A STUDY ON THE EFFECT OF PRIOR OXIDATION ON THE REDUCTION AND LEACHING KINETICS OF BANGLADESH ILMENITE

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Declaration

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Abstract

Bangladesh ilmenite containing 24.2% FeO , 33.0% Fe_2O_3 and 39.45 % TiO_2 has been oxidised in the temperature range of 700°C - 950°C for a period of upto 4 hours. X-ray diffraction and chemical analysis have shown that oxidation in normal furnace atmosphere for a period of 1 hour at 950°C converts all but 0.5% ferrous iron to ferric state. Oxidation at 700°C resulted in the formation of pseudorutile, hematite, rutile and some unidentified phases, where as pseudobrookite was found to have formed at temperature above 800°C. Optical microscope and scanning electron microscope revealed the presence of cracks in the oxidised samples.

Reduction by charcoal in the temperature range of 950°C to 1050°C for treatment times of upto 6 hour showed that the maximum metallic iron content of the samples reduced after oxidation were higher (42.1 percent) than in the samples reduced (37.8 percent) in the as- received condition. Reduction of ilmenite in the oxidised condition was found to proceed in two stages, the first stage is the reformation of ilmenite and the second stage is the progressive reduction of ilmenite to metallic iron and rutile. 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 rate of removal of metallic iron during leaching of reduced ilmenite in 5-15 percent HCl at temperatures upto 75°C was found to increase with an increase in temperature and also in the concentration of acid in the leaching solution. The activation energy of leaching of preoxidised, reduced and leached sample was found to be 30.4 kJ/mole whereas activation energy of leaching of as received and reduced sample was found to be 42.97 kJ/mole. Total iron content after leaching was estimated at 2.45 percent in the oxidised reduced leached sample while the total iron content of the leached sample reduced in the as received condition was estimated at 5.2 percent

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CHAPTER - 1 INTRODUCTION

1.1 Introduction

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

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

Rutile is essentially naturally occurring TiO_2 and deposits are relatively rare. Even though the supplies of rutile have increased, the deposits are fast depleting and demands outstrip supplies This shortage of natural rutile has forced technologists throughout the world to develop processes to enhance the titania content of ilmenites for use as a substitute for scarce natural rutile. The enriched ilmenite is known as synthetic rutile.

The most important commercial use of ilmenite is for the manufacture of titanium dioxide pigment. Titanium dioxide pigments, due to the unique properties of high refractive index, low specific gravity, chemical stability, high hiding power, light fastness, non-toxic nature and compatibility has now replaced all other white pigments like zinc oxide, white lead and zinc sulfide. Rutile, leucoxene, ilmenite and in some cases titanium dioxide are used for coating welding rods. Natural rutile is preferred to ilmenite for this purpose but synthetic rutile is an acceptable substitute. Titanium dioxide is an important and indispensable ingredient in the manufacture of electrical insulators, high gloss finishes in ceramic industries, brilliant white pigment which is used for the production of white rubber, and as a filler for paper.

Another attractive utilisation of ilmenite is in the production of titania rich slag. This slag is an ideal material to feed in the existing titanium dioxide plant as a substitute of ilmenite. The attractive feature of this process is that pig iron is also produced as a by product along with the slag (metallurgical process). This ensures the full utilisation of the value constituents of ilmenite.

Titanium that comes from ilmenite and other sources is used as a structural metal. It's extreme resistant to corrosion, high strength to weight ratio and high fatigue resistance at high temperature made its use imperative in supersonic transports, in desalination system, and in chemical process industries as a material for reaction vessels, pipes, pumps, heat exchangers, etc.

The important uses of ilmenite as well as its products are summarised as follow:

Ingredient	***Uses***
Titanium dioxide	Paints, plastics, printing inks, paper, leather cosmetics, vitreous enamels, synthetic gems, etc.
Titanium tetrachloride	Water proofing paints, adhesive promoter, polymerisation catalyst, titanium metal, etc.
Titanium metal	Corrosion resistant alloys, chemical process industries, space craft, heat exchangers, ship building, structural metal, etc.
Synthetic rutile	Welding rods, raw material for chloride route of titanium extraction, titanium dioxide extraction, etc.

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

1.2 Methods of Upgrading

Ilmenite ($FeO.TiO_2$) contains titania and iron oxide bound in spinal form. In addition, it may contain other oxides such as Fe_2O_3. Thus most beneficiation techniques are based on the preferential chemical reaction with iron to remove it. Over the years extensive research work has been directed towards the development of suitable techniques for removal of iron from ilmenite. As a result of these investigations, a number of techniques have been developed for upgrading ilmenite. Some of these methods 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 laboratories. The existing techniques for benificiation of ilmenite are based on following five principles.

1.2.1 Smelting

This is a pyro metallurgical technique in which ilmenite, mixed with metallurgical or petroleum coke and flux, is heated at a 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[2] 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.

The main merit of this process is that iron contained in ilmenite is obtained as a byproduct. However the process requires higher temperature resulting in higher consumption of energy and specialised knowledge. Moreover, the slag produced has to be processed further.

1.2.2 Reduction Followed by Chemical Treatment:

Most of the more successful processes for the production of synthetic rutile may be classified in this category. Iron present in ilmenite is either in ferrous or in ferric form. In these processes, the iron oxides present in ilmenite are reduced to lower oxide or to metallic iron. Various reducing agents like coal, hydrogen, charcoal, coconut pith, etc. have 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.

a) Leaching of the Reduced Ilmenite: HCl acid and $FeCl_3$ solutions are commonly used to leach out iron from reduced ilmenite. Leaching is usually carried out at atmospheric pressure, higher pressures have also been used. Synthetic rutile containing 85-95 per cent TiO_2 has been produced by these methods.

b) Rusting of the Reduced Ilmenite: 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[3-6]:

$$Fe_{Lattice} \rightarrow Fe^{++}_{Aq} + 2e$$

$$O_2 + 2H_2O + 4e \rightarrow 4\,OH^-$$

Ferrous hydroxide is formed and on further oxidation rust is formed.

Rusting is assisted by using some ammonium chloride and acidifying pulp with H_2SO_4 to a pH of 4. It is a cheap process and the yield is 90 per cent TiO_2 that can be increased to 94 per cent by acid leaching.

(c) Magnetic Separation: In these processes [7-11] reduction of ilmenite is carried out in the presence of suitable flux (e.g., NaCl, Na_2CO_3 CaF_2 Na_2SiO_3 boric acid or apatite). As a result, a product resembling sponge iron is obtained. The reduced ilmenite is crushed and wet ground and the mass is subsequently separated into two slurries containing iron and titania by means of a magnetic separator.

1.2.3 Direct Acid Leaching

Sulfuric acid and hydrochloric acids are commonly used for direct leaching of ilmenite. 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 (>98% TiO_2)

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[12] under suitable conditions can produce a product containing more than 98% TiO_2.

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

a) Conversion to Titanate: In this process ilmenite is treated with Na_2CO_3 at elevated temperatures (900°-1100°C) to obtain sodium titanate[13] according to the following reaction:

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

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

b) Conversion to Sulphate: Both iron and titanium in ilmenite can be converted to their respective sulphates[14], if ilmenite is treated with $(NH_4)_2SO_4$ 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.

c) Conversion to Sulfide: Treatment of ilmenite with some sulfur bearing material such as ZnS, Na_2SO_4+ C or, sulfur vapor leads to the preferential sulphidisation of iron in ilmenite[13, 15, 16] Heating of a mixture of ilmenite, Na_2SO_4 and carbon at 1000-1300°C results in the formation of FeS.

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

The reaction product is treated with boiling H_2SO_4 to yield a titania rich product.

Synthetic rutile is also prepared by heating the ilmenite at 500-1000°C in sulfur vapor[16] 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 ½ hour [17,18] resulting in a titania rich product.

1.2.5 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

a) Chlorinating With Cl_2 : Ilmenite is mixed with a carbonaceous reducing agent and chlorinated at 850-950°C to produce iron chloride and titanium tetrachloride. Titanium dioxide is obtained from titanium tetrachloride by hydrolysis.

Selective chlorination of ilmenite has also been carried out in two steps at two different temperature to effect the separation of both iron and titanium chloride. In this process, the ore is mixed with coal or charcoal and heated in the absence of air at 800°C and then cooled in reducing atmosphere to 350°C. At the same time dry chlorine gas is passed through the reducing mass. In this stage only iron is attacked and the ferric chloride vapor is condensed in a cooling chamber. The direction of flow of chlorine is then reversed and temperature is maintained at 550°- 600°C. In this stage titanium compounds are attacked and resulting titanium tetrachloride vapor is condensed in the cooling tower.

Preferential chlorinating of iron oxide in ilmenite has been investigated by some investigators[19, 20]. Ilmenite is briquetted with charcoal (6%) and $FeCl_3$ binder and then treated with chlorine at 500°- 600°C. This processes results in a product containing about 90% TiO_2. The rate of chlorinating is reported to be faster in presence of some catalysts like CuO, PbO, MnO_2, CaO, CeO and $Ca_3(PO_4)_2$. CeO is found to be the best catalyst among them. Chlorination with $CO+Cl_2$ has been carried out in fluidised bed at 900°-1000°C and a product containing 95-98 per cent TiO_2 has been obtained [21, 22]

Titanium dioxide has also been prepared by the selective chlorination of ilmenite with gaseous mixture of Na and Cl_2 in a chlorinator with a certain amount of air or oxygen [23, 24].

b) Chlorinating With 'HCl Gas: In a laboratory scale production a product containing 97% of TiO_2 has been obtained[25] by selective chlorination of ilmenite at 1000°C for 3 hours. Preoxidised ilmenite was found to require higher temperatures for effective removal of iron. However, no solid $FeCl_2$, which causes experimental difficulties in conducting chlorination, was found when preoxidised samples are used for chlorinating.

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

In presence of air $FeCl_3$ is obtained and the total iron chloride is decreased. Partial chlorination of ilmenite in a fluidised bed reactor by H_2 and Cl_2 mixture results in high grade TiO_2 (80-95% TiO_2) product [26].

A product containing 90% TiO_2 and 6.6% Fe_2O_3 has been obtained by selective chlorination of ilmenite with a mixture of $TiCl_4$ and Cl_2 [27] at a temperature of 1050°C.

Treatment of ilmenite with NH_3 and HCl at 600°C removes about 92% of iron. At a temperature of 800°C all the iron is removed [28 29]. A product containing about 96% TiO_2 has been obtained by treating a mixture of ilmenite and powdered coke (1%) in a kiln at 800°- 900°C with a gas mixture of Br_2 and N_2 or Br_2, N_2 and CO_2.[30] The $FeBr_3$ formed is cooled and passed into a cyclone where $FeBr_3$ separates as powder.

1.3 Advantage and Disadvantage of the Processes Developed:

The relative merits and demerits of the processes that has been developed so far are shown in Table – 1. 1.

1.4 Ilmenite Deposits in Bangladesh

The existence of natural concentrates of titanium bearing minerals such as ilmenite, rutile and leucoxene along with other potentially valuable mineral concentrates was detected in the beach sands of Bangladesh in 1960 The Pakistan Atomic Energy Commission took interest in the area in 1965 and carried out preliminary survey work till 1967. Laboratory investigations, particularly heavy mineral separation and determination of their percentages were carried out to have estimates of ore-reserves of the promising deposits. Exploration work to determine the quality and the quantity of the reserves began in 1968. Up to 1985 the presence of these minerals were detected in 17 places in the 550 km long coastal area (Table 1.2). It can be seen from this table that ilmenite constitutes the most significant portion of the heavy minerals

A pilot plant with the assistance of the Australian government was established in 1975 and commenced operation under the guidance of Australian consultant who commissioned the plant and supervised the test work on the bulk samples of sands from Moheshkhali and Badarmokam. The activities of the pilot plant continued in full swing up to 1987 and about 227 tons of ilmenite were separated. The activity of the plant was then kept suspended for some time The operation of the plant resumed in 1992 and the center is now pursuing all out efforts for commercialisation of the mineral sands.

1.5 Principles of Separation of Heavy Minerals

Since the mineralogy and the grain size of the minerals in all deposit occurring along the same stretch of coastline are not the same, the pilot plant studies are essentially carried out for each and every deposit. The study involves the concentration and separation of valuable heavy minerals from heterogeneous sand mixtures and subsequent removal of the contaminants. The properties that affect the primary concentration are grain size, shape, texture, and density. Final separations of the particles are done by utilising the differences in specific gravity, Table -1.1 Merits and demerits of the Processes Developed:

Process	Merits	Demerits
Halogenation:	I) Rutile of high purity can be obtained ii) Selective chlorination is cheap.	i) Chlorine is highly corrosive ii) Special reaction vessel lining is required.. iii) High temperature is required iv) Reaction conditions are not flexible and hence must be precise.
Reduction and leaching:	I) It can be exploited commercially ii) Reductants are coal or charcoal which are cheep and temp. required is generated by the reductants itself. iii) Reduction can be carried out on large scale using rotary kiln iv) The process is flexible and can be made continuous v) Spent acid and Fe_2O_3 can be recovered vi) Rutile with minimum Fe content can be prepared vii) Recovery of TiO_2 is possible	Only limitation is it is multistage process.
Fusion methods:		Not exploited on a commercial scale i) High temperature is required for fusion ii) Alkali used are corrosive iii) Energy input is high iv) Fusion in large quantity is difficult v) High cost of chemicals vi) Recovery is not satisfactory vii) Multistage process is involved
Direct leaching:	i) Single stage process ii) Can be operated at low temperature. iii) Reagent costs are comparatively low	i) Leachants are highly corrosive ii) Special materials are required for construction of vessels. iii) Long leaching time is required iv) In many cases extent of benefaction is low v) Excess quantity of leachants are to be used.

Table -1.2 Summary of heavy mineral reserves in the deposits along the coastal belt of Bangladesh[1].

SL No	Deposit	Sand Tonnage	Heavy Mineral Tonnage	Reserve of valuable minerals (in ton)							
				Zircon	Rutile	Ilmenite	Leuco-xene	Kyanite	Monazite	Magne-tite	Garnet
Main Coast:											
1	Badarmokam	1,765,000	411,000	4,932	3,288	94,530	18,002	-*	4,932	10,275	-*
2	Sabrang	347,558	68,582	4,184	1,372	19,614	3,470	727	206	1.001	3,018
3	Tcknaf	1,939,580	442,291	28,306	13,230	163,170	20.124	14,728	3.045	7,209	22,424
4	Silkhali	2,756,828	489,714	33,300	10,774	173,360	10,970	4,407	3,918	3,085	39,422
5	Inani	729,286	175,476	10,880	4,036	53,170	439	1,404	965	5,545	12,810
6	Cox's Bazar	5,119,000	920,000	23,000	6,440	161,000	10,488	-*	2,024	33,212	50,600
7	Kuakata	2,872,486	831,668	9,647	3,911	76,015	9,647	16,800	83 2	4,325	52,229
Moheshkhali Island											
8	Fore-shore beach	276,560	119,480	7,145	3,788	54,961	2,891	Trace	131	824	-*
9	Kutubjum	577,980	106,240	4,568	2,104	36,440	1,158	2,635	202	1,169	-*
10	Fakiraghona	273,940	68,460	1,513	1,458	15,746	952	5,006	55	288	4,655
11	Fakirahata	409,120	96,750	5,515	3,970	22,157	3,677	9,579	194	97	5 998
12	Baraghoriapara	888,440	181,770	6,017	6,744	52,168	6,416	13,815	927	1,236	11,815
13	Panirchara	1,595,410	204,390	12,264	6,479	60,091	5,519	16,351	531	3,863	13,490
14	Hoanak(Nalbila)	92,780	7,120	100	153	1,400	69	110	4	127	-*
15	Materbari	69,030	15,215	794	295	4,962	374	Trace	20	575	-*
16	Nijhum Dwip	379,337	96,348	2,052	424	12,978	77	2,592	19.3	4,384	-*
17	Kutubdia Island	404,656	119,997	3,900	1,908	23,796	2,436	2,592	96	3,384	6,300
	Total:	20,496,981	4,354,501	158,117	70,274	1,025,558	96,709	90.746	17,352.5	80,599	222,751

electrical and magnetic properties of the minerals. But this plant cannot separate the chemically bonded unwanted ingredients from the valuable constituents.

1.5.1 Separation Techniques Used in Cox's Bazar Pilot Plant:

Raw sands are collected from heavy mineral deposits and a slurry of sand and water is pumped into a gravity spiral, where heavy minerals are separated from the light minerals The heavy sands are passed through a dewatering cone to attritor to clean the surface coatings. Then it is passed over a drum magnet where magnetite is separated from the sand mixture. This magnetite free material is shaken in the Wilfley Table where heavy minerals are separated from light minerals. The dense heavies are collected as table concentrates and prepared as the feed material for the dry section.

In the dry section minerals are first fed into a rotary drum dryer and subsquently they are carried up by bucket elevator and fed into a high tension electrostatic separator where they are separated into the conductor and non conductor fractions. The non-conductor fraction contains zircon, garnet, and monazite. The conductor fraction contains ilmenite, and rutile. The conductor part is passed through cross belt magnetic separator Magnetite is separated here. Then it is passed into a high intensity roll magnetic separator where ilmenite and rutile are separated.

Similarly non magnetic fraction is passed through a roll magnet where they are separated again as magnetic (garnet and monazite) and non-magnetic (zircon) fraction. The material containing garnet and monazite is passed on a vibro-screen separator where garnet is separated as over size and monazite as under size. The zircon product is refined using air table. The flow sheet of the pilot plant is shown in the Fig. 1.1 and Fig. 1 2

1.6 Scope of the Present Work:

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

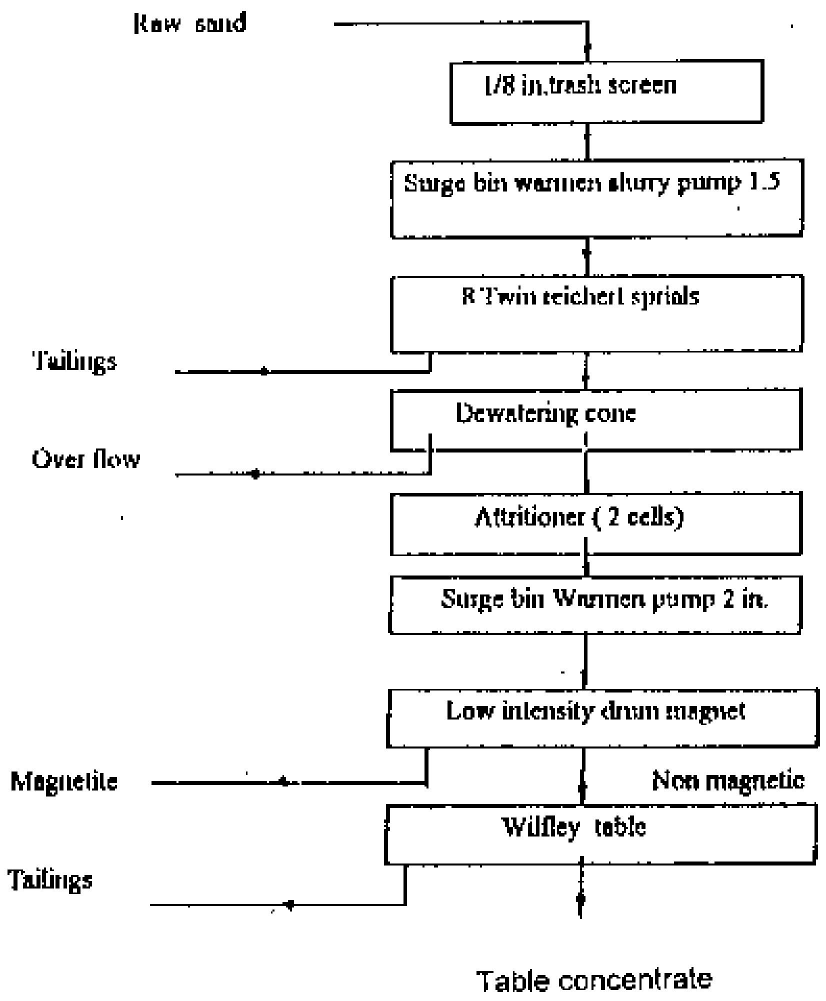


Fig. 1.1 The pilot plant flow sheet (wet section)

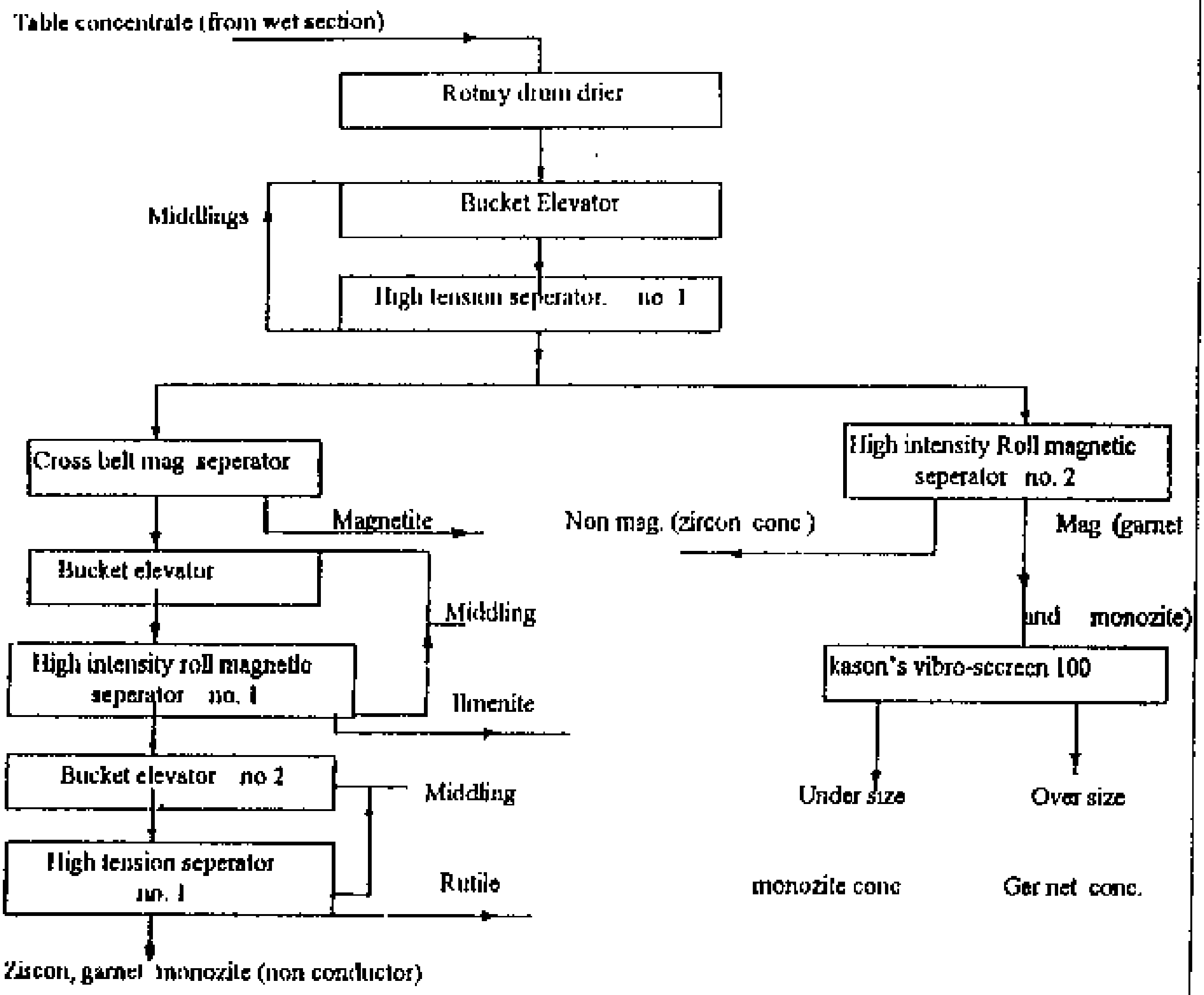


Fig. 1.2 The pilot plant flow sheet (dry section)

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

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

Studies[31,32] have shown that oxidation of ilmenite prior to reduction has the following beneficial functions:

1) introducing defects (cracks, grain boundaries etc) in the ilmenite grain, which enhances the rate of subsequent reductions.

2) converting all the ferrous iron to ferric iron which overcomes the problem of different ferrous to ferric ratios in ilmenite from different localities and

3) Altering the equilibrium conditions and the rate of reduction from ferric to ferrous state.

The rate of leaching has been found to be dependent upon the nature of ilmenite grains, and if the oxidation step is omitted the rate of leaching becomes slow. This also affects the quality of the end product.

No work on the effects of prior oxidation on the kinetics of reduction of Bangladesh ilmenite and the subsequent leaching of the reduced ilmenite has so far been reported. The heavy minerals separated from the beach sands of Bangladesh contain about 25 per cent ilmenite In a country so poor in mineral resources the need to upgrade the ilmenite cannot be over-emphasised. It was expected that a clear understanding of the effects of prior heating/oxidation on the kinetics of subsequent reduction and leaching would help establish the best possible route for the production of synthetic rutile from Bangladesh ilmenite. It has already been mentioned that the TiO_2 content of as-received Bangladesh ilmenite is below the minimum amount of TiO_2 content that is required by it to be suitable for industrial use. Under such circumstances it was considered desirable to under-take this study.

CHAPTER - 2 REVIEW OF LITERATURE

2.1 Introduction

Rutile and ilmenite are the most abundant minerals containing titanium. Rutile is richer in titanium content 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 has been developed and some of these methods are now being exploited on a commercial scale. Reduction of ilmenite with a suitable reducing agent followed by leaching or rusting is one of the commercially successful methods that have so far been developed. The material thus produced closely resemble natural rutile and is known as synthetic rutile.

Fetisov et al[32]. have studied the rates of reduction of oxidised and unoxidised ilmenite using hydrogen as a reducing agent. They found that the reducibility of oxidised ilmenite is higher than the unoxidised The difference in the rates decreased with increasing temperature but remained considerable. They concluded that, oxidative roasting of ilmenite prior to reduction has a beneficial effect on the rate of reduction.

The primary reduction of iron-oxide in the titaniferous minerals must be carried out at temperatures which ensure maximum reduction of iron oxide to its lower oxides. Any method, therefore, which promotes the rate of reduction of iron oxides in ilmenite concentrates is of industrial value. A detailed study on the process of oxidation of ilmenite, identification of the oxidation products, kinetics of reduction of oxidised and unoxidised ilmenite is of technical importance. As a result the oxidation products of ilmenite, the product morphology and the mechanism of oxidation of ilmenite has been studied [31], quite extensively.

2.2 Oxidation of Ilmenite

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

Ramdohr [33] and Overhault et al[34] found from X-ray diffraction patterns that ilmenite when heated in air at 900°C yielded pseudobrookite and rutile. D.G. Jones [35] found that oxidation product of ilmenite over 800°C yielded ferric pseudobrookite and rutile and according to data given by Webstar and Bright[36] ferric pseudobrookite in commercially oxidised Western Titanium ilmenite contains approx 4%, Fe^{2+}.

Curnow and Parry[37] studied the oxidation of ilmenite from beach sand of Australia by magnetic susceptibility and X-ray diffractometry and concluded that i) heating of ilmenite to 600°C enhances magnetic susceptibility and X-ray pattern gives lines similar to ilmenite and rutile. ii) prolonged heating at 800°C results in the formation of weakly ferromagnetic material and Debye Scherrer X-ray photograph of this material gives lines due to rutile and indicate the formation of new product with tetragonal lattice symmetry.

Karkhanawala and Momin[38] studied the oxidation of ilmenite and concluded that :

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

2) The products of oxidation at around 650°C contains mixture of hematite, rutile and an unidentified phase. At 850°C the oxidation products contain a mixture of hematite, pseudobrookite and rutile in an approximate ratio of 1:5:7 respectively.

3) There are three distinct regions of oxidation. 100°- 450°C, 540°-800°C, and 800°-900°C. The oxidation over first region is very slow.

Later investigations[39-42] indicated the formation of Fe_2O_3 as an alteration product when ilmenite is oxidised at temperature between 600°C to 800°C. Results regarding the product of oxidation of ilmenite up to 800°C are conflicting. Various results obtained by different investigators are given below:

1. $2FeTiO_3 + {}^1/_2\, O_2 = Fe_2O_3 + 2TiO_2$ [37, 38, 43]
2. $3FeTiO_3 + {}^3/_4\, O_2 = Fe_2Ti_3O_9 + {}^1/_2\, Fe_2O_3$ [39, 40, 41]
3. $2FeTiO_3 + {}^1/_2 O_2 = Fe_2TiO_5 + TiO_2$ [32-34]
4. $12FeTiO_3 + 3O_2 = Fe_2O_3 + 5Fe_2TiO_5 + 7TiO_2$ [38]

But reaction 4 could occur only under metastable condition.

RaO and Rigaud[31] 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 reaction (1) and (3). Thus either or both reactions may take place up to the decomposition of Fe_2O_3 or Fe_2TiO_5. The free energy change for the formation of pseudobrookite from its oxides is also favourable and reaction (3) takes 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 [44] found that higher temperature and longer time is required for the formation of pseudobrookite from their oxides and the lower temperature limit for the formation of pseudobrookite is explained by the fact that diffusion rate during formation of oxides at lower temperature is slow which might prevent the formation of pseudobrookite.

RaO and Rigaud[31] also performed thermogravimatric and differential thermal analysis of ilmenite prepared by mixing Fe_2O_3, Fe and TiO_2 in the required ratio. The curves obtained by them are shown in Figs. 2.2 and 2.3 respectively. Their general observations of the thermogravetric analysis in both oxygen atmosphere and air are as follows:

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

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

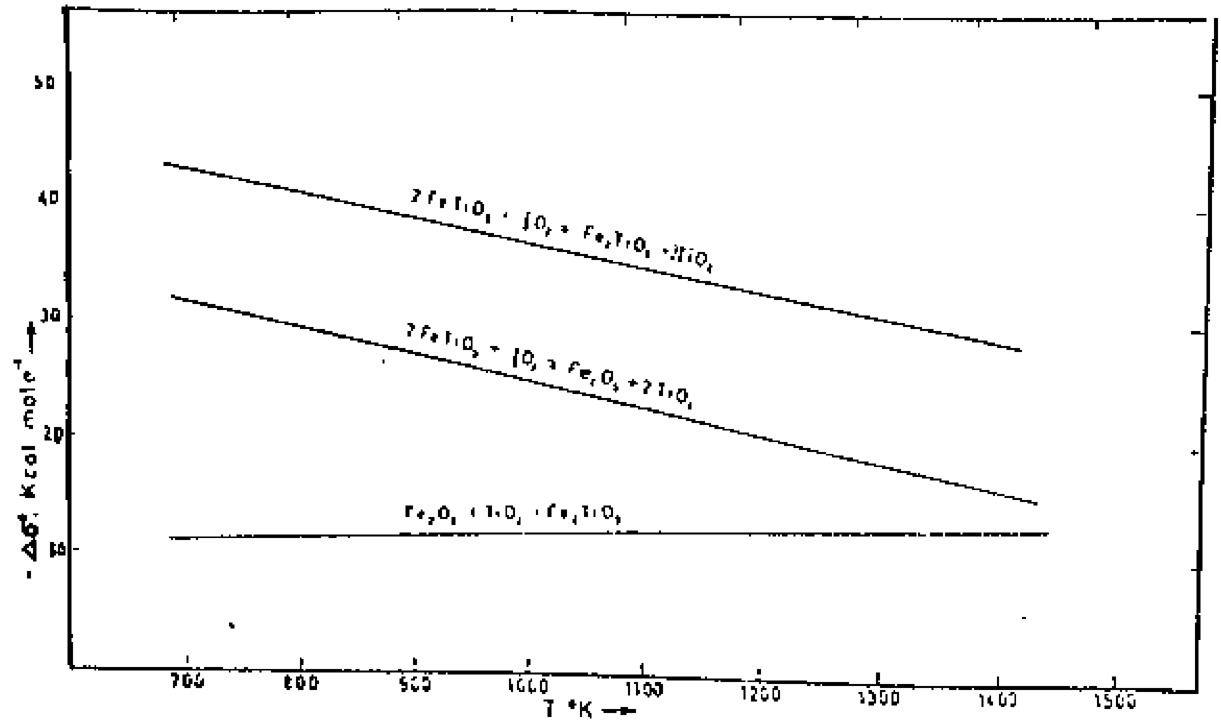


Fig. 2.1 Free energy changes vs temperature for various reactions

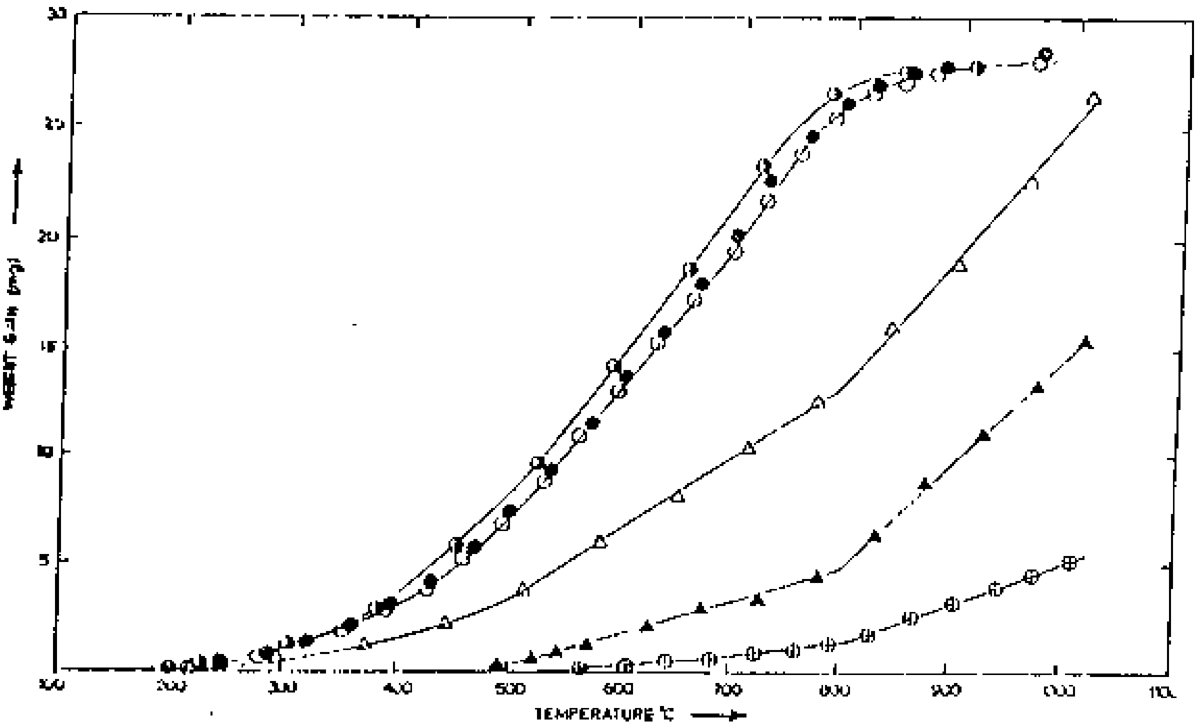


Fig. 2.2 Thermogravimatric curves for the oxidation of ilmenite . Particle size , oxidizing atmosphere and heating rates were: ⦶ Massive crystal , in air , 8° min⁻¹ ; ◑ -200 + 325 mesh , in air , 10° min⁻¹; ○ -150 + 200mesh , in air 6° min⁻¹; ● -150 + 200 mesh , in dry oxygen , 6° min⁻¹ ; △ +100mesh , in air, 10° min⁻¹ , ▲ +100mesh, Norwegian (Storgangen) ilmenite Ore, in air , 10° min⁻¹,

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

They summarised the differential thermal analysis results as follows:

1) The first stage of oxidation starts at 100°C and is exothermic and ended around 770°C.

2) The stage is endothermic and ended around 890°C. because of the larger peak it is difficult to asses ending of reaction but definitely this step continues up to 870°C.

3) A third exothermic reaction sets in at around 900°C

Differential thermogravimetric curves showed that weight gain is not a linear function of time and decreases with time at any given temperature. The rate of increase in weight with respect to temperature is, to some extent, compensated by corresponding decrease due to lapse of time. As a result DTG curves slopes very little. Around 800°C the curves appear to show a transition from rate of weight increase to rate of weight decrease. They returned to show weight increases at around 850°C. This transition may be due to a temperature gradient created as exothermic reaction changes to endothermic reaction. A change of reaction profile may also lead to such distribution.

2.2.1 Product Morphology:

In the gas solid reaction a dense film of reaction product is usually formed on the surface of the solid and the rate is determined by the migration of ions or electrons through the product layer One might expect that the reaction product may be uniform but recent investigations provided evidence of discontinuous formation of product especially at early stage of reaction Fischmeister[45] 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 are important and influence the subsequent leaching of the oxidised ilmenite.

RaO and Rigaud[31] studied the morphology of oxidised ilmenite by scanning electron microscopy at three different temperatures 700°C, 800°C and 1000°C corresponding to reactions (1), (2) and (3). Scanning Electron Micrograph obtained by them at the above temperatures are shown in Figs. 2.4 and 2.5 They found, the morphologies of Fe_2O_3 formed in the beginning stage at 700°C to be similar to the that reported by Gulbransen and Copan[46,47]. They could not locate TiO_2 and concluded that it might not have nucleated at surface.

X-ray energy spectrometric result reveals that the whisker structures contained primarily Fe and negligible amount of Ti {Fig. 2.6(a)]

The mechanism of growth of whiskers are not well established. Hardy[48] suggested that screw dislocation in metals causes the oxide to grow as whiskers. This concept assumes that the continuation of dislocation in the metal into the oxide layers serves as nucleation site for growth of oxides. However it has also been proved[49] that in a system in which more than one oxide is stable the whiskers always formed of higher oxides. RaO and Rigaud observed that whiskers grows from the lower oxides. The formation of higher oxides impose considerable stress on lower oxides[50, 51]. Nabarro-Herring mechanism suggests that the grain boundaries under stress might supply the necessary current of reactant atoms required for the formation of whiskers.

This is particularly true at high temperature where chemical potential variations between different spots on the surface are small. At high temperature and at enough oxygen pressure the product particle grows randomly Conditions favourable for the formation volatile suboxides may also lead to the formation of whiskers[52, 53], although thermodynamic calculation indicates that no such species is present at the system at this temperature. When ilmenite is oxidised at 850°C Fe_2O_3 segregates at grain boundaries in the shape of a columnar crystal aggregates surrounding pseudorutile phase.

The type of growth was suggested to be formed between two screw dislocations or from edge dislocation parallel to the base[45]. The surface morphology of an ilmenite crystal oxidised at 1000°C shows the morphology of pseudobrookite . Some blade like structures mainly TiO_2 also grew on the surface at preferred sites Relative intensities of Fe and Ti is shown in Fig 2.6(c). The intensities of b and c of Fig 2.6

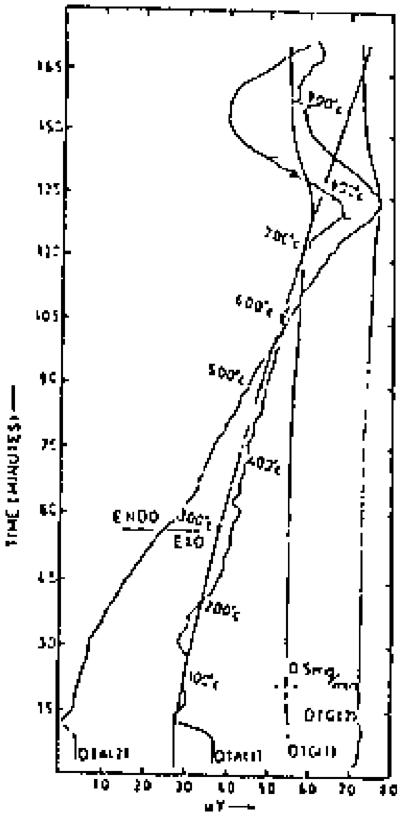


Fig. 2.3 Differential thermal analysis (DTA) and differential thermogravimetric Analysis (DTG) tracings for the oxidation of ilmenite powders (-150 +200 mesh size fraction). Heating rate was 6° per min and alumina was used as a reference material . DTA (1) and DTG (1) indicate the oxidation was carried out in air and DTA(2) and DTG(2) represent oxidation in dry oxygen.

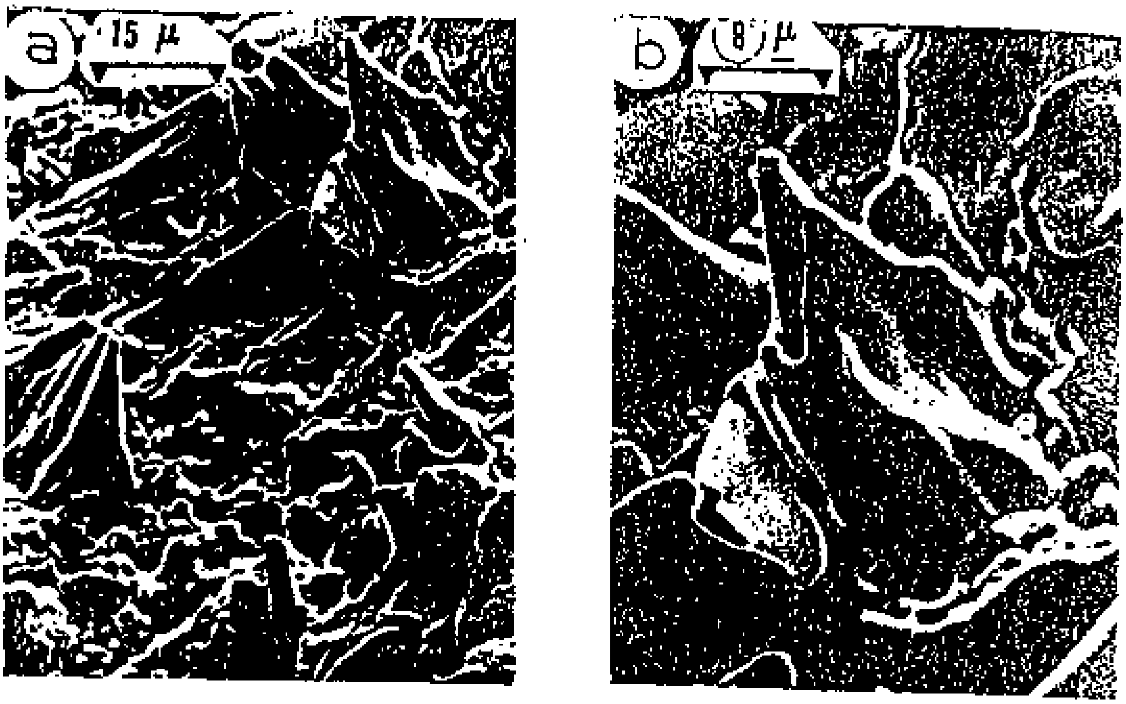


Fig. 2.4 Morphology of TiO_2 formed on the surface at 1000° C. (a) x 1,200; (b) x 2,400.

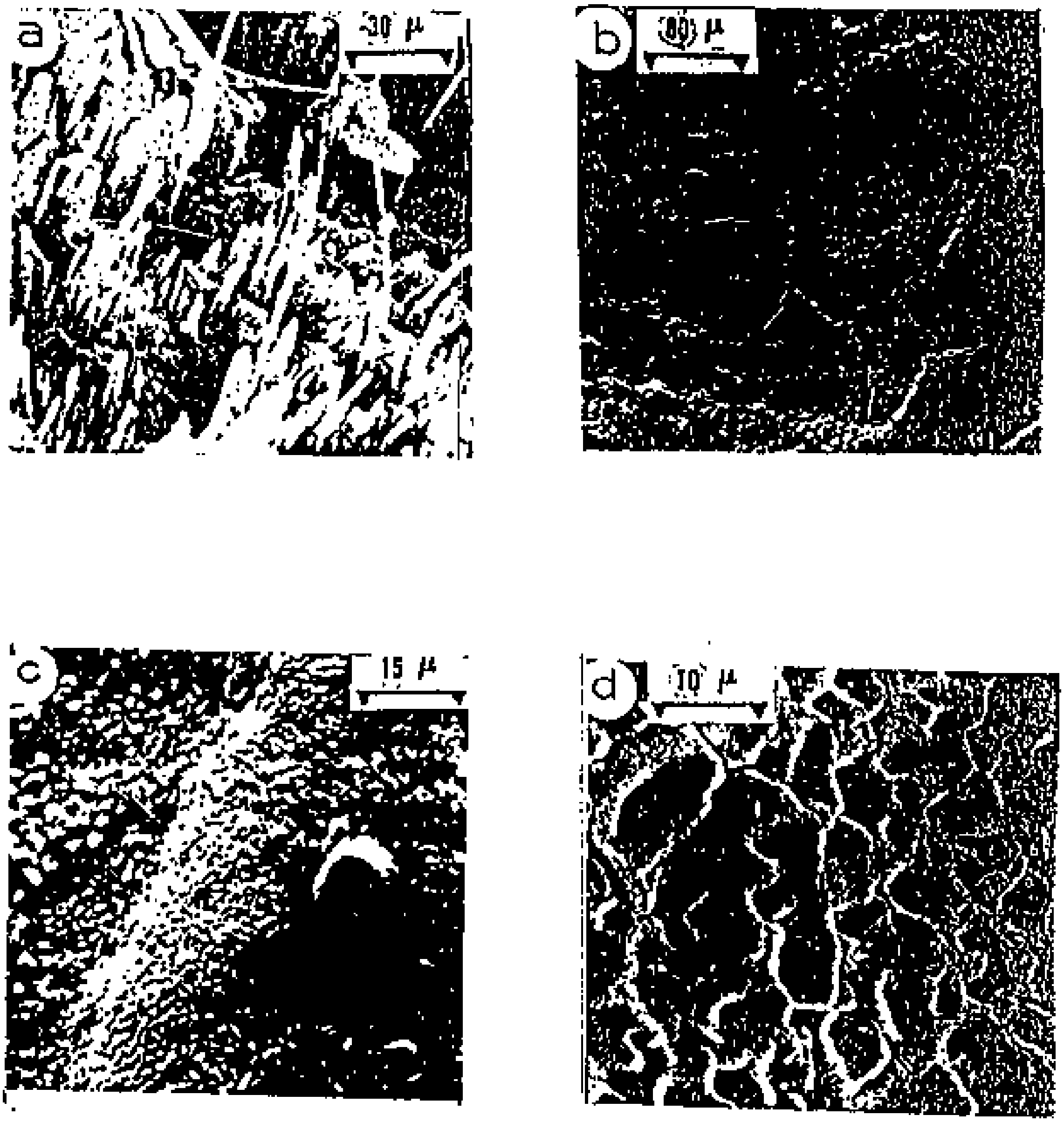


Fig. 2.5 Scanning Electron Micrographs of the product formed during oxidation of ilmenite crystals. (a) Morphology of the formation of hematite whiskers during the initial stages of oxidation at 700°C, X 650. (b) Morphology of the formation of hematite and $Fe_2Ti_3O_8$ upon oxidation of ilmenite at 850°C, X 250. (c) Hematite on the grain boundaries, X 1200. (d) Pseudobrookite formed at 1000°C, X 2000

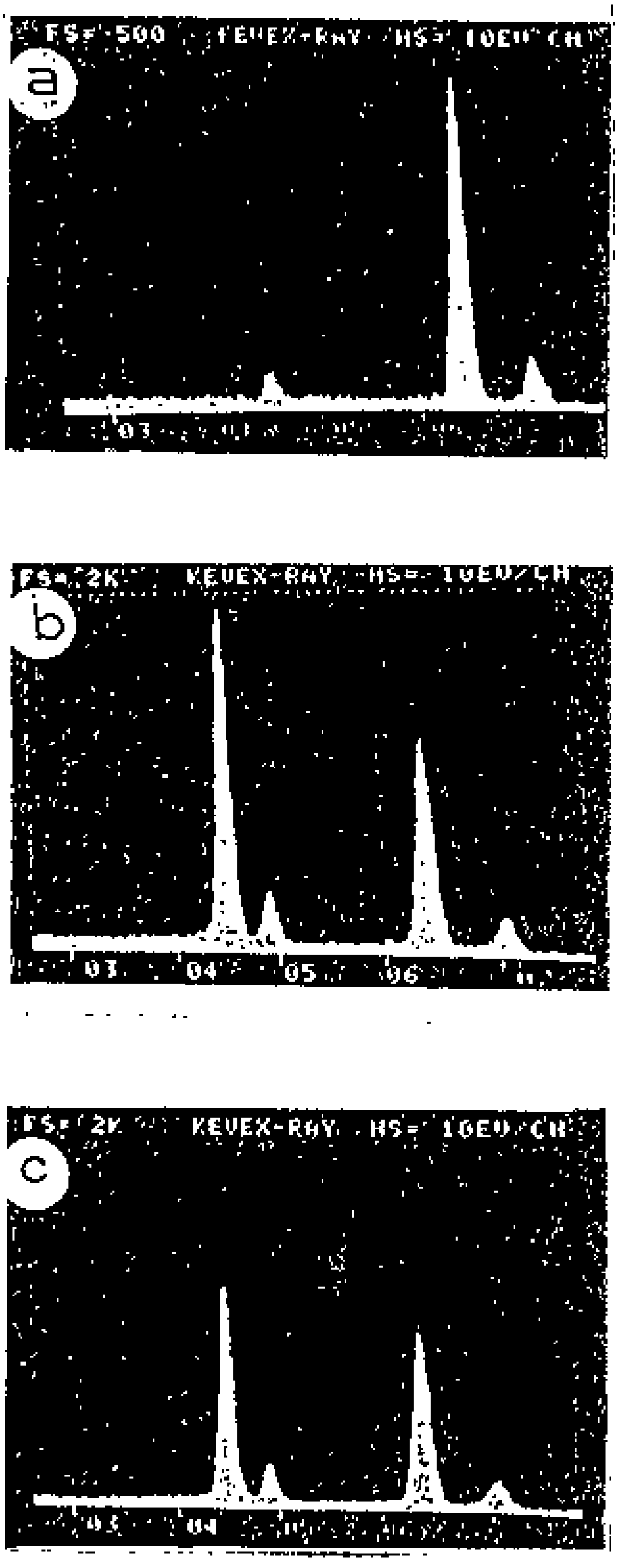


Fig. 2.6 Relative intensities of iron and titanium in the reaction products. X-ray energy for K radiation of iron and titanium are 6.4and 4.54 keV , respectively. (a) For Fe_2O_3 : (b) $Fe_2Ti_3O_9$, (c) Fe_2TiO_5 and the areas which they correspond to Figs. 2.5a, 2.5b and 2.5d respectively.

are comparable due to solid solubility of TiO_2 and Fe_2TiO_5. The morphology of TiO_2 is blade like with central pore. It was predicted[55] that this type of growth is due to the hollow type of dislocations.

The growth morphology of products can also influence significantly the kinetics of gas solid reaction . The whisker growth only affects[45] the kinetics in the early stages and before the product reaches appreciable thickness The kinetic data of the oxidation of ilmenite reported elsewhere[56] is also in agreement with this hypothesis.

RaO and Rigaud[31] found logarithmic rate law of oxidation in initial stage and suggest that it is due to penetration of oxygen through short circuit path. Oxidation is otherwise parabolic. They found one break in Arhenius plot corresponding to reaction (1) and (3) and could not distinguish the range of reaction (2). They suggested that this may be due to short range of reaction (2) or due morphological effect or the reaction (2) and (3) might be controlled by the same or similar mechanism.

2.2.2 *Mechanism Of Reactions:*

Actual mechanism for the formation of products of different textures are not known and the data related to the diffusion rate and conductivity of reactants and the products are also not available. Wort and Jones[57] studied the alteration of ilmenite and suggested that it takes place in two different stages.

Stage 1. $3Fe^{+2} . TiO_3 + 2 H^+ + {}^1/_2O_2 \rightarrow Fe_2{}^{3+} . Ti_3O_9 + Fe^{+2} + H_2O$

Stage 2. $Fe_2Ti_3O_9 + 4H^+ \rightarrow 3TiO_2 + 2Fe^{++} + 2H_2O + {}^1/_2O_2$.

Teufer and Temple [39] 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.

$$3Fe\ TiO_3 \rightarrow Fe_2Ti_3O_9 + {}^1/_2\ Fe_2O_3.$$

By heating pseudorutile above 800°C pseudobrookite is formed.

$$Fe_2Ti_3O_9 \rightarrow Fe_2TiO_5 + 2TiO_2$$

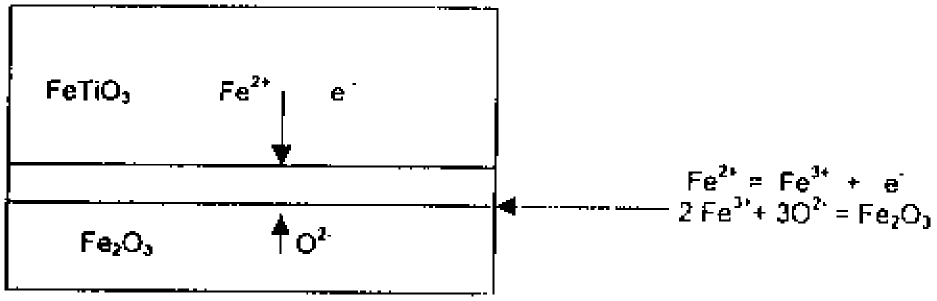
Rao and Rigaud[31] upon their extensive study on the oxidation mechanism and product morphology provided some tentative conclusion upon the general reaction mechanism:

During oxidation at temperatures below 770°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[58] 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.

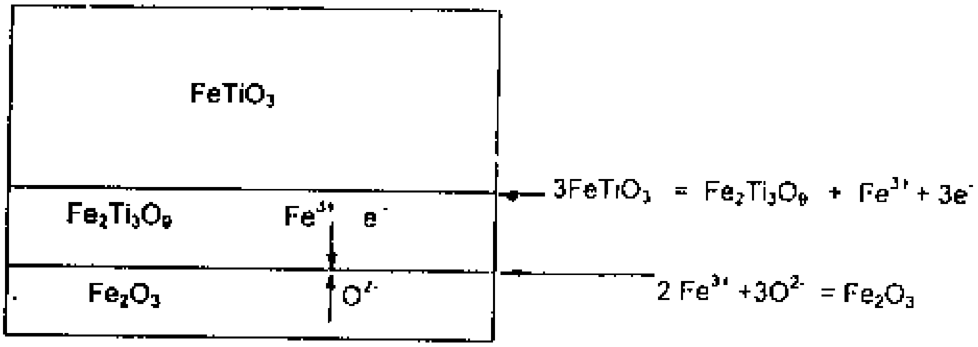
They found $Fe_2Ti_3O_9$ to be stable at temperatures from 770° to 900°C where iron will diffuse through it to the grain boundaries. This suggested that iron is mobile through pseudorutile. Pseudorutile has the highest titanium oxide content and there is possibility for the formation of solid solution 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 precipetated. At temperature greater than 900°C, TiO_2 is formed on the surface and mobility of Titanium increases. When the sample is heat treated above 950°C the initial whiskers of Fe_2O_3 formed on surface of the samples at 750°C is transformed to pseudobrookite. The movement of titanium is confirmed by the fact that when ilmenite is oxidised with markers at 950°, TiO_2 was formed above markers. The markers were covered with rutile at particular locations of the crystal. This is assumed due to rapid diffusion of Ti through certain preferred orientation of ilmenite. But the orientation favourable for diffusion of ilmenite was not confirmed due to its polycrystalline nature. The mobile Ti will leave some excess O_2 which in turn could be utilized in the oxidation step or escape to the gas stream. They found a central pore in each grain as well as in the 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 7 .

2.3 Reduction Of Ilmenite

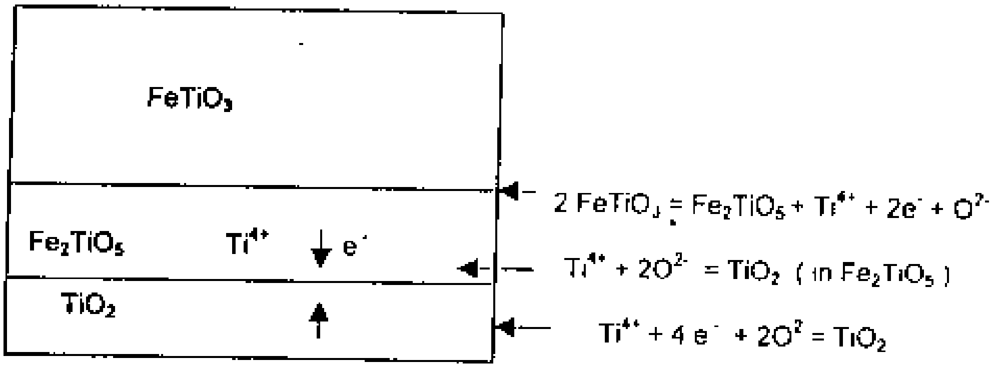
Reduction of ilmenite was studied by several workers using different reducing substances Guindy and Davenport[59] studied the mechanism of reduction of ilmenite using graphite as reductant. They observed that solid state reduction initiates near 860°C at contact point between the reactants. The solid 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.



a) T < 770° C



b) 770°C < T < 900° C



c) T > 900°C

Fig. 2.7 Schematic representation of proposed mechanism for the oxidation

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 ;

1) Solid state reaction:

$$C + Fe\,TiO_3 \rightarrow CO + Fe + TiO_2.$$

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

2) Gaseous reaction

$$.CO + FeTiO_3 \rightarrow CO_2 + Fe + TiO_2.$$

$$C + CO_2 \rightarrow CO$$

The reduction involving gaseous reduction depends upon the regeneration of CO of the system. The sequence of reaction in the reduction of ilmenite by pure CO was studied by D.G Jones[35] by x-ray diffraction analysis in the range of 900° - 1200°C. He found that reduction of naturally weathered and preoxidised 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.

$$Fe_2Ti_3O_9 + CO \rightarrow 2FeTiO_3 + TiO_2 + CO_2$$

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

The second stage is slower than first stage. In this 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.

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

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

At 900°C to 1000°C the reduction of pre-oxidised ilmenite is expressed as

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

Jones[35] Identified rutile and ferric pseudobrookite as the main constituents of pre-oxidised ilmenite and concluded that reduction proceeded in two stages. The first stage is the reformation of ilmenite

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

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.

At the later stage rutile is reduced to lower oxides.

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

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

At 1200°C the ilmenite is first reduced to metallic iron and ferrous pseudobrookite. On further reduction metallic iron is precipitated from ferrous pseudobrookite to yield M_3O_5 which progressively becomes richer in Ti_3O_5. Any Mn or Mg present is also incorporated in it [35, 60]. A significant amount of rutile is present as third phase At 1100°C M_3O_5 is stabilised by small amount of Mn and Mg[35, 60] But it still consists of a three-phase mixture. But M_3O_5 present is less than at 1200°C. The distribution of phases during reduction of Western titanium ilmenite[35] at different temperature is shown in Fig. 2.8 to Fig. 2.10

Reduction of Bangladesh ilmenite by using charcoal as reductant was carried out by Haseeb, et al[61]. 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 on reduction of Bangladesh ilmenite was studied by Sharmin et al[62]. They found that more than 97% of Bangladesh ilmenite belongs to U.S. Sieve No. 100, 140, 200. Finer fraction contains lower percentages of TiO_2 and higher percentages of total iron. Chemical analysis of ilmenite reduced by charcoal at 1050°C for 4 hour revealed that finer fraction contains lower iron oxides[62]. The degree of reduction of iron oxides present in ilmenite was found to be 71.35%, 75.39%, 78.91% for size fraction corresponding to U. S. Sieve No. 100, 140, 200 respectively. They concluded that as far as the optimisation of reduction parameters

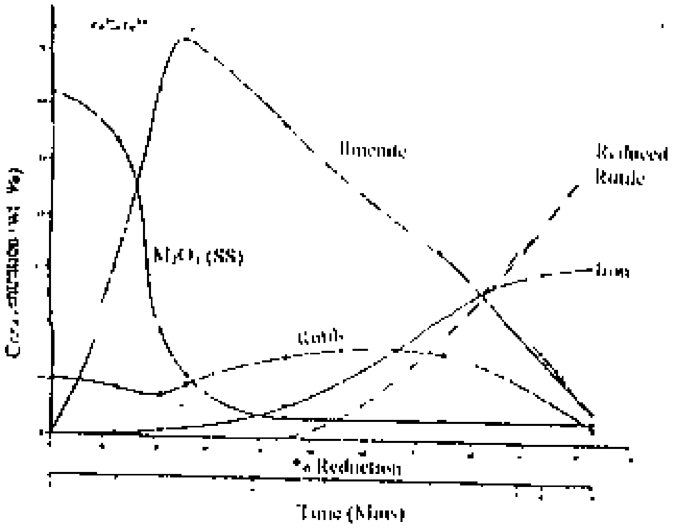


Fig. 2.8 Distribution of phases during reduction of Western Titanium N. L. ilmenite at 1000°C

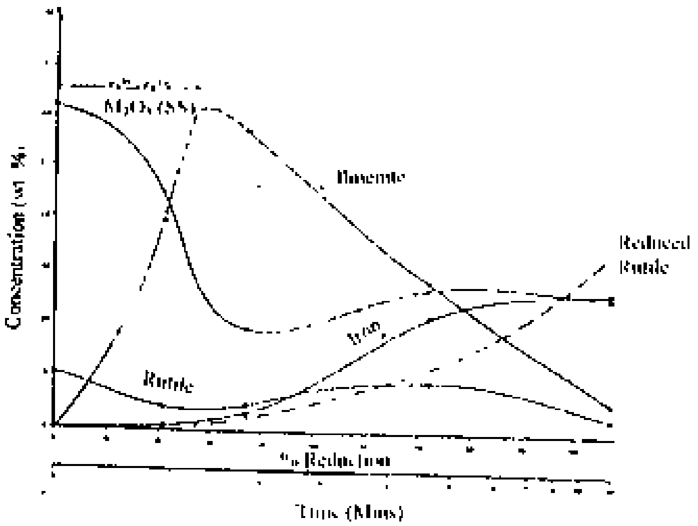


Fig. 2 9 Distribution of phases during reduction of Western Titanium N. L ilmenite at 1100°C

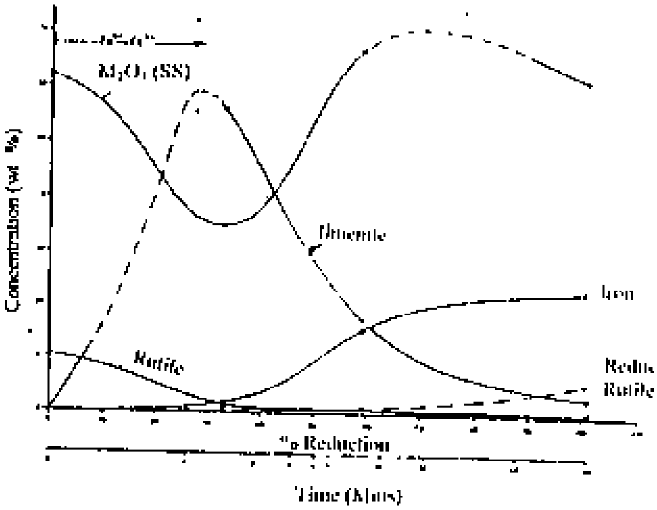


Fig. 2.10 Distribution of phases during reduction of Western Titanium N. L. ilmenite at 1200°C

of Bangladesh ilmenite is concerned, a separate reduction procedure for each fraction is not necessary.

2.3.1 Microscopic Examination And EPA Of Reduced Ilmenite:

M.I EL-Guindy and Davenport[59] examined the segregation of the product of ilmenite reduced by graphite and observed lightly sintered porous masses. The phases identified were:

1) A segregated iron phase present in oval-like forms which tend to migrate and coalesce. In some cases iron was observed to move to particle boundary area and to join together adjacent particle. He assumed the coalescence to be the apparent cause of sintering

2) TiO_2 phase is present near the boundary of the particle and in a vein like arrangement within the particle.

3) There are the area of variable composition within the phase.

4) Small unreduced area near the centre of the large particle.

D.G. Jones[35] studied the morphology of the Point Richard ilmenite reduced by CO and observed that the metallic iron is dispersed in a matrix of TiO_2. The morphology of metallic iron is influenced by the reduction temperature. At 1000°C, for example, much of iron occurs as plates up to 5 μm having a preferred orientation resembling that of altered region in the natural unreduced ilmenite. The remainder occurs as finely divided spherical particles. Voids are resulted from a change in the density as Fe (sp.gr.-7) is precipitated from ilmenite (sp.gr.- 4.5). Above 1000°C iron begins to coalesce in large globules which tend to segregate towards the periphery of the grains .At 1100°C nearly all the grains are completely enveloped by shells of metallic iron. These shells causes the grains to sinter together. Reduction of the ilmenite begins at the periphery of each of the grains and proceeds more or less symmetrically towards the centre At any instance during reduction there is an unreacted core surrounded by a shell of reaction product. This unreacted core is present even in some grains of the final product when the reduction has been taken to its maximum possible extent. EPMA has shown that the unreacted core contains unusually high concentration of Mn and /or Mg. This high concentration of Mn or Mg reduces the activity of Fe^{2+} making its reduction progressively more difficult. This effect becomes less noticeable with increasing temperature At temperature beyond 1000°C the Mn/Mg diffuses more rapidly and is able to concentrate more towards the centre of the ilmenite grains. However at higher temperature another troublesome phenomenon the formation of closed shell of metallic iron at the periphery of the grains is observed This impairs the rate of diffusion of the reacting species and leads to large-scale sintering of the product Pre-oxidation of the ilmenite can overcome the sintering problem. Pre-oxidation at above 800°C converts ilmenite to pseudobrookite and rutile and converts the single crystal of ilmenite into polycrystalline array of pseudobrookite containing a fine dispersion of rutile.

2.4 Leaching Of Ilmenite

Selective leaching of the ilmenite by mineral acid removes 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. On the other hand digestion with hydrochloric acid is selective and iron is brought to solution. Direct acid leaching is carried out at somewhat higher temperature. The preferential chlorinating of iron with hydrochloric acid gas is represented as

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

The standard free energy[63] for the reaction as a function of temperature is represented as

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

From the thermodynamic data[63] it is seen that the reaction is possible even when more than 99% H_2O is present in the mixture. It should be mentioned here 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[63] 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

$$^1/_3Fe_2O_3\ TiO_2 + 2HCl \rightarrow {}^2/_3FeCl_3 + {}^1/_3\ TiO_2 + H_2O$$

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-worker[30] 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 The leaching reaction of ilmenite can be expressed as

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

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

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

The standard free energy change for the preferential chlorinating of iron from ilmenite as a function of temperature is plotted in Fig 2.11.

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

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

The free energy change[36] for the reaction is represented as

$$\Delta F^\circ = - 7765 - 1.08\ T\ Log\ T + 18.8\ T$$

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

Mohan Das et al[64] 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 et al[65] 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[66] Fe_2O_3 is converted to FeO and was leached with 20% HCl at 108-110°C and obtained a product containing 95-97% TiO_2.

Ismail et al[67] studied the oxidation reduction and leaching kinetics of Srilanka ilmenite and found that the result is similar to Murso process and obtained a product containing 90-95 per cent TiO_2.

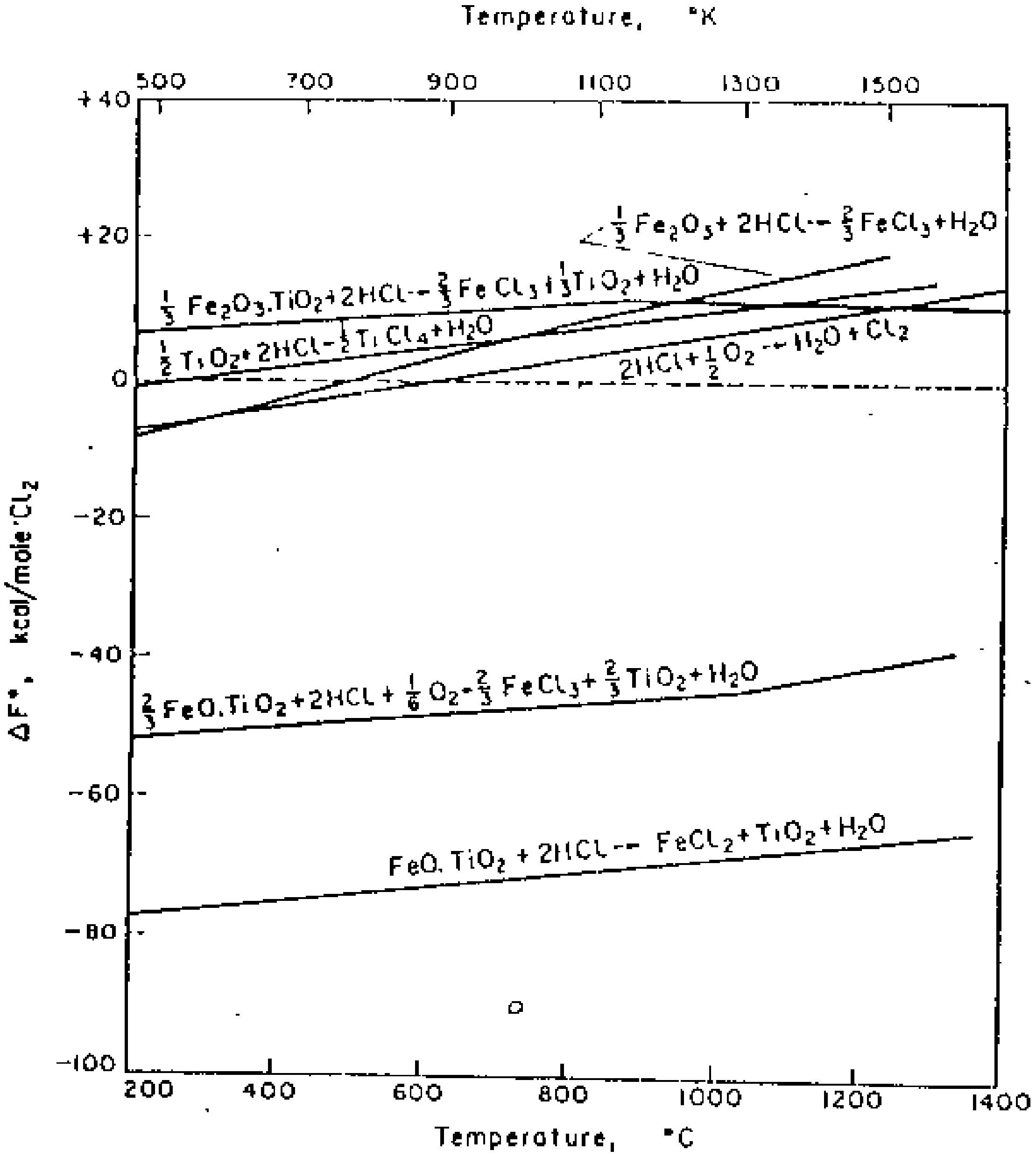


Fig. 2.11 Free energy changes involved during chlorination of ilmenite

Burastero[68] obtained a product >95% TiO_2 by employing oxidation reduction leach techniques in the laboratory scale.

2.5 Characterisation of Bangladesh Ilmenite:

It is well recognised that ilmenite occurring in nature undergoes alteration due to weathering. Alteration is a complex process but it can be simplified into two major reactions that occur sequentially[61].

Stage -1 $3Fe^{2+}TiO_3 + 2H^+ + {}^1/_2 O_2 \rightarrow Fe_2^{3+}Ti_3O_9 + Fe^{2+} + H_2O$

Stage-2 $Fe_2Ti_3O_9 + 2H^+ \rightarrow 3TiO_2 + 2Fe^{2+} + 2H_2O + {}^1/_2O_2$

In the first stage of the alteration of ilmenite one third of total iron is lost from ilmenite and the remaining iron is converted to ferric state forming pseudorutile In the second stage iron is removed from pseudorutile and yield rutile. Alteration of ilmenite depands on the geological history of the deposit. In the partially altered deposit different phases are co-existed and in the completely altered deposit the predominant phase is rutile and was concluded that as-received Bangladesh ilmenite is in partially altered state and contains rutile, pseudorutile and hematite. The presence of hematite in Bangladesh ilmenite has also been reported by other investigators[69] that clearly showed the presence of Fe^{3+} sextet belonging to hematite in the Mossbauer spectrum. Hematite present in ilmenite-hematite solid solution can shift the ilmenite peak to higher angles[70]. Similar shift of ilmenite peak with respect to standard data was also observed in the present study suggesting that some hematite also exists in ilmenite solid solution. Ahmed et al[69] identified six types of texture in the Bangladesh ilmenite and found that the main texture is seriate type where ilmenite and hematite exists side by side in a layered morphology.

2.6 Morphology of Ilmenite of Cox's Bazar Beach Sand.

Microscopic study of ilmenite of Cox's Bazar beach sand reveals wide variety of exsolution. features with the exsolved phases making up to 52% of grains[69]. These hemo-ilmenite and ilmeno-hematite's are ferrimagnetic and vary in composition between Ilm_{45} Hem_{55} and $Ilm_{75}Hem_{25}$ Mitra and Ahmed[69] distinguished five different types of intergrowth namely as I) ilmenite-hematite ii) magnetite-ilmenite iii) Hematite-rutile iv) hematite-ilmenite-rutile and v) ilmenite-rutile. The most common of these are exsolution of ilmenite and hematite. The ilmenite or hematite lamellae thickness in hematite or ilmenite matrix shows conspicuously a bimodal distribution. The coarser and first generation of lamellae were formed by diffusion process at 530°-600°C, the finer second generation lamellae were formed by slow diffusion process in 450°-500°C[69].

Enrich ilmenite(> 85% ilmenite solid solution) exsloves continuously where as ilmenite with higher Fe_2O_3 exsolves discontinuously The latter type of high fO_2 and other less defined conditions may produce bimodality of exsolved ilmenite. Such high fO_2 environment of crystallization of Fe_2O_3 rich ilmenite phases is distinctly different from that of exsolved continuously in a less oxygenating environment

The exsolution of ilmenite hematite shows various textural patterns such as emulsion, granular, quadrangular. Subgraphic and veined texture Of these seriate texture is more common. Where coarse ilmenite or hematite exsolution bodies contains rows of small bodies of hematite or ilmenite the lamellae occasionally shows curved boundaries which suggest the exsolution under stressed condition. The irregular shapes of the ilmenite in hematite host in some seriate texture possibly have formed by in insitu growth by drawing in or exsolved $FeTiO_3$ molecules from the adjacent mixed phase with ilmenite in solid solution. Mitra and Ahmed[32] suggested that this growth has led to the coalescence of adjacent exsolution bodies and thus produces aggregates of ilmenite lamellae of multiple generation, and the first generation of ilmenite was exsolved in hematite host. At a later stage when fracturing occur the second generation of ilmenite were exsolved along those fractures and finally the third generation exsolution takes place in between fractures. The second and third generation ilmenite phases derived titanium from the immediate neighbourhood by solid state diffusion.

CHAPTER - 3 EXPERIMENTAL

3.1 Introduction

The aim of this investigation was to study of the effect of prior oxidation on the reduction and leaching of ilmenite separated from beach sands of Bangladesh. In this chapter, the oxidation, reduction and leaching of ilmenite are described. The different experimental techniques used to follow the effects are also described.

Typical size fraction of the sample is given in Table - 3.1. Approximate composition of this ilmenite is given in Table - 3 2.

Table- 3.1 Typical size fraction of as-received Bangladesh ilmenite

US Sieve No	*% retained on Sieve*
70	2.25
100	34.24
140	52.77
200	10.41
270	0.44

Table -3.2 Chemical composition of as-received ilmenite.

Component	*Composition (%)*
Total iron	41.89
Fe_2O_3	33
FeO	24.19
TiO_2	39.45

3.2 Oxidation of Ilmenite

5 to 10 gm of dry as-received ilmenite was taken on a porcelain lid and was spread as a thin layer and was oxidised in a muffle electric furnace in the temperature range of 700°C to 950°C for up to four hours. The temperature of the furnace was controlled by an On- Off controller to ± 5°C A chromel-alumel thermocouple was used to measure the temperature of the furnace. The effect of time and temperature on the oxidation of Bangladesh ilmenite was followed by chemical analysis of the oxidised samples, optical microscopy and for a limited number of samples by scanning electron microscopy. The changes in phases were identified by X-ray diffraction techniques.

The extent of oxidation as a function of time and temperature was determined by chemical analysis for ferrous iron in the oxidised ilmenite. For this purpose ilmenite was finely ground in an agate mortar and pestle and was analysed. The details of the procedure for chemical analysis are given in Appendix-A.

Oxidised ilmenite was finely ground in an agate mortar and pestle. X-ray diffraction patterns were recorded on a X-ray diffractometer using Mo as turget. All the samples were investigated by X-ray diffraction using MoK_{α} radiation in a JEOL DX-GE-2P X-ray diffractometer. X-ray diffraction pattern was recorded with the following settings: voltage - 30 kV, current - 20 mA, scanning speed - $^1/_4$ °/minute, chart speed - 05 mm/minute. Scanning was initially done in the range of 5 to 35° and it was found that almost all the diffraction lines lie in the range of 8° to 31°. From the recorded x-ray patterns the 'd' spacings were calculated and the presence of various phases were identified.

Morphology of the oxidised ilmenite was studied by optical microscopy. For optical microscopic study, a few grains of ilmenite were bonded with cold setting resin and were prepared by using the standard techniques The mounted samples were then examined under an optical microscope A few samples were observed under a scanning electron microscope.

3.3 Reduction of Ilmenite

Reduction of both oxidised and as received ilmenite was carried out in a vertical tube furnace. The experimental arrangement is shown in Fig 3.1. For reduction charcoal of mesh size + 30 was used. Analysis of charcoal used for reduction is given in Table- 3.3

Table 3.3. Specification of the charcoal used.

Component	*percentage of weight*
Moisture content	9.4
Ash content	6.8
Volatile matter	26.2
Fixed carbon	57.35

For reduction 50 gm of ilmenite and 50 gm of charcoal was taken. A bed of charcoal was first charged in a vertical tube furnace. 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 prevent entrance of air in it. Reduction was carried out at three different temperatures (950°C, 1000°C and 1050°C). Higher temperatures were not used because previous investigations showed that at temperatures above 1050°C, some TiO_2 is also reduced[61]. Reduction was carried out for different periods of time such as $^1/_2$ hr, 1hr, 2 hr, 4 hr, and 6 hr. After reduction the reduced sample was separated from charcoal by screening. During charging care was taken to maintain identical charging conditions for all samples.

The extent of reduction was followed by the detection of metallic iron content of the reduced ilmenite by chemical analysis. The detail procedure for chemical analysis used is given in Appendix-B. The metallic iron content of ilmenite at different temperature was plotted as function of time. The best condition for reduction was found to be 4-6 hours at 1050°C for both oxidised and as received samples of ilmenite. The total iron values of both types of samples were determined as per procedure given in appendix C. Reduced samples were then taken for leaching in hydrochloric acid.

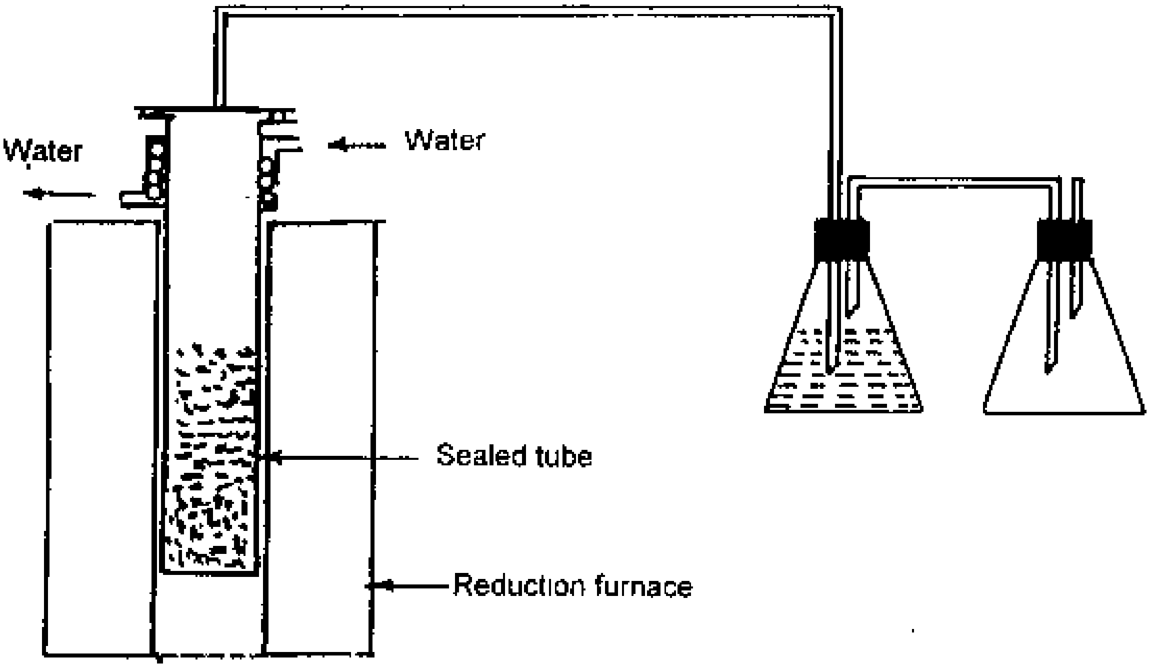


Fig: 3.1 Arrangement for reduction

3.4 Leaching

Samples of reduced ilmenite were leached in 5 – 15 per cent hydrochloric acid solution at temperatures ranging from room temperature to 75°C and for periods of up to 3 hr. The arrangement for leaching is shown in Fig. 3.2. During leaching 2 gm of sample was taken in 200 ml of 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 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 than plotted for obtaining the leaching kinetic curves.

The iron and TiO_2 contents of the leached samples were determined by 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

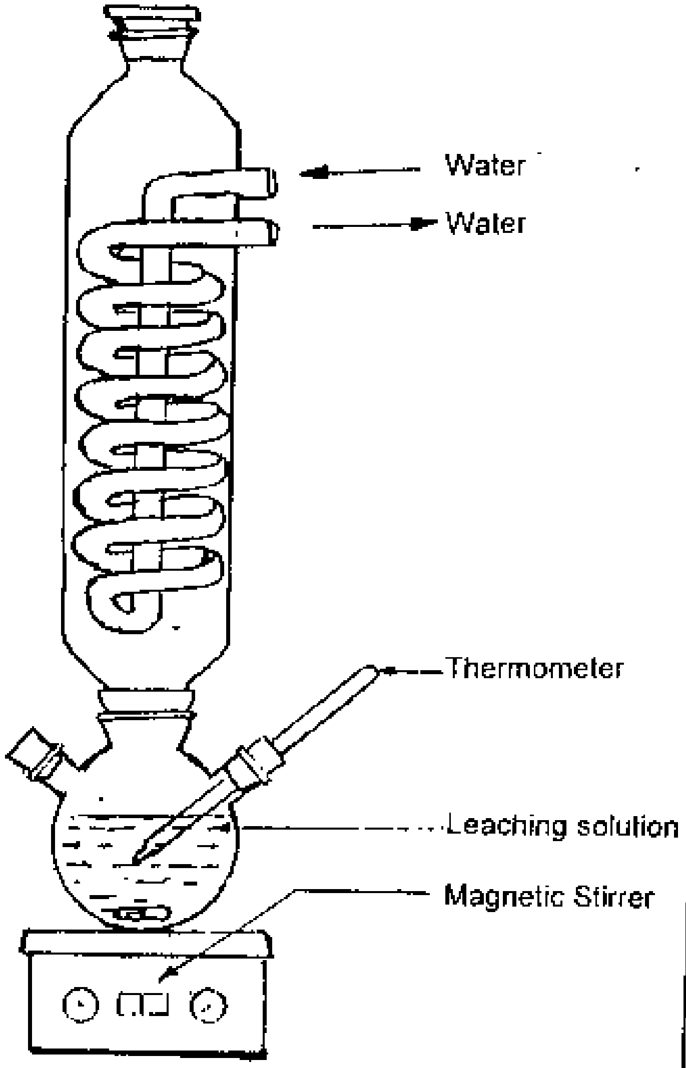


Fig. 3.2 Arrangement for leaching

CHAPTER - 4 RESULTS AND DISCUSSION

4.1 Introduction

The effect of oxidation on reduction and subsequent leaching of Bangladesh ilmenite has been investigated. The effects of time and temperature on the oxidation of ilmenite has been followed by chemical analysis, X-ray diffractometry and optical microscopy. A few samples were also observed under a scanning electron microscope. The sample of ilmenite both oxidised and as received were reduced with charcoal in the temperature range of 950°C to 1050°C for treatment time of up to 6 hours. The extent of reduction was followed by chemical analysis, X-ray diffractometry. The reduced samples were also observed under the optical (and a few samples scanning electron) microscope. The reduced samples were leached in hydrochloric acid. The kinetics of leaching was followed by chemical analysis. The result of these investigation are presented and discussed below:

4.2 Oxidation

Oxidation of ilmenite in the temperature range of 700° - 950°C has been performed in a mufle-type electric furnace. The temperature of the furnace was controlled to ± 5°C by an ON-OFF controller. The extent of conversion of ferrous iron to ferric ion was determined by chemical analysis of ferrous iron in the oxidised sample. X-ray diffraction patterns of the samples oxidised for various times at different temperatures were recorded for the identification of the phases formed during oxidation. The oxidised samples were observed under an optical microscope A few samples were observed under an electron microscope.

The results of chemical analysis of ferrous iron in the oxidised samples has been shown in Fig 4.1. From this figure it is clear that at all temperatures under investigation, the rate of oxidation is very rapid at the initial stage and the rate diminishes with time. At lower temperatures, a longer time is required for the attainment of the equilibrium condition. At higher temperatures, on the other hand, the equillibrium 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 is not oxidised to the ferric state, i.e., some ferrous

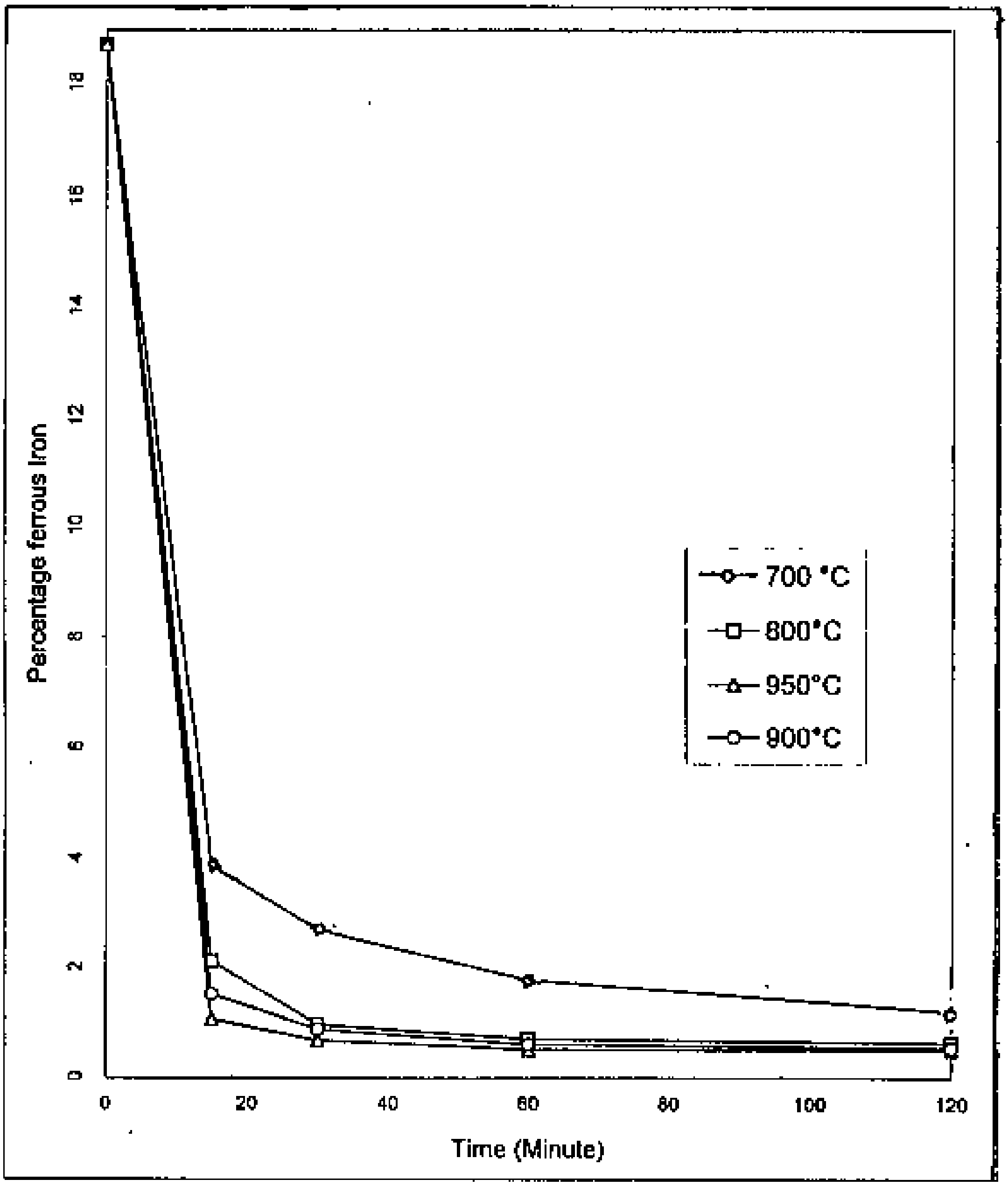


Fig: 4.1 Amount of ferrous iron present in the oxidised sample as a function of time at different temperature.

iron is always present in the oxidised sample. The presence of some ferrous iron can be explained by the fact that the attainment of complete oxidation would mean that the value of equilibrium constant is infinite This is practically impossible. From these results (Fig.4.1), it was concluded that the optimum time and temperature for oxidation of ilmenite is 1 hour at 950°C.

The higher initial rate of oxidation during the initial stages can be explained by the fact that 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 is the rate determining step.

4.2.1 Optical Microscopy

Particles of ilmenite both in the as received and in the oxidised 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 in a plain while the areas in between the particles were out of focus. A few samples were observed under a scanning electron microscope.

Fig. 4.2 shows the optical micrograph of as received ilmenite. Optical micrographs of ilmenite oxidised 1 hour at 700°C, 800°C, and 950°C have been shown in Fig 4.3

These figures shows that structure of ilmenite at 700°C is different from that of ilmenite structure oxidised above 800°C . The structure of ilmenite oxidised at 800°C is similar to that of ilmenite oxidised at 950°C indicating that above 800°C no significant phase change has occured. Fig. 4.4 and 4.5 show the scanning electron micrograph of ilmenite oxidised at 950°C for 15 and 60 minutes. An important observation from the figures is that oxidation 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.

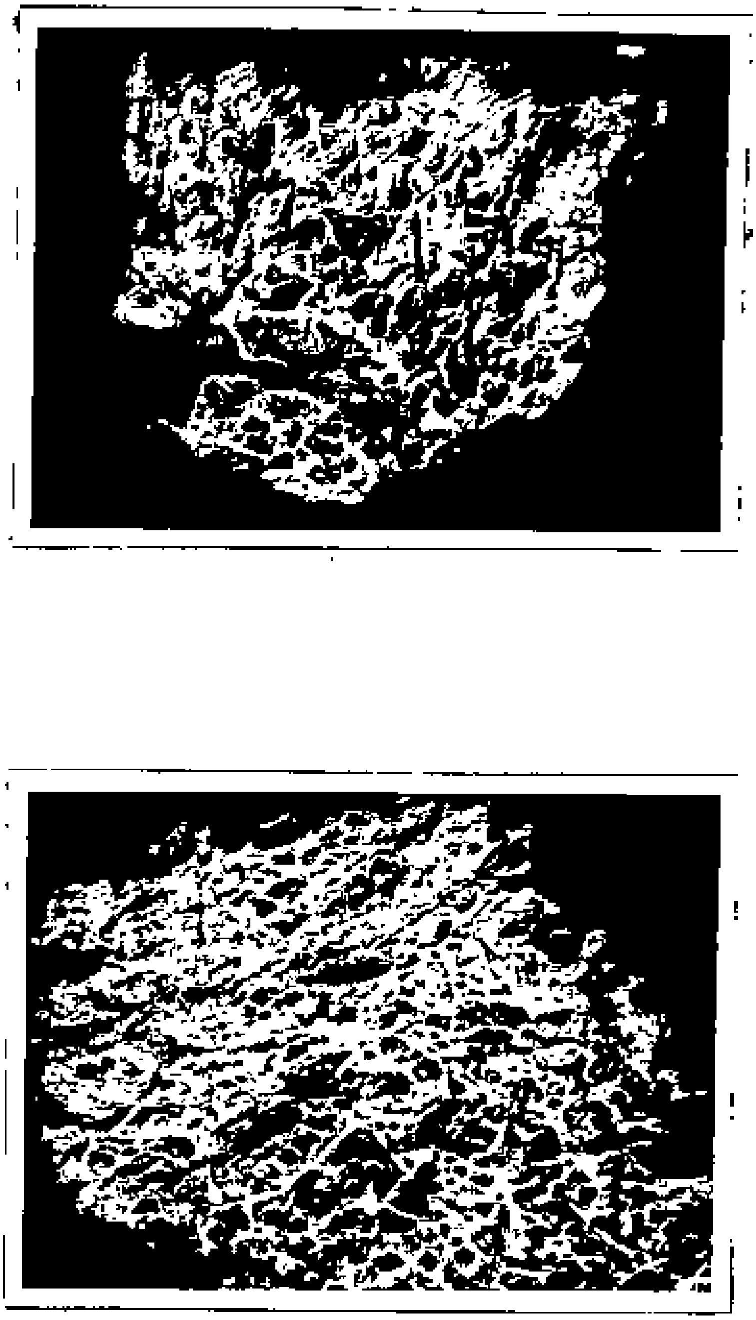


Fig. 4. 2 Microstructure of raw ilmenite. (x 400)

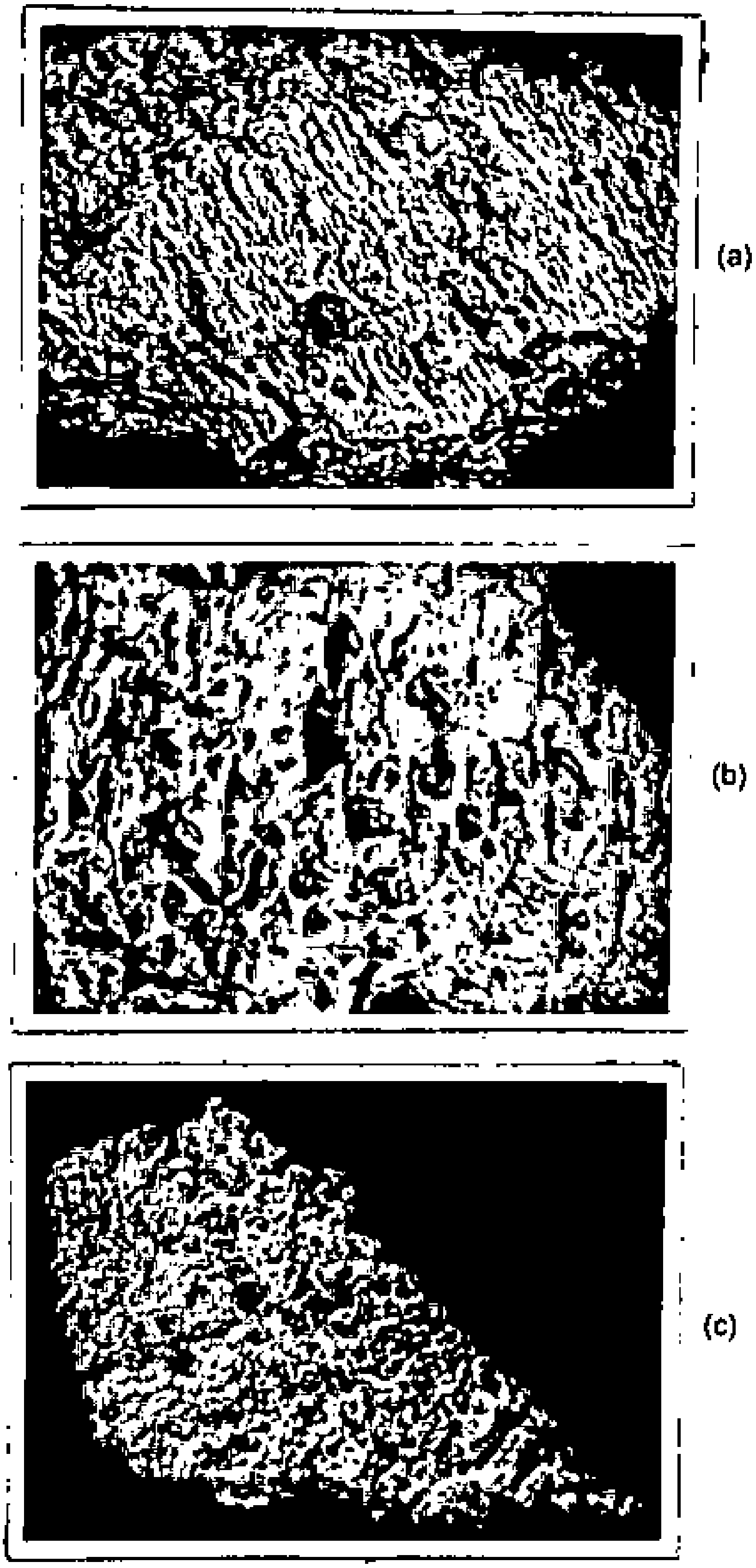
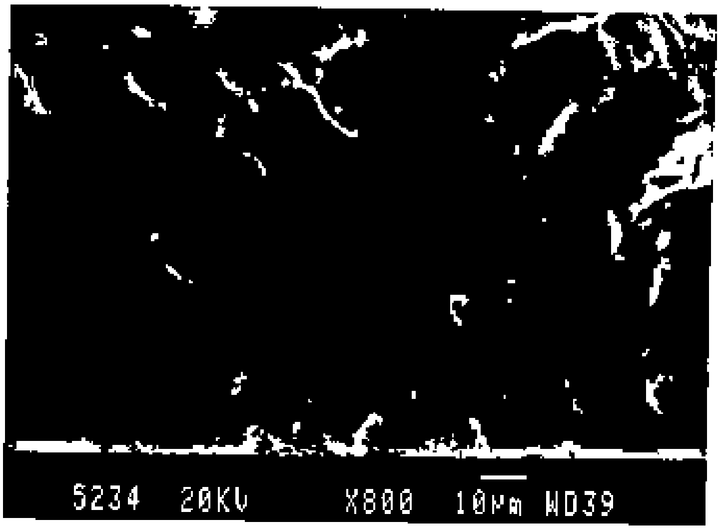
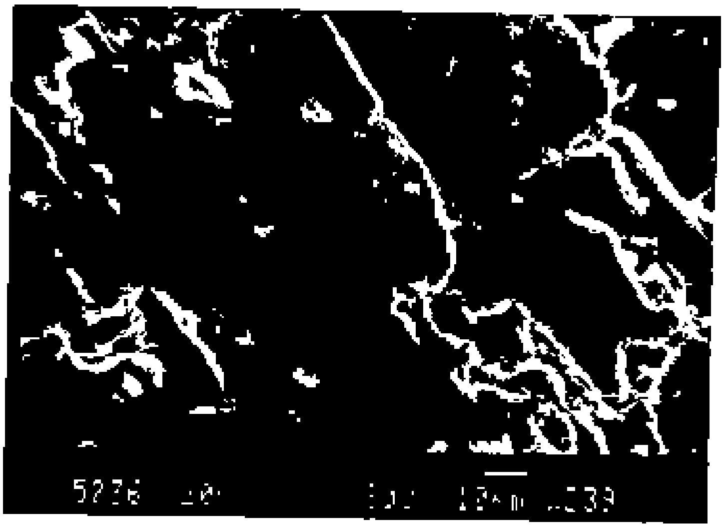


Fig. 4.3 Microstructure of oxidised ilmenite (X400). (a) Oxidised at 700°C for 1 hour, (b) Oxidised at 800°C for 1 hour, (c)oxidised at 950°C for 1 hour

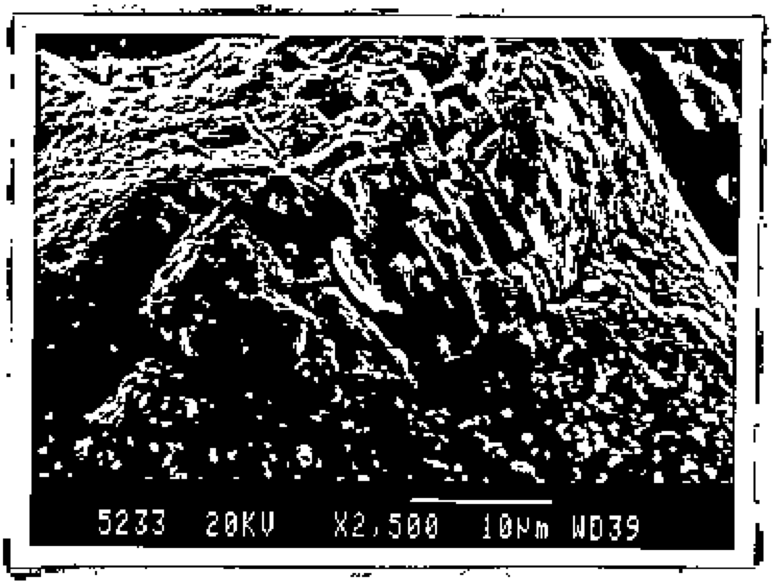


(a) Oxidised at 950°C for 15 minute. (X 800)

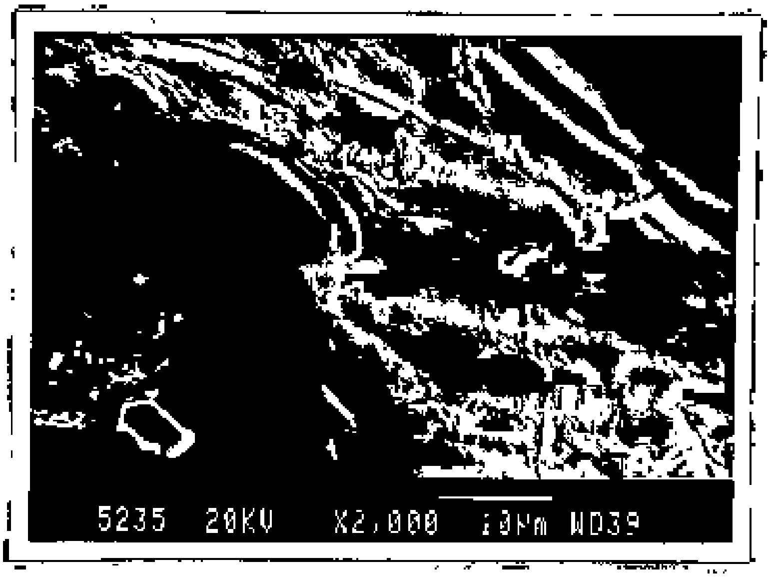


(b) Oxidised at 950°C for 60 minute. (X 800)

Fig. 4.4 Scanning Electron micrographs of oxidised ilmenite.



(a) Oxidised at 950°C for 15 minute. (X 2500)



(b) Oxidised at 950°C for 60 minute. (X 2000)

Fig. 4.5 Scanning Electron micrographs of oxidised ilmenite.

4.2.2 X-Ray Diffraction Study

The phases formed during oxidation of ilmenite were identified by x-ray diffraction. The x-ray diffraction patterns were recorded at a scanning speed of 0.25° per minute and a chart speed of 05 mm per minute and Mo was used as target. Fig. 4.6 shows the diffraction pattern of as received ilmenite Samples of natural ilmenite contain various impurities and the diffraction patterns may, therefore, show slightly different lattice parameters A large number of diffraction lines can be observed in samples of natural ilmenite which are in a partially altered state. Moreover some intense diffraction lines of the different phases expected to be present in as received and oxidised ilmenite overlap The presence of large number of peaks in the X-ray diffraction pattern and also the overlapping of the diffraction lines of the different phases often make the identification of phases troublesome and at times uncertain. Even then a satisfactory match could be obtained and the phases identified. X-ray diffraction lines selected for quantitative measurement are shown in Table-4.1

Table 4.1 X Ray Diffraction Lines Selected for Identification of the Phases. Target Mo Kα

Mineral species	*line d A°*	*2θ*	*Intensity ratio I/I_1*
Ilmenite	3 737	10.9	30
	2.754	14.83	100
	2 544	16 06	70
	1 868	21.93	40
	1 726	23 78	35
hematite-1	2.69	15 18	V.S.
	2.522	16.2	V.S.
	1.698	24 2	S
	1 485	27.7	S
Hematite-2	2 71	15.1	100
	1.66	24.7	34
	1 416	29.1	24

Mineral species	*line d A°*	*2θ*	*Intensity ratio I/I_1*
Rutile	3 245	12.5	100
	2 487	16 42	50
	1 687	24.3	60
Pseudorutile-1	3.82	10 67	40
	2.48	16 5	60
	1.688	24.3	100
Pseudorutile-2	3 5	11 65	100
	2.66	15 35	90
	2.51	16 3	80
	1.687	24.3	70
Pseudobrookite	4.88	8.4	M
	3 49	11 7	V.S.
	2 76	14.8	V.S
	2 455	16.64	S
	2.515	16 92	S
	1 972	20 76	S
	1.864	21.98	S
	1.686	24.33	M
	1 638	25	M
	1 545	26.6	S
Iron	2.03	20 2	100
	1.43	28 83	30
	1.17	35.4	20

X ray diffraction patterns of Bangladesh ilmenite oxidised at different temperatures in the range of 700°C to 950°C are given in Fig. 4.7 to 4.10. Fig 4.7 shows the diffraction patterns of ilmenite oxidised at 700°C and indicate the appearence of new phases These phases have been identified as rutile and pseudorutile. Diffraction lines from ilmenite, if present, coincide with the diffraction lines of pseudorutile and hematite. No significant change in the relative intensity of the diffraction lines were observed with an increase in time of oxidation at the temperature

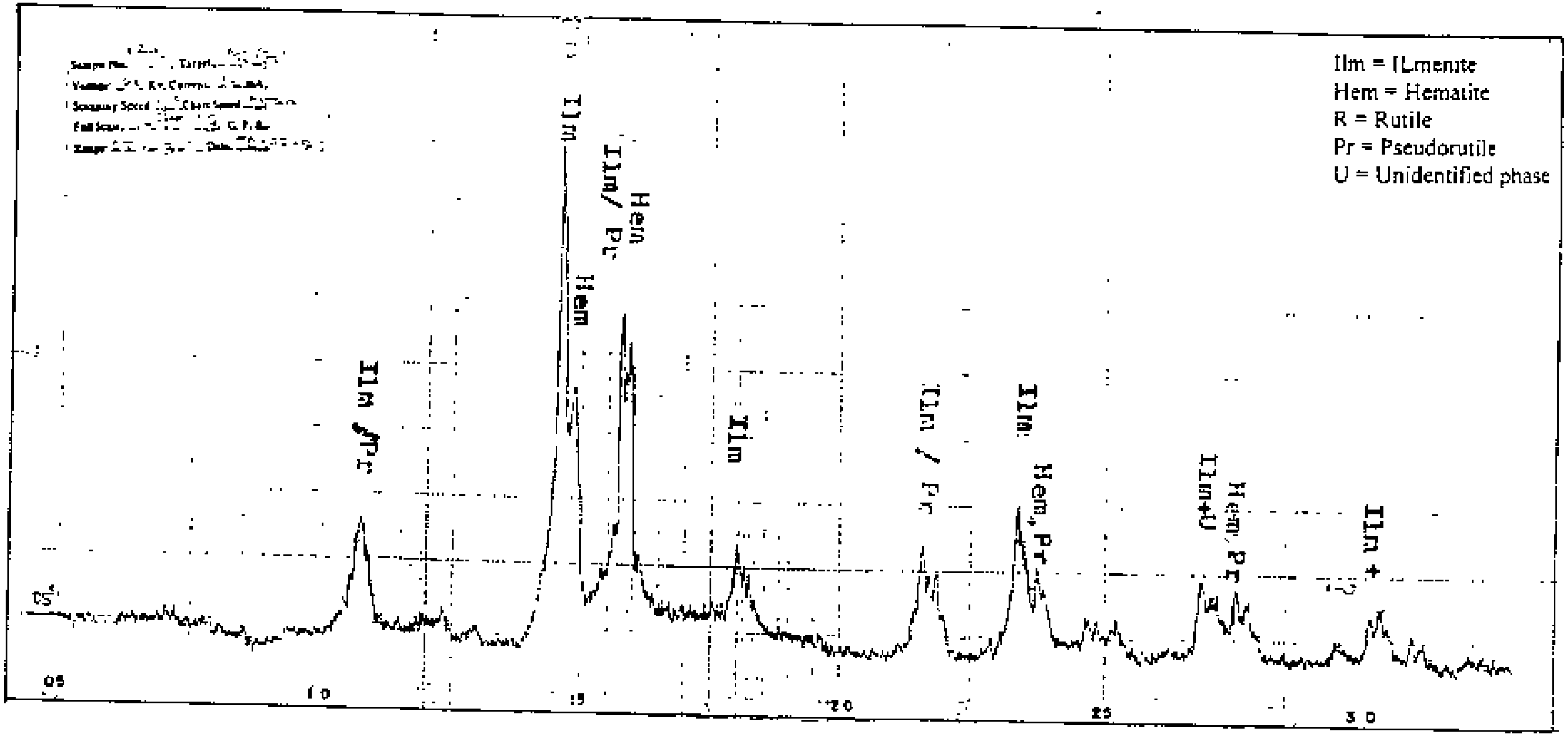
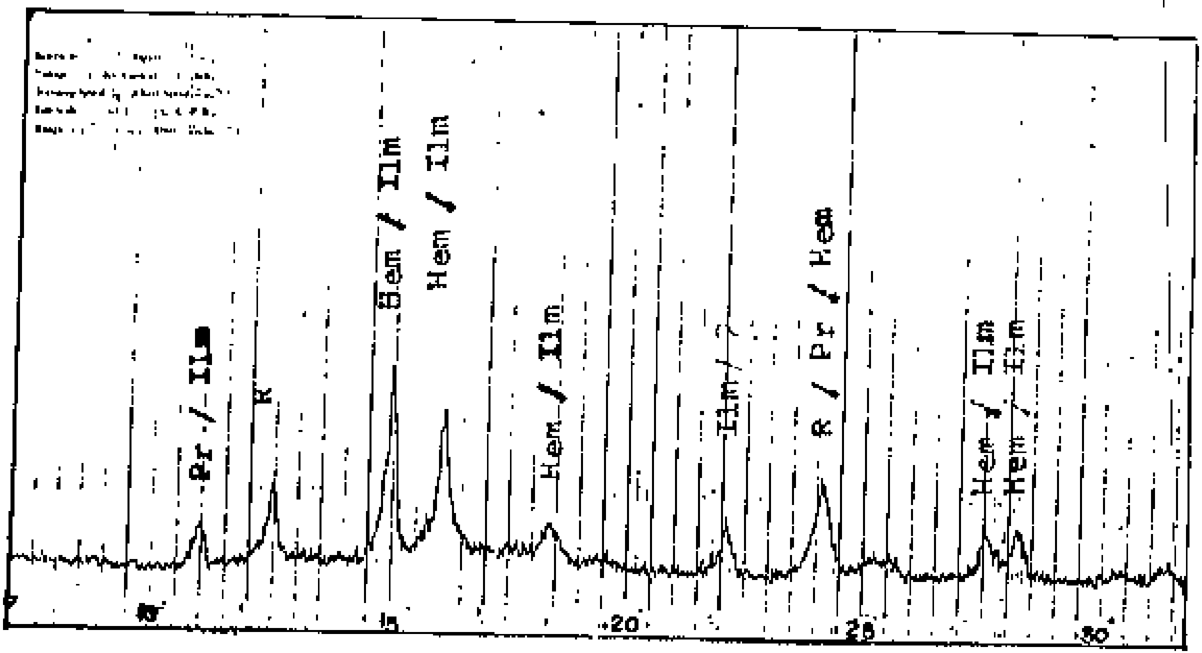
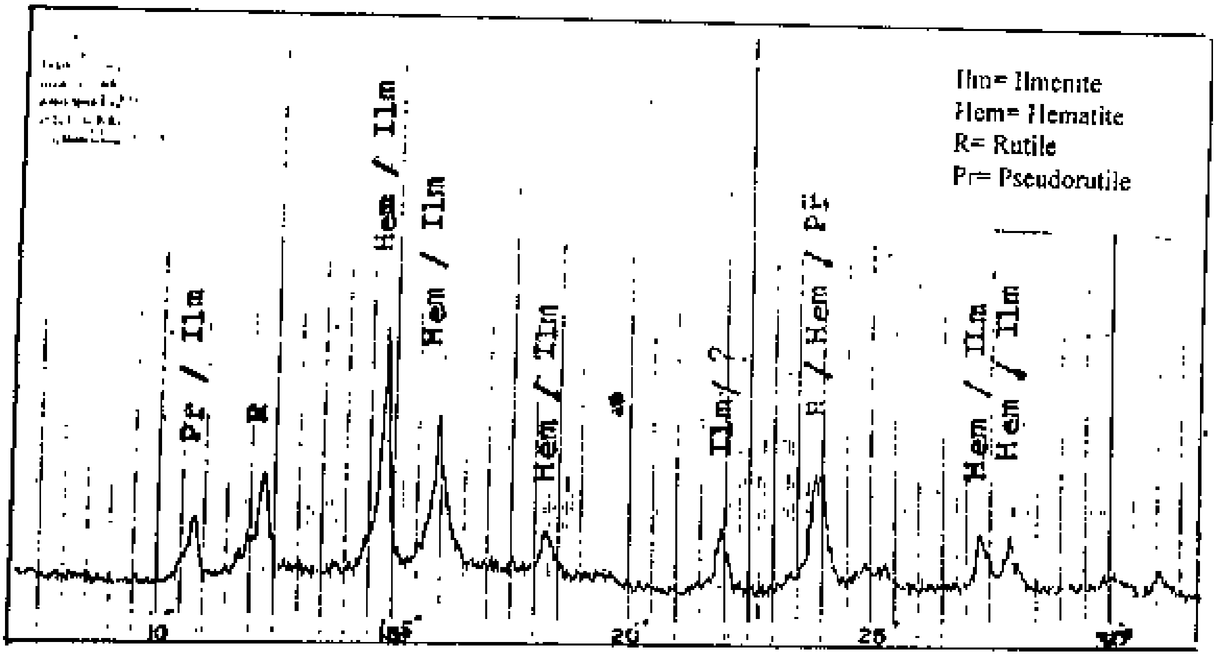


Fig 4.6 X-ray diffraction pattern of raw ilmenite of Cox's Bazar beach sand

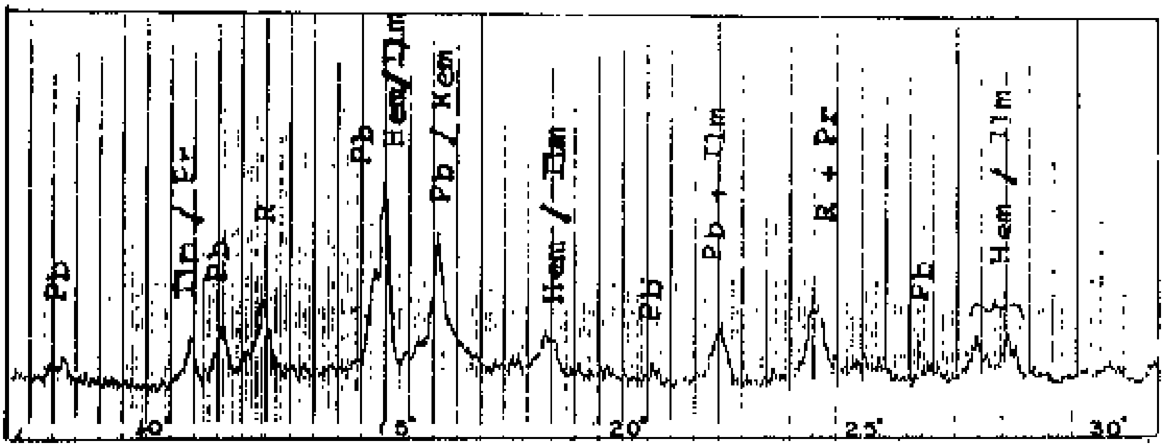


(a) · Oxidised at 700°C for 0 5 hour

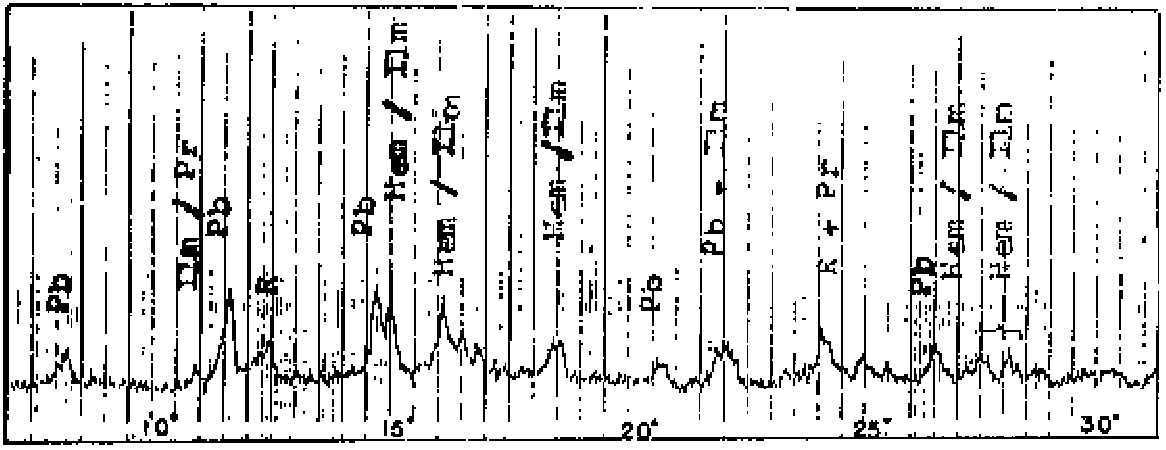


(b) Oxidised at 700°C for 2 hour.

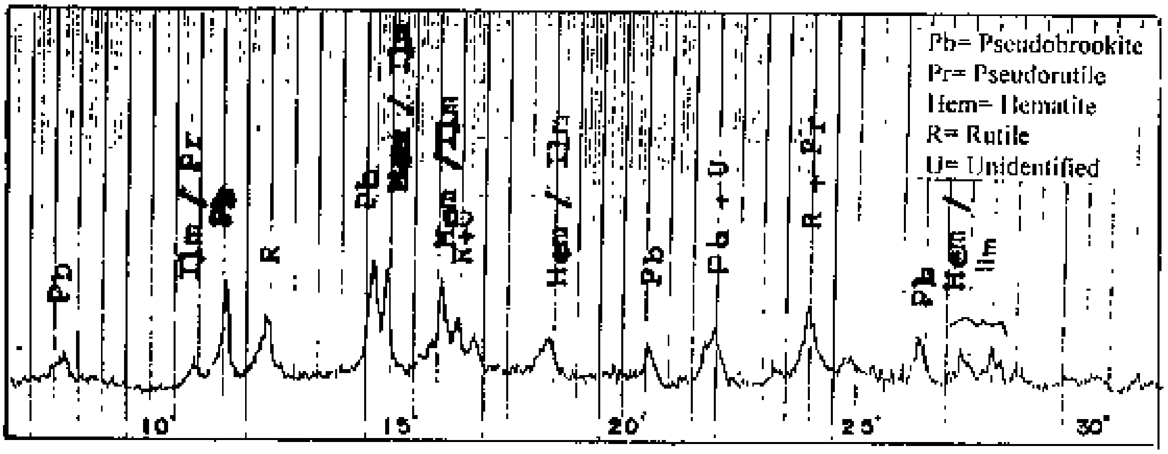
Fig 4.7 X-ray diffraction patterns of ilmenite oxidised at 700°C



(a) Oxidised at 800°C for 15 minute

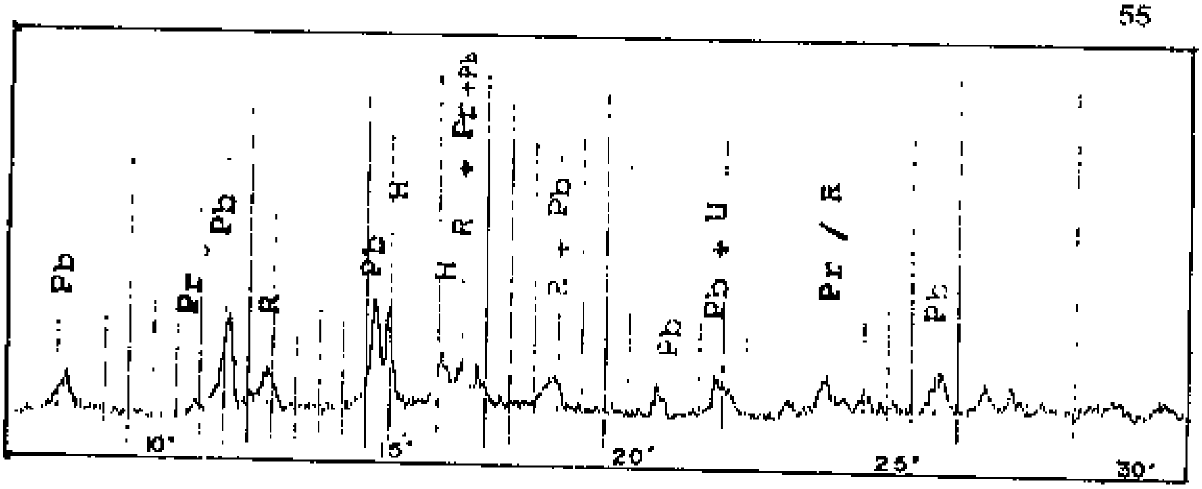


(b) Oxidised at 800°C for 30 minutes

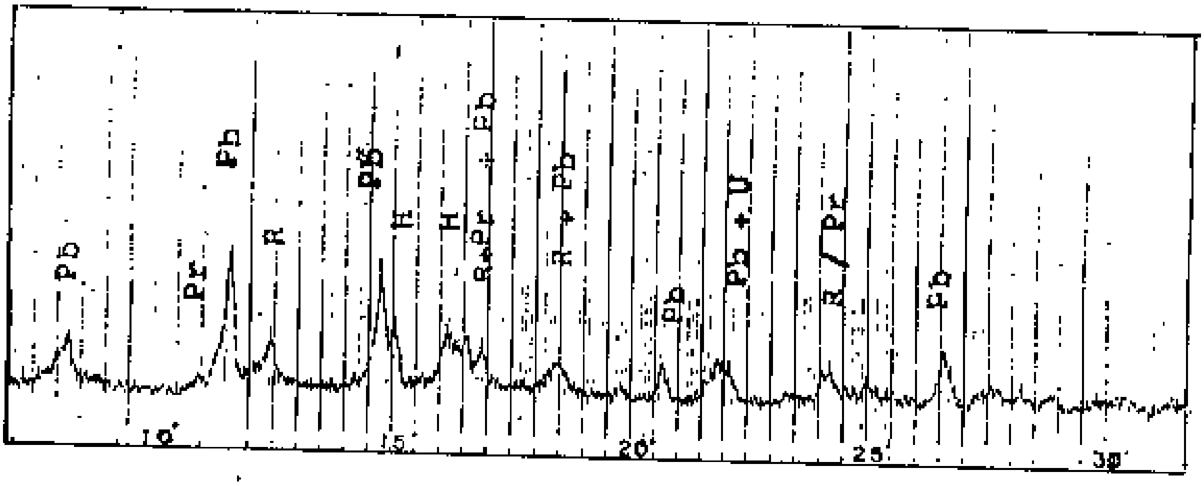


(c) Oxidised at 800°C for 1 hour.

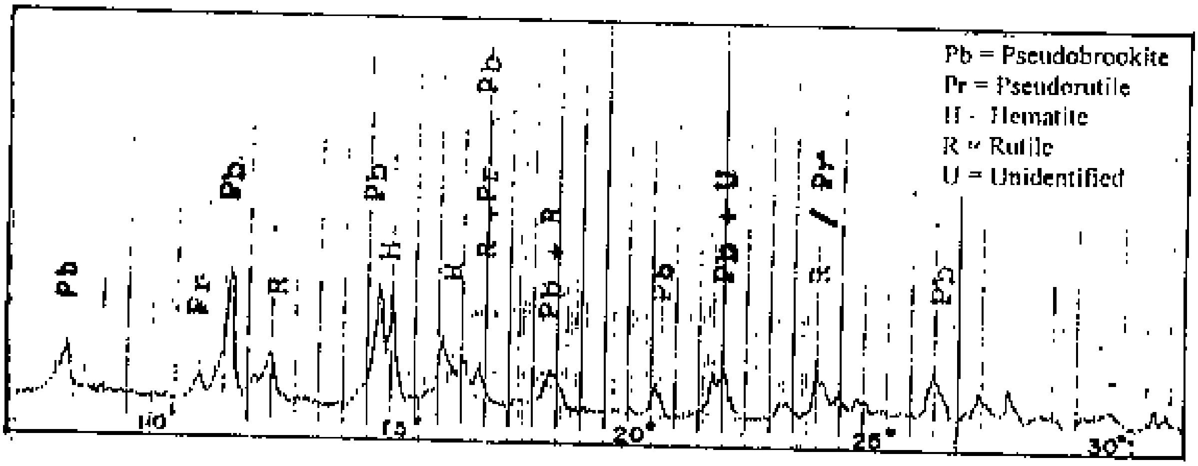
Fig: 4.8 X-ray diffraction patterns of ilmenite oxidised at 800°C



(a) Oxidised at 900°C for 30 minute

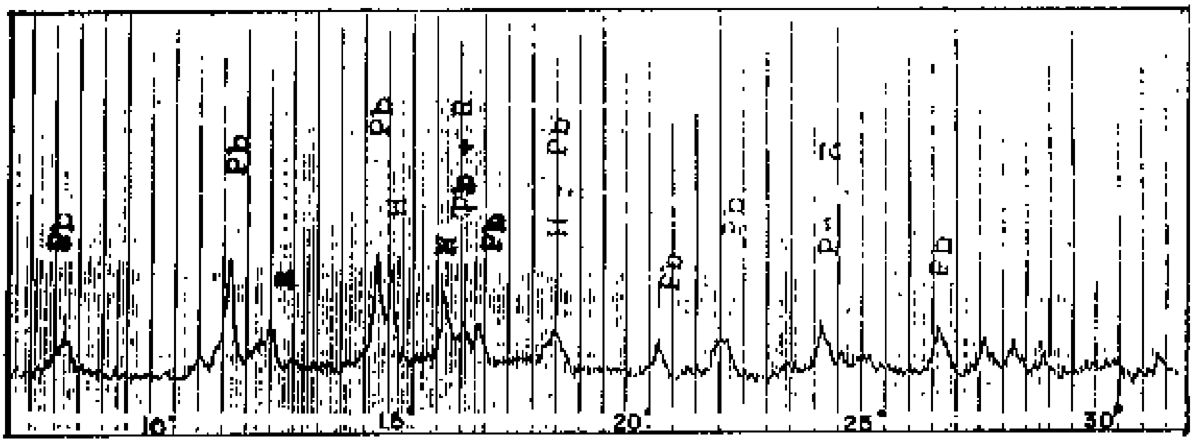


(b) Oxidised at 900°C for 1 hour.

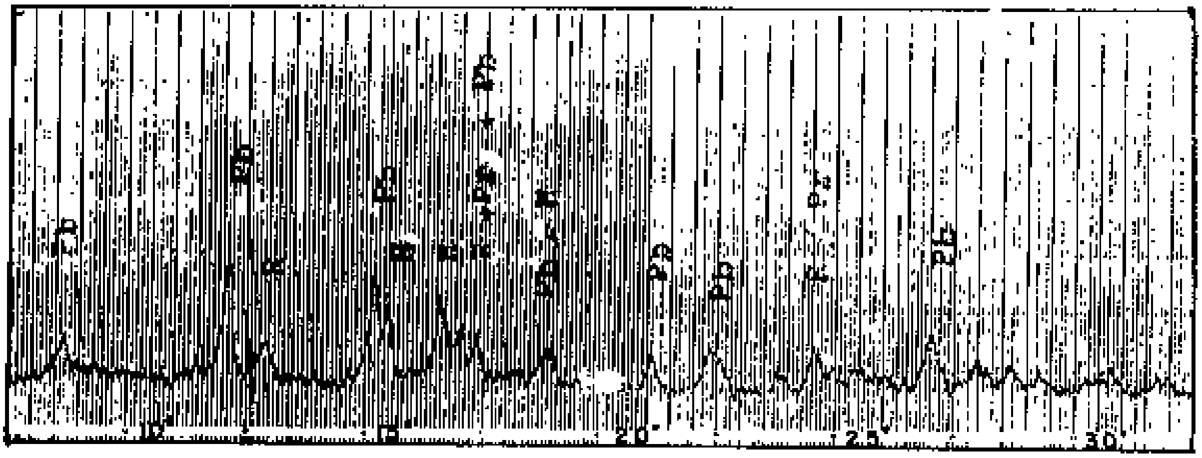


(c) Oxidised at 900°C for 2 hour.

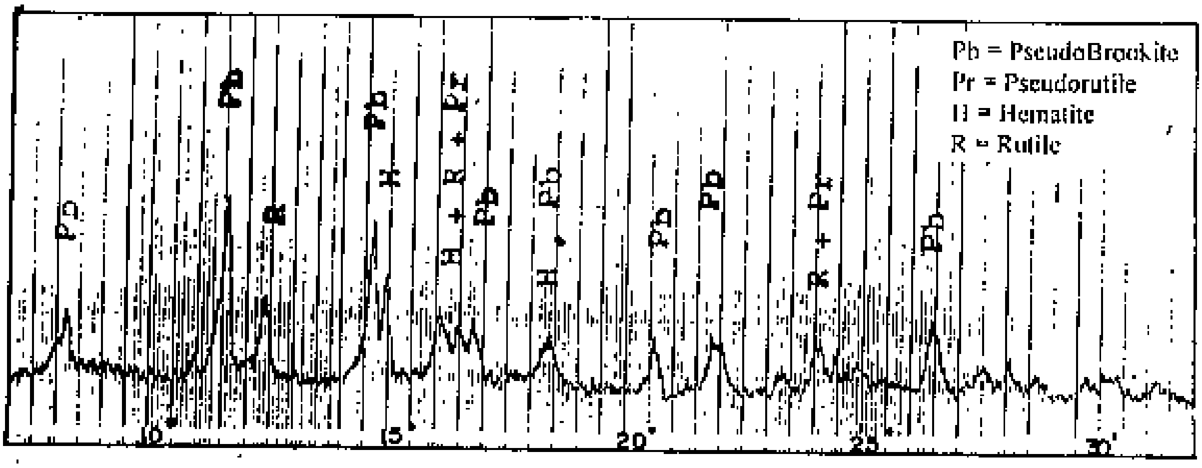
Fig: 4.9 X-ray diffraction patterns of ilmenite oxidised at 900°C



(a) Oxidised at 950°C for 15 minute



(b) Oxidised at 950°C for 30 minutes



(c) Oxidised at 950°C for 1 hour

Fig: 4.10 X-ray diffraction patterns of ilmenite oxidised at 950°C

Fig. 4.8 shows the X-ray pattern of ilmenite oxidised at 800°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 belonging to pseudorutile/ilmenite decreased. Fig.4.9 and 4.10 show the X-ray diffraction pattern of ilmenite oxidised at 900°C and 950°C respectively. No significant change was observed in the diffraction patterns even after prolonged heating. Fig. 4.11 shows the pattern of ilmenite oxidised for 1 hour at different temperatures. From the patterns it can be seen that pseudobrookite forms at higher temperatures and the relative intensity of pseudobrookite increases with temperature where as the intensity of pseudorutile was found to decrease.

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

1) Some of the diffraction lines belonging to pseudorutile coincides with those from rutile The x-ray diffraction pattern of ilmenite oxidised at 700°C is similar to as received ilmenite but chemical analysis showed the presence of small amount of ferrous 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 phases could not be made. The probable reaction may be as follow:

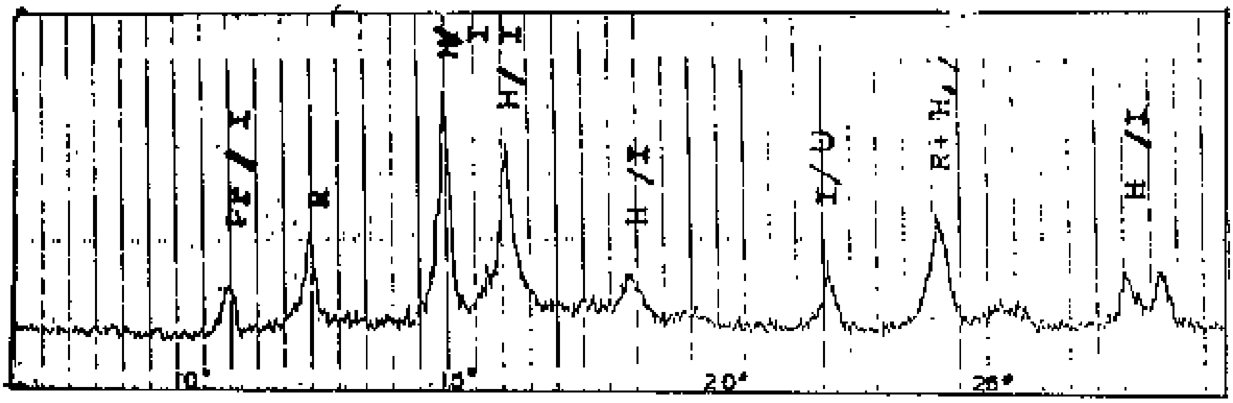
$2FeTiO_3+1/2\ O_2 \rightarrow Fe_2O_3+ TiO_2$ and

$3\ FeTiO_3- \rightarrow Fe_2O_3O_9 + \frac{1}{2}\ Fe_2O_3$

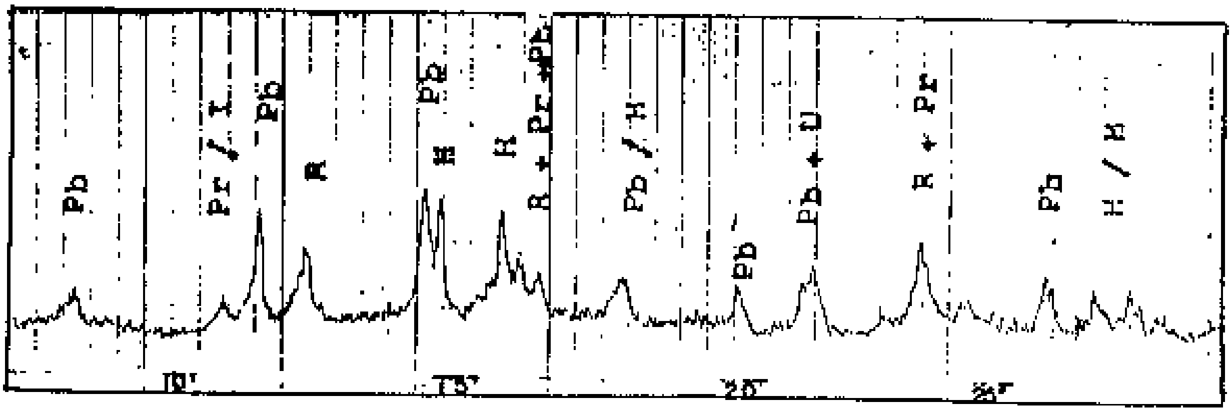
Some unidentified phases were also found to be present

2) With increasing temperature the percentage of pseudorutile and ilmenite (if present) decreases.

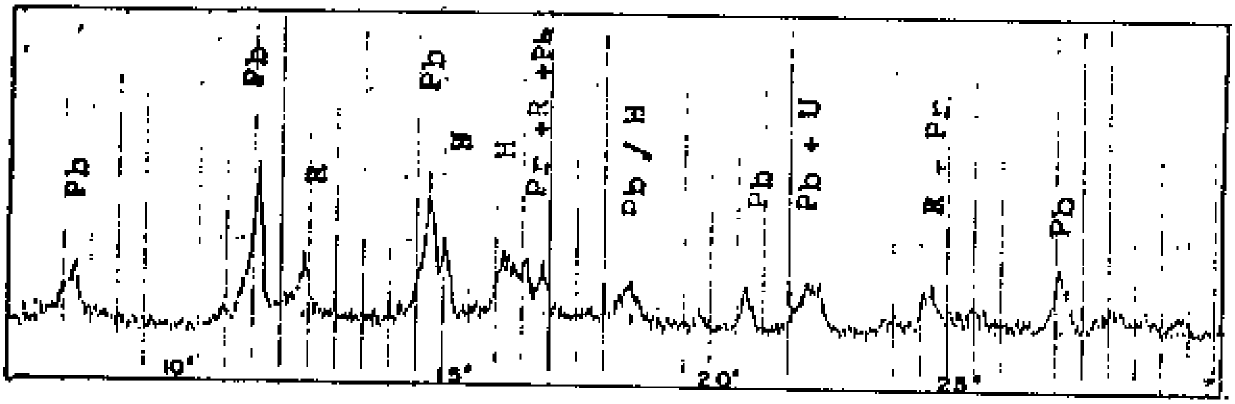
3) At temperature above 800°C diffraction lines belonging to the unidentified phases diminish with temperature and x-ray diffraction pattern shows the characteristic lines of phase pseudobrookite. The proportion of pseudobrookite increases with time for upto 0.5 hour then remains more or less constant



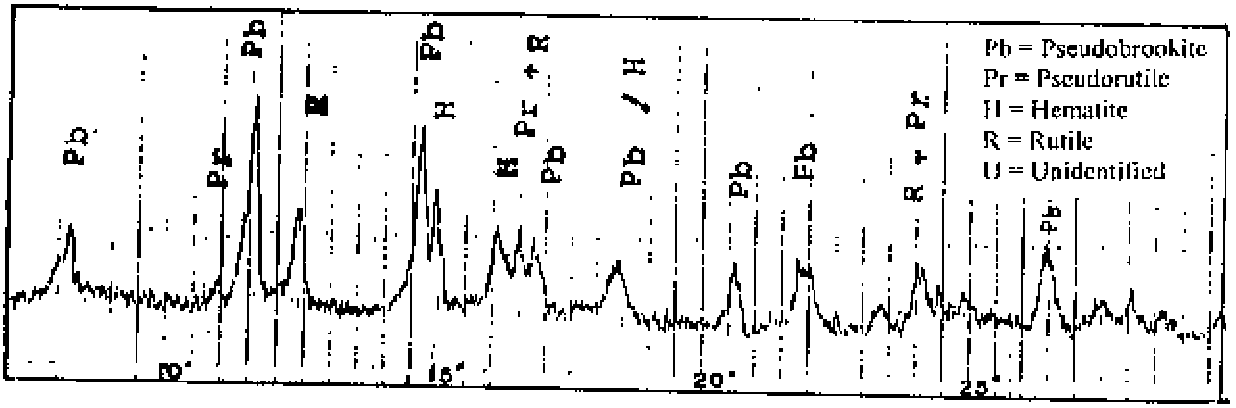
(a) Oxidised at 700°C for 1 hour.



(b) Oxidised at 800°C for 1 hour.



(c) Oxidised at 900°C for 1 hour.



(d) Oxidised at 950°C for 1 hour.

Fig: 4.11 X-ray diffraction pattern of ilmenite oxidised at different temperature.

The appearance of pseudobrookite can be expressed by the reaction:

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

$$2FeTiO_3 + \frac{1}{2} O_2 \rightarrow Fe_2O_3 + 2TiO_2$$

by heating pseudorutile above 800°C pseudobrookite is formed

$$Fe_2Ti_3O_9 \rightarrow Fe_2TiO_5 + 2TiO_2.$$

The existance 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[44]. Decrease in the relative intensity of hematite shows that pseudobrookite may also be formed by the reaction.

$$Fe_2O_3 + TiO_2 \rightarrow Fe_2TiO_2$$

The free energy change for this reaction is also favourable.

4.3 Results of Reduction

Ilmenite both in the as received and in the oxidised conditions were reduced by using charcoal as reductant. During reduction of ilmenite ratio of ilmenite to charcoal was kept as 1.1. This amount of charcoal is in excess of the theoretical requirement. Mohan Das et al[70] studied reduction of ilmenite with lignite as a reducing agent and found that metallic iron content of reduced ilmenite increases with an increase in the ilmenite:lignite ratio and maximum iron content in the ilmenite is found when quantity of reductant is 50 per cent of the total weight. A higher ratio of ilmenite:charcoal was used in these experiments to ensure maximum reduction of ilmenite. The size of the charcoal used was 30 mesh size. For optimising one factor affecting reduction, all others were kept constant and all experiments were carried out under identical conditions.

4.3.1 Effects of Temperature

For optimising temperature, reduction was carried out at different temperatures in the range 950°C to 1050°C. The results of reduction of ilmenite both in the as received and in the preoxidised conditions are plotted in Figs. 4.12 and 4.13. These figures show that the rate of reduction is low at lower temperatures and, with an increase in the temperature, there is a sharp increase in the metallic iron content of the reduced ilmenite. Although maximum reduction of iron oxide was obtained at

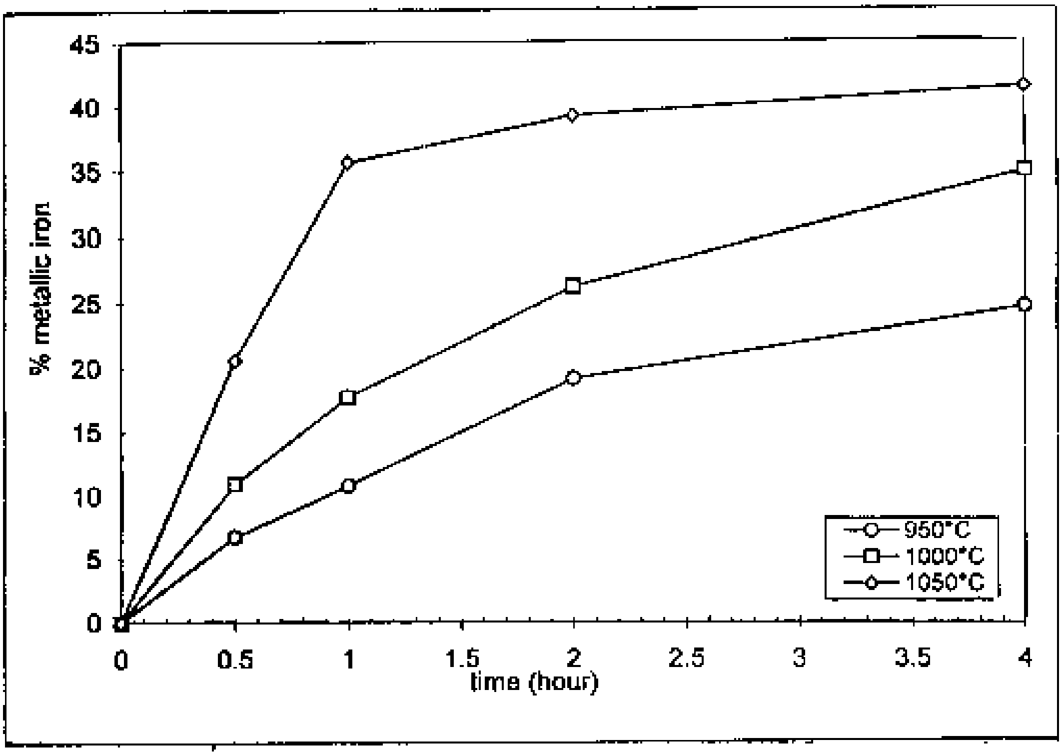


Fig: 4.12 Extent of reduction of oxidised ilmenite as a function of time at specified temperatures.

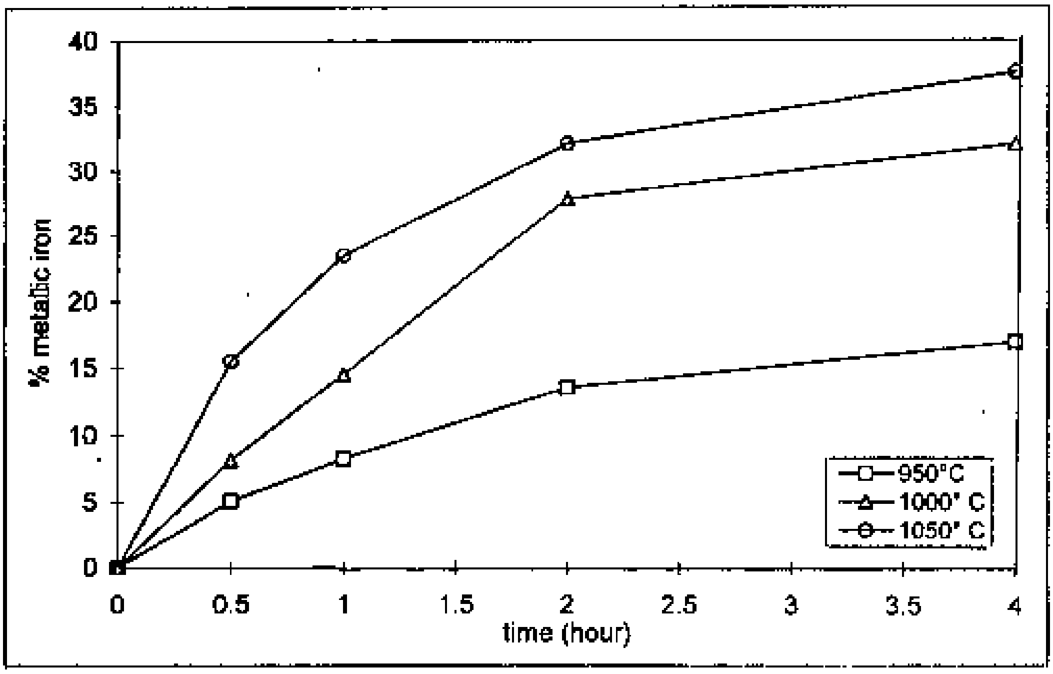


Fig: 4.13 Extent of reduction of as received ilmenite as a function of time at specified temperatures.

higher temperatures, the rate of increase in the metallic iron content shows a decreasing trend. This is because, as has been noted[31], at very high temperatures there is a possibility of reduction of TiO_2 to lower oxide.

The comparison of the rates of reduction of ilmenite in the oxidised and in the as-received conditions are given in the Fig 4.14 It can be seen that, under all the conditions investigated, the reduction of iron oxide to the metallic state is more in the case of the preoxidised samples than in the case of the samples reduced in the as received condition These results are in good agreement with the results obtained by other investigators The higher rate of reduction of oxidised ilmenite may be attributed to (i) the introduction of defects (cracks, grain-bourndaries etc.) in the ilmenite grains which enhances the rate of subsequent reduction and (ii) the alteration of equilibrium conditions and the rate of reduction from the ferric to ferrous state.

As can be seen from above, the rate of reduction of ilmenite both in the as received and in the oxidised conditions is low at lower temperatures and increases with an increase in temperature. Haseeb et al[61] investigated the reduction of Bangladesh ilmenite with charcoal and suggested that at lower temperatures (950°C - 1000°C) the reduction of ilmenite with charcoal proceeds via the solid state reaction between carbon present in charcoal and ilmenite. They identified this mode of reaction to be responsible for the slower rate of reduction at lower temperatures. At a temperature higher than 1000°C the reduction mechanism changes and is caused by CO formed in accordance with Boudouard reaction[59].

$$CO_2 + C \rightarrow 2CO$$

As a result an increase in the rate of reduction is observed

4.3.2 Effects of Time

The effects of time on the reduction of ilmenite at various temperatures are shown in Figs. 4.12 to 4.14. These figures show that at all temperatures the rate of reduction is fast at the initial stages of reduction. The rates slow down after about 2 hour of reduction. These figures also show that the rate of reduction increases with an increase in reduction temperature, however at higher temperatures the rate of increase in the reduction is not as much as at lower temperatures. When the reduction temperature is 1050°C there is a sharp increase in the reduction rate at the initial stage and after 1 hour this rate of increase is not as prominent and the curve becomes almost flat. Merk and Pickles[71] 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.

Figs. 4.15 and 4.16 show the extent of reduction of ilmenite in the as-received and in the oxidised conditions. Fig 4.17 shows the comparison of the extents of reduction of the as-received and the oxidised samples for reduction for specified period of time at various temperatures. These figures show that the extent of reduction of ilmenite in the oxidised conditions is always higher than the extent of reduction in the as-received condition. The reasons for the faster rate of reduction of oxidised ilmenite has already been discussed.

4.3.3 X Ray Diffraction Study of the Reduced Ilmenite:

X-ray diffraction patterns of ilmenite oxidised at 950°C for I hour and then reduced with charcoal for different periods of time at 1050°C is shown in Fig. 4.18. The X-ray patterns of the reduced ilmente do not show the diffraction lines belonging to pseudobrookite . It may be recalled that the main constituents of the pre-oxidisd ilmenite was rutile and pseudobrookite. Instead the patterns recorded after a short period of reduction show the diffraction lines belonging to ilmenite. A careful analysis of the diffractions patterns show that the d-values of the reformed ilmenite is close to the stoichiometric ($FeTiO_3$) compound

This figure also shows that with increasing time of reduction at this temperature, the intensity of the diffraction lines belonging to ilmenite diminishes and, at the same time, the intensity of the diffraction lines belonging to metallic iron and rutile increase indicating that the that amount of metallic iron and rutile in the reduced sample increases with time These observations (disappearance of the diffraction lines belonging to rutile and pseudobrookite and reappearance of the diffraction lines belonging to ilmenite, at the early stages of reduction of oxidised ilmenite, in the x-ray diffraction patterns) suggest that the reduction of oxidised ilmenite (containing rutile and psedobrookite) proceeds in two stages.

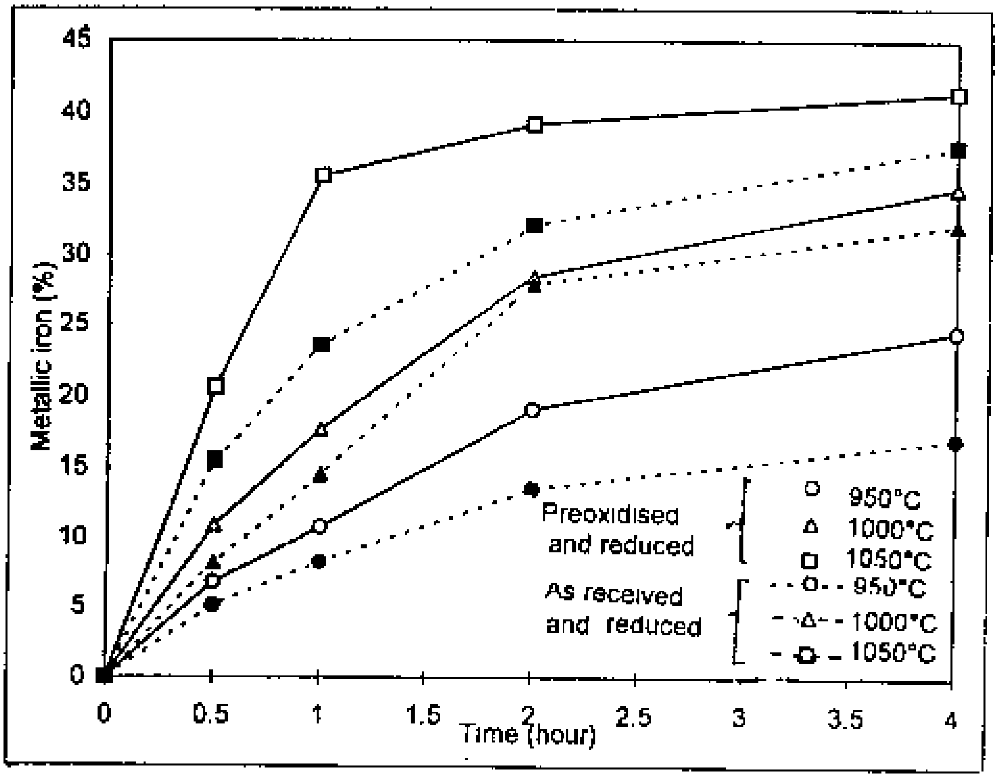


Fig. 4.14 Comparison of extent of reduction of pre oxides and as received ilmenite as a function of time at specified temperature.

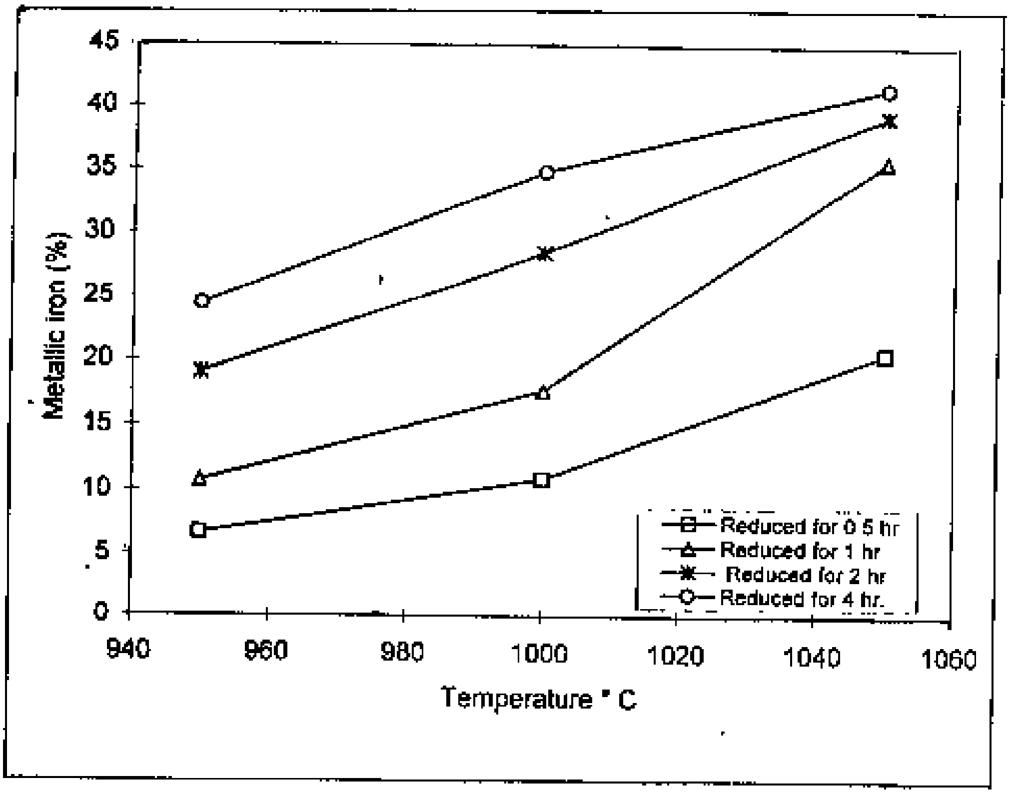


Fig. 4.15 Extent of reduction of pre oxidised ilmenite as a function of temperature at specified period of time.

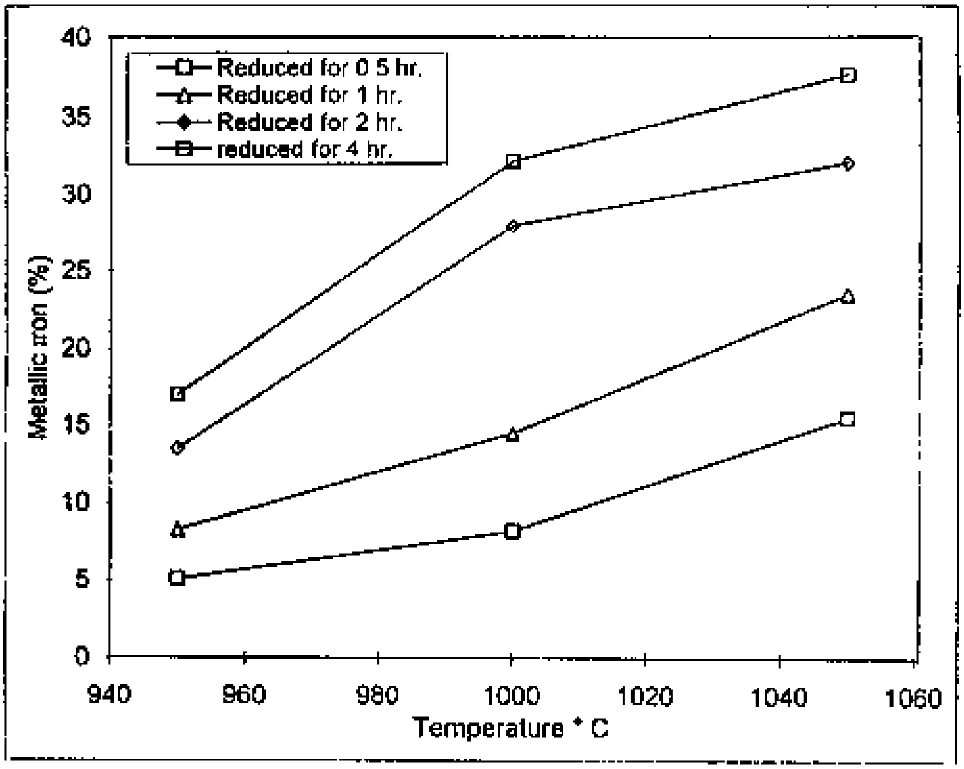


Fig: 4.16 Extent of reduction of as received ilmenite as a function of temperature at specified period of time.

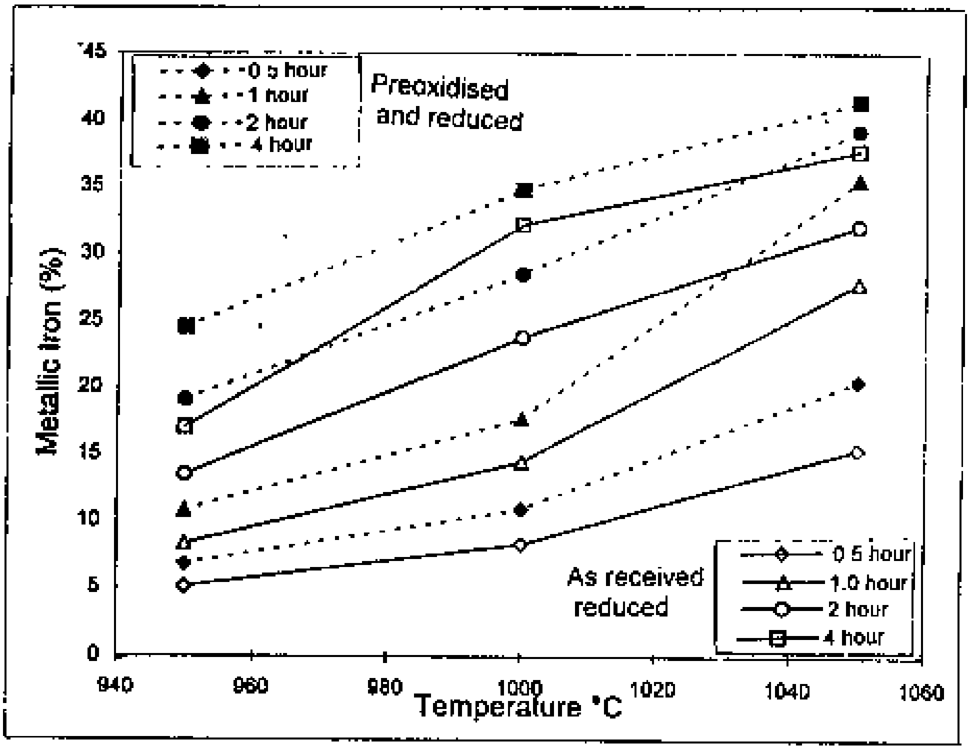
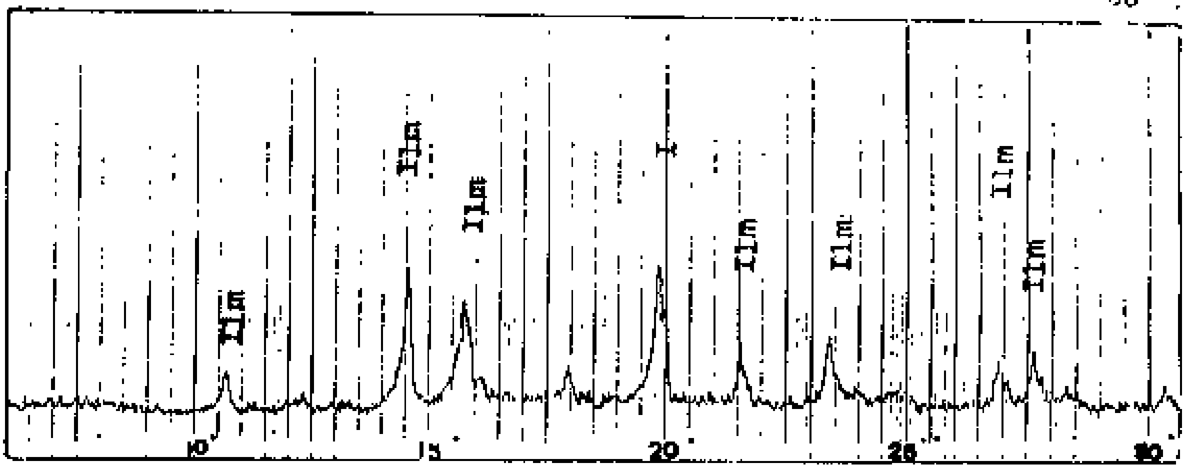
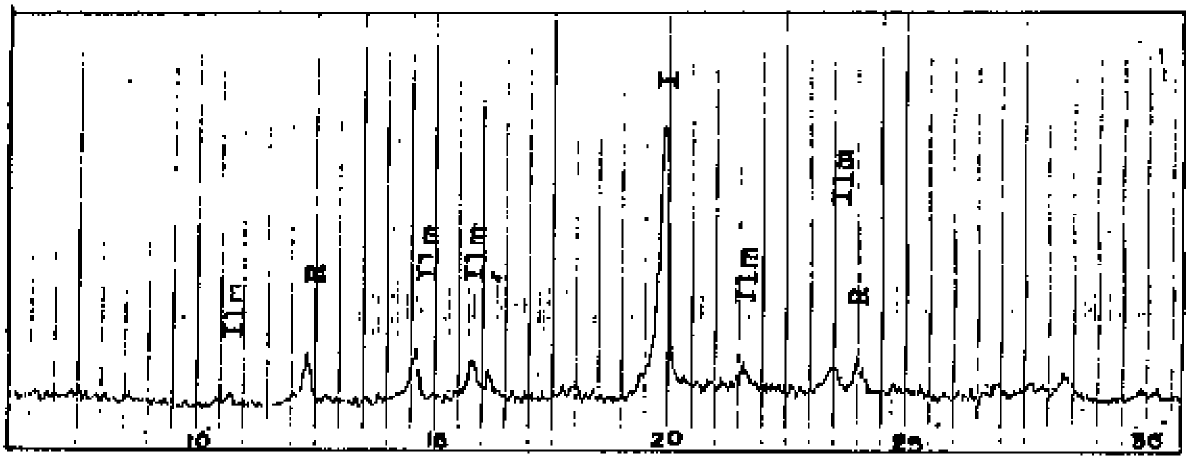


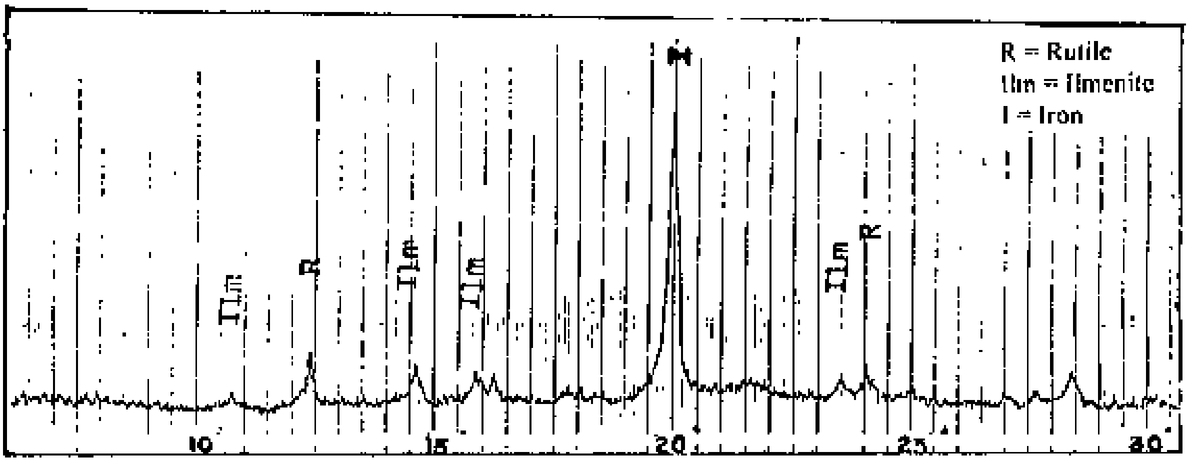
Fig: 4.17 Comparison of extent of reduction of pre oxidised ilmenite and as received ilmenite for specified time of reduction at different temperatures



(a) Reduced at 1050°C for 0.5 hour.



(b) Reduced at 1050°C for 1 hour.



(c) Reduced at 1050°C for 4 hour.

Fig: 4.18 X-ray diffraction pattern of pre oxidised ilmenite

The first stage is the reformation of stoichiometric ilmenite according to the following reaction:

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

Absence of rutile and hematite in the pattern indicates that ilmenite may also be formed from them. The overall process may be described as :

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

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

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

During this second stage of reduction, the proportion of ilmenite progressively diminishes with corresponding increase in the contents of metallic iron and rutile Fig. 4.18 shows slight decrease in the height of the diffraction lines belonging to the rutile phase occurs when the reactions have well advanced. This indicates a reduction in the amount of TiO_2 phase. Results of chemical analysis also indicated a lower TiO_2 content in the sample than the expected value This decrease in the TiO_2 content in the later stages of reduction may be due to reduction of rutile to lower oxides. Similar results during reduction of preoxidised ilmenite[35] were obtained by other workers also and the reaction in the second stage has been expressed as:

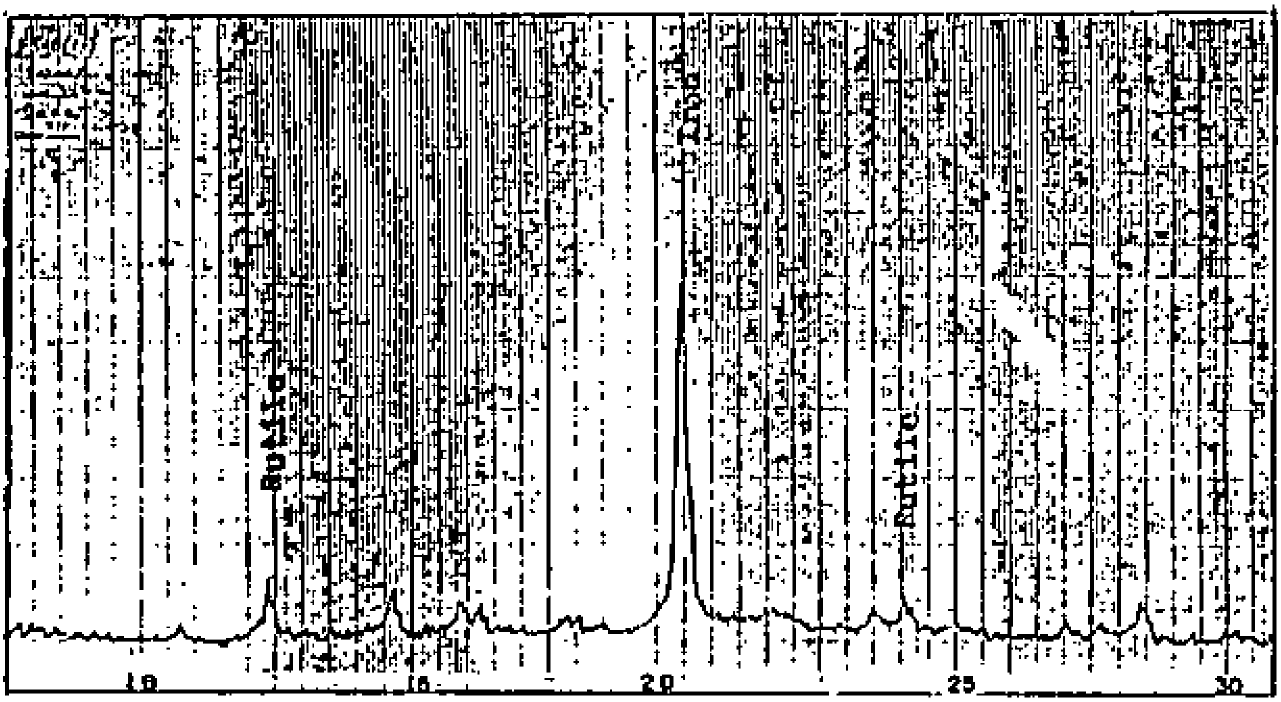
$$Fe\ TiO_3 + CO \rightarrow Fe + TiO_2 + CO_2$$

$$n\ TiO_2 + CO \rightarrow Ti_nO_{2n-1} + CO_2$$

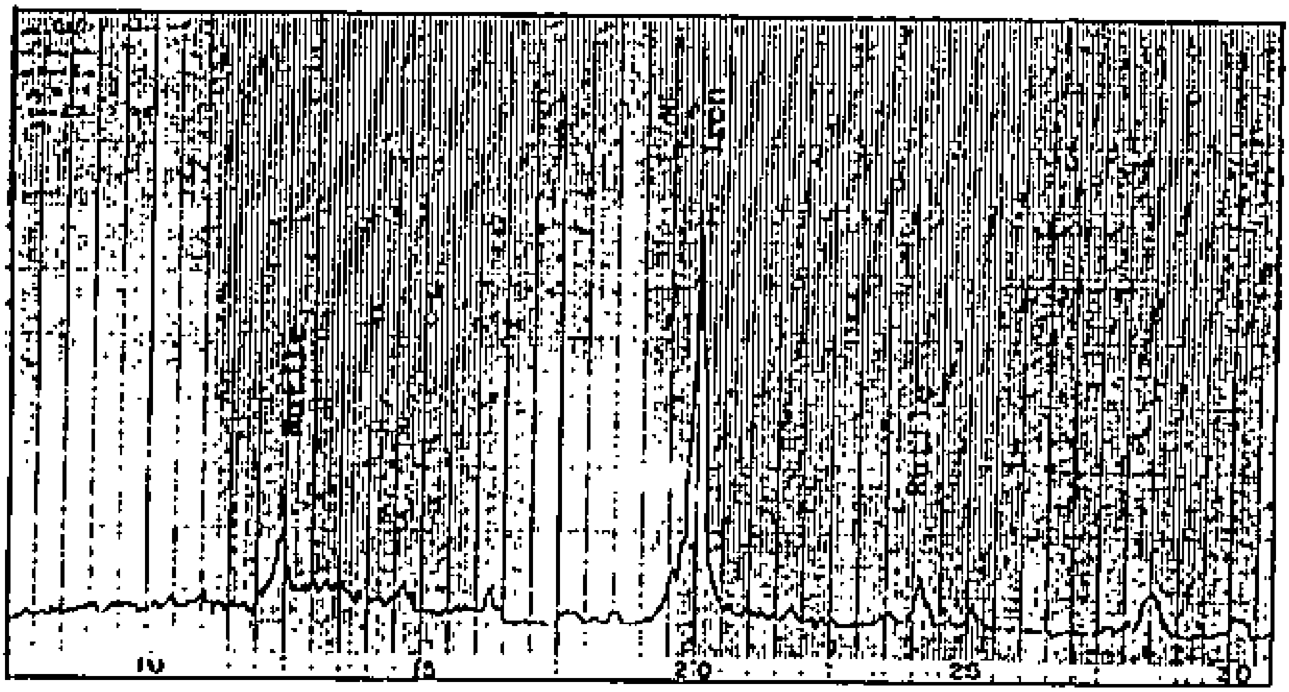
Reduction mechanism for the as received ilmenite is slightly different from preoxidised ilmenite. Previous work on the reduction study of the as received ilmenite showed that this process takes places through the following route:

pseudorutile → ilmenite → metallic iron.

Fig 4.19 shows the x-ray diffraction pattern of preoxidised ilmenite and as received reduced ilmenite . This diffractogram contain the characterstic lines of iron and rutile and some unidentifide phases indicating that rutile and iron is the end products. These unidentified phases may be compounds of iron, manganease, silicon, aluminium etc.



(a) Pre oxidised sample reduced at 1050°C for 4 hour.



(b) As received sample reduced at 1050°C for 4 hour

Fig: 4.19 X-ray diffraction pattern of reduced ilmenite

4.3.4 Microscopic Examination:

Particles of ilmenite reduced both in the as-received and in the oxidised conditions were mounted in cold-setting resin and observed under an optical microscope. Microstructures of ilmenite reduced for different periods of time at specified temperatures are shown in Figs. 4.20 - 4.22 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 for a shorter period of time shows this bright phase (metallic iron) as parallel plates Fig. 4.20 (a). This is because of the original lamellar morphology of ilmenite and hematite phases in the ilmenite grains. With increasing treatment times iron begins to coalesce into large globules and tend to segregate towards the peripheries of the grains to form close shells of metallic iron The formation of closed shell of metallic iron impairs the rate of diffusion of the reacting species and leads to large scale sintering of the product.

Oxidation of the ilmenite prior to reduction can overcome this problem. Oxidation converts single crystal of ilmenite to polycrystalline array of pseudobrookite and rutile[31] and which on reduction causes metallic iron to be precipitated along the sub-grain boundaries within the parent grain. Thus shells of metallic iron occurs at sub-grain boundaries and not at the periphery of the parent grain. As a consequence, the grains show no tendency to sinter together The presence of cracks in oxidised ilmenite increases the surface area and thus increases the rate and extent of reduction of ilmenite. Fig 4.22 shows an scanning electron micrograph of ilmenite reduced after oxidation. In these figures the cracks in these grains of ilmenite are readily visible

4.4 Results of Leaching

Ilmenite reduced both in the as received and in the oxidised conditions were leached in HCl. As received and reduced sample containing about 38 percent metallic iron (49.46% total iron) and preoxidised and-reduced sample containing 42 percent metallic iron (50.23% total iron) were used for the leaching experiments. The variables 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.

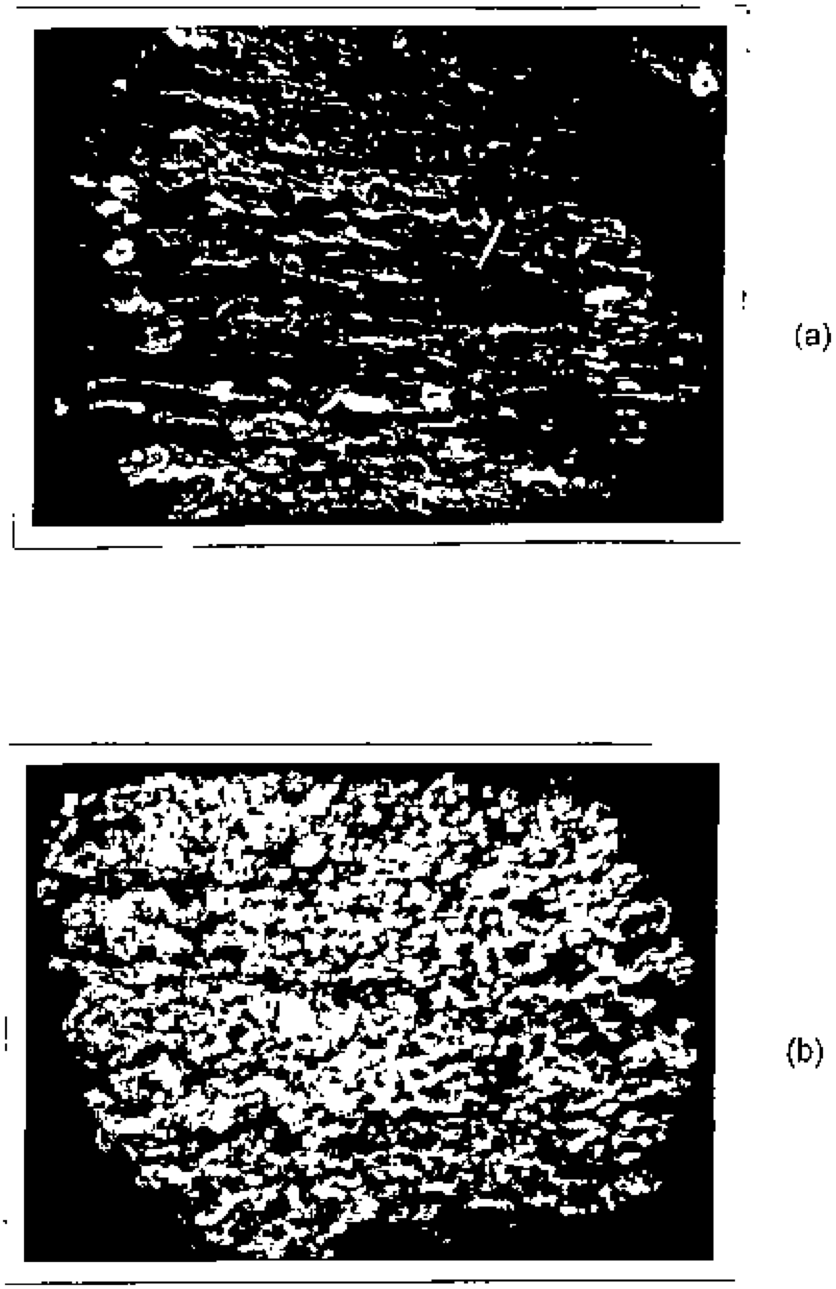


Fig. 4.20 Optical micrograph of as received and reduced ilmenite (X 400). (a) Reduced at 1050°C for 0.5 hour (b) Reduced at 1050°C for 4 hour.

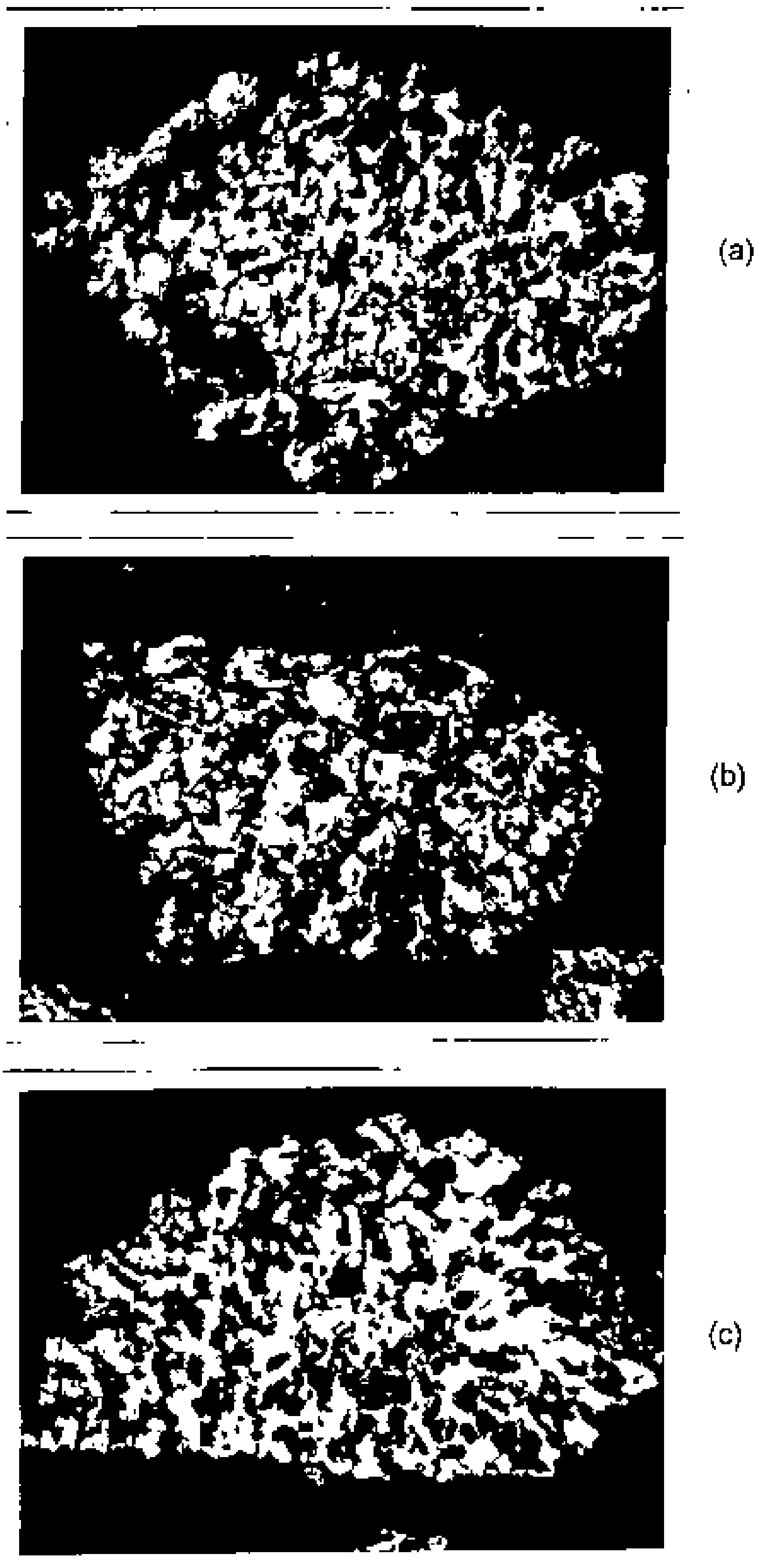
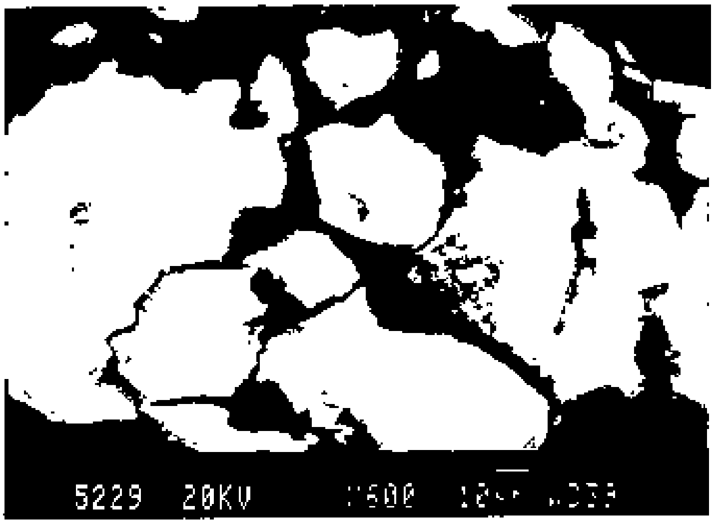
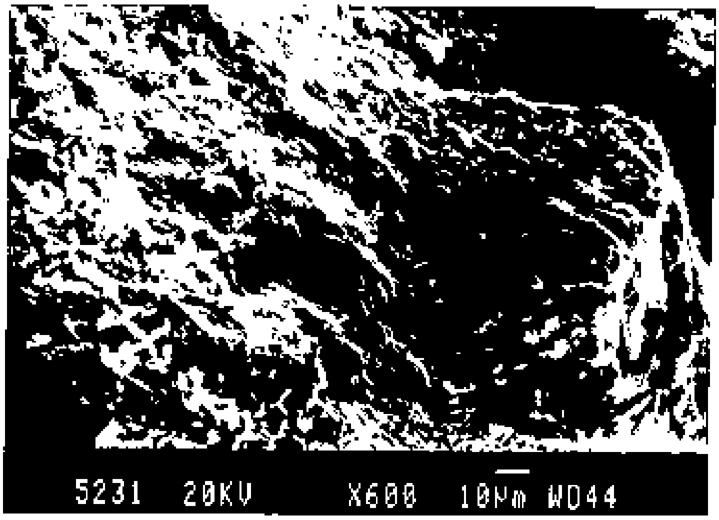


Fig. 4.21 Optical micrograph of preoxidised and reduced ilmenite (X400) (a) Oxidised and reduced at 950°C for 4 hour. (b) Oxidised and reduced at 1000°C for 4 hour. (c) oxidised and reduced at 1050°C for 4 hour.



(a) Pre oxidised and reduced ilmenite . (X600)



(b) As received and reduced ilmenite . (X600)

Fig: 4.22 Scanning Electron Micrographs of reduced ilmenite

4.4.1 Identification of Reaction Mechanism

The identification of the kinetic model constitutes an important step in the analysis of high temperature kinetic data on many metallurgical reactions. In many cases a preliminary identification is possible by using the so called reduced time plots. In reduced time plots the kinetic relationships are first expressed in terms of a factor α which may be defined as:

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

And the kinetic relationships are first expressed in the form

$$g(\alpha) = kt$$

where k is a rate constant and t the time. If $t_{0.5}$ be the time required to 0.5 fraction reacted (α=0.5) then one obtains the above reaction in the form

$$g(\alpha) = A\ (t/t_{0.5})$$

where A is calculated constant dependent on the form of the function g(α). This expression is dependent on kinetic rate constants and is dimensionless. For a given reaction mechanism a single equation represents all kinetic data irrespective of the nature of the system, temperature or any other factor that influence the reaction rate. Every mechanism has a unique dimensionless reduced time plot that is universally true for all reactions following this mechanism. These equations, therefore, offer useful approach to rapid selection of the appropriate rate equation.

In analysis of data one first finds out $t_{0.5}$ in the α - t plot for a given temperature. The plot is then redrawn, for the same given temperature, by plotting α versus $t/t_{0.5}$. All isothermal α - t plots merge into a single α versus $t/t_{0.5}$ if the kinetic data are truly isothermal and isokinetic. The α versus $t/t_{0.5}$ plot is matched against standard plots for different kinetic models.

The following rate equations were fitted to study the reaction mechanism:

1. first order reaction:

$$g(\alpha) = -\ln (1 - \alpha) = kt$$

2. kinetics controlled by chemical reaction:

$$g(\alpha) = [1 -(1 - \alpha)^{1/3}]^2 = (k/r_2)t$$

3. kinetics limited by diffusion through the product layer:

$$g(\alpha) = 1 - 2/3\ \alpha - (1- \alpha)^{2/3} = kt$$

Figs. 4.23 and 4.24 show the plots of α versus time for samples reduced in the oxidised and in the as-received conditions respectively. Fig. 4.25 shows the plot of $g(\alpha)$ versus $t/t_{0.5}$ for ilmenite reduced after oxidation. It can be seen that among the three suggested models, the kinetics of leaching after reduction in the oxidised state fits the first order reaction up to α value of 0.5. After that the reaction mechanism changes and the kinetics appear to be limited by diffusion through the product layer. 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 oxidised ilmenite. When 50 per cent of the reaction is complete, the reaction mechanism changes and the reaction follows Jander equation.

The plot of α versus $t/t_{0.5}$ for samples leached after reduction in the as-received condition is shown in Fig. 4.26. It shows that at the initial period the reaction takes place at all available sites exposed to leaching solution. But afterwards the reaction is controlled by diffusion. The reaction follows Ginstling-Brounshtein reaction.

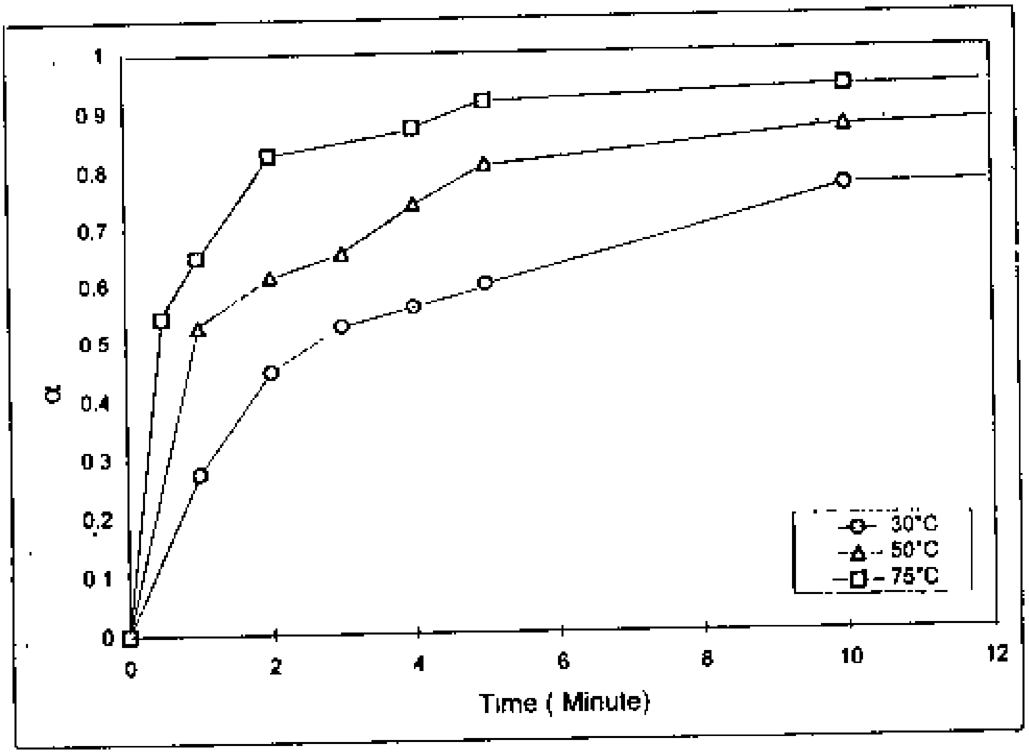


Fig. 4.23 Kinetic curve of isothermal leaching of preoxidised and reduced ilmenite leached with 10% HCl at specified temperature.

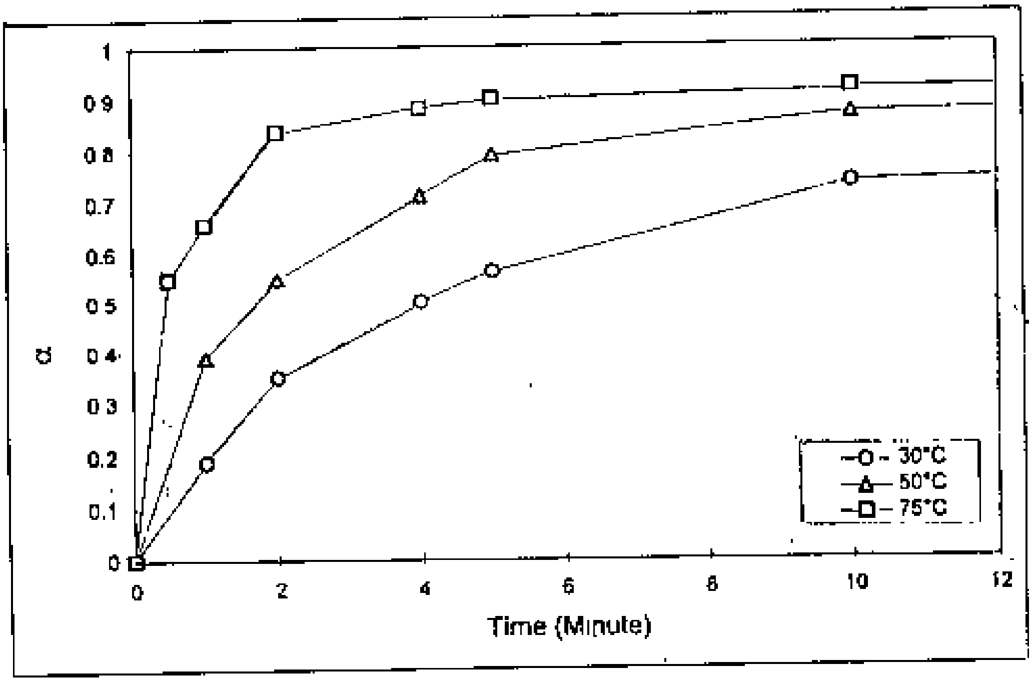


Fig. 4.24 Kinetic curve of isothermal leaching of as received and reduced ilmenite leached with 10% HCl at specified temperature.

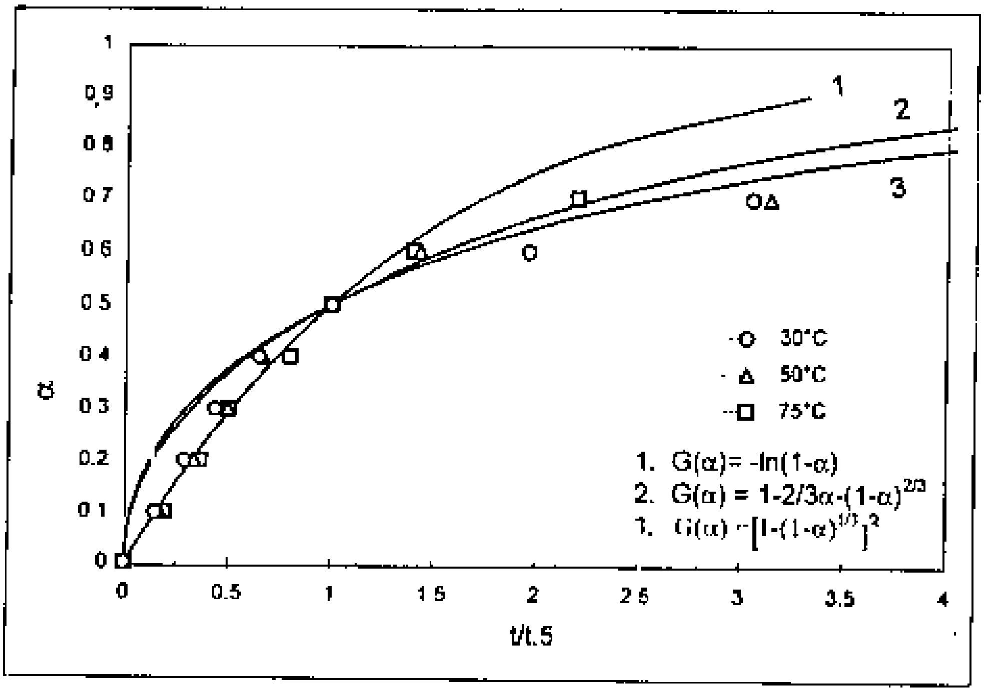


Fig: 4.25 Leaching time plot for isothermal kinetic data shown in fig. 4.23

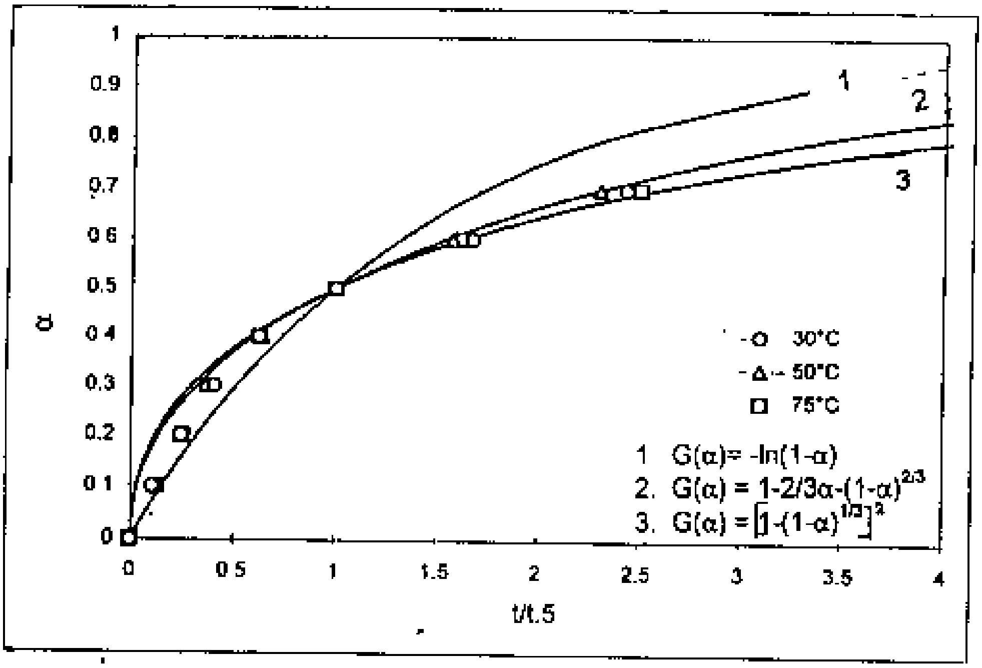


Fig: 4.26 Leaching time plot for isothermal kinetic data shown in fig. 4.24

4.4.2 *Evaluation of Activation Energy*

Both the integral and differential approach were considered to evaluate the activation energy.

a) *Integral Approach*

If the integral form of the kinetic law g(α) = kt is known, one can plot different isothermal values of g(α) against time. Since k = exp (-E/RT), the plot of ln k versus 1/T is a straight line and the slope represents the value of (-E/R). For the sample reduced in the oxidised condition, the plots of g(α) versus time and ln k versus 1/T are shown in Figs. 4.27 and 4.29 respectively. The apparent values of activation energy for the samples reduced after oxidation was calculated as 30.4 kJ/mole. The plots for the sample reduced in the as-received condition are shown in Figs. 4.28 and 4.30, and the apparent value for the activation energy is 42.97 kJ/mole.

b) *Differential Approach*

In the differential approach prior knowledge of any kinetic law is not necessary. The activation enrgy can be known without any prior knowledge of the form of g(α) and the reaction can be expressed as

$$\frac{d\alpha}{dt} = kf(\alpha) = Ae^{(-E/RT)} f(\alpha)$$

Considering fixed value of α

$$\ln \frac{d\alpha}{dt} = \ln A + \ln f(\alpha) - \frac{E}{RT}$$

Since f(α) has fixed value for fixed α, it follows that the plot of ln α versus time is straight line whose slope is –E/R.

Another differential approach can be written as

$$\frac{1}{A\exp(-E/RT)} \int_0^\alpha d\alpha = \int_0^t dt$$

t_o = const. exp (-E/RT)

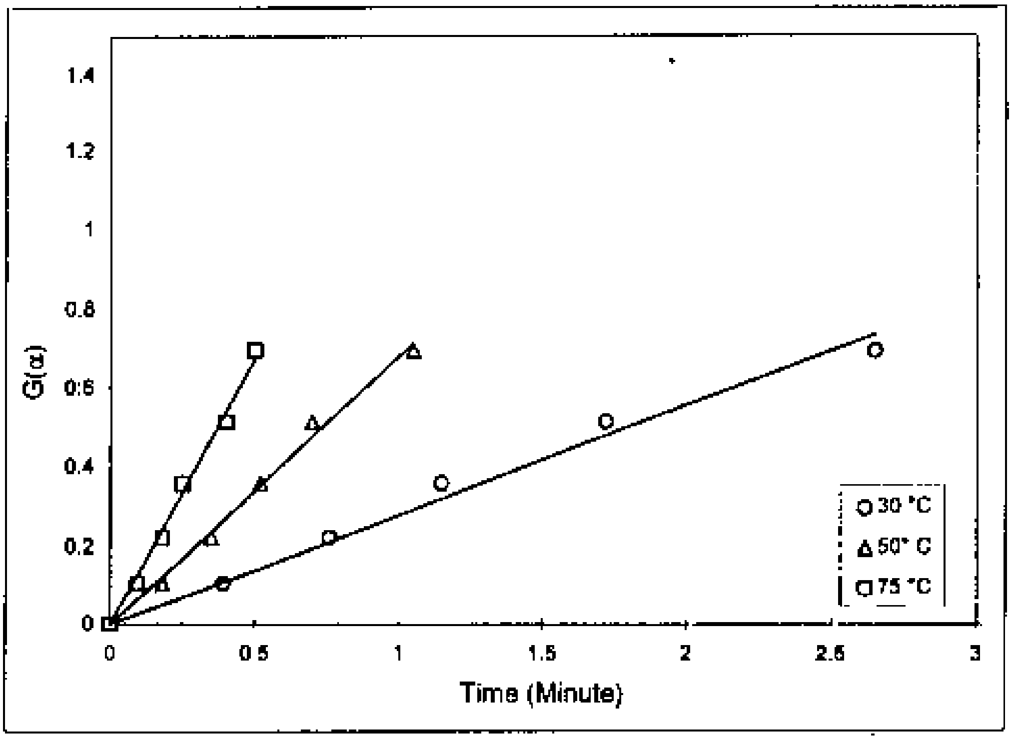


Fig: 4.27 Plots of isothermal kinetic data according to first order reaction for pre oxidised reduced and leached sample.

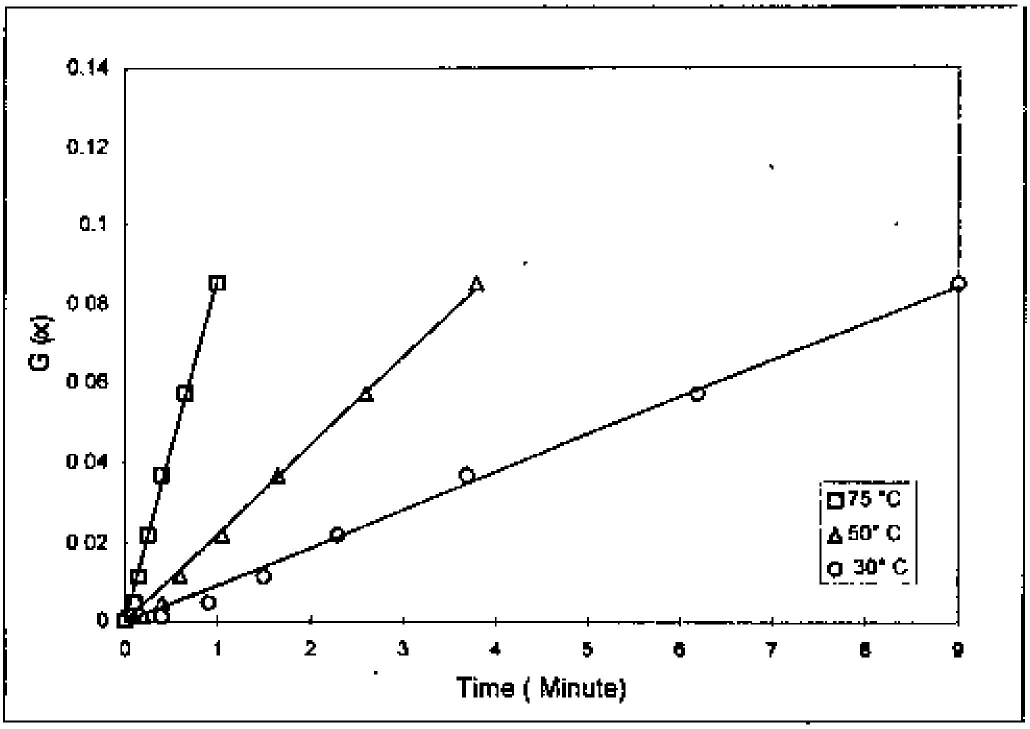


Fig: 4.28 Plots of isothermal kinetic data according to Ginstling-Brounsthein reaction for as received reduced and leached sample.

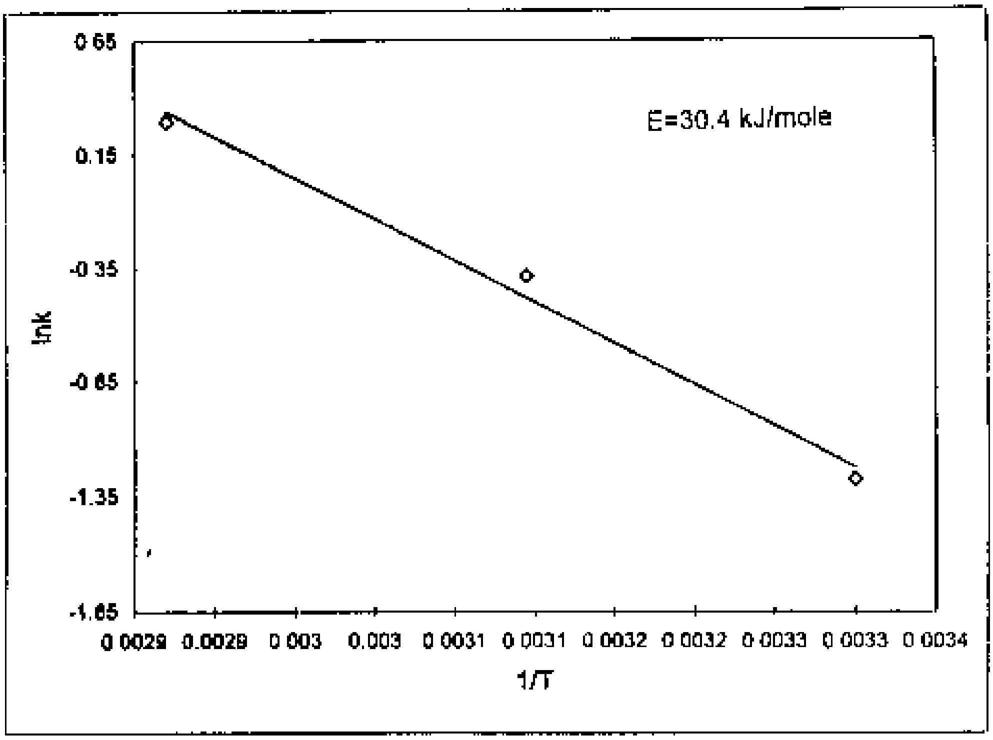


Fig: 4.29 Arhenius type plot for kinetic data of fig. 4.27

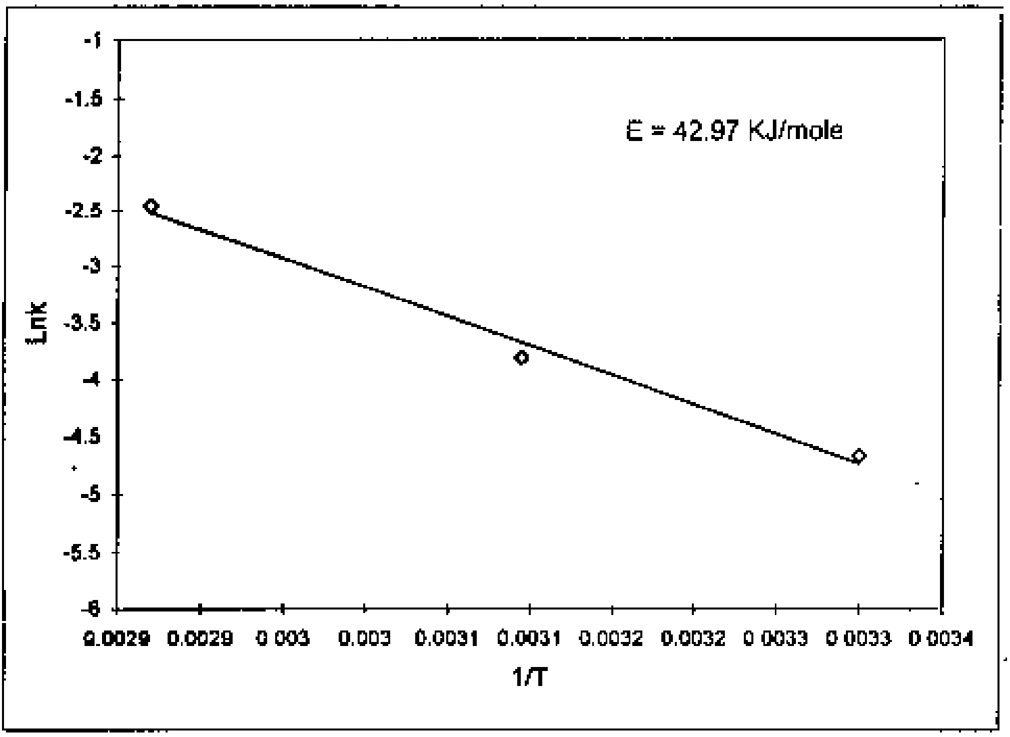


Fig: 4.30 Arhenius type plot for kinetic data of fig. 4.28.

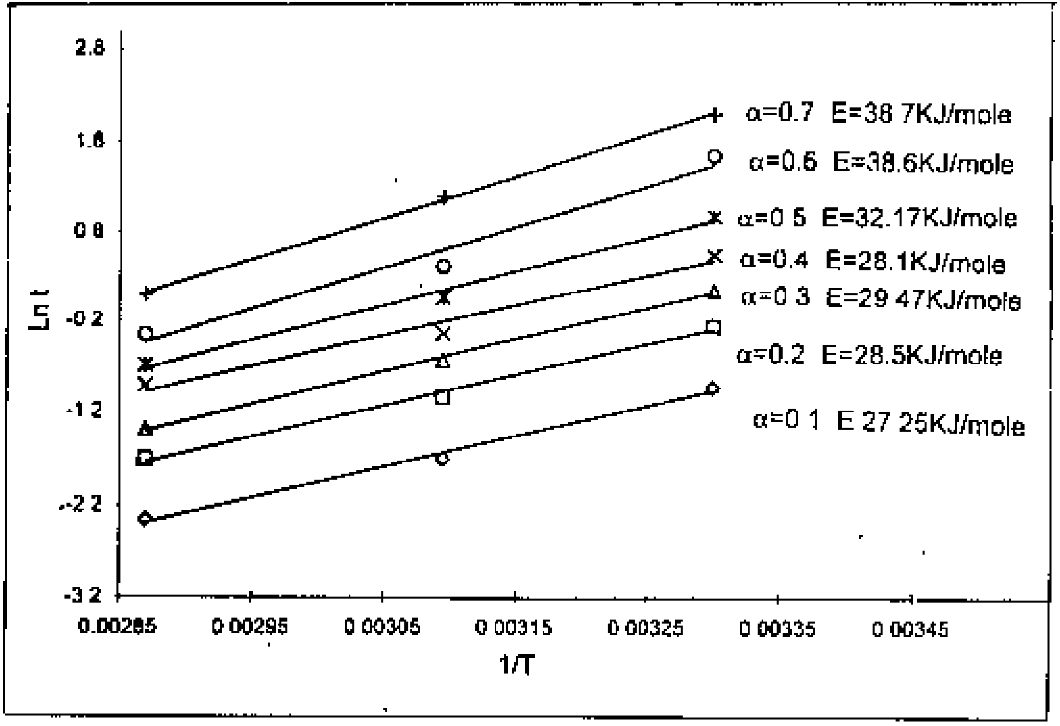


Fig: 4.31 Plots for calculation of apparent activation energy of leaching using differential approach for pre oxidised reduced and leached sample leached with 10% HCl.

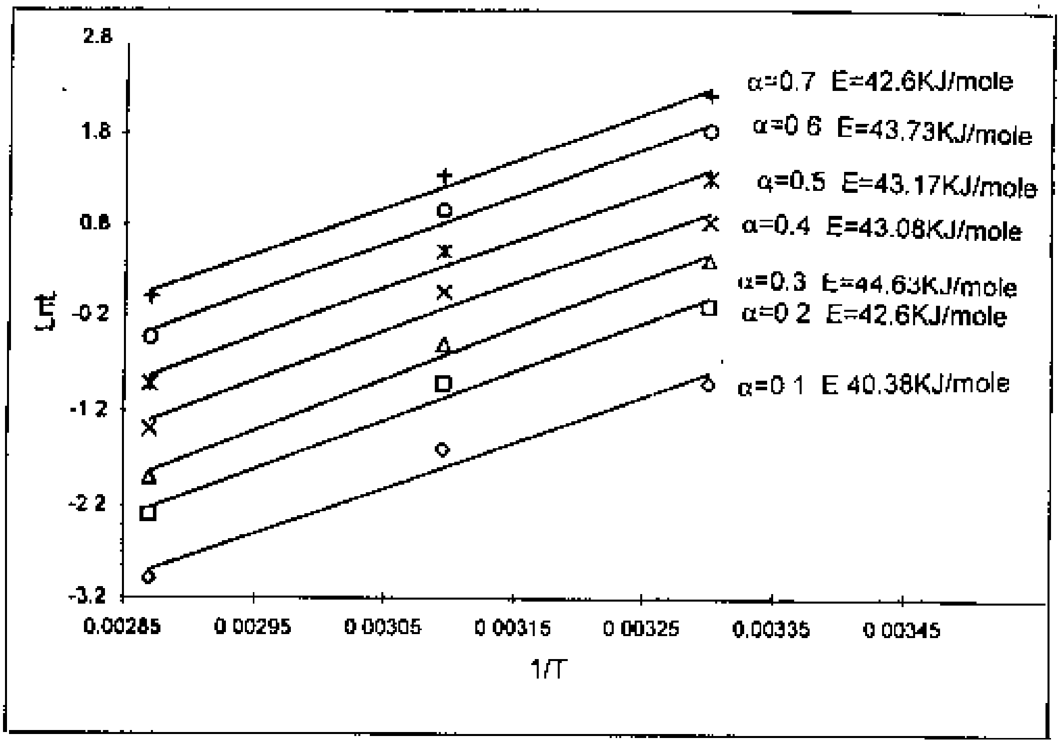


Fig: 4.32 plots for calculation of apparent activation energy of leaching using differential approach for as received reduced and leached sample leached with 10% HCl.

Thus a plot of $\ln t_0$ against 1/T is a straight line whose slope is - E/R. Plots of lnt versus 1/T have been plotted for oxidiesd-reduced-leached sample and as-received-reduced-leached samples. These plots are shown in Figs. 4.31 and 4.32 respectively.

It was found that the value of the activation energy of leaching ranges from 27.4 to 39 kJ/mole for the sample reduced after oxidation and 40.38 to 44.6 kJ/mole for the sample reduced in the as-received condition

4.4.3 Effect of Time on Leaching:

Effects of time on the rate of leaching of ilmenite, reduced in the as-received and in the oxidised conditions are shown in Figs. 4.23 and 4.24. 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 time of leaching, after which the rate of removal of iron from the sample is negligible.

Fig. 4.33 shows that in all cases leaching is faster in the samples reduced after oxidation and also more iron is removed from ilmenite leached after reduction in the oxidised condition than from ilmenite leached after reduction in the as-received condition.

4.4.4 Effect of Temperature

The effect of temperature on leaching is shown in Figs. 4.23 and 4.24. it can be seen that when leaching time is short, removal of iron increases sharply with an increase in temperature. The rate of leaching gradually decreases with time. The effect of prior oxidation on the rate of leaching of the reduced mass is shown in Fig. 4.33. It can be seen that the rate of leaching is enhanced by oxidation prior to reduction.

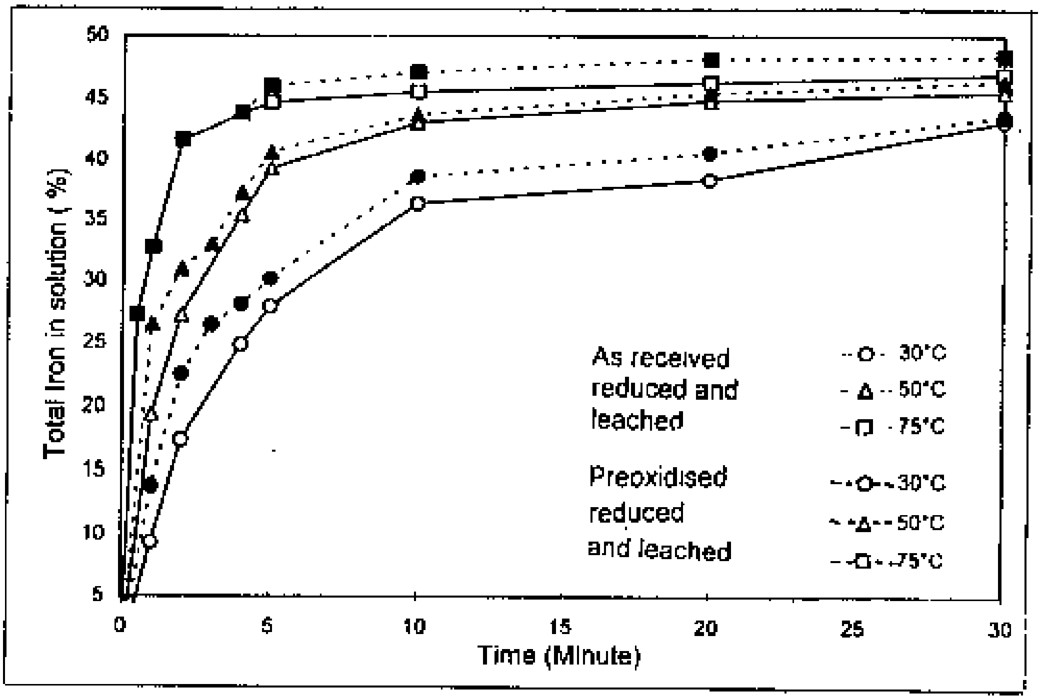


Fig: 4.33 Comparison of extent of dissolution of iron from preoxidised reduced sample and asreceived reducedsample leached with 10% HCl at specified temperature.

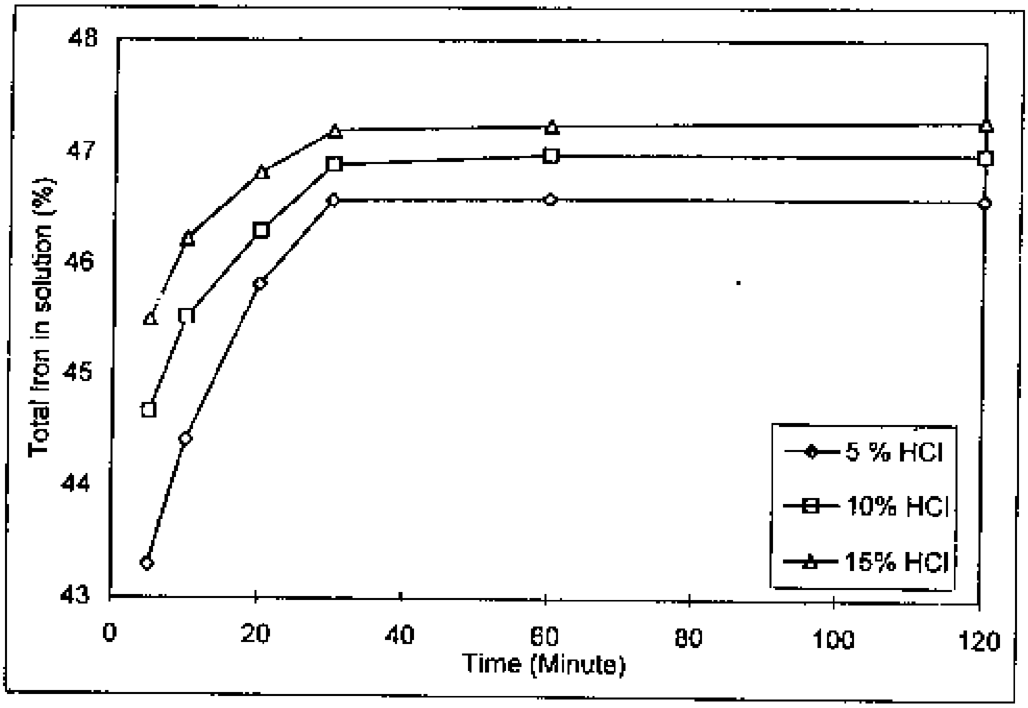


Fig: 4.34 Extent of dissolution of iron from as received and reduced sample leached with HCl of different conc. at 75°C.

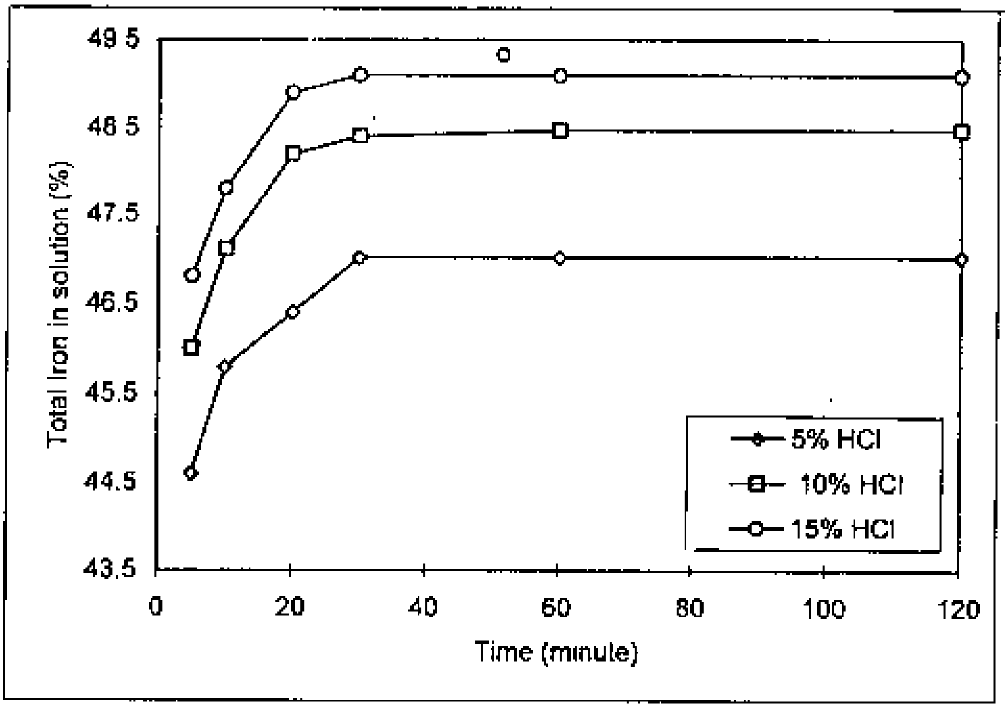


Fig. 4.35 Extent of dissolution of iron from pre oxidised and reduced ilmenite leached with hydrochloric acid of different conc. at 75°C.

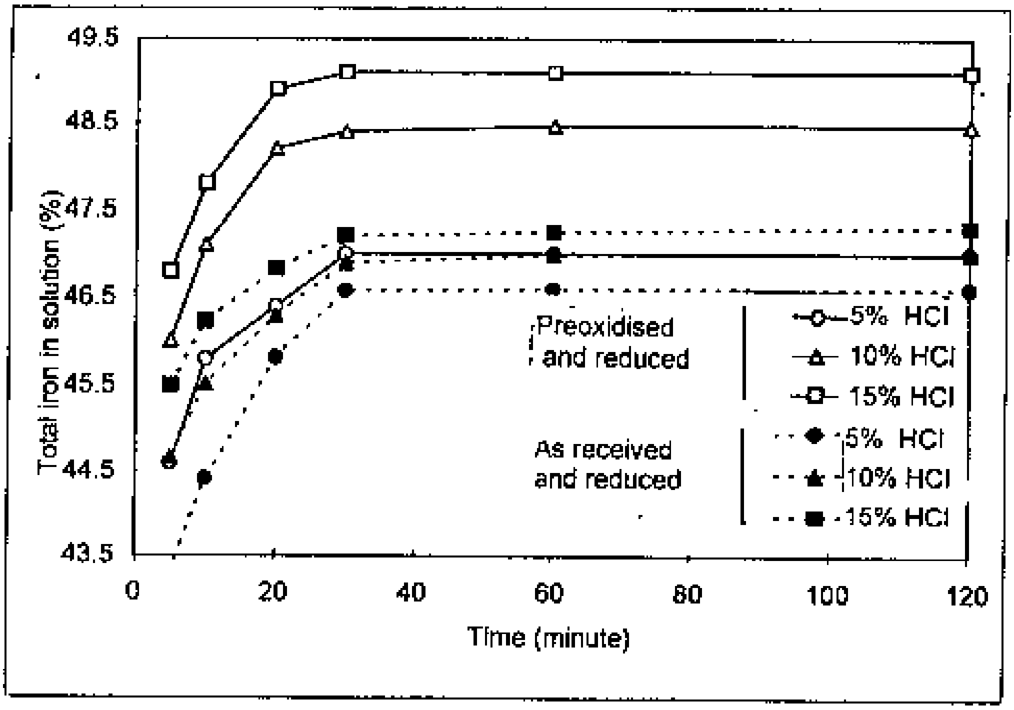


Fig. 4.36 Comparison of extent of dissolution of iron from pre oxidised reduced sample and as received reduced sample leached with hydrochloric acid of different conc. at 75°C.

4.4.5 Effect of Acid Concentration:

The effect of acid concentration on the rate of leaching is shown in Figs. 4.34 and 4.35. These figures show that the rate of removal of iron from the reduced ilmenite increases with an increase in the concentration of the acid. At all concentrations of the acid, it was found that the sample reduced in the oxidised condition has less iron than that reduced in the as-received condition. Fig. 4.36 shows the effects of oxidation on the extents of leaching of ilmenite at different acid concentrations.

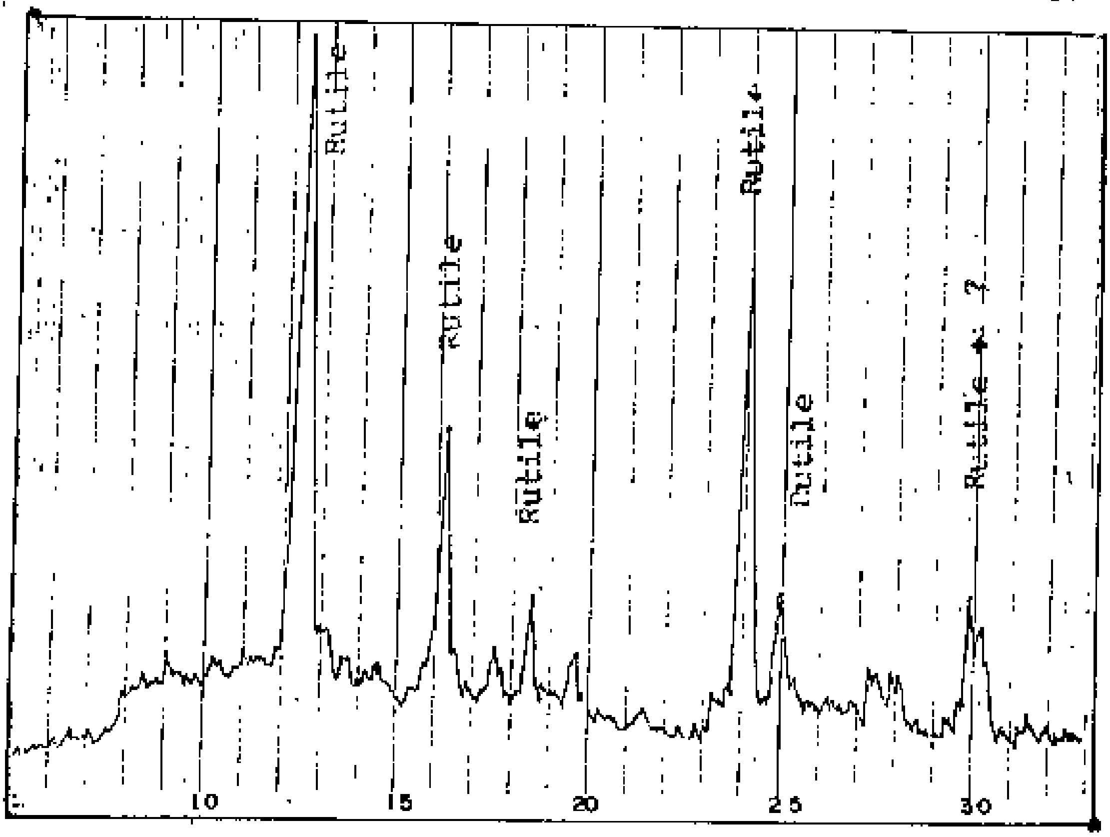
4.5 Comparison of the Products

The comparison of the leached samples are given in Table 4.2 which shows that the sample leached after reduction in the oxidised condition contains less iron. The presence of less TiO_2 in the sample reduced at 1050°C is 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

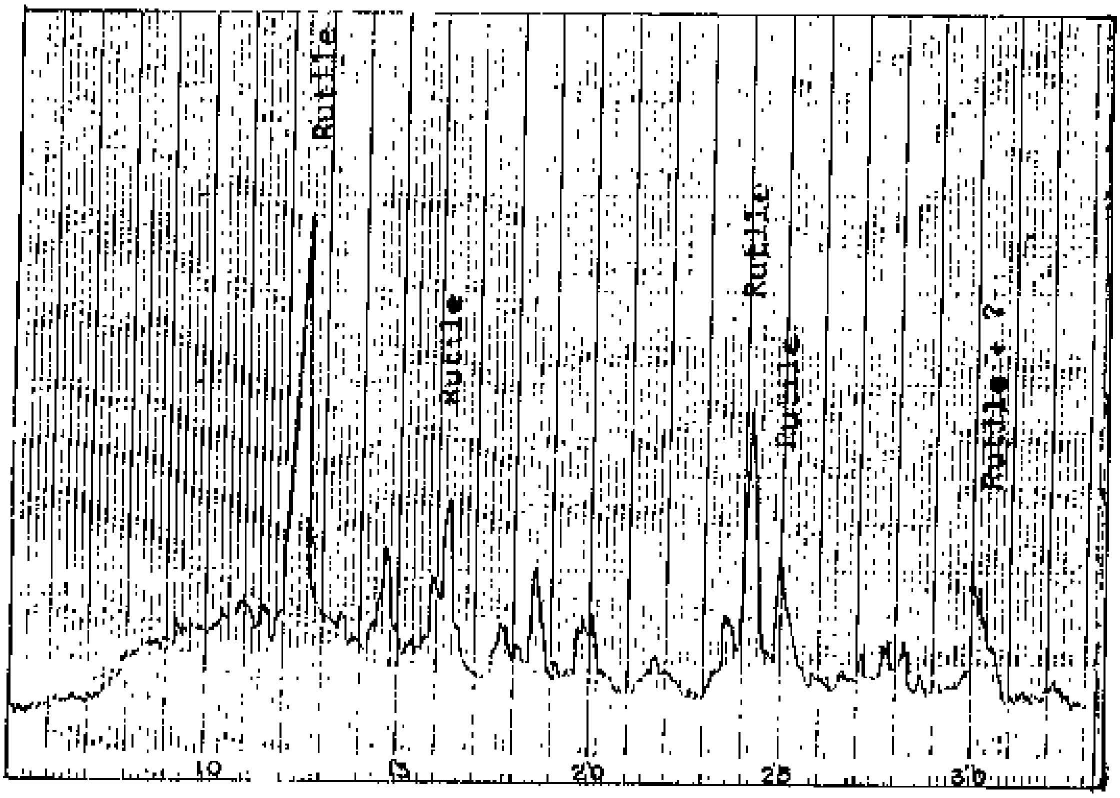
Table 4.2 Comparison of end products

Component	*As received reduced and leached*		*Reduced after oxidation and Leached*	
	1000°C	1050°C	1000°C	1050°C
TiO_2	82.54	82	90.8	89.9
Fe	7.4	5.2	5.57	2.45

Fig. 4.37 shows the x-ray diffraction pattern of leached ilmenite. These patterns show the presence of metallic iron, rutile and some unknown phases. These unknown phases may be complex phases of Fe, Mn, Al and SiO_2.



(a) Pre oxidised and reduced sample leached with 15 % HCl at 75°C



(b) As received and reduced sample leached with 15 % HCl at 75°C.

Fig: 4.37 X-ray diffractogram of leached ilmenite.

CHAPTER - 5 SUMMARY AND CONCLUSION

Effects of prior oxidation on the reduction and leaching of Bangladesh ilmenite has been investigated. The results obtained were compared with those obtained during reduction of Bangladesh ilmenite in the as-received condition.

The following methodology was followed

a) The extent of oxidation was determined by chemical analysis for ferrous iron.

b) The phases formed upon oxidation were identified by x-ray diffractometry.

c) The morphology of the product and the mechanism of oxidation of Bangladesh ilmenite was investigated by optical microscopy.

d) Oxidised samples were reduced by charcoal. The extent of reduction was determined by chemical analysis for metallic iron in the reduced sample and x-ray diffraction.

e) Reduced samples were leached in dilute hydrochloric acid and the extent of leaching was followed by chemical analysis

Almost all ferrous iron was found to have transformed into ferric state within 15 – 20 minutes of oxidation. X-ray diffraction studies showed that the product of oxidation at 700°C is pseudorutile, hematite, and rutile and some unidentified phases. Pseudobrookite was found to have formed during oxidation at temperatures above 800°C. The proportion of pseudobrookite was found to increase with time for up to 0.5 hour and then remain more or less constant. The appearance of pseudobrookite can be expressed by the reaction:

$$3Fe\,TiO_3 \rightarrow Fe_2Ti_3O_9 + {}^1/_2\,Fe_2O_3$$

On heating above 800°C pseudorutile transforms to pseudobrookite

$$Fe_2Ti_3O_9 \rightarrow Fe_2TiO_5 + 2TiO_2.$$

The existence of a lower temperature limit for the formation of pseudobrookite 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 suggest that pseudobrookite might also be formed by the reaction.

$Fe_2O_3 + TiO_2 \rightarrow Fe_2TiO_5$

The morphology of ilmenite oxidised at 700°C showed a different structure from that of ilmenite oxidised at temperatures above 800°C. The microcracks expected to be present was clearly visible in the Scanning electronic micrographs.

The rate of reduction of ilmenite was found to be dependent on temperature. At temperatures below 1000°C, reduction was through solid state reaction with carbon (of charcoal) and hence the reduction rate was slow. At higher temperatures (above 1000°C) reduction takes place through reaction with gaseous carbon monoxide. The rate of reduction was found to be faster in case of samples reduced after oxidation. The possible route of reduction of oxidised ilmenite has been expressed as follows:

The first stage is the reformation of ilmenite from oxidation products

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

$Fe_2O_3 + TiO_2 + CO \rightarrow 2\ Fe\ TiO_3 + CO_2$

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

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

During second stage of reduction some TiO_2 is reduced to lower oxides. The second stage may be expressed as:

$Fe\ TiO_3 + CO \rightarrow Fe + TiO_2 + CO_2$

$n\ TiO_2 + CO \rightarrow Ti_nO_{2n-1} + CO_2$

Reduction mechanism for the as received ilmenite is slightly different from preoxidised ilmenite. Previous work on the reduction study of the as received ilmenite showed that this process takes place through the route of

pseudorutile → ilmenite → metallic iron.

X-ray diffraction patterns of ilmenite reduced in the as received and also in the oxidised conditions were found to contain characteristic diffraction lines of iron and rutile and some unidentified phases, indicating that rutile and iron is the end products. The unidentified phases may be compounds of iron, Manganese, silicon, aluminium. etc.

The faster rate and higher extent of reduction in the oxidised condition has been attributed to:

1) Introduction of defects, (cracks, grain boundaries,) in the grains of ilmenite, which enhances the rate of subsequent reduction.

2) conversion of almost all ferrous iron to ferric state which overcomes the problems of ferrous to ferric ratios in the ilmenite from different locations.

3) alteration of equilibrium conditions and rate of reduction from ferric to ferrous state.

Leaching of ilmenite is a very rapid process and it was found that it is temperature dependent. The extent of removal of iron increases with an increase in temperature. Kinetic data of leaching shows that the reaction mechanism of preoxidised ilmenite follows the first order reaction upto $\propto$ value of 0.5, after that period it changes to Jander reaction. On the other hand leaching of ilmenite reduced in the as received condition follows Ginstling - Brounshtein reaction. The apparent activation energy for leaching was found to be 30.4 kj/mole for oxidised-reduced sample and 40.38 kj/mole for the sample reduced in the as-received condition and then leached.

CHAPTER – 6 LIMITATIONS OF THE PRESENT EXPERIMENTAL WORK AND SUGGESTIONS FOR FUTURE WORK

6.1 Limitations of the Present Work

Following were the main limitation of the experimental work

1) During oxidation the samples of oxidised ilmenite were taken out at specified time intervals. The temperature in the furnace dropped when the door was opened to take out samples and some time was required for the temperature to rise to the specified level

2) Every care was taken to maintain identical conditions during reduction. But even then some variations might have occurred during reduction. The bed of ilmenite may not have been uniform in all cases. However, it is not expected to cause much variation in the results.

3) Leaching was done by HCl acid During leaching samples were taken out after very short intervals of time and some time duration were required for taking out samples. This might have caused some error in the results particularly for those for short time leaching.

4) During determination of ferrous iron by volumetric method, it was sometimes difficult to identify the end point very precisely. The same type of difficulty was encountered in the estimation of metallic iron. During determination of TiO_2 in the reduced sample low TiO_2 content may have been found due to reduction of some TiO_2.

6.2 Suggestion for Future Work

Following studies may be further carried out on the reduction leach processes

1) Oxidation at higher temperatures may be carried out. SEM and DTA may be done to establish the possible courses of reaction.

2) Reduction may be performed at higher temperatures to enhance the reaction rate. A study on the effect of depth of initial coke bed on the rate of reduction may also be carried out.

3) Role of catalysis on the rate and extent of reduction may be investigated.

4) Leaching may be carried out in acids of higher concentrations and also at higher temperatures. Other acids may also be used for leaching.

5) Recovery of metallic iron from the leached liquor may be attempted.

6) After leaching the product may be further oxidised to study the effect of calcination.

References:

1 Information Booklet of Beach Sand Exploration Center, Bangladesh Atomic Energy Commission, June 1994

2 G W. Elger, D. E. Kirby, and S. C Rhoads, US Bur Mines Rep Invest. RI 8140 (1976) 31.

3 R.G.Becher, R. G. Canning and B. A Goodheart, Proceedings of the Australian Institute of Mining and Metallurgy, (1965) **21.**

4 G, L. Ganzu and K K Mazumdar, BARC Report on " A Continuous Process for Conversion of Ilmenite to Artificial Rutile" (1970)

5 A. J. Ravenstad and O. Moklebust (TitanCo Inc.) British patent 547898 (1942).

6 S. Samanta, R.N. Misra and P. p Bhatnagar, N. M. L Research Report 260/68 (1968).

7 R. H. Walsh, H. W Hockim, D. R. Brandt, P. L. Diotz and R. R. Girandot, Transaction of the Metallurgy Society AIME, **218** (1968) 994.

8 G. Ostberg, Journal of the Iron and steel Institute (London), **195** (1960), 50

9 Pollard, Leslie John Stewart and Donald Fergusson, Austr Patent 493,355(Cl C 22 B 5/10) 24 May 1978,Appl 76/13, 402, 7 May 1975, 14, chem. Abstr. **89** (1978) 150240e

10 Lakshevitz, Arthur Jr. De Almeida, Nelson Novais, De Almeida and Antonio Luiz (Centro Technico Aeroespacial Braz. Pedido, Pol Pat, 7608, 271 (Cl C 22 B 34/12) 4 July 1978, Appl 76/8, 271, 9 December 1976, 9, Chem Abstr, **90** (1979) 41849k.

11 Blaszkiewicz, Genowefa , Borowice, Krzysztof, Kepinski, Jozef, Maternowaski, Bogdan (Polytechnica Suzczecinska) Pol Pat, 84, 042 (Cl CO I G 23/04) 30 September 1976, Appl 166,670. 20 November 1973, 3; Chem Abstr. **90**(1979) 25570g.

12 J. C. Sehra, J. B. Gnanamoorthy, H. S. Gadiyar, Ch. S. RaO P. K. Jena, Transactions of the Indian Institute of Metals, **19** (1966) 114.

13 E. M. Khairy, M K. Hussain and K. A. Baraway, N. M. L. Technical journal, **10** (4) (1968).

14 K. V. Viswanathan Nayar, Bulletin of the Central Research Institute, University of Travencore, 11 (1952) 106.

15 A. K. Sharova and A.A. Fotiyev, Izvestiya Sibirskogo Otdbeleniya Akademy Nauk SSSR, No. **4** (1959) 52.

16 A. S. Gaskin and A.E Ringwood, Australian Patent 222517 (1959)

17 S. K. Jain, P. M Prasad and P. K Jena, Metallurgical transactions **1** (1970) 1527.

18 S. K. Jain, P. M. Prasad and P. K Jena, Paper to be presented at the 27th Annual Technical Meeting of the Indian Institute of Metals at Varanasi (1973).

19 C. C. Patel and G. V. Jere, Transactions of the Metallurgy Society AIME, **218** (1960) 219.

20 W. E. Dunn, Transaction of the Metallurgy Society AIME, **218** (1960) 6.

21 A. A. Rabie, M Y Saada and S. Y. Ezz, Advances in Extractive Metallurgy, The Institute of Mining and Metallurgy, London (1968) 501.

22 Dead Sea Works Ltd., British patent 1104780 (1968).

23 Joedden , Klaus, Heymer, Gero, Stephan and Hans Werner, Ger Offen, 3 201,482 (Cl C 01 G 23/047), 11 August 1983, Appl 3 February 1982, 13; Chem Abstr. **99** (1983)

24 Kwangtung, Instute of Non-Ferrous Metals Research, Chem Abstr, **88** (1978) 193793.

25 C. Sankaran, R. N. Misra and P. P. Bhatnagar, Advances in Extractive Metallurgy, The Institute of Mining and Metallurgy, London (1968) 480.

26 V. A. Altekar and A. S. Athawale, Transactions of the Indian Institute of Metals **20** (4) (1967) 220

27 Titan Company, British Patent 715257 (1954).

28 Ya. I. Ivashentsev, Transaction of Tomoskogo Gas University (Ser Chime), **154** (1962) 184.

29 Ya. I. Iva, Shentsev, Ibid, **170** (1964) 139.

30 Annie George and P. N. Mohan Das, Journal of Scientific and Industrial Research, **44** (1985) 443.

31 D. Bhogeswara Rao and M. Rigaud , High Temperature Science **6** (1974) 323

32 V. B. Fetisov, L.I. Leontyev, B.Z. Kudinov,and S V. Ivanova, Izv. Akad. Nauk SSSR Metal. **2**, 47 (1968). Eng. Transl. Russian Metallurgy (Metally) **2**, 35 (1968).

33 P. Ramdohr , Abhandi . Preuss. Akad . Weiss. Math, Nat. Klasse,**14**, 14 (1939);C. A. 35 , 117 (1941)

34 J.L. Overhault , G. Vaux and J. L. Rodda, Amer Mineralogist **35**, 117 (1950).

35 D. G. Jones , Trans Inst. Min. Metall., **82** (1973) C186.

36 A. H Webster and N F. H. Bright, J. Am Ceram. Soc.**44**, (1961), 110-6.

37 C.E.Curnow and L.G. Parry, Nature**174**, 1101 (1954)

38 M. D. Karkhanawala, A. C. Mommin Econ Geol. **54**, 913 (1939).

39 G. Teufer and A. K. Temple, Nature, **211** (1966)179.

40 A. K. Temple , Econ Geol **61**, 695 (1966).

41 I. E. Grey and A. F. Reid., J. Solid state Chem, **4** 186 (1972).

42 M. J. W. Larrett, and W. G. Spancer , AMDEL Bull. **12**. 74 (1971).

43 G. F. Strizhov, A.I. Okunev, V. Ya. Khoshkarov and S. J. Suchilnikov, Metallurgizdat, 1,120,(1965).

44 S. Akimoto, T. Nagata, and T. Katsura, Nature 179, **37** (1957) .

45 H. F. Fischmeister , in "Reactivity of solids" (J H. De Boer , et al, Eds) p. 195, Elsevier, Amesterdam, 1960.

46 E. A. Gulbransen and T.P.Copan, Nature**186**, 959 (1960).

47 E. A. Gulbransen and T.P.Copan, Proc. European Conf. Electron Microscopy , Delft **1**, 225, (1965).

48 K. H. Hardy, Prog. Met. Phys **5**, 45, (1956).

49 Paidassi, J., Acta Met **3**, 447 (1955)

50 P. D. Dankov, and P. V. Churev, Doki. Akad Nauk SSSR, **73**, 1221 (1950).

51 W. Jaenicke, and S. Z. Leistikow, Phys Chem **15**, 175 (1958).

52 W. W. Webb, and W. D., Forgeng, J Appl. Phys. **28**, 1449 (1957).

53 D. Bhogeswarw Rao, and J. R. Wynnyckyj., High temp. Sci. to be communicated.

54 J. B. Macchesney and A. Maun, Amer. Mineralogist **44**, 926 (1959)

55 F. C. Frank, Acta Cryst. **4**, 497 (1951).

56 D Bhogeswara Rao and M. Rigaud , Oxidation of metals , in press.

57 M. J. Wort. And M. P. Jones Mineralogical Magazine March 1980, Department of Mineral Resources Engineering , Royal School of Mines , London, SW7 2BP. **43** , 659 .,

58 L. B. Pfeil, ., J. Iron Steel Inst. **119**, 501 (1929).

59 M. I. El-Guindy and W. G. Davenport, Metall, Trans, **1** (1970) 1729.

60 I. E. Grey, and A.F. Reid, Trans. Instn. Min. Metall, **83** (1974). C39

61 A. S. M. A. Haseeb, M Z Huq and A. S. W Kurny, Trans. Instn. Min. Metall., Sect. C, **106** (1997) C39.

62 S, Islam, M. Jebin , A. S. M A. Haseeb, and ASW Kurny , Third Annual Paper Meet of the Mechanical Engineering Division , The Instute of Engineers, Bangladesh, Chittagong Oct .31-Nov. 2, 1996.

63 C. Sankaran, R.N.Misra, P.P. Bhatnagar " Selective Chlorination of Iron from Ilmenite with Hydrochloric Acid Gas." Proceedings of a symposium organised by the Institute of Mining & Metallurgy London, 17-20th April,1967,480

64 L. S. Rajeswari, P. N. Mohan das and A. D. Damodaran, Trans. Indian Inst. Met. **43**(4), (1990) 208.

65 Annie George, V S Kelukutty, L. G Radhika, P. N Mohandas, and P K Rohatgi, J Mater Sci, **19** (5) (1984) 1522.

66 R I . Jaffee and H M. Burte Titanium science and technology, Vol 1. Edited by R. I Jaffee & H M Burte (Plenum Press. New York. London) 1973.

67 M. G. M U. Ismail, J. Amarasekera and J S.N Kumarasinghe, International Journal of mineral Processing , **10** (1983) 161-164.

68 J.J Burastero, Chem Abstr, **89** (1978) 26787z.

69 S. Ahmed, T. Pal, and S Mitra , J Geol. Sco India, **40** (1992) 29.

70 D. S. S . Babu , P.N.M. Das and A.D . Damodaran., Chemical and metallurgical studies of ilmenite and there implication on industrial utilisation, Proc. 6th Kerala Science Congr., Thiruvananthapuram, India, Jan. 1994, 7

71 R. Merk and C. A. Pickles, Canadian Metallurgical Quarterly **27**(3), (1988), 179.

72 P. K. Jena, S. K. Jain and P. M Prasad, The Baranas Metallurgist, **5** (1973), 107.

73 D. G. jones , Trans. Inst. Min Metall. **83** (1974) C1.

74 E. O. Olanipekun, R. A. Oderinde, and O.K. Okurumeh, Trans. Indian Inst. Met. **46** (1), (1993), 45

75 B.D. Cullity, Elements of X-ray diffraction, Addision-Wesley Publishing Company, London (1978).

76 B. C.Agarwal, and S. P. Jain "A Text Book of Metallurgical analysis", 3rd Ed. Khanna Publishers, Delhi (1996).

77 O. Kubaschewski and E Ll. Evans, Metallurgical thermochemistry, 2nd edn. (Oxford , etc.: Pergamon Press, 1956) , 410

78 Hem Shankar Ray, Kinetics Of Metallurgical Reactions, Oxford & IBH Publishing Co. Pvt ltd, New Delhi, Bombay, calcutta.

Appendix-A

Estimation of Ferrous Iron

Keep all solutions ready before you start analysing

- 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 from hot plate and immediately add
    a) 100 ml of 4 pct. boric acid (4gm boric acid in 100cc water)
    b) 15 ml of H_3PO_4-H_2SO_4 mixture
    c) 100 ml of distilled water
    d) Cool in running water
- Add 1 ml of Barium diphenyl amine sulphonate indicator.
- Titrate with O.1N potassium dichromate solution to a violet-blue and point.

Calculation:

$$\% \text{ Fe}^{++} = \frac{\text{ml of } K_2Cr_2O_7 \times N \times 0.05584 \times 100}{\text{wt of sample}}$$

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

<u>Test the residue for iron content</u>

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

  a) 10 ml of H_3PO_4-H_2SO_4 mixture.

  b) 10 ml of Zimmerman solution

  c) 5 drops of Barium diphenyl-amine sulphonate indicator.
- Titrate with standard potassium dichromate solution

Appearance of violet colour is the END POINT.

<u>Calculation</u> :

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

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

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 sulphate.
- Spread the weighed sample evenly over solidified potassium BI-sulphate.
- Heat gently to melt
- Swirl the contents of the crucible carefully
- Increase the temperature to the maximum (900^0)
- Heat (at 900°C) for 30 minutes
- Allow to solidify.
- Place the crucible(and the lid) inside a beaker containing 20 pct H_2SO_4.
- Heat till dissolution is complete.
- Make upto 250 ml.

Use this solution for the determination of TiO_2 also

- Pipette out 25 ml of the solution in a conical flask
- Add 5ml conc. HCl, heat to 80°C.
- Reduce the iron solution by adding (DROPWISE)FRESHLY PREPARED $SnCl_2$ Solution. [Add till the colour disappears, add one drip excess]
- Cool immediately in ICE (to 20^0C)
- Dilute to about 100 ml.

- Add 10 ml of Saturated $HgCl_2$ solution (rapidly, at a time) and mix thoroughly.
- Silky while precipitate will be obtained. Allow to stand for 5 minutes.
- Add 5 ml of conc. H_2SO_4 and 10 drops of n-phenylanthralinic acid indicator.
- Titrate with std. potassium dichromate solution to pink colour. This colour change is not very prominent, has to be noticed carefully.

Calculation:

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

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

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

Appendix-D

Determination of Total Iron from Leached Solutuion

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

  10 ml of Zimmerman soln

  10 ml of acid mixture.

  5 drops of sodium/ Barium diphenyl amine indicator.
- Titrate with std. Potassium dichromate to get the amount of total iron.

Calculation:

% of total iron is calculated from the following relationship:

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

Estimation of TiO_2

- The apparatus consists of a 500 ml Erlenmeyer flask with a 2-hole rubber stopper. A pointed glass rod nearly touching the bottom of the flask is placed in one hole of the stopper and the short end of the delivery tube is placed in the other hole. The other end of the delivery tube is placed into a 400ml. beaker containing saturated sodium bicarbonate solution. The aluminium foil is attached to the glass rod fixed with the stopper.
- Take 25 ml of solution (prepared for estimation of total iron) in a 500-ml Erlenmeyer flask
- Add 30 ml of Hcl (conc.)
- Boil the solution.
- Attach 2 gm of high purity aluminium foil to the end of the glass rod of the reductor.
- Remove the flask from the heating mantle.
- Immediately insert the rubber stopper carrying the glass rod with aluminium and the

delivery tube of 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 aluminium foil and the solution is rapid
- Towards the end of the reaction swirl the flask to ensure complete mixing and reduction.
- When all the aluminium 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°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 indicator
- Titrate with standard ferric ammonium sulphate indicator.

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

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

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 100ml and store in a dark coloured bottle.

2. Standardisation of Ferric Alum:

Dissolve 30.16gm of ferric ammonium sulphate in 800ml distilled water and 15ml conc. H_2SO_4. Add H_2O_2 to ensure complete oxidation of the iron. Boil the solution to remove excess H_2O_2 and dilute to 1 litre. Standardise the solution against standard TiO_2 reduced in the same way as described for the sample

3. Preparation of $SnCl_2$:

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

4. Phosphoric acid-Sulphuric acid Mixture

150ml of conc. H_2O_4 150ml of H_3PO_4 in 700 ml distilled water.

Total volume will be 1000ml

5. Zimmerman Solution

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

6. Diphenyl amine sulphonate Indicator

Dissolve 1 gm of the diphenyl-amine salt in 100ml of conc. H_2SO_4

7. Barium diphenylamine sulphonate Indicator

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

8. N-phenylanthralinic acid indicator

0.1gm phenylanthralinic acid in 100ml of 0.005 molar sol^n of NaOH

9. 20% HCl Sol^n

Conc. HCl contains 35% HCl. Take 100cc HCl and add distilled water to make upto 165cc.

Appendix - G

Result of Chemical Analysis of Oxidised Sample

Table Amount of ferrous iron present in the oxidised sample

Temp / Time (Minute)	*Ferrous iron (%)*			
	700°C	800°C	900°C	950°C
0	18.7	18.7	18.7	18.7
15	3.85	2.1	1.5	1.05
30	2.67	0.95	0.87	0.67
60	1.76	0.7	0.6	0.5
120	1.18	0.625	0.54	0.5

Result of Chemical Analysis of Reduced Sample

Table: Data of reduction (Oxidised sample)

Temp/ Time	Metallic Iron (%)			
	0.5 hr	1 hr	2 hr	4 hr
950° C	6.8	10.8	19.09	24.5
1000°C	10.94	17.7	26.13	34.8
1050°C	20.6	35.6	39.2	42.1

Table : Data of reduction (As received sample)

Temp/ Time	Metallic Iron (%)			
	0.5 hr	1 hr	2 hr	4 hr
950° C	5.1	8.3	13.5	17
1000°C	8.2	14.5	27.9	32.16
1050°C	15.5	23.5	32.1	37.8

Appendix -I

Result of Chemical Analysis of Leached Sample

Table: Result of leaching Preoxidised and reduced sample leached with 10% HCl

Time/ temp.	*Total iron in the leached sample (%)*		
	30 °C	50°C	75°C
0	0	0	0
1	13.8	26.5	32.7
2	22.55	30.93	41.6
3	26.49	32.98	42.3
4	28.1	37.3	43.8
5	30.15	40.65	46.01
10	38.63	43.71	47.1
20	40.6	45.43	48.2
30	43.54	46.38	48.4
60	45.34	47.26	48.47
120	46.99	48.1	48.47

Table: Result of leaching As received and reduced sample leached with 10% HCl

Time/ temp	*Total iron in the leached solution (%)*		
	30 °C	50°C	75°C
0	0	0	0
1	9.4	19.4	27.27
2	17.4	27.27	32.69
3			41.25
4	24.9	35.4	43.8
5	27.92	39.31	44.67
10	36.4	43.06	45.52
20	40.6	44.83	46.3
30	43.15	45.5	46.95
60	44.95	46.75	46.99
120	45.65	46.78	47

Table: Result of leaching As received and reduced sample leached at 75° C.

Time (minute)	Total iron in the leached solution (%)		
	5 % HCl	10% HCl	15 % HCl
5	43.3	44.67	45.5
10	44.42	45.52	46.2
20	45.82	46.3	46.82
30	46.58	46.95	47.2
60	46.58	46.99	47.5

Table: Result of leaching Preoxidised and reduced sample leached 75° C

Time (minute).	Total iron in the leached solution (%)		
	5 % HCl	10% HCl	15 % HCl
5	44.8	46.01	46.89
10	46	47.1	47.89
20	46.4	48.2	48.8
30	46.8	48.4	49.0
60	46.8	48.47	49.1