteration of the margins of well-rounded grains is fairly common, suggesting that alteration occurred after rounding of the grains, that is during the late stages of transportation, or after deposition[26]
- Some beach deposits display a vertical variation in the composition of ilmenite concentrates, particularly about the water table[23]. In these deposits the leucoxene contents of ilmenite concentrates are significantly higher above the water table or near the surface, suggesting that these areas of higher acidity enhance the alteration of ilmenite. This suggests that the alteration of ilmenite is due to weathering, and that this for the most part has taken place in situ in the sand deposit[26]

- ξ It also notes that older deposits generally contain the most altered ilmenite, and cites values from Western Australian raised beaches of different elevations (and consequently different ages) as an example; and
- ξ Mucke *et al.* [26] note that the alteration displayed by ilmenite in littoral zones is not observed in the source rocks and is rarely found in alluvial ilmenite grains.

2.4.7 The Importance of Study on the Extent of Alteration

The importance of altered ilmenite in the fact that it constitutes more than one third of the world production of titanium mineral categorized by the U.S. Bureau of Mines as ilmenite and totaling 2.2 million tons in 1963.[18] By virtue of its being an alteration product of varying composition, altered ilmenite has in the past presented problems both in are dressing and in the sulfuric acid digestion method of pigment manufacture, a process that consumes more than 90 percent of the ilmenite and altered ilmenite produced. More recently, a better understanding of the natural alteration of ilmenite has become important in view of work directed at upgrading ilmenite and altered ilmenite concentrates to products much higher in TiO_2.

There has been appreciable work on the alteration of ilmenite. Most of the workers[34-35] agrees that the mineral ilmenite undergoes oxidation and leaching whereby iron is removed from the structure resulting in a relative enrichment in TiO_2. There has been much discussion [36] on the nature of the alteration product and generally it has been agreed that in nature no secondary iron titanium compounds are involved in the alteration although the very fine grain size of the alteration product has made positive identification extremely difficult. Temple [18] explained how iron gets out of the ilmenite structure. According to him, iron is removed along structural discontinuities. It is postulated that removal of iron from the grain is caused by a migration gradient initiated at the structural interfaces and facilitated by the slight reduction in the size of the Fe atom due to oxidation from the ferrous to the ferric state. Since this process takes place at low pressure and temperature conditions reaction kinetics are slow and thousands of years by be required for this process to occur in nature. TiO_2 content increases with increasing age. Due to these slower rate disequilibria assemblages

should be common in natural ilmenite deposit. The difference in the degree of ilmenite alteration in various heavy mineral placer deposits implies differential weathering due to age differences and/or multistage alteration of ilmenite.

Gevorkyan and Tananayev[17], who reported a close connection between the iron and water contents in altered ilmenite and concluded that the iron oxide is hydrated during alteration process and that iron is removed as a mobile hydroxide, have discussed the role of water in the alteration of ilmenite. From the above discussion it is clear that the alteration of ilmenite takes place near the surface and requires presence of water, a temperature of 50^0C[26] not exceeded. This favorable environment is also common for our beach sands as the beach sand minerals are exposed to a temperature around 35-40^{0}C. So there is higher possibility to obtain altered ilmenite grains in the ilmenite separated from the coastal black sand of Bangladesh.

In this respect it can be mentioned that there are many examples of alteration of ilmenite in placer deposit like Eneabba, Western Australia, Trail Ridge, Florida, which contain mostly altered ilmenite and yield concentrates containing between 54-66 percent TiO_2 while Folkson, Georgia contains an ilmenite assaying of 76.1 percent. TiO_2 Attempts to produce synthetic rutile from Bangladesh ilmenite have yielded encouraging results. However no study on the extent of alteration of ilmenite in the deposits of Bangladesh has so far been reported. So study of alteration may be a promising field for the exploration of beach sand.

CHAPTER 3: EXPERIMENTAL

3.1 Introduction

The objective of this study was to characterize Cox's Bazar ilmenite and to study the weathering effect, if any. The beach sand minerals were collected from the Cox's Bazar deposit of heavy minerals and ilmenite was separated at the Beach Sand Exploitation Centre, Kalatoli. The as-received sample was magnetically fractionated to different magnetic fractions and also to different size fractions. These fractions were then characterized in terms of phase content, chemical analysis and reduction behavior. The phases present in the as received sample were identified by X-ray diffraction analysis thermogravimetric analysis was performed on the different magnetic fractions to detect the presence of water, if any. In this chapter the experimental procedures used for the present investigation has been discussed.

3.1.1 Magnetic Separation of As-received Sample

Frantz isodynamic magnetic separator was used to obtain the magnetic fractions. Frantz isodynamic magnetic separator is more practicable for the magnetic separation between minerals, which have low but different specific susceptibilities. The Frantz isodynamic separator, used in this study, consists of a vibrating chute mounted centrally between the pole pieces of an electromagnet as shown in the Fig 3.1. It relates the current in the electromagnet and the transverse slope of the chute to the specific susceptibility at which the separation is being effected. This unit may be inclined in any direction by the universal mounting, and the electromagnet current is continuously adjustable from 0 to 1.5 amperes. Mineral separations are normally made by arbitrary adjustment of the current of the electromagnet and the transverse slope of the chute until the most suitable splitting is obtained. At any such setting the separator divides a sample into two fractions determined by the settings. With suitable calibration Frantz isodynamic separator will accordingly provide absolute measurements of the specific susceptibility of mineral grains.

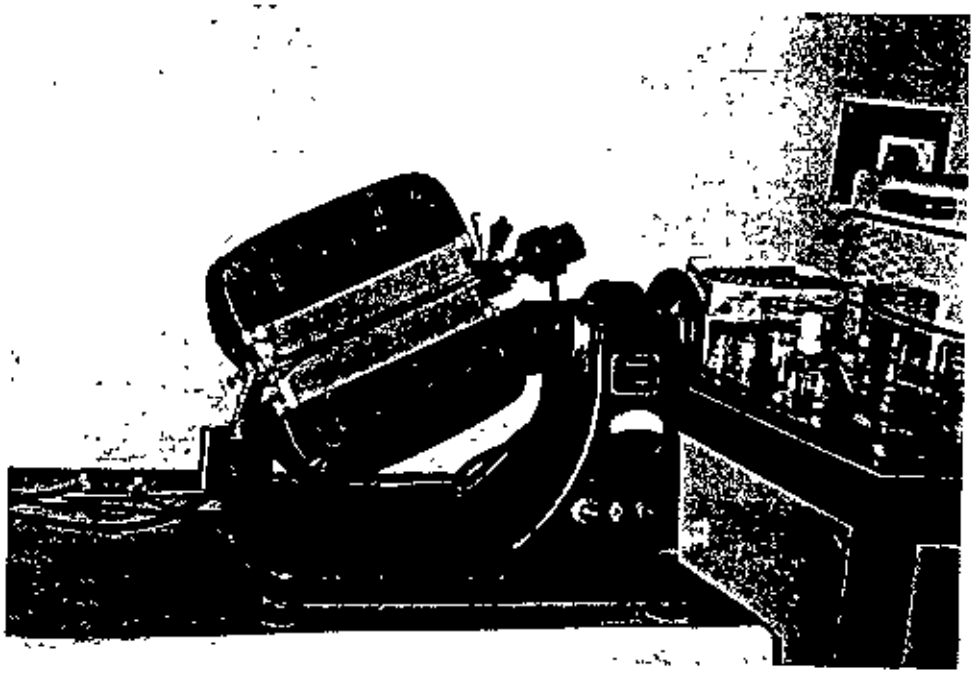


Fig: 3.1 The Frantz Isodynamic Magnetic Separator

3.1.2 Chemical Analysis of As-received Sample

Wet chemical analysis was performed to determine the contents of Cox's Bazar ilmenite. The detail procedure for chemical analysis has been given as Appendix 1. The prime interest was to know the material contents specially, the percentage content of ferrous oxide (FeO), ferric oxide (Fe_2O_3), and titanium oxide (TiO_2) in as-received sample. Percentage of ferrous iron, total iron and titanium oxide were found by actual wet chemical analysis and the Fe_2O_3 content was calculated by difference. During calculation it was assumed that iron is bound with oxides as a chemically standard compound. Besides the chemical analysis of as-received sample, chemical analysis was also carried out in the different stages as mentioned below:

- As-received sample was oxidised and then analyzed chemically to determine the extant of oxidation of ferrous to ferric oxide.
- Chemical analysis was carried out for all these size and magnetic fractions to determine the concentration of ferrous oxide, ferric oxide and titanium oxide

to investigate the difference if any among the different size and magnetic fractions.

- The reduced masses were also analyzed to determine the content of metallic iron, total iron, and titanium oxide and thus to determine the extent of reduction.

3.1.3 X- Ray Analysis of As-received Sample

X-ray diffraction analysis was conducted to find out different phases present in the Cox's Bazar ilmenite. The X-ray diffraction patterns were recorded by a Jeol DX-GE-2P X-ray diffractometer. Before recording the X-ray patterns, the samples of ilmenite were prepared by using the following procedures.

- 1-1.5 gram ilmenite sample was finely ground in an agate mortar.
- This fine powder was placed on the XRD slide and loaded in the XRD machine.
- The pattern was recorded with the following setting of the X-ray diffractometer.
- The diffraction lines were identified by using the powdered diffraction file of JCPDS - International Center for Diffraction Data.

Target:	**Molybdenum (Zr)**
Current	20 mA
Voltage	30 kV
Scanning Range	$8\text{-}37^0$
Scanning Speed	0.5^0 per min
Chart Speed	05 mm per min
Full scale intensity	2 υ 10^{-4} cps

X-ray diffraction patterns of all the different size and magnetic fractions were also recorded to identify the different phases present in the different fractions. The same setting was used for all the samples.

3.1.4 Reduction Behavior of the Different Magnetic Fractions

To study the effects of prior oxidation on the reduction of the different magnetic and size fractions, some samples of ilmenite were oxidized for 2 hour at 950^{O}C in a muffle type electric furnace. After oxidation the ferrous iron content of the ilmenite determined by chemical analysis. All the magnetic fractions and size fractions were reduced at 1050^{0}C for 4 hours. 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 was mixed with equal amounts of charcoal of 30-mesh size. Samples and charcoal were placed in the crucible layer by layer. A layer of charcoal was placed at the bottom of the crucible and then a layer of ilmenite was placed on the charcoal. In this manner, alternate layers of ilmenite and charcoal were placed in the crucible. The topmost layer was charcoal to resist the oxidation. A metallic lid made of same material of the crucible covered the crucible. This arrangement is shown in the Fig 3.2. A number of such crucibles were placed in a muffle electric furnace set at temperature of 1050^{0}C. The temperature of the furnace was controlled to $\pm$ 5^{0}C by an off-on controller.

After 4 hours, the crucibles were taken out one by one and allowed to cool to room temperature. After cooling, the reduced mass was separated from charcoal. Separation was carried out in two stages. At first sieving separated the bigger particles of charcoal. In the second stage particles of ilmenite were separated from the final particle of charcoal by a small hand magnet. The extent of reduction was followed by the chemical analysis of the reduced mass for the content of metallic iron.

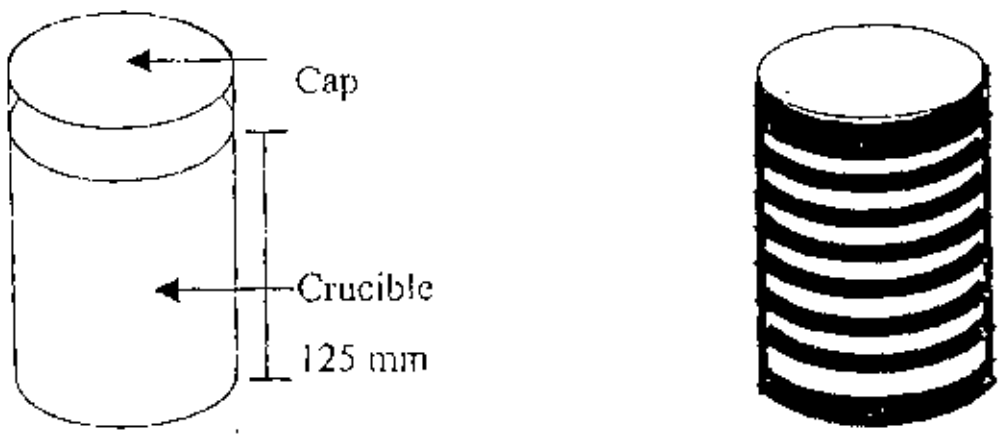


Fig 3.2: Arrangement for Reduction

X-ray Diffraction Analysis and Optical Metallography of the reduced mass were carried out to identify different phases present. The degree of reduction was calculated by using the formula,

$$\%\ Of\ \text{Re}duction = \frac{\%\,Of\ Metallic\ Iron}{\%\,Of\ Total\ Iron}$$

3.1.5 Thermogravimetric Analysis for the Different Magnetic Fractions

A Shimadzu TGA – 50 Machine, performed thermogravimetric analysis. It has a TGA chamber the main heating unit, a control unit that is used to set different parameters and inert gas set-up. 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 charge was placed on it.

1) Initial weight was taken.
2) The crucible was inserted in the TGA chamber slowly and when it is completely in the TGA chamber was closed.
3) He gas was introduced into the chamber to provide protective atmosphere.
4) The heating rate was set at 20^{0}/min and the machine was turned on.
5) The machine was turned off at 980^{0}C and the chamber was allowed to cool within protective inert gas atmosphere.
6) Finally the machine produced the report as a Graph.

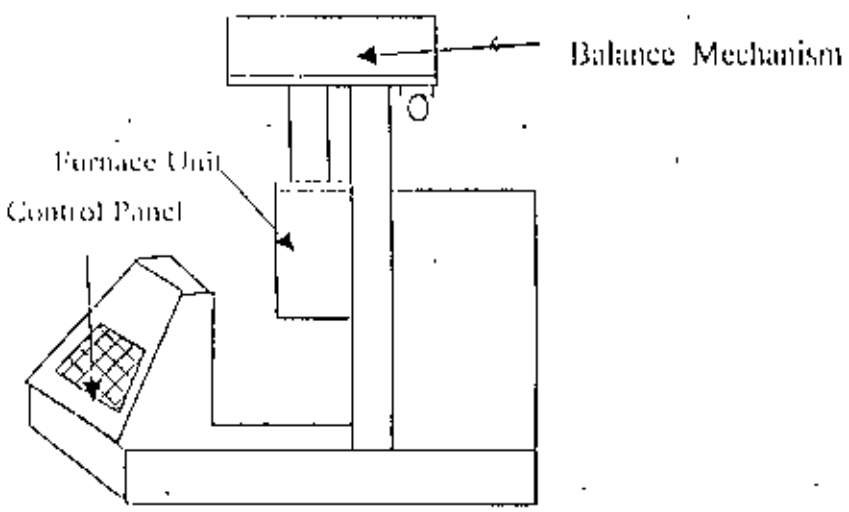


Fig 3.3: The Cross-sectional View of the Furnace Unit of TGA Machine

The chamber was allowed to cool and the machine produced the report as a graph. To support the Thermogravimetric data some samples were sent to the Regional Research Laboratory, Thiruvanthapuram, India for TGA analysis.

3.2 Sieve Analysis

Sieve analysis of the as received sample was performed in a standard sieve shaker. At first the sieves of different mesh sizes were arranged in such a way that the lowest sieve remained at the top most position while the highest remained at the bottom. Then 200 gm sample was placed in the top most sieve and the power was turned on for a shaking period of 15 minutes. Then the samples retained on different sieve were collected. Most of the ilmenite was retained on US Sieve Number 70, 100, and 140. The subsequent investigations were conducted on these three size fractions only.

3.3 Optical Metallography of the Different Fractions

Microstructure of all the size fractions was examined under an optical microscope after reduction to study the extent of reduction. Particles of the corresponding samples were prepared for the observation as before and the photographs of the significant areas of the sample were taken. Difficulties were encountered during mounting and polishing due to loss of loosely held particles. It was however possible to obtained a satisfactory surface composed of scattered particles in plain but the areas between particles were out of focus.

CHAPTER-4 RESULTS AND DISCUSSION

4.1 Introduction

One of the objectives of this study was to find the extent of weathering, if any, in the Cox's Bazar Ilmenite. The sample was chemically analyzed in the as received condition, after magnetic fractionation and also after size fractionation. X-ray diffraction technique was used to identify the phases present in all these fractions. Sample of both magnetic fraction and size fractions were also reduced by charcoal under identical condition. The extent of the reduction was followed by chemical analysis, qualitative X-ray diffraction analysis and optical microscopy. X-ray pattern were also used to detect the presence, if any, of pseudo-rutile, one of the probable alteration products. Thermogravimetric analysis of the magnetic fractions was carried out to detect the presence of water in the sample. The result of this investigation are presented and discussed in this chapter. Tables containing actual experimental data are presented in the Appendix-2.

4.2 Magnetic Separation of As Received Sample:

Magnetic fractionation of the as-received samples showed that almost 90% ilmenite of the sample was separated at currents up to 0.3A, which contains four major fractions. Other two fractions separated at comparatively higher currents were approximately 10% only Fig 4.1 shows the results of magnetic fractionation.

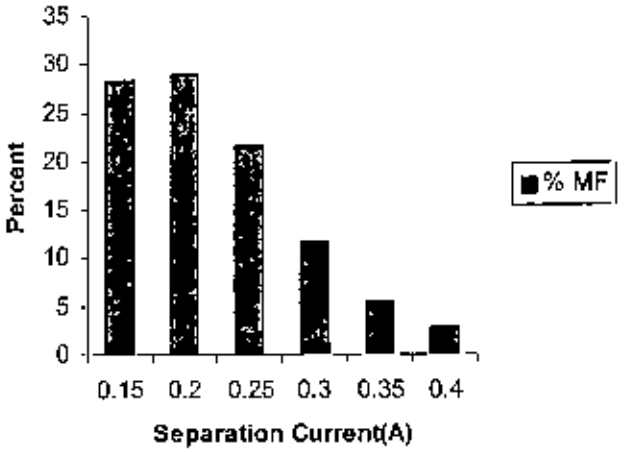


Fig 4.1 Results of Magnetic Fractionation

4.3 Chemical Analysis of Different Magnetic Fractions:

Magnetic fractions separated at different currents were analyzed chemically. Percentage of total iron and ferrous iron were determined by wet chemical analysis and the percentage of the ferric oxide was determined by difference. Fig 4.2 shows the results of the chemical analysis. It can be seen that the amount of ferrous oxide and total iron, as determined by wet chemical analysis, decrease gradually in the fractions separated at higher separation currents. This is to be expected because the fractions correspond to increasing separation currents. However the amount total iron was found to be maximum for the fraction separated at separation current of 0.25A.This is an interesting observation and needs further investigation. The amount of ferric oxide varied in a similar manner showing a maximum for the fraction separated at a separation current of 0.25A.

Moheskhali ilmenite was found to contain a higher amount of ferrous oxide than ferric oxide[50]. Another important observation was that titanium oxide content decreases with increasing current of separation. Thus it appears that a higher amount of impurities are present in the magnetic fractions separated at higher separation current.

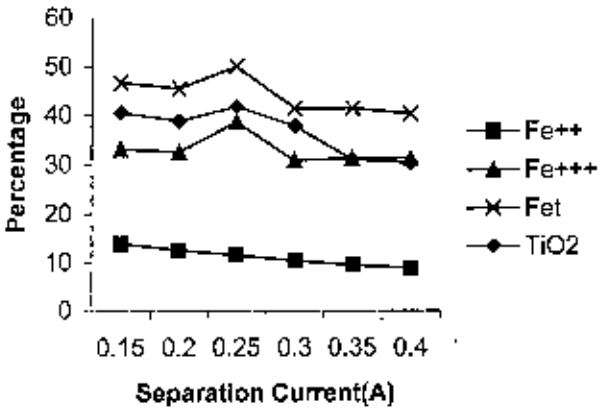


Fig 4.2: Per cent of Ferrous Iron, Ferric Iron and Total Iron (Fe_t) of As-received Sample

4.4 X-ray Diffraction Analysis of Magnetic Fractions

Fig 4.3 shows X-ray diffraction pattern recorded on the samples of different magnetic fractions of the as received ilmenite. All these pattern show diffraction lines mainly ilmenite present with rutile, pseudobrookite and hematite. It may be noted that an earlier study[4] with Cox's Bazar ilmenite showed the presence of diffraction lines belonging to pseudorutile. Slight shifting of the diffraction lines of ilmenite could be noted in all patterns recorded and this is not unusual in the naturally occurring minerals. The pattern analysis was strictly confined to qualitative analysis The shifting of the diffraction angle in different magnetic fractions for the same plane could have happened due to the slight distortion in the Ilmenite. From the data the lattice parameter can be calculated by using the following formula.

$$\frac{1}{d2} = \frac{h2 + hk + k2}{a2} + \frac{l2}{c2}$$

Now using the above formula we can calculate the lattice volume for different magnetic fractions. To find out the volume of unit cell following formula may be used.

Volume= a x a sin 60^0 x C

The calculated values of lattice volumes were found to be different from the volume calculate for the standard ilmenite using the standard diffraction file (316.0069). The placer deposit is not a chemically standard substance; it is a heterogeneous compound containing both FeO and Fe_2O_3 within the ilmenite grain as well as some impurities, which may affect the lattice parameter value.

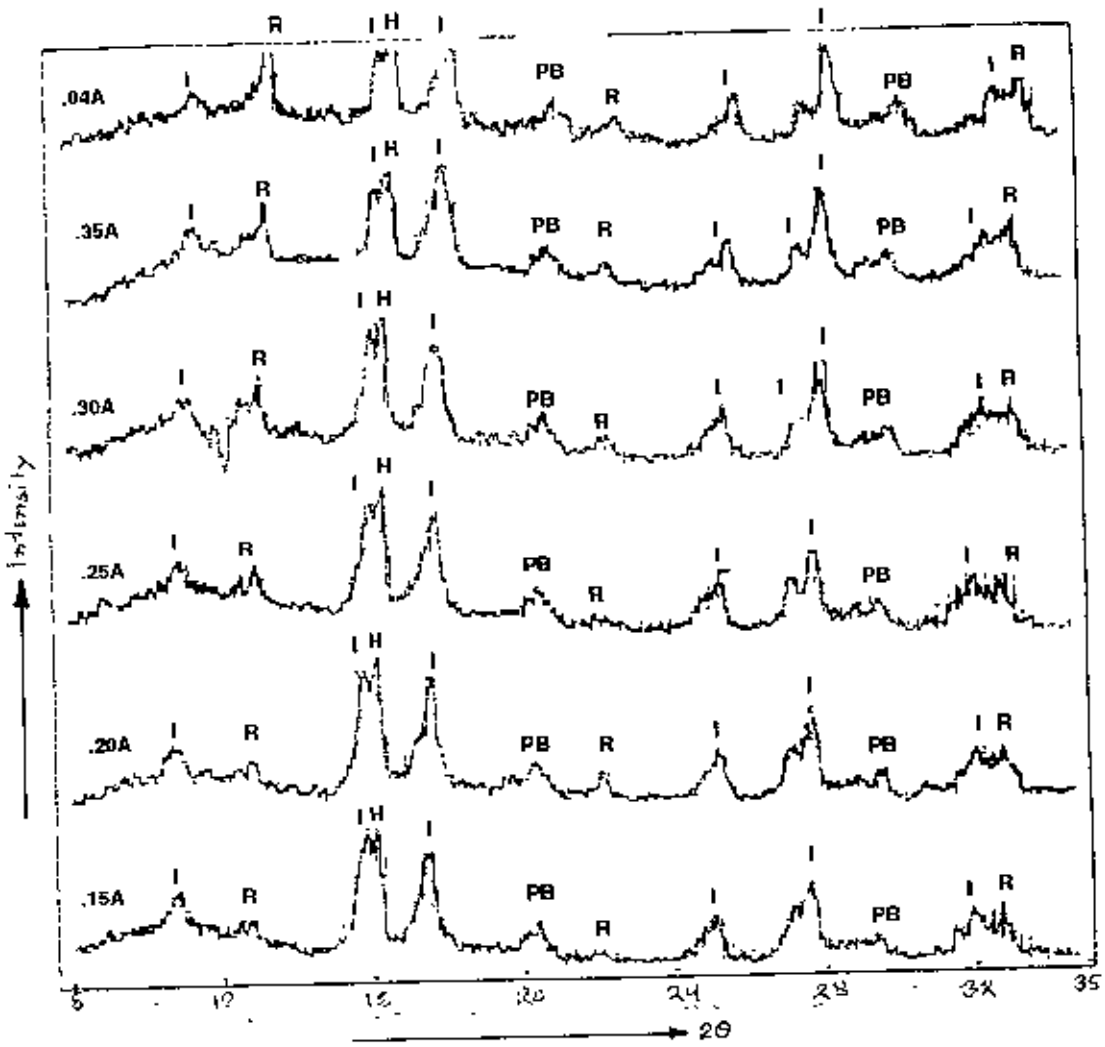


Fig 4.3: X-ray Diffraction Patterns of the Different Magnetic Fractions (as-received) (I-ilmenite, H- heamatite, PB- Pseudobrookite, R- rutile)

4.5 Extent of Reduction of the Different Magnetic Fractions

The extent of reduction of the different magnetic fractions was studied by the chemical analysis of the reduced mass (both in the as received and oxidized conditions) for the content of the metallic iron. X-ray diffraction analysis and optical metallography of the reduced mass were also carried out to supplement results of chemical analysis.

4.5.1 Oxidation of the Different Magnetic Fractions

Oxidation was done to transform the ferrous oxide to ferric oxide. It has been shown[43-44] that oxidation subsequently helps reduction due to the following reasons.

1. Conversion of iron in ilmenite from ferrous to ferric state, which eliminates the element of uncertainly in the relative amount of ferric and ferrous irons in the as-received ilmenite.

2. Alteration of equilibrium condition and consequently an increase of the rate of reduction of iron from the ferric state as compared to that of ferrous state.

3. Introduction of defects in ilmenite grains that enhances rate of subsequent reduction.

An earlier investigation[9] showed that the optimum time and temperature for the oxidation of ilmenite was 1 hour at 950°C. Results of wet chemical analysis has shown that the ferrous iron content of the oxidized ilmenite was only 1.4% while the rest of the iron was in the ferric state. This means that oxidation could be considered complete. These oxidized samples were reduced for 4 hours at 1050°C.

4.5.2 Reduction Behaviors of Different Magnetic Fractions

The results of chemical analysis of the reduced magnetic fractions clearly showed that the content of the metallic iron as well as that of total iron (except the separated at 0.25A) decreases with increase of applied current for separation (Fig 4.4)

$$\%Of\ \mathrm{Re}duction = \frac{\%Of\ Metallic\ Iron\ in\ the\ \mathrm{Re}duced\ Mass}{\%Of\ Total\ Iron\ in\ the\ \mathrm{Re}duced\ Sample}$$

Results obtained indicate that magnetic fractions separated at lower current are reduced to a higher extent than those separated at higher currents. It may be due to the higher ferric oxide content in these fractions. But the actual extent of reduction of the different magnetic fractions did not show any significant difference. So from the point of view of optimization of the reduction process, adaptation of separate reduction procedure for each of the magnetic fractionation may not be necessary.

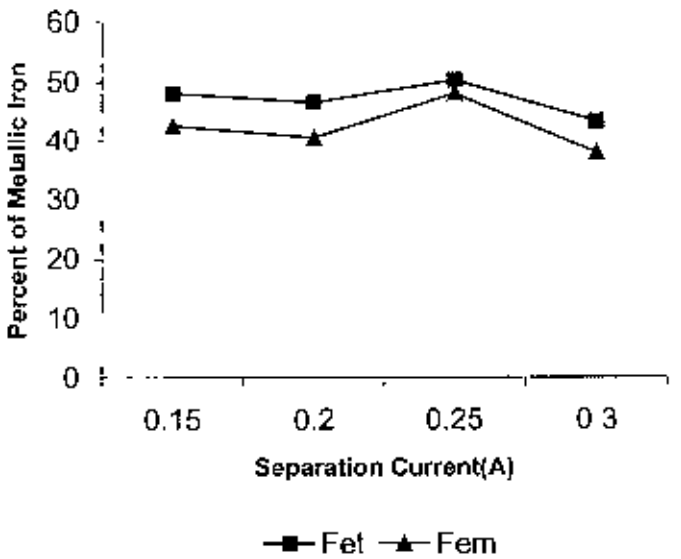


Fig 4.4: Percentage of Metallic (Fe_m) and Total Iron (Fe_t) in the Different Magnetic Fractions after Reduction in the As-received Condition

Cox's Bazar ilmenite was reduced in 1) as received condition 2) after oxidation 3) Using carbonate in the reduction mixture.

The extent of reduction in the as received condition (indicated by the amount of metallic iron in the reduced mass) was found to be the highest for the fraction separated at a separation current of 0.25A. It has already been mentioned that the results of chemical analysis have shown that this fraction contains the highest amount of ferric oxide. The extent of reduction of iron oxide in each of these fractions in the oxidized conditions was found to be higher than the corresponding fraction in the as-received condition (Fig: 4.5). At the same time the fraction separated at a separation current of 0.25A did not show any higher reduction. This is to be expected. All the fractions were oxidized at 950^{o}C for a period of two hours.

This converted almost all the ferrous oxide in all these fractions to ferric oxide. As a result no fraction showed any difference in the reduction behavior. Studies[5] have shown that oxidation of ilmenite prior to reduction (a) introduces defects (Crack, grain boundaries etc) (b) converts all the ferrous iron to ferric iron which overcome the problem of different ferrous to ferric ratios in ilmenite from different localities and (c) alters the equilibrium conditions and the rate of reduction from ferric to ferrous state. It is therefore to be expected that the extent of reduction is higher in the samples reduced after oxidation.

A comparison (Fig 4.5) of the reduction behaviors of the different magnetic fractions reduced (a) in the as received condition, (b) after oxidation and (c) after oxidation and addition of 10% sodium carbonate in the reduction mixture shows that the extent of reduction of each the fractions is the lowest in the as received condition, except for the fraction separated at a separation current of 0.25A. Oxidation prior to reduction gives a higher extent of reduction while the extent of reduction was found to be highest for the samples reduced in a mixture containing 10% sodium carbonate. Earlier studies [6,7] have shown that addition of sodium carbonate enhances the extent of reduction of ilmenite. The enhancement in the rate of reduction in the presence of a carbonate has been attributed to an early onset of the gasification reaction in the section two. Carbonate plays an important role in the second stage of the gasification reaction. Because carbonate releases CO at higher temperature at around 1000^0C. In the present study sodium carbonate suffered following reaction.

$$Na_2CO_3 \longrightarrow Na_2O+CO_2$$

$$C+CO_2 \longrightarrow 2\,CO$$

This CO increases the supply of CO as well as enhances the generation of CO from charcoal. N.N.Shams[10] also observed the similar effect on the Moheskhali ilmenite. So reduction rate for Cox's Bazar ilmenite increases. The chemical analysis of the study of N.N.Shams[50] showed that Moheskhali sample has similar composition like Cox's Bazar sample.

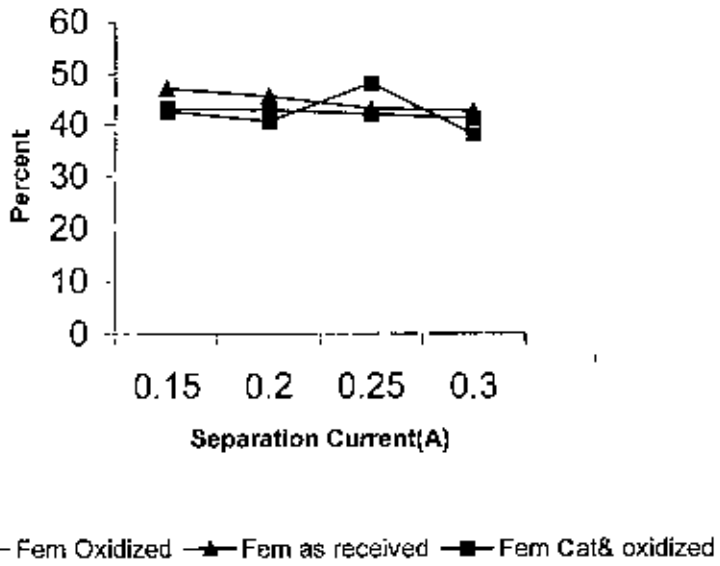


Fig 4.5: Percentage of Metallic Iron (Fe_m) in the Reduced magnetic Fractions (Reduced in the As-received, Oxidized and Oxidized + Catalysed Conditions)

4.5.3 X-ray Diffraction Analysis of the Reduced Magnetic Fractions

X-ray diffraction patterns of the reduced magnetic fractions are presented in the Fig 4.6. Two phases, iron and titanium oxide, were identified in these X-ray patterns. There were no diffraction lines belonging to iron oxide, which distinguishes X-ray patterns of reduced samples from the patterns of unreduced samples. Due to reduction iron oxide transforms to metallic iron. Thus the X-ray patterns of all reduced magnetic fractions show diffraction lines belonging to metallic iron. The more intense peak of titanium oxide and metallic iron in the fractions separated at 0.25A indicates higher reduction of this fraction in the as received condition.

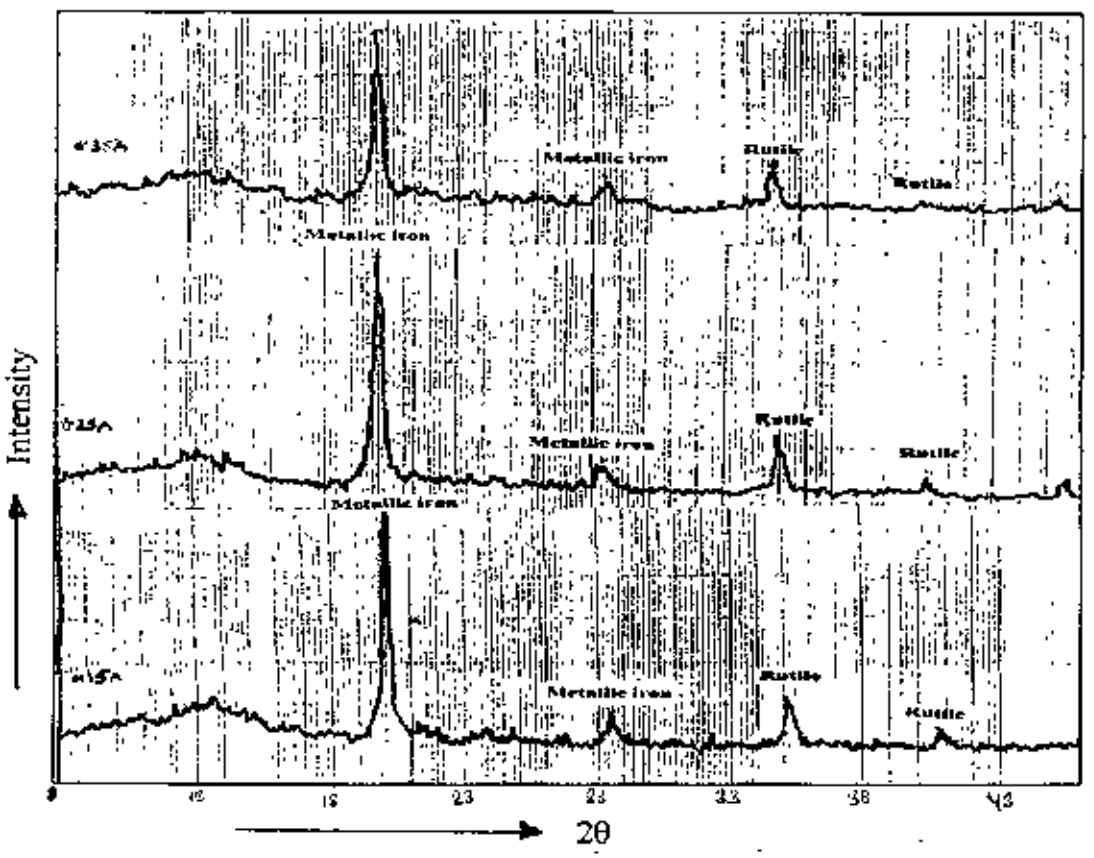


Fig 4.6 X-ray Diffraction Patterns of the Different Magnetic Fractions after Reduction (4 hour at 1050^{0}C)

4.5.4 Thermogravimetric Analysis of the Magnetic Fractions

Thermogravimetric analysis (Fig 4..7 to Fig. 4.11) was carried out to observe any changes in weight during heating. During this heating inert atmosphere was maintained by the supply of He. These data did not show any significant weight loss. D.S.S Babu et.al[19] studied the alteration of Indian ilmenite of Chavara, Manvalakurichi, Orissa deposits. During their study, they identified weight loss at a temperature near around 600^0C. This decrease indicates the presence of bound water. Naturally bound water increases as the degree of alteration increases. This is because pseudorutile structure may contain hydroxyl ions. Thus the contents of bound water is related to the presence of the pseudorutile phase. This study did not show any significant weight loss at above-mentioned temperature. Thermogravimetric analysis therefore indicates that there is no alteration product in the Cox's Bazar ilmenite.

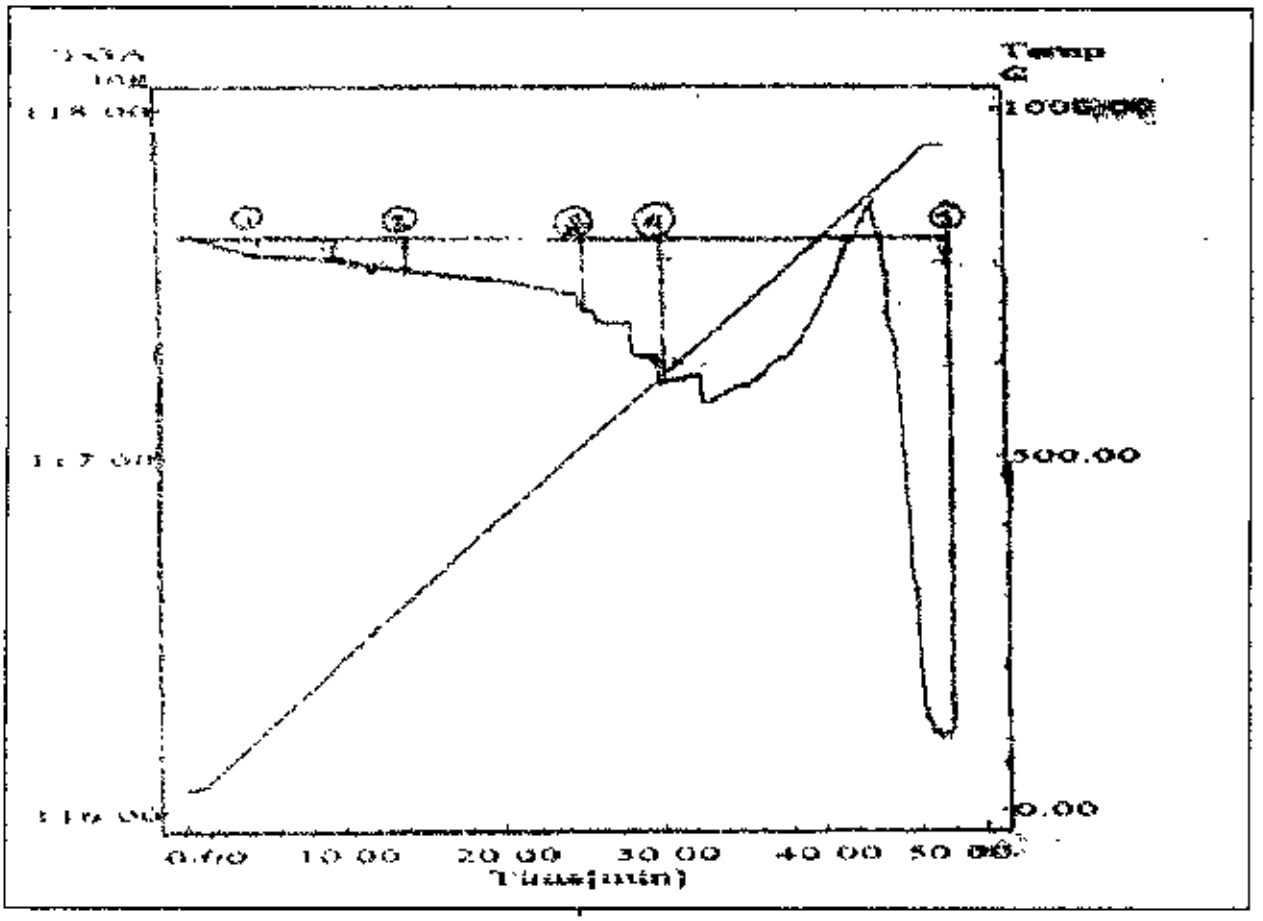


Fig 4.7 TGA Pattern of Fraction Separated with a Current of 0.2A

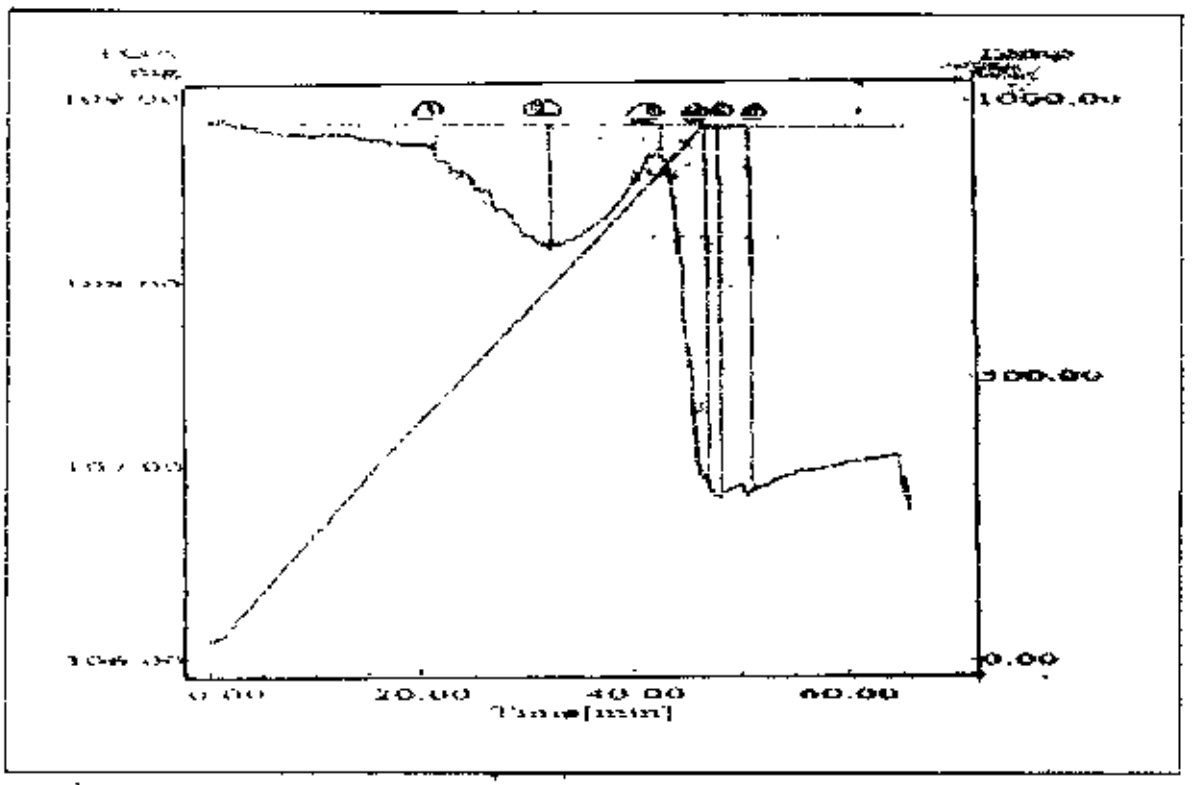


Fig 4.8 TGA Pattern of Fraction Separated with a Current of 0.25A

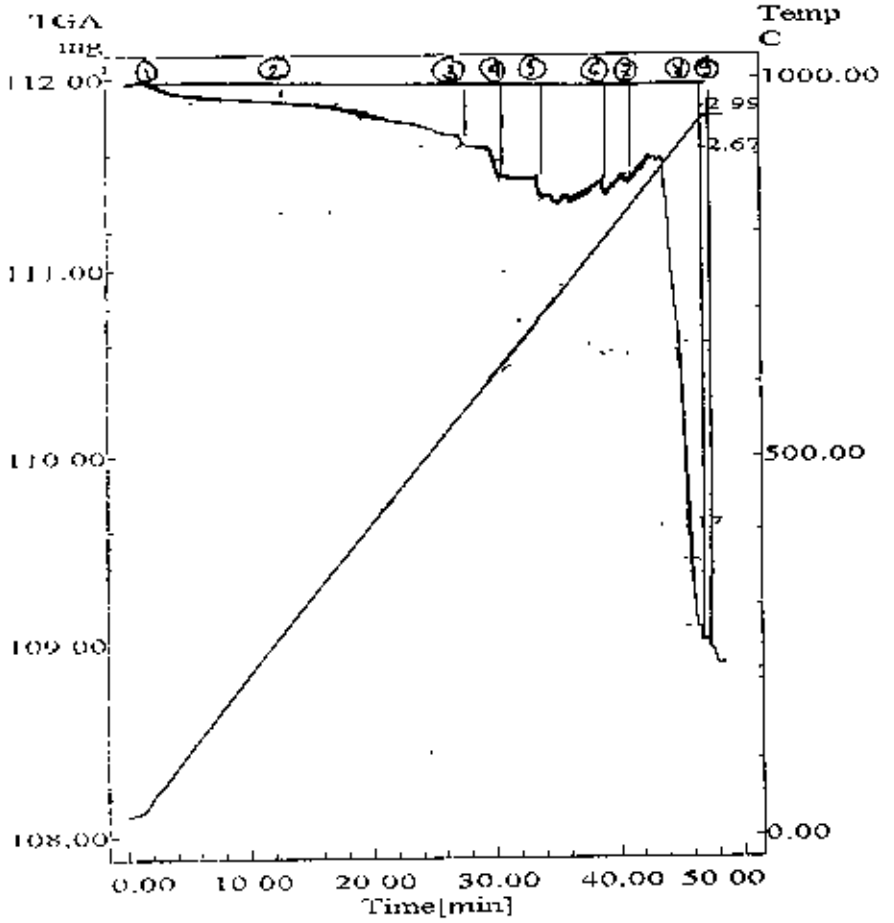


Fig 4.9 TGA Pattern of Fraction Separated with a Current of 0.3A

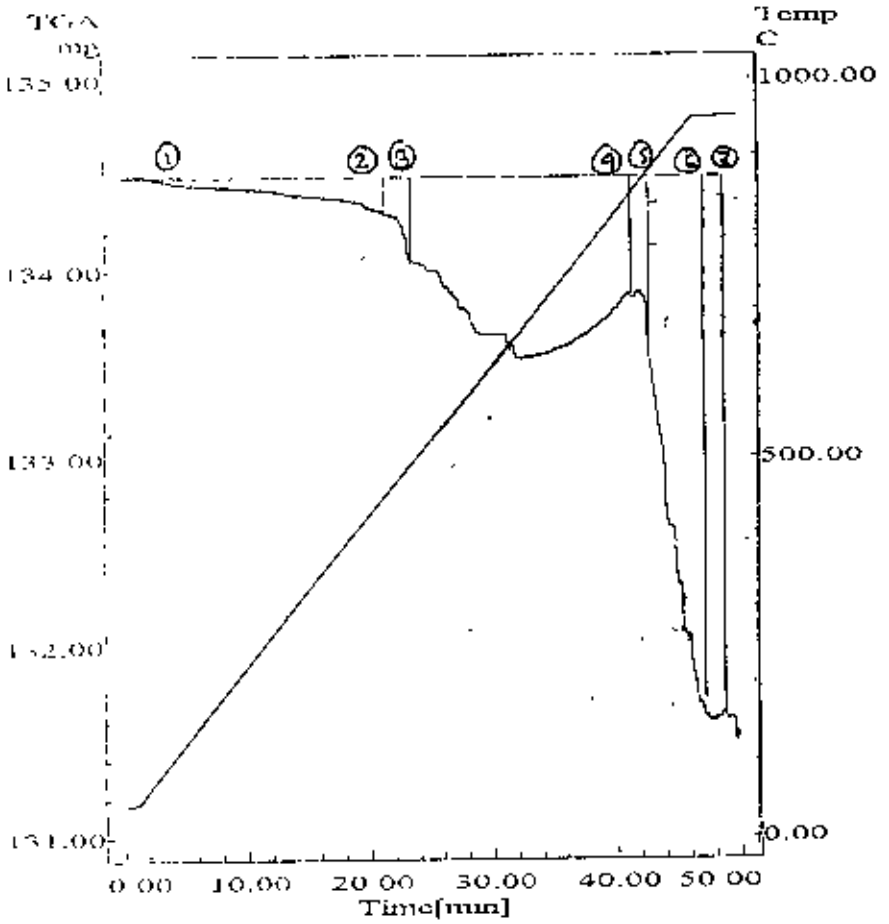


Fig 4.10 TGA Pattern of Fraction Separated with a Current of 0.35A

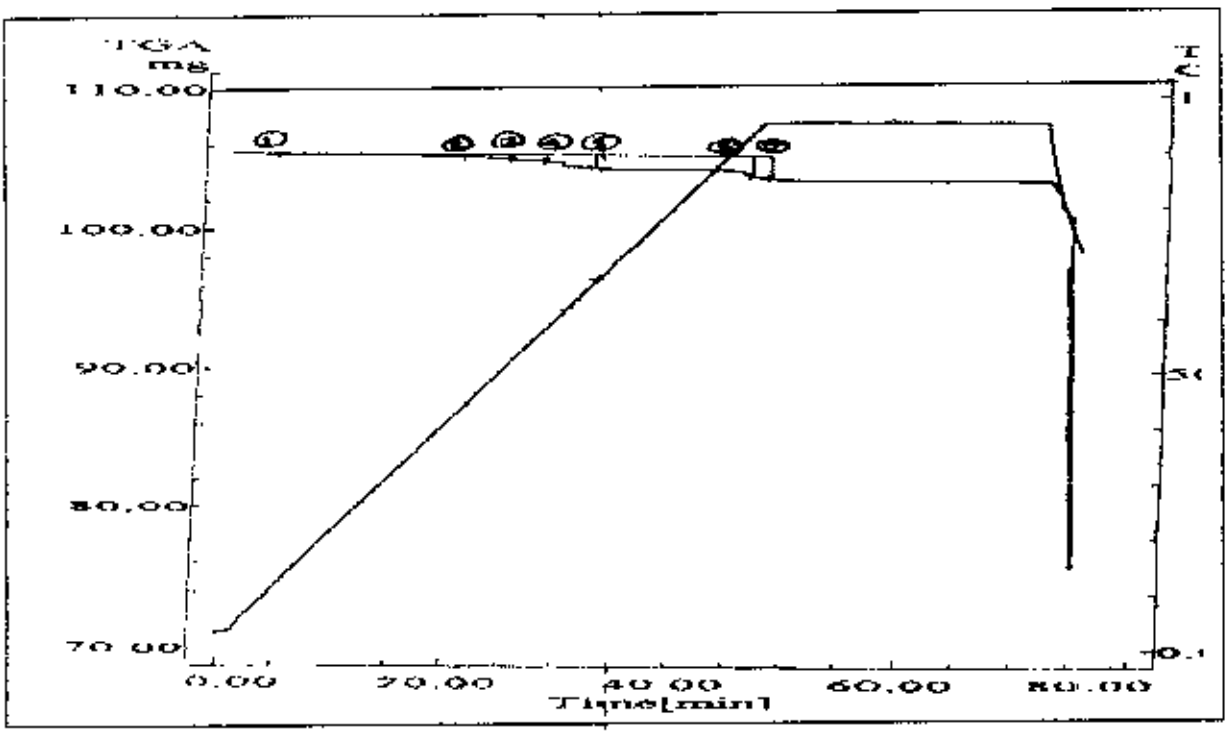


Fig 4.11 TGA Pattern of Fraction Separated with a Current of 0.4A

4.5.5 Optical Metallography of the Different Magnetic Fractions

Ilmenite was mounted by cold setting resin and was polished properly to get scratch free surface. Then the sample was placed under microscope and photographs were taken the different grains of ilmenite. Typical microphotograph in optical microscopy is presented below Fig 4. (12-18)

Microphotograph of all samples were almost similar in appearance. There were no significant changes that could be noticed from these microphotographs. Reduced sample contained more white phases (metallic iron) than the samples in the unreduced condition.

4.5.6 Mineralogy of the Different Magnetic Fractions

The mineralogical microscopic study of fractioned sample showed (Fig.4.19) grains of different colors. During this study, foxy red grains of rutile, black grains of ilmenite and glassy grains of quartz or zircon could be identified. At the same time quartz mixed ilmenite particles were also observed. However all the grains of ilmenite were smooth in appearance indicating that no alteration has taken place in these grains.

4.5.7 Scanning Electron Micrograph

Samples of reduced ilmenite belonging to the highly magnetic fractions (separated at low separation currents) were observed under a scanning electron micrograph. The surfaces of sample reduced for 4 hours reduction (Fig. 4.21) were more porous in appearance than the samples reduced for half an hour (Fig. 4.22). In the as-received sample (Fig: 4.20) no crack or porosity could be seen. Some crack could be seen in the oxidized sample (Fig 4.23). Ananda and Gilkes[22] have noted that scanning electron micrographs of slightly altered grains show massive irregular surfaces due to formation of pseudorutile while highly altered grains have very porous surfaces. It can thus be concluded that the major magnetic fractions (~ 90 per cent) of Cox's Bazar ilmenite are not altered to any significant extent.

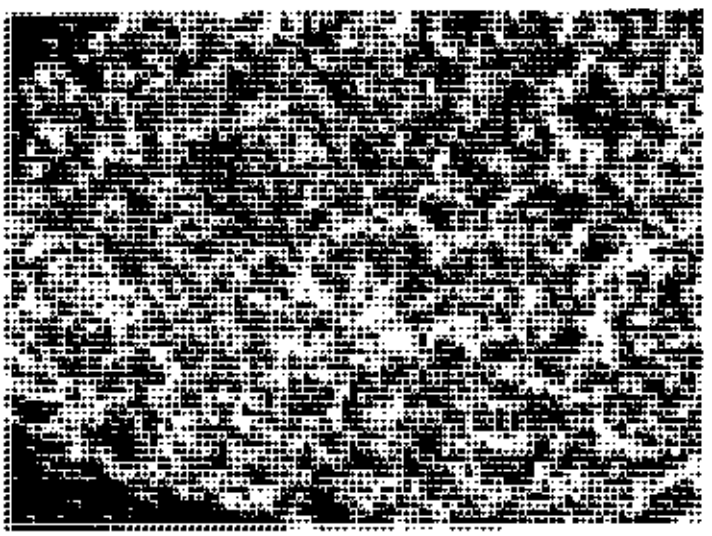


Fig 4.12 Microphotograph of As-received Sample (Mag. 400 X)

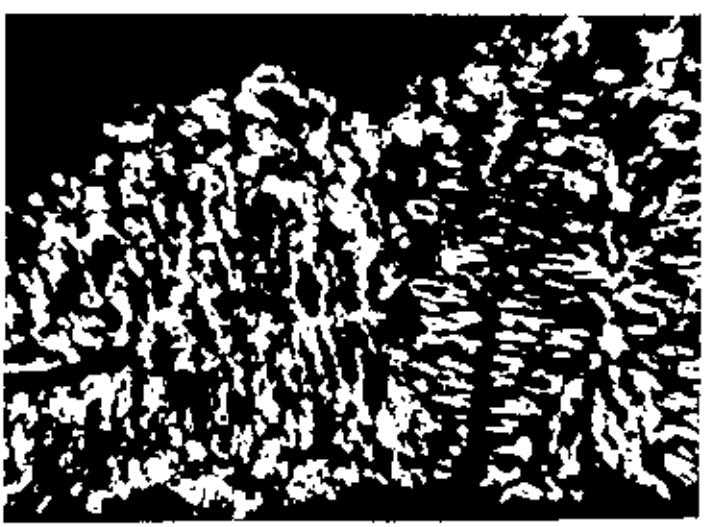


Fig 4.13 Microphotograph of the Magnetic Fraction Separated at 0.15 A (After Reduction, Mag. 400 X)

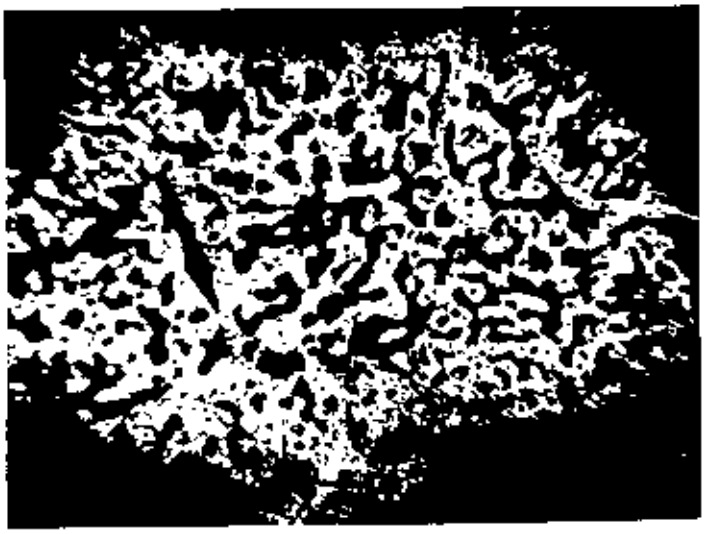


Fig 4.14 Microphotograph of the Reduced Magnetic Fraction Separated at a Current of 0.20 A (Mag. 400 X)

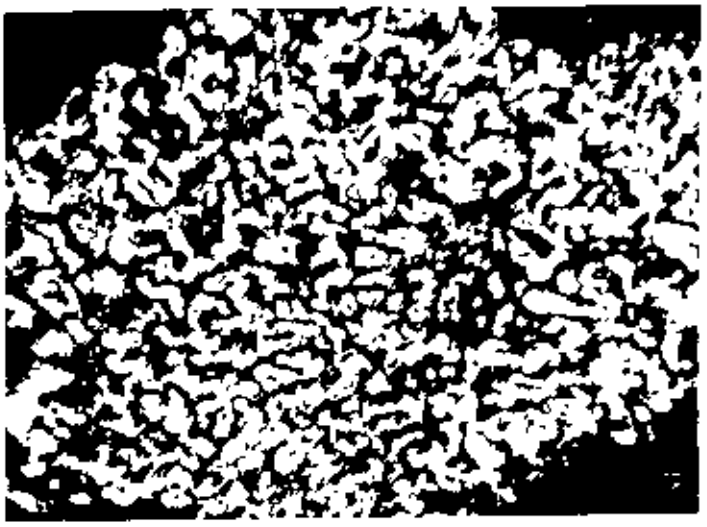


Fig 4.15 Microphotograph of the Reduced Magnetic Fraction Separated at a Current of 0.25 (Mag. 400 X)

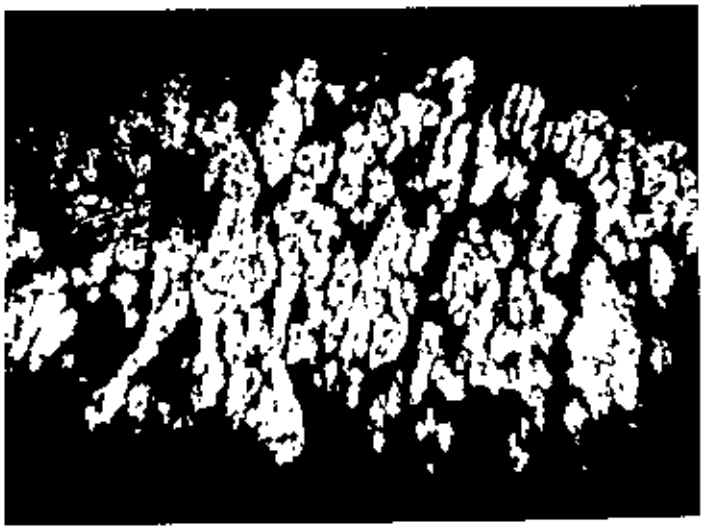


Fig 4.16 Microphotograph of the Reduced Magnetic Fraction Separated at a Current of 0.30 (Mag. 400 X)

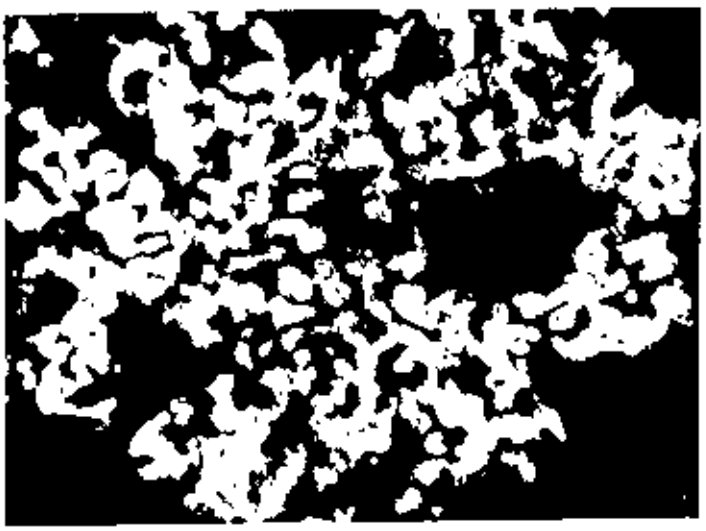


Fig 4.17 Microphotograph of the Reduced Magnetic Fraction Separated at a Current of 0.35 (Mag. 400 X)

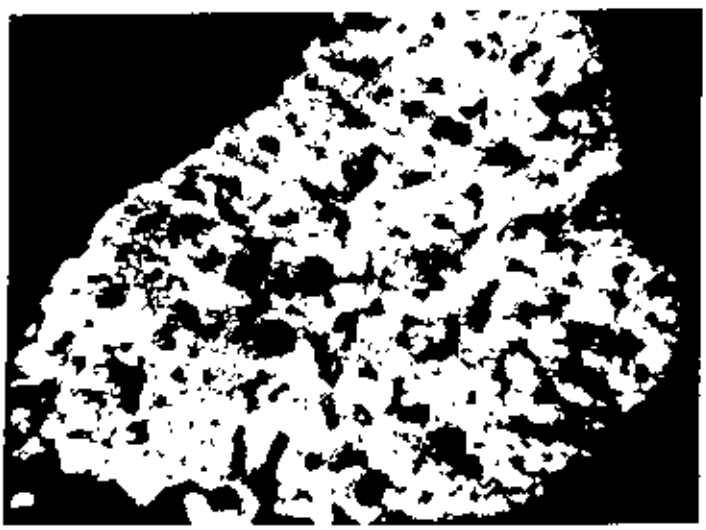
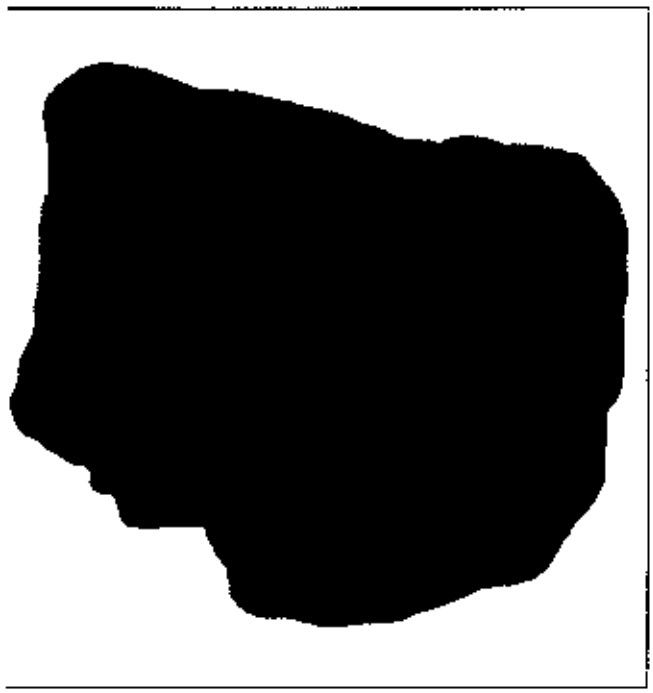
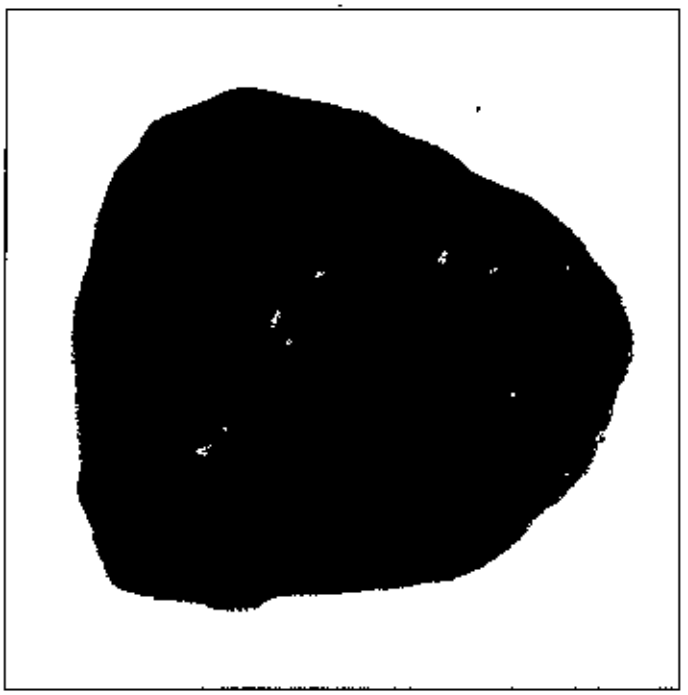


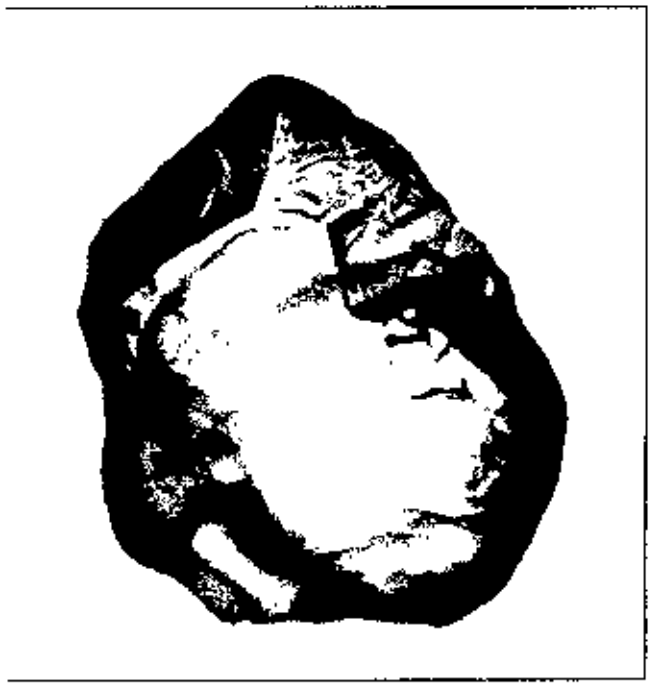
Fig 4.18 Microphotograph of the Reduced Magnetic Fraction Separated at a Current of 0.40A (Mag. 400 X)



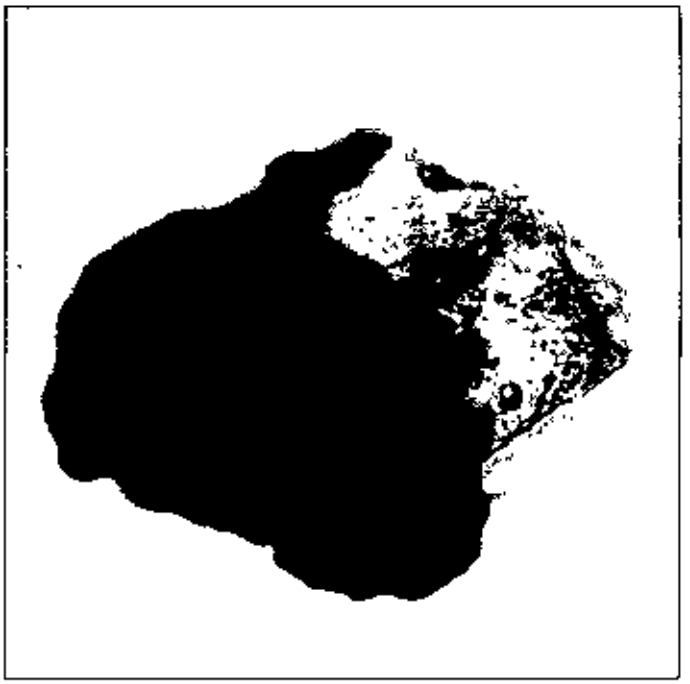
(A-Ilmenite)



(B-Rutile)



(C-Zircon)



(D-Quartz mixed Ilmenite)

Fig 4.19: Mineralogy of the Cox's Bazar Ilmenite (As Received)

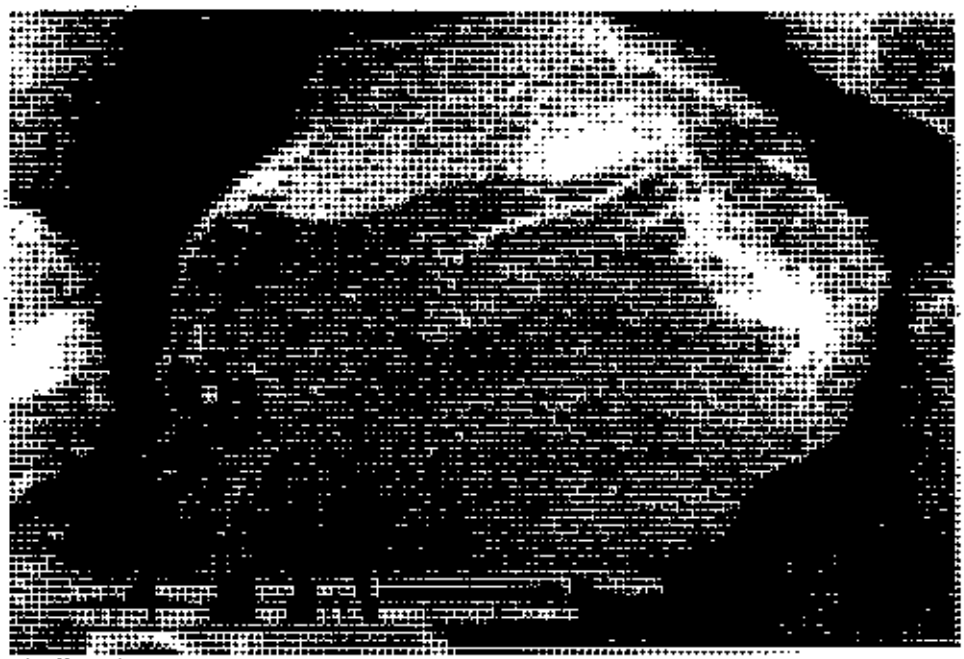


Fig 4.20 Scanning Electron Micrograph of As Received Sample (Mag. X 350)

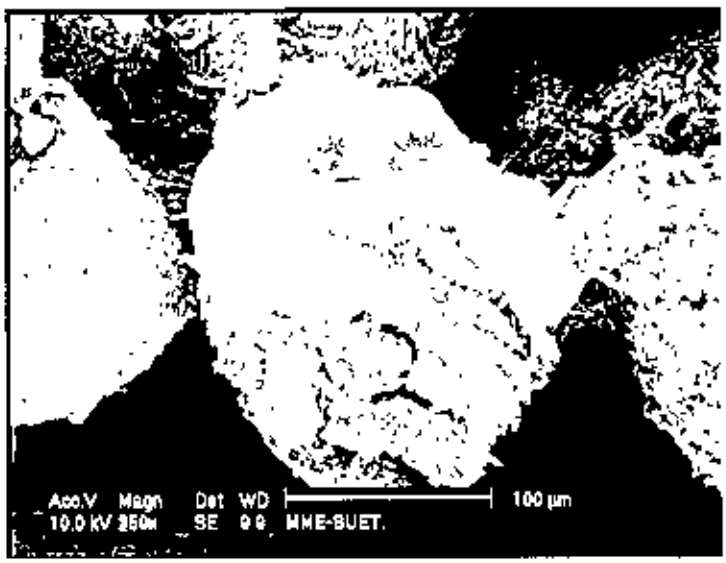


Fig 4.21a Scanning Electron Micrograph of Samples
(After Reduction for 4.0 hour, Mag. X 350)

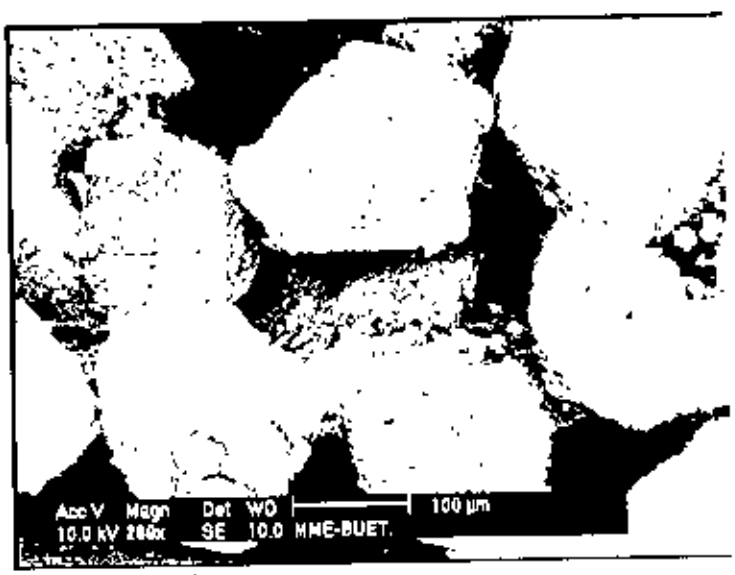


Fig 4.21b Scanning Electron Micrograph of Samples
(After Reduction for 4.0 hour, Mag. X 200)

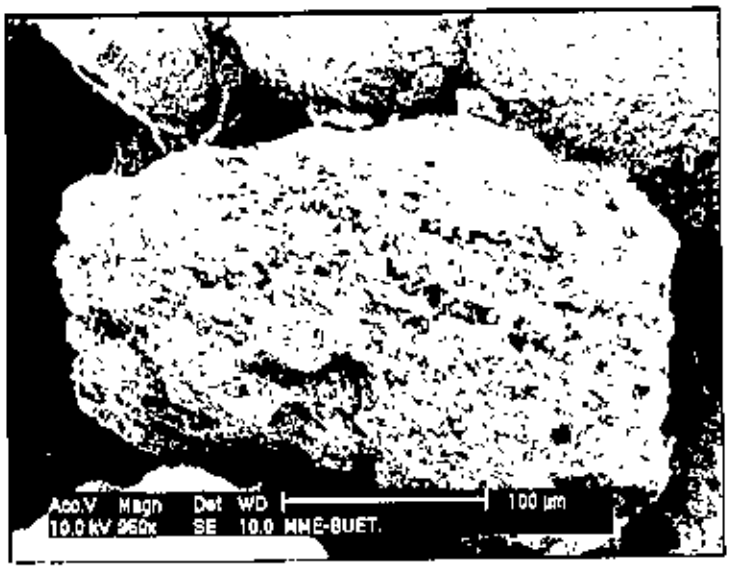


Fig 4.22a Scanning Electron Micrograph of Samples
(After reduction for 0.5 hour, Mag. X 350)

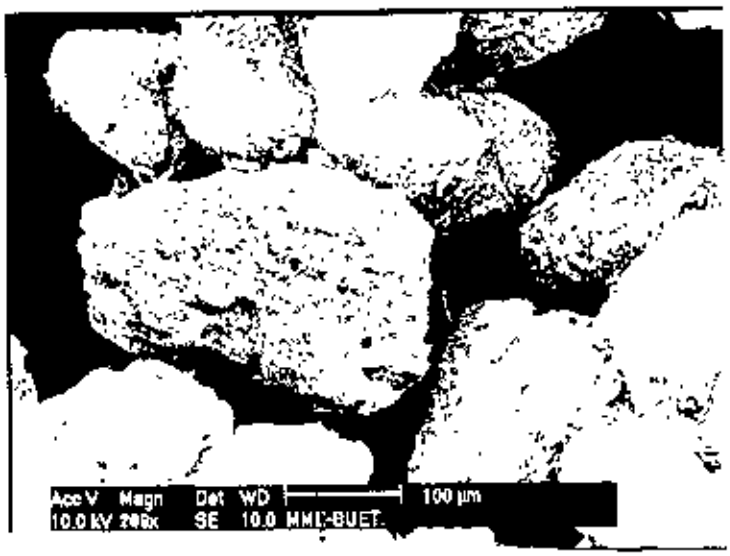


Fig 4.22b Scanning Electron Micrograph of Sample
(After reduction for 0.5 hour Mag. X 200)

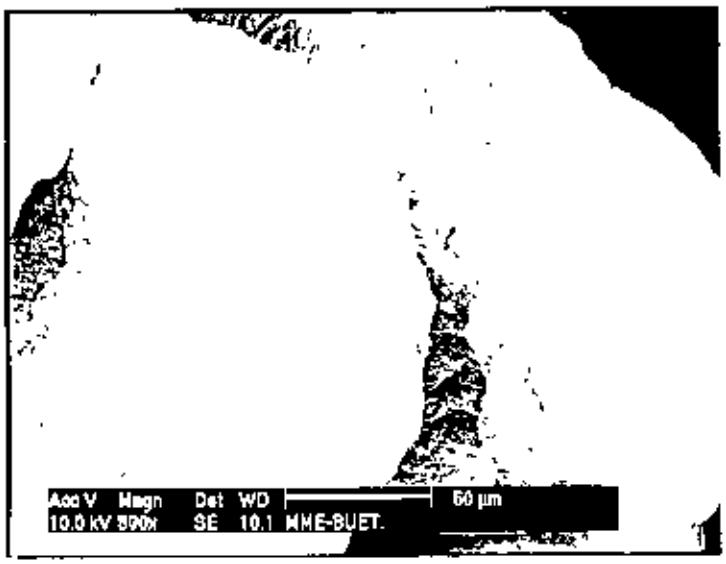


Fig 4.23a Scanning Electron Micrograph of Oxidized Sample(Mag. X 350)

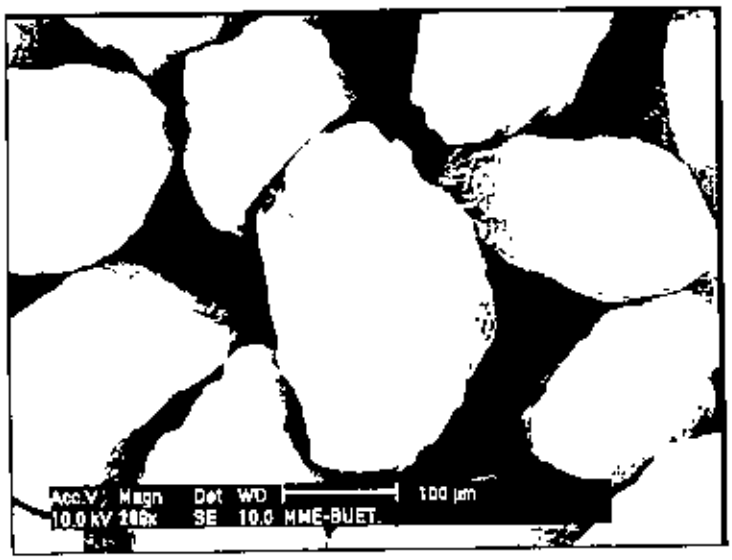


Fig 4.23b Scanning Electron Micrograph of Oxidized Sample (Mag. X 200)

4.6 Sieve Analysis of As Received Sample

A sieve shaker was used to perform size fractionation. The sieves were arranged in the usual way, sample was placed in the top most sieve and power was turned on for 15 minutes. The sample retained on different sieves were collected and weighed. It was found that 94.5% (shown Fig 4.24) of the total sample was retained on the US sieve number 70, 100, 140. While only 3.5% was retained on the other sieves. Subsequent investigation was conducted on the major fractions only.

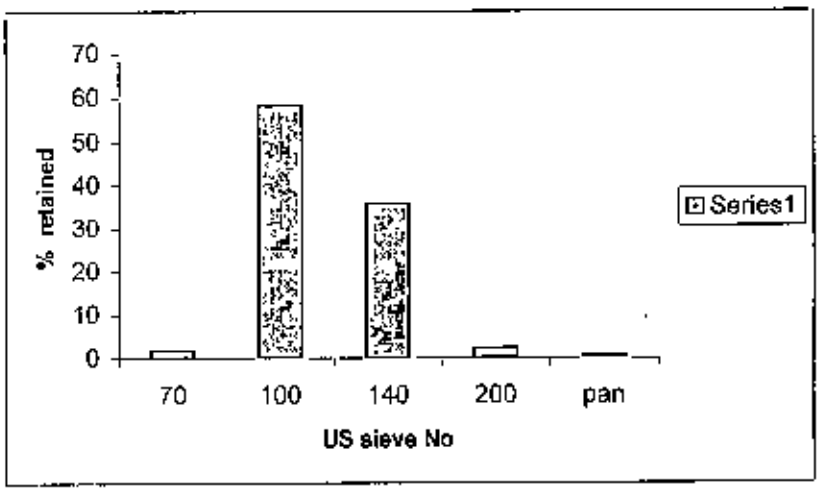


Fig 4.24: Results of Sieve Analysis

4.6.1 Chemical Analysis of these Different Size Fractions

Among these four fractions particles retained on US sieve no 200 are the finest one. Chemical analysis (before and after reduction) of the different size fractions were performed. From the wet chemical analysis data, it was found that with increasing sieve number, percentage of ferrous oxide and total iron increases. (Fig 4.25. Fig 4.26) show that the extent of reduction is maximum for the US sieve no 200, while minimum for sample retained on US sieve no 70. On the other hand chemical analysis of reduced samples showed that the finer fractions contain higher ferric oxide which leads to enhanced reduction. .It was concluded that size fractionation

will not be helpful to increase the extent of reduction. This behavior of the Cox's Bazar Ilmenite was also found to be similar to that Moheskhali Ilmenite [50].

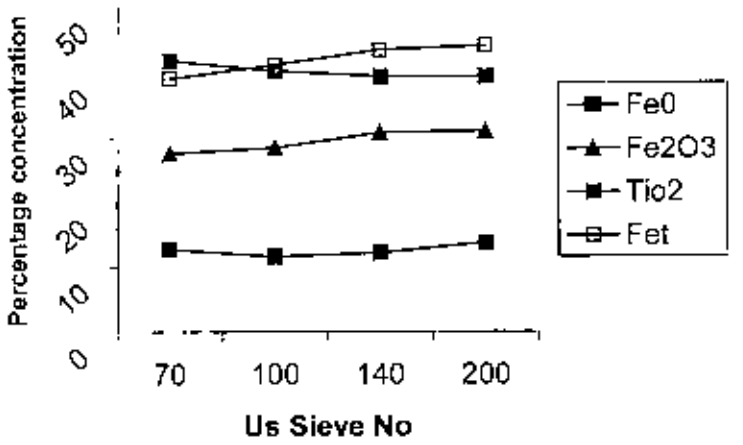


Fig 4.25: Chemical Analysis of Different Size Fractions
(FeO-Ferrous Oxide, Fe_2O_3-Ferric Oxide, TiO_2-Rutile, Fe_t-Total Iron)

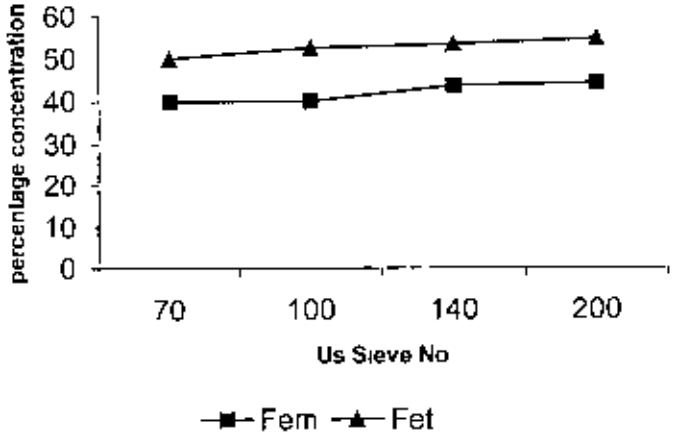


Fig 4.26:Chemical Analysis of the Different Size Fractions
(After reduction)

4.6.2 X-ray Diffraction Analysis of Different Size Fractions:

Fig. 4.27 shows the X-ray patterns of the different size fractions. Diffraction lines belonging to ilmenite, pseudobrookite, rutile, and iron titanium oxide could be identified in these patterns. Diffraction lines belonging to pseudorutile could not be detected in any of these fractions. X-ray analysis of reduced fractions (Fig 4.28) showed that iron and rutile phases are present in all the diffraction patterns. The amounts of the different phases present in these patterns were however not calculated. The result is therefore only qualitative in nature.

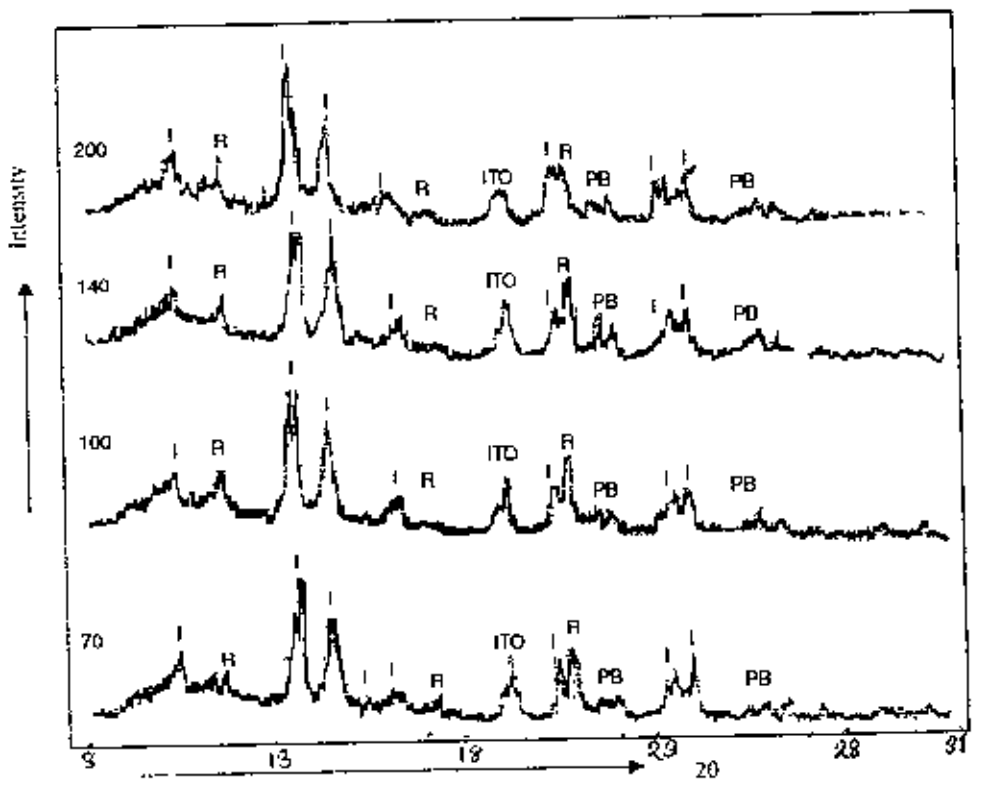


Fig 4.27: X-ray Diffraction Patterns of the Different Size Fractions (I-ilmenite, ITO –iron titanium oxide, PB-Psudobrokite, R- rutile)

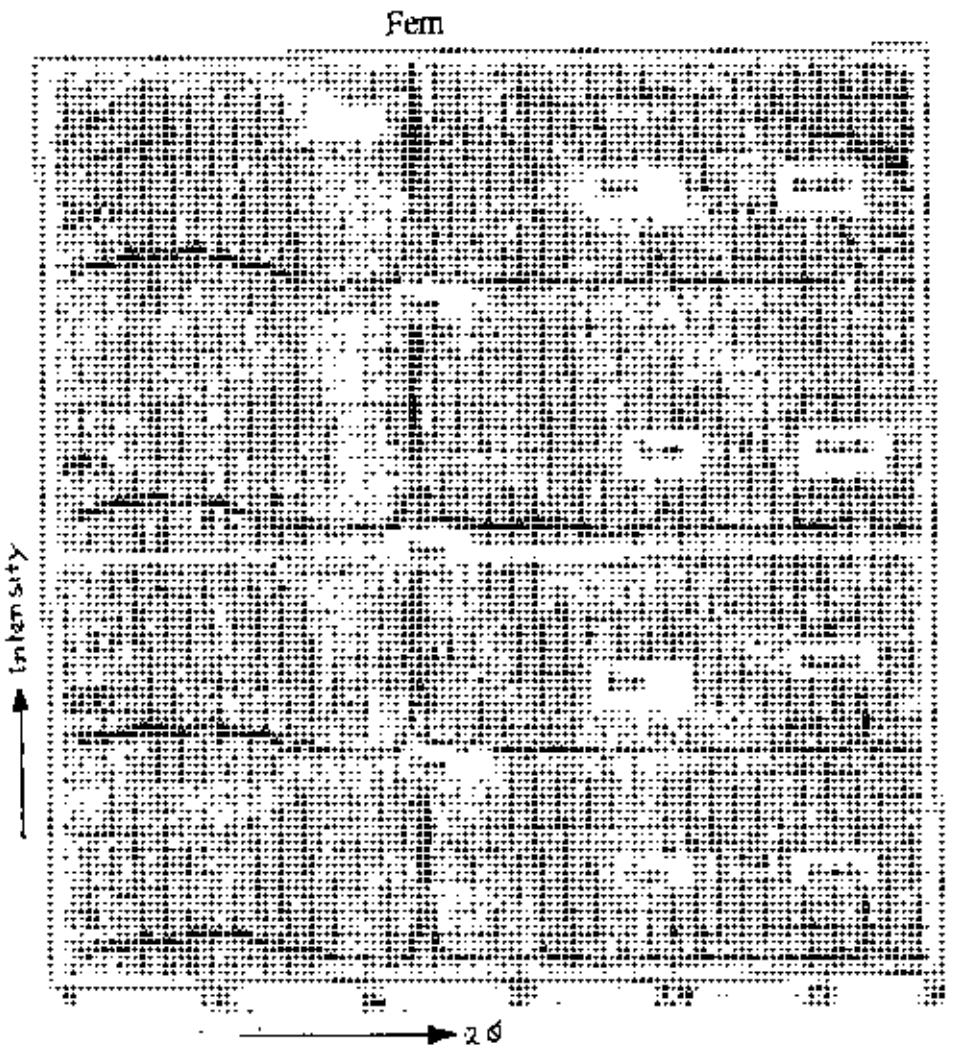


Fig 4.28 X-ray Diffraction Patterns of the Different Size Fractions (After Reduction)

4.6.3 Sphericity of Different Size Fractions

Sphericity, a geometrical factor, of the three-ilmenite fractions was determined. For this purpose, the raw ilmenite sample of different size fractions were photographed under a stereoscope. Sphericity of a particle was then calculated from the following formula.

Sphericity $= d_n/a$

Where d_n = nominal dia of the particle

$$d_n = (a + b + c) / 3$$

a=length of major axis

Sphericity of at least twenty grains of each size fractions was measured (Fig 4.29) and average value was taken as sphericity of the particular fraction and data are tabulated.

The sphericity of the three samples is found and lies in a narrow range, 0.820 to 0.839. Sphericity of N.N Shams[50] showed that Moheskhali ilmenite also lies in narrow range 0.773 to 0.845. However finer size fractions are found to have a slightly higher Sphericity than the courser ones. So finer fractions have longer history of weathering, erosion etc during transportation.

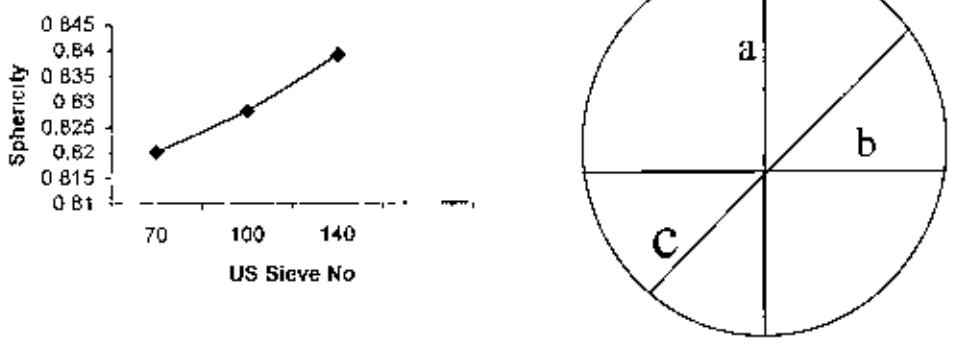


Fig 4.29 Sphericity of Different Size Fractions

CHAPTER-5 SUMMARY AND CONCLUSION

Introduction

Analysis of the as-received sample has shown that Cox's Bazar ilmenite contains around 40 % TiO_2. This percentage of titanium di oxide in this deposit of ilmenite is below the minimum that is required for commercial application. From the different techniques of upgradation, reduction followed by leaching was selected. This process is simple and is easy to manipulate when compared with other techniques available for upgradation. Reduction characteristics of ilmenite depends upon numerous factors including size and shape characteristics of the ilmenite particles, composition, presence of the different phases and their morphologies, presence of defects like voids, cracks etc [10].

5.1 Study of Reduction Behavior

Reduction was carried out in the as received condition, in presence of carbonate, after oxidation and after magnetic and size fractionation. The prime concern of these experiments was to identify the most suitable route for reduction. The effects of time and temperature on the extent of reduction were not, however, studied. Since characteristically, Cox' s Bazar ilmenite was found to be similar to Moheskhali ilmenite in the as received condition, optimum time and temperature established earlier was used for all these reduction experiments.

5.2. Effect of Oxidation

Higher extent of reduction in oxidized condition has been attributed to the introduction of defects (cracks, grain boundaries etc.), conversion of almost al ferrous iron to ferric state and alteration of equilibrium conditions and rate reduction from ferric to ferrous state [9]. Experimental data of oxidation indicates the conversion of ferrous oxide to its higher oxides Fe_2O_3 that leads the increase of reduction rate.

5.3. Effect of Carbonate

From a previous [10] study, it was found that addition 10% carbonate to the reduction mixture gives the most satisfactory result. That is why 10% Na_2CO_3 was used in this experiment and the results show an increase of percentage in reduction compared to the uncatalyzed condition. At a lower temperature the reduction proceeds via the solid-state reaction between carbon present in charcoal and the oxides of iron present in ilmenite. At temperature above 1000^{O}C, the reaction mechanism changes and carbon monoxide, generated through the reaction between carbon dioxide and carbon of charcoal, acts as the main reducing agent. In other words, the overall reduction rate is greatly enhanced by the availability of the reducing gas that is produced by the gasification of carbon in accordance with the Boudouard reaction. The presence of carbonate in reduction mixture enhances this gasification by supplying carbon dioxide produced from the breaking of carbonates at high temperature.

5.4. Effect of Size Fractions

Particle size plays an important role in the kinetics of reaction. Reaction rate increases with reduced size as the finer particle provide more contact area to begin the reaction. Keeping this in mind, effect of size of the particles of ilmenite on reduction was studied.

Increasing sieve number in sieve analysis indicates the increase of fineness of the particle. With increasing fineness the active surface area for the reduction also increases. The reduction reaction starts at the contact points of ilmenite and the reducing agent. So the extent of reduction was higher for the finer particles. The present study has shown that although finer fractions of Bangladesh ilmenite contain higher percentage of iron oxides, they actually get reduced at a faster rate. As a result the reduced sample of finer fraction contain a lower amount of iron in the oxide form. Thus from the viewpoint of optimization of reduction process, adaptation of separate reduction procedure for each fraction is not necessary.

5.5. Reduction Behavior of Magnetic Fractions

Alteration of ilmenite makes it a heterogeneous substance as it produces variety of products within the ilmenite grains containing different concentration of iron. Different magnetic fractions were reduced. Results obtained have shown that reduction of three major fractions were relatively higher than higher fraction.

5.6. Study of Alteration

Alteration is a complex process but the simplest alteration mechanism can be explained as follows[18, 20, 22, 28, 26].

Ilmenite ⟶ Pseudorutile ⟶ Rutile + Hematite

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

This is the two-stage simplest alteration mechanism. In the first stage of the alteration of ilmenite one third of the total iron is lost from ilmenite and the remaining iron is converted to ferric state forming pseudorutile. The second stage involves the removal of remaining iron and loss of some oxygen to form rutile. A general feature of altered ilmenite grain is that the altered product includes materials that give a pseudorutile diffraction pattern. The presence of pseudorutile has been detected in the altered grains of ilmenite from South and West Australia [31], South Africa [23], Indonesia, Brazil [47] and Quilon [47] (South India).

These alteration stages can be deduced qualitatively from the changes in mineral proportions revealed by the diffraction spectra of magnetic fractions of altered ilmenite grains. Alteration can be indicated by the changes in Fe^{2+}/Fe^{3+} and Fe/Ti ratios, as well as variations in magnetic susceptibility, density, hardness and reflectivity, structural and morphological changes [47]. In nature, progressive alteration of ilmenite results in the formation and co-existence of different phases. X-ray diffraction has been used to identity the products of weathering.

The presence of any altered product like pseudorutile could not be detected in the X-ray patterns of the different magnetic fractions. So it can be inferred that there is no alteration in this present deposit. However positive identification of all altered phases is difficult because of indistinct and similar structural as well as physical properties.

Besides this in X-ray pattern, slight shifting of peaks related to nearer 2T angles also might influence the diagnosis. To overcome the above problem thermogravimetric analysis (TGA) was carried out. It has been suggested[19] that altered ilmenite suffers a weight loss at around 600°C due to loss of bound water. The results of thermogravimentric investigation could not detect the presence of bound water in the grains of ilmenite.

5.7 Conclusions

1. Cox's Bazar ilmenite contains about 40%TiO_2 and from the point of view chemical analysis it is similar to Moheskhali deposit.

2 The bulk of ilmenite of the Cox's Bazar deposit belongs to magnetic fractions separated at currents of equal to or less than 0.3A. Except for the fraction separated at a separation current of 0.25A, the contents of total iron and ferrous iron in the different fractions gradually decrease with an increase in the separation current.

3. Oxidation prior to reduction and addition of carbonates in the reduction mixture increase the extent of reduction under all the conditions investigated The extent of reduction, after oxidation, of the different magnetic fractions does not show any significance difference. Thus, so far the extent of reduction is concerned separate reduction procedures for the individual magnetic fraction may not be necessary.

4. TGA studies did not indicate the presence of combined water. X-ray patterns did not show the presence of pseudorutile. It was concluded that ilmenite of Cox's Bazar deposit has not been altered to any significant extent.

5. Finer fractions of Cox's Bazar ilmenite contain higher amounts of iron and have a higher degree of reduction. Higher reduction rate of finer fractions of ilmenite is believed to be principally due to shorter diffusion length in these particles. It is concluded that as far as the optimization of reduction parameters of Bangladesh ilmenite is concerned, a separate reduction procedure for each fraction is not necessary.

5.8. Suggestions for Future Work

- ξ In this experiments reduction behavior was studied. But no reaction mechanism or kinetics was studied. Kinetics of the reduction reaction might lead to new conclusion.
- ξ Leaching behavior of the reduced size and magnetic fractions may be investigated to find out if they show any difference in their leaching characteristics.

APPENDIX-I

ESTIMATION OF FERROUS IRON:

All the solutions be kept ready before analysis

- Take 0.5 gm of finely ground sample in a 500 ml flask
- Add
  - a) 40 ml of distilled water
  - b) 25 ml conc. H_2SO_4
- Heat gently to boiling, boil for one minute.
- Add 10 ml of HF, boil for 10 minutes.
- Remove form hot plate and immediately add
  - a) 100 ml of 4 pct. boric acid (4gm boric acid in 100cc water)
  - b) 15 ml of H_3PO_4-H_2SO_4 mixture.
  - c) 100 ml of distilled water.
  - d) Cool in running water.
- Add 1 ml of Barium diphenylamine sulphonate indicator.
- Titrate with O. 1N potassium dichromate solution to a violet-blue and point.

Calculation

$$\% Fe^{++} = \frac{ml\ of\ k_2Cr_2O_7 \times N \times 0.5584 \times 100}{wt\ of\ sample}$$

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 of H_3PO_4-H_2SO_4 mixture.
  b) 10 ml of Zimmerman solution
  c) 5 drops of Barium diphenylamine sulphonate indicator.
- Titrate with standard potassium dichromate solution
  Appearance of violet color is the END POINT.

Calculation:

$$\% \text{ Metallic iron} = \frac{ml\ of\ K_2Cr_2O_7 \times N \times 0.5584 \times 100}{wt\ of\ sample}$$

$$\text{Factor } K_2CrO_7 = \frac{55.84 \times Normality\ of\ K_2Cr_2O_7}{100}$$

ESTIMATION OF TOTAL IRON:

- Melt 10-15 gm of potassium-hydrogen sulphate (in silica crucible) to get a clear solution.
- Allow the melt to solidify.
- Weigh out 0.5 gm of FINELY GROUND sample.
- Spread the weighed sample evenly over solidified potassium bi-sulphate.
- Heat gently to melt
- Swirl the contents of the crucible carefully.
- Increase the temperature to the maximum (900^0)
- Heat (at 900^0c) for 30 minutes.
- Allow solidifying.
- Place the crucible (and the lid) inside a beaker containing 20 pct H_2SO_4.
- Make upto 250ml.

N.B. Use this solution for the determination of TiO_2 also

- Pipette out 25 ml of the solution in a conical flask
- Add 5ml conc. HCl, Heat to 80^0C.
- Reduce the iron solution by adding (DROPWISE) FRESHLY PREPARED $SnCl_2$
- Solution [Add till the color disappears, add one drip excess]
- Cool immediately in ICE (to 20^0C)
- Dilute to about 100 ml.
- Add 10ml of Saturated $HgCl_2$ solution (rapidly, at a time) and mix thoroughly.
- Silky white precipitate will be obtained Allow to stand for 5 minutes.
- Add 5ml of conc., H_2SO_4 and 10 drops of n-phenylanthralinic acid indicator.
- Titrate with std. Potassium dichromate solution to pink color. This color change is not very prominent, has to be noticed carefully.

Calculation :

$$\% \text{ Total iron} = \frac{ml\ of\ K_2Cr_2O_7 \cup N \cup 0.5584 \cup 10}{wt\ of\ sample}$$

$$\text{Factor of } K_2Cr_2O_7 = \frac{55.84 \cup Normality\ of\ K_2Cr_2O_7}{100}$$

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

$\%Fe^{III}$ = % total iron - $\%Fe^{II}$

ESTIMATION OF TiO_2

- The apparatus consists of a 500 ml Erlenmeyer flask with a 2-hole rubber stopper. A pointed glass rod nearly touching the flask is placed in one hole of the stopper and the short end of the delivery tube is placed into a 400ml. Beaker containing saturated sodium bicarbonate solution. The aluminum foil is attached to the glass rod fixed with the stopper.
- Take 25ml of solution (prepared for estimation of total iron) in a 500-ml Erlenmeyer flask.
- Add 30 ml of Hcl (conc.)
- Boil the solution
- Attach 2gm of high purity aluminum foil to the end of the glass rod of the redactor.
- Remove the flask form the heating mantle.
- Immediately insert the rubber stopper carrying the glass rod with aluminum and the delivery tube to the flask.
- Place the other end of the delivery tube below the level of the saturated sodium bicarbonate 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 dissolved gently boil the solution for 3-5 minutes keeping the delivery tube still immersed in the sodium bicarbonate solution.
- Ensure that the rubber is rightly fitted.
- Cool the flask (in ice) to less than 60^0C.
- As the sample (in the Erlenmeyer flask) cools, the sodium bicarbonate solution is drawn into the Erlenmeyer 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 2 ml of 24 pct ammonium thiocyanate indicators.
- Titrate with standard ferric ammonium sulphate indicator.

Calculation :

$$\% \ TiO_2 = \frac{ml\ of\ titrant \cup factor \cup 1000}{Wt\ (mgm)\ of\ the sample}$$

$$\text{Factor} = \frac{Wt\ of\ Std.TiO_2 \cup \%m\ Std\ TiO_2}{ml\ of\ titrant \cup 1000}$$

PREPARATION OF SOLUTIONS

1. Ammonium Thicoyanate indicator

Dissolve 24.5 gms of ammonium thiocyanate in 80ml of hot distilled water. Filter through two What Man 42 filter paper using vacuum. Cool, dilute to 100ml and store in a dark colored bottle.

2. Standardization of Ferric Alum:

Dissolve 30.16gm of ferric ammonium soleplate in 800ml distilled water and 15ml 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 litre. Standardize the solution against standard TiO_2 reduced in the same way as described for the sample.

3. Preparation of $SnCl_2$:

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

4. Phosphoric acid-Sulphuric acid Mixture

150ml of conc. H_2O_4 150ml of H_3PO_4 in 700ml distilled water. Total volume will be 1000ml.

5. Zimmerman Solution

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

6. Diphenyl amine sulphonate Indicator

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

7. Barium diphenylamine sulphonate Indicator

0.2gm of barium diphenylamine salt in 100ml distilled water.

8. N-phenylanthralinic acid indicator

0.1gm phenylanthralinic acid in 100ml of 0.005 molar sol" of NaOH.

9. 20% HCl Solution

Conc. HCl contains 35% HCl. Take 100cc HCl and add distilled water to make upto 765cc

10. $K_2Cr_2O_7$ Solution

1.9033 gm 1 litre (0.1N Solution)

49.033 for 1 litre

11. 0.005 molar NaOH Sol".

0.02gm NaOH crystal in 100 ml H_2O

12. 4% Boric acid:

4 gm boric acid in 100ml water.

13. Potassium ferricyanide solution:

0.02gm potassium ferricyanide in 100ml water.

14. 20% H_2SO_4

80ml H_2O + 20 H_2SO_4

APPENDIX – 2

Table-A 1: Data for Magnetic Fractionation of Ilmenite Sample

Separation Current (A)	Percentage
0.15	28.3
0.2	28.9
0.25	21.6
0.3	11.6
0.35	5.55
0.4	2.859

TableA2: Chemical Analysis of Different Magnetic Fractions

Current (A)	Fe++	Fe+++	Fet
0.15	13.9	33.117	46.6
0.2	12.44	32.55	45.5
0.25	11.49	38.5	50
0.3	10.402	30.8	41.32
0.35	9.4	31.15	41.32
0.4	8.855	31.15	40.2

Table A3: Chemical Analysis of As Received, Oxidized And Catalyzed Fractioned Sample

Current (A)	Fe_m Oxidized	Fe_m as received	Fe_m Cat.& oxidized
0.15	43	47	42.5
0.2	42.75	45.5	40.5
0.25	42	43	48
0.3	41	42.5	38

Table A4: Chemical Analysis of the Reduced As Received Sample

Current (A)	Fet	Fem
0.15	48	42.5
0.2	46.52	40.5
0.25	50.25	48
0.3	43.32	38

Table A5: TGA Analysis of Different Magnetic Fractions

0.15A (123.9 gm sample)

Points	Temp^{0}C	Wt loss	%Wt loss
1	100.19	.026	.021
2	406	.119	.096
3	558.16	.509	.411
4	651.58	.685	.553
5	885.83	.093	.553
6	943.51	1.121	.905
7	948.69	1.006	.812

0.2A(117.6 gm sample)

Points	Temp^{0}C	Wt loss	%Wt loss
1	103.43	.051	.043
2	511.29	.208	.177
3	614.41	.422	.359
4	878.71	.026	.022
5	948	1.2	1.4

.25A(108.9 gm sample)

Points	Temp (^{0}C)	Wt loss (mg)	%Wt loss
1	80.94	.023	.021
2	442.62	.161	.148
3	657.74	.658	.605
4	866.24	.180	.165
5	946.92	1.953	1.794
6	948.92	2.02	1.855

.3 A (112 gm sample)

Points	Temp (^{0}C)	Wt loss (mg)	%Wt loss
1	45.80	.009	.008
2	263.7	.097	.86
3	560.19	.33	.298
4	617.72	.492	.439
5	685.15	.596	.532
6	786.52	.584	.521
7	883.2	.510	.456
8	939.6	2.949	2.634
9	947	2.99	2.67

0.35A(134.5 gm sample)

Points	Temp (^{0}C)	Wt loss (mg)	%Wt loss
1	115.45	.043	.032
2	448.68	.194	.144
3	486.54	.438	.325
4	651.35	.623	.463
5	873.9	.935	.695
6	947.92	2.847	2.117
7	948 74	2.850	2.119

0.4A(106 gm sample)

Points	Temp (^{0}C)	Wt loss (mg)	%Wt loss
1	83.81	.081	.077
2	417.48	.246	.228
3	498.89	.406	.384
4	559.31	.513	.486
5	640.99	.947	.896
6	921.17	1.456	1.380
7	947.63	1.647	1.561

TableA6: Sieve Analysis

Us Sieve No	Mesh opening	%Retained sieve
70	210	1.87
100	149	58.47
140	105	35.9
200	74	2.29
pan	--	.64

Table A7: Chemical Analysis of Different Size Fractions

Us Sieve No	Fe^{+}	FeO	Fe^{++}	Fe_2O_3	Fe Total	TiO_2
70	12.84	16.5	27.18	38.82	39	41.73
100	11.84	15.625	28.45	40.64	41.132	40.14
140	12.28	15.78	30.67	43.65	43.35	39.26
200	13.84	17.22	30.9	44.14	44.35	39.26

Table A8: Chemical analysis of Different Size Fractions (After Reduction)

Us Sieve no	Fem	Fet
70	39.86	50
100	40	52.5
140	43.5	53.36
200	44.1	54.47

Table A9: Sphericity of Ilmenite of Different Size Fractions:

US Sieve No	Sphericity
70	0.820
100	0.828
140	0.839

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