Characterisation of Bangladesh Ilmenite in the Process of its Upgradation into Synthetic Rutile

by

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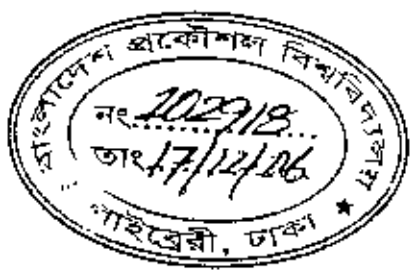
DOCTOR OF PHILOSOPHY



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

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ABSTRACT

Heavy minerals found in the beach sands of Bangladesh are one of the most important mineral deposits that have, so far, been identified in Bangladesh. Ilmenite is the most abundant mineral in these deposits and constitutes about 25 per cent of all the heavy minerals. It has been estimated that about one million tons of ilmenite can be separated from the beach sands of Bangladesh.

In 1977, a pilot plant was set up at Cox's Bazar by the Bangladesh Atomic Energy Commission to separate the individual heavy minerals from these deposits. Unfortunately, however, the ilmenite produced at Cox's Bazar pilot plant contains less than 40 percent TiO_2 together with a large amount of iron in the form of oxides, silica, magnesium and unacceptable amounts of manganese and chromium. Ilmenite containing less than 55 percent titanium di-oxide is not considered suitable for industrial use. As a result, this valuable mineral separated from the beach sands of Bangladesh, which is used in the manufacture of paints, welding electrodes, ceramics, etc. could not find any market in Bangladesh or elsewhere.

In view of rapid depletion of known reserves of natural rutile (TiO_2) efforts are being made throughout the world to transform ilmenite into rutile through thermo-chemical treatment. As a result of these investigations, a number of commercial processes for the production of rutile from ilmenite have been developed. This rutile is known as synthetic rutile. No efforts are known to have been made to convert Bangladesh ilmenite to synthetic rutile. It was, therefore, considered necessary to explore the possibility of converting Bangladesh ilmenite to synthetic rutile through thermo-chemical treatment. It is believed that the successful conversion of Bangladesh ilmenite into synthetic rutile will make this valuable mineral of Bangladesh useful at home and abroad, enhance the confidence in our ability to use our own natural resources and also the prestige of the nation.

In this dissertation investigations were carried out to characterize Bangladesh ilmenite in the process of its up-gradation into synthetic rutile. Raw sand containing the heavy minerals was collected from the back dune surface layers of heavy mineral deposits at Teknaf village area (Lengurbil deposit) from points located 2-3 Km away from the water line and 5-6 meter above mean sea level. The area selected for the study falls between the latitude 20°52'7" to 20°52'21"N and longitude 92°16'10" to 92°15'58"E at Teknaf. The heavy mineral proportions

of the concentrates were determined to be 89-92% by point counting grains using both reflected and transmitted light microscopy. Among the minerals found in the Teknaf beach sands ilmenite is the most important one It constitutes around 24% percent of heavy mineral tonnage, the other important constituent minerals of the heavy minerals being rutile and zircon. Factory grade ilmenite was produced at the Beach Sand Mineral Exploitation Centre, Cox's Bazar. The techniques of seperation are based on the difference in physical properties like density, electrical and magnetic properties. The reduction-leach route of up gradation of ilmenite was followed in this investigation. The sample of ilmenite was analyzed chemically by standard methods of wet chemical analysis in the as received condition, after oxidation and reduction and also after magnetic and size fractionation. X-ray diffraction analysis was performed to identify the phases present in the various fractions. Thermo-gravimetric analysis of the magnetic fractions was carried out to detect the presence of water in the sample. Combined water in ilmenite is an indicator of the extent of alteration. The effect of oxidation on the extent of reduction and also on subsequent leaching of Bangladesh ilmenite has been investigated. The effects of time and temperature on the oxidation of ilmenite have been followed by chemical analysis, X-ray diffraction and optical microscopy. A few samples of ilmenite were also observed under a scanning electron microscope. The sample of ilmenite both oxidized and as received was reduced with charcoal in the temperature range of 800^0C to 1100^0C for treatment time of up-to 5 hr. The magnetic fractions and the size fractions were also reduced under identical conditions. The extent of reduction was followed by chemical analysis and X-ray diffraction analysis. The reduced samples were also observed under optical and scanning electron microscope. The reduced samples were leached in hydrochloric acid. An attempt has been made to understand the kinetics and mechanisms of leaching process.

Ilemenite sample under investigation contained 25.32% FeO, 32.53% Fe_2O_3 and 39.96% TiO_2. From the sieve analysis it was found that more than 96% of the ilmenite belongs to the US sieve no. 100, 140 and 200.The sphericity of all three samples was found lie in a narrow range, 0.822-0.843. However, finer size fractions were found to have a slighdy higher sphericity than the coarser one. Magnetic fractionation showed that about 96% of Teknaf ilmenite belongs to the fractions separated by a current of 0.10 - 0.30 amperes and relative sp.gr. range of 4.1-4.5 in comparison of synthetic rutile sp.gr. 4.7

X-ray diffraction patterns of different magnetic fractionated as received ilmenite shows the presence of pseudorutile phase and TGA report indicate the presence of bound water.

Detailed investigation on the X-ray pattern and TGA report led to the conclusion Teknaf ilmenite is in a partially altered state but not hydrated enough.

Samples of ilmenite have been oxidized in the temperature range of 750-950^{0}C for a period of up-to 2 hr. Scanning electron microscopic studies revealed the presence of cracks in the oxidized samples. Chemical analysis results have shown that the oxidation of the as received ilmenite in normal furnace atmosphere at 950^{0}C for 1 hr. converts all but 0.57 percent FeO.

The samples of ilmenite were reduced by charcoal in the temperature range 800^{0}C to 1100^{0}C for treatment time of up-to 5 hr. The optimum conditions for reductions were found to be 1050^{0}C and 4 hr.The maximum extent of reduction was found to be 87.61%. It was also identified the optimum ilmenite coke ratio for reduction is 1:1.

Finer fractions of Teknaf ilmenite contain higher percentage of iron oxide. They actually get reduced at a faster rate and the reduced samples of finer fraction contain a lower amount of iron in the oxide form. So adaptation of separate reduction procedure for each of the size fractions is not necessary.

Ilmenite fractionated at lower current contains higher percentage of iron oxide. Fractions separated at lower currents are reduced to a higher extent than those separated at higher currents and the reduced samples separated at lower currents actually contain lower amount of iron in the oxide form. Thus adaptation of separate reduction procedure for each of the fraction will not be helpful to enhance the reduction process.

Reduction with charcoal under optimum condition showed that the maximum metallic iron content of the sample reduced after oxidation were higher (39.36%) than in the samples reduced (38.36%) in the as received condition. Reduction of ilmenite in the oxidized condition was found to proceed in two stages. The first stage is the reformation of ilmenite according to the either or both of the following reactions:

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

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

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

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

On the other hand, the reduction of as received Bangladesh ilmenite involves (i) conversion of pseudorutile into rutile and ilmenite and (ii) change of ilmenite into metallic iron and rutile.

The reduced ilmenite samples were leached in 5 to 15 percent hydrochloric acid solution in temperature range of 30 to 85^{0}C for periods of up to 2 hr. Attempts were made to identify the effects of oxidation on the extent of leaching. Oxidation prior to reduction of Teknaf ilmenite was found to increase the rate of leaching. The iron removal from leached ilmenite after reduction in the oxidized condition is more than from ilmenite leached after reduction in the as received condition. The kinetic data of leaching of ilmenite reduced after oxidation was found to follow first order reaction model i.e. $G(\alpha) = -\ln(1-\alpha)$ up-to an α value of 0.5 (up-to 50 percent reaction) and then change to spherical model i.e.,$G(\alpha) = [1-(1-\alpha)^{1/3}] = (k/r)t$ On the other hand, leaching of ilmenite reduced without oxidizing was found to follow the spherical model i.e., $G(\alpha) = [1-(1-\alpha)^{1/3}] = (k/r)t$ .al-through the leaching process. Oxidation of ilmenite prior to reduction was also found to have decreased the activation energy of leaching from 23 kJ/mol, found for samples leached after reduction in the as received condition, without oxidizing, to 16 kJ/mol. for sample leached after oxidation and reduction.

The X-ray diffraction pattern of the leached sample did not show the presence of metallic iron or ilmenite, the maximum intensity peak was that of rutile. TiO_2 content of synthetic rutile prepared from Teknaf ilmenite is very much compareable with commercially available synthetic rutile. The values for the other constituent of iron oxide are well comparable. The variations may be due to the difference in the raw materials used. In general it can be stated that synthetic rutile prepared from Teknaf ilmenite by this oxidation-reduction-leach route is equally good if not better than the commercially available sample. So synthetic rutile obtained in these studies contains 91.50 percent TiO_2, which is very much compareable in chemical constitution with the commercially available synthetic rutile.

Chapter 1

INTRODUCTION

1.1 Introduction

Ilmenite, rutile and leucoxene are the only naturally occurring titanium bearing minerals that have been seriously considered as suitable feedstock for either the metal producing or pigment industries. This is because only these minerals are found in large enough commercial concentrations; compared with other naturally occurring minerals containing titanium, to be suitable for industrial exploitation. The other minerals that contain titanium are arizonite titaniferous magnetite, sphene, perovskite etc. Major deposits of ilmenite, rutile and leoucoxene are located in Australia, Brazil Canada, Norway, USA, India, Malaysia, Ceylon, China, South Africa and Russia.

Ilmenite, usually referred to as ferrous titanate ($FeO.TiO_2$), is abundant in nature and is regarded as an alternative raw material for the production of titanium di oxide, which can be used directly as pigment or for the manufacture of titanium. Ilmenite is named for its place of recovery, at Ilmen Lake in the Ilmen Mountains of Russia. Ilmenite forms as a primary mineral in mafic igneous rocks and is concentrated into layers by a process called "magmatic segregation". Ilmenite also occurs in pegmatites and some metamorphic rocks as well as in the sedimentary rocks that are formed from the weathering and erosion of them. It has a specific gravity of 4.5 to 5 and crystallizes in the rhombohedral class of the hexagonal system. The colour is usually iron black, but brown and red varieties with a metallic lustre are also found. It is opaque and slightly magnetic. The theoretical composition of ilmenite shows that it contains about 52.6 percent TiO_2, 47.35 percent FeO. In otherwords it contains 31.56 percent Ti, 36.81 percent Fe and 31.63 percent oxygen. However, in most cases the ferrous iron is partly replaced by ferric iron. The individual grains of ilmenite may also contain submicroscopic inclusions of rutile, essentially pure TiO_2 with very small quantities of iron. Other grains may also be altered, resulting in the breakdown of the ilmenite structure with partial leaching and oxidation of the iron This can increase the TiO_2 content of ilmenite to 60 per cent or more. Pseudorutile and leucoxene are the alteration products of ilmenite containing higher titanium and are usually limited 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 are marketed as an acceptable substitute for rutile. Rutile is essentially naturally occuring TiO_2 and deposits are relatively rare. As a result of

increasing consumption, particularly in the paint industries, the deposits are fast depleting and demands outstrip supplies. This shortage of natural rutile has forced technologists throughout the world to develop a number of processes to increase the titania content of ilmenites 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 manufacturing of titanium dioxide pigment due to the 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. Infact the largest percentage (upto 95%) of world use for titanium oxide is for the production of this white pigment.

Ilmenite is a source of titanium metal. Due to extreme resistant 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. Ilmenite is used in the preparation of high gloss finishes in ceramic industries, It is used in the manufacture of electrical insulators, brilliant white pigment, in the production of white rubber, and as a filler for paper.

Ilmenite is used to produce titania rich slag, which is an ideal feed material in the 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 [Krishnan and Roy, 1942] of ilmenite as well as its products are summerised as follows:

Titanium Metal:

Berzelius first prepared titanium by reducing potassium fluo-titanate with sodium. In a very finely crystalline or amorphous condition it is a grey-powder. At ordinary temperatures the metal is rather brittle but can be forged and drawn into wire at red heat. It is twice as heavy

as magnesium and only slightly heavier than aluminium. The metal has a high proportional limit, which gives a measure of its elasticity, which is much higher than that of cold-worked stainless steel. Hence titanium, when fabricated, can offer lightweight sections, which can bear bigh stresses. It has been suggested for use in the very highly stressed parts of aircraft and also for diaphragms in radio-television industry, for spools, spindles etc. in textile machinery and so on.

The metal is resistant to the corrosive action of seawater, nitric acid, boiling chlorides, wet chlorine gas, strong alkalies and organic acids. It is attacked by dry chlorine, sulphuric and hydrochloric acids and boiling nitric acid. Titanium and a few of its alloys are used now instead of stainless steel in some aircraft parts and military equipment Titanium is claimed to give the same or better protection as high-class armour steel against projectiles for the same thickness of metal. Titanium can be surface-hardened for use as pistons because of its lightness, strength and resistance to frictional wear, but some other metals are better in regard to heat conductivity.

Titanium dioxide:

Titanium dioxide is at present the most important manufactured compound of titanium in commercial use. It has been produced from ilmenite and rutile and is well known as paint pigment called titanium white. The pigment is used in paints, enamels and lacquer; and as filler in paper, rubber, leather, textile, plastic, printing inks etc. The chief properties contributing to the importance of this pigment are its high opacity and covering power. Amongst white pigments it has apparently the highest refractive index (2.7). It is also practically inert and resistant to atmospheric action. The paint wears evenly and without cracking or pealing. It resists the action of seawater, hydrogen sulphide, sulphuric acid etc.

Titanium dioxide is often mixed with various other pigment materials and fillers like barium sulphate, calcium sulphate, zinc oxided, lithopone etc. A pigment containing 75 per cent barium sulphate and 25 percent titanium dioxide is called titanox while the corresponding calcium sulphate pigment is also used. Mixtures of lithopone and titanium dioxide are also used as paints.

It has low specific gravity. Its very fine particle size enables it to be dispersed easily in liquid media. It is also non-toxic and can be safely used in various industries. It is used to give whiteness and opacity to various grades of paper textile etc. In the rayon industry titanium pigment has been found useful because of its inertness and ability to reduce the lustre of the fibers i e. acts as a valuable de-lustrant

Titanium dioxide pigment finds extensive use in cosmetics where its useful properties and particularly its non-toxic character are prized. It is used in face powders together with certain other constitute to give the desired adhesiveness and absorbing and covering power. It is also used in various preparations like cold creams, skin lotions, ointments, polishes, tooth powders, pastes etc.

Titanium dioxide is widely used in the ceramic industry. It imparts a yellow colour to vitrified ware and enamels. Opacifying enamels have been developed in recent years for direct application on metal without a prime coat. In nitro-cellulose and other lacquers, titanium dioxide is used in view of the high opacity imparted by it. In the manufacture of plastic it is used as the opacifying agent and for giving different colours. An ivory-white enamel made from the dioxide is used in making artificial teeth.

Titanium Chemicals:

In the dyeing industry the chloride and sulphate of titanium find application, as they are effective stripping agents, which can be used on silk, cotton and wool. Other titanium salts such as fluoride, lactate, tartarate and double salts of alkali and titanium are also employed for this purpose. Titanium chloride destroys basic dyestuffs dyed with tannic acid-tartar emetic mordant. If hard water is used in the process, some hydrochloric acid should be added to the titanium chloride in order to prevent the precipitation of titanic acid by hydrolysis. In some cases titanium dioxide serves as an excellent mordant. Alizarine scarlet, dyed on wool with titanium mordant, is the fastest colour that wool can take. Alizarine yellow also gives similar results Potassium-titanium-oxalate is used as mordant in the dyeing of vegetable tanned leather with basic colouring matter.

Titanium tetra chloride ($TiCl_4$) is an important chemical of titanium, which has various uses including that of being the raw material for the manufacture of metallic titanium. It is manufactured as a liquid, which forms dense white fumes on coming into contact with moisture in the air. This property is extensively used for producing smoke screens and for skywriting. The addition of a little ammonium to this compound is said to make the fumes denser.

A compound of logwood and titanium produces deep black permanent ink, which is indelible and cannot be washed easily. Titanous chloride is used for removing iron stains from cloths in laundries. Titanium dioxide has been used in catalysts for esterfication of acetic acid. Alkyl titanates formed by the action of $TiCl_4$, on alcohols show excellent waterproofing qualities and can be applied on all types of natural and artificial fibres as well as on metallic surfaces. Barium titanate has been used in high voltage condensers (e g. television sets)

because of their special electro-mechanical characters in high electric fields (Jaffe, 1950). Titanium compounds have been used in the manufacture of insulating materials and also in making thermocouples, resistance heating units, electron discharge tubes etc.

Carbides:

Titanium carbide, boride and silicide are very hard substances, which have found use as abrasives. Titanium carbide is already being used as a substitute for tungsten carbide. A mixture of titanium and tungsten carbides are sintered and pressed and the mixed carbides are used as tips for cutting tools, in dies and in abrasive wheels etc.

Titanium in Alloys:

Titanium is an important alloying element in steel. This is largely due to titanium forming stable carbides and nitrides and acting as a de-oxidiser. It acts as a purifier of steel by forming slag.

A few types of ferro-alloys of titanium are made and used in the steel industry. In steel making, both high-carbon and medium-carbon ferro carbo-titanium are used generally as a final addition to steel after manganese and silicon have been put in. In rimming steels (those with very little or no alloying elements and containing generally less than 0.25 per cent C) the addition of titanium serves to keep blowholes clean and free from oxidation so that on rolling they disappear completely. The titanium also helps the evolution of gas contained in the metal before it freezes. It refines the grain size promotes the formation of ferric and its compounded (mainly carbide) become distributed evenly in the steel.

Titanium added to stainless steels, prevents or inhibits intergranular corrosion, which is particularly useful in welds Its use in high chromium heat resistant steels is increasing as it causes a refinement of grain. In certain manganese steels, titanium has been used to replace nickel and vanadium satisfactorily because titanium is able to impart a hard chilled surface layer to iron and steel. Such steel has been used for making axles rollers, wheels etc.

Certain alloys containing cobalt, molybdenum and iron with titanium and beryllium show excellent resistance to several acids, alkalis and other corrosives substances. Titanium alloys with nickel, cobalt and iron are said to have yielded a very suitable material for the manufacture of permanent magnets, which can retain their magnetism over a large range of temperature. A typical composition is said to be 45 percent Fe, 16 percent Ni, 28 percent Co and 11 percent Ti but the titanium content may be higher in some compositions.

Titanium dioxide gems:

During the last few years titanium dioxide has been melted in an electric arc and crystalised to form transparent gemstones. These can be produced in different colours. They have a high refractive index and brilliance and are claimed to be better than artificial corundum as synthetic gemstones. Titanium dioxide is also used in pyrotechnics to produce brilliant light.

The various products of commercial importance indicated above give a broad idea of the attractive avenues open for the utilization of ilmenite.

1.3 Methods of Upgrading

Ilmenite comains titania (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 following five principles [Ganzu and Mazumdar, 1970 and Jena et al., 1973] .

1.3.1 Smelting

This is a pyrometallurgical technique where in ilmenite is heated with a reducing agent and fluxes in an electric arc furnace at high temperature (>1500°C) to get molten iron and titania rich slag containing most of the gangue material. This slag layer is given to further treatment. The process can be represented as follows:

Ilmenite + coal + flux → pig iron + titania rich slag + carbon monoxide.

Synthetic rutile is also produced by smelting a mixture of ilmenite pellets, coke and lime in an electric arc furnace [Elger and Rhoads, 1976]. The slag obtained is tapped at 1600°C and treated with O_2 and titanium pyrophosphate, which converts titanium oxide to crystalline rutile and phosphate glass. The treated slag is then ground and leached with H_2SO_4 to dissolve phosphate glass and to obtain rutile crystal.

1.3.2 Reduction followed by removal of iron

Most of the successful process for the production of synthetic rutile may he classified in this category. 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. has been used as

reducing agents. Reduction temperatures in the range of 1000°-1100°C are usually employed. Iron is then removed from the reduced mass by leaching, rusting or magnetic separation [Samanta et al, 1968 and Ganzu and Mazumdar, 1970]

Leaching: Hydrochloric 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.

Rusting: Oxidative removal of iron from reduced ilmenite is carried out by rusting in a vessel agitated by blowing air at controlled rates. The following reaction takes place [R.G. Beacher et al, 1965 and Samanta et al, 1968]

$$Fe_{\text{lattice}} \Rightarrow Fe^{++}_{aq} + 2e$$

$$O_2 + 2H_2O + 4e \Rightarrow 4\,OH$$

Ferrous hydroxide is formed by the reaction between the ferrous and hydroxyl ions and by further oxidation rust is formed. Using some ammonium chloride (0.5%) and acidifying pulp with sulphuric acid to a pH of 4 assist rusting. It is a cheap process and yields a high-grade product (containing over 90 percent TiO_2, which can be upgraded further to 94 percent by simple acid leaching) that can be readily processed to pigment-grade titania by the chloride route.

Magnetic Seperation: In these process [Walsh et al,1968 and Pollard et al, 1978] reduction of ilmenite is carried out in the presence of suitable flux (e.g. NaCl, Na_2CO_3,CaF_2,Na_3SiO_2 etc.). As a result, a product resembling sponge iron is obtained. The reduced ilmenite is crushed and wet ground and the mass is subsequently sepereted into two slurries containing iron and titania by means of magnetic seperator.

1.3.3 Direct acid leaching

In the direct leaching of ilmenite sulfuric acid and hydrochloric acids are 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 [Sehra et al, 1966] under suitable conditions can produce a product containing more than 98% TiO_2.

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

Conversion to Titanate:

Ilmenite is treated with Na_2CO_3 at elevated temperatures (900°-1100°C) to obtain sodium titanate [Khairy et al, 1968] according to the following reaction:

$$Fe\ TiO_3 + Na_2CO_3 \rightarrow Na_2TiO_2 + FeO + CO_2$$

The sodium titanate is leached out with water or dilute acid resulting a product containing 93% TiO_2.

Conversion to Sulfate:

Both iron and titanium in ilmenite can be converted to their respective sulfates [Viswanathan Nayar, 1952] by treating with $(NH_4)_2\ SO_4$ at 300-500°C or $NaHSO_4$ at 400-800°C. About 90% Fe and 95% Ti of ilmenite can be recovered by leaching with 7N H_2SO_4. TiO_2 is separated from leach liquor by controlled hydrolysis.

Conversion to Sulfide:

Treatment of ilmenite with some sulfur bearing materials (pyrite, ZnS, Na_2SO_4+ C) or, sulfur vapors leads to the preferential sulphadisation of iron in ilmenite [Sharova and Fotiyev, 1959, and Gaskin and Ringwood, 1959]. For example on heating of a mixture of ilmenite, Na_2SO_4 and carbon at elevated temperature (1000-1300°C) results in the formation of FeS according to the following reaction.

$$FeTiO_3 + Na_2SO_4 + 2C \rightarrow FeS + Na_2TiO_3 + 2CO_2.$$

The reaction product is treated with boiling H_2SO_4 to yield a titania rich product. Synthetic rutile is also prepared by heating ilmenite at 500-1000°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 1000°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 $^1/_2$ hour resulting in a titania rich product [Jain and Jena, 1970 and Jain and Jena, 1973].

1.3.5 Halogenation

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, etc. The residue left after treatment is synthetic rutile.

Chlorinating with Cl_2:

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

Preferential chlorinating of iron oxide in ilmenite has been investigated by some investigators [Patel and Jere, 1960 and Dunn, 1960]. Ilmenite is brequetted with charcoal (6%) and $FeCl_3$ binder and then treated with chlorine at 500°C-600°C. This process results in a product containing about 90% TiO_2. Titanium dioxide has also been prepared by the selective chlorinating of ilmenite with gaseous mixture of Na and Cl_2 in a chlorinator with a certain amount of air or oxygen [Joedden et al, 1983 and Kwangtung, 1978].

Chlorinating with HCl Gas:

A product containing 97% of TiO_2 has been obtained [Sankaran and Bhatnagar, 1968] by selective chlorination of ilmenite by HCl gas at 1000°C for 3 hr in the laboratory. Preoxidised ilmenite requires higher temperatures for effective removal of iron. No solid $FeCl_2$, which causes experimental difficulties in conducting chlorinating, is found when preoxidised samples are used for chlorinarion.

Increasing the percentage of H_2 in the gas mixture of HCl and H_2 the percentage of iron chlorinated is decreased and the condensate mainly consists of $FeCl_2$.

A product containing 90% TiO_2 and 6.6% Fe_2O_3 can be obtained by selective chlorination [British patent, 1954] of ilmenite with a mixture of $TiCl_4$ and Cl_2 at a temperature of 1050°C. Treatment of ilmenite with NH_3 and HCl at 600°C removes about 92% of iron. At temperature 800°C all the irons are removed [Ivashentsev, 1962 and Ivashentsev, 1964].

1.4 Ilmenite Deposits in Bangladesh

Heavy mineral deposits along the coastal belt of Bangladesh constitute a potential national asset [Beach sand minerals report'1983]. The exploration, exploitation, development and uses of these resources are essential for upliftment of national economy. Beach Sand Minerals Exploitation Centre located at Kalatali in Cox' Bazar explored 17 deposits at the

entire southeastern and southern coasts along with their adjacent islands have. Among these deposits 6 deposits are located along the Cox's Bazar –Teknaf coast (Badarmokam, Sabrang, Teknaf, Shilkhali, Inani and Cox'bazar), 7 deposits on Moheshkhali Island (Foreshore deposit, Kutubjum, Fakirghona, Fakirhata, Baroghoria Para, Panirchara and hoanak), 1 deposit on Matarbari Island and 1 deposit on Kutubdia Island. Fig 1.1 shows the map of this area. Only two deposits have been found in the southern coast of the country: 1 in Nijhum Dwip of Haria and 1 in Kuakata of Patuakhali district. Most of these deposits occur at a distance of about 1-2 miles inland from the present shoreline. The distribution of valuable minerals in these deposits is shown in Table-1.1 [Bari Biswas.1993]. Table-1.1 shows that a total of 2,04,96,981 tons of crude sands containig 43,54,501 tons of heavy minerals are available in the deposits in which Ilmenite constitute 10,25,558 tons.

1.5 Beach Sand Minerals Exploitation Center

Beach sands containing valuable heavy minerals were first discovered in 1961 during a geological survey for radioactive minerals in Cox'bazar beach area by the geologist of erstwhile Geological Survey of Pakistan [Schmidt and Asad, 1962]. The exploration drilling began in 1968 at Cox'sbazar and Teknaf under the joint supervision of Mr. Noakes and Mr. Macdonald who also trained geologist and other para staff of the commission in the techniques of drilling and sampling. A bulk sample of sand from Cox'sbazar was sent to Mineral Deposits Limited (MDL), Australia, for testing and in 1970 initial plans for a pilot plant were drawn up on the basis of MDL flow sheets and recommendations. In 1973, Bangladesh Atomic Energy Commission requested the Government of Australia to build a pilot plant at Cox'sbazar. Installation of the plant began in May 1975 and was completed in October 1977. The center is mainly engaged exploration and exploitation of valuable heavy minerals like zircon, rutile, ilmenite, leuxene, monazite, garnet etc. The activities of the center continued in full swing till 1987. After then the Government decided to sell out the center to private sector. But due to some difficulties this decision could not be materialized and the activities of the center were kept pending till 1991. In late 1991 the Government took decision to continue the activities of the center and the activities of the center started again in late 1992. The plant has separated hundreds of tons ilmenite with some other heavy minerals.

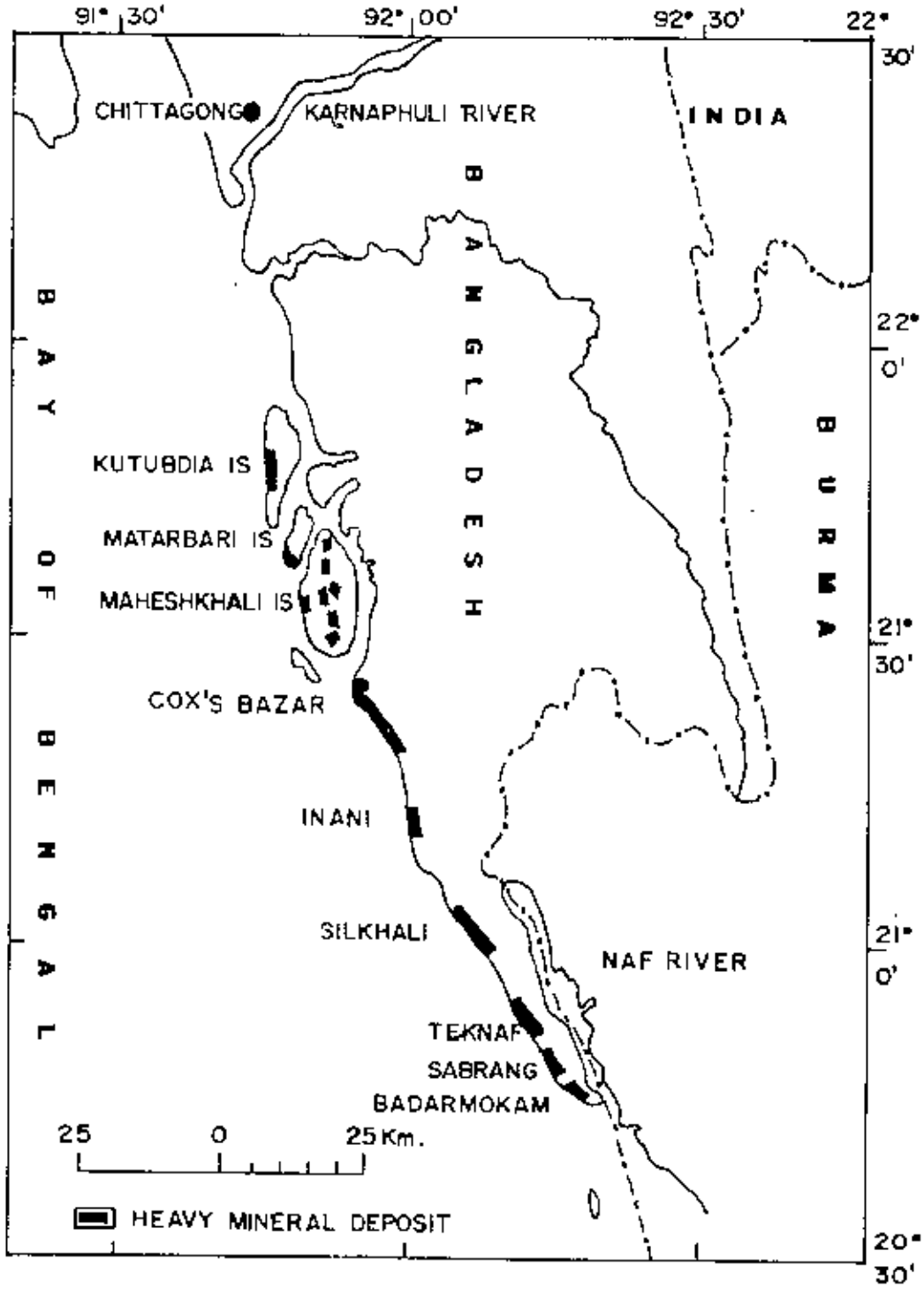


Fig. 1.1 Map showing location of heavy mineral deposits along the southeastern coast of Bangladesh.

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	17,002	-*	4,932	10,275	-*
2	Sabrang	1,347,558	68,582	4,184	1,372	19,614	3,370	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	26,000	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
Mobeshkhali Island											
8	Fore-shore beach	276,560	119,480	7,145	3,788	554,961	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 No	Deposit	Sand Tonnage	Heavy Mineral Tonnage	Reserve of valuable minerals (in ton)							
				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	Fakirhata	409,120	96,750	5,515	31870	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	Matarbari	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	796	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

1.6 Prospects of Bangladesh Ilmenite

Heavy minerals found in the beach sands of Bangladesh are one of the most important mineral deposits that have, so far, been identified in Bangladesh. Ilmenite is the most abundant mineral in these deposits and constitutes about 25 per cent of all the heavy minerals [Report, 1985].

In 1977, a pilot plant was set up at Cox's Bazar by the Bangladesh Atomic Energy Commission to separate the individual heavy minerals from these deposits. Unfortunately, however, the ilmenite produced at Cox's Bazar pilot plant contains less than 40 percent TiO_2 together with a large amount of iron in the form of oxides, silica, magnesium and other trace elements such as manganese chromium etc. Different constituents of Bangladesh ilmenite are shown in the Table-1.2. This table shows the minimum and maximum percentage of of the constituents as complied from data found in different references. [Information booklet, 1994. Ahmed et al., 1992 and Haseeb et al., 1997]

Table 1.2 Constituents of Bangladesh ilmenite.

Constituents	Constituents
TiO_2	39.00-45.37
Fe_2O_3	25.62-33.00
FeO	24.019-29.75
SiO_2	1.20
MnO	1.17- 1.30
Cr_2O_3	0.02 –0.57
P_2O_5	0.03

Ilmenite containing less than 55 percent titanium di-oxide is not considered suitable for industrial use. As a result, this valuable mineral separated from the beach sands of Bangladesh, could not find any market in Bangladesh or elsewhere.

In view of rapid depletion of known reserves of natural rutile (TiO_2) efforts are being made throughout the world to transform ilmenite into rutile through thermo-chemical treatment. As a result of these investigations, a number of commercial processes for the production of rutile

from ilmenite have been developed. This rutile is known as synthetic rutile. It was therefore, considered necessary to take up this systematic study to assess the possibility of converting Bangladesh ilmenite to synthetic rutile through thermo-chemical treatment. It is believed that the successful conversion of Bangladesh ilmenite into synthetic rutile will make this valuable mineral of Bangladesh useful at home and abroad, enhance the confidence in our ability to use our own natural resources and also the prestige of the nation.

1.7 Scope of the Present Work

The Pilot Plant established at Cox's Bazar separate the valuable heavy minerals including ilmenite from heterogeneous sand mixtures. The techniques of seperation used at BSMEC Cox's Bazar are based on the physical properties only of the minerals.

Chemical analysis performed at the laboratories of the Department of Metallurgical Engineering at BUET, Dhaka and also elsewhere has shown that the ilmenite separated at the pilot plant at Cox's bazar contains about 40 percent titanium-di-oxide [ASW Kurny, 1998] and is, therefore, not suitable for industrial use. The ilmenite separated from the beach sands of Bangladesh has to be processed further to remove the chemically combined useless minerals, particularly iron, before it can find some use.

Bangladesh is very poor in mineral resources. The best possible use of the heavy minerals separated from the beach sands of Bangladesh is, therefore, very important for the economy of the country. Mridha and Islam [1985] attempeted to separate TiO_2 from the Bangladesh ilmenite by the wet chemical route. Their process involved dissolution of ilmenite in a mixture of hot concentrated nitric and sulphuric acid subsequent seperation of titanium as metanitric acid, which on heating at 75-80°C yielded TiO_2. Earlier investigations at the Department of Materials and Metallurgical Engineering at the B.U.E.T., Dhaka on the production of synthetic rutile through the reduction-leach route yielded encouraging results and the TiO_2 content of Bangladesh ilmenite could be raised to about 92 per cent [Haseeb and Kurny, 1998 and Sarkar and Kurny, 1998]. Early studies [Kurny, 1998] indicated that TiO2 content of ilmenite separated from the beach sands of Bangladeshh could be enhanced by thermochemical treatments. Detailed characterization of Bangladesh ilmenite concentrate has therefore been undertaken.

Chapter 2
LITERATURE REVIEW

2.1 Introduction

Ilmenite and rutile are the commercially most important minerals that contain titanium. There are several other minerals that contain appreciable quantities of titanium. Of this ilmenite, arizonite, titaniferous magnetite is of commercial importance. Table 2.1 shows the composition, specific gravity and titanium percent of chief titanium minerals [Krishnan and Roy, 1942].

Table 2.1 Chief Titanium Minerals

Mineral	Composition	Specific Gravity	Titanium per cent
Rutile	TiO_2	4.25	59.95
Ilmenite	$FeTiO_3$	4.5 - 5.00	31.6
Arizonite	$Fe_2O_2\,3TiO_2$	... ...	36.6
Titaniferous Magnetite	Fe_2O_4 with Ti	5.0 - 5.5	Upto 20
Sphene	$CaTiSiO_3$	3.54	24.5
Perovskite	$CaTiO_3$	4.0	35.3

Ilmenite ($FeTiO_3$) is the most common mineral of titanium. It occurs in most igneous rocks (particularly in basic ones) and in some schistose rocks. Generally it occurs in the form of disseminated grains. Lenses and veins of ilmenite and titaniferous magnetite are also found. It is black in colour with a sub-metallic lustre. Its specific gravity is 4.5 to 5 and hardness 5 to 6. It contains 31.6 percent titanium (52.7 percent, TiO_2) and 37.2 percent iron.

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

Arizonite is a mineral found in very small quantity in Arizona. It has the formula $Fe_2O_3.3TiO_3$, which gives 60 percent TiO_2. According to Gillson [1949] as it is similar in appearance to ilmenite, it is surmised to be present in the beach sands giving a higher titanium content than ilmenite.

Sphene ($CaTiSiO_3$) is also called titanite. It has a yellow-brown colour with hardness 5.5 and specific gravity 3.54. It occurs as an accessory mineral in various types of igneous rocks, particularly in granite, syenite and diorite and also in certain amphibole-schists, chlorite-schists, epidiorites etc. It contains 24.5 percent titanium. Sphene is often associated with rare earths and may carry quantities of yttrium earths, columbium, tantalum, cerium etc.

Perovskite ($CaTiO_3$) is a yellow to orange or grey mineral with a hardness of 5.5 and specific gravity of 4. It is found generally in alkaline rocks (especially in those of a basic character like melilite basalts) and also sometimes in metamorphic rocks. The mineral does not occur in large enough quantities to be used commercially. It contains 35.3 percent titanium.

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

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

Various processes for the beneficiation of ilmenite have been developed and some of these methods are now being exploited on a commercial scale. Most of the beneficiation techniques involve oxidation, reduction and leaching. Extent of alternation also influences the production techniques. The study on oxidation, reduction, alternation of ilmenite and leaching behavior of oxidized and oxidized reduced ilmenite is therefore of technical importance. In this literature review results of studies on oxidation, reduction, leaching and alternation of ilmenite have been summarized.

2.2 Oxidation of Ilmenite

It is generally agreed that the purpose of oxidation of ilmenite is to (i) convert iron in ilmenite from ferrous to ferric state which overcomes different ferrous to ferric iron ratios in ilmenite (ii) alter equilibrium condition and the rate of reduction from ferrous to ferric state (iii) introduce defects in ilmenite grains to enhance the rate of subsequent reduction.

A number of researchers [Ramdohr et al., 1941 and Overhault et al., 1950] found from X-ray diffraction patterans that ilmenite when heated in air at 900° C yielded pseudobrookite and rutile. D.G Jones (1973) found that oxidation of ilmenite at temperature over 800°C yielded ferric pseudobrookite and rutile. According to data given by Webstar and Bright (1961) ferric pseudobrookite in commercially oxidized Western Titanium ilmenite contains approx. 4% Fe^{2+}.

Karkhanawala and Mommin (1939) studied the oxidation of ilmenite and concluded that:

1. The Products of oxidation of ilmenite is weekly paramagnetic and for products heated for equal periods the magnetic susceptibility decreases with increasing temperature.
2. The products of oxidation at around 850° C contains mixture of hematite, pseudobrookite and rutile in an approximate molar ratio of 1:5:7 respectively.
3. Thermogravimetric analysis showed there are three distinct regions of oxidation 100°- 450°C, 540-800°C and 800°-900°C. The oxidation rate over the first region is very slow.

Investgations [Teufer and Temple, 1966, Temple, 1966, Grey and reid, 1972 and Larrett and Spancer, 1971] indicate the formation of $Fe_2O_3.3TiO_2$ as an alteration product and when natural ilmenite was oxidized between 600°C-800°C. Larret and Spencer, (1971) also maintain that the compound $Fe_2O_3.TiO_9$ is formed only when a synthetic ilmenite powder is oxidized. In some cases the natural ilmenite when oxidized in the state of fine powders gave this compound. Results regarding the products of oxidation of ilmenite up to 800°C are conflicting. Various results obtained by different investigators are given below:

1. Rutile and hematite $2Fe\ TiO_2 + {}^1/_2O_2 = Fe_2O_3 + 2TiO_2$ [Strizhov et al, 1965; Curnow and Parry, 1954; Karkhanawala and Mommin, 1939]
2. Hematite and pseudorutile $3FeTiO_2 + {}^3/_4\ O_2 = Fe_2Ti_3O_9 + {}^1/_2\ Fe_2O_3$ [Teufer and Tample, 1966; Grey et al , 1972;]
3. Rutile and pseudobrookite $2FeTiO_3 + {}^1/_2\ O_2 = Fe_2TiO_5 + TiO_2$ [Overhault et al., 1950; Fetisov et al., 1968 and Ramdohr et al., 1941]

4. A mixture of hematite, pseudobrookite and rutile $12FeTiO_3 + 3O_2 = Fe_2O_3 + 5Fe_2TiO_5 + 7TiO_2$ [Karkhanawalla et al 1939]

But reaction 4 could occur only under metastable condition, Rao and Rigaud [1974] calculated the free energy changes for the above reactions. They found that the standard free energies over a specified temperature range is favourable for both reactions (1) and (3). Thus either or both reactions may take place upto the decomposition of Fe_2O_3 or Fe_2TiO_5. The free energy change for the formation of pseudobrookite from its oxides,

$$Fe_2O_3 + TiO_2 = Fe_2TiO_5$$

is also favourable and one would expect reaction (3) to take place in preference to reaction (1) and (4). The plot of free energy change versus temperature is shown in Fig, 2.1.

Akimoto et al, [1957] found that higher temperature and longer time is required for the formation of pseodubrookite from their oxides and the lower temperature limit for the formation of pseodubrookite is explained by the fact that diffusion rate during formation of oxidation at lower temperature is slow which might prevent the formation of pseodubrookite.

Rao and Rigaud (1974) also performed thermogravimetric analysis of ilmenite prepared by mixing Fe_2O_3, Fe and TiO_2 in the required ratio. The general observations of the thermogravimetric analysis in both oxygen atmosphere and air are as follows:

(a) An abrupt weight gain is observed when particle size is less then 200 meshes and it is difficult to observe a break in the thermogram. In case of very fine partice having a large surface area the reaction rate is very high and major part of reaction is complete before temperature 800°C reached.

(b) An inflection of thermogram could be noticed at around 770°C when particles of 100 mesh size or more were used and a heating rate $10^0 min^{-1}$ was employed.

(c) Up to 1100°C, the reaction products were identified as pseudobrookite and rutile. Any other product formed at lower temperature e.g. hematite and rutile react to form pseudobrookite above 900°C.

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 investigations provide evidence

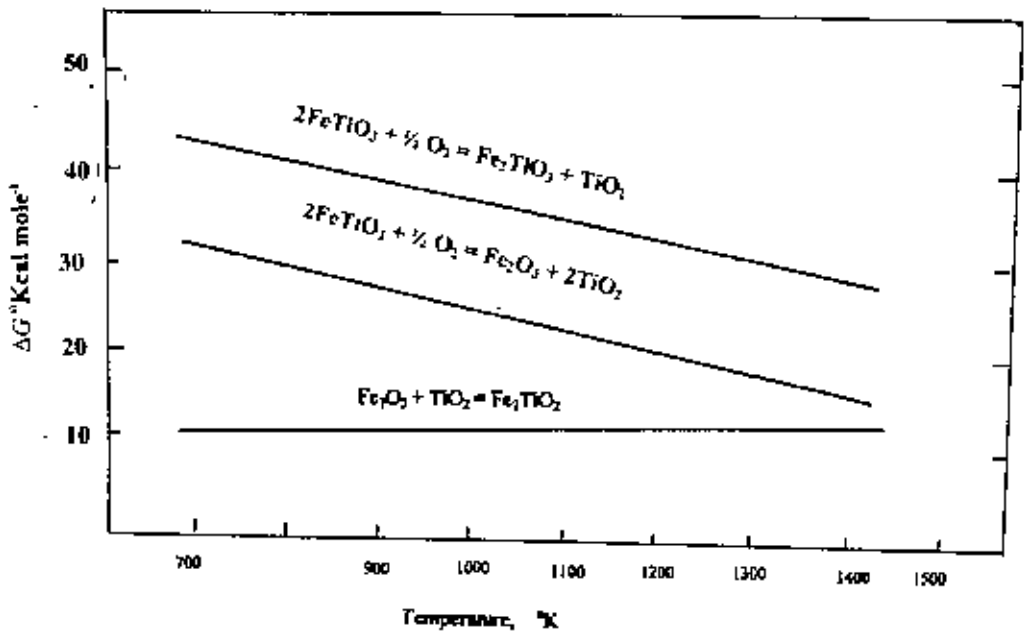


Fig. 2.1 Free energy changes vs temperature for various reactions.

of discontinuous formation of product especially at early stage of reaction. Fischmeister [1960] reviewed and discussed the subject; he also considered the influence of product growth morphology on the reaction kinetics. Discontinuous product growth results due to the formation of product as island, whiskers and lamellar or columnar growth of crystal. The morphology of the product of ilmenite is important and influences the subsequent leaching of the oxidized ilmenite.

Rao and Rigaud (1974) studied the morphology of oxidized ilmenite by scanning electron microscopy at three different temperatures 700°C, 8000C and 1000°C corresponding to reactions (1), (2) and (3). Scanning electron micrograh obtained by them at the above temperatures are shown in Fig. 2.2 and Fig.2.3. They found the morphology of Fe_2O_3 formed in the beginning stage at 700°C to be similar to that reported by Gulbransen and Copan [1965]. They could not locate TiO_2 and concluded that it might not have neucleated at surface.

The growth morphology of products can also influence significantly the kinetics of gas solid reaction. The whisker growth only affects [Fischmeister, 1960] the kinetics in the early stages and before the product reaches appreciable thickness. The kinetic data of the oxidation of ilmenite reported elsewhere [Bhogeswara, 1974] is also in agreement with this hypothesis.

Rao and Rigaud [1974] found logarithimic 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 reaction or due morphological effect of the reaction (2) and (3) might be controlled by the same or similar mechanism. 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 [1980] studied the alteration of ilmenite and suggested that it takes place in two different stages.

$$\text{Stage 1: } 3Fe^{+2}TiO_3 + 2H^+ + \tfrac{1}{2}O_2 = Fe_2^{+3}Ti_3O_9 + Fe^{+2} + H_2O$$

$$\text{Stage 2: } Fe_2Ti_3O_9 + 4H^+ = 3TiO_2 + 2Fe^{++} + 2H_2O + \tfrac{1}{2}O_2$$

Teufer and Temple (1996) established a disorder structure-transition phase between rutile and ilmenite and formulated the alternation of ilmenite as a topochemical reaction in which number of oxygen atom in ilmenite is essentially preserved in pseudorutile and rutile.

$$3Fe\,TiO_3 = Fe_2Ti_3O_9 + \tfrac{1}{2}Fe_2O_3$$

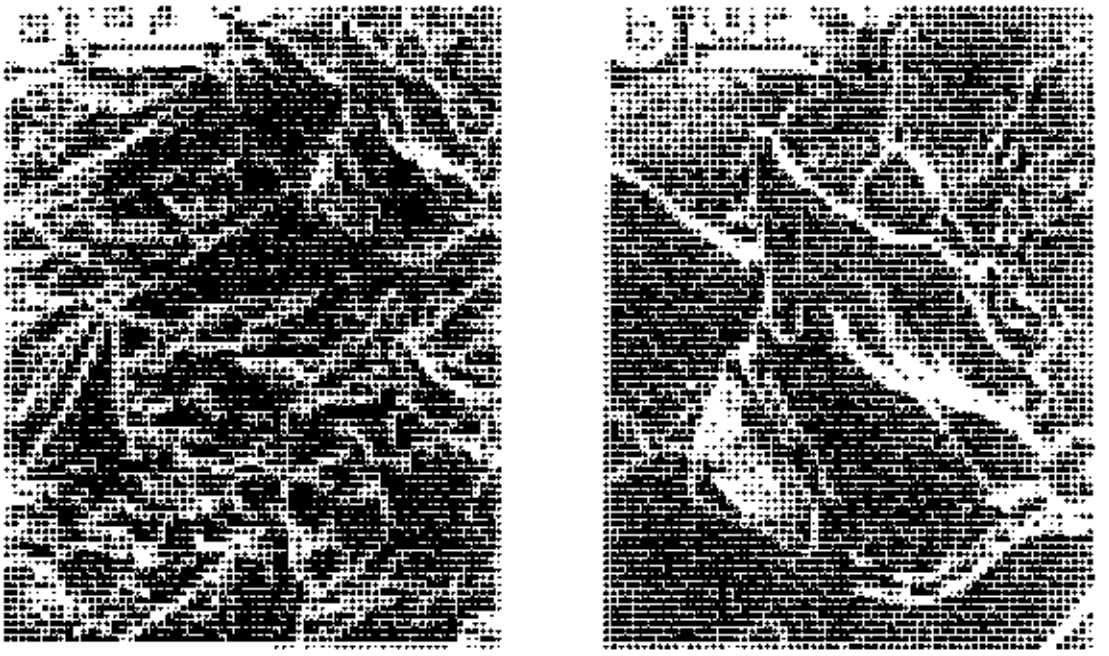


Fig. 2.2 Morphology of TiO_2 formed on the surface at 1000° C (a) X 1200 (b) X 2400

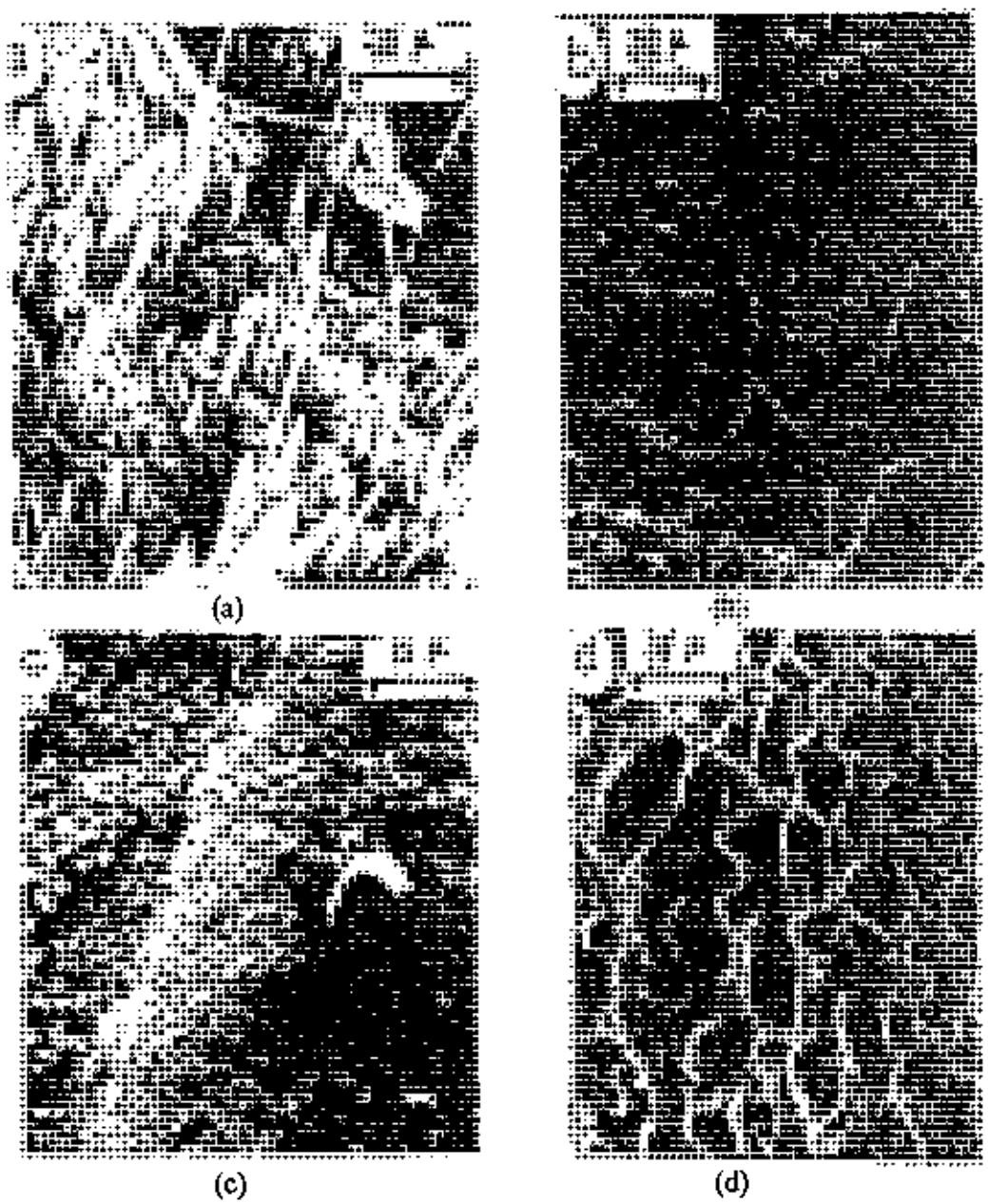


Fig.2.3 Scanning Electron Micrographs of the product formed during oxidation of ilmenite crystals
(a) Morphology of the formation of hematite whiskers during the initial stages of oxidation at 700° C, X 650

(b) (b) Morphology of the formation of hematite and $Fe_2Ti_3O_9$ upon oxidation of ilmenite at 850° C X 250,

(c) Hematite on the grain boundaries X 1200

(d) Pseudobrookiten formed at 1000°X 2000

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

$Fe_2Ti_3O_9 = Fe_2TiO_5 + 2TiO_2$

Rao and Rigaud (1974) upon their extensive study on the oxidation mechanism and product morphology provided some tentative conclusion upon the general reaction mechanism.

During oxidation at temperatures below 770^{0}C, Fe_2O_3 is formed on the surface and when the surface of ilmenite is covered by Fe_2O_3 oxygen diffuse through the product layer [Pfeil, 1929] and further reaction takes place at $FeTiO_3$- Fe_2O_3 interface and the diffusion rate of O_2 in FeO and $FeTiO_3$ is low.

They found $Fe_2Ti_3O_9$ to be stable at temperatures from 770^{0}C to 990^{0}C 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 lower temperature limit exists for the formation of Fe_2TiO_5.Fe_2O_3 is precipitated. At temperature greater than 900^{0}C TiO_2 is formed on the surface. When the sample is heat treated above 950^{0}C the initial whiskers of Fe_2O_3 formed on surface of the samples at 750^{0}C is transformed to pseudobrookite. The movement of titanium is confirmed by the fact that when ilmenite is oxidised with markers at 950^{0}C, the formation of TiO_2 was observed above the markers. The markers were covered with rutile at particular locations of the crystal. This is assumed due to rapid diffusion of titanium through certain preferred orientation of ilmenite. But the orientation favorable for diffusion of ilmenite was not confirmed due to its polycrystalline nature. The mobile titanium 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 centre of TiO_2 structure. They suspected that oxygen might have escaped from this portion. Their tentative mechanism of oxidation is given in Fig. 2.4.

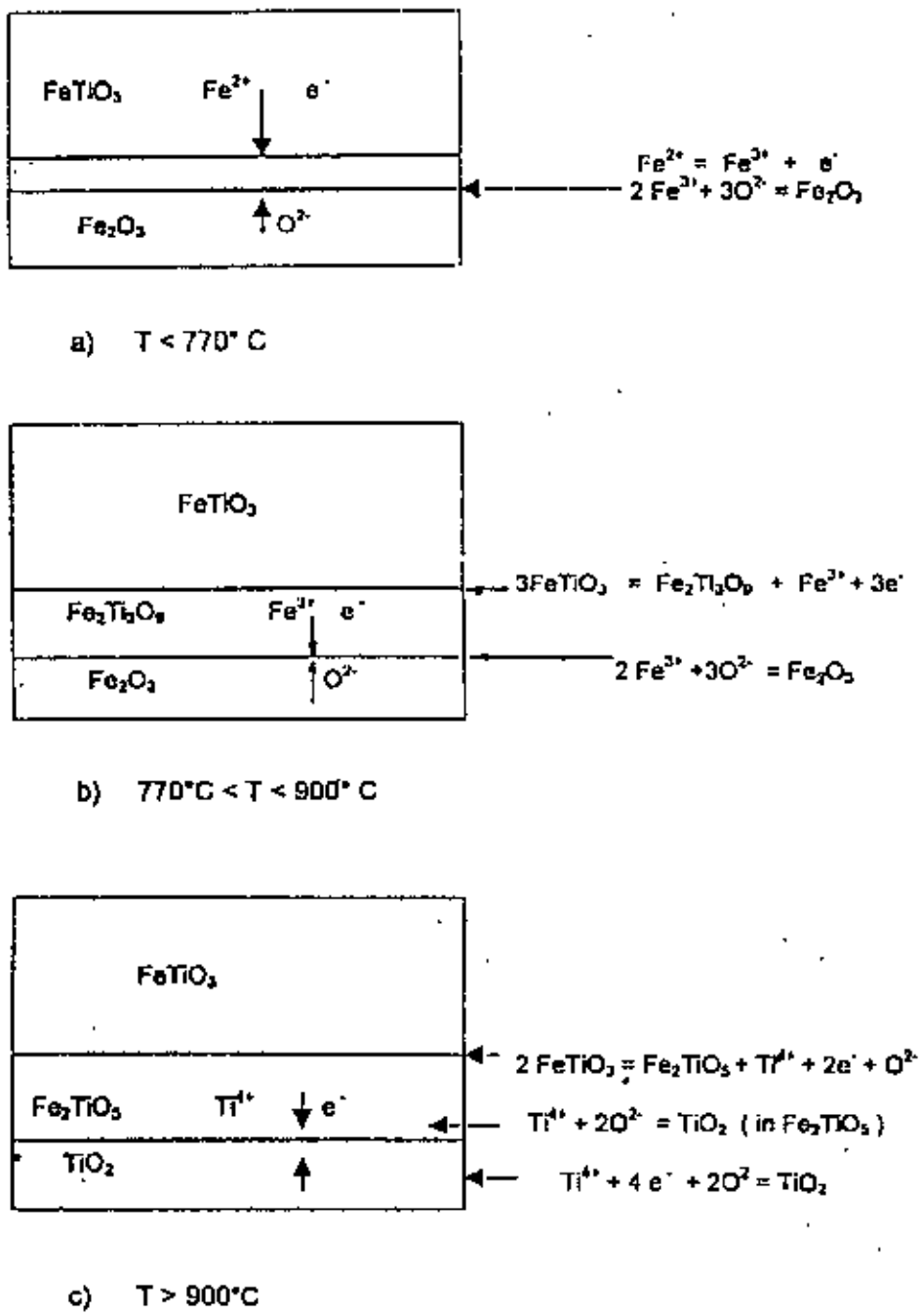


Fig. 2.4 Schematic representation of proposed mechanism for the oxidation.

2.3 Reduction of Ilmenite

Reduction of iron oxides in ilmenite to metallic iron is carried out by using reductant. From the Ellinghum diagram it is apparent that the stability of titanium di-oxide is much higher than that of the oxides of iron and cannot be reduced by carbon at temperature around 1100° C. Thus when ilmenite is heated by mixing it with carbonaceous fuel at temperature range 950°C-1100°C, iron oxide is reduced to metallic state but the titanium di-oxide remains unchanged. Thus iron oxide can be theoretically reduced to metallic form without changing the titanium oxide. Since both the oxides of iron and titanium are more stable than corresponding metals, metallic iron can easily be dissolved in hydrochloric acid and therefore the titania conent can be increased.

Several workers using different reducing substance studied reduction of ilmenite. Guindy and Davenport [1970] studied the mechanism of reduction of ilmentie using graphite as reductant. They observed that solid-state reduction initiates near 860°C at contact point between the reactants. The solid-state reduction is the main reaction mechanism up to 1020°C. Above this temperature a rate increase has been observed and the mechanism changed to gaseous reduction by generation of CO. Microscopic examination and electron probe analysis of reduced particle showed the segregation of Fe and TiO_2. Iron particle as large as 80μ was obtained by keeping the reduced sample at 1020°C to 1075°C for several hours. They pointed out that the reactions that occur during the reduction of ilmenite are as follow:

(a) Solid state reacion:

$$C + Fe\,TiO_3 = CO + Fe + TiO_2$$

This reaction initiate at contact point between reactants and proceeds as long as there remains contact point between the reactants.

(b) Gaseous reaction :

$$CO + Fe\,TiO_3 = CO_2 + Fe + TiO_2$$

$$C + CO_2 = 2CO$$

The reduction involving gaseous reductant depends upon the regeneration of CO in the system. The sequence of reaction in the reduction of ilmenite by pure CO was studied by D.G. Jones [1973] andGrey et al.,[1973] by X-ray diffraction analysis in the range of 900°- 1200°C. He found that reduction of naturally weathered and peroxidised sample proceeds in two distinct

stages. First stage is the rapid reformation of ilmenite from Fe^{3+} compounds in the sample according to the following reactions:

$$Fe_2Ti_3O_9 + CO = 2FeTiO_3 + TiO_2 + CO_2$$

$$Fe_2O_3 + 2TiO_2 + CO = 2FeTiO_3 + CO_2$$

The second stage is slower than the first stage. In the second stage the proportion of ilmenite progressively diminishes with corresponding increase in the metallic iron and rutile. Finally when the reduction has well advanced the rutile peak diminishes slightly due to reduction of rutile to lower oxides according to following reaction.

$$FeTiO_3 + CO = Fe + TiO_2 + CO_2$$

$$nTiO_2 + CO \rightarrow Ti_nO_{2n-1} + CO_2$$

At 890°C to 1000°C the reduction of pre-oxidised ilmenite is expressed as:

$$Fe_2TiO_5 + TiO_2 + CO = 2FeTiO_3 + CO_2$$

Jones [1973] identified rutile and ferric pseudobrookite as the main constituents of pre-oxidised ilmenite. Pre-oxidation converts the ilmenite to pseudobrookite (Fe_2TiO_5) and rutile (TiO_2) at temperature above 800°C (Ostberg., 1960) according to the following reaction;

$$2FeTiO_3 + 1/2O_2 = Fe_2TiO_5 + TiO_2$$

The single crystals of ilmenite are converted into a polycrystalline array of pseudobrookite and a fine dispertion of rutile. During the reduction process ilmenite is reformed by the following reaction. The first stage is the reformation of ilmenite.

$$Fe_2TiO_5 + TiO_2 + CO = 2FeTiO_3 + CO_2$$

In this case there are subgrains within the parent ilmenite grains and the iron precipitates at these subgrain boundaries. In unoxidised ilmenite, shells of metallic iron from along the grain boundaries which impairs the diffusions of reacting species and also results in the sintering of the product. Both of these effects limit the kinetics of the reduction of unoxidised ilmenite particularly at higher temperatures.

The second stage proceeds by two alternative route depending on the temperature and the concentration of the impurities. At 1000°C the overall process is the reduction of ilmenite to metallic iron and rutile.

$$Fe\,TiO_3 + CO = Fe + TiO_2 + CO_2$$

Prior oxidation transforms ilmenite ($FeTiO_3$) to pseudobrookite ($FeTiO_5$), which results in substantial cracking and lattice expansion. This cracking and expansion enables the subsequent reduction to proceed at both an accelerated rate and to a greater extent without much sintering. This oxidation of ilmenite prior to reduction has a beneficial effect on the rate of reduction.

Reduction of Bangladesh ilmenite by using charcoal as reductant was carried out by Haseeb, et al [1997]. By x-ray diffraction study and microscopic study they established that the reduction behaviour of Bangladesh ilmenite is similar to that of Australian ilmenite, the reduction behaviour of what has been described above.

Effect of size fraction on reduction of Cox's Bazar ilmenite was studied by Sharmin et al [1996]. They found that more than 97% of the ilmenite belongs to U.S. sieve No. 100, 140 and 200. The finer fraction contains lower percentages of TiO_2 and higher percentages of total iron. Chemical analysis of this ilmenite reduced by charcoal at 1050°C for 4 hrs. revealed that finer fraction contain lower iron oxides. The degree of reduction of iron oxides present in ilmenite was found to be 71.35%, 75.39% and 78.92% for size fraction corresponding to US sieve No.100, 140 and 200 respectively. They also concluded that as far as the optimization of reduction parameters of Cox'bazar ilmenite is concerned, a separate reduction procedure for each fraction is not necessary.

A thermogravimentic study of the reduction of ilmenite with graphite was carried out by El-gundy and Davenport [1970] with a view to find out the kinetics and mechanism of the reduction reactions. They observed that up to 1020°C solid-state reaction was the prominent one, which initiated at about 860°C at the contact points. Above 1020°C the reduction was essentially gaseous. Rate constants were calculated taking CO as the diffusing species. A detailed study of the mechanism of reduction of Egyptian ilmenite using different gases showed that the reduction was dependent on factors like temperature, time etc. H_2 was found to be more efficient than CO. While in the case preoxidised ilmenite CO was better. Presence of CO_2 in the stream decreased the reduction rate and the mechanism of reduction was found to be more or less the same [Hussain et al, 1972].

The reaction sequences and products obtained in the reduction of ilmenite using CO gas were studied by Jones (1973) using x-ray diffraction. The reduction of weathered and pre-oxidised

ilmenite was found to proceed in two steps, the first one being the formation of ilmenite and in the second stage were metallic Fe and titanium oxides were formed. At temperatures above 1150^{0}C, ferrous pseudobrookite was formed which got converted to M_3O_5 solid solution with iron and titanium. It was also observed that below 1150^{0}C, pseudobrookite and ulvospinel were present in small amounts at all temperatures. An x–ray diffraction study by some other workers [Grey and Reid, 1973.,Grey and Reid, 1974] revealed that during pre-oxidation of ilmenite at 1000^{0}C rutile and a solid solution of Fe_2TiO_5-$FeTiO_5$ were formed, while after reduction, the products obtained were metallic iron, reduced rutile and a solid solution of Fe Ti_2O_5-Mn Ti_2O_5-Ti_3O_5 It was also observed that the concentrations of Mn and Mg affected the quantities of these constituents in the reduced product. The effect of various factors like ilmenite feed rate, reducing atmosphere, temperature, and addition of Mg from an external source etc. on the reduction was also investigated.

In a continuos methods [Reeves, 1967] for the production of synthetic rutile the ferric oxide present in ilmenite was first reduced to ferrous oxide at 950^{0}C with coke followed by gaseous reductions at 950^{0}C-1100^{0}C with CO and H_2 where reduction to metallic iron to about 95% took place. This was then subjected to acid leaching increasing the TiO_2 content. The reduction of Indian ilmenite using different industrial reductions was studied by Gokarn et al., [1969]. It was found that charcoal even when used in excess gave a reduction only upto 73.3% which increased when 2% Na_2CO_3 was used as a flux. With oxidized ilmenite the rates of reduction by C were faster. Reduction upto 85.5% was achieved using large excess of city gas and hydrogen. In the continuous moving bed experiments higher reduction percentages were obtained using coke. The reduction process of synthetically prepared ferrous titanate with CO gas reduction at 800-1100^{0}C was investigated by Levitskil et al., [1969] and the process was analysed on the basis of thermedynamics. Khalimov and co-workers [1973] studied the reduction of ilmenite with CO-CO_2 mixture. They found that below 860^{0}C, Fe^{3+} was reduced Fe^{2+} while above 860^0 C metallic iron was obtained. The reduction was found to be diffusion controlled and the activation energies were calculated. Poggi et all., [1976] reported a detailed study of the reduction of ilmenite using solid and gaseous reducing agents. They found that the presence of impurities affected the reduction process considerably. Presence of MgO had negative effect while Fe_2O_3 had a positive effect on the rate of reduction.

2.4 Leaching of Ilmenite

Titanium oxide is produced industrially by the sulphuric acid leaching of its minerals and the subsequent thermal hydrolysis of of titanium sulphate solutions; this is commonly known as the sulphate process. It is also produced by the vapour phase oxidation of titanium tetrachloride. Although the manufacture of titanium oxide by this latter process is gradually increasing, the former is still the most widely used The sulphate process however, has serious disadvantages because the treatments of crude iron sulphate and of the waste acid solution are difficult. On the otherhand, hydrochloric acid, which is very useful for decomposition of natural ores, allows comparatively easier recovery of the useful free acid from its waste solution than does sulphuric acid. In practice, the recovery of free hydrochloric acid from the waste solution of steel cleansing is now feasible.

Selective leaching of the ilmenite by mineral acid removes [Sehara et al., 1966 and Viswanathan Nayar, 1952] iron from ilmenite. In direct acid leaching sulphuric acid and hydrochloric acid is used as the 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. Digestion of ilmenite with concentrated sulphuric acid [Tong-po Tam et al., 1957, Kramer, 1948 and British patent 1967] is the conventional method for preparing TiO_2 pigments. Ilmenite is digested with hot concentrated H_2SO_4 to form a product consisting of $FeSO_4$, $Fe_2(SO_4)_3$ and $Ti(SO4)_2$ solution, that is then preferentially hydrolysed to form hydrous TiO_2 in coarse readily filterable form.

An attempt has also been made to digest ilmenite with dilute H_2SO_4 (5-20%) to utilize the waste acid from pigment production [Tikkanen et al, 1963] without any further concentration and was found that higher temperatures (around 200°C) are essensial for this purpose. Several investigators [Sankaran et al, 1972] reported that leaching with dilute sulphuric acid (7 to 50% conc.) under pressure (30 to 260°C) is very effective in the selective dissolution of iron so as to obtain a rutile grade product. In India at Trivandrum, M/s Travancore Titanium products is manufacturing TiO_2 pigment from ilmenite by the concentrated H_2SO_4 digestion process.

On the other hand digestion with hydrochloric acid is selective [Viswanathan Nayer, 1952] and iron is brought in to solution. Direct acid leaching is carried out at somewhat higher temperature. Tha 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 [Rajeswari et al, 1990] for the reaction as a function of temperature is represented as

$$\Delta G^{\circ} = -81420 + 0.99 \log T + 7.4T \ (298 - 1640^{\circ}K)\ ^{\circ}K \text{ cal mol}^{-1}$$

From the thermodynamic data [Sankaran et al., 1967] it is 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.

From the thermodynamic data it is apparent 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 on reaction with HCl will lead to the formation of less volatile $FeCl_2$. The reduced iron in the ilmenite is dissolved by dilute acid even at room temperature but complete removal of iron may require higher temperatures and pressures and longer time. Annie George and co-workers [1985] reported a process where completely reduced Fe_2O_3 and FeO to metallic iron can be leached out with dilute HCl at lower temperature and in a short period [Webster, 1961]. 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.

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

The standard free energy change for the preferential chlorinating of iron from ilmenite as a function of temperature is plotted in Fig. 2.5.

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

$$\tfrac{1}{2}\ TiO_2 + 2HCl \longrightarrow \tfrac{1}{2}\ TiCl_4 + H_2O$$

The free energy change [Webster and Bright, 1961] for the reaction is represented as

$$\Delta G^{\circ} = -7765 - 1.08 \log T + 18.8T\ ^{\circ}K \text{ cal mol}^{-1}$$

Which shows that this reaction in not possible above 523°K.

Rajeshwari et al [1990] studied leaching of the ilmenite using $FeCl_3$ solution. They found that leaching of the completely reduced ilmenite yields a product with 2% Fe and 92.6% TiO_2

Annie George et al [1984] carried out reduction of ilmenite using coconut pith as reductant. The reduced product was leached out and obtained a product containing 2% Fe.

In Murso process [Jaffe and Burte, 1973] Fe_2O_3 is converted to FeO and was leached with 20% HCl at 108-110°C to obtain a product containing 95-97% TiO_2.

Ismail et al [1983] studied the oxidation reduction and leaching kinetics of Sri Lanka ilmenite and found that the result is similar to Murso process and obtained a product containing 90-95 per cent TiO_2.

Burastero [1978] obtained a product >95% TiO_2 by employing oxidation-reduction leach techniques in the laboratory scale.

Wash Chang Corporation of USA [Ching-Lung and Mackey, 1965] has developed sussessfully a process for producing synthetic rutile (93% TiO_2) from ilmenite on an industrial scale by double stage pressure leaching (at 30-35 psi) with hydrochloric acid (about 8 N) at 105-110°C. The temperature and pressure are maintained by injecting steam into the digester.

The Benilite Corporation of America [Davar, 1969] claimed development of a process in which, ilmenite or any other titaniferous material is first subjected to a certain degree of pre-reduction by any conventional reduction roasting (e.g. with coke at 815-1090°C) to convert most of the ferric iron to ferrous iron (which is more readily soluble in acid). The pre-reduced ilmenite is then treated with 20% HCl acid in a vessel (digester lined with acid resisting material), which rotates slowly during digestion.

Ishihara Sangyokaisa Ltd. of Japan (Kenzo Ishihara, 1970) worked out a process for manufacturing synthetic rutile. In the said process, ilmenite is first partially reduced to convert F_2O_3 content of ilmenite to FeO. After the partial reduction, the reduced ilmenite is leached with dilute mineral acid. The condition of leaching is reported to be unique and the company claims that the process can be easily operated economically on an industrial scale.

Besides the above important developments many more paper (Sehra et al, 1966. British patent, 795164,1958) have appeared on hydrochloric acid leaching of ilmenite at atmospheric as well as higher pressure In the case of leaching at atmospheric pressure, the process is less efficient and the product is of inferior quality (about 88.50% TiO_2) compared to the pressure leaching process which under suitable conditions yield a high grade product containing more than 98% TiO_2.

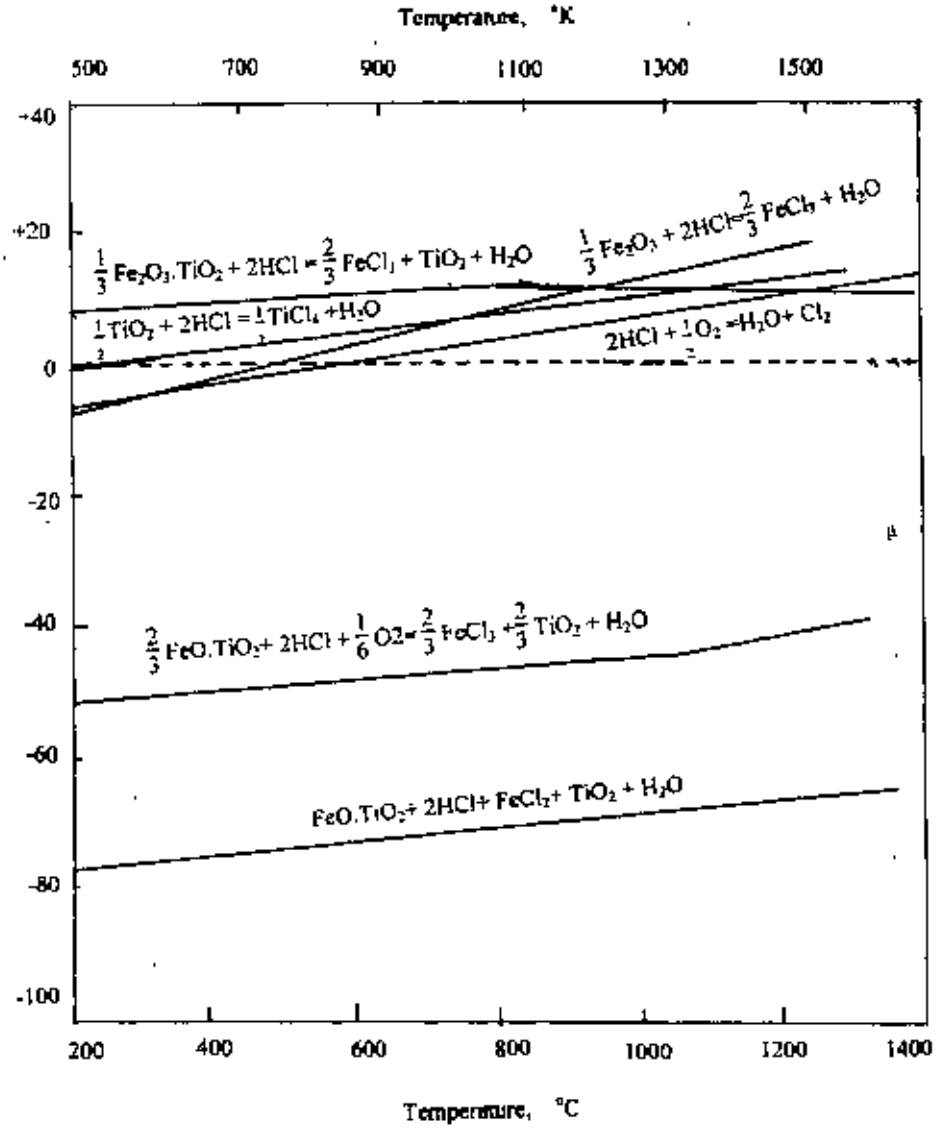


Fig. 2.5 Free energy changes involved during chlorination of ilmenite.

2.5 Ateration 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, 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 [George and Mohan Das, 1985]. Complete removal of iron from the pseudorutile lattice results in a grain composed of crystallites of the mineral rutile Only these four mineral phases [Temple, 1966], ilmenite, pseudorutile, leucoxene and rutile have been identified in the commercial titanium mineral concentrates studied. 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.

2.5.1 Alteration Product of Ilmenite

Several attempts have been made to characterize the sequence, mechanism, depth and products of alteration. The important alteration indicators [Babu et al, 1975] changes in Fe2+/Fe3+ and Fe / Ti ratios; variations in magnetic susceptibility, density, hardness and reflectivity; structural and morphological changes, increases in impurities like Cr and V and decrease in Mn, Ni, Zn, Cu, Mg, Co and Ca [Grey and Reid, 1975, Wort and Jones, 1980 and Anand and Gilks-1984]. A common ilmenite alteration mechanism can be explained as follows:

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

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 [Hugo and Cornell, 1991] 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. Accordingly, degree of alteration may only be perceived as the degree of rutilization. There is also considerable uncertainty in the terminology applied to the alteration products. Lynd and Lefond [1983] 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 (1961) presented the petrographic, as opposed to the commercial, viewpoint and pointed out the range of rock types where ilmenite and its alteration products occur. It is thus clear that the initial product is ilmenite and leucoxene is the end product of the alteration process. According to Mucke and Chandhuri (1991) and Hugo and Cornell (199) during the transformation of ilmenite to leucoxene following products can be identified:

Ilmenite → Hydrated Ilmenite → Pseudorutile → Leached Pseudorutile → Leucoxene

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

Unaltered ilmenite is the dominant mineral. When altered, ilmenite changes 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. No distinction is made between ferrian-ilmenite and ilmenite. Although varying in intensity and pattern from grain to grain, the most common alteration is along grain boundaries and fracture, along crystallographic directions.

Hydrated Ilmenite: This is also known as leached ilmenite, which is not completely altered to pseudorutile. This commonly replaces ilmenite along crystallographic directions, leading to the formation of microcracks. 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 and Khatuntesva [1960] and was adopted by Frost et al., [1983] to indicate the mixture of ilmenite and pseudorutile, which contain crystalline water while the term "leached

ilmenite" was used by Mucke and Chadhuri [1991] and Chernet [1999] to identify a distinct intermediate leaching product between ilmenite and pseudorutile.

Pseudorutile: A deformed [Grey and Watts, 1983] 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. Characteristically it shows rough and porous texture. Compared to ilmenite, it appears brighter, in contrast to its typical greyish color. Under reflected light isotropic pseudorutile is blue-gray in color with a slightly higher reflectance than ilmenite [Hugo and Cornel, 1991]. Pseudorutile is developed along crystallographic orientations, in ordered or disordered patterns, along boundaries and fractures, and is characterized by the development of microfractures. The mineral is difficult to identify positively as these optical properties are often indistinct and its major XRD peaks exhibit d-spacings similar to those of ilmenite, rutile and hematite.

Leched Pseudorutile: It is another optically identifiable intermediate phase [Mucke and chadhuri, 1991 and Chernet, 1999] lying between pseudorutile and leucoxene. This results from leaching of iron from pseudorutile. The abundance of microfractures is 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 [Grey and Reid, 1975]. Leucoxene displays abundant internal reflections, changes from brownish to white with the decrease in iron content. Replacement of ilmenite and the intermediate phases by a secondary rutile of definite crystal structure is common. Leucoxene is distingushed optically from rutile or antase by its characteristic sugary internal reflections although it may consist almost entirely of crypto or microcrystalline rutile and/or anatase in the last stages of reflections.

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

2.5.2 Mechanism of Alteration of Ilmenite

Different mechanisms of alteration of ilmenite have been proposed by different investigators [Temple, 1966 and Grey and Watts, 1983]. These mechanisms can be classified as follows

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

Type II: The Direct weathering of ilmenite to leucoxene in sediments above the water table.

Type III: 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 microcrystals.

Type I Alteration:

Many authors [Temple, 1966 and Grey and Watts, 1983] 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 (Fig.2.6.a), or in the form of oriented stringers along the basal cleavage planes of ilmenite. The second stage of alteration is marked by the development of leucoxene, which forms as irregular patches along grain boundaries, or structural weakness. The development of leucoxene along grain boundaries is less common than expected for the in situ alteration of ilmenite [Hugo and Cornel, 1991].

In a number of grains the boundaries between leucoxene and the phases it is replacing are truncated by the grain surface, showing that the alteration occurred in a large grain (Figure 2.6.b). This type of alteration may be explained by the two-stage model proposed by Grey and Reid [1975]. 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:

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

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 redeposited 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:

$$Fe_2Ti_3O_9 + 4H^+ \longrightarrow TiO_2 + Fe^{2+} + \tfrac{1}{2}O_2 + H_2O \text{ ---------- (2)}$$

Pseudorutile Rutile Dissolved Iron

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

Type II Alteration:

In this type of alteration ilmenite or slightly altered ilmenite, is observed altering directly to leucoxene. The alteration occurs from grain boundaries or along weaknesses, such as fractures within the grains. In some instances leucoxene may grow as replacement fronts across grains (Fig. 2.6.c).

Frost et al.,[1983] and Frost et al., [1986] and Hartman [1953] studying iron-titanium oxides during bauxitization, found that ilmenite may alter directly to leucoxene or optically identifiable anatase. Frost et.al., [1983] noted relatively unaltered ilmenite cores surrounded by leucoxene in a concentrate and concluded that these assemblages represent a single step dissolution re-precipitation process without the formation of pseudorutile. This style of alteration of ilmenite leucoxene, rutile, or anatase may be expressed by the equation

$$FeTiO_3 + 2H^+ \longrightarrow TiO_2 + Fe^{2+} + H_2O \text{ ----------(3)}$$

Ilmenite Rutile Dissolved Iron

Significantely altered ilmenite (Leucoxene) is shown in the Fig. 2.6(d).

Type III Alteration:

In this type of alteration two distinct intergrowths are noted. The first type of intergrowth is characterized by the replacement of ilmenite by prismatic TiO_2 microcrystal. According to this mechanism the alteration does not occur along grain boundaries, but rather as patches within grains. The second type of intergrowth is charaterised by the development of anhedral, often-vermiform rutile microcrystals in patches within the ilmenite grains. In a few instances

microcrystals of hematite are found in rutile intergrowth of some ilmenite deposit [Hugo and Cornell, 1973]. Subsequent dissolution of hematite results in grains consisting of only ilmenite and microcrystalline rutile.

2.5.3 The effect of alteration on ilmenite quality

It has been shown that the magnetic susceptibility of ilmenite decreases with increasing alteration. Hugo [1988] estimated the magnetic behavior of ilmenite and altered ilmenite in the Reehards Bay deposits by determining their mass proportions in different magnetic fractions from a heavy mineral concentrate.

These results show that:

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

2. Altered ilmenite grains containing leucoxene have a large range of magnetic susceptibility and such grains may report to ilmenite concentrate or magnetic middlings fractions; and

3. 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 middlings or rutile concentrate.

It is clear from the results of Hugo [1988] that the degree and type of alteration will affect the recoverability of altered ilmenite grains.

Frost et al. [1983] 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 [Frost et al., 1983] 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 nonrecoverable and they contribute to impurity levels in concentrates.

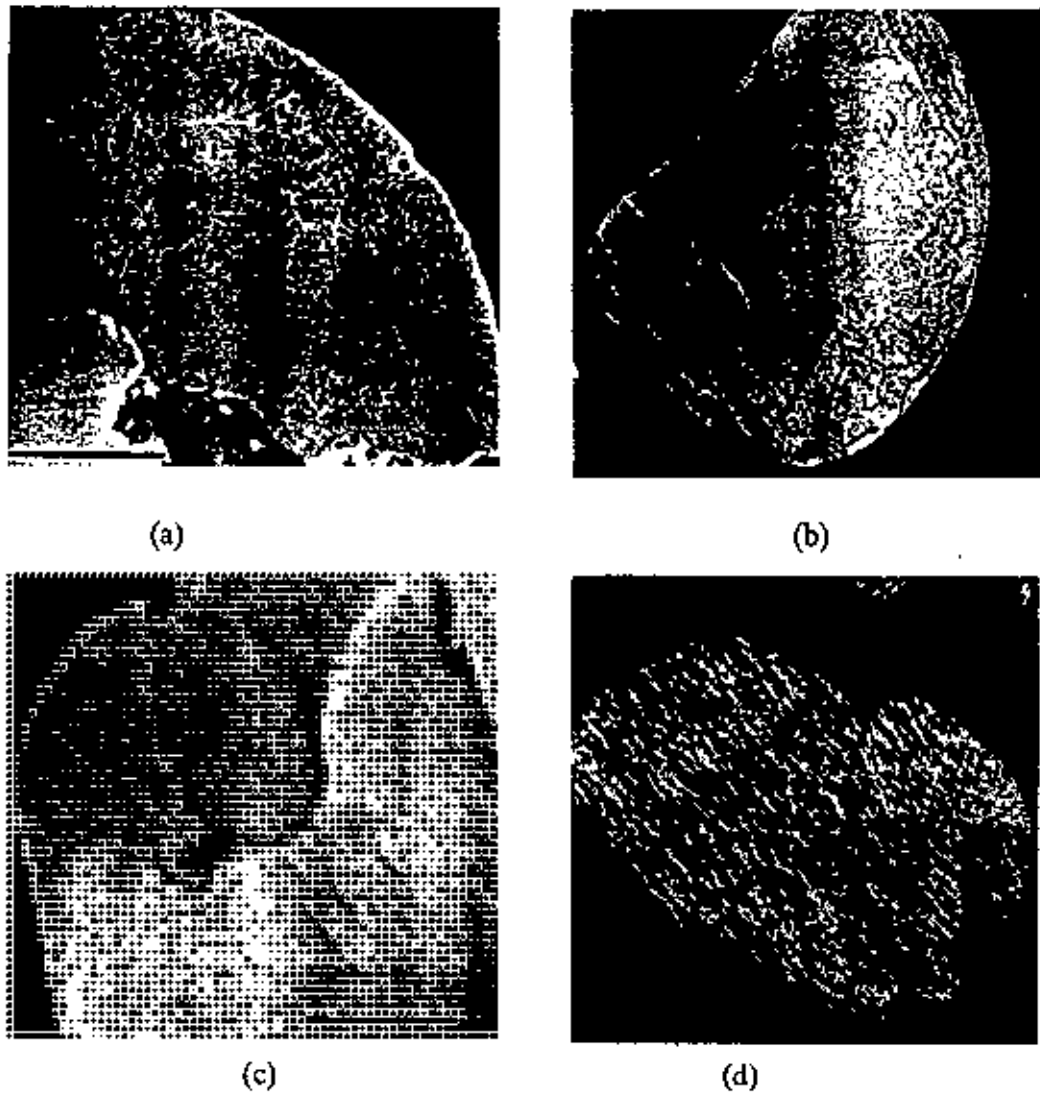


Fig: 2.6 Scanning electron micrographs of partially altered and highly altered ilmenite grains.
(a) Patchy alteration of ilmente to hydrated ilmenite
(b) Co-existence of unaltered and al ilmiente.
(c) Hydrate ilmenite grain Altering to leucoxene
(d) Highly altered ilmenite grain showing a porous surface.

2.5.4 The Importance of Study on the Extent of Alteration

Altered ilmenite 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 [Temple, 1966]. By virtue of its being a product of varying composition, altered ilmenite has in the past presented problems both in ore 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 [Bailey et al, 1956 and Flimer, 1959] have agreed 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 [Karkhanawala, 1959] 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 [1966] 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 facilated 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 condition reaction kinetics are slow, thousands of years may be required to take this process in nature. TiO_2 content increases with increasing age. Due to this slower rate disequilibrium assemblages should be common in natural ilmenite deposit. The difference in the degree of ilmenite alteration in various heavy mienral placer deposits implies differential weathering due to age differences and / or multistage alteration of ilmenite.

The role of water in the alteration of ilmenite has been discussed by Gevorkyan and Tananayev (1982) 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.

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°C [Mucke and Chadhuri, 1991] not exceeding. This favorable environment is also common for our beach sands as the beach sand minerals are exposed to a temperature around 35-40°C. So there is a 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 alterd ilmenite and yield concentrates containing between 54-66 percent TiO_2 while Folkson, Georgia ilmenite assay 76.1 percent TiO_2 Attempts to produce synthetic rutile from Bangladesh ilmenite have yielded encouraging results. However no detailed study on the extent of alteration of ilmenite in the deposits of Bangladesh has so far been reported. So the study of alteration may be a promising field of study for the exploration of beach sand minerals in Bangladesh.

2.6 A review of important process for rutile substitutes

A detailed analysis of the developments in this area shows that a number of research workers have tried to solve the problem from different angles utilising various properties of the material Enormous studies have been undertaken for the production of synthetic rutile, some of which are purely of academic interest. In this review for making rutile substitute a brief summary of the most important processes developed and studies reported by various workers is given. These processes may be discussed under the following headings.

1. Processes employing caustic or alkali metal salts.
2. Processes employing liquid -liquid extraction.
3. Processes employing ferric salt leaching.
4. Processes employing sulfur, sulfides or sulfates.
5. Processes employing sulfuric acid.
6. Processes employing hydrogen chloride gas.
7. Processes employing hydrochloric acid.
8. Process employing the solid-state reduction of iron to metal.

9. Processes employing the reduction of iron to metal under slagging conditions.
10. Processes employing chlorinating techniques.

Processes employing caustic or alkali metal salts:

When a mixture of ilmenite and solid sodium hydroxide is heated above 350° C, the sodium hydroxide melts and reacts with the ferrous titanate. The reaction product consists of a solid phase containing iron oxides and a liquid phase containing most of the titanium dioxide can by separating the two phases, iron and titanium dioxide be recovered separately.

In a process employing this principle [British pat, 1960] ilmenite and solid caustic soda are mixed in a ratio of about 1 part ilmenite to 9 parts of caustic, and the mixture is heated to about 750° C. Upon completion of the reaction between the caustic and ferrous titanate, the temperature is lowered to about 500°C. The solid phase is then allowed to settle from the liquid. The liquid phase is separated from the solid by decantation and is filtered to remove suspended solids.

Upon cooling, the filtered liquid is solidified and the solid leached with boiling water to dissolve sodium hydroxide and leave a residue containing titanium dioxide.

Schechter and leddy [1962] patented a process in which a mixture ilmenite and sodium hydroxide is heated at about 400°C for 3 to 8 hours. Air or oxygen is added during the reaction period, after which the entire reaction product is allowed to cool and solidify. It is then crushed and leached with water to dissolve sodium hydroxide. After filtering to remove the sodium hydroxide solution, the residue is leached with hydrochloric acid to dissolve the iron. The residue from the hydrochloric acid leach, after solid-liquid separation, contains about 90 percent TiO_2 and as little as 0.5 percent Fe_2O_3

In a process developed by Safiullin and Belyaev [1968] a product containing over 92 percent TiO_2, less than 2 percent Fe_2O_3, and 0.1 to 0.6 percent Cr_2O_3 was obtained from ilmenite ores containing from 2.0 to 12.9 percent Cr_2O_3. In this process the high-chrome ore is mixed with sodium carbonate and sintered at 900° C for 3 to 4 hours. The sinter is leached first with water at 60° to 85° C and then with 20 percent HCl at 105° to 108° C to yield the final product.

Processes employing liquid -liquid extraction:

Titanium can be recovered from solutions containing both iron and titanium by liquid liquid-extraction. To recover titanium from a titaniferous ore using this technique, the ore is first leached with an acid to obtain a solution containing the iron and titanium. The solution is then contacted with an organic extractant, and the liquid phase containing the titanium is treated to recover titanium dioxide. The extractant is recovered for reuse and the iron is usually left in an aqueous solution.

A process patented by Long, Olson and Surls [1960] uses concentrated sulfuric acid to react with ilmenite, forming a solid mass containing water soluble titanyl sulfate and ferric and ferrous sulfates. Approximately 90 percent sulfuric acid is reacted with the ilmenite for one-half hour to 3 hours, using antimony oxide (Sb_2O_3) or antimony sulfide (Sb_2S_3) as a promoter. The reaction product is heated to 250° C for about 1 hour and is then leached with water, maintaining the temperature at about 60° C. Temperatures of 80° C and higher are undesireable as colloidal hydrated titanium oxide is formed, and the presence of the colloid during the liquid extraction steps causes the formation of hard-to-break emulsions. Following the water leach, the waste solids are removed and the solution containing both iron sulfates and titanyl sulfate is contacted with a mono - or dialkyl substituted orthophosphoric acid in a solvent, such as kerosine. After about 30 minutes of contact, the organic and aqueous phases are separated and the organic phase containing the titanium and ferric iron is scrubbed with 5 molar hydrochloric acid to remove the iron in the acidic, aqueous phase. The organic phase, still containing the titanium is first separated from the aqueous phase and then contracted with a saturated solution of ammonium carbonate to extract the titanium. The ammonium carbonate solution, containing the titanium is separated from the organic phase and is evaporated by gentle heating causing the titanium to precipitate as hydrated titanium dioxide. The precipitate is separated from solution and is calcified at about 900° C for 4 hours to obtain a titanium dioxide product.

Another method of recovering titanium from the organic phase following the removal of iron is by adding an ammonium bifluoride solution instead of ammonium carbonate. In this case the titanium is precipitated from the aqueous phase as ammonium hexafluorotitanate [$(NH_4)_2TiF_6$]when the solution is evaporated. The ammonium hexafluorotitanate is added to a solution of aqueous ammonia forming hydrated titanium dioxide that is removed from solution and calcified to recover the rutile substitute product.

A somewhat different process [Schaefer and zirngibl 1966] using a solution consisting of 3 parts of benzene and 1 part of decyl alcohols to extract titanium from leach solutions. Titanium tetrachloride is then recovered from the organic extractant by scrubbing with water.

Processes employing ferric salt leaching:

In the processes using ferric salts titaniferous ore is roasted under reducing conditions to convert the iron to metal. The reduced ore is leached with a solution containing ferric iron to extract the metallic iron converting it to the ferrous state. The reaction may be shown as:

$$Fe^{0} + 2Fe^{+3} = 3Fe^{+2}$$

The resultant solution, containing ferrous iron is separated from the TiO_2 residue. The solution is then processed to regenerate ferric iron for leaching additional ore and to recover the iron as a byproduct.

A processe [Shiah, 1966 and U.S. Pat, 1966] patented by C. D. Shaih, uses a solution containing both ferrous and ferric chloride. In this process the ore is first roasted in an oxidizing atmosphere at about 1050^{0} C for 2 hours to convert the iron to the ferric state. The oxidized ore is then roasted at about 900^{0} C for about 2 hours under reducing conditions to convert the oxidized iron to metallic iron. In this case hydrogen gas is used as the reductant. The reduced ore is cooled in an inert atmosphere to avoid reoxidation of the iron and is leached at 80^{0} C in a chloride solution containing 70-gpl ferrous irons and 50-gpl ferric irons. After the reaction the ferrous chloride solution, which still contains a small quantity of ferric iron is decanted from the residue.

$$2FeCl_3 + Fe = 3FCl_2$$

To regenerate ferric chloride, air is bubbled through the ferrous chloride solution, oxidizing portion of the iron as shown in the following equation:

$$12FeCl_2 + 3O_2 = 2Fe_2O_3 + 8\,FeCl_3$$

Ferric oxide precipitates as a hydrate and is recovered by filtration. It is then washed and calcined to produce high purity Fe_2O_3. The solution from which the hydrated ferric oxide is recovered contains both ferric and ferrous chlorides and after discarding as much as 5 percent of the solution to avoid impurity build up, it is recycled to the leaching step. In his German patent [Shiah, 1966] substitutes and electrolytic iron recovery system for the aeration scheme.

The titanium dioxide residue that remains after leaching is recovered by washing first with a weak acid solution and then with water. After drying a rutile substitute containing over 90 percent TiO_2 is recovered.

Nakazawa and Terunuma [1958] developed a similar process in which ilmenite is oxidized, reduced and then leached with a solution containing either hydrochloric acid and ferric chloride or sulfuric acid and ferric sulfate. After reduction, the metallic iron in the ore is dissolved by a reaction similar to the one in the preceding process, and the iron is recovered from the leach solution by electrolysis.

Ilmenite was subjected to solid-state reduction and the metallic iron obtained was oxidized to a soluble Fe (II) complex, which was then separated as solid Fe_2O_3 by oxidation [James W. Reeves, 1966]. A concentrate containing more than 90% TiO_2 was obtained from ilmenite by roasting in air at 800- 1200^{0}C followed by reduction with a mixture of CO and H_2 gas at 750-1250^{0}C and leaching with $FeCl_3$ to dissolve Fe as $FeCl_2$, which was then regenerated [Oceanic process Corp., 1965].

Processes employing sulfur, sulfides or sulfates:

In the following group of processes sulfur, or a salt containing sulfur as a sulfide or sulfate is reacted with a titaniferous ore at a temperature in the range of 400^0 C to 1000^0 C. The reaction product contains the iron and titanium in forms that can be separated by leaching and liquid solid separation techniques to produce a rutile substitute and in some cases an iron oxide by product.

Gaskin and Ringwood [1960] developed a process in which ilmenite ore is reached with sulfur vapor to produce ferrous sulfide, which is removed from the rutile product by pressure digestion. The ilmenite ore is added to a furnace with coke and pyrite. The coke is used to maintain a reducing atmosphere in the furnace, and the pyrite serves as the source of sulfur. The furnace with an ore retention time of 1 to 4 hours is operated at about 700^{0}C. The products from the reaction are ferrous sulfide, titanium dioxide, and carbon monoxide as shown in the following reaction:

$$FeTiO_3 + S + C = FeS + TiO_2 + CO$$

After completion of the reaction, the furnace product is cooled in the absence of air before it is screened to remove excess coke, which is recyled to the furnace. The cooled furnace product,

after coke removal, is leached in a vessel with water at a temperature of 110°C to 200°C, while air or oxygen is admitted at a pressure of 20 to 100 psig. The reaction product from pressure digestion contains titanium dioxide, iron sulphate, iron oxides, and sulfur. Following solid-liquid seperation, the sulphur and iron oxide fines are removed by screening. The rutile is recovered separatly and is leached with 20 percent sulfuric acid to remove adhering iron, leaving a rutile product containing some insoluble impurities.

A processes similar to the one developed by Sarova and Fotiyev, was patented by Takimoto, Tanaka and Hattori [1959]. In the process ilmenite, sodium sulfate and coke are mixed in the ratio 1:1.07:0.24. The mixed solids are roasted at 1050^0 C followed by a water leach to recover sodium sulfide and sodium hydroxide. A dried residue from water leaching contained 51.5 percent TiO_2 and 27.1 percent Na_2O, and after treating the residue under pressure with 10 percent sulfuric acid, a final product contained 92.6 percent TiO_2, 0.9 percent FeO, 1.05 percent Na_2O, and 0.07 percent SiO_2.

Processes employing sulfuric acid:

There are many processes employing sulfuric acid to treat titaniferous ores. Most of the processes are designed to produce a titania pigment and are not applicable to the present review of processes for making rutile substitutes. In these processes a mixture of titaniferous ore, sulfuric acid and a reductant is reacted in an autoclave at elevated temperature and pressure. The iron is dissolved from the ore as ferrous sulfate, and the titanium dioxide remain in the residue. A substantially iron free titanium dioxide product is obtained after solid liquid separation of the slurry leaving the autoclave.

Processes employing hydrogen chloride gas:

When hydrogen chloride gas is passed over a titaniferous ore at elevated temperatures (600^0 to 1600^0 C) the iron present in the ore reacts with the gas to from a volatile chloride, which leaves the furnace in the exit gas stream. The iron chloride is removed from the gas stream to recover the chlorine for regeneration of hydrogen chloride gas and the solids remaining after chloridization are recovered and used as a rutile substitute.

In a process developed by Weil (1960) ore having a low gangue content must be used because only iron is removed leaving other impurities in the product. In the process the ore is crushed, mixed with enough finely divided carbon to completely reduce all the iron oxides to metallic

iron and roasted at about 1275° C for 6 hours. The carbon requirement is not critical but enough should be used to totally reduce the iron to metal However, the addition of too much carbon is to be avoided so that titanium carbide, which will chloridize with the iron, will not form.

The ore does not fuse at the temperature of reduction and the furnace product is a highly porous, coherent mass. This material is cooled while maintaining a reducing atmosphere to prevent reoxidation of the iron and is crushed. The crushed reduced ore is next chloridized with anhydrous hydrogen chloride gas

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

The chloridization reaction occurs during the 5-hours retention of the ore in the chloridizing furnace which is maintained at about 1000°C. In several examples where the quantity of carbon used during reduction was varied and the reduced ore chloridized the resulting chloridization residue contained at least 98 percent TiO_2 and less than 0.25 percent iron.

In the different approach [Robinson et al., 1960] to producing a rutile substitute, ilmenite ore is roasted in an oxidizing atmosphere at 760° C to convert all the iron to ferric oxide. The oxidized ore is chloridized with hydrogen gas to form ferric chloride according to the following reaction:

$$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$$

The reaction is carried out in a fluidized bed at a temperature of about 600°C, and the synthetic rutile product contains over 90 percent TiO_2 with about 1.6 percent total iron as Fe_2O_3. However no ferric chloride recovery system is proposed and a circulating load of 600,000 ft^3 of hydrogen chloride gas per ton of product is required.

Processes employing hydrochloric acid:

Processes using hydrochloric acid to upgrade titaniferous ores involves leaching the ore to dissolve the iron as a chloride. The residue containing most of the titanium present in the ore is filtered from the iron containing solution and is removed as a rutile substitute.

In one process [British pat, 1958] titaniferous ore ground to minus 200 mesh is charged to an autoclave. Sufficient 36 percent hydrochloric acid is added to provide about 300 percent excess of the stoichiometric quantity to react with the contained iron and the autoclave is heated to

175°C. At this temperature the initial internal pressure in the autoclave is about 40 atmospheres. The autoclave is maintained at the reaction temperature for about 12 hours after which it is cooled and the reaction products are removed. The solid and liquid are separated and the residue is washed with water. The resultant residue contains over 99 percent of the titanium originally in the ore and only about 4 percent of the iron product.

In a process [Sehra et al., 1966] developed for treating an ilmenite containing 60 percent TiO_2, 10.5 percent FeO, 25.4 percent Fe_2O_3, 0.17 percent V_2O_5 and 0.13 percent Cr_2O_3, a product containing 97 to 98 percent TiO_2 is obtained. Minus 60 mesh ilmenite is mixed with 5.25 N hydrochloric acid so that 50 percent excess HCl over that required to dissolve the ferrous and ferric oxide is present. The acid ilmenite mixture is charged to a reactor and heated at about 250°C for 24 hours. Agitation of the reactants is necessary and the resulting residue, after removal of the solution, contains about 98 percent TiO_2, 0.5 percent Fe_2O_3, and less than 0.02 percent each of V_2O_5 and Cr_2O_3. Approximately 90 percent of the hydrochloric acid is recovered from the solution following solid liquid separation of the reaction products.

A process [Australian Upgrading Process, 1969] developed in Australia is expected to produce a synthetic rutile containing 96 to 97 percent TiO_2, on a commercial scale. This process employs a hydrochloric acid leach of reduced ilmenite ore to remove the iron as ferrous chloride leaving a residue of synthetic rutile. The ilmenite ore is first roasted in an oxidizing atmosphere for 1 hour, using a fluid- bed technique. It is then roasted in another fluid bed for one half hour this time using hydrogen gas to partially reduce the oxidized ilmenite. The partially reduced ore is then leached with hydrochloric acid at a temperature of about 105°C for a period of 4 hours. After leaching, the spent acid solution containing ferrous chloride is separated. Magnetic separation removes chromite from the product leaving a synthetic rutile containing 96 percent to 97 percent TiO_2.

Sinha and co-workers [1967] had reviewed the various methods available for the preparation of titanium concentrates from ilmenite. They proposed an improved method in which ilmenite was subjected to oxidation roast before partial reduction and leaching with 20% HCl. The product contained 95-97 % TiO_2.

In another process [Oster, 1968] finely powdered ore was refluxed with HCl to dissolve the iron and the residue was washed and calcined to give a product containing 92.2% TiO_2. By leaching

ilmenite in two steps with different concentrations of HCl at 105-110°C at high pressures Ching-Lung and Mackay (1965) could remove more than 95 % of iron from it. Aravamuthan and Raghavan (1969), and Aravamuthan and sundram (968) prepared TiO_2 with 75% purity from ilmenite by reduction at 600°C with fuel oil followed by HCl leaching which was repeated for two or three times. They observed that the acid consumption would be reduced to 60% when the leaching was done in closed pans and by grinding the ilmenite before leaching. Sehra and Jena [1966] upgraded Quilon ilmenite to a product containing 97.28% TiO_2 by a single stage HCl leaching at about 250°C for 48 hours without stirring or for 24 hours with stirring. A process for recovering the HCl was developed.

Synthetic rutile containing about 95% TiO_2 was prepared from ilmenite by reduction in a fluidized bed followed by leaching with dilute HCl at about 105°C to remove iron [Komarov et al, 1973]. In a study reported by Kurata et al (1974) the iron oxide present in ilmenite was reduced to ferrous form using H_2 which was leached out with 20% HCl at 105° C giving a product with 96.2% TiO_2 and 0.6% iron. Effect of various factors, concentration of acid, presences of coagulents and flow velocity on leaching have been studied.

In the Murso process [Sinha, 1973] which is one of the important routes for the production of synthetic rutile. Crushed ilmenite after giving an oxidative roasting at 900-950°C was subjected to reduction with H_2 or mixtures of hydrogen, CO, CO_2 and steam at around 850-900°C. The ferrous iron formed was leached with dilute hydrochloric acid at about 110°C. HCl was regenerated from the product.

Marshall and co-workers [1972] prepared TiO_2 (80.7%) from powdered ilmenite by leaching with HCl in the presence of $SnCl_2$.

Process employing the solid-state reduction of iron to metal:

Included in this section are processes in which the iron contained in the ore is reduced to the metallic state without melting the furnace charge. After reduction the ore is either leached or is subjected to a physical separation process such as magnetic separation to remove the iron from the titanium dioxide product.

In a process developed by Becher (1963) and Beacher et al (1965) ilmenite ore is mixed with minus 8- plus 20-mesh coal char and is roasted at a temperature of 1000° to 1150°C. A ratio of 3

parts char to 10 parts ilmenite is sufficient if the reduced ilmenite is cooled in the absence of oxygen and carbon dioxide. Oxidation of the ore prior to reduction is beneficial in that the ore is more easily reduced.

After reduction the ore is screened and magnetically seperated to remove the unburned char for recycling to the furnace. The char free reduced ore is then added to a vessel and mixed with water in the ratio of 1 part reduced ilmenite to 6 to 8 parts of water. The temperature of the slurry is maintained at 60^0 to 80^0 C and air is passed into the vessel for a period of 6 to 8 hours causing the metallic iron to rust from the reduced ilmenite. The iron rust formed by the oxidation of the metallic iron remains suspended in the solution as a fine precipitate and is separated from the heavier titanium dioxide residue by decantation. The use of a catalyst, such as ammonium chloride and a trace of hydrochloric acid accelerates the rate of oxidation and helps to maintain the solution pH near 4.

After separation from the titanium dioxide residue the fine iron oxide is filtered and then calcined at temperatures of 400^0 to 900^0C to produce different grades of iron oxide pigment. The titanium dioxide product, which remains after the iron is removed, is a rutile substitute containing about 90 percent TiO_2 and about 5 percent total iron.

In a process developed by O'Brien and Marshall [1984] magnetic separation of the reduced ore is employed to produce a product containing about 80 percent TiO_2. Ilmenite concentrate 99 percent minus 200 mesh, is mixed with coal char about 80 percent minus 48 mesh in equal parts. To these mixtures of ilmenite and coal char is added minus 100 mesh iron byproduct that is recycled from the final magnetic seperation step. The mixture is added to a furnace where the temperature is slowly raised to 1200^0C at which temperature the charge is held for 4 hours. The furnace product is cooled to 700^0C over a period of about 18 hours while excluding air. This material is then cooled to room temperature in the presence of air.

After lightly mulling the furnace product the unburned char is removed by magnetic separation. The magnetic, nonchar fraction of the furnace product is ground in a ball mill and the fine material is subjected to wet magnetic separation. The nonmagnetic fraction is titanium dioxide product containing about 78 percent TiO_2 and 8 percent iron on a carbon free basis.

Processes employing the reduction of iron to metal under slagging conditions:

When iron is reduced under slagging conditions, titaniferous ore is charged to a furnace usually with a solid reductant and a flux material and is smelted. The iron is reduced to molten metal, which forms a liquid layer separated from the lighter slag containing the titanium dioxide. Separation of the two liquid layers results in a high-grade titanium dioxide slag and a pig iron byproduct. Varying conditions during the smelting of the ore results in different metal and slag compositions and different grade of the products.

Swinden and Jones [1978] carried out the smelting of ilmenite in an arc furnace to give metallic Fe and a tiataniferous slag. They found that there was no difficulty in producing slags with TiO_2 concentration upto 95 % from western Australia beach sand ilmenite but the reduction kinetics suggested that it would be uneconomical to process beyond 85% titanium oxide concentration.

Elger et al [1976] carried out a pilot plant scale study of the reduction smelting of ilmenite with coke and lime in an electric arc furnace at 1600°C. The slag after proper treatment and leaching with dilute sulphuric acid gave a rutile with 88% TiO_2. An evaluation of the economics of the process had also been carried out.

The Osaka Titanium Croporation developed a process [Noda Toshio, 1968] to produce a high-grade titanium dioxide slag from ilmenite. The slag is of such quality that it can be used in place of rutile for the production of titanium sponge. The process utilizes ilmenite containing about 54 percent TiO_2, which is mixed with petroleum coke in the ratio of 1 part coke per 6.5 parts ilmenite. The ilmenite coke mixture is charged to an electric arc furnace where the iron is reduced to molten metal and the titanium remains in a separate slag phase. To obtain a high-grade titanium dioxide slag a high degree of reduction is required. This reduction results in the formation of titanium sesquioxide which cause an increase in slag viscosity with increasing titanium sesquioxide content. The slag viscosity is maintained at a desired level by leaching the slag with oxygen during the melting step to retard the reduction of titanium dioxide to the sesquioxide. The high-grade titanium dioxide slag produced by the process has an equivalent TiO_2 content of 97 percent.

Greffe Andre [1959] developed a process that utilizes a solid reduction of iron followed by fusion of the reduced mass. Ilmenite ore is crushed to minus 40 mesh and mixed with minus 80 mesh coke. The ratio of ore coke is 10 to 1 and the mixture is hearted to 1200° C for about 1

hour to reduce the iron to metal. After reduction the reaction products are transferred directly to another furnace where they are heated to 1,650° C causing the reduced ore to melt. The two liquid phases formed when the ore melts are separated to yield two products. The one product pig iron contains about 2 percent C, 0.2 percent Si traces of Ti and the balance metallic iron. The slag phase is a high titania product containing about 95 percent TiO_2 and less then 4 percent FeO

Processes employing chlorinating techniques:

The chlorination processes for treating titaniferous materials are basically of two types. One type of process employs the chlorination of both the iron and titanium in the ore forming volatile chlorides each of which are collected separately. This process will not be considered here because the titanium product is either titanium tetrachloride or a pigment grade titanium dioxide.

Chapter 3

MATERIALS AND EXPERIMENTAL METHODS

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

3.1 Materials

Ilmenite: Raw sand containing the heavy minerals was collected from the backdune surface layers of heavy mineral deposits at Teknaf village area (Lengurbil deposit) from points located 2-3 Km away from the water line and 5-6 meter above mean sea level. The area selected for the study falls between the latitude 20°52'7" to 20°52'21"N and longitude 92°16'10" to 92°15'58"E at Teknaf. This placer deposit forms one of the major heavy mineral concentrations of Bangladesh. The heavy mineral proportions of the concentrates were determined to be 89-92% by point counting grains using both reflected and transmitted light microscopy. The Teknaf beach placer deposit, consisting of ilmenite, rutile, zircon and quartz mixed ilmenite. Ilmenite constitutes around twenty seven percent of heavy mineral tonnage. The heavy minerals show the grains of different colours in the Fig. 3.1. 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.

The sample was dried and screened (~8 mesh) to remove shell and other trash. Factory grade ilmenite was produced by the flow sheet developed at the Beach Sand Minerals Exploitation Centre, Cox's Bazar and the details can be found elsewhere [Information booklet,1994]. The techniques of seperation are based on the difference in physical properties like density, electrical and magnetic properties. The ilmenite seperated from Teknaf beach sands is a black shiny powder material having particles of various sizes. The major constituents of ilmenite are oxides of iron and titanium. The results of wet chemical analysis are shown in Table 3.1. The chemical analysis of the as-received Teknaf ilmenite contains a substantial amount of iron in the form of ferrous and ferric state. The ferrous iron content is 25.32%, ferric iron content is 32.53% and the amount of TiO_2 is 39.96%. The atomic absorption analysis indicate that the sample also contains traces element i.e., chromium, coper, magnesium, manganese, zinc nickel etc. The results of chemical analysis are given in Table 3.1. It is clear that the as received Teknaf ilmenite did not contain any metallic iron.

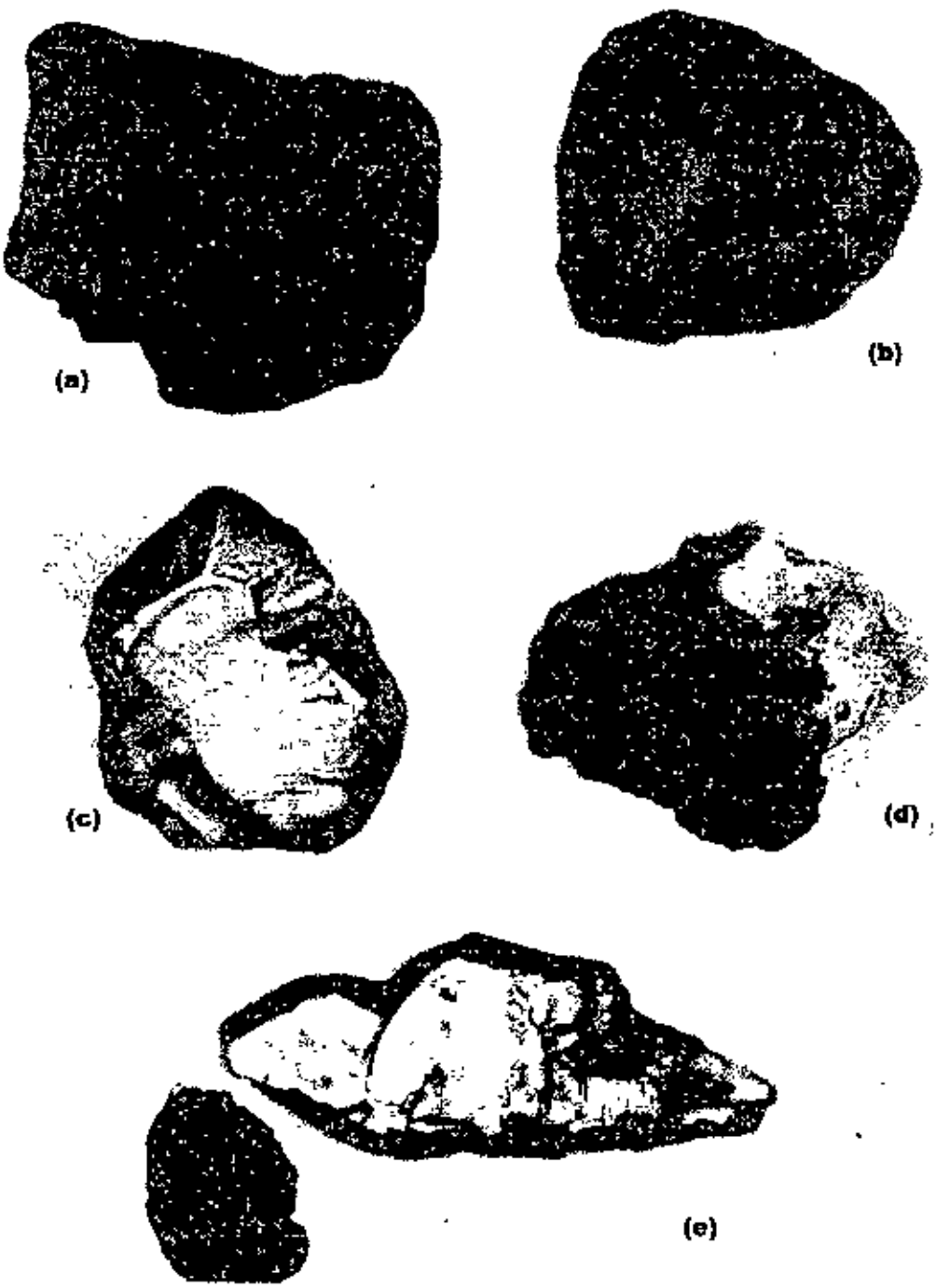


Fig. 3.1 Mineralogy of as received heavy mineral sample:'(a) Ilmenite , (b) Rutile, (c) Zircon, (d) Quartz mixed Ilmentie, and (e) Garnet

Table 3.1 Chemical analysis of as received ilmenite.

Component	% in ilmenite
FeO	25.32
Fe_2O_3	32.53
Fe_{tot}	42.43
TiO_2	39.96

Charcoal: The reducing agent used for the studies was charcoal. The charcoal was collected from local marcket. The charcoal was dried and ground. The ground charcoal was sieved and only +30 mesh size charcoal powder was selected as a reductant. It was then dried at 110°C for 4-6 hrs, cooled and stored for use in the experiments. The chemical analysis of the charcoal is given below.

Table: 3.2 Specification of charcoal used as a reductant (mesh size +30).

Component	%
Fixed carbon	57.35
Ash content	6.80
Volatile matter	26.20
Phosphorus	0.30

3.2 Experimental methods

To characterize the ilmenite, the following investigations were carried out.

01. Chemical analysis
02. X-ray diffraction pattern analysis
03. Magnetic separation
04. Sieve analysis
05. Oxidation
06. Reduction
07. Leaching
08. Thermogravimetric analysis
09. Optical microscopy
10. Scanning electron microscopy

3.2.1 Chemical analysis

Wet chemical analysis was performed to determine the contents of as received ilmenite. The detailed procedure for chemical analysis has been given as Appendix A. – Appendix F. Chemical analysis was done by the standard wet chemical methods namely aluminium reduction methods for TiO_2, dichromate titration for iron and atomic absorption methods for trace element

contents. The prime interest was to determine percentage of ferrous oxide (FeO), ferric oxide (Fe_2O_3), and titanium di oxide (TiO_2) in the ilmenite sample used in these investigations.

Chemical analysis was also carried out in the different stages as mentioned below:

(a) For all the size fractions and magnetic fractions to determine the concentration of ferrous oxide (FeO), ferric oxide (Fe_2O_3) and titanium oxide (TiO_2) to investigate the difference, if any, after separation into different size fractions and magnetic fractions.

(b) Oxidized ilmenite sample to determine the extent of oxidation of ferrous oxide (FeO) to ferric oxide (Fe_2O_3).

(c) After reduction, to determine the contents of metallic iron (Fe_M), total iron (Fe_T) and titanium oxide (TiO_2) and thus to determine the extent of reduction. Reagent grade chemicals were used for analysis.

(d) Leached sample of ilmenite to determine the concentration of TiO_2 and metallic iron.

3.2.2 X- Ray diffraction pattern analysis

X-ray diffraction analysis was conducted to identify the different phases present in the ilmenite. The x-ray diffraction patterns were recorded by a Jeol DX-GE-2P X-ray diffractometer. Before recording the patterns, the samples were finely ground in an agate mortar. The diffraction depends on the crystal stucture and on the wavelength. By comparing the diffraction angle (d-value) with JCPDS (Joint Committee of Powder Diffraction Standard) standard data we can know the composed phases of the sample. If a sample has a preferred orientation, strong diffraction line from the oriented plane can be observed. The d-value are calculated by using Bragg law: $2d\sin\theta = n\lambda$.

The pattern was recorded with the following setting of the x-ray diffratometer.

Target:	Mo (Zr)
Current:	20 mA
Voltage:	30 kV
Angle of Diffraction:	$8\text{-}38^0$
Scanning Speed:	$1/2^0$ per min
Chart Speed:	05 mm per min
Full scale intensity:	2×10^{-4} cps

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

3.2.3 Magnetic separation of as-received ilmenite

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

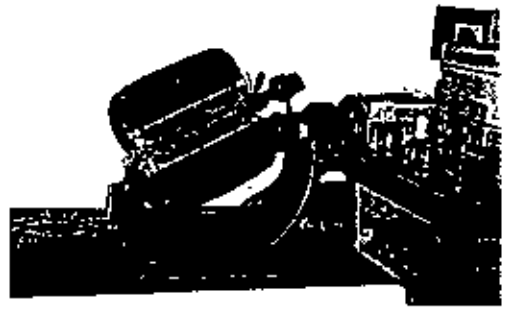


Fig 3.2 The Frantz isodynamic magnetic separator

Mineral separations are normally made by arbitrary adjustment of the current. At any such adjustment the separator divides a sample into two fractions. The more magnetic fraction consists of particles each having a specific susceptibility above a value determined by the settings. The less magnetic fraction consists of particles of susceptibility below this value. The sample of ilmenite was separated into five different magnetic fractions (at a current of 0.10-0.30 amp.) with a chute angle 15^0 and feed rate about 50 gm/hr. The magnetic fractions were recycled through the separator to ensure a clean seperation.

3.2.4 Sieve analysis

Sieve analysis of the as received sample was performed in a standard US Sieve shaker. At first the sieves of different mesh sizes were arranged in such a way that the sieve of US sieve no 60 remained at the top most position while the pan remained at the bottom. The other sieves were placed from top to bottom according to their increasing sieve number. Then 50 gm of as-received ilmenite 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 sieves were collected and measured.

3.2.5 Specific gravity mesurement

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

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

Where, W_1 = Wt. of empty bottle

W_2 = Wt. of sample and bottle

W_3 = Wt. of sample, bottle and water

$W_2 - W_1$ = Wt. of sample

$W_3 - W_2$ = Wt. of water (vol. of water)

50 = Volume of the sp.gr. measuring bottle

$50 - (W_3 - W_2)$ = Vol. of sample

3.2.6 Oxidation of as-received sample

Oxidation of ilmenite samples was carried out in temperature controlled furnace. 20 gm of dry as-received ilmenite was taken on a porcelain lid. The sample was spread on the lid as a thin layer and was oxidized in a muffle electric furnace. The temperature of the furnace was controlled by an on-off controller to $\pm 5^0$C. After oxidation the sample was taken out from the furnace and cooled to room temperature.

3.2.7 Reduction of as received and pre-oxidised ilmenite

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

The temperature of the furnace was controlled to $\pm 5^0$C by an off- on controller. After reduction crucibles were taken out one by one at different time intervals 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 the bigger particles of charcoal were separated by sieving. In the second stage particles of reduced ilmenite were separated from the final particle of charcoal by a small hand magnet.

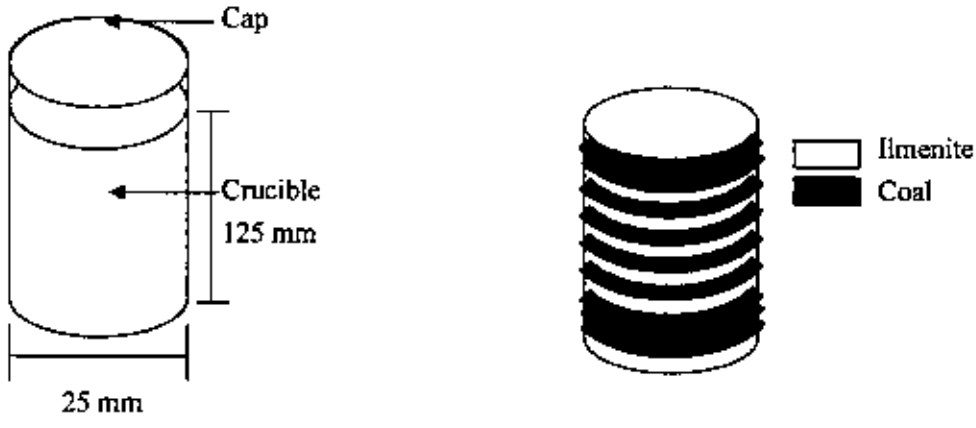


Fig. 3.3 Arrangement of Reduction

The extent of reduction was followed by the chemical analysis of the reduced mass for the content of metallic iron. X-ray diffraction analysis and optical metallography of the reduced mass were carried out to complement the results of wet chemical analysis. From the experimental result, degree of reduction was calculated by using the formula [Shams, 2000].

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

3.2.8 Leaching of reduced ilmenite

Samples of Teknaf ilmenite was used for this investigation. Samples of ilmenite reduced both in the as received and pre-oxidised conditions were used to study the effects of prior oxidation on the extent of subsequent leaching of the reduced mass. Leaching was performed in the temperature range of 30°C to 80°C for period's upto 2 hrs. in acid solutions containing 5-15 percent HCl. A three-necked flask equipped with a reflux condenser, a thermometer and a magnetic stirrer was used as the reaction vessel for leaching. The arrangement for leaching is shown in Fig.3.4.

During leaching 2 gm of ilmenite samples were taken in 200 ml HCl solution. The leaching solution was stirred by a magnetic stirrer. Care was taken to maintain similar stirring speed in all

cases. Temperature of the leaching solution was controlled to the specified value and was continuously monitored by a thermometer. During leaching 5 ml of solution was taken after certain interval of time and was analysed to determine iron content in the solution. This was

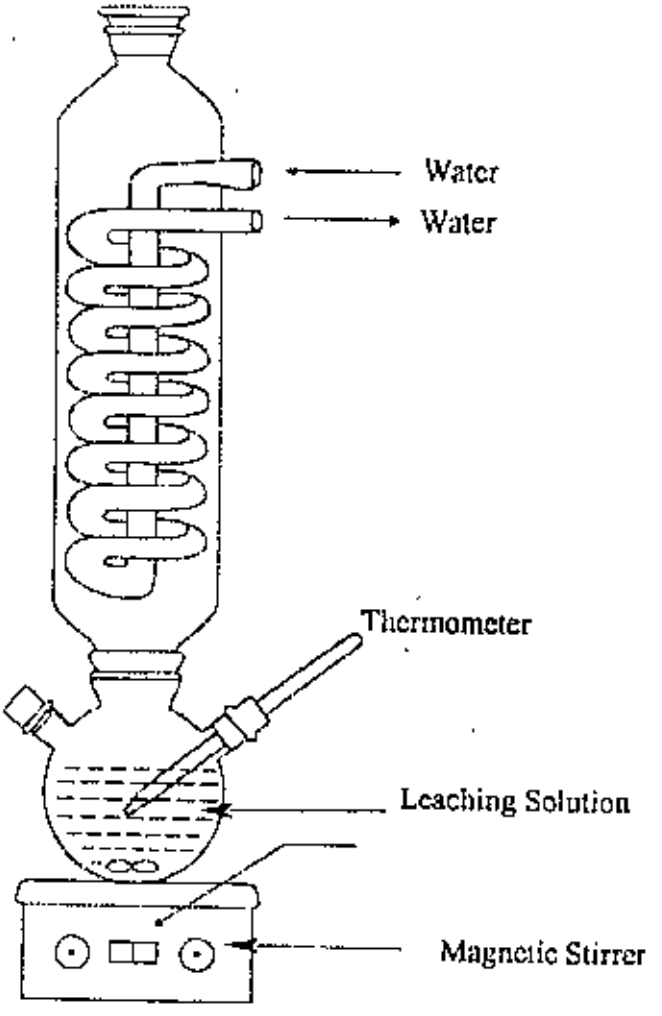


Fig. 3.4 Experimental setup for leaching.

used to determine the amount of iron removed from the experimental samples. The procedure for determination of the amount of iron in leaching solution is given in Appendix-D. These results were then plotted for obtaining the leaching kinetic curves. The iron and TiO_2 contents of the leached samples were determined by wet chemical analysis. The effect of oxidation on the quality of the synthetic rutile produced was identified by comparison of the contents of iron and TiO_2 of the samples reduced in the as received and in the oxidised conditions. The variables considered were acid concentration, time and temperature of the leaching solution. Attempts have also been made to identify the reaction mechanism and to determine the activation energy for the reaction.

3.2.9 Thermo-gravimetric Analysis for the Different Magnetic Fractions

Thermogravimetry is "A method of measuring the mass of a substance as a function of temperature or time by varying the temperature of the substance according to a controlled program, usually performed by measuring the change in the mass of the test piece as a function temperature"(JIS). The change of mass indicates thermal decomposition, dehydration, combustion, oxidation, reduction, sublimation, evaportion, and so on. The change of the mass of a sample is measured by the use of the thermobalance. The thermobalance is a device, which continuously weighes a sample when it is being heated or cooled. Thermogravimetric analysis was performed in a SHIMADZU TGA–50 Machine [Fig.3.5 and Fig. 3.6]. It has a TGA chamber, the main heating unit, a control unit that is used to set different parameters, an inert gas set-up, and some electrical wiring.

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

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

(a) Initial weight was taken.
(b) The crucible was inserted in the TGA chamber slowly and when completely in the TGA chamber it was closed.
(c) Inert gas was introduced to the chamber to provide inert atmosphere.
(d) The heating rate was set at a value of 20^{O}/min and the heater was turned on.
(e) When temperature rose up to 1000^{O}C the machine was turned off and the chamber was allowed to cool.
(f) The machine produced the report as a graph.

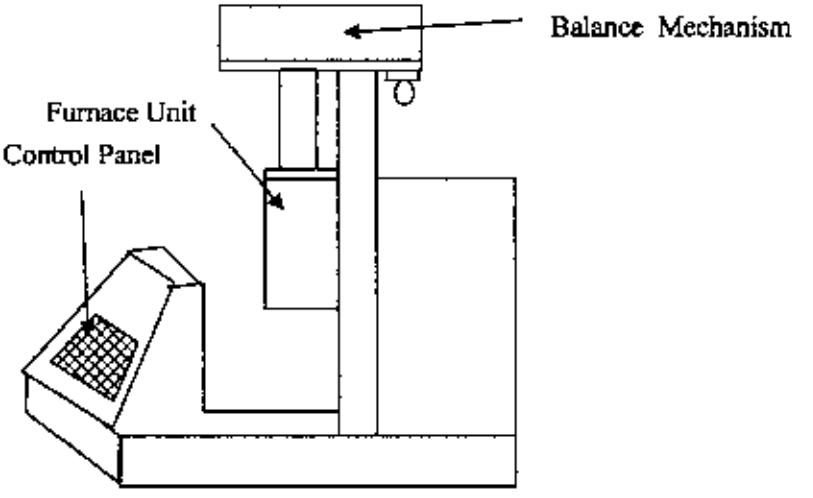


Fig. 3.5 External view of TGA Machine.

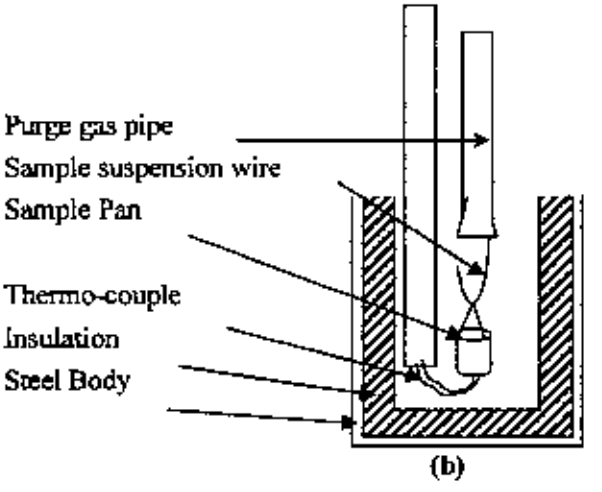


Fig. 3.6 The cross-sectional view of the furnace unit of the TGA machine.

3.2.10 Optical Microscopy

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

3.2.11 Scanning electron microscopy (SEM)

The SEM images vividly display the three-dimensional characteristic of the object surface, under examination and the high reslution images are usally produced by the secondary electrons. In order to observe specimen surface, as it actually exists, special care must be taken.
Ion spattering device were used for specimen preperation. The metal used to coat the specimen is placed on the cathode plate. Ions generated by glow discharge hit the plate and eject the metal atoms from it. These ejected metal atoms deposit on the surface of the specimen, which has been placed on the anode plate.

When scanning a specimen surface with a finely focused electron beam, information will be emitted from each point of the scanning. The emmited information is converted into an electric signal, amplified, and then fed into an observation on CRT (cathode ray tube). On the CRT, the information is used to control the brightness of the corresponding spot. Thus the information emitted from the specmen surface is displayed on the CRT as an image. The magnification of the displayed image is the ratio of the size of the image on the CRT to the size of the electron beam scanning on the specimen surface. The type of information obtained can be changed by switching the signal. In this way, a specific characteristic of the specimen surface can be seen on the CRT in a magnified scale.

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

Chapter 4

RESULTS AND DISCUSSIONS

4.1 Introduction

The objective of the study was to "Characterise Bangladesh ilmenite in the process of its up gradation into synthetic rutile". It was decided to follow the reduction-leaching route of up gradation. The samples were analyzed by standard methods of wet chemical analysis in the as received condition, and also after reduction and on the various magnetic and size fractions. X-ray diffraction analyses of all the fractions were performed to identify the phases present. Thermo-gravimetric analyses of the magnetic fractions were carried out to detect the presence of combined water in the sample. The effects of time and temperature on the oxidation of ilmenite have been followed by wet chemical analysis, X-ray diffraction analysis and optical microscopy. A few samples of ilmenite were observed under a scanning electron microscope. The sample of ilmenite both oxidized and as received was reduced with charcoal in the temperature range of 800^0C to 1050^0C for treatment time up-to 5 hrs. All the magnetic and the size fractions were reduced under otherwise identical conditions. The extent of reduction was followed by wet chemical analysis and X-ray diffraction analysis. Ilmenite samples of as received, oxidized, reduced and leached conditions were also observed under optical and scanning electron microscope. The reduced samples were leached in hydrochloric acid. The kinetics of leaching was followed by wet chemical analysis. The results of these investigations are presented and discussed as in the following subheading.

(a) Characterisation of as received ilmenite.
(b) Oxidation of as received ilmenite.
(c) Reduction of as received and oxidized ilmenite.
(d) Reduction behavior study.
(e) Leaching of ilmenite.
(f) Identification of reaction mechanism.
(g) Comparison of the products.

4.2 Characterisation of as-received ilmenite sample

To characterize as received ilmenite, the sample were analyzed by standard methods of wet chemical analysis and by atomic absorption method. Sieve analysis of the as received

ilmenite was performed in a standard US sieve shaker. The sphericity of different sieved fractions was also measured. Franz isodynamic separator was used to separate the different magnetic fractions present in the ilmenite sample. Thermo gravimetric analysis of the magnetic fractions was carried out to detect the presence of water in the various magnetic fractions of the sample. The phases present were identified by x-ray diffraction analysis. Few samples were observed under scanning electron microscope and optical microscope.

4.2.1 Chemical analysis of as-received sample

The results of wet chemical analysis and atomic absorption analysis of the as received ilmenite are shown in the Table 4.1 It can be inferred from the chemical analysis of the as-received sample that Teknaf ilmenite contains a substantial amount of iron in the form of ferrous and ferric form. The ferrous iron content is 25.32%, ferric iron content is 32.53% and the amount of rutile (TiO_2) is 39.96%. It is also inferred from the atomic absorption analysis (only dissolved in extractant) that the sample also contains of traces elements like chromium, copper, magnesium, manganese, zinc nickel etc.

A comparison of the chemical constituents of as received ilmenite collected from Teknaf deposit with those commercially available from other sources as compiled from data found in different references [Samsuddin et al., 1992 and Vijayn Nayar, 1991] is given in the Table 4.1(a) Teknaf ilmenite contains only about 39.96 % TiO_2. While commercial grade of ilmenite contains a minimum of 55% TiO_2. Thus the Teknaf ilmenite has to be processed further to remove the chemically combined unwanted minerals.

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

Constituent	USA	Canada	Brazil	Srilanka	Norway	Australia	Kerala	Cox'Bazar
TiO_2	44.30	42.50	40.30	53.61	43.90	54.20	55.89	39.12-42.85
FeO	35.90	31.10	32.40	20.67	36.00	24.00	0.33	29.83-32.02
Fe_2O_3	13.80	20.70	16.60	20.95	1.11	18.00	40.37	23.70-28.04
Al_2O_3	1.21	1.05	0.30	0.54	0.85	0.85	1.14	-
SiO_2	2.0	0.88	1.30	0.38	3.28	0.50	1.20	-
CaO	-	-	-	0.05	-	0.01	0.19	-
MgO	0.07	2.0	0.10	0.92	3.69	0.16	0.18	0.04-0.27
V_2O_5	0.16	0.36	0.06	-	0.20	0.15	0.26	-
MnO_2	0.52	0.04	0.60	0.95	0.33	1.60	0.28	1.04-1.30
Cr_2O_3	0.27	0.15	0.50	0.05	0.03	0.03	0.32	0.03-0.08

Table 4.1 Chemical composition of as received Teknf ilmenite concentrate

Substance	%	Substance	ppm	Substance	ppm
FeO	25.32	Cr	1.499	Zn	0.8836
Fe_2O_3	32.53	Cu	0.0225	Mg	6.81
Fe_{tot}	42.43	Mn	7.955	Ni	0.242
TiO_2	39.96	Ca	<MDL		

4.2.2 X- Ray diffraction analysis of as-received sample

X-ray diffraction pattern of as received ilmenite is shown in Fig.4.1. Analysis of the pattern shows that ilmenite is the main phase while of diffraction lines belonging to hematite, ferrous oxide, rutile and pseudorutile could also be detected. This nature is somewhat same as the Cox'sbazar ilmenite. K. Z. Sarker et al (1999) detected hematite (Fe_2O_3) along with ilmenite in Cox'sbazar deposit. A small amount of hematite,rutile and pseudorutile was also detected in the Teknaf ilmenite. The pattern analysis was strictly confined to qualitative analysis. Slight shifts in the locations of the diffraction lines were also noted. This can be explained as the placer deposit are not the chemically standard substance; it is a heterogeneous compound as well as some other impurities which may affect the lattice parameter values.

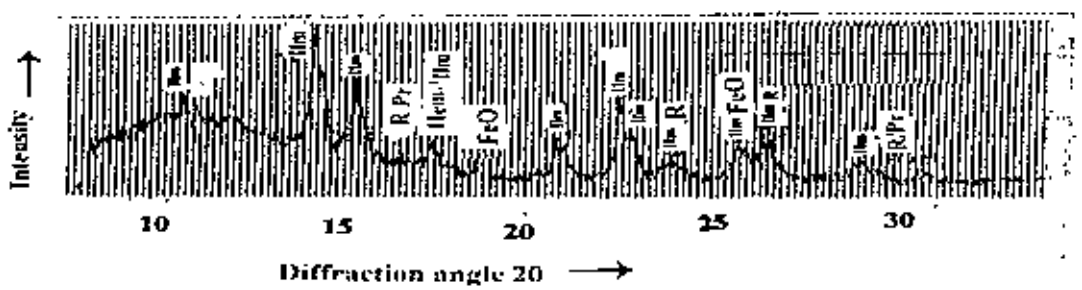


Fig. 4.1 X-ray diffraction pattern of as received ilmenite.

4.2.3 Scanning electron microscopy of as received ilmenite

As received ilmenite was observed under scanning electron microscope. The observed surface (Fig.4.2) was more or less uniform in appearance, having either pores or only micropores. Anand and Gilks [1984] have noted that SEM of slightly altered grains show massive irregular surfaces due to formation of pseudorutile while highly altered grains have very porous surfaces. The spot analysis also shows the presence of aluminum, silicon, magnesium and titanium.

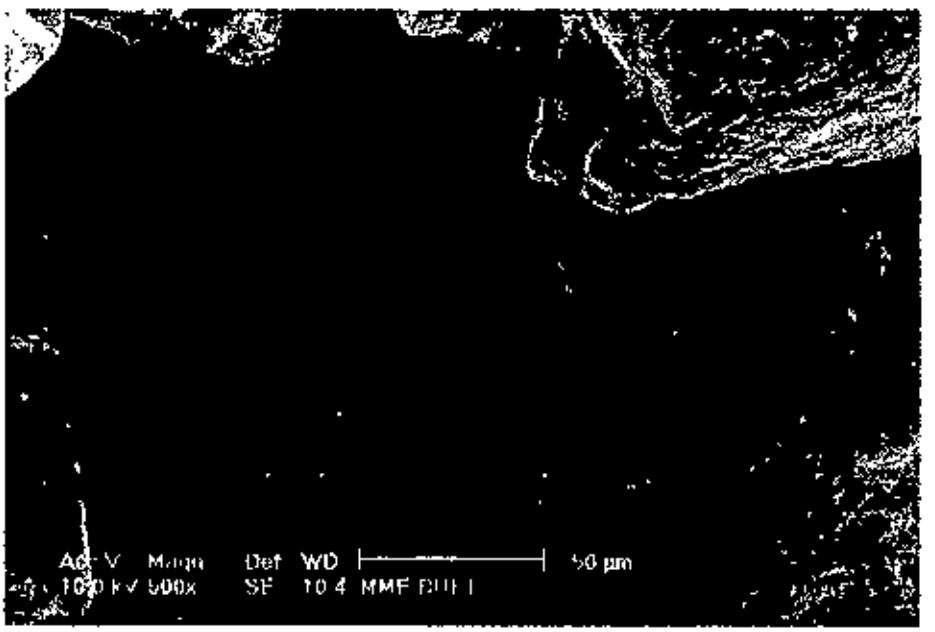
4.2.4 Sieve analysis

Size fractionation of as received sample was performed with a standard Taylor sieve shaker. 50 gm. sample was placed on the top most sieve and power was turned on for 15 minutes. The samples on the different sieves were weighed and the results are presented in Table 4.2. It was found that almost 96 percent sample was retained on three sieves; US sieve no.100, 140 and 200, the individual amount belonging to each of these sieves being 5.094%, 47.057% and 44.51% respectively. Only 4% was retained on the other sieves, which were not sufficient for subsequent investigations, and therefore subsequent investigations were conducted only on these three main size fractions.

Table 4.2 Sieve analysis of as received ilmenite.

US Sieve No	Mesh opening µm	% Size fraction
70	210	0.053
100	149	5.094
140	105	47.057
200	74	44.51
>200	53	2.99

(a)



(b)

Fig. 4.2 SEM of as received ilmenite sample (natural ilmenite)
(a) Magnification X 100
(b) Magnification X 500

4.2.4.1 Chemical analysis of different size (sieve) fractions

The major fractions were analyzed chemically by standard techniques to find out the amounts of titanium oxide, ferrous oxide, ferric oxide and total iron and the results are presented in Fig. 4.3. It can be seen that the finer fractions contain a lower percentage of TiO_2, higher percentage of total iron and lower percentage of ferrous oxide. Similar variation in the composition of finer and coarse size fractions of ilmenite has also been reported by Ahmed et al (1992).

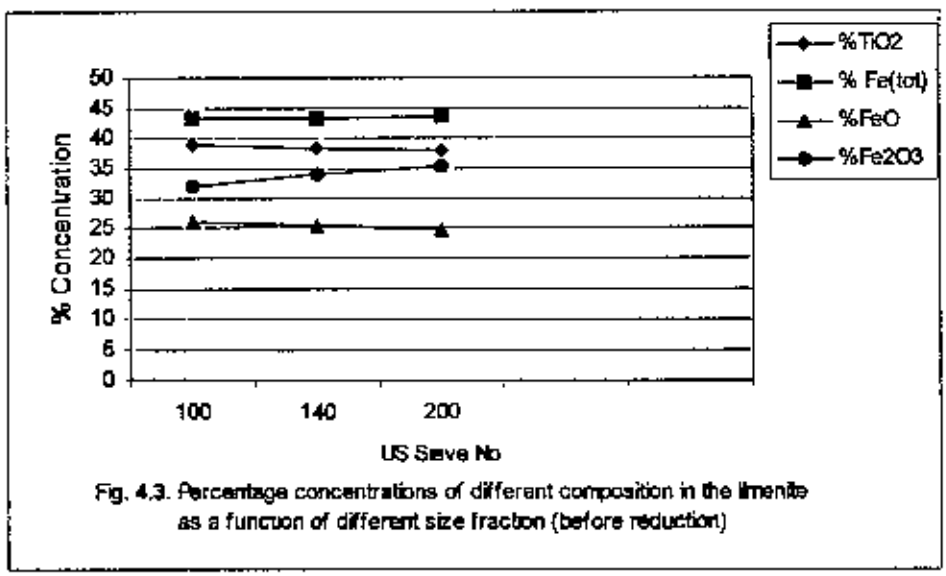


Fig. 4.3. Percentage concentrations of different composition in the ilmenite as a function of different size fraction (before reduction)

Although finer fractions of Teknaf ilmenite contain a higher percentage of total iron, the percentage of ferrous oxide was actually found to be slightly lower in finer fractions. This also in good agreement with the findings of the earlier studies, Ahmed et al. [1992]. The ferric oxide content of the finer fractions is obviously higher.

4.2.4.2 Sphericity of different size (sieve) fractions

In the present study, the shape characteristics of ilmenite particles have been expressed in in terms of sphericity. Sphericity means that the particle has the shape of a sphere and hence the lowest surface area to volume ratio. Particles with lowest sphericity will be elongated in shape and hence have larger surface area. The sphericity of different size fractions of Teknaf ilmenite was calculated by using the formula given by Grade and Ranga Raju [1985] and is explained below.

Sphericity = d_n / a

Where d_n = nominal diameter of the particle

The nominal diameter is calculated as $d_n = (a+b+c)/3$

Where a = length of its major axis,

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

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

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

Sphericity of at least forty grains of each size fractions was measured and the average value was taken as the sphericity of that particular fraction and the data are tabulated in the Table 4.3.

Table 4.3 Sphericity of ilmenite particles of different size fractions

US Sieve No.	Sphericity
100	0.822
140	0.832
200	0.843

The sphericity of all the three fractions of Teknaf ilmenite is found to be in a narrow range, 0.822-0.843. Sphericity of Mohcshkhali ilmenite [N.N. Shams, 2000] also lies in narrow range 0.773 to 0.845. From the sphericity value it was found that finer size fractions are found to have a higher sphericity while the coarser ones has the lower value of sphericity. This is possibly linked with the fact that finer fractions may have longer history of weathering, erosion etc. during transportation.

4.2.4.3 X-ray diffraction analysis of different size fractions

X-ray diffraction patterns of different size fractions of ilmenite are shown in the Fig. 4.4. A large number of diffraction lines observed in the samples of as received different size fractionated ilmenite. Moreover some of the more intense diffraction lines of the different phases expected to be present may overlap. From the figure it is evident that ilmenite is the main phase in all the size fractions. Diffraction lines characteristic of a few other compounds including rutile, pseudorutile, and hematite can also be detected. The presence of hematite in Bangladesh ilmenite has also been reported by Ahmed et al.,[1992]. The presence of hematite in ilmenite –hematite solid solution can shift the ilmenite peaks to higher angles and the observation of such a shift in relation to the standard powdered diffraction data in present case suggests that some hematite also exists in solution in ilmenite.

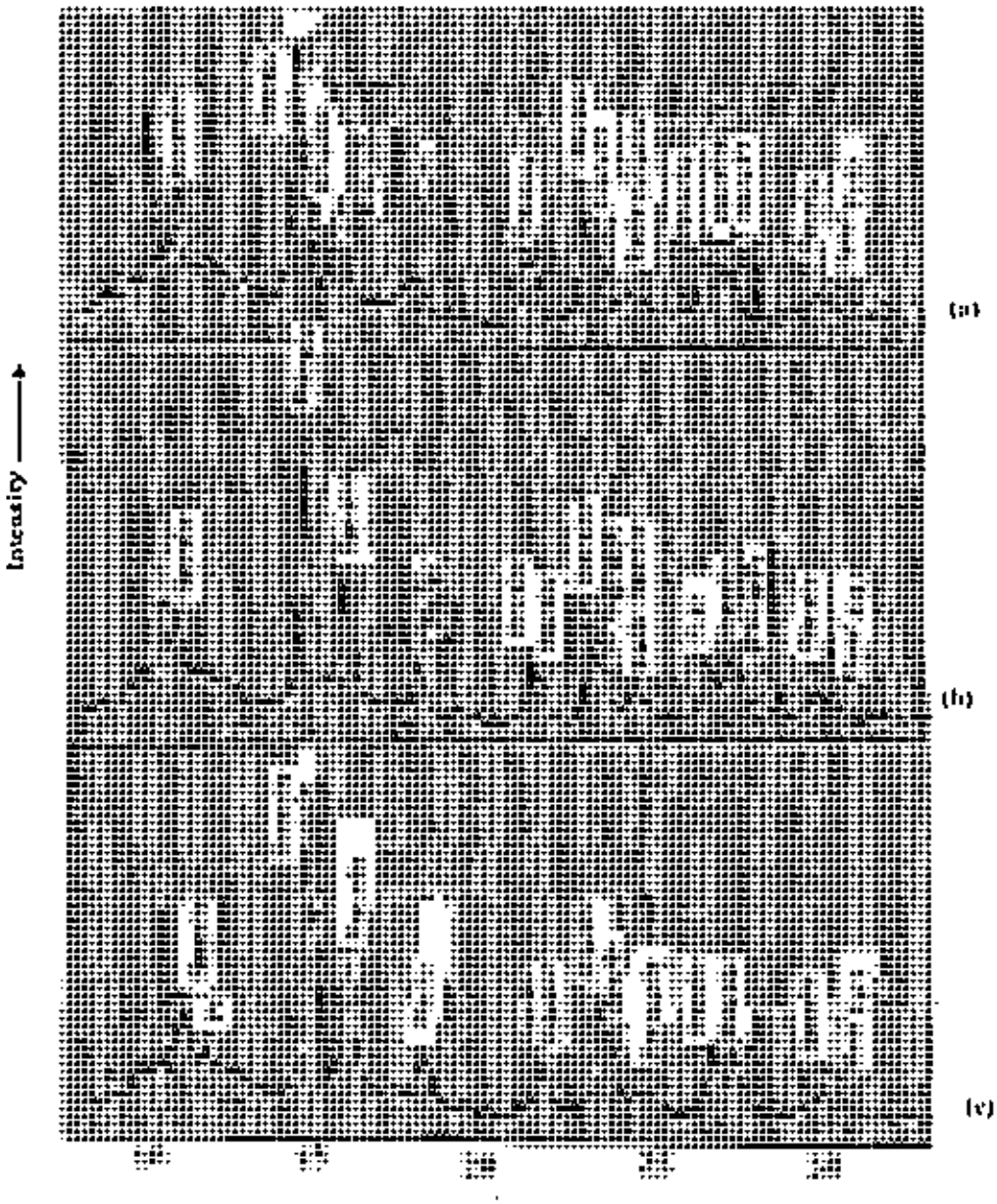


Fig. 4.4 X-ray diffraction patterns of different size fractionated ilmenite.
(a) Fraction retained on US sieve No. 100.
(b) Fraction retained on US sieve No. 140.
(c) Fraction retained on US sieve No. 200.

4.2.5 Magnetic fractionation of as received ilmenite

Magnetic fractionations were carried out using by an isodynamic separator. Table 4.4 shows the relative amounts (wt. percent) of the different magnetic fractions. It can be seen that about 96% of Teknaf ilmenite belong to the fractions separated by a current of 0.10-0.30 amperes. The amounts in the other fractions were not of sufficient quantity for further investigation. Further investigations were therefore confined to the major magnetic fractions only. Specific gravity of different magnetic fraction of ilmenite was determined using specific gravity measurement bottle and water as a medium. It shows that bulk of this ilmenite has specific gravity range of 4.1-4.5 in comparison to synthetic rutile specific gravity 4.7.

Table 4.4 Percentage of different magnetic fractions and the relative specific gravity.

Current of fractionation (amp.)	Percentage	Specific gravity
0.10	17.33	4.11
0.15	31.63	4.48
0.20	20.46	4.20
0.25	19.46	4.51
0.30	7.34	4.51
0.35	3.68	4.47

4.2.5.1 Chemical analysis of the different magnetic fractions

The magnetic fractions separated at different currents were analyzed chemically. Fig. 4.5 shows the composition of different magnetic fractions. It is evident from the analysis that with increasing current of separation the content of Fe_2O_3 and FeO decreases. The figure also shows that Teknaf ilmenite contain higher amount of ferrous oxide than ferric oxide. TiO_2 content was also found to decrease with increasing current of separation. From the materials balance (Fig 4.6) it is also found that in the samples which were separated at higher currents, the total amount of FeO+ Fe_2O_3 + TiO_2 decreases gradually that is more impurities are present in the magnetic fractions separated at higher currents. It is also inferred from the atomic absorption analysis that all the magnetic fractions contains of trace elements, like Cr, Cu, Mn, Ca, Zn, Mg, Ni etc. The concentration of trace elements, which are shown in Table 4.4(a), is the amount dissolved in the extractant only. The total amount of trace elements is not here. The presented result only indicates the presence of trace elements in the samples.

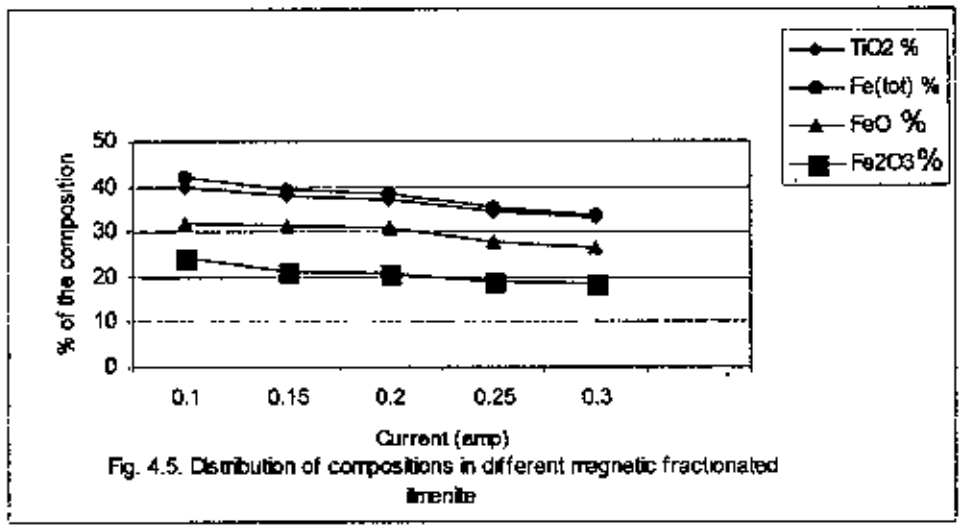
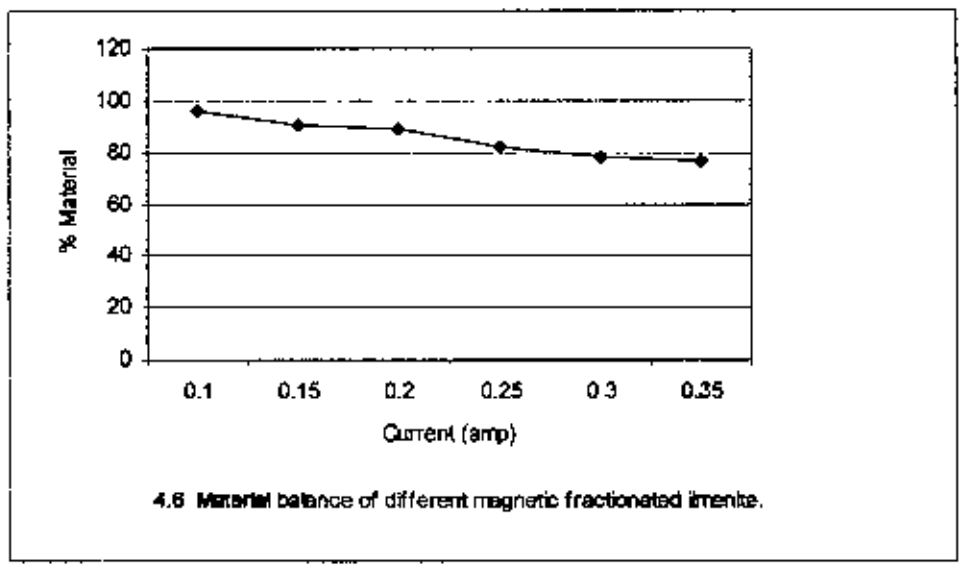


Fig. 4.5. Distribution of compositions in different magnetic fractionated ilmenite



4.6 Material balance of different magnetic fractionated ilmenite.

Table: 4.4(a) Chemical analysis of trace elements in the magnetic fractions (amount dissolved in extractant only).

Fractionated amp.	Cr ppm.	Cu ppm.	Mn ppm.	Fe ppm.	Ca ppm.	Zn ppm.	Mg ppm.	Ni pm.
0.10	0.0943	0.01	9.21	404	<MDL	0.9682	11.52	0.1897
0.15	4.0830	0.04	10.61	519	<MDL	0.7864	5.54	0.4060
0.20	0.5322	0.01	8.02	456	<MDL	0.8545	6.73	0.1973
0.25	1.2868	0.03	3.98	234	<MDL	0.9256	3.45	0.1758

4.2.5.2 X-ray diffraction analysis of different magnetic fractionated ilmenite

The diffraction pattern of the magnetic fractions is shown in Fig 4.6 (a). There are many diffraction lines in the pattern, the most prominent being those of ilmenite. Diffraction lines characteristic of a few other compounds including rutile, pseudorutile,ferrous oxide and hematite can also be detected. The pattern analysis was strictly confined to qualitative analysis. Slight shifts of the diffraction lines were also noted. This may be explained as the placer deposit are not the chemically standard substance it is a heterogeneous compound as well as some impurities which may affect the lattice parameter value.

4.2.5.3 Thermogravimetric analysis (TGA) of the different magnetic fractions

TGA experiment has been carried out for the samples fractionated at different magnetic fractions (0.10- 0.30 amp) to observe any changes in weight. During heating inert atmosphere was maintained by the supply of nitrogen. TGA pattern in the Fig. 4.7 to Fig.4.10 (a) shows that the weight loss occurs for all the fractions after certain temperature. The wt. loss due to the presence of bound water.

Under investigations the five magnetic fractionation samples are 0.10, 0.15, 0.20, 0.25 and 0.30 amp. having FeO content of 31.96, 31.35, 30.89, 28.01 and 26.410% respectively. Fig.4.7 and Fig.4.8 show that, initially wt. loss occurs but after certain temperature an effective weight gain have been noticed. This could be due to the oxidation of substantial amount of FeO present in those samples. The change in weight gain/loss in different magnetic fractions is shown in Table. 4.4(b).

A number of researcher [Suresh Babu, 1993 and Ramakrishnan et al., 1997] studied the alteration of Indian ilmenite of Chavara, Manavalakurichi, Orissa deposits. During their study, they identified weight loss at a temperature near around 600^{0}C. This decrease in weight indicates the presence of bound water. Naturally bound water (H_2O^-) increases as the degree of alteration increases, on the other hand pseudorutile structure actually contain hydroxyl ions (FeOOH-TiO_2). Ram Krishnan et al., 1997 found that the release of hygroscopic free water (-50^{0}C) and structurally bound water (-300^{0}C) causes loss in weight as in the case of every sample. The structural water (hydroxyl) represents the major weight loss. He also found that an effective wt. gain has been noticed in two samples (1.88% and 1.49%) due to the presence of substantial amount of FeO, which could be oxidation at high temperature more than 800^{0}C.

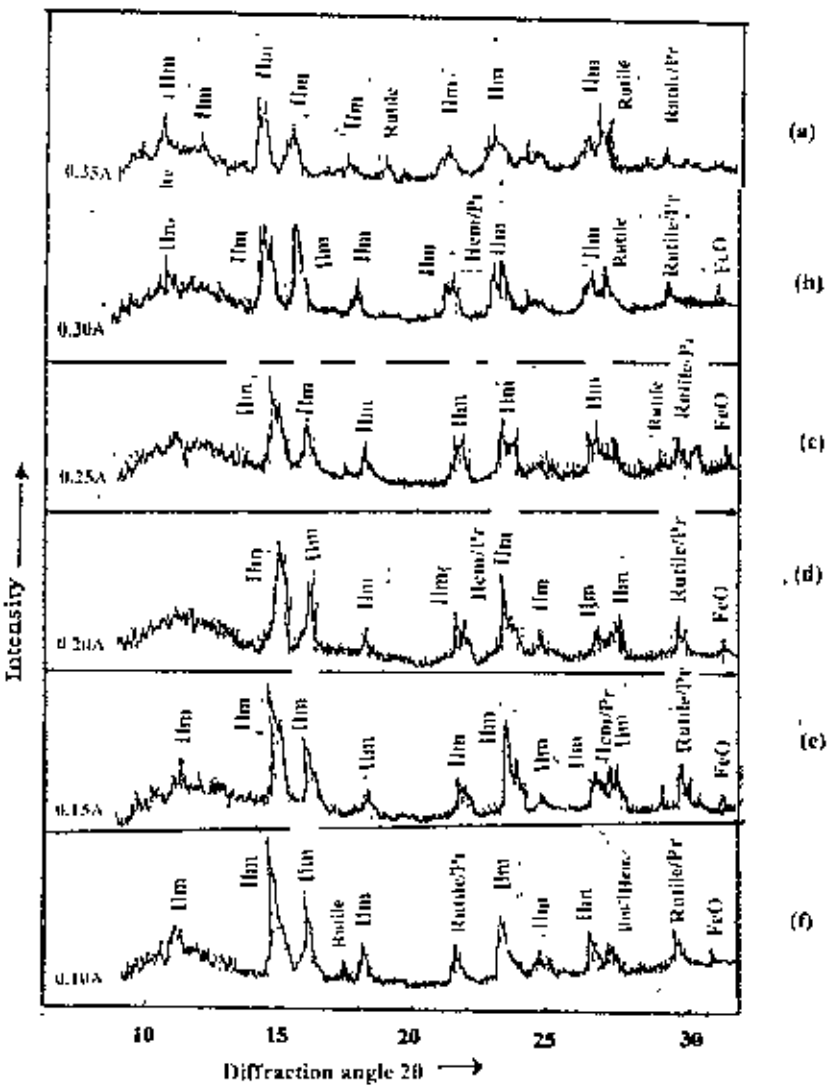


Fig. 4.6(a) X-ray diffraction patterns of different magnetic fractionated ilmenite (a) Fractionated at 0.35 amp (b) Fractionated at 0.30 amp(c) Fractionated at 0.25 amp(d) Fractionated at 0.20 amp(e) Fractionated at 0.15 amp(f) Fractionated at 0.10

It is generally recognized that in natural deposits ilmenite undergoes alteration due to weathering. This alteration is a complex process, but it can be summarized by two major, sequential reactions [Dimenche and Bartholome, 1976].

$$\text{Stage (1): } 3Fe^{2+}TiO_3 + 2H^+ + 1/2O_2 = Fe_2^{3+}Ti_3O_9 + Fe^{2+} + H_2O \quad (1)$$

$$\text{Stage (2): } 3Fe_2Ti_3O_9 + 2H^+ = 3TiO_2 + 2Fe^{2+} + 2H_2O + \tfrac{1}{2}O_2 \quad (2)$$

In stage (1) ilmenite is converted into pseudorutile by the loss of one third of the total iron and oxidation of the remaining iron to the ferric state. In stage (2) removal of the remaining iron and loss of some oxygen take place to yield rutile. The extent of alteration of ilmenite depends on the geological history of the deposit, and the degree of alteration of different deposits in the world is quite varied- those of Zululand (South Africa), Orissa (India) and Brazil being altered relatively little but, those of Australia and Florida (USA) showing extensive alteration. [Hugo and Cornell, 1991]. A partially altered deposit shows the coexistence of different phases i.e, ilmenite, hematite, rutile and pseudorutile. But complete alteration will lead to a predominantly rutile phase. X-ray diffraction pattern of Teknaf ilmenite showed the co-existence of different phase and the TGA analysis of this present study show weight loss. It is concluded that the Teknaf ilmenite is in a partially altered state but not hydrated enough.

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

Table: 4.4(b) TGA report for magnetic fractions at different current.

Points	0.10 amp		0.15 amp		0.20 amp		0.25 amp		0.30 amp	
	^{0}C	Wt. %.	^{0}C	Wt. %	^{0}C	Wt. %	^{0}C	Wt. %	^{0}C	Wt. %
1	23	100	30.7	99.98	31	99.99	66	100	21	100
2	450	99.78	443	99.80	407	99.78	388	99.78	419	99.77
3	523	99.44	611	99.50	518	99.49	471	99.13	670	99.03
4	682	99.52	727	99.60	710	99.42	760	98.48	760	99.21
5	704	99.42	850	100.3	880	99.44	865	98.48	850	99.69
6	881	100.5	989	98.08	991	95.19	910	98.36	975	94.75

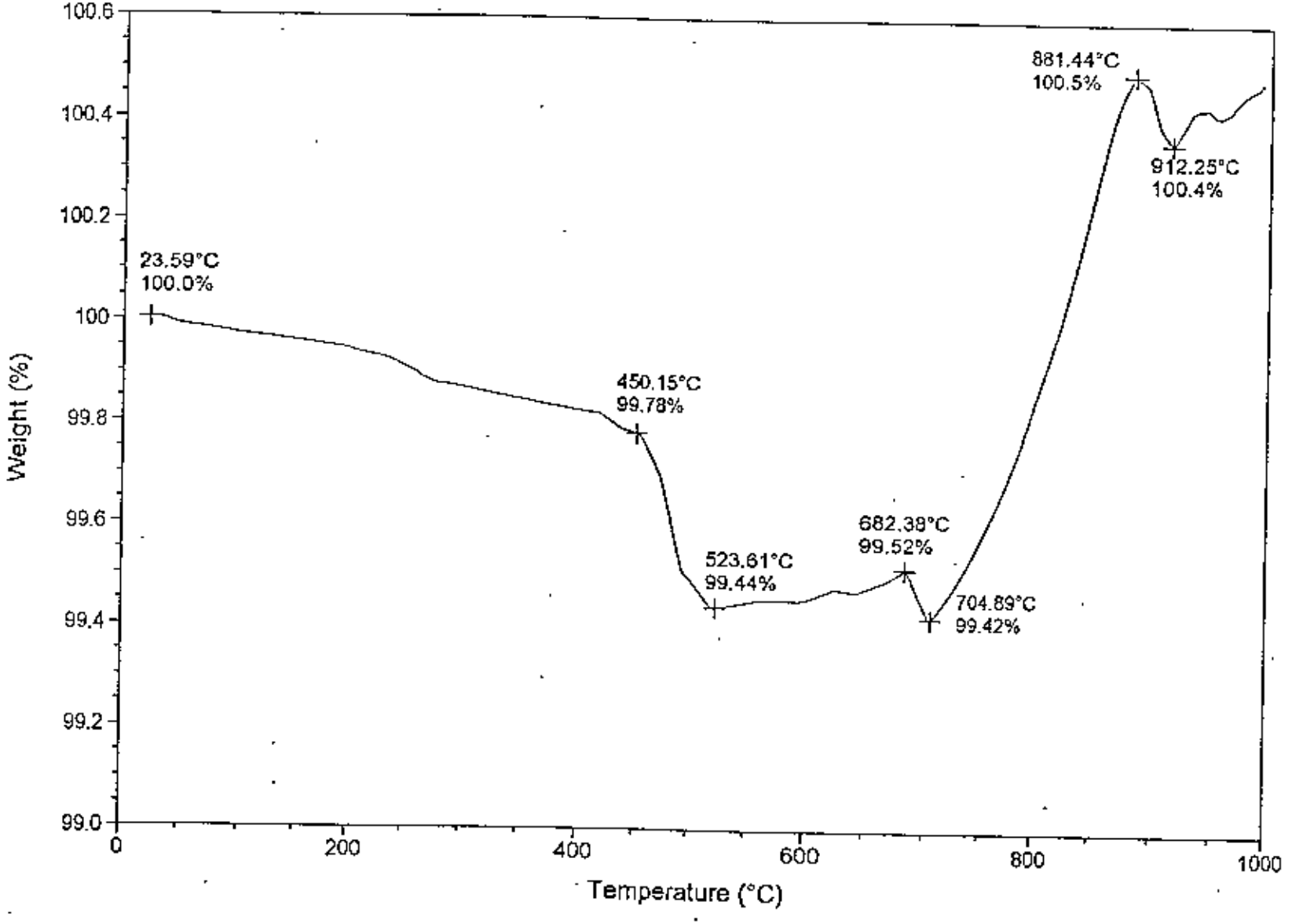


Fig. 4.7: TGA graph of ilmenite sample fractionated at 0.10 amp.

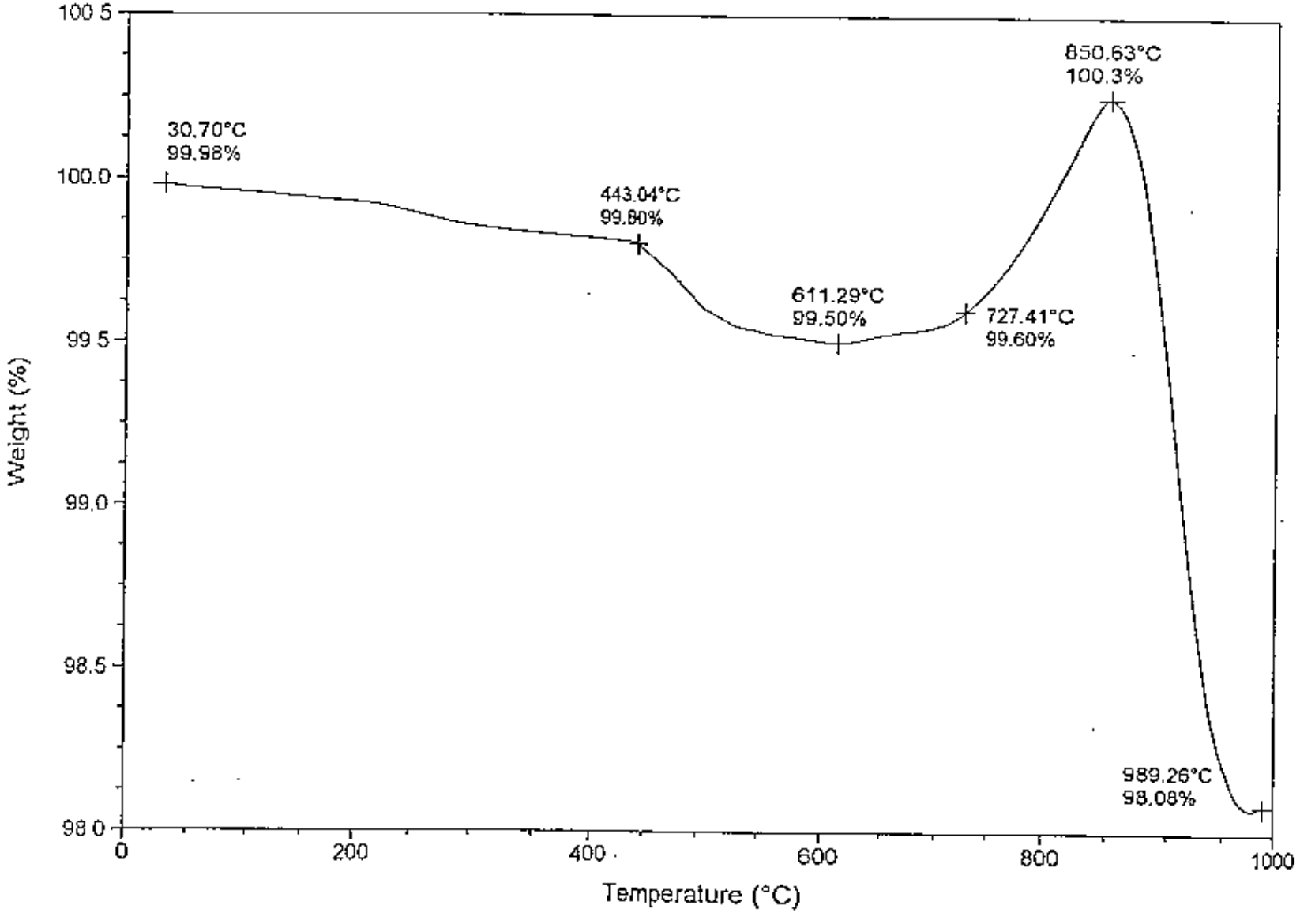


Fig. 4.8: TGA graph of ilmenite sample fractionated at 0.15 amp.

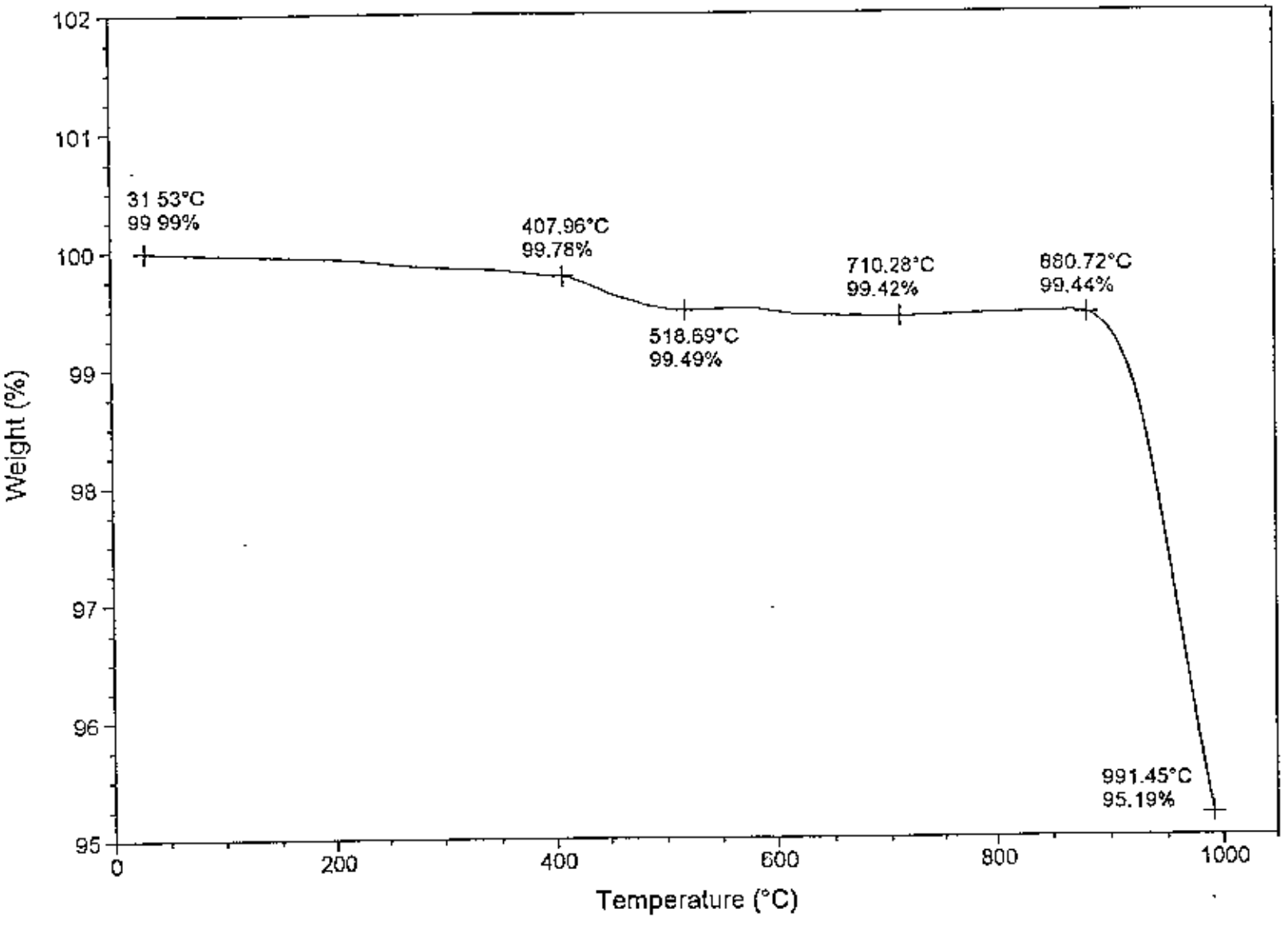


Fig. 4.9: TGA graph of ilmenite sample fractionated at 0.20 amp.

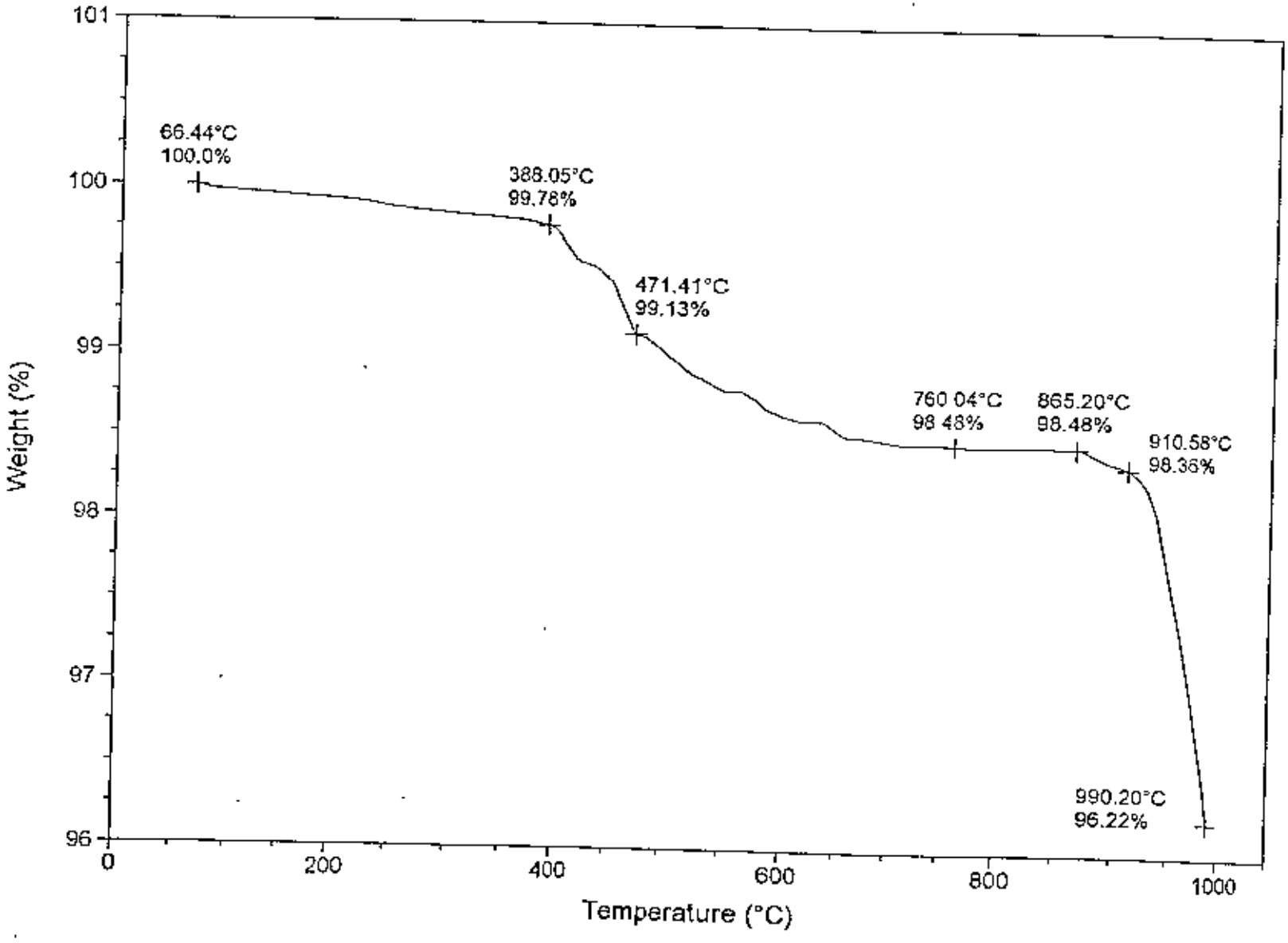


Fig. 4.10: TGA graph of ilmenite sample fractionated at 0.25 amp.

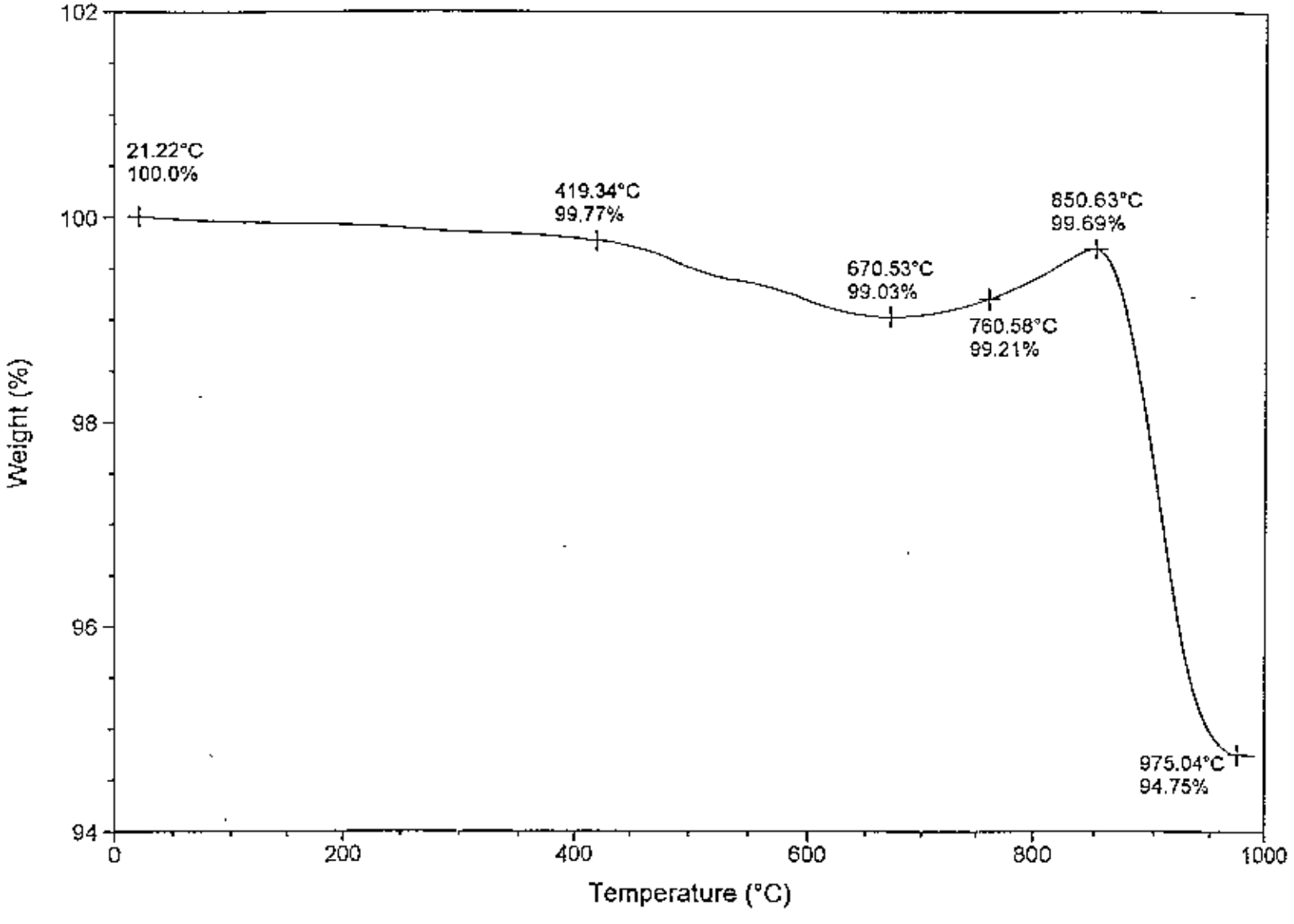


Fig. 4.10(a): TGA graph of ilmenite sample fractionated at 0.30 amp.

4.2.5.4 Optical metallography of the different magnetic fractions

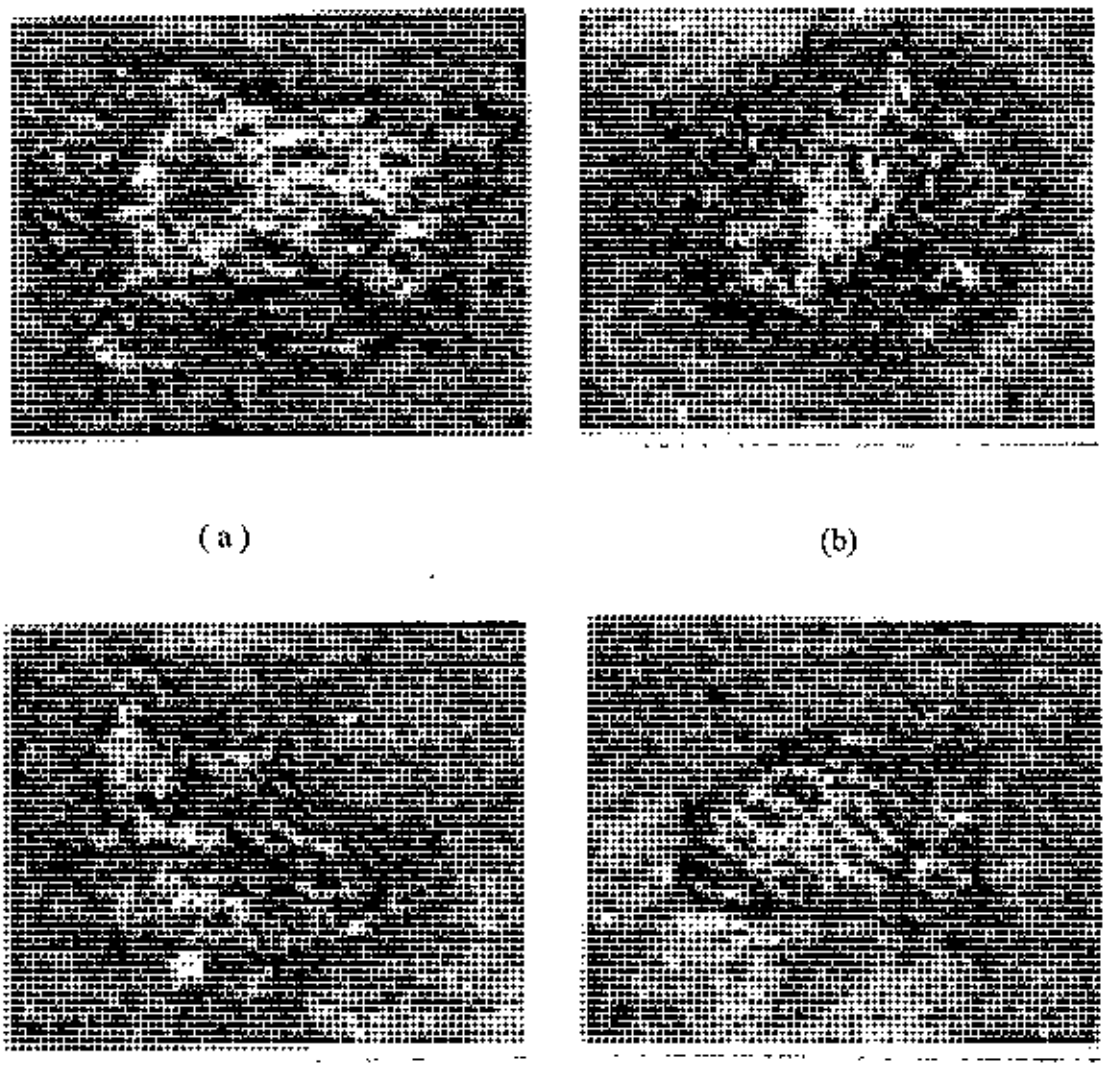
Samples belonging to different magnetic fractions were mounted in cold set resin and were polished to get scratch free surface. Then the samples were observed under the microscope and photographs were taken. Typical microphotographs are presented in the Fig.4.11. Optical microscopy mainly showed white and gray structure of ilmenite and hematite respectively. Microstructures of all the samples are almost of similar in appearance. No significant difference could be identified from this microphotographs.

4.2.5.5 Scanning electron microscopy

Samples of ilmenite belonging to different magnetic fractions were observed under a scanning electron microscope. The observed surfaces in the Fig. 4.12 (a) to Fig. 4.12(d) were more or less uniform in appearance. Anand and Giles [1984] have noted that SEM of slightly altered grains show massive irregular surfaces due to formation of pseudorutile while highly altered grains have very porous surfaces. The spot analysis showed the presence of Ti, Cr, Cu, Ni and iron.

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 [Hugo and Cornell, 1991] 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. Accordingly, degree of alteration may only be perceived as the degree of rutilization. There is also considerable uncertainty in the terminology applied to the alteration products.

A partially altered ilmenite shows the coexistence of different phases i.e., ilmenite, hematite, rutile and pseudorutile[Hugo and Cornell, 1991]. But complete alteration will lead to a predominantly rutile phase. X-ray diffraction pattern of Teknaf ilmenite showed the co-existence of different phase including pseudorutile phase and the TGA results indicate weight loss. So it can be concluded that the Teknaf ilmenite is in a partially altered state but not hydrated enough.



(a) (b)

(c) (d)

Figure 4.11 Micrographs of ilmenit sample fractionated at different current
(a) fractionated at 0.10 amp.
(b) fractionated at 0.15 amp.
(c) fractionated at 0.20 amp
(d) fractionated at 0.25 amp..

Fig 4.12 (a) SEM of Teknaf ilmenite fractionated at 0.10 amp. current.

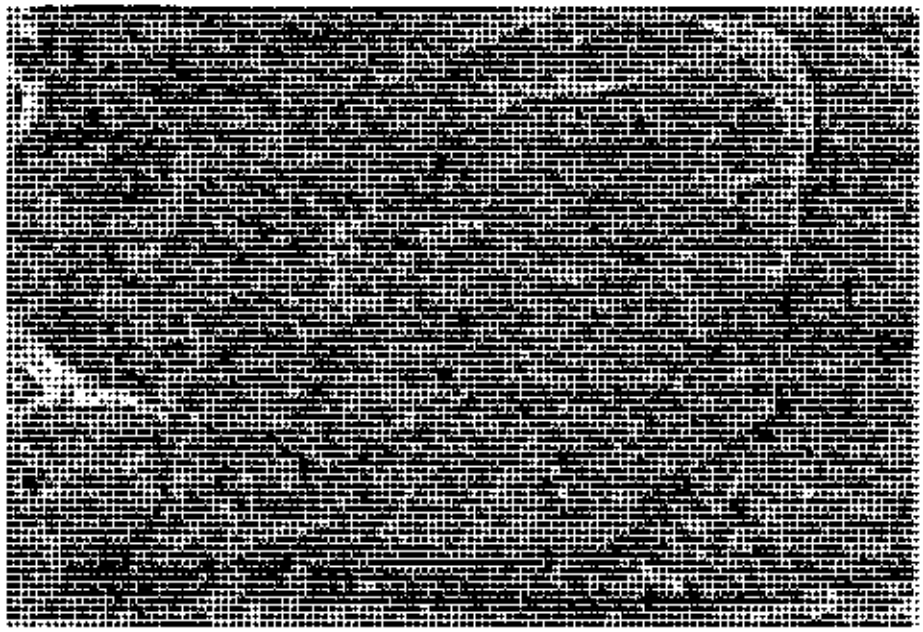


Fig. 4.12 (b) SEM of Teknaf ilmenite fractionated at 0.15 amp. current.

Fig. 4.12 (c) SEM of Teknaf ilmenite fractionated at 0.20 amp. current.

Fig. 4.12 (d) SEM of Teknaf ilmenite fractionated at 0.25 amp. current.

4.3 Oxidation of as-received sample

Initial studies were taken up to optimize the various parameters that affect and control the oxidation reaction. The main factors studied were time and temperature of oxidation.

4.3.1 Optimization of oxidation parameter

Oxidation of ilmenite in the temperature range of 750°-950°C has been performed. The extent of conversion of ferrous iron to ferric ion was determined by chemical analysis of the oxidized samples. X-ray diffraction patterns of the samples oxidized for various times at different temperatures were recorded for the identification of the phases formed during oxidation. The oxidized samples were observed under an scanning electron microscope and also under optical microscope.

Chemical analysis:

Fig.4.13. indicates the amounts of ferrous oxide left in the sample after oxidation for different times at different temperature. At all temperatures under investigation the rate of oxidation was found to be very rapid at the initial stage and the rate diminishes with time. At lower temperatures, a longer time was required for the attainment of the equilibrium condition. At higher temperatures (950^{0}C), on the other hand, the equilibrium was attained in approximately thirty minutes. The results of chemical analysis also show that, during oxidation under the conditions investigated, all the ferrous iron present in ilmenite was not oxidized to the ferric state, i.e., some ferrous iron was always present in the oxidized sample (e.g. at 950^{0}C for 2 hrs. ferrous iron is 0.359).

The presence of some ferrous iron can be explained by the fact that the attainment of complete oxidation would mean that the value of the equilibrium constant is infinite. This is practically impossible. At the initial stage of oxidation at 950°C was very rapid and rate diminished with time. After 0.5 hr. the oxidation rate was very slow, and getting stabilized. However after 1 hr. the effect of time was found to be negligible on oxidation and after that time did not have any major influence on oxidation. From these results, it was concluded that the optimum time and temperature for oxidation of ilmenite could be taken as 1 hour at 950°C.

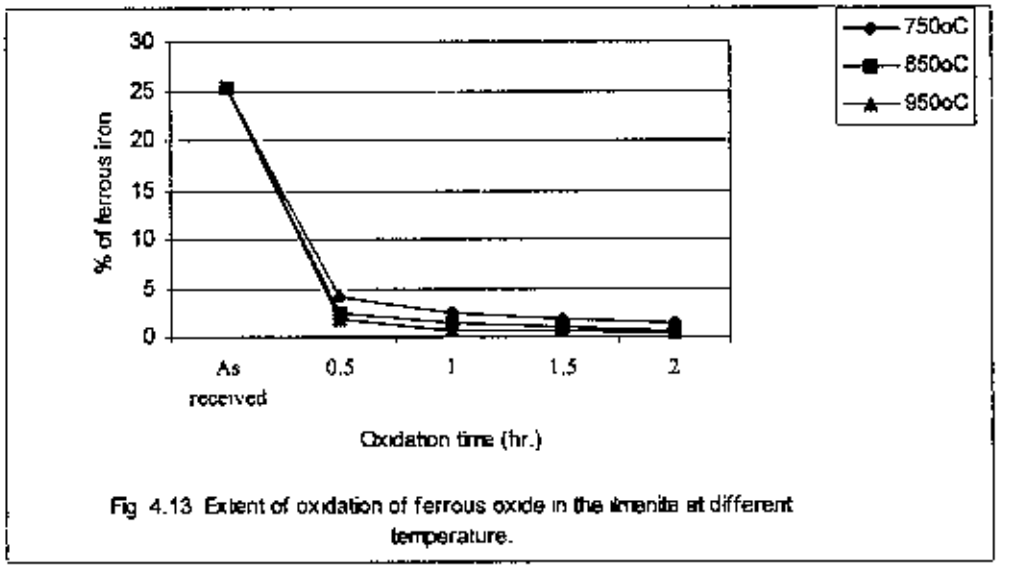


Fig 4.13 Extent of oxidation of ferrous oxide in the ilmenite at different temperature.

The experimental condition for oxidation was thus chosen as 1 hour at 950^0 C. Results of wet chemical analysis have shown (Table 4.5) that the ferrous iron content of the oxidized ilmenite, was only 0.5747 % while the rest of the iron was in the ferric state.

Table. 4.5 Chemical analysis of oxidized ilmenite at 950°C for 1 hr.

Materials	% of materials present in the ilmenite
Fe^{++} Iron	0.4467 %
FeO	0.5747 %
Fe Iron	40.26
Fe_2O_3	57.56
Total Iron	40.71

The higher initial rate of oxidation during the initial stages can be explained by the fact that the surface area available for reaction is higher at the initial stage of oxidation and with time of oxidation the reaction product covers the surface of solid ilmenite in the form of a dense film. The film thickens with time and migration of ions or electrons becomes the rate-determining step.

Optical microscopy:

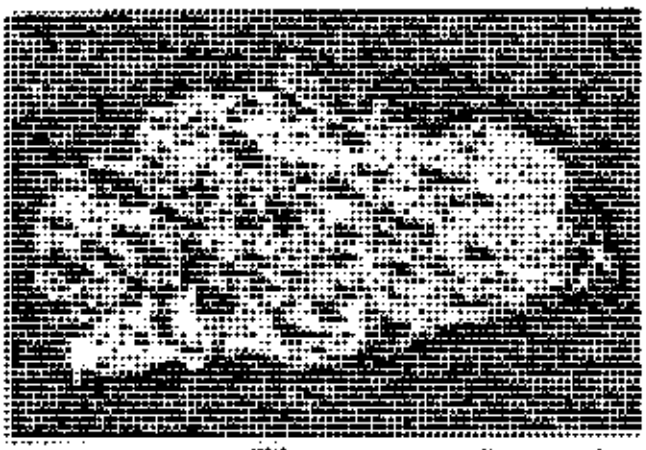
Particles of ilmenite both in the as received and in the oxidized conditions were mounted in cold setting resin. Standard techniques were used to prepare the specimens for observation under the optical microscope. Difficulties were encountered during mounting and polishing due to loss of loosely held particles. It was, however, possible to obtain a satisfactory polished surface composed of scattered particles. Optical micrographs of ilmenite oxidized for 1 hour at 750°C, 850°C and 950°C have been shown in Fig.4.14 These figures show that the structure of ilmenite at 750^0C is different from that of ilmenite structure oxidized above 850°C. The structure of ilmenite oxidized at 850°C is similar to that of ilmenite oxidized at 950°C. No significant difference could be identified from this micrographs.

Scanning electron microscopy:

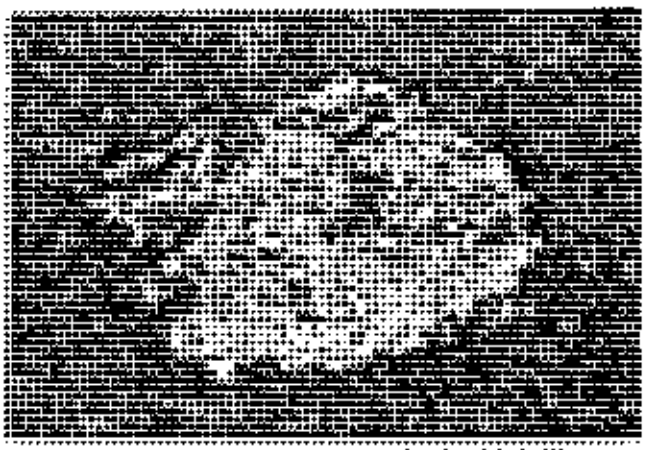
Fig. 4.15 shows the scanning electron micrograph of ilmenite oxidized at 750°C, 850°C 950°C for 60 minutes. An important observation from the figures is that oxidation at higher temperature and longer time produces fine cracks in the grains of ilmenite. This may be due to the fact that oxidation converts the single crystal of ilmenite to polycrystalline array of pseudobrookite and rutile. The formation of cracks increases the surface area of the product.

X-ray diffraction study:

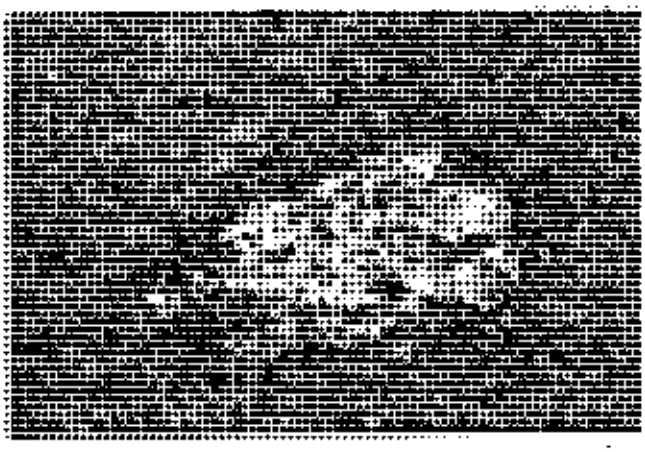
X-ray diffraction patterns of Teknaf ilmenite oxidized at different temperatures in the range of 750°C to 950°C are given in Figs.4.16- 4.18. Fig.4.16 shows the diffraction patterns of ilmenite oxidized at 750°C. Oxidation for 0.50 hr. the FeO phases have been diminishes and a new phase of pseudobrookite have been appeared. Diffraction lines of ilmenite, if present gradually, coincide with the diffraction lines of the new phases. No significant change in the relative intensity of the diffraction lines was observed with an increase in time of oxidation at the temperature. With the increase of oxidation time pseudobrookite phase appeared and this frequency of appearing increase with the time. Rutile phase also increase with time.
Fig.4.17 shows the X-ray diffraction pattern of ilmenite oxidized at 850°C. A new phase was found to have formed and has been identified as pseudobrookite and the intensity of diffraction lines belonging to pseudobrookite was found to increase with time while the intensity of diffraction lines



(a)



(b)



(c)

Fig. 4.14 Microstructure of oxidised ilmenite
(a) oxidised 750°C for 1 hr
(b) oxidised 850°C for 1 hr
(c) oxidised 950°C for 1 hr

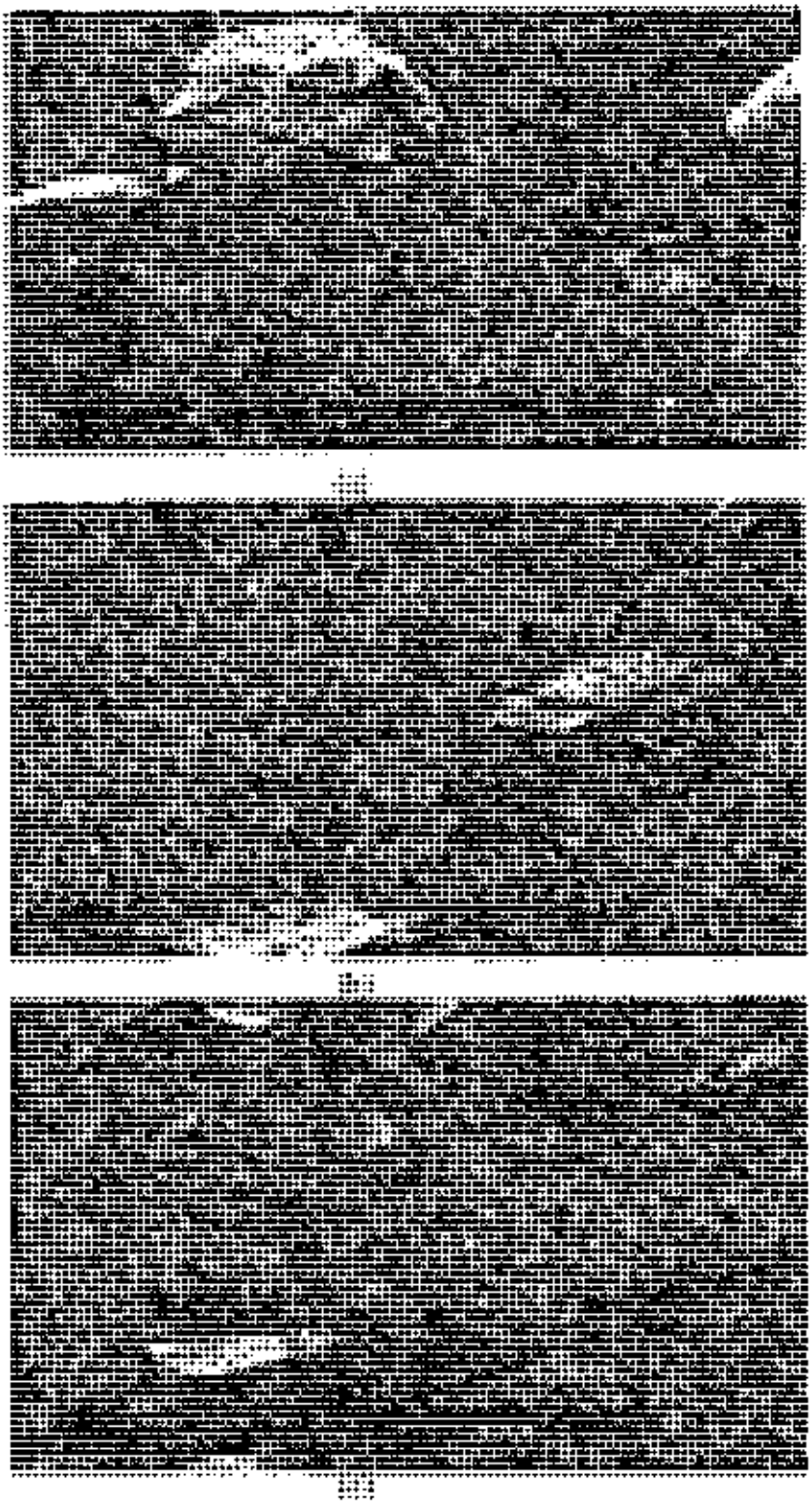


Fig. 4.15 Scanning electron micrograph of oxidized ilmenite (oxidized for 1 hr.)
(a) Oxidised at 750°C
(b) Oxidised at 850°C
(c) Oxidised at 950°C

belonging to pseudorutile dimnished. Fig. 4.18 shows the X-ray diffraction pattern of ilmentic oxidised at 950°C. From the patterns it can be seen that pseudobrookite and rutile phase increases with time and temperatue where as the intensity of pseudorutile phase have been disappeared at this temperature and ilmenite phase completely diminishes after one hour.

The results of of X-ray diffraction patterns analysis may be summarized as follows:

a) The x-ray diffraction pattern of ilmenite oxidized at 750°C for 0.50 hr. and 1 hr. is similar to as received ilmenite. Some of the diffraction lines belonging to pseudorutile coincide with those of rutile.Chemical analysis of ilmenite oxidised at 750°C for 0.50 hr. to 2 hr. showed the presence of small amount of ferrous iron and maximum ferric iron at this temperature. Therefore it can be concluded that at lower temperature the oxidised sample contains ferric pseudorutile, rutile and hematite. Small amount of ilmenite may also be present. Since diffraction lines belonging to ilmenite and hematite coincide, definite identification of the phase could not be made. Some unidentified phases were also found to be present. The probable reaction may be as follow:

$$2FeTiO_3 + \tfrac{1}{2} O_2 \longrightarrow Fe_2O_3 + 2TiO_2 \text{ and}$$

$$3FeTiO_3 \rightarrow Fe_2Ti_3O_9 + \tfrac{1}{2}Fe_2O_3$$

b) With increasing temperature the pseudorutile phase disappeared and percentage of ilmenite phase (if present) decreases

c) At temperature above 850°C diffraction lines belonging to ilmenite phase diminish with time and x-ray diffraction pattern shows the characteristic lines of pseudobroookite phase. The proportion of pseudobrookite phase increases with time for upto 1 hour then remains more or less constant.

The appearance of pseudobrookite can be expressed by the reaction:

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

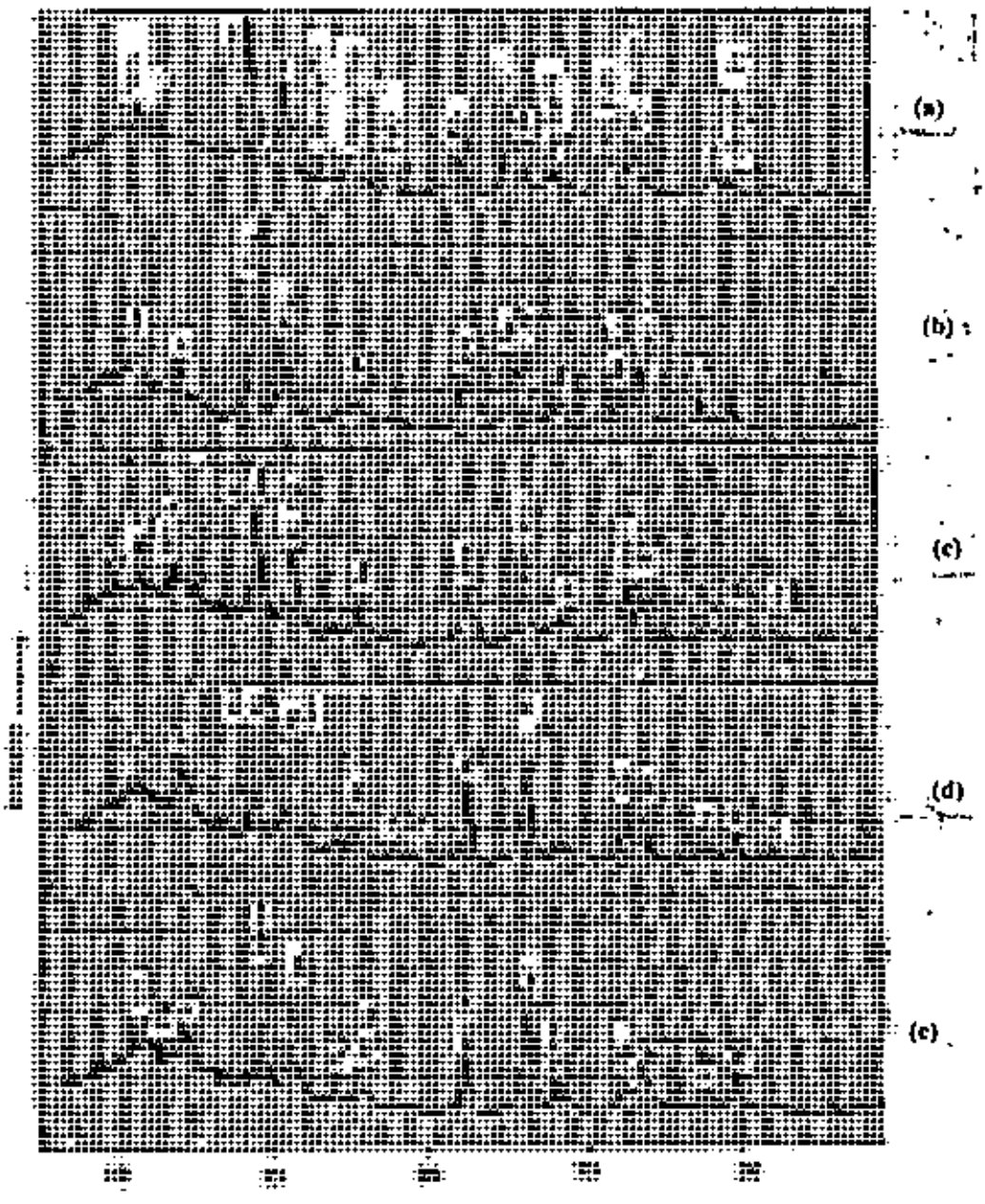
$$2FeTiO_3 + \tfrac{1}{2} O_2 \longrightarrow Fe_2O_3 + 2TiO_2$$

By heating pseudorutile above 850°C pseudobrookite is formed.

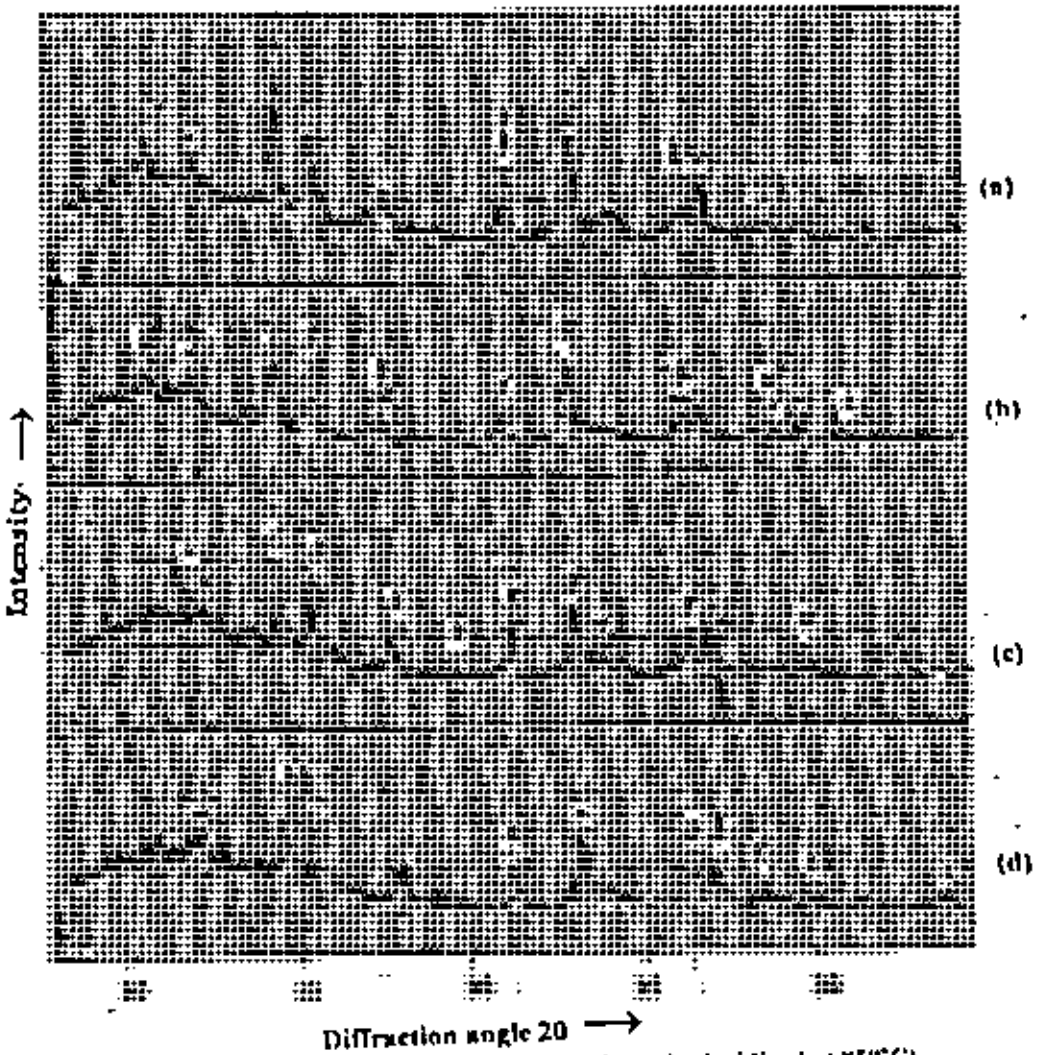
$$Fe_2Ti_3O_9 \longrightarrow Fe_2TiO_5 + 2TiO_2$$

The existence of lower temperature level for the formation of pseudobrookite may be due to the fact that diffusion rate at lower temperature is slow which may prevent the formation of pseudobrookite [K.Z.Sarker, 1999]. Decrease in the relative intensity of hematite shows that pseudobrookite may also be formed by the reaction.

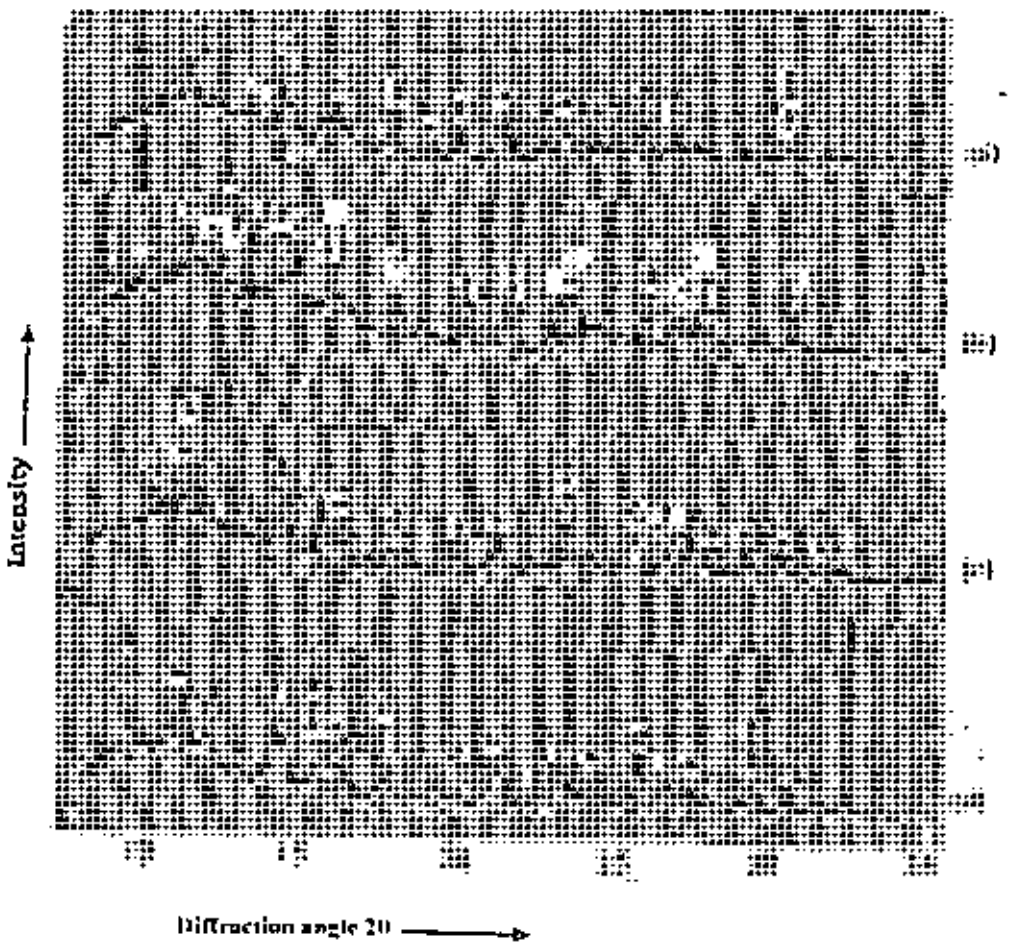
$$Fe_2O_3 + TiO_2 \longrightarrow Fe_2TiO_5$$



4.16 X-ray diffraction pattern of
(a) As received ilmenite
(b) Oxidised for 0.50 hr. at 750°C
(c) Oxidised for 1 hr. at 750°C
(d) Oxidised for 1.5 hr. at 750°C
(e) Oxidised for 2 hr. at 750°C



4.17. X- ray diffraction pattern of oxidized ilmenite (oxidized at 850°C).
(a) Oxidized for 0.50 hr. at 850°C.
(b) Oxidized for 1 hr. at 850°C.
(c) Oxidized for 1.5 hr. at 850°C.
(d) Oxidized for 2 hr. at 850°C.



4.18. X- ray diffraction pattern of oxidized ilmenite (oxidized at 950°C).
(a) Oxidized for 0.50 hr. at 950°C.
(b) Oxidized for 1 hr. at 950°C.
(c) Oxidized for 1.5 hr. at 950°C.
(d) Oxidized for 2 hr. at 950°C.

4.4 Reduction of as received ilmenite

As received ilmenite which was used for the experiments contained mainly Fe_2O_3, FeO and TiO_2. As it is difficult to remove Fe_2O_3 from ilmenite by direct leaching, a reduction step is necessary. Reduction of iron oxides in ilmenite to metallic iron was carried out by using charcoal as a reductant. From the Ellinghum diagram it is apparent that the stability of titanium di-oxide is much higher than that of the oxides of iron and cannot be reduced by carbon at temperature around 1100^0C. Thus when ilmenite is heated by mixing it with charcoal at a temperature range of 950^0C- 1100^0C, iron oxide is reduced to metallic state but the titanium di-oxide remains unchanged. Thus iron oxide can be theoretically reduced to metallic form without changing the titanium oxide. Since both the oxides of iron and titanium are more stable than corresponding metals, metallic iron can easily be dissolved into hydrochloric acid and therefore, the titania content can be increased.

To examine the feasibility of reduction of Teknaf ilmenite, reduction conditions were selected with a maximum temperature of 1050°C for 5 hours in presence of excess charcoal (reductant), which were found from literature to be sufficient for the reduction of ilmenite using various reductants.

For reduction 9 gm of ilmenite and 9 gm of charcoal of mesh size +30 was taken. A bed of charcoal was first charge in vertical stainless steel tube. Small amounts of ilmenite and charcoal were then charged as alternate layers. The top layer was made of charcoal. The tube was then sealed to minimise entrance of air in it. The tube was cooled to the room temperature; the reduced ilmenite was taken out and separated using by a hand magnet. The results of chemical analysis are given in Table 4.6.

Table 4.6 Chemical analysis of as received reduced Ilmenite (reduction at 1050^0 C)

Component	% in ilmenite
TiO_2	42.32
Fe_{tot}	44.67
Fe_{met}	39.20
% Degree of reduction	87.77

Ilmenite, the starting material, contained no metallic iron, while the ferrous and ferric iron content were 25.32% and 32.53 % respectively. The Table no.4.6 shows that ilmenite had undergone reduction during heating with the formation of 39.20% metallic iron and the degree of reduction is 87.75%. The extent or degree of reduction of an oxide sample can be defined as the function of oxygen removed during the reduction process and is given by

$$DOR = \frac{O_2^{\,i} - O_2^{\,r}}{O_2^{\,i}} X\ 100 \qquad (1)$$

Where DOR = degree of reduction,

$O_2^{\,i}$ = initial oxygen content of the sample.

$O_2^{\,r}$ = oxygen content of the reduced sample.

Degree of reduction based on different forms of reduction. Equation (1) has been used for iron ores [R. Haque et al., 1991]. In the case of ilmenite, oxides of both iron and titanium are present. Although TiO_2 is more stable than oxides of iron, it is possible that some of TiO_2 is reduced to lower oxides. However earlier study [Huq et al., 1994] on Bangladesh ilmenite has shown that for 4 hrs of reduction at 1050^{0}C, TiO_2 is not reduced. In the present case it can thus assumed that loss of oxygen of ilmenite sample during reduction was due to the reduction of iron oxides only. Using this argument the degree of reduction of iron oxides in the ilmenite sample can now be defined as;

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

Where DOR_{Fe} = degree of reduction of iron oxides in ilmenite.

$O_2^{\,i}Fe$ = oxygen content of iron oxides in as received ilmenite.

$O_2^{\,r}Fe$ = oxygen content of iron oxides in reduced ilmenite

While calculating $O_2{}^r{}_{Fe}$ it was assumed that iron, other than in metallic form, is present in the reduced ilmenite as FeO only. This is a valid assumption supported by an earlier study on Bangladesh ilmenite [Huq et al., 1994]. A study on iron ore [Dam Gonzales and Jeffes, 1987] has also shown that if the degree of reduction is more than 40 % (which is true in the present case as will be seen earlier), then no metallic iron is produced before all higher oxides are reduced to FeO.

X-ray diffraction analysis of reduced ilmenite show the diffraction lines belonging to metallic iron and rutile phase only (Fig.4.20). Hematite and ilmenite which were found in the as received sample, had disappeared. This means that oxides of iron in ilmenite reduced to metallic iron. Scanning electron micrograph (Fig. 4.21) shows the rough surface, which is in contrast to the smooth plane surface of the unreduced sample. After reduction larger pores were observed. The pores were formed due to the removal of oxygen from the oxides of iron during reduction .The spot analysis of SEM shows the presence of metallic iron at the surface of the sample and no oxides of iron. Ferric and ferrous oxide present in ilmenite was reduced to metallic iron. The reduction-taking place is $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO. \rightarrow Fe$.

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

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

$$Fe_2O_3.TiO_2 + 3\,C \longrightarrow 2\,Fe + TiO_2 + 3\,CO \text{ and,}$$

$$Fe_2O_3.TiO_2 + 3\,CO \longrightarrow 2\,Fe + TiO_2 + 3\,CO_2$$

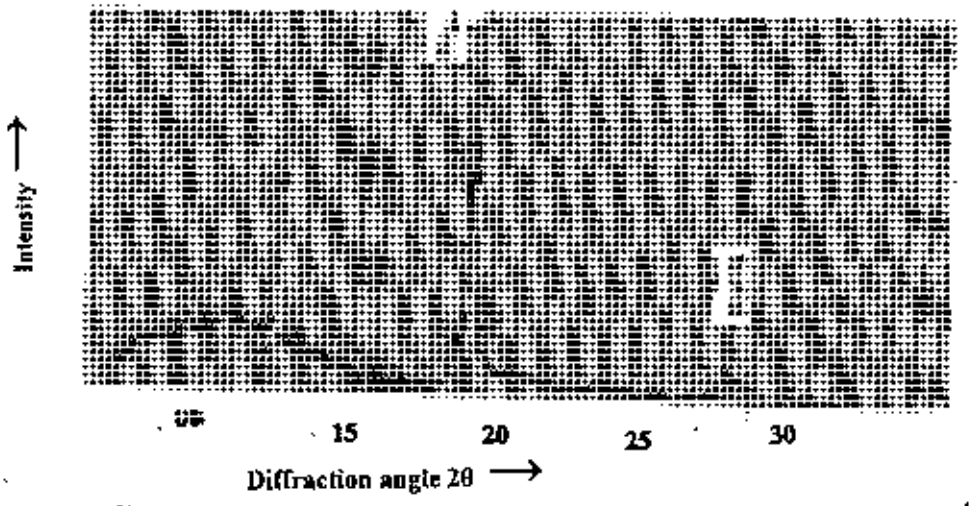


Fig. 4.20 X-ray diffraction patterns of Teknaf ilmenite reduced at 1050°C for 5 hr.

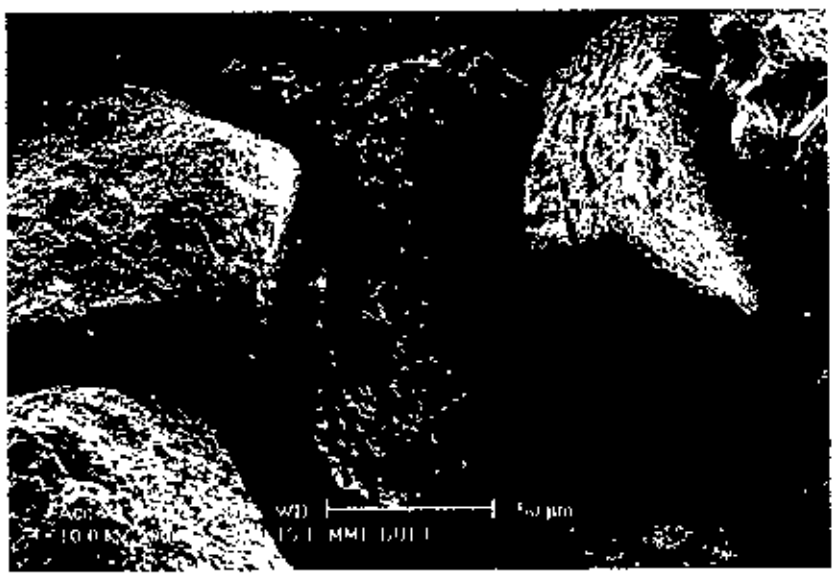


Fig. 4.21 SEM of the sample reduced at 1050°C for 5 hrs.

4.4.1 Optimization of various parameters for reduction of ilmenite

After examining the feasibility of reduction of ilmenite by charcoal, further studies were taken up to optimize the various parameters affecting and controlling the reduction reaction. The main factors studied were ilmenite to charcoal ratio, time and temperature of reduction. While optimizing one factor, all the other parameters were kept constant during these experiments.

4.4.1.1 Ilmenite to coke ratio

Reduction experiments were carried out using ilmenite and charcoal with weight ratios as 1:0.25,1:0.5, 1:1, 1:2, 1:3 and 1:4 keeping time and temperature constant. Ilmenite and charcoal in the required ratios were taken in the sample case and heated in the furnace at 1050°C for 4 hours as in the previous case. The products after cooling were separated and analyzed, the results of which are given in the Fig. 4.22. Fig. 4.22 shows that rate and also the extent of reduction of iron oxid to metallic iron of as received ilmenite reduced at 1050^{0}C for 4 hrs as a function of ilmenite to coke ratio. It shows that upto 1:1 ratio reduction percentage of iron oxide to metallic iron increased after which it got more or less stabilized.

In other words, after 1:1 ratio the increase in reduction was very nominal. Hence it is concluded that the optimum ilmenite to charcoal ratio for reduction is 1:1 at 1050°C and 4 hours.

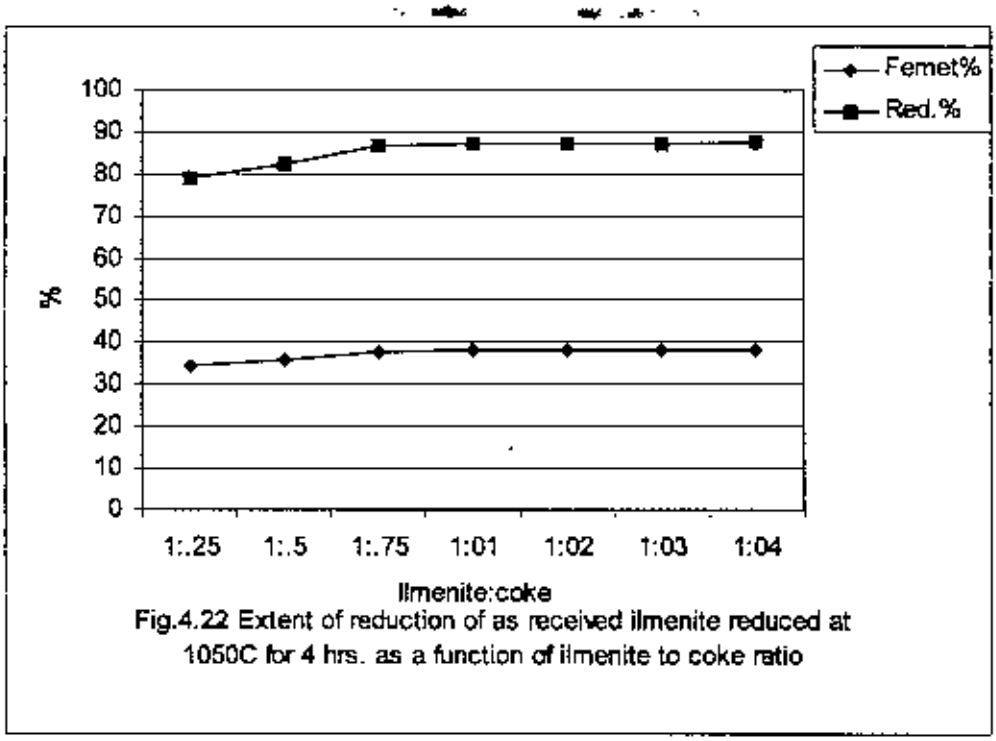


Fig.4.22 Extent of reduction of as received ilmenite reduced at 1050C for 4 hrs. as a function of ilmenite to coke ratio

4.4.1.2 Optimization of temperature

For optimization of temperature reduction experiments were carried out for time period of ½ hr, 1 hr, 2hr and 4 hours in the temperature interval 800-1100°C. Ilmenite and charcoal in 1:1 (w/w) ratio was heated at 800°C for each of the time periods 1/2 hr, 1 hr, 2 hr and 4 hr. The reduced mass was then cooled and analyzed. Another experiment with fresh charcoal and ilmenite was carried out at 900°C for the above time periods. In other words, each experiment was carried out with fresh raw materials and was not a continuation from the previous one.

Fig 4.23 and Fig. 4.24 give a plot of percentage of metallic iron and percent of reduction as a function of time. It is clear from the figures that for any specified time the percent of reduction and percent of metallic iron increased with an increase in temperature. Between 800 and 1100°C, at any temperature metallic iron content was lesser after reduction for 3 hours than after reduction for 4 hours. Up to about 1050^{0}C extent of reduction increases sharply. After that there is no considerable effect of temperature on reduction. At about 1050°C, the reduction got stabilized, after that the increase in metallic iron content is nominal. At 1100°C the extent of reduction curve merges with the extent of curve at 1050°C, the reduction got stabilized, after that the increase in metallic iron content is nominal.

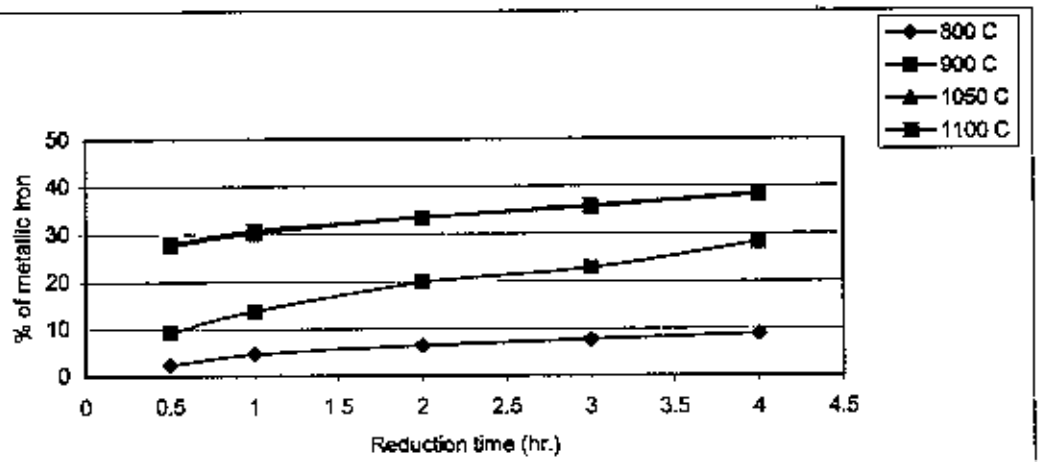


Fig 4 23 Effects of time and temperature on the extent of reduction (% of metallic iron) in the as received ilmenite.

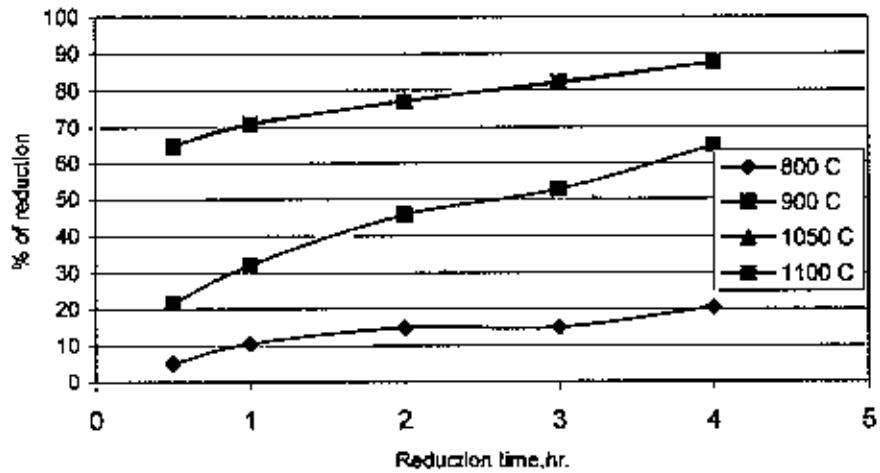


Fig. 4 24 Effects of time and temperature on the extent of reduction (% of reduction) for as received ilmenite

Merk and Pickles [1988] investigated reduction of ilmenite with CO and noted that above 1000°C, the degree of reduction remains essentially constant due to the formation of metallic shell of iron that segregates to ilmenite grain boundaries and inhibit CO diffusion.

The Fig.4.24 showed that the optimum temperature required for the reduction of ilmenite was around 1050°C, after that the percentage of reduction increase was nominal. The Fig. 4.24 also showed that at any specified time in both the temperature the % of reduction was more or less same. The percentage of reduction was 87.39% and 87.47% for 4 hrs. at temperature of 1050^0C and 1100^0C respectively. For a better understanding of the optimization of temperature the following were carried out.

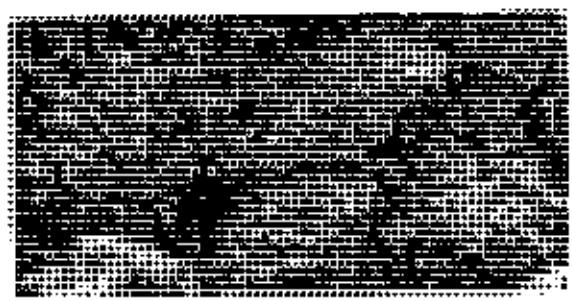
Scanning electron microscopic studies:

Ilmenite samples reduced at different temperature level (800°C-1100°C) for 4 hrs. were subjected to scanning electron microscopic observation in order to understand the effect of temperature on the surface of the particles. The results are given in Fig. 4.25. The trend was more or less same as seen in the case of reduction time (Fig. 4.30). It may be noted that the surface of the unreduced ilmenite particle was relatively smooth nonporous surface (Fig.4.2). In Fig 4.25(a), which is after reduction of 4 hr at 800°C, the appearance of slightly porous surface is an indication that some reduction has taken place. As the reduction temperature increases, the size and number of pores increases i.e. the porosity increases with temperature. Which is evident from the Figs. 4.25(b), 4.25(c) and 4.25(d).

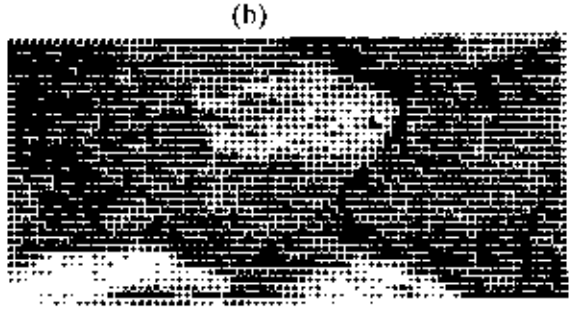
Optical microscopy:

Particles of reduced ilmenite were mounted in cold-setting resin and observed under an optical microscope. Microstructures of ilmenite reduced at different temperature (800°C-1100°C) for 4 hrs. are shown in Fig. 4.26. The progress of reduction can be observed in the microstructures of the reduced mass. In these microstructures metallic iron is clearly visible as a bright phase, the rest of the phases are grayish, voids and fissures being dark in appearance. Microstructures of as received ilmenite particles reduced at lower temperature show this bright phase (metallic iron). With increasing of temperature iron begins to coalesce into large globules and tend to segregate towards the peripheries of the grains.

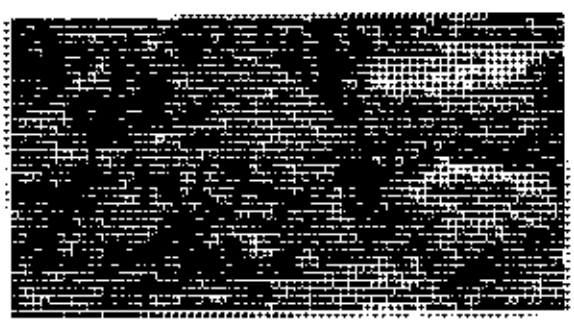
(a)



(b)



(c)



(d)

Fig. 4.25 SEM of reduced ilmenite (reduced for 4 hr.) at
(a) 800°C, (b) 900°C,
(c) 1050°C (d) 1100°C.

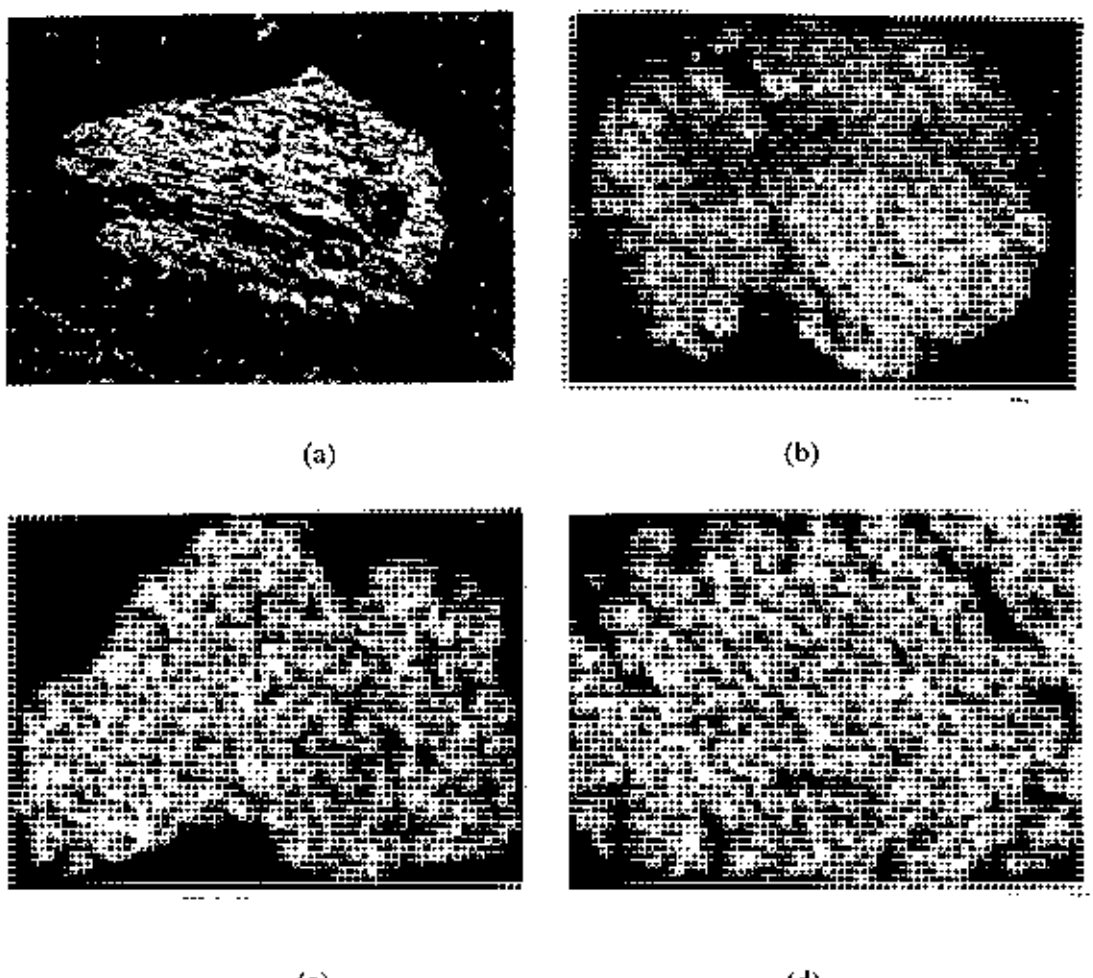


Fig. 4.26 Microstructure of as received reduced ilmenite
(a) Reduced at 800°C for 4 hr
(b) Reduced at 900°C for 4 hr
(c) Reduced at 1050°C for 4 hr
(d) Reduced at 1100°C for 4 hr

X-ray diffraction studies:

X-ray diffraction analysis of ilmenite reduced at different temperatures for 4 hours were carried out. Typical x-ray diffraction patterns of ilmenite reduced at 800°C, 900°C, 1050°C and 1100°C for 4 hrs. are given in Fig. 4.27. During the reduction of ilmenite by charcoal the proportions of the phase's change and a new phase, metallic iron appears and increases in proportion with the extent of reduction. These changes in the reduced mass can be followed via the x-ray diffraction pattern. Sample reduced at 800°C gave a peak of the new phase, metallic iron and pseudobrookite phase appear. This figure also shows that with the increasing temperature at 900°C the intensity of the diffraction lines belonging to pseudobrookite phase and at the same time, the intensity of the diffraction lines belonging to metallic iron and rutile increases with indicating that the amount of metallic iron and rutile in the reduced sample increases with temperature. With the increase of temperature reduction preceded, the intensity of ilmenite peak slowly diminished and disappeared at 1050°C showing the complete decomposition of ilmenite to TiO_2 and metallic iron. At 1050°C the peak for metallic iron become reaching maximum. The presence of Fe_2O_3 and pseudobrookite was detected in the sample reduced at 800°C after which it was absent indicating the disappearance of ferric iron through reduction at higher temperature. Chemical analysis values also showed the presence of ferric iron only upto 800°C confirming the above observation.

From the above observation it is clear that ilmenite phase slowly diminished with the increase of temperature and reaching zero at 1050°C. The intensity of metallic iron phase up to 800°C was less, after which the intensity increases up to 1050°C. Chemical analysis also showed the presence of maximum metallic iron at this temperature. After 1050°C the intensity of metallic iron phase for 1100°C is more or less same. The change in the height of the rutile peak is shown as a function of reduction temperature. At all temperatures except 1100°C it increases progressively. At 1100°C, in contrast, the height of the rutile peak actually decreases, implying a decrease in the amount of rutile. This decrease in the peak height of rutile was accompanied by the appearance of weak, overlapping peaks in the neighborhood of the rutile peak; these new peaks flanking the rutile peak [Grey and Reid, 1974]. Thus from the above observation of chemical analysis, optical microscopy, SEM and x-ray diffraction studies the optimum temperature for reduction is 1050°C.

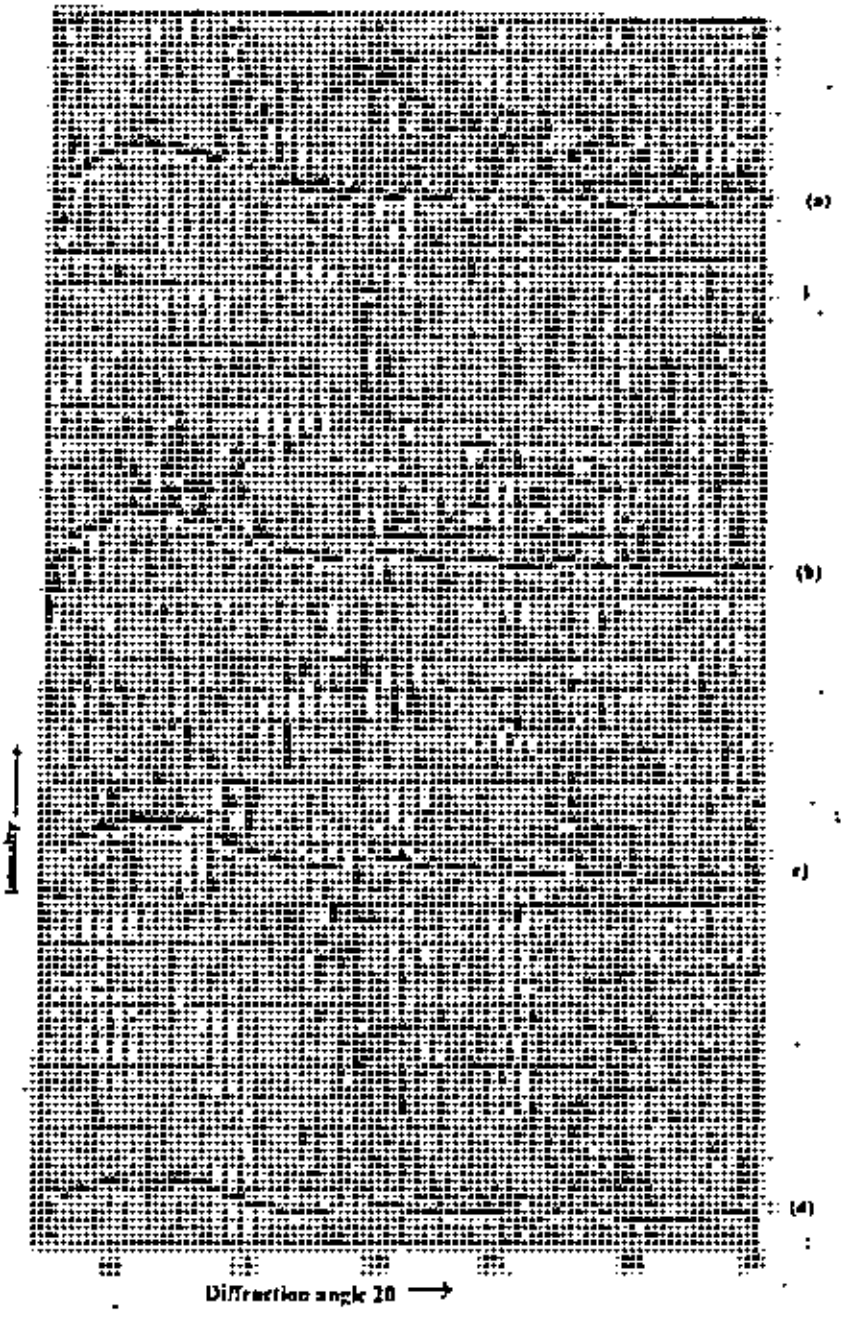


Fig. 4.37 X-ray diffraction patterns of Teknaf ilmenite reduced at different temperature.
(a) Reduced at 800°C for 4 hr.
(b) Reduced at 900°C for 4 hr.
(c) Reduced at 1050°C for 4 hr.
(d) Reduced at 1100°C for 4 hr.

4.4.1.3 Optimization of time

From the experiments described earlier, it was observed that optimum reduction took place at 1050°C at an ilmenite to coke ratio of 1:1. Hence these conditions were kept constant during the experiments for optimization of time. Ilmenite and charcoal were taken in the reaction tube in 1:1 ratio by weight and heated at 1050°C for various time intervals like 0.50, 1.00, 2.00, 3.00, 4.00 and 5.00 hours. The first sample was heated for 0.5 hours, after which it was taken out and analyzed. Another sample was heated for 1.00 hours. In other words, fresh samples were used for studying reduction at each time interval. After the reaction the product was analyzed as before.

Fig. 4.28 gives a plot of percentage reduction and percentage of metallic iron as a function of time. Ilmenite, which was the starting material, contained no metallic iron, while ferrous iron content was 25.32% with the balance of 32.53% in the ferric form. It is clear from the figure that as time increased reduction of ferric and ferrous iron to metallic iron gone on increasing. Up to about 4 hours the increase was sharp, after which it slowed down. The reduction rate increases at the initial stage and after 4 hour the curve becomes almost flat. At this stage chemical analysis shows that more than 87.61% of iron was in the metallic state, and the balance is oxide of iron. At 4 hours, the reduction got stabilized, after which at 5 hrs. the increase in metallic iron was nominal (87.75). Reduction became highest at 4 hours, after which time did not have any significant effect. In other words, the optimum time required for the reduction of ferrous iron and ferric iron present in ilmenite to metallic iron was about 4 hours.

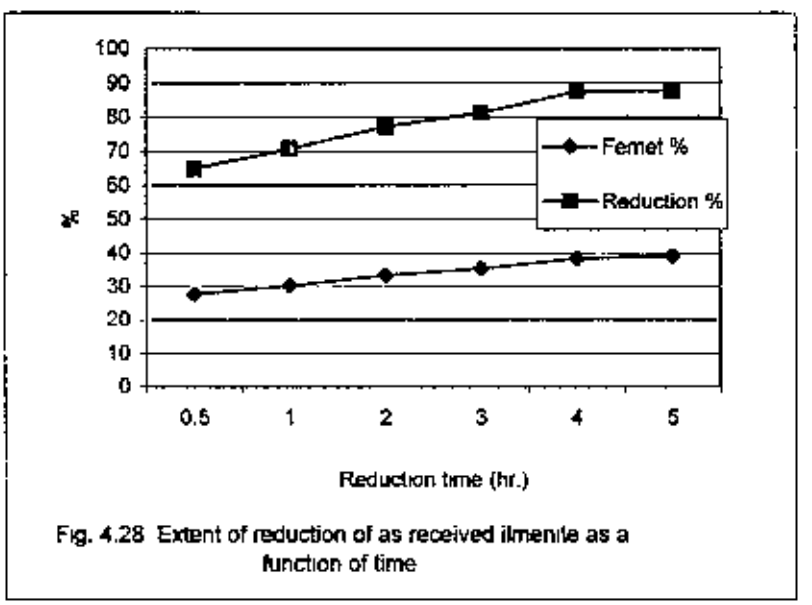


Fig. 4.28 Extent of reduction of as received ilmenite as a function of time

Following instrumental observation were also carried out for understanding the optimization phenomenon.

Optical microscopic studies:

The microstructure of the unreduced and reduced samples in the Fig. 4.29 shows the internal structure of the polished particles. The progress of reduction can be observe in the microstructures of the reduction mass. In a sample reduced for 0.5 hr. (Fig.4.29.b) small bright spots due to metallic iron were observed. Dark gray or black areas seen in the particle were voids. . The pores were formed due to the removal of oxygen from the ferric oxide during reduction. Metallic iron spots were seen only in some particles while in many others reduction had not proceeded to the metallic state, which is also evident from the low metallic iron percentage obtained in chemical analysis. After reduction for 1 hour (Fig. 4.29.b), more shining white metallic dots were observed with an increase in the size and number of voids. The small metallic iron particles combined together to form bigger particles as reduction proceeded, which is evident from Fig.4.29 (d). In some of the reduced ilmenite grains, these globules started diffusing from the interior to the periphery and got concentrated there. In the 3 hr reduced sample these metallic iron particles combined together. While in others they were still distributed. This trend became clearer in the 4 hr reduced sample in Fig.4.29. (f). The particle was having more voids and pores due to reduction.

Jones [1974] had observed that during reduction Australian ilmenite above 1000°C the metallic iron formed coalesced together forming larger globules. These globules diffused to the periphery of the particles and got concentrated there. He also observed that at 1100°C, almost all the grains were completely enveloped by shells of metallic iron of 5-10 μm thickness.

Scanning electron microscopic studies (SEM):

The SEM studies of the unreduced and reduced ilmenite samples were carried out to study the changes taking place on the surface of the particles during reduction. Results are shown in Fig.4.30. The unreduced ilmenite (Fig 4.2) has got a smooth plane surface having either no pores or only micro pores. After one hr. of reduction, uneven surface developed, which indicated the begining of reduction. In the three hour reduced sample, the surface showed the formation of cracks and more uneven surface. Larger pores of a few micron sizes with interconnections were observed. The pores were formed due to the removal of oxygen from the ferric oxide during reduction. The surface of the four hour reduced sample became completely uneven and more porous giving an appearance of a honeycomb structure.

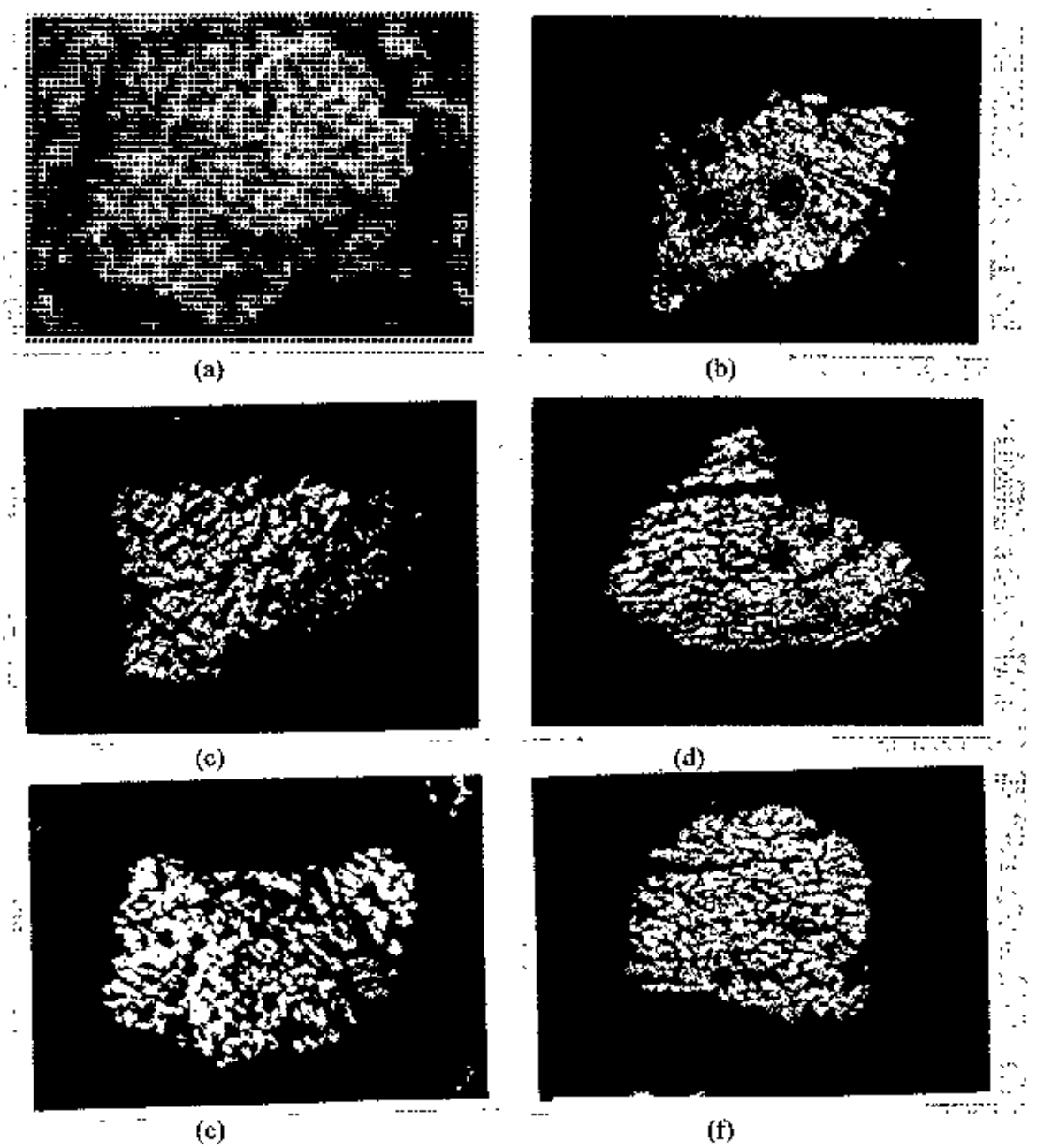
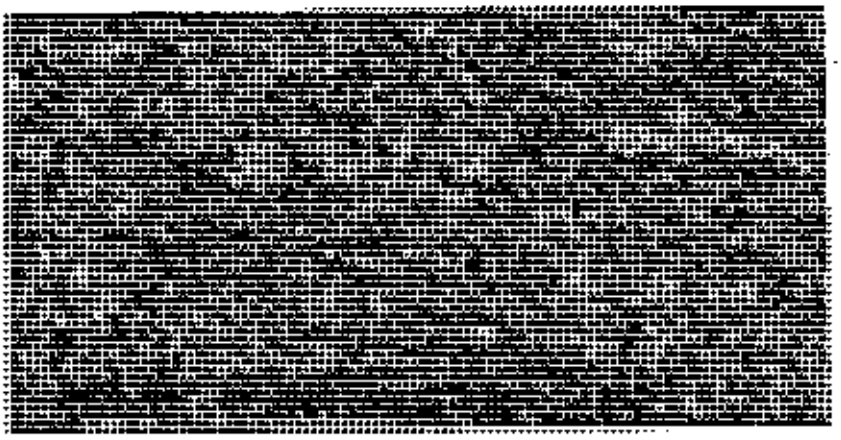
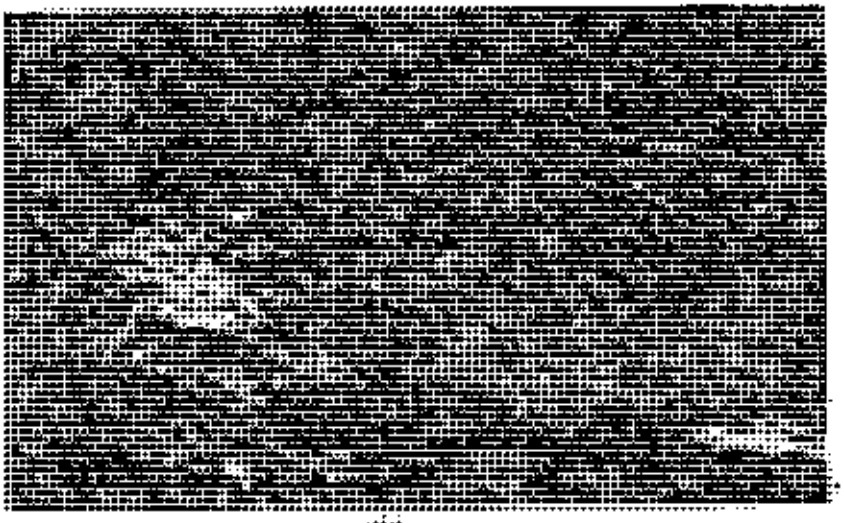


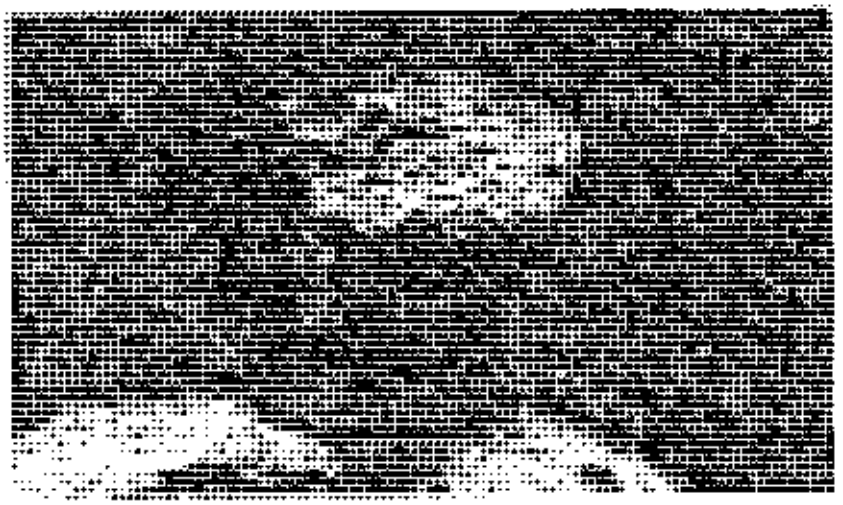
Fig. 4.29 Microstructure of unreduced and reduced ilmenite sample

(a) As received ilmenite
(b) Reduced at 1050°C for .50 hr .
(c) Reduced at 1050°C for 1 hr .
(d) Reduced at 1050°C for 2 hr .
(e) Reduced at 1050°C for 3 hr .
(f) Reduced at 1050°C for 4 hr .



(a)





(c)

Fig. 4.30 SEM of reduced sample (reduced at 1050°C)
(a) For 2 hr. (b) For 3 hr. (c) For 4hr.

X-ray diffraction studies:

X-ray diffraction patterns of as received ilmenite reduced with charcoal for different periods of time at 1050°C are shown in Fig.4.31. X-ray diffraction analyses of the reduced ilmenite samples were carried out for understanding the changes taking place to various constituents during reduction.

The patterns recorded after half an hour of reduction show the diffraction lines belonging to ilmenite, metallic iron, rutile and pseudorutile phase.

In the unreduced ilmenite sample, the maximum intensity peak was that of ilmenite, while there was no peak for metallic iron, which was also confirmed by chemical analysis. After reduction for 0.5 hours, the maximum intensity peak was that for metallic iron. As reduction proceeded, the intensity of ilmenite peak slowly diminished and disappeared after 3 hours showing the complete decomposition of ilmenite to TiO_2 and metallic iron, while the peak for metallic iron became slowly prominent with increase of time. It was also noted that the pseudorutile phase disappeared completely after 1-hour reduction. But chemical analysis indicated the presence of ferrous iron in all the samples.

Raw ilmentie showed a peak for ilmentie. Intensity of ilmenite diffraction lines decreasing with the time of reduction and the reaching the zero at 2 hours, while with the increase of time the diffraction line for metallic iron also increases up to 4 hrs. After 4 hours, it decreased which can be due to the following reason. For longer time reduction the rutile reduced to Ti_5O_9 and Ti_6O_{11}, which can affect the overall absorption of the specimen and hence can cause a drop in the metallic iron content. However, chemical analysis showed the presence of more or less the same quantity of metallic iron in the 4 and 5 hour reduced samples. Hence this drop of value in x-ray after 4 hours cannot be taken as a decrease in metallic iron content. Wouterlood [1979] in the case of Australian ilmenite has observed the same phenomenon. From the above investigation of chemical analysis, optical microscopy, scanning electron microscopy and x-ray diffraction analysis it is evident that the optimum time for reduction of ilmenite 4 hr. at 1050°C. Hence it is concluded that 4 hours is required for the optimum reduction of ilmenite at 1050°C. All further reduction studies were carried out for 4 hours to ensure that complete reduction of oxides of iron in the ilmenite sample can take placee.

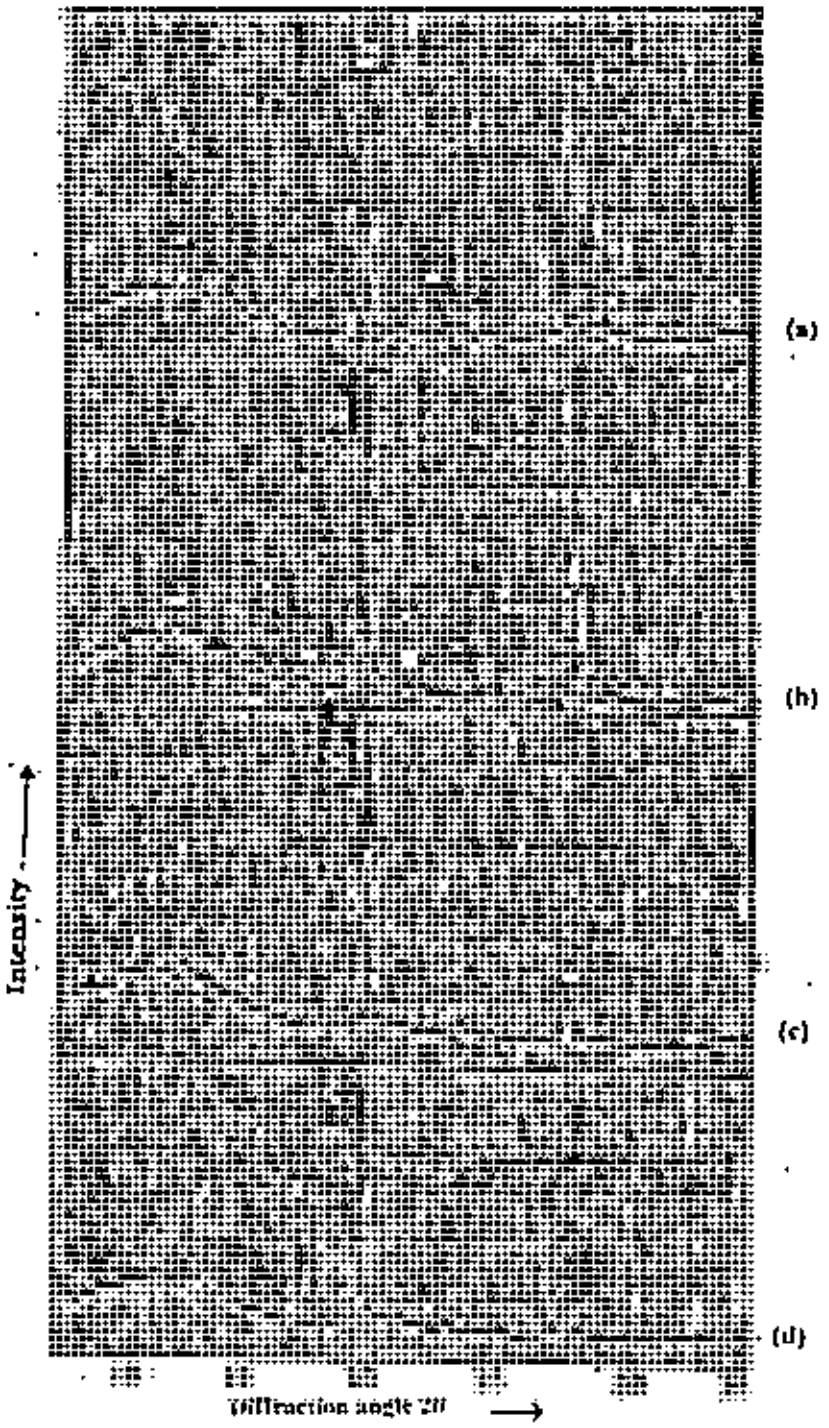


Fig 4.31 X-ray diffraction pattern of reduced ilmenite.
(a) Reduced for 0.50 hr. at 1050°C
(b) Reduced for 1 hr. at 1050°C
(c) Reduced for 3 hr. at 1050°C
(d) Reduced for 4 hr. at 1050°C

4.5 Reduction Behavior study

Teknaf ilmenite was reduced to study the

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

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

(c) Reduction behavior of the different magnetic fractions.

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

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

The effect of time and temperature on the extent of reduction of ilmenite in the as received condition were studied. In all cases the ratio of ilmenite and charcoal ratio was kept constant at 1:1. The result of isothermal reduction experiment is presented in the form of percent metallic iron and percent of reduction in the reduced mass of ilmenite. The chemical analysis results plot in the previous Fig. 4.24 indicate that the extent of reduction for a specified period increases with an increase in the reduction temperature and also with an increase in time for a specified temperature.

After certain period at all temperatures, the rate of reduction was found to decrease with time of reduction. The decrease in the rate of reduction at a later stage may be attributed to be difficulty encountered by the gaseous species (CO and CO_2) to diffuse through the porous product layer consisting of iron and titanium-di oxide or to the decrease in the surface area available for reduction. The extent of reduction in the as received ilmenite increases significantly as the reduction temperature increases. The higher extent of reduction may be attributed to the fact that at higher temperatures carbon monoxide produced by the gasification of carbon of the charcoal becomes the main reducing agent while at lower temperatures solid carbon acts as the main reducing agent.

Hasseb et al. [1997] investigated reduction of ilmenite with charcoal and suggested that at lower temperature (950-1000°C) the reduction of ilmenite proceeds via the solid-state reaction between carbon present in charcoal and ilmenite. They identified this model of reaction to be responsible for the slower rate of reduction at lower temperatures, at temperatures higher than 1000°C,the reduction mechanism changes and is caused by CO in accordance with the Boudouard reaction. This change in mechanism increases the extent of reduction. On the other hand, the Boudouard reaction (eqn.1) proceeds, at a significant rate at temperatures higher than 1000°C.

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

Thus at reduction temperatures of 1050°C and 1100°C, carbon monoxide acts as the main reducing agent. The rate of this gas-solid reaction is higher than that of the solid-solid reaction. At the initial stage of reduction, pseudorutile is rapidly converted into ilmenite and rutile as follows.

$$Fe_2O_3 3TiO_2 + C/CO \Rightarrow FeO.TiO_2 + TiO_2 + CO/CO_2 \qquad (2)$$
(pseudorutile)

This reaction involves conversion of ferric into ferrous state, which is generally fast. Ilmenite is then reduced to rutile:

$$FeO.TiO_2 + C/CO \Rightarrow TiO_2 + Fe + CO/CO_2 \qquad (3)$$

This reaction is basically the reduction of iron from the ferrous state into the metallic state and is a slow process. Upon reduction at high temperature i.e., 1100°C rutile is further reduced to lower oxides with the loss of oxygen. Haseeb et al., (1997) has observed that the general reduction mechanism of Bangladesh ilmenite by charcoal is very similar to that of Australian Capel ilmenite by carbon monoxide as proposed by Jones (1974). Jones found that Australian ilmenite also undergoes reduction in two major stages; conversion of pseudorutile into ilmenite, and reduction of ilmenite into metallic iron and titanium oxide. Occurance of lower oxide of titanium also reported by Jones [1974] also reported at reduction temperatures as low as 1000°C.

4.5.2 Effects of particle size on the extent of reduction:

Graphical presentation of degree of reduction and percent of Fe_{met} of different size fractions of as received reduced ilmenite is shown in Fig.4.32 and Table 4.6(a) shows the initial and final values of oxygen contents of iron oxide in different size fractionated ilmenite.

Table: 4.6 (a) Initial and final oxygen content of iron oxide of ilmenite and degree of reduction.

Ilmenite size fractions	% of total O_2 combined with Fe before reduction	% of total O_2 combined with Fe after reduction	Degree of reduction
U.S. Sieve No. 100	15.34	1.96	87.22
U.S. Sieve No. 140	15.72	1.68	89.31
U.S. Sieve No. 200	16.07	1.47	90.85

The degree of reduction for the three size fractions is presented in the forth column of Table: 4.6 (a). It is seen from the figure 4.32 that percentage of metallic iron and degree of reduction increase with the increase of the fineness of the particles.

Fig 4.33 shows that the percentages of total iron in the reduced samples are higher as compared with the corresponding values in the raw samples. This is due to the removal of oxygen during reduction. After reduction the finer fractions are found to contain higher amount of total iron as before. From the Fig.4.32 it is evident that the content of metallic iron as well as degree of reduction increases with the increase of fineness of the particles. It is clear from the table that although finer ilmenite grains contain a higher amount of oxygen associated with iron, these fractions actually contain a lower amount of oxygen in the reduced mass. As a result the reduced samples of finer fraction contain a lower amount of iron in the oxide form. Consequently the degree of reduction is seen to be higher in the finer fractions (Fig.4.32). In other words, under the reduction conditions used, the finer fractions of ilmenite get reduced at a faster rate. Thus from the viewpoint of optimization of reduction process, adaptation of separate reduction procedure for each of the size fractions is not necessary.

X-ray diffraction patterns of the different size fractions of ilmenite after reduction is presented in Fig.4.35. The phases identified in the x-ray patterns, were metallic iron and rutile. There were no diffraction lines in the x-ray pattern representing any of iron oxide, ilmenite or pseudorutile, which distinguish these patterns from the patterns of size fractions prior to reduction. Due to reduction, iron oxide was reduced to metallic iron. Thus the x-ray patterns of all reduced size fractions show diffraction lines belonging to metallic iron. Before reduction diffraction lines belonging to TiO_2 was detected in the x-ray pattern of only one size fraction which was separated at US sieve No. 100 But after reduction more than one intense peak for TiO_2 were identified for all the three fractions. Fig.4.36 Shows the micrographs of different size fractions of reduced ilmenite. These microphotographs are similar to each other and it is difficult to get any useful information from these microphotographs. However reduced samples contain whiter phase than as-received sample due to presence of iron.

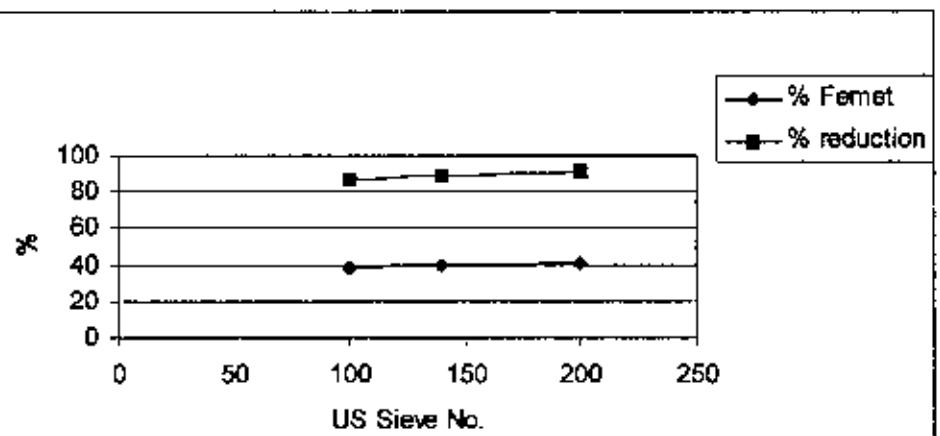


Fig.4.32 Extent of reduction of as received ilmenit as a function of size fraction.

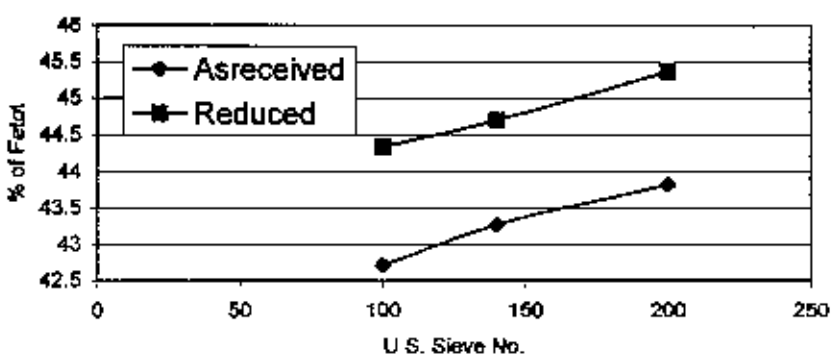


Fig 4.33 Variation of total iron of as received and reduced size fraction ilmenite.

4.5.3 Effect of different magnetic fractions on the extent of reduction

The extent of reduction was followed by the chemical analysis of the reduced mass for the content of metallic iron. X-ray diffraction analysis and optical metallography of the reduced mass were also carried out.

Chemical analyses results of the different reduced magnetic fractionated samples are plotted in the Fig 4.36. This figure shows that the contents of metallic iron as well as Fe_{tot} decrease with an increase in the separation current.

The calculated percentage reduction is plotted in the Fig. 4.36 and the degree of reduction was calculated by using the formula,

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

From the Fig.4.36 it is evident that magnetic fractions separated at lower current (0.10-0.25) are reduced to a higher extent than those separated at higher currents, it may be due to higher ferrous oxide contents in those four fractions which are separated at higher currents. So it is beneficial to reduction for the first four fractions. But these four major fractions contain about 89% of the ilmenite sample. So it may not economical to develop a separate reduction techniques for the rest two.

X-ray diffraction analysis of the different magnetic fractions after reduction is presented in the Fig.4.37. Two phases were identified in the x-ray pattern, are metallic iron, and TiO_2. There were no diffraction lines in the x-ray pattern representing any of ilmenite, pseudorutile and iron oxide phase, which distingnish these patterns from the patterns of magnetic fractions prior to reduction. Due to reduction, iron oxide was reduced to metallic iron. Thus the x-ray patterns of all reduced magnetic fractions show diffraction lines belonging to metallic iron. Before reduction diffraction lines belonging to TiO_2 was detected in the x-ray pattern with less intense diffraction lines. But after reduction intense peak for TiO_2 were identified.

Fig.4.38 shows the micrographs of reduced magnetic fractions. These microphotographs are similar to each other and it is difficult to get any useful information from these photographs. However reduced samples contain whiter phase than as-received samples due to presence of iron.

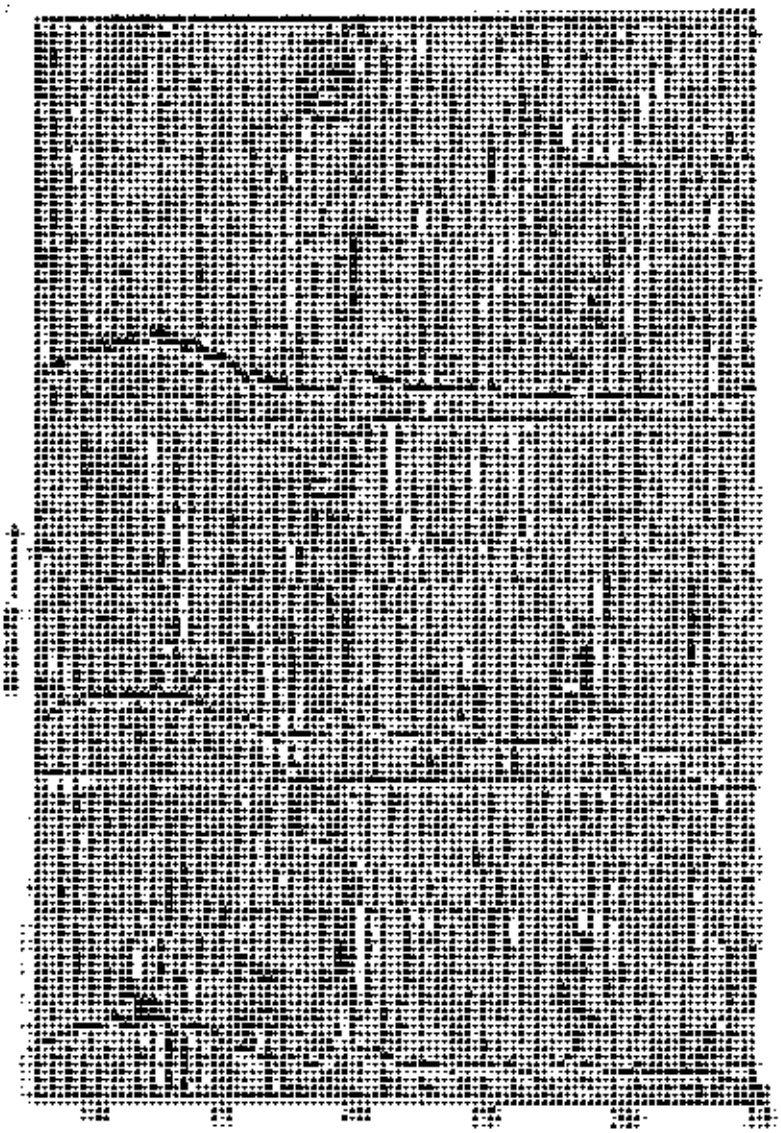
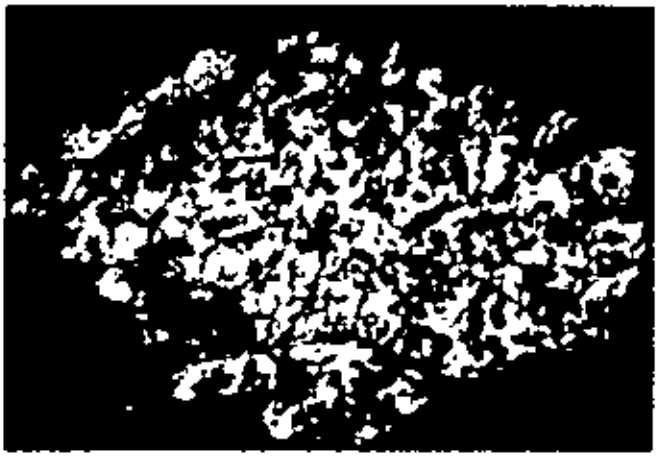
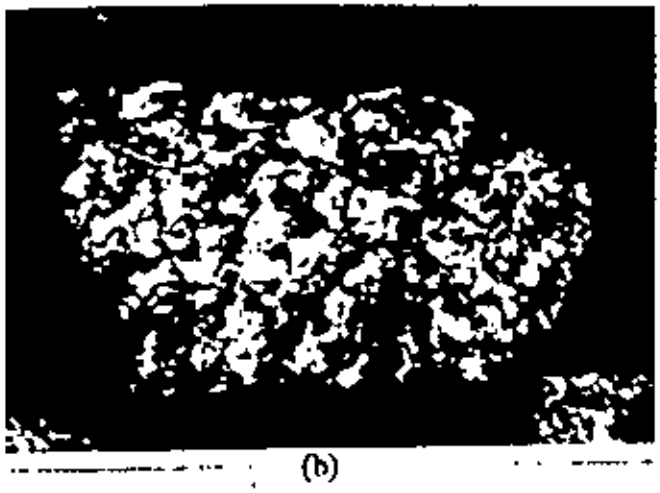


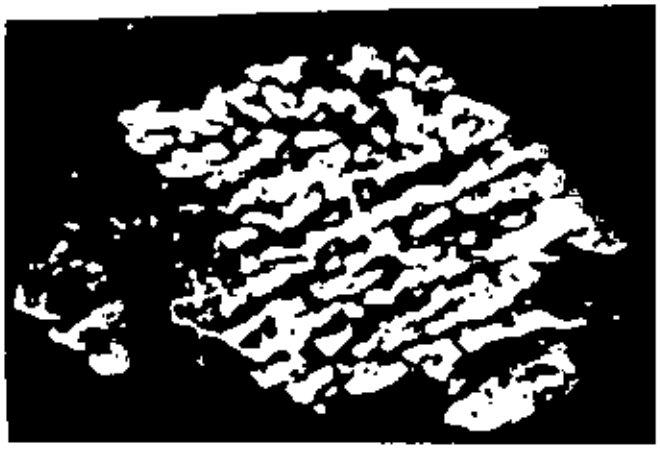
Fig. 4.34 X-ray diffraction patterns of different size fractionated reduced ilmenite(reduced at 1050°C for 4 hrs.)
(a) U.S. Sieve No. 100
(b) U.S. Sieve No. 140
(c) U.S. Sieve No.300



(a)



(b)



(c)

Fig.4.35 Microstructure of different size fractionated reduced ilmenit (at 1050° C, 4 hr)
(a) Ilmenite of 100 U.S. sieve size.
(b) Ilmenite of 140 U.S. sieve size.
(c) Ilmenite of 200 U.S. sieve size.

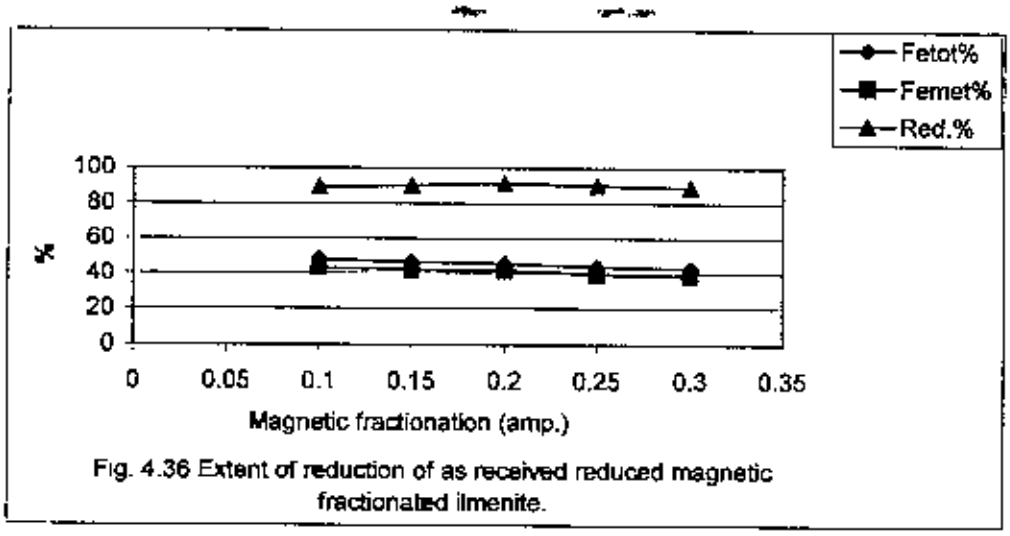


Fig. 4.36 Extent of reduction of as received reduced magnetic fractionated ilmenite.

4.5.4 Effects of Prior Oxidation on the Extent of Reduction

Chemical analysis of the samples of Teknaf ilmenite, oxidised in the temperature range 750 – 950°C, indicated that the content of ferrous iron decreases rapidly with an increase in time and temperature of oxidation. The rate of change of the ferrous iron to ferric iron decreased rather rapidly and then remained more or less unchanged. Diffraction patterns of oxidised samples, contained diffraction lines belonging to pseudobrookite, rutile, and hematile. X-ray diffraction studies by Jones [1974] also showed that ilminate when heated at 1000°C yielded pseudobrookite and a small amount of rutile.

Scanning electron micrographs of oxidised ilmenite showed in the previous Fig.4.15(c) the presence of cracks in the oxidised particles of ilmenite.

Fig.4.39 shows a comparison of the extents of reduction of as received and pre-oxidised ilmenite reduced at 1050°C.It can be seen that at any time the extent of reduction is higher in the case of pre-oxidised samples than in the case of as received ilmenite.

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

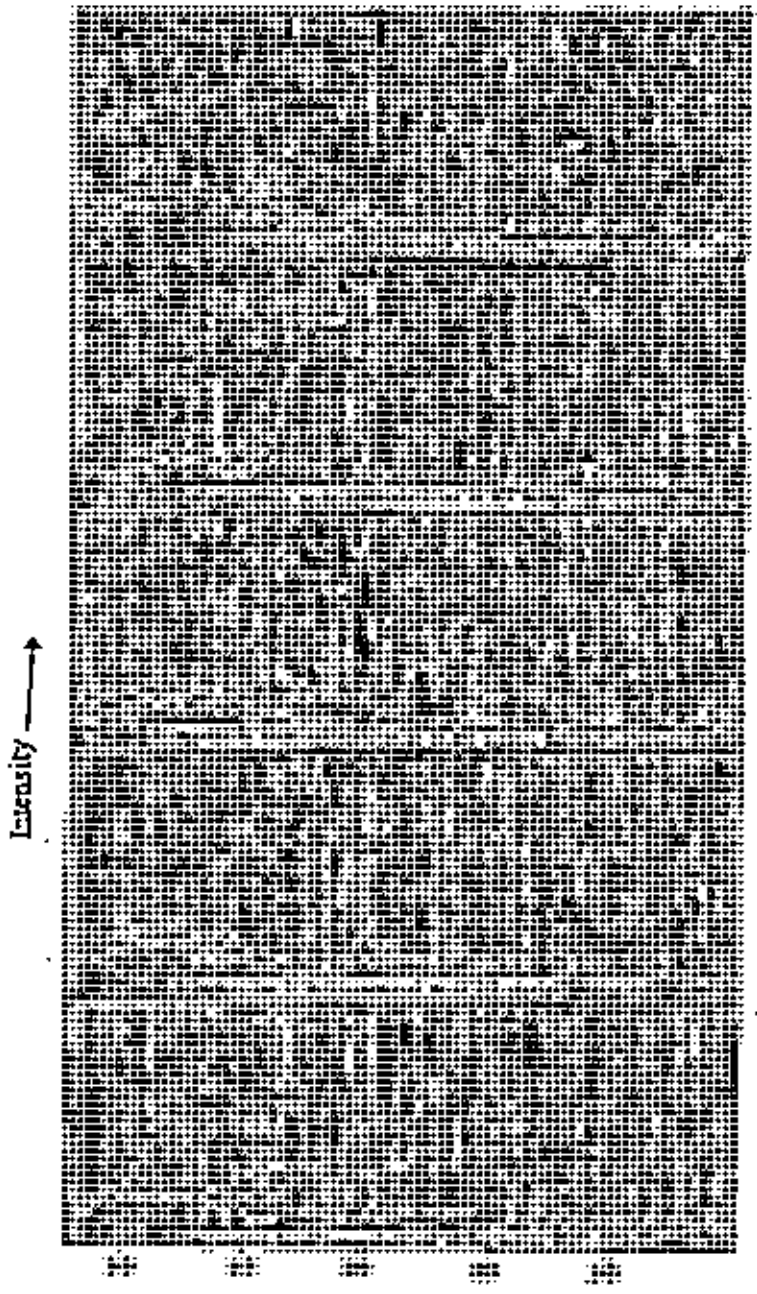


Fig. Fig. 4.37 X-ray diffraction patterns of different magnetic fractionated reduced ilmenite (reduced at 1050°C for 4 hr.)

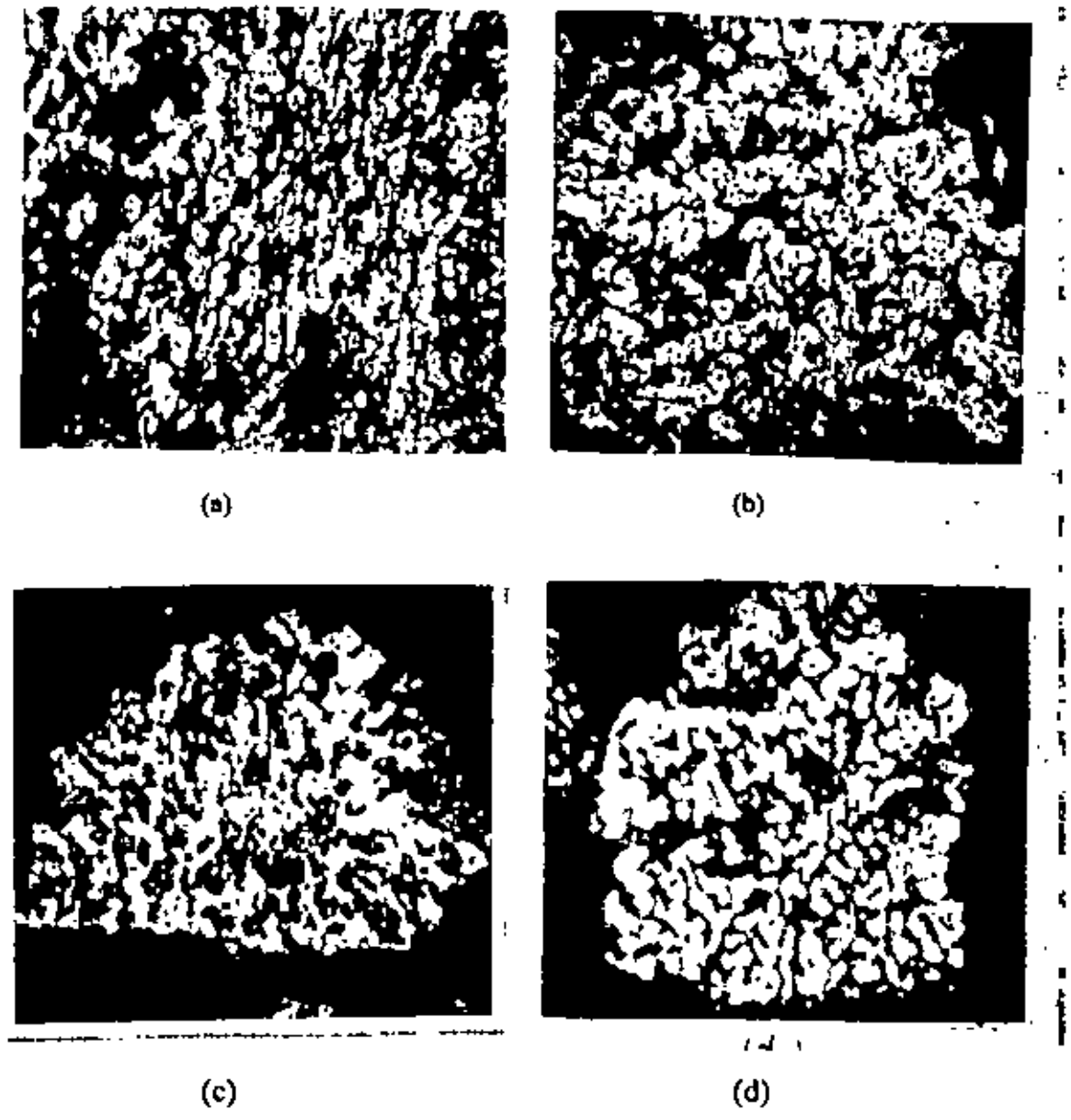


Figure 4.38 Optical micrographs of different magnetic fractionated reduced ilmenit (reduced at 1050°C for hr.)

(a) Fractionated at 0.10 amp.
(b) Fractionated at 0.15 amp.
(c) Fractionated at 0.20 amp.
(d) Fractionated at 0.25 amp.

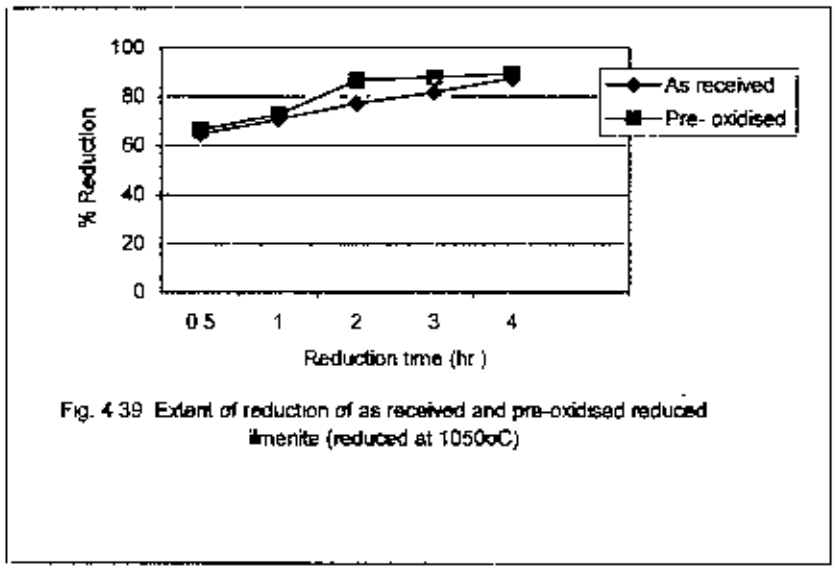


Fig. 4 39 Extent of reduction of as received and pre-oxidised reduced ilmenite (reduced at 1050oC)

X-ray diffraction patterns of samples reduced (in the oxidised condition) at 1050^0 C for different periods of time are shown in Fig 4.40. The diffraction pattern of the sample reduced for 0.5-hour show the presence of diffraction lines belonging to ilmenite, metallic iron and rutile. It may be recalled that the main constituents of the pre-oxidised ilmenite was rutile, hematite and pseudobrookite. The presence of diffraction lines belonging to pseudobrookite, rutile and hematite phases could not be detected in this pattern. Fig.4.40 (b) shows that the intensity of diffraction lines belonging to ilmenite diminishes with an increase in time of reduction and completely disappears after 2hr. reduction. On the other hand, the intensity of diffraction lines belonging to metallic iron increases with increasing time of reduction. This means that the amount of metallic iron increases with time of reduction. It may therefore be concluded that the reduction of Teknaf ilmenite in the oxidized condition proceeds in two stages. The first stage is the reformation of ilmenite according to the either or both of the following reactions:

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

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

The disappearance of hematite and pseudobrookite phases and the appearance of ilmenite in the x-ray diffraction pattern of the sample reduced after oxidation gives credence to the above suggestion. Jones (1973) suggested that ilmenite can reform through the above reactions. The second stage is progressive reduction of ilmenite to metallic iron and rutile according to following reaction.

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

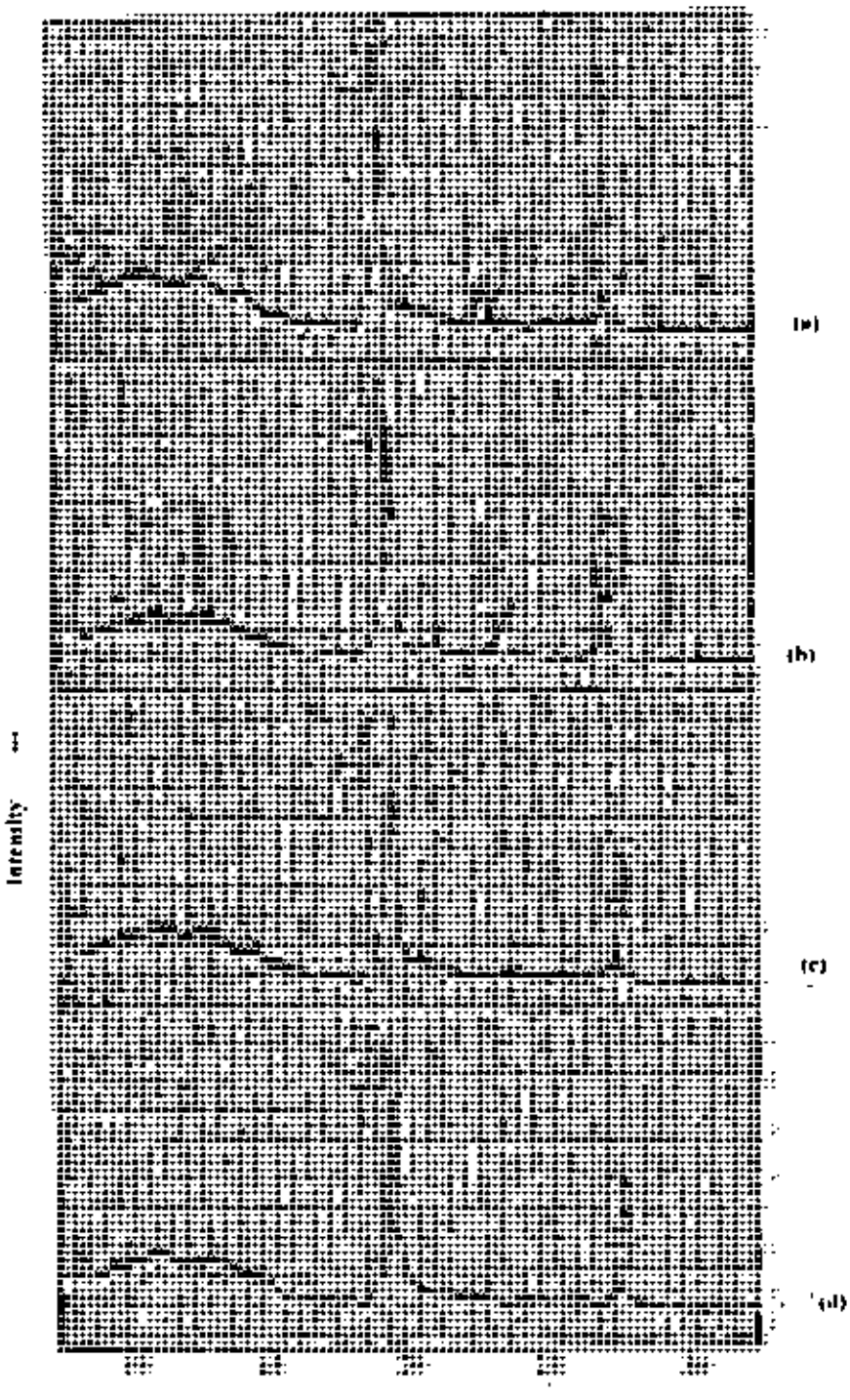


Fig. 4.40 X-ray diffraction patterns of pre-oxidised reduced ilmenite.
(a) Reduced for 0.5 hr. at 1050°C.
(b) Reduced for 1 hr. at 1050°C.
(c) Reduced for 2 hr. at 1050°C.
(d) Reduced for 4 hr. at 1050°C.

Thus the mechanism of reduction of naturally weathered and pre-oxidised sample of Teknaf ilmenite appear to be slightly different. The first step in the reduction of oxidised ilmenite is the rapid reformation of ilmenite either from pseudobrookite, rutile and carbon monoxide or from hematite, rutile and carbon monoxide or from both these reactions. The second stage is the reduction of reformed ilmenite to metallic iron and rutile. Reduction of as-received Teknaf ilmenite by charcoal, on the other hand, involves: (i) conversion of pseudorutile into rutile and ilmenite and (ii) change of ilmenite in the metallic iron and rutile.

Thus oxidation of Teknaf ilmenite converts almost all the ferrous iron content in ilmenite to ferric iron. This alters the mechanism of reduction. Moreover the generation of cracks in the oxidised samples prevents sintering, increases the surface area of the oxidesed particles and hence enhances the rate of subsequent reductions. Fig 4.42 shows that for all the size fractions the extent of reduction in as received and pre-oxidized reduction condition is more than as received reduction. Fig 4.43 shows a comparison of the extent of reduction in as received and pre-oxidized magenetically fractionated reduced ilmenite. It can be seen that the extent of reduction for all the magnetic fractions is higher in the case of pre-oxidized reduction than in the case of as received ilmenite.

Particles of ilmenite reduced both in the as received and in the oxidized conditions were mounted in cold-setting resin and observed under an optical microscope. In both cases bright spot due to metallic iron were observed. Dark gray or black areas seen in the particles were voids. They were formed due to the difference in densities of ilmenite and metallic iron, which was deposited due to reduction. Fig. 4.44 shows the comparison of the microstructures of ilmenite reduced in the as received and pre-oxidised condition for similar reduction conditions. From the figure it is evident that the volume fraction of metallic iron formed on reduction in the case of oxidized sample is much more compared to that of as received condition. On oxidation single crystal ilmenite converts to polycrystalline array of pseudobrookite and rutile. The presence of cracks in the oxidized ilmenite increases the rate and extent of reduction of ilmenite.

Fig. 4.45 shows the scanning electron micrograph of as received and pre-oxidised reduced sample. The SEM pictures in both cases show the rough surface, which is in contrast to the smooth plane surface of the unreduced sample. After reduction pores were observed. The pores were formed due to the removal of oxygen from the oxides of iron during reduction. The surface of the oxidized and then reduced sample becomes completely uneven and more porous than the sample reduced in the as-received condition.

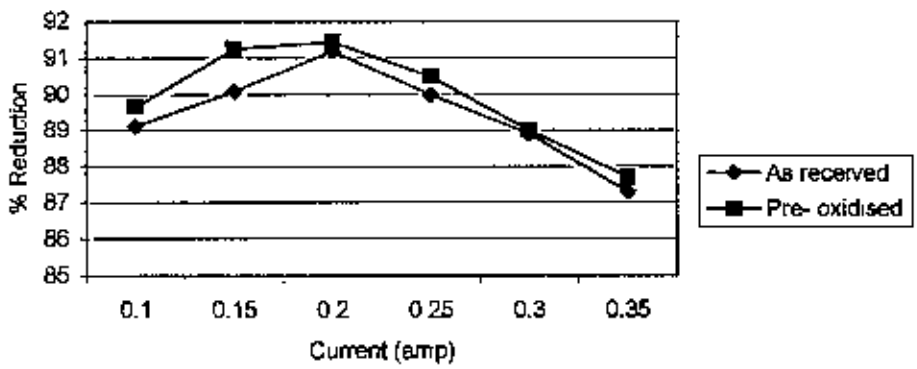


Fig. 4.42 Extent of reduction of as received and pre-oxidised fractionated ilmenite.

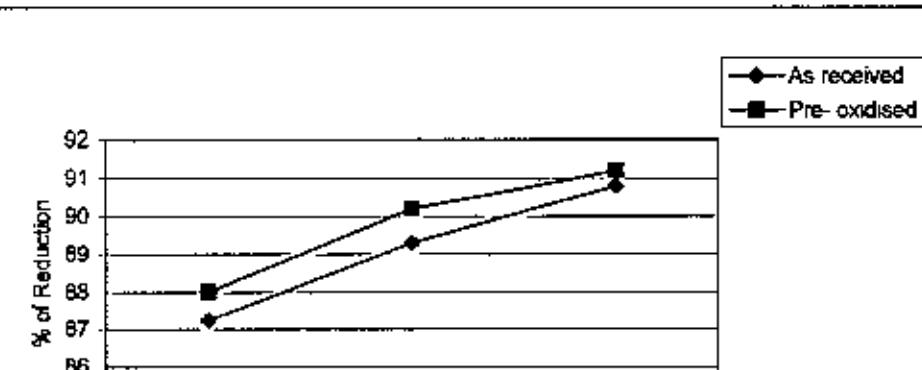
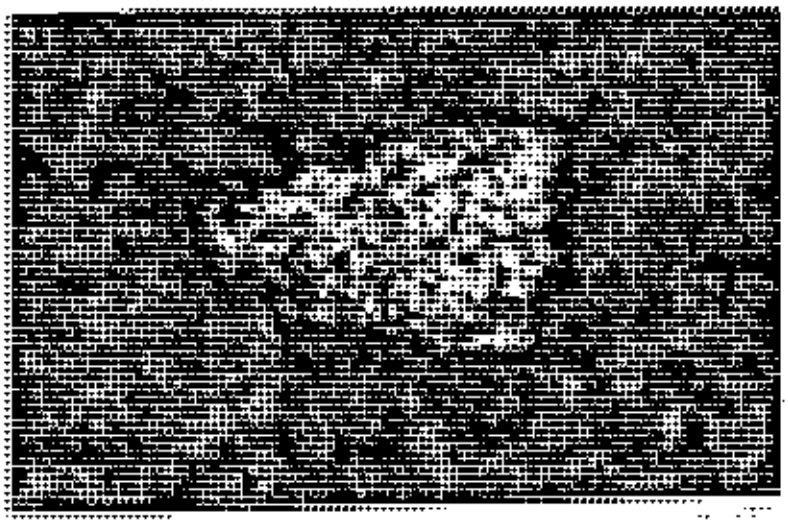
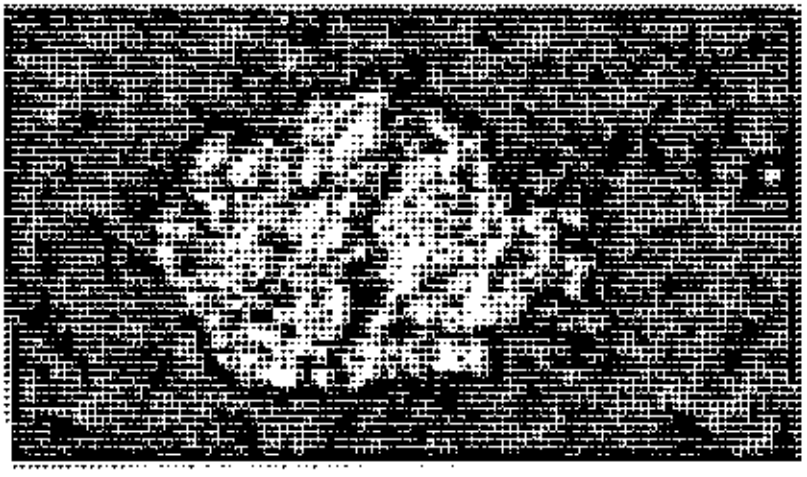


Fig.4.43 Extent of reduction of as received and pre-oxidised reduced of different size fractionated ilmenite.



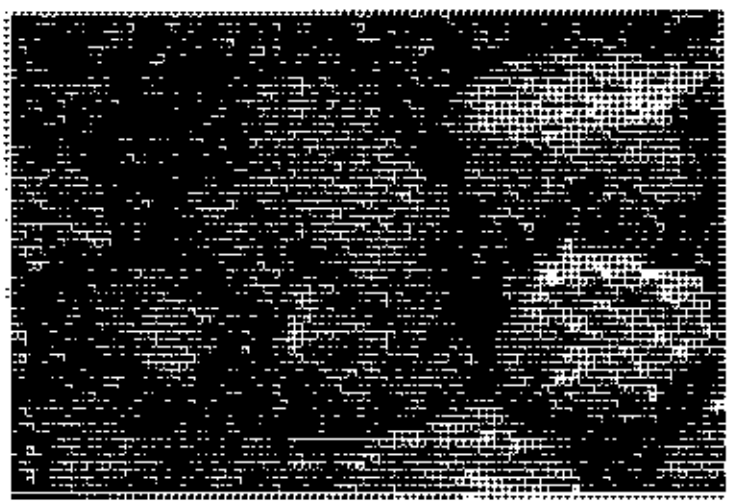
(a)



(b)

Figure. 4.44 Microstructure of reduced ilmenite (reduced at 1050°C for 4 hr.)
(a) as received reduced ilmenite
(b) pre- oxidised reduced ilmenite

(a)



(b)

Fig. 4.45 SEM of reduced ilmenite (reduced at 1050°C for 4 hrs.)
(a) As received reduced
(b) Pre-oxidised reduced

4.6 Leaching

4.6.1 Introduction

Teknaf ilmenite reduced both in the as received and in the oxidized conditions were leached in dilute HCl solutions. Samples reduced in the as received condition containing about 38.36 percent metallic iron (43.78% total iron) and samples reduced after oxidation containing 39.47 percent metallic iron (44.16% total iron) were used for the leaching experiments. The variables were acid concentration, time of leaching and temperature of the leaching solution. Attempts have also been made to identify the reaction mechanism and to determine the activation energy for the reaction.

4.6.2 Leaching of Reduced ilmenite

Ilmenite contains oxides of iron, silica and trace elements like copper, zinc, nickel, aluminum, calcium, manganese, magnesium, chromium etc. The techniques of upgradation involve preferential removal of iron. From the reduction studies it was evident that on reduction under optimum condition most of the ferrous and ferric oxides of the ilmenite were reduced to metallic iron. This reduced ilmenite was leached with HCl to remove metallic iron, which is one of the most widely used methods for the production of synthetic rutile. The leaching behavior of the ilmenite at various conditions has been studied. The results of these investigations are presented and discussed below.

Leaching was performed at 75^{0}C for a period 2 hrs. in an acid solutions containing 15 percent HCl. A three-necked flask equipped with a reflux condenser, a thermometer and a magnetic stirrer was used as the reaction vessel for leaching. The arrangement for leaching is shown in Fig.3.4.

During leaching 2 gm of ilmenite samples were taken in 200 ml 15% HCl solution. The leaching solution was stirred by a magnetic stirrer. Care was taken to maintain similar stirring speed in all cases. Temperature of the leaching solution was controlled to the specified value and was continuously monitored by a thermometer. During leaching 5 ml of solution was taken after 2 hrs leached and was analyzed to determine iron content in the solution. This was used to determine the percentage of iron removed from the experimental samples. Method used for the determination of total iron from leached solution has been given in appendix-D and the method for the determination of total iron from the leached sample has been given in the appendix-C. After leaching for 2 hours the solution was cooled and filtered. The leached ilmenite was washed several times with water, dried in an oven at

110^0C for 2 hrs and analyzed. The leached sample gave a product with 2.57% iron and percentage of iron removal is 96.61%. The main reactions taking place during leaching are

$$Fe + 2HCl \rightarrow FeCl_2 + H_2$$

$$FeO + 2HCl \rightarrow FeCl_2 + H_2O$$

i.e. iron present in the reduced ilmenite as metallic and ferrous form should get dissolved in the acid with the formation of chloride.

Fig. 4.46 Scanning electron micrograph of reduced leached ilmenite
(Leached at 75°C, 2hr. at 15% acid solution)

The SEM picture of synthetic rutile i.e. the product obtained after leaching the reduced ilmenite for 2 hr at 75°C is given in Fig. 4.46. The particle is completely porous throughout the body with the appearance of a beehive. The globular structures seen on the surface of the reduced ilmenite had disappeared during leaching. As the soluble material in the particle was iron, it may be an indication that most of these structures consisted of iron. SEM spot analysis study of the leached particle showed the absence of iron on the surface while there was a high concentration of iron on the surface of the reduced particle before leaching. This means that during leaching all the iron on the surface was dissolved out. The experiment shows that it is possible to leach the metallic iron present in the Teknaf reduced ilmenite with hydrochloric acid.

4.6.3 Optimum reduction condition for maximum leaching of iron

After examining the feasibility of leaching of reduced ilmenite in hydrochloric acid solution first series of leaching experiments was carried out by using ilmenite that was reduced at different temperature for different time.

The quantities of metallic iron and ferrous iron were different in the samples reduced for different periods of time at various temperatures. These samples were subjected to leaching to check whether complete reduction was required for the preparation of synthetic rutile with minimum iron content.

First series of leaching experiments were carried out with a sample reduced at 1050^0C for different period of time. In each case leaching experiments were carried at 75^0C in 15% HCl soln. for 1hr. The percentage of iron removal is plotted as a function of time of reduction in Fig. 4.47. Percentage removal of iron was calculated by the following relationships [George, 1987].

$$\% \text{ Iron removal} = \frac{\text{Iron removed} \times 100}{\text{Total iron content before leaching}}$$

The iron content of the as-received ilmenite before leaching was 42.43% and after leaching gave a product with 39.20% iron, which means that only about 7.61% of iron could be removed by directly leaching with acid under this condition.

The sample reduced for 1hr before leaching gave a product with 20.48 % iron after leaching against an iron content of 42.77% before leaching. With the increase of reduction time iron removal on leaching was enhanced. From the experimental results it was evident that reduction of the sample before leaching enhanced iron removal. It was also evident from the experimental results that complete reduction of iron favored the maximum removal of iron on leaching.

Fig. 4.47 shows the removal of iron from the sample reduced for different periods. On leaching removal was about 52% for the sample reduced for 1 hr,after which it sharply rose up to 78% for 2 hrs. reduced sample,88% for 3 hrs. reduced sample 95.97% for 4 hrs. reduced sample and 96.07% for 5 hrs. reduced sample. Between 4 and 5 hrs reduced sample the removal was marginal, which showed that there was a stabilization of iron removal at this region. Which indicate that reduction time more than 4 hrs did not have any major influence on leaching.

Hence it was concluded that 4 hrs of reduction at 1050^{0}C when most of the iron (87.39%) reduced to metallic state was the most favorable condition for the maximum removal of iron on leaching.

Next series of leaching experiments were carried out using ilmenite samples reduced at different temperatures for 2 hrs and 4 hrs. Fig.4.48 is a plot of percentage removals of iron vs. reduction temperature. Sample reduced at 800^{0}C and900^{0}C for 2 hrs after leaching the percentage of iron removal was 12.12% and 46.84% respectively

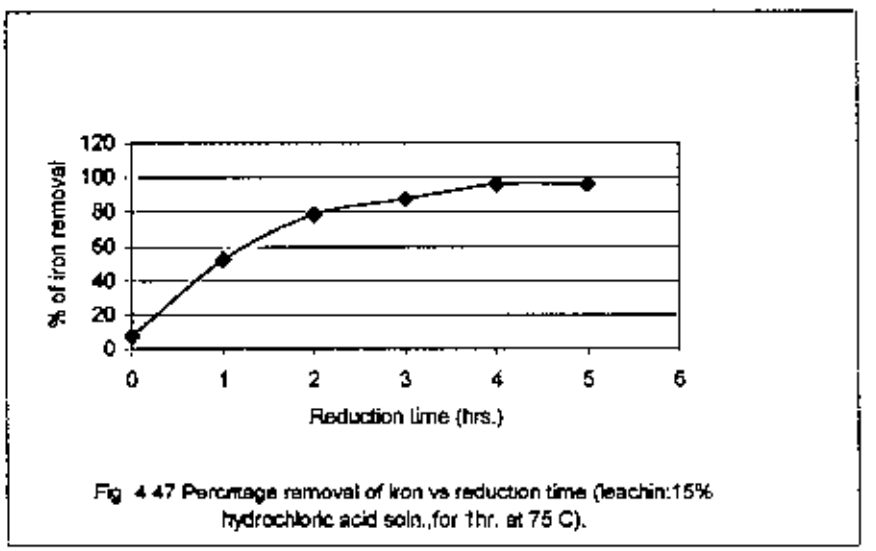


Fig 4.47 Percentage removal of iron vs reduction time (leachin:15% hydrochloric acid soln.,for 1hr. at 75 C).

As the reduction temperature increased, the percentage of iron removal from the sample with a value of 87.54% at 1050^{0}C and 87.73% at 1100^{0}C for the sample reduced for 2 hrs. In the case of sample reduced for 4 hr the percentage of iron removal was 18.65% at 800°C, 67.85% at 900°C, 95.97% at 1050°C and 96.01% at 1100°C. From the Fig. 4.48 it was evident that the iron removal of 4 hrs reduced and leached sample at any temperature was higher than the samples leached after 2 hr reduction. From 800-900^{0}C, the iron removal was limited, after which there was a sharp rise up to 1050^{0}C; getting slowly stabilized afterwards in the case of 4 hrs reduced samples. In the case of samples reduced for 2 hrs at temperatures up to 900^{0}C the iron removal was very slow. There was a fast increase for the sample reduced at 1050^{0}C after which the effect of temperature was negligible. Complete stabilization was observed at about 1050^{0}C. From the previous experiments (Fig 4.47) it was also observed that maximum removal of iron took place in the case of 4 hrs reduced sample at 1050^{0}C. Hence all the leaching experiments were carried out with a sample reduced at 1050^{0}C for 4 hrs.

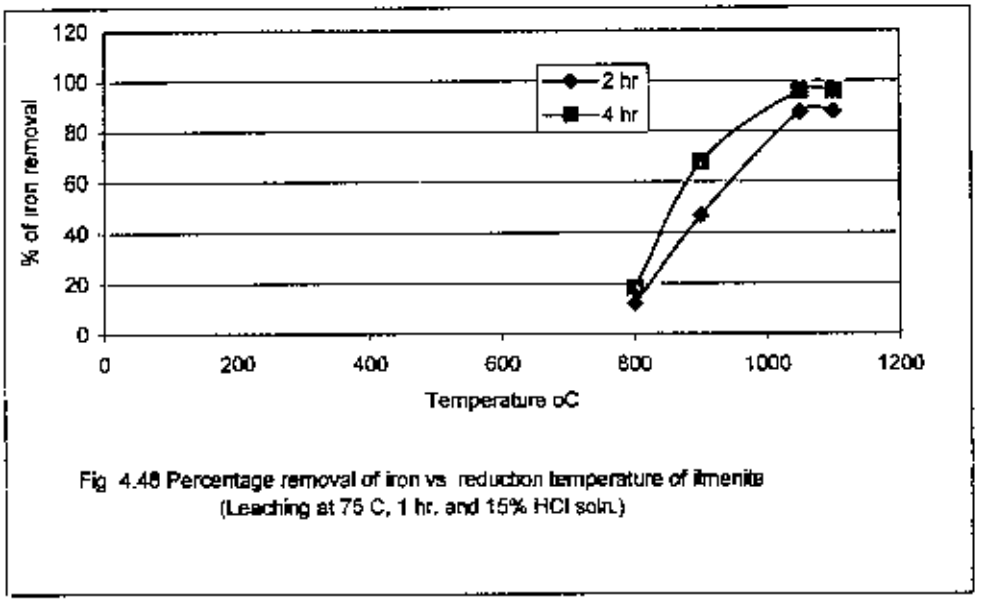


Fig 4.48 Percentage removal of iron vs reduction temperature of ilmenite (Leaching at 75 C, 1 hr. and 15% HCl soln.)

4.6.4 Optimization of leaching Condition

From the previous experiment (Fig. 4.47) it was evident that it is possible to leach out iron from the reduced Teknaf ilmenite. Next series of experiments were taken up to optimize the leaching conditions. The sample used for this purpose was reduced at 1050°C for 4 hr.The major factors that affected leaching are time of leaching, temperature of leaching and concentrations of acid in the leaching solution.. To optimize one parameter the other two were kept constant during the experiments.

Optimization of leaching time:

It was observed (Fig. 4.47) that about 96% of iron could be removed from reduced ilmenite on leaching for 1 hr at 75°C in a leaching solution in which the concentration of HCl was 15%. For optimization of the leaching time, the temperature was kept constant at 75°C and the acid concentration was maintained at 15% and time was varied from 10 min to 2.5 hrs. Experiments were carried out for each time interval with fresh sample and fresh acid and were not a continuation from the previous one. After leaching for specified time the percentage of iron in solution was calculated. The percentage removal of iron was plotted against time of leaching (Fig 4.49). The reduced ilmenite before leaching had an iron content of 43.78%. The iron removal percentage is 93.39% after leaching for 10 minutes. The dissolution was slow after 30 minutes. After that there was no major effect of time on leaching. The curves becomes flat after about 30 minutes.

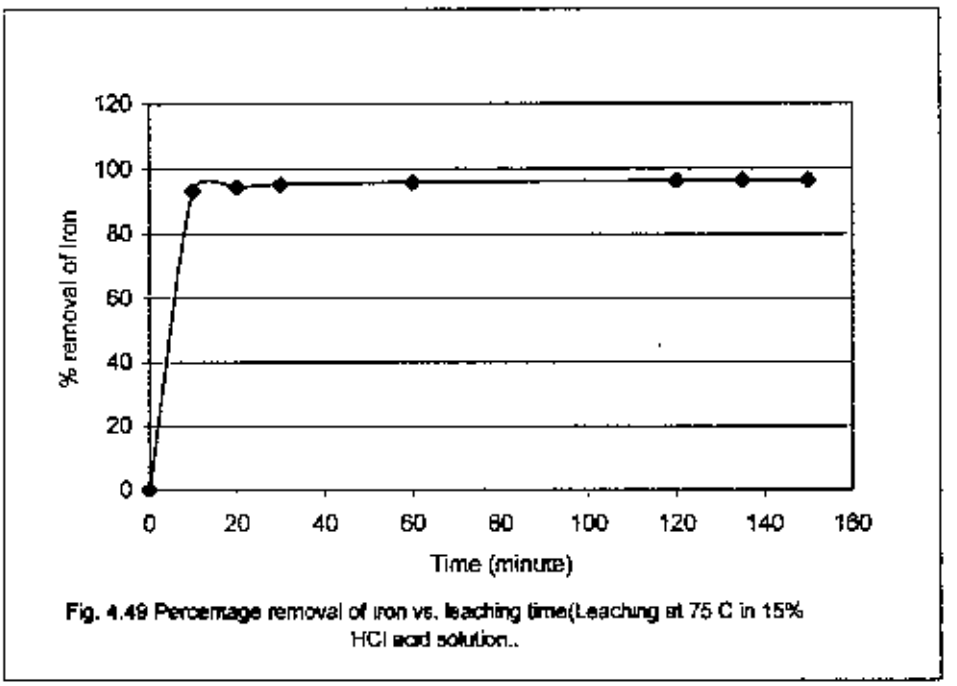
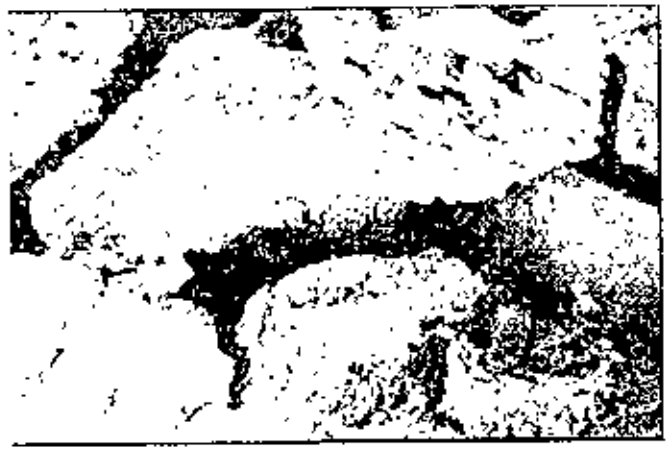


Fig. 4.49 Percentage removal of iron vs. leaching time(Leaching at 75 C in 15% HCl acid solution..

The reaction then becomes slow, as most of the iron had been removed in the first 10 minutes itself. The faster dissolution of iron in the initial period could be due to the removal of iron rich surface and formation of pores in large numbers. The percentage of iron removal 95.39% for 30 minutes and it increases slowly up to 96.61% for 2 hrs. leaching. After that the percentage of iron removal was marginal. From the figure 4.49 it was evident that the percentage of iron removal curve after 2 hrs. leaching is flattened. So it can be concluded that removal of iron got stabilized after 2 hrs. leaching after which the effect of time on leaching in terms of iron removal was negligible or practically nil. The scanning electron micrograph of leached ilmenite is shown in Fig.4.50. The Fig. shows that the particles are completely porous throughout the body with the appearance of beehive. It is also evident from the figure that the porousness of the leached sample increases with the increase of leaching time. From these experimental results it is evident that a leaching time of 2 hrs was favourable for maximum removal of iron.



(a)

(b)

(c)

Fig. 4.50 SEM of as received reduced leached ilmenite (leached at 75°C in 15% acid soln.)
(a) Leached for .50 hr.
(b) Leached for 1 hr.
(c) Leached for 2 hr.

Optimization of leaching temperature:

To optimize leaching temperature experiments were carried out keeping the acid concentration and time of leaching constant at 15% (V/V) and 2 hrs respectively and varying the leaching temperature with an accuracy of $\pm 2^0$C from 30 to 85^{0}C. Fresh reduced samples and acid were used at every temperature.

The percentage removals of iron as a function of temperature are plotted in Fig 4.51. The percentage removal of iron at 30°C is 93.12% while at 60°C it increases to 95.97%. It reached a value of 96.61% at 75°C after which the value remained more or less constant up to 85^{0}C. The scanning electron micrograph (Fig. 4.52) shows that the leached particles are completely porous throughout the body with the appearance of beehive. It is also evident from the figure that with the increase of leaching temperature the porousness of the surfaces of the leached sample increases.

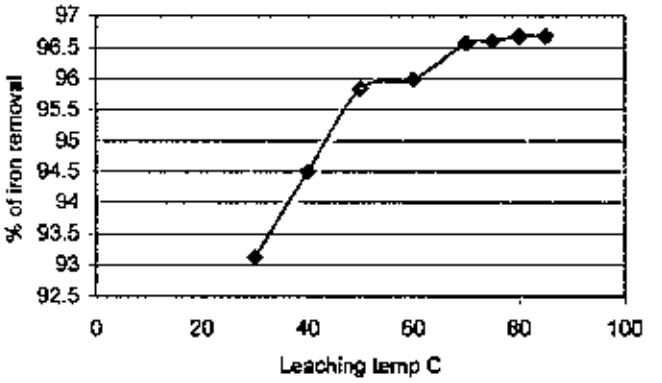
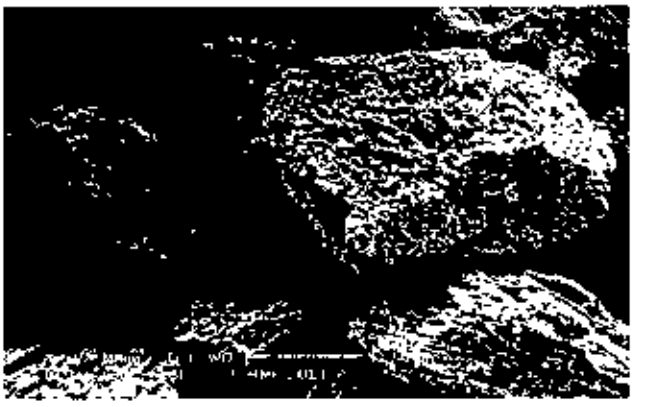
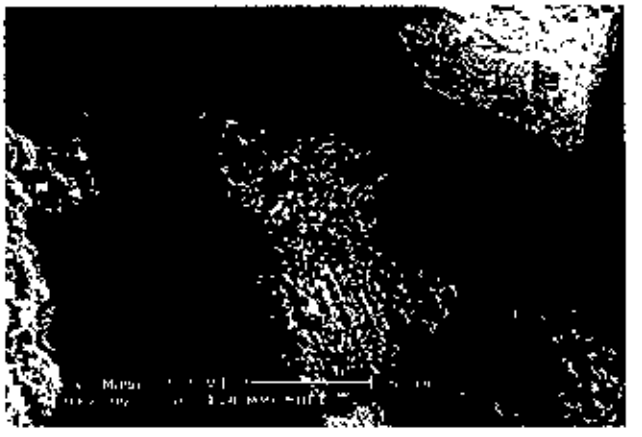


Fig. 4.51 Percentage removal of iron vs. leaching temp.
(leaching 15% Hcl soln , 2hrs)

It is also established fact that long time leaching with dilute acid even at room temperature was sufficient for removing most of the iron present in ilmenite. However studies were not carried out at temperatures below 30^{0}C as this would not be having any practical application. From the flat portion of the graph after 75^{0}C it could be concluded that removal of iron got stabilized at 75^{0}C after which the effect of temperature on leaching in terms of iron removal was negligible or practically nil. However the temperatures of 75-80^{0}C was taken as optimum at leaching time of 2 hrs with 15% HCl.solution.



(a)



(b)

(c)

Fig 4.52 SEM of as received reduced leached ilmenite (leached for 2 hrs. in 15% acid soln.)

(a) Leached at 30°C
(b) Leached at 50°C
(c) Leached at 75°C

Optimization of acid concentration:

Studies for the optimization of acid concentration were carried out keeping the time and temperature constant at 75°C and 2hrs respectively. Reduced ilmenite samples were leached with hydrochloric acid of different concentrations between 1 to 30% (V/V). Leaching with 1% HCl about 17.31% iron removed from the sample but with 5% HCl most of the iron was removed giving an iron content of 2.67% in the leached sample. With an increase of acid concentration the rate of iron removal increased slowly reaching a value of 96.61% for 15% after which the effect was very marginal. However it should be noted that even with very dilute hydrochloric acid solution major portion of iron could be removed in 2 hrs time. From the Fig 4.53 (which shows the percentage removal of iron versus concentration of acid). it is clear that about 97% of iron could be removed using 15% acid solution. The scanning electron micrograph of the sample leached at different acid concentrations are shown in Fig. 4.54. The figure shows that the leached particles are completely porous with the appearance of beehive. It is also evident from the figure that with the increase of acid concentration the porous ness of the surfaces of the leached sample increases.

The percentage removal of iron from the reduced mass increased slowly as the concentration of acid increased from 5 to 15 percent and after 15% the increase is marginal, which means that under these condition an increase of acid concentration from 15-30% did not have any major advantage. Hence it could be concluded that the optimum concentration of HCl that should be used to leached reduced ilmenite should be 15% (V/V) at 75°C and 2 hrs.

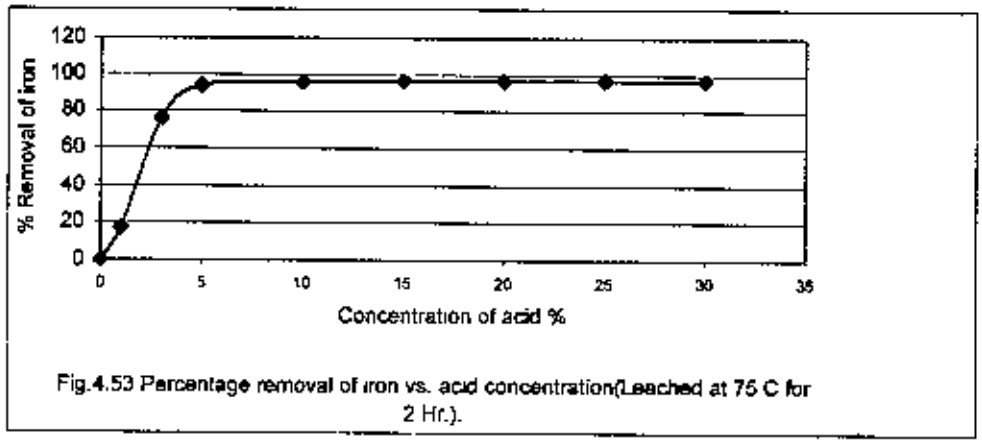
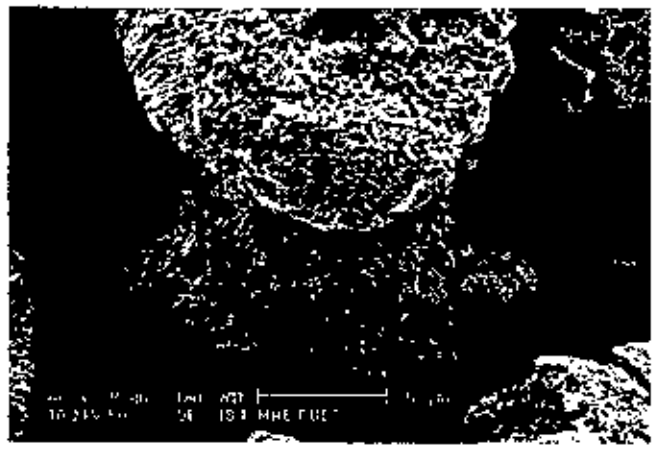


Fig.4.53 Percentage removal of iron vs. acid concentration(Leached at 75 C for 2 Hr.).

(a)



(b)

(c)

Fig. 4.54 SEM of as received reduced leached ilmenite (leached at 75°C for 2 hr.)
(a) Leached in 5% HCl acid solution.
(b) Leached in 10% HCl acid solution.
(c) Leached in 15% HCl acid solution.

4.6.5 Leaching behavior study

To study the leaching behavior of prior oxidized reduced ilmenite containing 44.16% total iron and as received reduced ilmenite containing 43.78% total iron in the sample were used. The sample used for this purpose was reduced at 1050°C for 4 hr. in both cases. The major factors that affected leaching behavior were time of leaching, temperature of leaching and concentration of acid, for studying one parameter the other two were kept constant.

Effect of time on leaching:

Effects of time on the rate of leaching of ilmenite in 10% acid concentration, reduced in the as received and in the oxidised conditions are shown in Figs. 4.55 and Fig. 4.56 respectively. It can be seen from these figures that, at all temperatures investigated, the rate of leaching is very fast at the initial stages of leaching. It can also be seen that the rate of leaching is faster at higher temperatures. This is to be expected. The rate of leaching decreases rather rapidly and the curve becomes almost flat in a short period of leaching, after which the rate of removal of iron from the sample is negligible. Fig.4.57 also shows that in all cases leaching is faster in the samples reduced after oxidation and also more iron is removed from ilmenite leeched after reduction in the oxidized condition than from ilmenite leached after reduction in the as-received condition. This is because of the fact that the oxidation of samples produces micro cracks [Rao and Rigaud, 1974] at the surface of the particles as a result contact surface area increase. Thus, the leaching of sample reduced in the as received condition progressed at a slower pace than the sample reduced after oxidation.

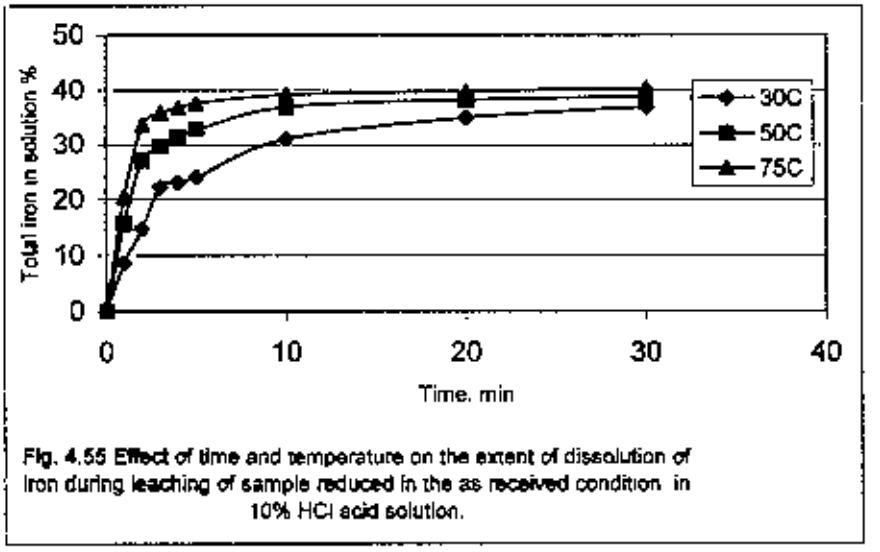


Fig. 4.55 Effect of time and temperature on the extent of dissolution of iron during leaching of sample reduced in the as received condition in 10% HCl acid solution.

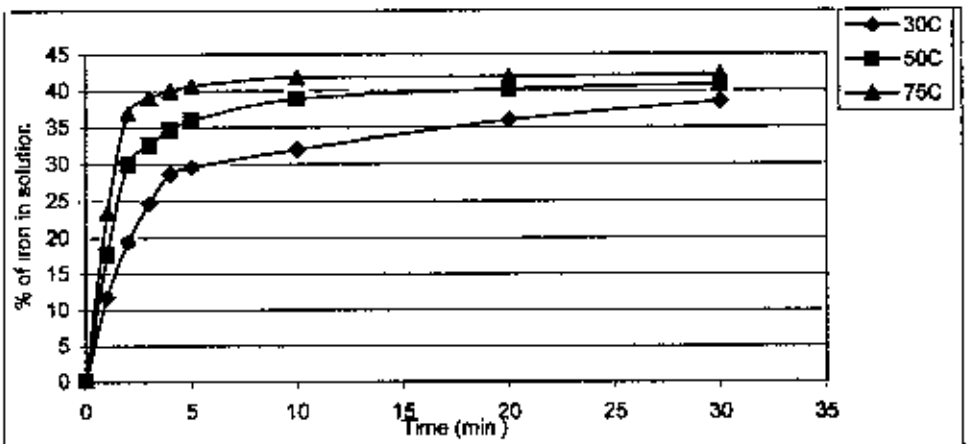


Fig. 4.56 Effect of time and temperature on the extent of dissolution of iron during leaching of sample reduced after oxidation in 10% acid solution.

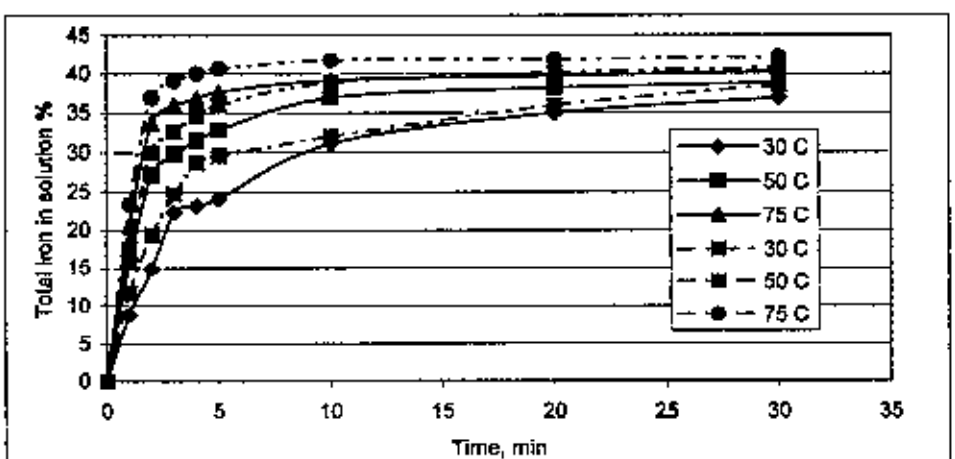


Fig. 4.57 Comparison of extent of dissolution of iron from samples reduced in the as received and oxidised conditions in 10 % HCl at specified temperature.

Effect of Temperature:

The effect of temperature on the rate of leaching of ilmenite reduced in the as received and in the oxidized conditions are shown in Fig.4.57.It can be seen from the figure that removal rate (total iron in solution) of iron increases with an increase in temperature. The rate of leaching gradually decreases with time. The figure also shows that the rate of leaching is (total iron in solution) enhanced by oxidation prior to reduction.

Effect of acid concentration:

The effect of acid concentration on the rate of leaching of ilmenite reduced in the as received and in the pre-oxidized conditions are shown in Figs. 4.58 and 4.59 The figures show that in the both cases the rate of removal of iron from the reduced ilmenite increases with an increase in the concentration of the acid. Fig.4.60 shows that at all concentrations of the acid, the sample reduced in the oxidised condition has less iron than that reduced in the as-received condition

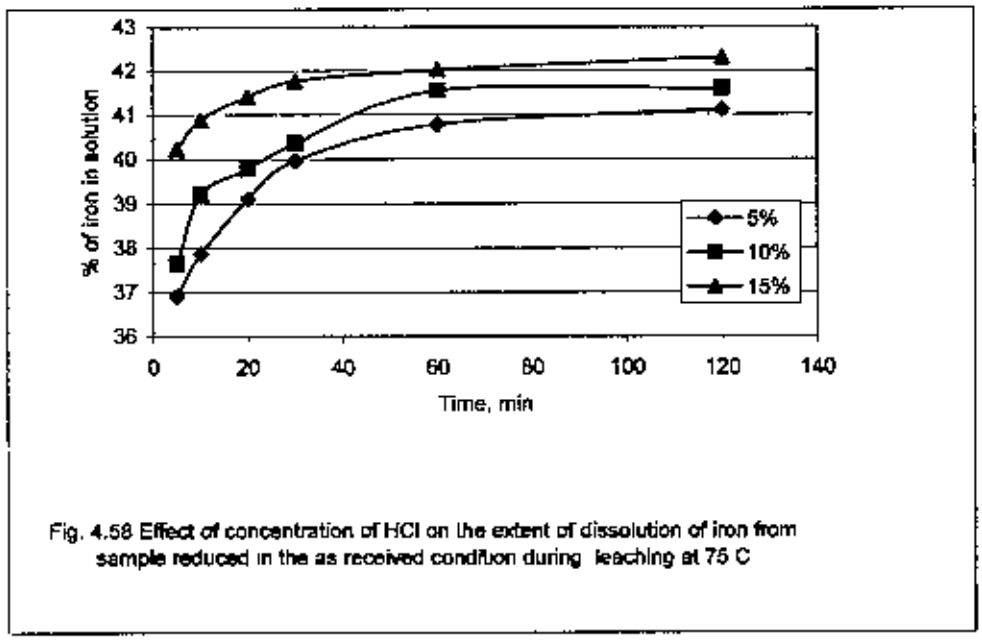


Fig. 4.58 Effect of concentration of HCl on the extent of dissolution of iron from sample reduced in the as received condition during leaching at 75 C

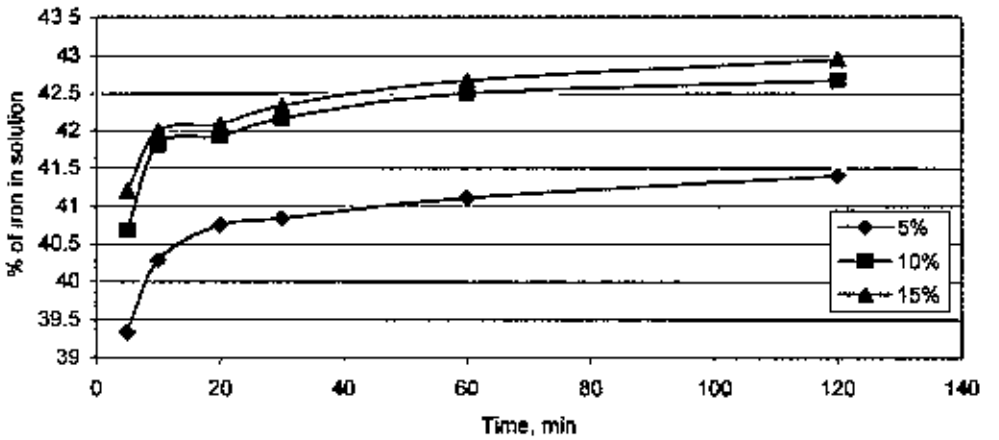


Fig. 4.59 Effect of concentration of HCl acid on the extent of dissolution of iron during leaching at 75 C from the sample reduced after oxidation

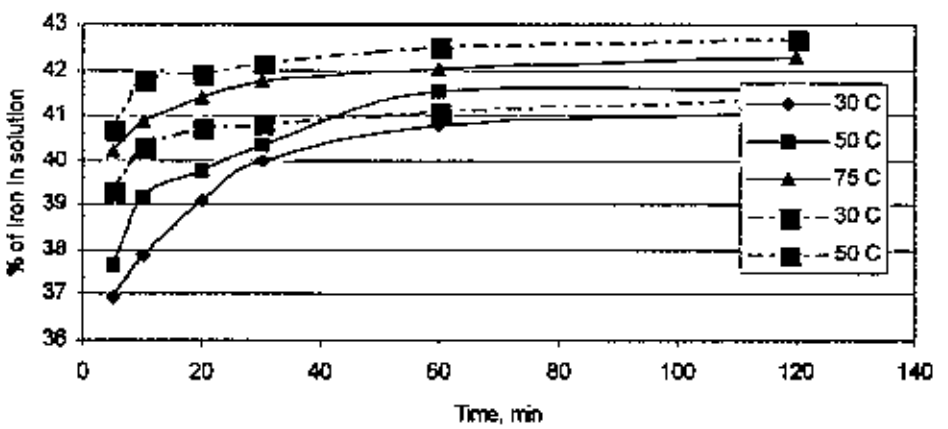


Fig. 4.60 Comparison of extent of dissolution of iron for thesample reduced in the as received condition and after oxidation during leaching with HCl of different concentrations at 75 C

4.7 Identification of reaction mechanism:

Kinetic studies are aimed to determine the influence of various process parameters on a reaction and also to explain the reaction mechanism. When a kinetic law is established and the variation of the rate constant with temperature is studied then it becomes possible to obtain a value of activation energy, which indicate the reaction mechanism. This, however, requires some mathematical procedures.

To identify the mechanism of leaching reaction the so-called reduced time plots were used. The identification of the kinetic model constitutes an important step in the analysis of many metallurgical reactions. In many cases a preliminary identification is possible by using the so-called reduced time plots. The kinetic relationships are first expressed in terms of the degree of reduction α, which may be defined as:

$$\alpha = \frac{\text{Weight of iron in solution}}{\text{Weight of total iron in sample}}$$

It can be seen that three commonly suggested models such as first order, sherical reaction and Ginstling- Brounshtein reaction for iron dissolution in acid solution. The equations of the above- models are as follows.

1. First order reaction:
   $F_1 = g(\alpha) = -\ln(1-\alpha) = kt$

2. Kinetics controlled by chemical reaction (spherical reaction)
   $R_3 = g(\alpha) = [1-(1-\alpha)^{1/3}] = (k/r_2)t$

3. Kinetics limited by diffusion through the product layer (Ginstling- Brounshtein reaction):
   $D_4 = g(\alpha) = 1-2/3\,\alpha - (1-\alpha)^{2/3} = kt$

Fig. 4.58 and Fig.4.57 show the plots of α versus leaching time at temperatures 30°C, 50°C and 75°C for oxidized reduced and then leached and reduced as received and then leached ilmenite respectively. From these plots, the time taken for a 50 percent reduction, indicated by $t_{0.5}$, at different leaching temperatures were obtained. Then reduced time plots, i.e. α versus $t/t_{0.5}$, were plotted, Fig.4.61 and 4.62.

It can be seen in Fig.4.61 that among the three suggested models, the kinetics of leaching after reduction in the oxidized state fits the first order reaction up to a value of α of 0.5 only.

This implies that during the initial period of leaching the reaction occurs randomly. Such a situation prevails when (i) the solid is so porous that the fluid can penetrate freely within the solid and there is no resistance to diffusion, (ii) the reaction is not restricted to a core/product interface and (iii) the reaction occurs randomly and the rate is proportional to the unreacted mass.

This situation is supported by the fact that oxidation produces a large number of micro-cracks in the grains of oxidized ilmenite. After that the reaction mechanism changes and the kinetics appear to be limited by diffusion through the less iron rich surface layer. When 50 per cent of the reaction is completed, the reaction mechanism changes and the reaction follows spherical model. In this case, leaching of iron becomes slow, as most of the iron had been removed and the kinetics appears to be limited by diffusion through the less iron rich surface layer.

The plots of α versus $t/t_{0.5}$ for samples leached after reduction of as received ilmenite is shown in Fig. 4.62. It shows that the reaction follows spherical model. The diffusion controlled spherical reaction model seems to be the most appropriate one to fit the result. The sample in this case did not contain any cracks so leaching progressed slowly and the kinetics appears to be limited by diffusion through the product layer.

4.8 Evaluation of activation energy

Both the conventional integral approach and differential approach were considered to evaluate the activation energy (E) of the leaching reaction.

Integral Approach:

During isothermal kinetic studies the progress of a reaction is generally measured in terms of degree of conversion on dissolution, which is expressed as, α and the value of α varies from zero to unity. Values of α are plotted against time (t) for the given temperatures. Subsequently these data are fitted into an appropriate form of integrated kinetic equation. In the integral expression of kinetic equations an appropriate function of α, G(α), is shown to be proportional to time (t). In this method, the reaction rate constant k of various temperature were obtained from the linearsed plots of G(α) versus time (t).

The reaction rate constants, k, at various temperatures for oxidized and reduced samples obtained from the linearised plots, Fig. 4.63

The rate constant was then plotted against temperature according to Arrehenius type equations. [Fig. 4.65. Hence a plot of lnk against 1/T should give a straight line. The slope of this straight line equals, E/R, where E is the activation energy and R is the ideal gas constant. The apparent values of activation energy for leaching of oxidized and reduced ilmenite was estimated to be 16 kJ/mol. Similar plots for reduced ilmenite without oxidation are given in Fig.4.64 and Fig. 4.66 and the activation energy was estimated as 23 kJ/mol.

Differential Approach:

In the differential approach, t_α, the time required for a given value of α was calculated first and then plots of In t_α against temperature (1/T) is a straight line whose slope is –E/R. Plots of ln t versus 1/T have been plotted for oxidized reduced leached sample and as-received reduced and leached samples. These plots are shown in Figs. 4.67 and 4.68 respectively. As before, the slopes of these curves equal –E/R. .For oxidized and reduced samples, the activation energy of leaching was estimated in the ranges of 13 to 17 kJ/ mol. for α values of 0.10 to 0.50. On the other hand, for non-oxidised and reduced samples, the activation energies were estimated in the range of 17 to 23 kJ/ mol for α values of 0.10 to 0.50. Thus the activation energy values obtained by the two approaches are nearly identical. This result also explains why the extraction of iron is larger in the case of oxidized ilmenite samples. This may be taken as evidence to support the kinetic mechanisms identified for the two sets of samples. Besides, a marked increase in the values of activation energy beyond α =0.5 is clearly noticeable in Fig.4.67. This is also indicative of a change in the reaction mechanism at that point from first order to spherical for oxidized and reduced samples.

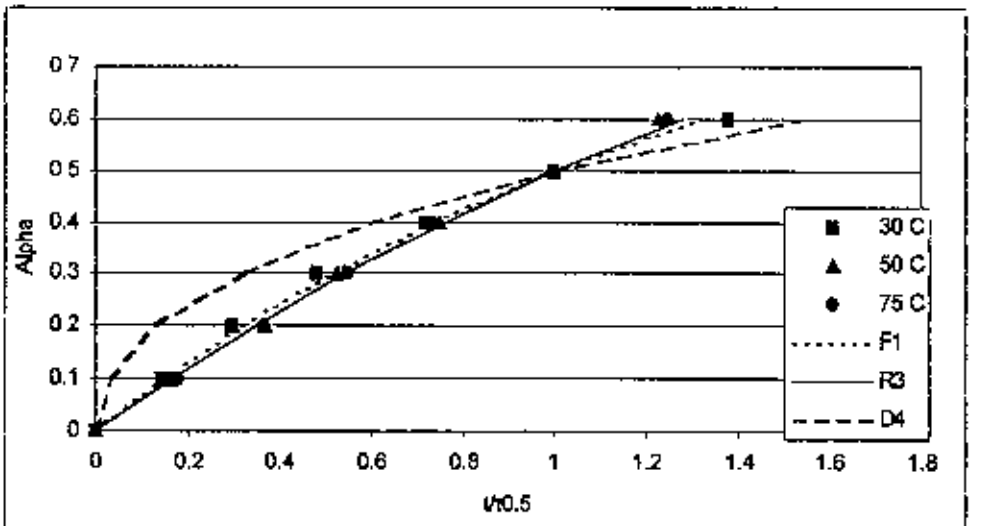


Fig 4.61 Leaching time plot for isothermal kinetic data.

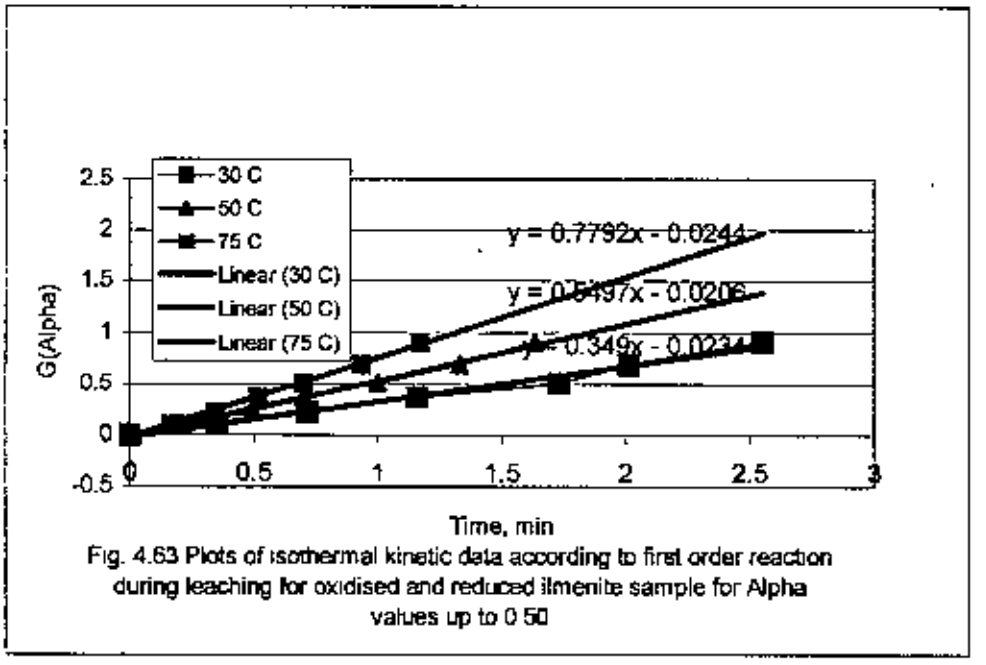


Fig. 4.63 Plots of isothermal kinetic data according to first order reaction during leaching for oxidised and reduced ilmenite sample for Alpha values up to 0.50

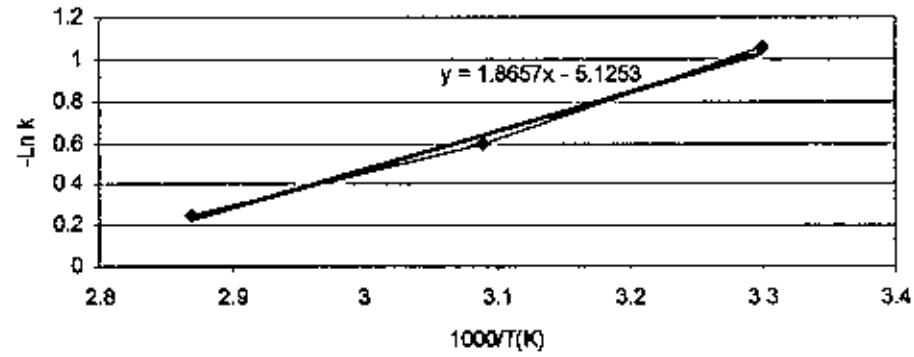


Fig. 4.65 Arhenius type plot for kinetic data of Fig. 4.58

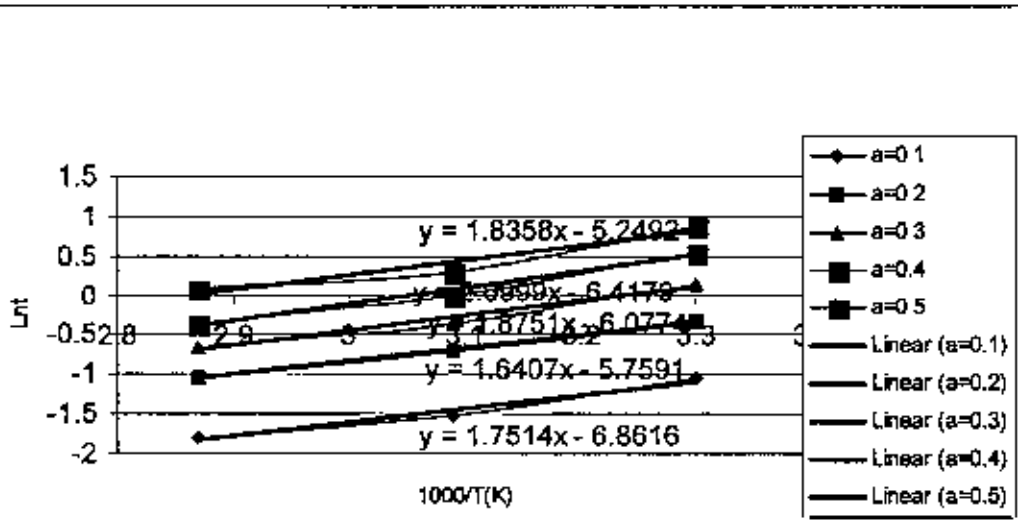


Fig.4.67 Plots for calculation of apperent activation energy of leaching using differential approach for oxidised and reduced ilmenite sample leached with 10 % hydrochloric acid.

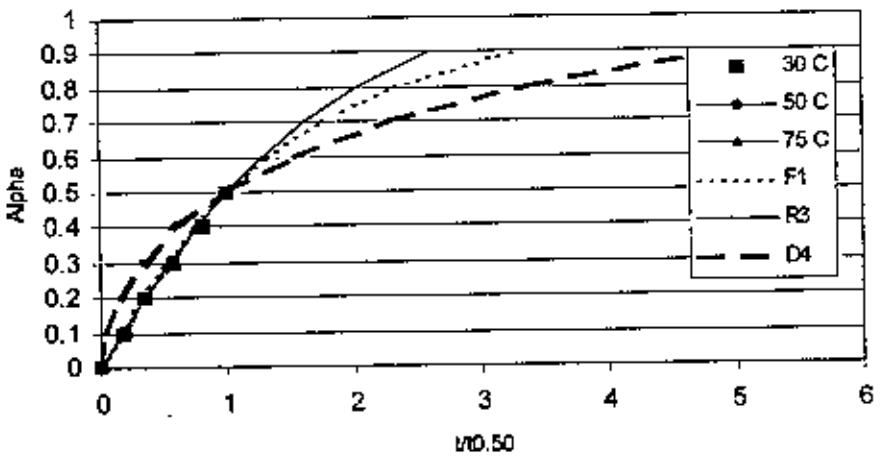


Fig. 4.62 Leaching time plot for isothermal kinetic data shown in Fig. 4.57

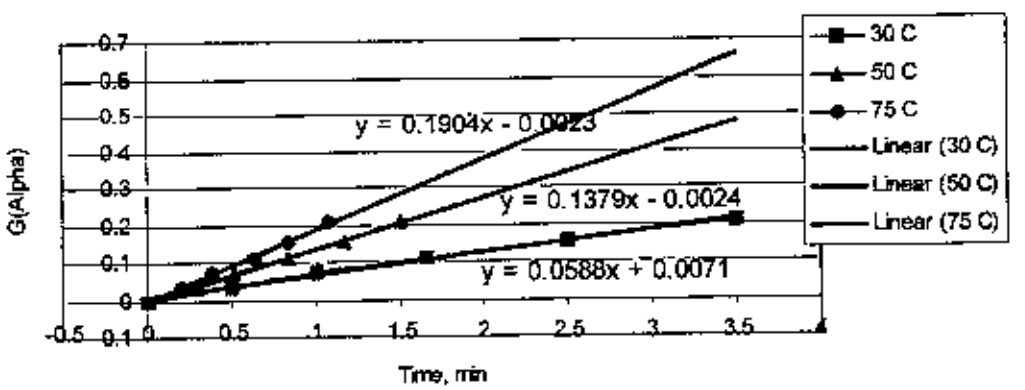


Fig. 4.64 Plots of sothermal kinetic data according to spherical reaction model reaction during leaching for as received reduced ilmenite

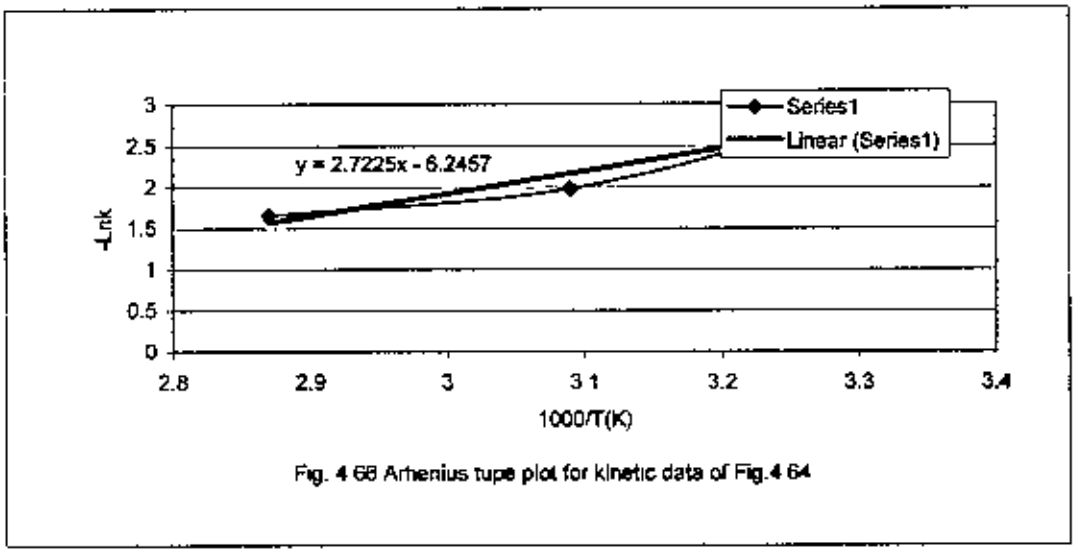


Fig. 4 68 Arhenius tupe plot for kinetic data of Fig.4 64

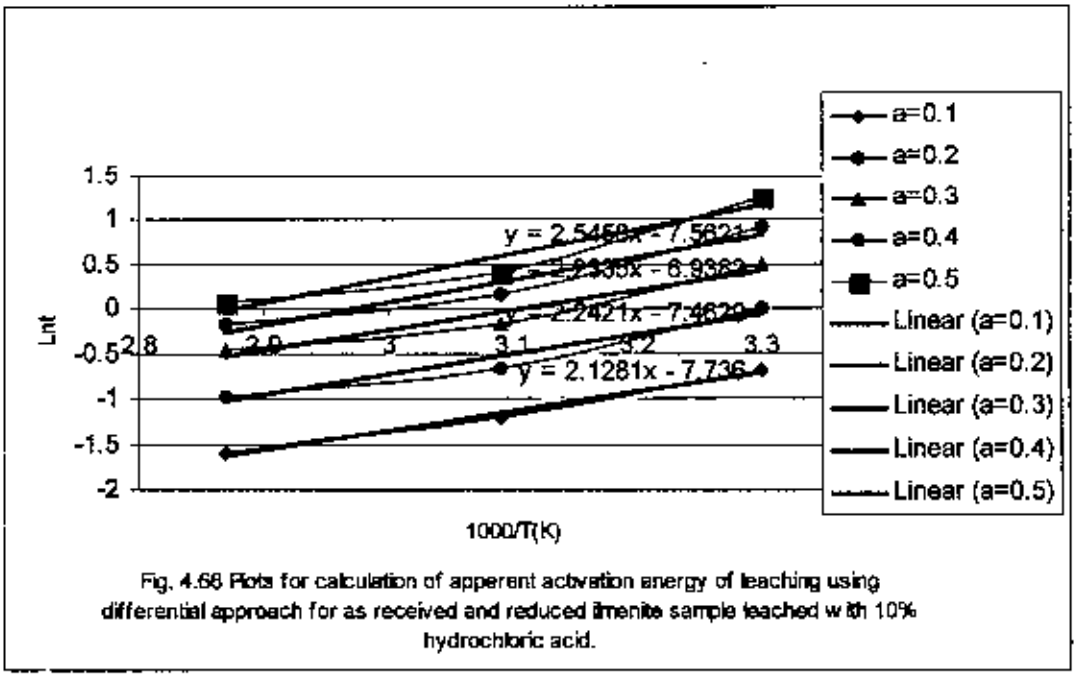


Fig. 4.68 Plots for calculation of apperent activation energy of leaching using differential approach for as received and reduced ilmenite sample leached w ith 10% hydrochloric acid.

4.9 Comparison of the leached Products

From the earlier investigation it was concluded that the sample reduced at 1050°C for 4 hr is the suitable for maximum removal of iron on leaching. It was also observed that the optimum time, temperature and acid concentration for maximum removal of iron from the reduced sample is 2 hour at 75°C in 15% acid solution.

A leached sample was prepared followed by the above conditions. The leached sample was subjected to wet chemical analysis to check the purity of the materials. The leached sample contained most of the impurities present in the raw material in small quantities. Iron content 2.57% for as received reduced and 2.18 for oxidized reduced leached sample and TiO_2 content 90.45 % for as received reduced leached and 91.50% for oxidized reduced leached sample. In general, it can be stated that Teknaf leached products prepared by this oxidation-reduction-leach route is equally good if not better than the commercially available synthetic rutile sample. A sample reduced at 1100°C for 4 hr. also leached in 15% acid solution at 75°C for 2 hr. followed by chemical analysis. The analysis shows that the TiO_2 content of the sample was 89.78%. The presence of less TiO_2 in the sample reduced at 1100°C probably due to the fact that during reduction at higher temperatures a small amount of TiO_2 is also reduced to lower oxides of titanium. Similar results were also obtained by Grey and Reid [1974]

Table 4.7 Comparison of the reduced leached products.

Component	Reduction temperature	Without oxidised	Pre-oxidised
Fe%	1050°C	2.57	2.189
TiO_2 %	1050°C	90.45	91.50

Fig.4.69 shows comparison of the x-ray diffraction pattern of as received reduced and pre-oxidised reduced leached ilmenite. These patterns show the presence of rutile phase only and some unknown phases. These unknown phases may be complex phases of Fe, Mn, Al and SiO_2. It did not show the presence of metallic iron or ilmenite.

The scanning electron micrograph of a synthetic rutile sample prepared at optimum conditions of oxidation-reduction-leaching condition is given in Fig: 4.70. The particle was highly porous with a pore size of a few microns. However, the particle sizes decreased during leaching which could be due to crumbling of the reduced ilmenite particles.

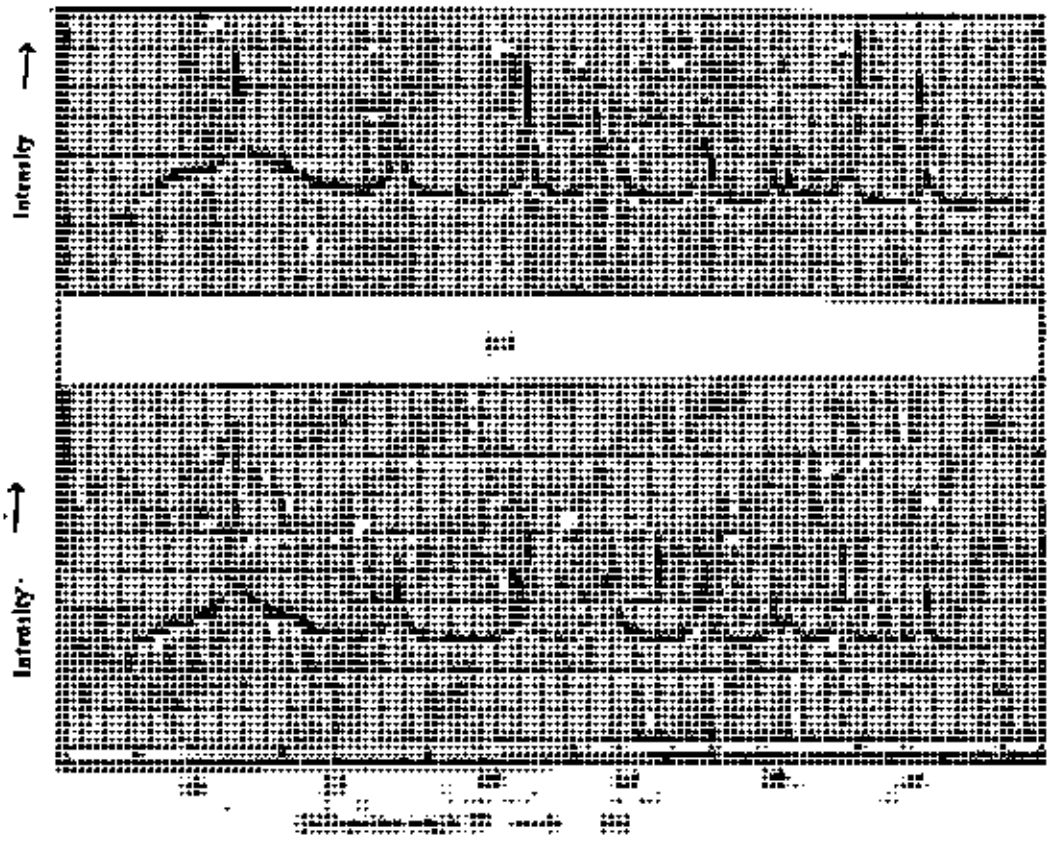
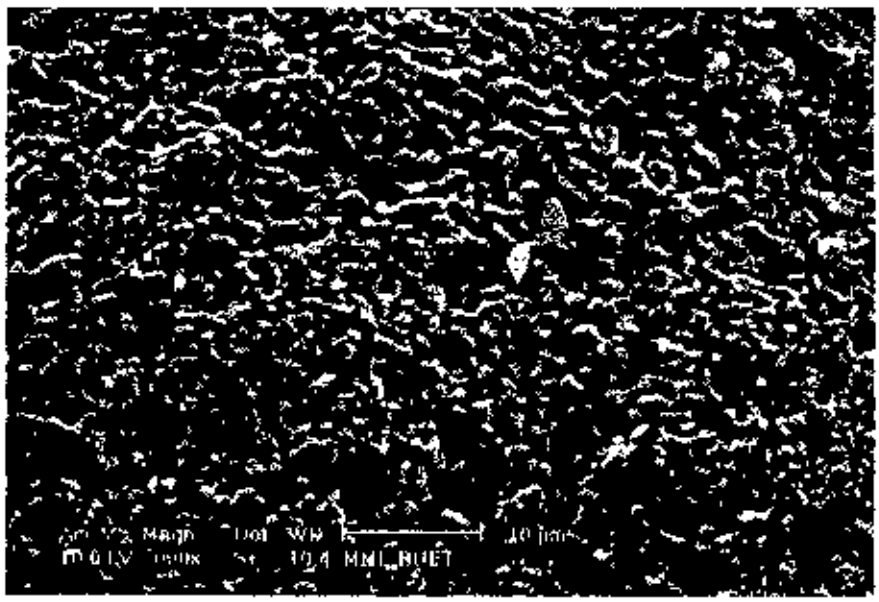


Fig. 4.69 X-ray diffraction patterns of leached ilmenite (leaching condition: 15% HCl soln. at 75°C for 2 hrs.)
(a) AS received reduced and leached.
(b) Oxidized reduced and leached.

(a)



(b)

Fig. 4.70 EM of pre-oxidised reduced leached ilmenite (leached at 75 °C for 2hrin 15% HCl acid solution)

(a) SEM magnification X 350

(b) SEM magnification X 2000

Chapter 5

SUMMARY AND CONCLUSIONS

5.1 Introduction

Investigations were carried out to characterize Teknaf ilmenite in the process of its up gradation into synthetic rutile. Bangladesh ilmenite produced at Cox's Bazar pilot plant contains about 40 percent TiO_2 together with a large amount of iron in the form of oxides, silica and trace element like calcium, zinc, nickel, manganese, chromium, magnesium, copper etc. As a result this valuable mineral, separated from the beach sands of Bangladesh could not find any market in Bangladesh or else where. To make this mineral commercially significant, the TiO_2 content must be increased. From the different techniques available for the up gradation of low grade ilmenites, oxidation-reduction leach route was selected, as it is simple and easy to manipulate when compared with other techniques available for up gradation. As a part of this programme it was decided to study the oxidation-reduction and leaching of ilmenite, the product Morphology, and the mechanism of each process. The results obtained were compared with those obtained during reduction of Teknaf ilmenite in the reduced leached in the as received condition.

An attempt has also been made to understand the kinetics and mechanism of the leaching process. The following methodology was followed.

a) Characterization of raw ilmenite.
b) Optimization of oxidation parameter.
c) Optimization of reduction parameter.
d) Reduction behavior study.
e) Optimization of leaching condition in dilute hydrochloric acid.

5.2 Characterization of as received ilmenite

Chemical analysis of Teknaf ilmenite revealed that it contains a large amount of iron in the ferrous and ferric state.The content of as received ilmenite is ferrous iron 25.32%, ferric iron 32.53% and TiO_2 is 39.96%. It is also inferred from the atomic absorption analysis that it contains trace element i.e. Cr, Ca, Cu, Mg, Mn, Zn, Ni etc. X-ray diffraction pattern shows that ilmenite is the main phase; other phases of rutile, pseudorutile, ferrous oxide and hematite could be detected. SEM of as received sample surface was more or less uniform in

appearance, having either pores or only micro pores. Anand and Gilks (1984) have noted that SEM of altered grains show massive irregular surfaces due to formation of pseudorutile while highly altered grains have very porous surface. More than 96 percent of Teknaf ilmenite was retained on US sieve no. 100, 140 and 200, individual amounts belongs to each sieve being 5.094%, 47.05% and 44.51% respectively.

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

The bulk of the (more than 96%) Teknaf ilmenite belongs to magnetic fractions separated at separation currents of 0.10 –0.30 amperes.

The content of ferrous oxide and ferric oxide was found to decrease with increasing current of separation. With increasing current of separation titanium oxide content was found to decrease. From the material balance it was found that more impurities are present in the magnetic fractions separated at higher currents.

TGA graph of different magnetic fraction showed a weight loss. Babu et al (1993) identified weight loss at a temperature near around 600^{0}C in the case of altered ilmenite. This decrease in weight loss indicates the presence of bound water. Naturally bound water increases as the degree of alteration increases, on the other hand pseudorutile structure actually contain hydroxyl ions. A partially altered deposit shows the coexistence of different phases, but complete alteration will lead to a predominantly rutile phase. The x-ray diffraction pattern of different magnetic fraction of Teknaf ilmenite also showed the presence of hematite, rutile and pseudorutile phase. That is Teknaf ilmnite have the co-existence of different phases. TGA reports of different magnetic fractions of Teknaf ilmenite indicate the presence of bound water. So it could be concluded that the Teknaf ilmenite is in a partially altered state but not hydrated enough.

5.3 Oxidation

Oxidation of ilmenite in the temperature range of 750^{0}C-950^{0}C has been performed. The extent of conversion of ferrous iron to ferric iron was determined by chemical analysis of the oxidized samples. The rate of oxidation was found to be very rapid at the initial stage and the rate diminished with time.

Optical micrographs of ilmenite oxidized at 750°C for 1hr is different from that of ilmenite oxidized above 850°C. The structure of ilmenite oxidized at 850°C is similar to that of ilmenite oxidized at 950°C. No significant difference could be identified from this micrograph.

From SEM of oxidized ilmentite it was observed that at higher temperature and longer time oxidation produces fine cracks were found in the grains of ilmenite. This is due to the fact that oxidation converts the single crystal of ilmenite to polycrystal array of pseudobrookite and rutile. X-ray diffraction studies showed that the product of oxidation at 750°C is pseudorutile, hematite and rutile and some unidentified phases. At 750°C pseudobrookite also formed with the increase of time. Pseudobrookite was found to have formed during oxidation at temperatures above 850°C. The proportion of pseudobrookite was found to increases with time for up to 1.5 hr and then remain more or less constant. The appearance of pseudobrookite can be expressed by the reaction.

$$3\ Fe\ Ti O_3 \rightarrow Fe_2\ Ti_3\ O_9 + {}^1/_2\ Fe_2O_3$$

On heating above 850°C pseudorutile transforms to pseudobrookite.

$$Fe_2\ Ti_3O_9 \longrightarrow Fe_2\ TiO_5 + 2TiO_2$$

The non-existence of pseudobrookite at lower temperature has been attributed to the fact that the rate of diffusion is slow at lower temperature, which prevents the formation of pseudobrookite. The decrease in the relative intensity of hematite suggests that pseudobrookite might also be formed by the reaction.

$$Fe_2O_3 + TiO_2 \longrightarrow Fe_2TiO_5$$

From the investigation of chemical analysis optical microcopy, scanning electron microscopy and x-ray diffraction analysis it can be inferred that the optimum time and temperature for oxidation of ilmenite is 1hr. at 950°C. The content of oxidized ilmenite at optimum condition is 0.5747% ferrous ion, 57.56% ferric iron and 40.71% total iron.

5.4 Reduction

To examine the feasibility of reduction of as received ilmenite with charcoal, reduction conditions selected were a temperature of 1050°C and a reduction time 5 hrs in presence of sufficient amount of charcoal. Ilmenite which was the starting material contained no metallic iron, while ferrous iron content was 25.32% with the balance of 32.53% in the ferric form undergone reduction during heating with the formation of 39.20% metallic iron. X-ray diffraction studies, SEM structure, and spot analysis of SEM showed that ilmenite could be reduced with charcoal.

The main parameters such as reduction time, temperature and ilmenite to coke ratio optimized.

Equal weights of ilmenite and coke were found to be necessary for maximum reduction of iron oxide in the ilmenite or in other words the optimum ilmenite to coke ratio was 1:1.

From the investigation of chemical analysis, optical microscopy, scanning electron microscopy and x-ray diffraction studies the optimum time and temperature for reduction is 4hr at 1050^{0}C.

5.5 Reduction behavior study

The prime concern of these experiments was to identify the most suitable condition for reduction. The optimum ilmenite to coke ratio and optimum time and temperature was used for all the reduction experiments. Reduction behavior study was carried out on the following different conditions.

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

The extent of reduction for a specified period was found to increase with an increase in the reduction temperature and also with an increase in time for a specified temperature. At all temperatures, the rate of reduction was found to slower after certain period with time of reduction. The decrease in the rate of reduction at a later stage may be attributed to be difficulty encountered by the gaseous species (CO and CO_2) to diffuse through the porous product layer consisting of iron and titanium di-oxide or to the decrease in the surface area available for reduction. The extent of reduction in as received ilmenite was found to increase significantly as the reduction temperature increases.

The higher extent of reduction at higher temperatures may be attributed to the fact that at higher temperatures carbon monoxide produced by the gasification of carbon of the charcoal becomes the main reducing agent while at lower temperatures solid carbon acts as the main reducing agent. Hasseb et al, [1997] investigated the reduction of Bangladesh ilmenite with charcoal and suggested that at lower temperatures 950-1000^{0}C the reduction of ilmenite proceeds via the solid-state reaction between carbon present in charcoal and ilmenite. They identified this model of reaction to be responsible for the slower rates of reduction at lower temperatures. At temperatures higher than 1000^{0}C, the reduction mechanism changes and is caused by CO in accordance with the Boudoured reaction. This change in mechanism increases the extent of reduction.

Effects of particle size on the extent of reduction:

The 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. The finer fractions contained higher percentage of iron oxide in ferric state, which may also increase the extent of reduction. On the other hand reduced samples of finer fractions contain higher amount of metallic iron. i.e. lower amount iron remained as oxide form. So from the point of view, optimization of reduction process, adaptation of separate reduction procedure for each of the size fractions may not be useful.

Extent of reduction of the magnetic fractions:

On reduction magnetic fractions separated at lower current were reduced to a higher extent than those separated at higher currents. It may be due to the higher ferric oxide content in four fractions, so it may be beneficial to reduction. But these four major fractions contain about 89% of the ilmenite sample. So it will not economical to develop a separate reduction techniques for the rest two. Moreover the actual extent of reduction of the different magnetic fractions did not show any significant difference. So the magnetic fractionation will not help to enhance the reduction process.

Effect of prior oxidation on the extent of reduction:

The extent of reduction of ilmenite in the as received and in the oxidized conditions have been studied. It can be seen that the rate and also the extent of reduction of iron oxide to metallic iron is higher in samples reduced in the oxidized condition than in the samples reduced in the as received condition. The oxidation of Teknaf ilmenite converts almost all the ferrous iron in ilmenite to ferric iron. This alters the mechanism of reduction. Moreover the generation of cracks in the oxidized samples helpenhances the rate of subsequent reductions.

5.6 Leaching

Leaching of reduced Teknaf ilmenite was found to be a very rapid process and about 50 percent of leaching was completed within the first 5 to 10 minutes of leaching. The extent of removal of iron was found to increase with time, temperature and concentration of acid in leaching solution.

Hydrochloric acid concentration of 15% was found to be optimum for leaching out iron from the sample. At 15 percent hydrochloric acid concentration the optimum time and temperature for leaching out iron is 2 hrs and 75^{0}C respectively. The sample leached after reduction in the oxidized conditions contains less residual iron. On the other hand the TiO_2 content in the leached product was found to increase in the oxidized condition.

The leaching of ilmenite was enhanced by the presence of cracks formed during oxidation and the leaching mechanism was found to follow the first order reaction up to an α value of 0.5%, after that the mechanism was changed to spherical reaction. On the other hand, leaching of ilmenite reduced without prior oxidation was found to be slower and the mechanism followed the Spherical model. The apparent activation energy for leaching was found to be about 16 kJ/mol for sample reduced after oxidation for α values up to 0.5 and 23 kJ/mol for samples reduced without prioroxidation.

SEM studies of the rutile sample showed a highly porous non- continuous surface, and spot analysis showed the absence of iron on the surface, X-ray analysis indicated that the sample contained only rutile peaks and peaks for metallic iron and ilmenite were absent. A comparison of the chemical constituents of synthetic rutile prepared in these studies from Teknaf ilmenite with that of a commercially available synthetic rutile sample [Bracanin et al., 1980] is given in the Table 4.8. TiO_2 content of synthetic rutile prepared from Teknaf sample is slightly lower than the commercial sample. The values for the other constituents are well compareable. In general it can be stated that synthetic rutile prepared from Teknaf ilmenite by this oxidation-reduction-leach route is equally good as those prepared from ilmenites of other origin.

Table 4.8 Comparison of the chemical constituents of synthetic rutile samples.

Constituents	Commercially available synthetic rutile		Teknaf synthetic rutile
	Australian	Kerala	
TiO_2	92.80	93.50	91.50
Residual iron	2.10	1.30	2.18

5.7 Conclusions

1) Teknaf ilmenite contains a larger amount of iron. Teknaf ilmenite contains around 40% TiO2, 25.32% FeO and 32.53% Fe_2O_3

2) X-ray diffraction patterns of as received ilmenite show that ilmenite is the main phase.

3) SEM of as received ilmenite shows uniform appearance. Spot analysis shows that it contains titanium, iron, oxygen, silicon and niobium.

4) More than 96 percent of Teknaf ilmenite was retained on US sieve no. 100, 140 and 200.

5) Finer fractions of Bangladesh ilmenite contain lower percentage of TiO_2 and higher amounts of total iron.

6) From the sphericity value, finer size fractions are found to have a higher sphericity.

7) X-ray diffraction analysis of all the size fractions, ilmenite is the main phase and other phases like hematite, ferrous oxide, rutile and pseudorutile also present.

8) The bulk (more than 96%)of Teknaf ilmenite consists of magnetic fractions separated at separation currents of 0.10 –0.30 amperes.

9) The content of titanium oxide, ferrous oxide and ferric oxide decreases with increasing current of separation..

10) Teknaf ilmenite is in a partially altered state and not hydrated enough.

11) Finer fractions of Teknaf ilmenite have higher extent of reduction.

12) The optimum time and temperature for oxidation of ilmenite is 1 hr at 950^0C.

13) The optimum condition of reduction of Teknaf ilmenite by charcoal is 4 hr at 1050^0C.

14) Oxidation prior to reduction of Teknaf ilmenite enhances the rate of subsequent reduction.

15) Adoptions of separate reduction procedure for the different size fractions and magnetic fractions of Teknaf ilmenite are not necessary

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

17) Oxidation prior to reduction of Teknaf ilmenite increases the extent of reduction and also increases the extent of leaching of iron.

18) It is possible to produce synthetic rutile from Teknaf ilmenite through oxidation-reduction leach techniques.

19) Synthetic rutile obtained in these studies contains 91.50 percent TiO_2, which is very much comparable in chemical constitution with those prepared from ilmenite of other origins.

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Appendix-A

Estimation of ferrous iron:

Keep all the solutions 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 1ml of Barium diphenyl amine sulphonate indicator.
- Titrate with 0. IN potassium dichromate solution to a violet-blue end point.

Calculation:

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

Appendix -B

Estimation of metallic iron:

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

Test the residue for iron content

a) Add one drop of potassium ferricyanide solution.

b) Green color will indicate presence of iron

c) Boil ppt with 100cc distilled water and filter

(d) Test again for Fe content

e) Repeat, if necessary.

- Add

a) 10 ml 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:

$$\% \text{ Metallic iron} = \frac{\text{Vol of } k_2Cr_2O_7 \times \text{Factor of } K_2Cr_2O_7 \times 10 \times 100}{\text{Weight of sample}}$$

$$\text{Factor } K_2Cr_2O_7 = \frac{5\ 5.84 \times \text{Normality of } K_2Cr_2O_7}{1000}$$

Appendix -C

Estimation of Total Iron:

- Melt 10- 15 gm of potassium-hydrogen sulphate (in a 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 (900^0C)
- Heat (at 900^0C for 30 minutes).
- Allow solidify.
- Place the crucible (and the lid) inside a beaker containing 20 pct H_2S0_4
- Heat till dissolution is complete.
- Make upto 250ml.

Use this solution for the determination of TiO_2-also

- Pipette out 25 ml of the solution in a conical flask
- Add 5ml conc. HCl, Heat to80^0C.
- Reduce the iron solution by adding drop wise freshly prepared $SnCl_2$ Solution. (Add till the color disappears, add one-drop excess)
- Cool immediately in ICE (to 20^0C)
- Dilute to about 100 ml.

- Add 10 ml of Saturated HgC_{l2} solution (rapidly, at a time) and mix thoroughly.
- Silky white precipitare 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

$$\% \text{ Total iron} = \frac{\text{vol. of } k_2Cr_2O_7 \times \text{factor of } k_2Cr_2O_7 \times 10 \times 100}{\text{Wt of sample}}$$

$$\text{Factor of } K_2CrO_7 = \frac{5\ 5.84 \times \text{Normality of } K_2\ Cr_2\ O_7}{1000}$$

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

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

Appendix -D

Determination of Total Iron from Leached Solution

- Take out 5 ml of sol.
- Dilute to 50 ml.
- Add conc. HCL (5ml)
- Heat to 60-80^0 C (just to boiling)
- Immediately reduce with $SnCl_2$ (Keep cool in tcc.)
- Excess $SnCl_2$ to be neutralized by $HgCl_2$ (to cold soln.) (should not be too excess)
- Shake well to get a silky white ppt. of $HgCl_2$
- Add:

  10ml of Zimmerman soln

  10ml of acid mixture.

  5 drops of sodium/Barium diphenyl amine indicator.

  Titrate with std. Potassium dichromate go get the amount of total iron.

Calculation:

% of total iron is calculated from the following relationship:

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

Appendix -E

Estimation of TiO_2

- Tile 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 stopper is rightly fitted,
- Cool the flask (in ice) to less than $60^{0}C$.

- 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:

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

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

Appendix -F

Preparation of Solutions

1 Ammonium Thiocyanate indicator

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

2. Standardization of Ferric Alum:

Dissolve 30.16gru of ferric ammonium sulphate in 800ml distilled water and 15ml Conc. H_2SO_4. add H_20_2 to ensure complete oxidation of the iron. Boil the solution to remove excess H_20_2 and dilute to 1 litre. Standardize the solution against standard Ti02 reduced in the same way as described for the sample.

3. Preparation of $SnC1_2$:

Conc. Solution of $SnC1_2$ is prepared by dissolving 12 of pure tin or 30gms of AR crystalline SnC12 ($SnC1_2$, $2H_20$) in 100ml of cone. HCl and dilute to 200ml with distilled water.

4.Phosphoric acid Sulphuric acid Mixture

150ml of cone. H_2SO_4 and 150 ml 150 ml of H_3PO_4 in 700ml distilled water. Total volume will be 1000ml.

5.Zimmerman Solution

50gms $MnS0_4$ in 250ml H_20+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 I 00ml of cone. H_2SO_4

7 Barium diphenylamine sulphonate Indicator

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

8.N-phenylanthralinic acid indicator

0. 1 gm phenylanthralinic acid in I00ml of 0.005 molar sol" of NaOH.

9. 20% HCI Solution

Conc. HCI contains 35% HCL take 100cc HCI and add distilled water to make upto 165cc.

10. $K_2Cr_2O_7$ Solution

4.9033 gm Hitre (0. IN Solution)

11.0.005 molar NaOH Soln.

0 02gm NaOH crystal in 100 ml H_20

12. 4% Boric acid:

4 gin boric acid in I 00ml water

13. Potassium ferricyanide solution:

0.02gm potassium ferricyanide in I 00mlwater.

14. 20% H_2SO_4

80ml $H2O_2$+20ml H_2SO_4

CHEMICAL ANALYSIS RESULTS OF TEKNAF ILMENITE

Table 1: Chemical analysis of as received Teknaf ilmenite(4.1)

Component	% In ilmenite
FeO	25.32
Fe_2O_3	32.53
Fe (tot.)	42.43
TiO_2	39.96

Table.2: Sieve analysis of Teknaf ilmenite(4.2) .

US Sieve No.	Mesh opening (μm)	Av. size fraction %
70	210	0.053
100	149	5.094
140	105	47.057
200	74	44.510
>200	53	2.99

Table.3: Chemical analysis of different size fractions of Teknaf ilmenite before reduction (4.3)

US Sieve No.	% TiO_2	% Fe (total)	% FeO	% Fe_2O_3
100	39.15	42.71	26.04	32.13
140	38.50	43.27	25.50	33.53
200	38.00	43.83	24.60	35.37

Table 4:: Chemical analysis of magnetically fractionated ilmenite(element only dissolved in extractant 4.4)

Fractionated amp.	Cr ppm	Cu ppm	Mn ppm	Fe ppm	Ca ppm	Zn ppm	Mg ppm	Ni ppm
0.10	0.0943	0.01	9.21	404	<MDL	0.9682	11.52	0.1897
0 15	4.0830	0.04	10.61	519	<MDL	0.7864	5.54	0.4060
0.20	0.5322	0.01	8.02	456	<MDL	0.8545	6.73	0.1973
0.25	1.2868	0.03	3.98	234	<MDL	0.9256	3.45	0.1758
Raw	1.499	0.022	7.955	403	<MDL	0.8836	6.81	0.2422

Table. 5: Chemical analysis of magnetically fractionated ilmenite (4.5).

Fractionated amp.	TiO_2 %	$\%Fe_{tot}$= ml.x11.168	Fe^{++} =mlx 5.584	Fe O %= Fe^{++}x 1.2865	Fe^{+++}= Fe_{tot}- Fe^{++}	Fe_2O_3 %=Fe^{+++}x 1.4298	Sp.Gr.	% of total material
0.10	39.64	41.94	24.8	31.96	17.11	24.44	4.11	96.04
0.15	38.03	39.20	24.37	31.35	14.83	21.20	4.88	90.58
0.20	36.99	38.55	24.01	30.89	14.54	20.78	4.20	88.67
0.25	34.64	35.19	21.77	28.01	13.42	19.18	4.51	81.83
0.30	33.06	33.42	20.52	26.40	12.90	18.44	4.51	77.90

Table 6. Variation of ferrous iron in the oxidized sample with time and temperature (4.13).

Temp°C / Time (hr.)	Ferrous iron (%)		
	750°C	850°C	950°C
as received	25.32	25.32	25.32
0.5	4.10	2.37	1.867
1.0	2.48	1.40	0.5747
1.5	1.90	0.969	0.538
2.0	1.50	0.6465	0.3591

Table 7 Extent of reduction of ilmenite with different proportion of reductant (Reduction:1050° C for 4hr 4.22).

Ilmenite:coke	$\%Fe_{tot}$	$\%Fe_{met}$	%of reduction
1:25	43.45	34.40	79.16
1:50	43.54	35.79	82.19
1:75	43.61	37.68	86.40
1:1	43.78	38.10	87.02
1:2	43.85	38.25	87.25
1:3	43.83	38.27	87.30
1:4	43.90	38.35	87.35

Table 8 Extent of reduction of ilmenite as a function of time and temperature (4.23).

Temp.°C / Time (hr)	Metallic iron (%)			
	800 °C	900°C	1050°C	1100°C
0.5	2.2	9.24	27.64	28.00
1.0	4.52	13.79	30.23	30.80
2.0	6.45	19.82	33.39	33.90
3.0	7.80	22.79	35.64	36 00
4.0	8.90	28.19	38.26	38.40

Table 9 Extent of reduction of as received ilmeni as a function of time (4.24) .

Time (hr.)	Reduction %			
	800°C	900°C	1050°C	1100°C
0.5	5.185	21.72	64.79	64.90
1.0	10.62	32.19	70.68	71.10
2.0	15.00	45.80	77.16	77.00
3.0	18.13	52.63	81.93	82.43
4.0	20.56	64.73	87.39	87.47

Table.10 Extent of reduction of ilmenite (4.28).

Temp°C	Time (hr.)	Fe (met) %	Reduction %
1050	.5	27.64	64.79
1050	1	30.23	70.68
1050	2	33.39	77.16
1050	3	35 40	81.19
1050	4	38.36	87.61
1050	5	39.20	87.75

Table 11 Extent of reduction of as received ilmenite as a function of size fraction (Reduction: 1050°C for 4 hr. 4.32)

US. Sieve No.	FeO	Fe_{met} %	Degree of reduction %
100	8.80	38.69	87.22
140	7.56	39.03	89.31
200	6.62	41.20	90.85

Table 12 Variation of total iron of as received ilmenite and reduced size fractionated ilmenite (4.33)

US. Sieve No.	% of total iron in as received ilmenite	% of total iron in reduced ilmenite
100	42.71	44.34
140	43.27	44.70
200	43 83	45.37

Table 13 Chemical analysis of fractionated reduced sample (Reduced at 1050°C for 4 hr. 4.36)

Fractionated amp.	TiO2%	Fe (tot) %	Fe (met) %	% of reduction
0.10	45.53	48.02	42.80	89.12
0.15	44.73	46.64	42.04	90.09
0.20	41.51	45.50	41.50	91.20
0.25	40.44	43.83	39.45	90.00
0.30	38.83	43.08	38.30	88.90
0.35	32.80	42.71	37.30	87.30

Table 14 Extent of reduction (%of reduction) of as received and pre-oxidized reduced ilmenite (Reduction: 1050°C,4.39)

Time (hr.)	% Of reduction (As received)	% Of reduction (Pre-oxidized)
0.50	64.79	66.48
1.0	70.68	72.62
2.0	77.16	86.76
3.0	81.93	87.93
4.0	87.61	89.38

Table 15Extent of reduction (%of reduction) of as received and pre-oxidized reduced of different size fractionated ilmenite (Reduction: 1050°C,4.42)

US sieve No.	% Of reduction (as received)	% Of reduction (oxidized)
100	87.25	88.00
140	89.30	90.20
200	90.80	91.20

Table.16 Extent of reduction of pre-oxidized and as received fractionated ilmenite (Reduction: 1050 C for 4 hr. 4.43)

Fractionated amp.	% Of reduction (As received)	% Of reduction (pre-oxidized)
0.10	89.12	89.66
0.15	90.09	91.25
0.20	91.20	91.45
0.25	90.00	90.50
0.30	88.90	89.00
0.35	87.30	87.70

Table: 17 Chemical analysis of reduced ilmenite (Reduction for 0.50,1,2,3,4 and 5 hrs.)

Temp°C	Time (hr.)	Fe (tot.) %	Fe (met) %	Reduction %
1050	.5	42.66	27.64	64.79
1050	1	42.77	30.23	70.68
	2	43.27	33.39	77.16
1050	3	43.60	35.40	81.19
1050	4	43.78	38.36	87.61
1050	5	44.67	39.20	87.75

Table: 18: Chemical analysis of pre-oxidized reduced ilmenite.

Temp°C	Time (hr.)	Fe (tot) %	Fe (met) %	Reduction %
1050	.5	42.82	28.47	66.48
1050	1	42.99	31.22	72.62
1050	2	43.77	37.97	86.76
1050	4	44.16	39.47	89.38

Table 19: Extent of reduction of pre-oxidized different size fractions (Reduction:1050°C 4hr).

US sieve No.	$Fe_{tot.}$ %	Fe_{met} %	Reduction %
Raw	43.78	38.26	87.61
100	44.88	39.50	88.00
140	44.75	40.50	90.20
200	46.27	42.20	91.20

Table: 20: Extent of reduction (Fe_{met} %) of pre-oxidized reduced ilmenite as a function of time and temp.

Temp.°C / Time (hr)	Metallic iron (%)		
	800 °C	900°C	1050°C
0.5	5.10	10.94	28.47
1.0	8.30	17.70	31.22
2.0	10.80	26.13	37.97
3.0	11.20	30.80	38.50
4.0	13.70	34.80	39.47

Table:21 :Extent of reduction (reduction %) of pre-oxidized reduced ilmenite as a function of time and temp..

Temp.^{0}C / Time (hr)	Metallic iron (%)		
	800 ^{0}C	900^{0}C	1050^{0}C
0.5	11.98	25.62	66.48
1.0	19.39	41.16	72.62
2.0	25.20	60.50	86.76
3.0	26.10	71.13	87.93
4.0	31.86	80.14	89.38

Table: 22 Chemical analysis of reduced ilmenite as a function of time and temperature.

Temp^{0}C	Time hr.	Fe (Tot.) %	Fe (Met.) %	Reduction %
800	.5	42.43	2.20	5.185
800	1	42.54	4.52	10.62
800	2	42.90	6.45	15.00
800	3	43.00	7.80	18.13
800	4	43.27	8.90	20.56
900	.5	42.54	9.24	21.72
900	1	42.83	13.79	32.19
900	2	43.27	19.82	45.80
900	3	43.30	22.79	52.63
900	4	43.55	28.19	64.73
1050	.5	42.66	27.64	64.79
1050	1	42 77	30.23	70.77
1050	2	43.27	33.39	77.16
1050	3	43.50	35.64	81.93
1050	4	43.78	38.36	87.39
1100	.5	43.14	28.00	64.90
1100	1	43.33	30.80	71.10
1100	2	44.00	33.90	77.00
1100	3	43.67	36.00	82.43
1100	4	43.90	38.40	87.47

. Table: 23 Chemical analysis of pre-oxidized reduced ilmenite as a function of time and temperature.

Temp^{0}C	Time hr.	Fe (Tot.) %	Fe (Met.) %	Reduction %
800	.5	42.54	5.10	11.98
800	1	42.80	8.30	19.39
800	2	42.85	10.80	25.20
800	3	42.90	11.20	26.10
800	4	43.00	13.70	31.86
900	.5	42.70	10.90	25.62
900	1	43.00	17.70	41.16
900	2	43.18	26.13	60.50
900	3	43.30	30.80	71.13
900	4	43.42	34.80	80.14
1050	.5	42.82	28.47	66.48
1050	1	42.99	31.22	72.62
1050	2	43.76	37.97	86.76
1050	3	43.78	38.50	87.93
1050	4	44.15	39.47	89.38

Table: 24: Chemical analysis of fractionated pre-oxidized reduced ilmenite (reduced at 1050^{0}C for 4 hrs.)

Fractionated amp	TiO2 %	Fe (tot.) %	Fe (met.) %	% of reduction
0.10	46.60	48.69	43.61	89.66
0.15	45.26	47.74	42.80	91.25
0.20	42.58	46.06	41.87	91.45
0.25	41.55	45.50	41.20	90.50
0.30	40.55	44.39	39.54	89.00
0.35	33.75	42.71	37.46	87.70

able: 25: Chemical analysis of as received reduced ilmenite (reduced at 1050^{0}C for different period).

Reduction time (hr.)	Concentrate in reduced ilmenite %				% of oxygen combined with Fe before reduction	Degree of reductio n
	Fe_{tot}	Femet	FeO	% of total oxygen		
3	43.50	35.64	12.4	2.8	15.379	81.79
4	43.78	3836	8.55	1.90	15.379	87.64
5	44.67	39.20	8.46	1.88	15.379	87.75

Table: 26 Cakculation of degree of reduction for fractionated reduced sample.

Cyrrent amp.	% present in as received ilmenite					FeO in reduced ilmenite	O_2 in reduced ilmenite	Degree of reductio n
	FeO	O_2 in FeO	Fe_2O_3	O_2 in Fe_2O_3	Total oxyzen			
0.10	31.96	7.1022	24.44	7.332	14.434		1.570	89.12
0.15	31.35	6.9665	21.20	6.36	13.326		1.320	90.09
0.20	30.89	6.864	20.78	6.234	13.098		1.15	91.20
0.25	28.01	6.224	19.18	5.754	11.978		1.1978	90.00
0.30	26.40	5.866	18.44	5.532	11.398		1.265	88.90

LEACHING

Table 27 Percentage removal of iron vs. reduction time of ilmenite sample (Sample reduced at 1050°C, 4 hr. leaching time: 1 hr. at 15% HCl soln and at 75°C, : 4.47)

Reduction time (hr.)	Fe_{tot} % In reduced sample	Fe in leached soln. %	% of iron removal
0	42.43	3.23	7.61
1	42.77	22.29	52.53
2	43.77	33.38	78.29
3	43.60	38 21	87.63
4	43.78	42.02	95.97
5	44.67	44.91	96.07

Table: 28 Percentage removal of iron vs. reduction temperature of ilmenite sample (leached in 15% HCl soln. At 75°C for 1 hr. 4.48)

Temp °C	% Fe_{tot} in the case for 2 hr reduced sample			% Fe_{tot} in the case for 4 hr reduced sample		
	In reduced sample	In leached solution	% o f Fe removal	In reduced sample	In leached solution	% of Fe removal
800	42.90	5.20	12.12	43.12	8.07	18.65
900	43.27	20.27	46.84	43.55	29.55	67.85
1050	43.27	37.88	87.54	43.78	42.02	95.97
1100	43.44	38.09	87.73	43.90	42.14	96.01

Table: 29 Percentage removal of iron vs. leaching time (leached: 15% HCl at 75°C, Sample reduced at 1050°C for 4 hr. Fe_{tot} 43.78%,4.49)

Leaching time (min)	Fe_{tot} in reduced sample	Iron present in leached soln %	% of iron removal
00.00	43.78	00.00	00.00
10	43.78	40.89	93.39
20	43.78	41.41	94.58
30	43.78	41.76	95.39
60	43.78	42.02	95.97
120	43 78	42.30	96.61
135	43.78	42.33	96.68
150	43.78	42.36	96.75

Table: 30 Percentage removal of iron vs. leaching temperature (leached: 15% HC for 2 hrs. As received sample reduced at 1050°C for 4 hr. Fe_{tot} 43.78% 4.51)

Temperature °C	Iron present in leached solution %	% of iron removal
30	40.77	93.12
40	41.38	94.51
50	41.96	95.84
60	42.02	95.99
70	42.28	96.57
75	42.30	96.61
80	42.33	96.68
85	42.33	96.68

Table:31 Percentage removal of iron vs. HCl acid concentration (leached at 75°C for 2 hr. in different HCl concentration. Reduced sample: Fe_{tot} =43.78, 4.53)

Concentration of acid %	Iron present in reduced sample %	Iron present in leached solution %	% of iron removal
1	43.78	7.58	17.31
3	43.78	33.28	76.01
5	43.78	41.11	93.90
10	43.78	42.02	95.97
15	43.78	42.30	96.61
20	43.78	42.33	96.66
25	43.78	42.38	96.80
30	43.78	42.38	96.80

Table 32 Comparison of extent of dissolution of iron from pre-oxidized reduced sample and as received reduced sample leached with 10% HCl at specified temperature (4.55, 4.56 and 4.57).

Time (Min)	% of iron in solution					
	30°C		50°C		75°C	
	As received reduced	Pre-oxidised reduced	As received reduced	Pre-oxidised reduced	As received reduced	Pre-oxidised reduced
1	8.75	11.76	15.76	17.66	20.57	23.40
2	14.88	19.42	27.14	30.02	33.71	36.92
3	22.32	24.72	29.77	32.67	35.89	39.05
4	23.20	28.70	31.52	34.63	36.77	40.03
5	24.09	29.58	32.84	35.94	37.65	40.68
10	31.10	32.02	36.93	38.88	39.20	41.82
20	34.98	35.94	38.22	40.19	39.78	41.93
30	36.90	38.56	38.87	40.84	40.36	42.17
60	39.27	39.27	41.07	41.19	41.55	42.50
120	39.97	40.92	41.80	42.03	41.59	42.67

Table 33 Comparison of extent of dissolution of iron from pre-oxidized reduced sample and as received reduced sample leached with HCl of different concentration at 75°C(4.58, 4.59 and 4.60).

Time (min.)	% Of iron in solution					
	5% HCl		10%HCl		15%HCl	
	As received reduced	Pre-oxidized reduced	As received reduced	Pre-oxidized reduced	As received reduced	Pre-oxidized reduced
5	36.91	39.34	37.65	40.68	40.23	41.20
10	37.87	40.29	39.20	41 82	40.89	42.00
20	39.10	40.75	39.78	41.93	41.41	42.09
30	39.97	40.84	40.36	42.17	41.77	42.34
60	40.78	41.11	41.55	42.50	42.02	42.67
120	41.11	41.40	41.59	42.67	42.30	42.95

Table 34 Chemical analysis data for kinetic curve of isothermal leaching of oxidized and reduced ilmenite leached with 10 percent hydrochloric acid at specified temperature (Fe_{tot}=44.16%,4.56)

Time (min)	30°C		50°C		75°C	
	% in sol^n	α	% in sol^n	α	% in sol^n	α
1	11.76	.266	17.66	.40	23.40	.54
2	19.43	.44	30.02	.68	36.92	.84
3	24.72	.56	32.67	.74	39.05	.88
4	28.70	.65	34.63	.78	40.03	.91
5	29.58	.67	35.94	.81	40.68	.92
10	32.02	.725	38.88	.88	41.82	.95
20	35.94	.8138	40.19	.91	41.93	.95
30	38.56	.8731	40.84	.92	42.17	.95

Table : 35 Chemical analysis data for kinetic curve of isothermal leaching of reduced ilmenite without oxidizing leached with 10 percent hydrochloric acid at specified temperature (Fe_{tot}=43.78%,4.57)

Time (min)	30°C		50°C		75°C	
	% in sol^n	α	% in sol^n	α	% in sol^n	α
1	8.75	.20	15.76	.36	20.57	.47
2	14.88	..34	27.14	.62	33.71	.77
3	22.32	.43.51	29.77	.68	35.89	.82
4	23.20	.50.53	31.52	.72	36.77	.84
5	24.09	.56.55	32.84	.75	37.65	.86
10	31.10	.71	36.93	.84	39.20	.89
20	34.98	.80	38.22	.87	39.78	.91
30	36.90	.84	38.87	.89	40.36	.92

Table: 36 Data for leaching time plot for isothermal kinetic curve shown in .Oxidized-reduced and leached ilmenite sample(4.61).

Alpha	30°C		50°C		75°C	
	Time (t), sec	t/t0.5	Time (t), sec	t/t0.5	Time (t), sec	t/t0.5
0.1	21	.1448	13	.1625	10	.178
0.2	43	.296	29.5	.3678	20.5	.366
0.3	70	.482	42	.525	31	.553
0.4	104	.7172	60	.75	41	.737
0.5	145	1	80	1	56	1
0.6	200	1.379	98	1.22	70	1.25

Table: 37 Data for isothermal kinetic plots according to first order reaction during leaching for oxidized and reduced ilmenite(4.63).

Alpha	Time,(sec/min)						$G(\alpha) = -Ln(1-\alpha)$
	30 °C		50°C		75°C		
0.1	21	.35	13	.216	10	.166	0.105
0.2	43	.716	29.5	.4916	20.5	.341	0.223
0.3	70	1.16	42	.70	31	.5166	0.37
0.4	104	1.73	60	1	42	70	0.51
0.5	145	2.01	80	1.33	56	.9333	0 69
0.6	200	2.55	98	1.63	70	1.166	0.91

Table 38 Arhenius type plot for kinetic data (4.63).

Temp°C	T°K	1/T	k=tanθ	Lnk
30	303	.0033	.349	-1.052
50	323	.00309	.5497	-.5983
75	348	.00287	.7793	-.2494

Table 39 Data for apperent activation energy calculation of leaching. Using differential approach for oxidized reduced leached with 10% HCl acid (4.67).

°K	1/T	α =0.1		α =0 2		α =0.3		α =0.4		α =0.5	
		Time,t	Lnt	Time,t	Lnt	Time,t	Lnt	Time,t	Lnt	Time,t	Lnt
303	.0033 0	.35	-1.04	.716	-.334	1.16	.148	1.73	.548	2.41	.879 6
323	.0030 9	.216	-1.532	.4916	-.71	.70	-.3566	1	0	1.33	.285 1
348	.0028 7	.166	-1.795	.35	-1.04	.5166	-.66	.70	-.356	.9166	-.087

Table 40 Data for leaching time plot for isothermal kinetic curve(As received reduced and leached ilmenite sample, 4.62)

Alpha	30° C		50°C		75°C	
	Time (sec)	t/t0.5	Time (sec)	t/t0.5	Time (sec)	t/t0.5
0.10	30	.171	18	.20	12	.18
0.20	60	.343	31	.34	23	.35
0.30	100	576	50	.55	38	.58
0.40	140	.80	70	.77	50	.76
0.50	175	1	90	1	65	1

Table 41 Data for isothermal kinetic plots according to Spherical reaction model during leaching for as reaceved reduced ilmenite (4.65).

Alpha	30° C		50°C		75°C		$R_3=[1-(1-\alpha)^{1/3}]$	
	Time		Time		Time			
	Sec	Min	Sec	Min	Sec	Min		
0.10	30	.50	18	.30	12	.20	.0345	
0.20	60	1.0	31	.5166	23	.38	.07168	
0.30	100	1.66	50	.833	38	.633	.11209	
0.40	150	2.50	70	1.166	50	.833	.1565	
0.50	210	3.50	90	1.50	65	1.08	.2062	

Table 42 Arhenius type plot for kinetic data (4.66).

Temp.°C	Temp °K	1/T °K	K (Slope)	LnK
30	303	.00330	.2739	-1.29499
50	323	.00309	.5497	-.5983
75	348	.00287	.7793	-.2494

Table 43 Data for apparent activation energy calculation of leaching, Using differential approach for as received reduced leached with 10% Hcl acid (4.68).

1/T oK	α= 0.10		α =0.20		α = 0.30		α = 0.40		α =0.50	
	t	Lnt	t	Lnt	t	Lnt	t	Lnt	t	Lnt
.00330	.50	-.693	1	0	1.66	.5068	2.50	.9162	3.50	1.252
.00309	.30	-.1.20	.5166	-.660	.833	-.182	1.166	.1535	1.50	.4054
.00348	.20	-1.609	.380	-.967	.633	-.457	.833	-.182	1.08	.0769