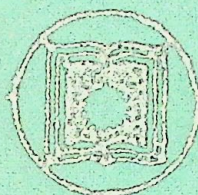


PROCESSING OF ILMENITE BY VARIOUS ROASTING, LEACHING AND SOLVENT EXTRACTION PROCESSES



A Dissertation

*Submitted to the University of Rajshahi in
Partial Fulfilment of the Requirements for
the Degree of Doctor of Philosophy*

By

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OCTOBER, 1992

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RAJSHAHÍ, BANGLADESH

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*Dedicated to my Grandparents
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DECLARATION CERTIFICATE

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CONTENTS

Page No.

ABSTRACT

CHAPTER—I

INTRODUCTION	1
------------------------	---

CHAPTER—II

REVIEW OF LITERATURES	24
---------------------------------	----

CHAPTER—III

OBJECT OF THE PRESENT INVESTIGATION	38
---	----

CHAPTER—IV

EXPERIMENTAL	41
------------------------	----

4.1 . CHEMICALS USED, THEIR SOURCES AND SPECIFICATIONS	41
--	----

4.2 . PREPARATION OF DIFFERENT STANDARD SOLUTION	43
--	----

4.3 . EXPERIMENTAL TECHNIQUES	46
---	----

a. Analytical Technique : Spectrophotometer	46
---	----

i) <i>Spectrophotometric estimation of titanium(IV)</i>	47
---	----

ii) <i>Spectrophotometric estimation of iron (III)</i>	48
--	----

b. Phase mixing	52
---------------------------	----

i) <i>In solid-liquid system</i>	52
--	----

ii) <i>In liquid-liquid system</i>	52
--	----

c. High temperature apparatus : Electric Tube Furnace	53
---	----

d. Gas flow regulator	53
---------------------------------	----

e. Thermostates	55
---------------------------	----

f. Acidity measurement : pH Meter	55
---	----

g. Size reduction : The Ball Mill	55
---	----

h. Size sorting : The Sieve Shaker	56
--	----

i. X-ray Diffractometer	56
-----------------------------------	----

4.4 . EXPERIMENTAL PROCEDURES	57
---	----

a. Experimental set-up and procedures for different thermal treatments of ilmenite prior to leaching	57
--	----

b. Experimental set-up and procedures for leaching	61
c. Procedure for liquid-liquid extraction and stripping	61
d. Procedure for regeneration of extractant and precipitation of metals	62

CHAPTER—V

EXPERIMENTS, RESULTS AND DISCUSSION	64
5.1 LEACHING OF NON-TREATED ILMENITE POWDER BY DIFFERENT MINERAL ACIDS	64
5.2 THERMAL TREATMENT (ROASTING) OF ILMENITE POWDER WITH LPG-PYROLYSED PRODUCTS AND SUBSEQUENT LEACHING	67
5.3 THERMAL TREATMENT (ROASTING) OF ILMENITE POWDER BY THE REFORMED PRODUCTS OF THE LPG-H ₂ O MIXTURE IN PRESENCE OF NICKEL POWDER AND SUBSEQUENT LEACHING	88
5.4 SALT-WATER VAPOUR ROASTING OF ILMENITE	107
5.5 CHARACTERIZATION OF THE SALT-WATER VAPOUR ROASTED PRODUCT OF ILMENITE BY X-RAY DIFFRACTION	131
5.6 KINETICS OF DISSOLUTION OF THE SODIUM CARBONATE-WATER VAPOUR ROASTED ILMENITE BY HYDROCHLORIC ACID SOLUTION	137
5.7 RECOVERY OF TITANIUM FROM LEACH SOLUTION	158
SUMMARY	171
EXPERIMENTAL DATA	181
BIBLIOGRAPHY	237
APPENDICES	258

CONTENTS OF FIGURE

Figure No.	Page No.	Figure No.	Page No.
1	5	31 & 32	113
2	50	33 & 34	115
3	51	35 & 36	117
4	54	37 & 38	119
5	58	39 & 40	121
6	66	41 & 42	124
7 & 8	69	43a & 43b	127
9 & 10	70	44	130
11 & 12	75	45 & 46	144
13	79	47 & 48	148
14 & 15	82	49 & 50	150
16 & 17	85	51 & 52	154
18 & 19	91	53	156
20 & 21	92	54 & 55	157
22 & 23	94	56 & 57	160
24 & 25	99	58 & 59	162
26 & 27	101	60 & 61	164
28	103	Flowsheet A	167
29 & 30	110	Flowsheet B	169

CONTENTS OF TABLE

Table No.	Page No.	Table No.	Page No.
A	3	XXIII	203
B	7	XXIV	204
C	9	XXV	205
D	11	XXVI	206
E	64	XXVII	207
F	77	XXVIII	208
G	80	XXIX	209
H	87	XXX	210
I	98	XXXI	211
J	106	XXXII	212
K	125	XXXIII	213
L	136	XXXIV	214
I	181	XXXV	215
II	182	XXXVI	216
III	183	XXXVII	217
IV	184	XXXVIII	218
V	185	XXXIX	219
VI	186	XL	220
VII	187	XLI	221
VIII	188	XLII	222
IX	189	XLIII	223
X	190	XLIV	224
XI	191	XLV	225
XII	192	XLVI	226
XIII	193	XLVII	227
XIV	194	XLVIII	228
XV	195	XLIX	229
XVI	196	L	230
XVII	197	LI & LII	231
XVIII	198	LIII & LIV	232
XIX	199	LV & LVI	233
XX	200	LVII & LVIII	234
XXI	201	LIX	235
XXII	202	LX	236

ABSTRACT

The processing of ilmenite (TiFeO_3) to produce pigment grade white TiO_2 and black Fe_2O_3 by various thermal, leaching and liquid-liquid extraction with subsequent precipitation treatments has been investigated. Thermal pre-treatment of ilmenite with LPG-pyrolysed product at 700°C for 75 min. at LPG-flow rate $230\text{ cm}^3\text{ min}^{-1}$ produces a roasted mass which gives ~83.5% titanium and 80% iron dissolutions in 6 g eq dm^{-3} hydrochloric acid at its boiling point, solid to liquid phase ratio (S/L) of 0.02 kg dm^{-3} and at pulp agitation speed of 350 rpm for 5h. Under similar condition sulphuric acid dissolves only 66% titanium and 73% iron. X-ray powder diffraction patterns (XRD) of ilmenite and roasted mass suggest the chemical/physical change occurring during roasting.

A different method of thermal treatment of ilmenite is to react with the reformed products of the LPG- H_2O vapour mixture in presence of nickel catalyst. The optimum conditions for roasting are 700°C temperature, $110\text{ cm}^3\text{ min}^{-1}$ LPG-flow rate, 0.041 atm. water vapour pressure and 40 min time. XRD shows the changes but the composition of roasted mass can not be identified. Hydrochloric acid gives better leaching results than sulphuric acid of identical concentration. About 93% titanium and 95% iron are dissolved in 6 g eq dm^{-3} hydrochloric acid at its boiling point, S/L ratio of 0.02 kg dm^{-3} and at 350 rpm for 4h. Under similar condition, only ~46% titanium and ~64% iron are dissolved in sulphuric acid.

The advantage of the thermal hydrolysis of Na-salt (NaCl , Na_2SO_4 , NaNO_3 and Na_2CO_3) at $\sim 800^\circ\text{C}$ has been exploited. The alkali produced in-situ has been reacted with ilmenite to give easily soluble roasted mass. Although from all the salts used, the hydrolysed product is NaOH , different roasted masses with different leaching characteristics are obtained due to the existence of different atmospheres (oxidising, non-oxidising, inert etc.) in

the furnace. The best leaching has been obtained from the roasted mass with carbonate. The optimum roasting conditions with carbonate are ilmenite to carbonate weight ratio 1.5, temperature 850°C, carrier gas (N₂) flow rate 420 cm³ min⁻¹, water vapour pressure 31.5 mm Hg and time 45 min; whereas the optimum leaching conditions with 6 g eq dm⁻³ hydrochloric acid at boiling point, S/L ratio of 0.02 kg dm⁻³ and at 292 rpm for 45 min. Under this condition 96% titanium and 74% iron are dissolved.

The XRD pattern of sodium carbonate water vapour roasted product shows the existence of Na₃Fe₃TiO₈ together with another non-identified phase. The complete conversion of ilmenite to these phases occurs only within 45 min.

The rate of the dissolutions of titanium and iron from the Na₂CO₃-H₂O vapour roasted product (powder) have been investigated as function of hydrochloric acid concentration, temperature and pulp agitation speed. The exponent of hydrochloric acid concentration term varies with its concentration region; higher value in lower region for both metal ions, suggesting the change in mechanism with concentration. From temperature dependence studies, the apparent activation energies have been evaluated, which also suggest the change in dissolution mechanism with reagent concentration and temperature. The effect of pulp agitation speed also suggests the same. The initial rate constant has been calculated to be of the order of $\sim 5 \times 10^{-5} \text{ cm}^2 \text{ g}^{-1} \text{ mol}^{-a} \text{ min}^{-1}$ ('a' is the exponent of concentration term).

Finally, alternative steps for the recovery of titanium and iron from hydrochloric acid leach solution have been suggested in which iron has been removed by methylisobutyl ketone (MIBK) extraction (stripped with distilled water), distilled to recover hydrochloric acid and subsequent thermal hydrolytic co-precipitation of TiO₂.nH₂O followed by filtration, washing, drying and ignition. Overall titanium recovery from ilmenite is over 91%.

INTRODUCTION

(1) ORES OF TITANIUM AND THEIR OCCURRENCES :

The metal, titanium occurs in nature mainly in two forms : ilmenite (TiFeO_3) and rutile (TiO_2).

The rocky deposits of massive ilmenite have been found in Virginia¹⁻³ and North Carolina States⁴ of USA. These deposits contain about 18% titanium dioxide⁵.

The ilmenite-magnetite deposit is rather more common than the massive ilmenite deposit in the world. In the USA, ilmenite-magnetite deposit is found in the Adirondack Mountain of New York State⁶, the Sandford Hill in Essex county⁷ and in the Lake and Cook counties of Minnesota⁸ containing about 7-23%, 18%, and 3-20% titanium dioxide respectively. Deposits of ilmenite-magnetite and ilmenite-hematite containing about 20-30% titanium dioxide are found in Quebec province of Canada⁹. In Europe, Norway¹⁰ has the richest deposit (~42% titanium dioxide) at her South Western part. Sweden and Finland have also some reserves. There is an extensive reserve of ilmenite in the Ilmen Mountain (from which the mineral is named) of the USSR¹¹. This deposit contains about 14% titanium dioxide, 54% iron and 0.6% Vanadium pentoxide. Ilmenite-magnetite ore deposits containing an average of about

11% titanium dioxide can be found in South Africa¹², Mozambique¹³ and also in some other places like Belgium Congo and Madagascar. The important Asian deposit is found in Manchuria, Korea, Indo-china, India¹⁴ and in the Arabian Desert¹⁵. The other mineral, rutile is found abundantly in Virginia¹⁶, Southern Norway, Quebec¹⁷, Goyaz and Minas Geraes states of Brazil¹⁸, East Greenland¹⁹, Cameroon²⁰, Algeria, Madagascar²¹ and Kyzylkum of the USSR²². The rutile content of these deposits varies from about 5-20%.

Due to the high stabilities of titanium minerals, they were left behind in the county rocks and in time on weathering and erosion, are accumulated in the black sand of streams and beaches. The composition (mineralogical) of the beach sand is related with the composition of the county rocks nearby the beach on the stream. The amount of heavy minerals (sp. gr. >3 g/cc) in beach sands may vary from some three to about fifty percent. Almost all the beach sand of the world contains variable proportions of heavy minerals like ilmenite, zircon, monazite, etc. It is apparent therefore that the beach sand may be used as economical source of ilmenite, zircon, monazite etc.

The black beach sands of the South-Western coast of India, Malayasia, Indo-China, Srilanka²³, Australia²⁴ (at Naracoopa, from New South Wales to Queensland and in the East coast), Newzealand²⁵, Japan²⁶ (in the island of Hondu, Kynshu and Hokkaido), USA (at Florida²⁷, Arakansas²⁸, California, etc.), Senegal²⁹, West Africa²⁹, Egypt³⁰, South-East coast of Brazil³¹, Argentina, Guatemala, Mexico, Portugal, Italy, Yugoslavia etc. find commercial values as a source of titanium, zirconium and in some cases of thorium and

lanthanides. In concentration plants the float-sink, magnetic and electrostatic (dry & wet) methods are usually applied to obtain separate fractions of magnetite, ilmenite, zircon, monazite, thoria, rutile etc. Table A shows the percentages of TiO_2 , FeO , Fe_2O_3 , SiO_2 etc. in the ilmenite fractions obtained from the different coastal areas of the world.

Table A. *Analysis of ilmenite fraction of the beach sands.**

Origine	Percentage of						
	TiO_2	FeO	Fe_2O_3	SiO_2	MnO	V_2O_5	Cr_2O_3
USA :							
Virginia							
Piney River	~44.53	~36.76	~14.26	~1.60	~0.31	~0.17	~0.140
Roseland	51.40	37.90	1.60	4.60	0.70	0.07	-
New York	44.30	36.70	4.40	3.20	0.35	0.24	0.001
California	48.20	39.10	10.40	1.40	0.10	0.05	0.030
Florida	52.00	-	-	-	-	-	-
Georgia	34.40	11.30	7.80	43.10	1.89	-	-
CANADA :							
Ivry	37.50	~30.30	~20.00	~2.00	0.04	0.36	0.150
BRAZIL :							
	~55.10	~17.15	~23.40	1.40	~0.50	~0.13	~0.300
INDIA :							
Travancore	~57.05	~18.55	~19.10	1.23	~0.45	~0.16	~0.100
MALAYASIA :							
	~52.85	~36.9	~4.76	~0.75	~3.56	0.04	0.020
NORWAY :							
	~41.06	~34.17	~15.06	~2.46	~0.31	~0.36	~0.060
USSR :							
	44.00	31.40	16.90	1.84	0.72	-	0.050
PORTUGAL :							
	52.20	42.10	-	0.27	5.00	-	-
SENEGAL :							
	~55.35	~10.75	29.25	~1.10	0.76	0.27	~0.275

*Source : J. Barksdale, Titanium, its Occurance, Chemistry and Technology, The Ronald Press, New York, 1949, p. 33.

(2) BEACH SAND IN BANGLADESH :

Recently, a huge reserve of heavy minerals has been discovered in the South-Eastern coastal area of Bangladesh. The area covers the different islands like Maheshkhali and Nizhum Dwip and also the coastal areas of the main land ranging from Sitakundu to Teknaf (about 250 km long); these regions are shown in Fig. 1. The heavy mineral contents in the raw sands varies from about 5 to 50%. Table B shows the mineralogical percentages of some valuable minerals present in the beach sands of different localities in Bangladesh. The table indicates clearly the variation of the heavy mineral content (e.g., 4.50% at Teknaf-Inani whereas 51% at Banskhali) in different places. The third and the ninth columns of the table indicate that the ilmenite content in raw sand is almost proportional to the total heavy mineral content in raw sand. It is the highest in Banskhali (18.5%) and the lowest in Teknaf-Inani region (~0.3%).

The light fraction of the raw sand from almost all these localities are composed of mainly quartz (~90%) and the other are feldspar (~7%), mica (0.5%) etc. On the otherhand, the heavy fractions (sp. gr. > 2.85 g/cc) are comprised of several valuable minerals like ilmenite (TiFeO_3), zircon (ZrSiO_4), rutile (TiO_2), monazite (Th.LnPO_4), magnetite (Fe_3O_4), etc. together with many non-valuable minerals like garnet ($\text{A}_3^{++} \text{B}_2^{+++} \text{Si}_3\text{O}_{12}$),

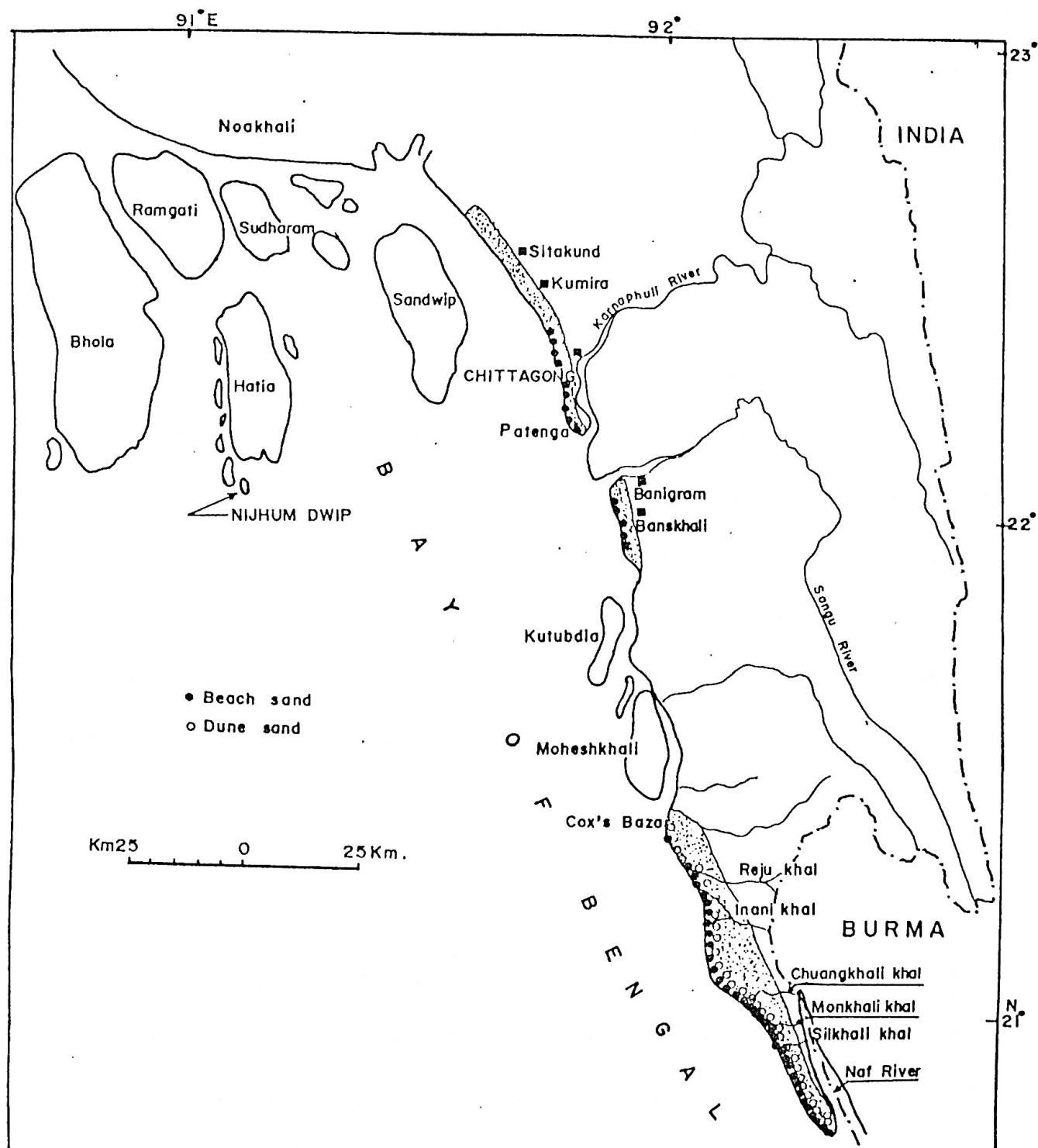


Fig. 1. South-eastern coastal region and islands of Bangladesh.

leucoxene [(Ca or Na)(Ti,Al,Fe or Nb)(O,OH or F)SO₄], kyanite (Al₂O₃.SiO₂), epidote [HCa₂(Al,Fe)₃Si₃O₁₆], amphiboles [M_x(SiO₃)_y; M=Ca, Mg, Fe & alkali metals], biotite (ferrous mica), apatite [3Ca₃(PO₄)₂.CaF₂] etc.

The beach sand exploitation center of Bangladesh Atomic energy Commission at Cox's Bazar has been succeeded in fractionating the heavy minerals (Pilot Plant scale) from the raw beach sands of different localities. The composition of the ilmenite fraction varies widely. For example, an Australian analysis³⁶ shows the following percentage : TiO₂ 38.5%, Fe₂O₃ 25.62%, FeO 29.75%, SiO₂ 1.2%, P₂O₅ 0.03%, MnO 1.3%, Cr₂O₃ 1.08%, whereas a native analysis³⁷ gives the composition as Fe₂O₃ 47.48%, FeO 15%, ZrO₂ 15.78%, TiO₂ 29.46%, ThO₂ 0.046%, Cr₂O₃ 0.114%, MnO 0.43%, MgO 0.47%, Al₂O₃ 0.41%, SiO₂ 2.56%. It is clear however that in the second analysis Zirconia fraction has not been separated from the ilmenite fraction. Although the analysis are not identical, it is certain that the ilmenite fraction obtained from the beach sands of Bangladesh contains a considerable proportion of chromium and manganese, which causes a bad coloring effect on the product, TiO₂ when conventional sulphate process is used for its manufacture. This fact eventually points out that the conventional sulphate process could not be used for the processing of ilmenite obtained from our sea-shores. So other methods are to be developed for the commercial recovery of the products from this ilmenite.

Table B : Mineralogical percentages of some of the valuable minreals in the beach sands of different localities in Bangladesh.

Locality	Percentages of								Ref.
	Magna-tite	Ilme-nite	Zircon	Rutile	Garnet	Mona-zite	Other*	Total ^f	
Badormokam	1.5	3.8	0.35	0.08	-	-	11.77	17.50	32
Maheshkhali									
fordune	0.5	7.1	0.70	2.50	-	0.007	24.59	35.40	32
Maheshkhali									
backdune	0.03	2.6	0.65	-	1.6	-	-	-	32
Cox's bazar	0.60	2.6	0.28	0.08	1.4	-	-	-	32
Teknaf-Inani beach	-	0.3	0.07	0.02	0.2	-	2.22	2.85	33
							(2-3 Ph. size)		
Teknaf-Inani dune	-	0.7	0.16	0.05	0.7	-	4.43	6.00	33
Banskhali	-	18.5	0.76	0.67	5.8	-	25.26	51.00	33
Patengha	-	15.0	2.66	0.90	3.5	-	20.96	43.00	33
Nizhum Island	1.12	5.2	2.32	0.33	3.7	0.160	11.50	24.38	34

* Others include leucoxene, kyanite, epidote, amphiboles, biotite, apatite etc.

f The rest being the light fraction which contains mainly quartz (~90%), feldspar (~7%), mica (~0.5%) etc.³⁵

(3) CONVENTIONAL METHODS FOR ILMENITE PROCESSING :

As pointed out earlier, the beach sand is a potential source of many metals, particularly of titanium and zirconium, and beach sand can be effectively fractionated into different parts one part being rich in a particular mineral by various comminution and concentration processes like float-sink using a heavy liquid medium (e.g. bromoform sp. gr. 2.85),

magnetic separation and electrostatic separation. The ilmenite fraction often obtained from the beach sands contains mainly titanium dioxide, ferrous oxide and ferric oxide in variable proportions depending on the place of occurrence. Besides the above oxides, ilmenite may contain some silicon dioxide, manganous oxide, zirconium oxide, chromium oxide, cobalt oxide, magnesium oxide etc. In the following few paragraphs a comparative study of the conventional methods for the preparation of pigment grade TiO_2 from ilmenite fraction will be discussed.

The most common method for the production of TiO_2 from ilmenite is the Sulphate Process. Until 1959, this process was the only method for the manufacture of pigment grade titanium dioxide. However, now-a-days, another competitive method known as Chloride Method has been developed by Dupont company of the USA. The major companies which produce titanium dioxide by either of the processes are American Cyanamide, Dupont, Kerr McGee, Glidden Co, National Lead and New Jersey Zinc Company of the USA, British Titan products of the G.B and Laporte Industries of Australia. The present annual World production of titanium dioxide is over two million tons per annum.

The Sulphate and Chloride Methods demand separate raw materials. For Sulphate Process, the raw material is ilmenite but not rutile as it is not attacked appreciably by sulphuric acid of any concentration, whereas the Chloride Process prefers natural rutile or a mixture of rutile and ilmenite or beneficiated ilmenite to avoid excessive chlorine requirement and waste handling. Certain other restrictions should be noted here. Ilmenites with a high chromium content can not be used in the Sulphate Process, because of

the deterioration of the color of the product by the presence of chromium compounds. On the otherhand, magnesium, manganese and other alkaline earth metals in the starting material may cause operational difficulties in the Chloride Process. For either process, however, less sulphuric acid or chlorine is required and less by-products or waste products are formed with increasing percentages of titanium dioxide in the feed material.

Table C indicates the main ilmenite deposits which are being worked today.

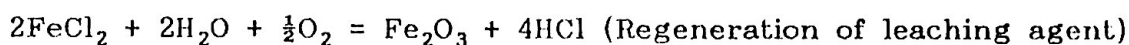
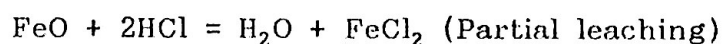
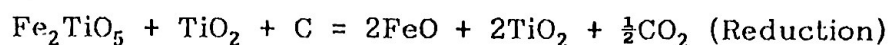
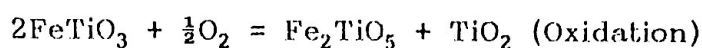
Table C. *Ilmenite deposits which are being worked today in the world.*

Country	Reserves of titanium bearing ore (million tons)	Titanium dioxide content of deposits (%)	Titanium dioxide content of minerals after treatment (%)
Canada	200-220	35	37
USA			
New York	100	17	43
Virginia	5	8	44
Florida	180	0.5-3	63
Norway	250	17	43
Finland	50	13.5	44
India	100	20-40	59
South Africa	20	5	49
Australia	15	30	50-60

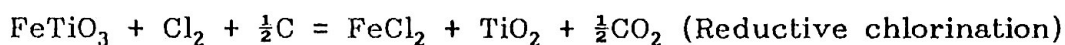
Now-a-days, the feed material for the Sulphate Process has been significantly up-graded (w.r.t. Titanium dioxide content) by the slag process. The use of slag reduces both the quantities of sulphuric acid required and

the waste produced. It is an electrothermal process which produces slags containing about 70% titanium dioxide. The slag is however easily attacked by sulphuric acid because of the fact that titanium exists as a mixed magnesium-iron titanate and not rutile. Since the natural rutile reserve is very small, the feed material for the chlorination method is the synthetic rutile. Rutile can be synthesized from ilmenite by the following schemes :

SCHEME-I



SCHEME-II



In both scheme, products containing more than 92% titanium dioxide are produced. The present world supply of raw materials for titanium dioxide manufacturing are as follows : Australian rutile (9.5%), other rutile (1.5%), synthetic rutile (1.5%), slags (25%), Australian ilmenite (16.5%), USA ilmenite (21.5%), Norwegian ilmenite (15%) and other ilmenites (9.5%).

The Sulphate Process :

The typical analyses of three sources of raw materials commonly used for the sulphate process are given in Table D.

Table D. Composition of ilmenite used for sulphate process.

Constituent	Norwegian ilmenite (%)	Australian ilmenite (%)	Canadian slag (%)
TiO ₂	44	54.20	60.10
Ti ₂ O ₃	-	-	8.30
Fe	-	-	0.20
FeO	34.60	23.30	12.60
Fe ₂ O ₃	11.80	17.30	-
Cr ₂ O ₃	0.08	0.04	0.20
V ₂ O ₅	0.02	0.10	0.50
SiO ₂	5.00	1.00	4.60
Al ₂ O ₃	0.70	0.70	4.00
P ₂ O ₅	0.04	0.08	0.03
MgO	3.70	0.20	5.00
MnO	0.30	2.00	0.20

Apart from the various impurity levels, the efficiency of extraction by sulphuric acid tends to be increased by an increase in the FeO to Fe₂O₃ ratio.

In this process, ground ilmenite or slag is digested with concentrated sulphuric acid (>95%, 60% excess for the stoichiometric requirement) at an elevated temperature; the resultant titanium and iron compounds are leached with water or dilute acid and the ferric ion is reduced to ferrous ion by the addition of scrap iron to crystallize out ferrous sulphate after

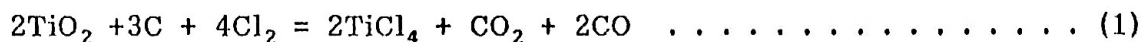
clarification and cooling. After centrifugal separation of coppeas $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ crystals, the mother liquor is treated with steam to hydrolyse titanyl sulphate. Some seed crystals are however added before hydrolysis. The hydrated acidic titanium is precipitated. The precipitates are filtered washed and calcined to produce TiO_2 .

The overall efficiency of the process is over 80%. The sulphuric acid requirement is about 4-5 tons per ton titanium dioxide produced.

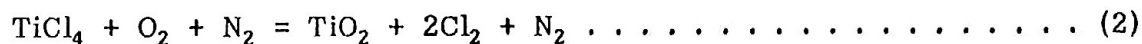
The Chloride Process :

This process essentially consists of the production of TiCl_4 from the raw material, purification of TiCl_4 produced, and subsequent oxidation by oxygen enriched air to TiO_2 .

Preparation of TiCl_4 is carried out by chlorination of the raw material in a reducing atmosphere at about 950°C .



The combustion of TiCl_4 in oxygen enriched air starts at 1000°C and once initiated the temperature rises sharply to $\sim 1500^\circ\text{C}$.



Although many methods claim the economic recovery of Cl_2 from FeCl_2 , there is no plant in operation at the present time which uses ilmenite directly as raw materials. The chlorination reaction is usually carried out in fluid-bed reactors and the out coming gas consists of the vapours of titanium and the other impurity metal chlorides, carbonmonoxide and carbon dioxide (unchanged chlorine gas is seldom mixed with exit gas). The vapour

is condensed and the most impurities are removed as dry solids. Excepting VCl_5 all metal impurity chlorides can effectively be removed from TiCl_4 by fractional distillation or simple distillation. For separation of VCl_5 , H_2S gas should be passed into the crude TiCl_4 solution to reduce vanadium to its lower valency state.

The waste and by-products from a plant producing 50,000 tons of pigment per annum by Sulphate Process may be as high as 140,000 tons copperas (as crystallized $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), 75,000 tons strong acid (calculated on 100% purity), 40,000 tons weak acid (calculated on 100% purity) and 83,000 tons FeSO_4 (soluble, calculated as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). The quantities of waste products are however strictly related to the type of raw material used. Theoretically, it is possible to recover the sulphur value, from copperas or from the waste acid or alternatively convert them into saleable products. Unfortunately, neither of these processes is economic.

The degree of difficulty and cost involved in recovering sulphur values are due to the following :

- a) The strong acid rejected from the process is between 10-20% strength. For re-use it must be concentrated to 96% strength. Since vast quantities of water have to be evaporated, these processes are highly energy intensive.
- b) During the evaporation step, metallic salts precipitate in the form of slurries which are difficult to separate from the liquid. Certain salts remain in solution even at high acid strength, and recycling of such salts leads to deterioration of colour of the pigment.
- c) High temperature roasting of the various salts is also energy intensive,

and both this step and the acid evaporation lead to high quantity gaseous emission of water vapour containing residual sulphur dioxide.

- d) Process economics have been plagued with significant variations in fresh sulphur prices. Since 1973, energy costs have quadrupled. The ratio energy cost/sulphur value has fluctuated widely and recently in a worsening direction. The situation is further complicated because in the production of sulphuric acid from sulphur a very significant quantity of energy is released which can be easily utilized in the associated titanium dioxide plant.

Many paper studies have been made on alternative processes. Mention will be made here only of the limited numbers which have achieved some commercial application by 1976.

- a) Neutralization with limestone/lime and dumping of neutralized products — this requires large scale availability of limestone and disposal areas for the neutralized solids. It is operated by one small company.
- b) Neutralization with limestone to produce saleable gypsum — this requires availability of limestone and suitable market. It is operated on a small scale in the USA and Japan.
- c) Neutralization with metallic iron in the production of beneficiated ilmenite. This is operated by one Japanese company, but leads to higher discharge of iron salts.
- d) Limited quantities of copperas are used for water treatment, or can be converted into soil conditioners.
- e) Production of iron oxide pigments from copperas — this is operated in Germany.

f) Neutralization with other alkalies to produce saleable by-products (ammonium sulphate, sodium sulphate) — this requires close proximity to markets, because of relatively low value of these chemicals. It is operated by one Japanese company.

The product titanium dioxide is widely used in the paint, plastic paper, textile and rubber industries. In the paint industry, it is by far the most effective white pigment in terms of covering power (refractive index, 2.5-2.9). Paint industries utilizes about 62% in Europe and 51% in the USA of their total production of ilmenite. The plastic, paper, textile and rubber industries utilize about 13%, 8%, 5%, 3% respectively in Europe and 23%, 10%, 3% (ceramics instead of textile), 3% respectively in the USA. In these areas no substitute products represent serious threats to titanium dioxide's established position.

Nevertheless, a future break through is needed for the development of other methods for the manufacture of titanium dioxide from ores which do not meet the specification requirements for the sulphate or chloride process. For examples, our beach sand deposits can not be used effectively by the sulphate process for high chromium content. Moreover both conventional process are energy intensive and criticized by the waste disposal problems.

(4) AN OUTLINE ON HYDROMETALLURGICAL METHODS :

In many cases, for example, in the treatment of lean or very complex ores for metal extraction or in the recovery of valuable metals from wastes where pyrometallurgical methods can not be used, the hydrometallurgical methods find successful applications in the extraction of metals or metallic

compounds from such sources. The name hydrometallurgy is derived from the fact that at least some of the reactions are carried out in aqueous solution during the sequence of operations performed for the recovery or extraction of metal from their resources.

There are three main types of hydrometallurgical operations :

(i) LEACHING :

It is a method to dissolve the whole or some part of the solid. The element to be recovered is usually obtained in solution, but it may, in a few cases, be left as an insoluble residue. The operation is also called Lixiviation. To leach a material, it is usually treated with a solution of acid, base, water, salt or a complexing agent at a suitable temperature and pressure. Sometimes pressure leaching is shown to be effective. The commercial leaching agent is chosen by considering the following factors :

- a) the chemical and physical characteristics of the material to be leached,
- b) the cost of the reagent,
- c) the corroding action of the reagent and consequently the material of construction,
- d) selectivity for the desired constituent to be leached,
- e) ability to be regenerated.

Selectivity of a leaching agent toward a particular mineral in an ore depends on the concentration of the reagent, temperature, pressure, contact time etc. A new and successful leaching agent may cause revolution in Hydrometallurgy. The introduction of sodium cyanide for leaching gold and

silver ores is an old example. A modern example is the selective leachings of Co, Ni and Cu in an ammonical medium.

Selectivity of a particular metallic constituent dissolution in a specified leaching agent may some times be increased by certain thermal treatments. These include (a) calcination (b) roasting and (c) fusion. The process, calcination usually helps easy size reduction, which ultimately facilitates the dissolution due to greater surface area of ores exposed to the leaching agent. Accompanied with the expulsion of organic and other volatile matters, dehydration or dehydroxylation, a phase transition etc. may also occur which may eventually affect the leaching characteristics.

In general, sulphide ores under normal conditions are not attacked by an acid, alkali or salt solution. However, on converting the sulphide ores to oxide ores, the difficulty may easily be overcome. The conversion of a sulphide mineral to the oxide mineral could easily be performed by heating the material in presence of air (mostly autogeneous) which is termed as roasting. Sometimes, the ore may be subjected to the chlorodizing-roasting, in which the material is heated with a chlorinating agent like common salt, hydrogen chloride (Produced by the reaction of NaCl with water vapour over 700°C), chlorine gas etc. The products are either volatile chlorides of the desired metal contaminated with the chloride of the other metals or a mixture of easily leachable non-volatile chlorides. To increase the selectivity, the ore may in some cases, be subjected to the "reductive roasting" or "smelting". The result of the treatment is the reduction of a particular mineral to its metallic or reduced state which eventually shows different leaching characteristics. The most important example is the slag process in titanium metallurgy from ilmenite.

Sometimes alkali fusion is desired to render the mineral values amenable to further easy treatment. In alkali fusion, the ore (oxide or silicate) is fused with an alkali or alkaline earth reagent (e.g. CaO , Na_2CO_3 , NaOH , NaCl , Na_2SO_4 etc.) in iron pot or rotary kilns. The example of alkali fusion is found in the aluminium extraction metallurgy by Bayer's Process.

(ii) PURIFICATION OF LEACHED SOLUTION :

The solution obtained on leaching often contains contaminants. The contaminants are required to be separated from the desirable constituent prior to the final recovery stage, the precipitation. The solution purification is usually carried out either by (a) ion-exchange or (b) liquid-liquid extraction.

In the ion-exchange method of solution purification, the leached solution is percolated through a bed of cation or anion exchange resin, during which the metal ion in the cationic or anionic forms are absorbed on the resin with the elimination of hydrogen ion or an anion (usually Cl^- or SO_4^{2-}) respectively in equivalent amount. During the operation the constituents which are inactive toward the resin are not absorbed and separated. Sometime strong complex forming agent is used to make a particular constituent inactive. Depending on the stability of the resin-metal (absorbed) complex, different absorption beds may be obtained in the column, one bed contains one metal ion only and the other contains other metal ion. The cation exchange processes are acidity dependent. It is inconvenient to fractionate the absorbed resin beds to get different solutions of pure metallic compounds. The different solutions of pure metallic

compounds can however be obtained by percolating the absorbed beds with a suitable reagent in solution form. This process is called elution. Acid or salt solution are used to elute the absorbed solution in cation and anion exchange systems respectively. The elution also regenerates the resin for reuse.

The most convenient method for purification of leach solution is the liquid-liquid extraction. While the ion-exchange method of solution purification is tedious and applicable only to very small scale operations, the liquid-liquid extraction method is very simple and applicable to both small and large scale operations.

The liquid-liquid extraction is a technique of extracting metals from their solution (obtained usually by suitable leaching of ores) selectively by treating with a solvent (containing an extracting agent) which is capable of forming metallic species more soluble in the solvent phase than in the aqueous phase. The equilibrium stage of the process is called partition or distribution and the species which distributed is called "distribuend". The solvent is comprised of an extracting agent (which is either a liquid or solid organic compound when pure) in an organic diluent especially hydrocarbons or chlorinated hydrocarbons. Organic solvent and the aqueous metal solution form easily separable immiscible phases. The extractant itself and the metal ions are partitioned in between the immiscible phases. Sometimes a third constituent (modifier) is used to alter the physical nature of the solvent.

There are large varieties of compounds which may be used as extractant for the metal ions in solution. These include (a) alcohols (1-Octanol, for Co/Ni separation), (b) ethers (diethylether, for extraction of

many metals e.g. Fe(III), from HF, HNO₃, HCl and H₂SO₄ solutions), (c) carboxylic acid (fatty acids like palmitic, stearic or mixed versatic acid and the naphthenic acids of general formula C₅H₁₁-(CH₂)_n-COOH), (d) ketones (acetylacetone, thenoyltrifluoroacetone, methylisobutylketone), (e) oximes (Lix-reagents containing (=N-OH) group, very specific for Cu⁺⁺ extraction), (f) organophosphorous esters (tributylphosphate, dibutylphosphate, di-(2-ethylhexyl) phosphoric acid, dodecylphosphoric acid etc.) (g) amines (trialkylmethylaniline or Primen JM, dilaurylamine or Armeen 212, tri-n-octylamine, Alamine 336 : a mixture of tri-n-octylamine and tri-n-decylamine etc.) (h) Oxine (8-hydroxyquinoline and its derivatives) and others like dithizone (C₆H₅-N₂-C(=S)-NH-NH-(C₆H₅), cupferron (C₆H₅-N(OH)-NO) etc.

The transfer of metals ions from an aqueous phase to an organic phase is measured by the extraction ratio, E which is defined as follows :

$$E = \frac{\text{Concentration of metal ion in organic phase, } [M^{n+}]_o}{\text{Concentration of metal ion in aqueous phase, } [M^{n+}]_a}$$

The higher the value of E at equilibrium, the higher is the extractibility of the metal ion in question by that particular extractant.

The method of transferring the extracted metal ion from organic phase to aqueous phase is called stripping. In the stripping process, two purposes are achieved.

- i) Recovery of the metal values from the organic phase and
- ii) Regeneration of the extractant for recycle.

The stripping co-efficient is defined by

$$D' = \frac{\text{Concentration of metal ion in aqueous phase, } [M^{n+}]_a}{\text{Concentration of metal ion in organic phase, } [M^{n+}]_o}$$

The higher the value of D' at equilibrium, the higher is the tendency of the metal ion to be transferred to the aqueous phase. The stripping co-efficient is the inverse of the distribution co-efficient, D . Stripping agents depend on the nature of the extraction mechanism. Ethers and neutral organic phosphorous compounds such as TBP are readily stripped by water. Acid organophosphorous compound may be stripped by acids or bases. On treatment with suitable reagent, the stripping and the precipitation of a metallic compound may occur concurrently.

(iii) RECOVERY OF METALLIC COMPOUND OR METAL FROM PURIFIED LEACH SOLUTION :

For recovery of a metal in its elemental state, the hydrogen reduction or electrolytic method is usually practised. A brief account of the hydrogen reduction process is given below :

When hydrogen gas is passed through an aqueous solution of metal ion, any one of the following changes may occur depending on the nature of the metal ion, reaction temperature and pressure : (a) reduction of a metal ion to a lower valency state without precipitation (e.g. Ce^{4+} to Ce^{3+} or Fe^{3+} to Fe^{2+}), (b) precipitation of an oxide (e.g. MoO_4^{2-} to MoO_2 or MnO_4^- to MnS), (c) precipitation of a sulphide (from sulphate solution of Zn^{2+} to ZnS) and (d) precipitation of a metal in its elemental form. The precipitation of

oxide and sulphids by hydrogen reduction is of interest to the Geochemists and some of these products are also of interest to the chemical industries. In order to get a precipitate of a metal in its elemental form, certain conditions must be fulfilled which are discussed elsewhere³⁸. Antimony, arsenic, bismuth, gold, lead, silver, nickel, mercury, tin, cobalt, copper etc. can be precipitated from their aqueous complex or simple salt solution by hydrogen at high temperature (100–330°C) and pressure (~50–250 atm.).

Carbon monoxide, in lieu of hydrogen may be used for gaseous reduction of metal ions, but in such case, the rate of reduction becomes too slow for the very slow initiating step : $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$. In certain cases, sulphur dioxide at higher temperature and pressure can reduce the metal ions into their elemental forms, e.g. $\text{Cu}^{2+} + \text{SO}_2 + 2\text{H}_2\text{O} = \text{Cu} + \text{H}_2\text{SO}_4 + 2\text{H}^+$. The use of a more electropositive element to a solution of lesser electropositive metal ion solution (e.g. Zn, Ni or Fe to Cu^{++} , Cu to Pd^{++} , Mg to Be^{++} or Zn to $\text{Ag}(\text{CN})_2^-$ or $\text{Au}(\text{CN})_2^-$) has been found to be extremely helpful to get the metallic precipitate (known as cementation process).

When the precipitation by gaseous reduction is not possible and specially when the metallic compound rather than its elemental form is desired, then metal ion in purified leach solution may be precipitated as a compound by the use of a suitable precipitating agent which eventually depends on the final product and the nature of the metal ion. Many metal ions (excluding alkali and alkaline earth metal ions) precipitates as hydroxide at lower acidities or in alkaline medium. The precipitated hydroxides may be easily separated, dried and calcined to get pure metal oxide. Other reagents like H_2S , NH_4OH , $(\text{NH}_4)_2\text{CO}_3$, Oxalate etc. together with

certain specific reagent like dimethylglyoxime for Ni^{++} , $(\text{NH}_4)_2\text{HPO}_4$ for Mg^{++} etc. find application in precipitation of metallic compounds. Sometimes the fractional precipitation using different precipitating agents may also be suitable and essential for the purification of leach solution.

Another old and simple method for the recovery of metal from leach solution is crystallization. While the solubility of the most metallic salts increases with increasing temperature, above about 100°C the solubility starts to decrease and at above 250°C , it becomes practically nil and the precipitation of crystals takes place. The solubility of salts in water is also decreased usually with the addition of an organic solvent (alcohol) miscible with water. Otherwise, the addition of a complexing agent, decomposition of a metallic complex ion or formation of a double salt may favour crystallization.

REVIEW OF LITERATURES

Before going to the objectives and experimental details of the work, the following paragraphs summarize the important reports of our interests so far appeared in journals, particularly in the last two decades. These include the fractionation of black beach sand, direct leaching of ilmenite with different inorganic acids, enrichment of titanium dioxide content of ilmenite for chlorination process, chlorination, different roasting and fusion processes and also the solvent extraction and precipitation characteristics of titanium and iron from leach solutions.

This paragraph points out the recent works on the fractionation of heavy minerals in heavy beach sands into the constituent minerals e.g. ilmenite, rutile, zircon, thoria, magnetite, monazite, leucoxane etc. Yampol'skaya³⁹ has reported a flowsheet for treating marine sands. Classification, tabling, electrical and magnetic separations, cleaning and flotation steps have been used to get magnetite (>90%), zircon (91-93%), garnet plus ilmenite (86%) fractions. Two papers^{40,41} describing the fractionation of beach sands of two different places in India by the electrostatic and magnetic methods have been reported. Using the combination of various processes such as grinding, flotation and magnetic separation, Hwang and Oh⁴² have separated magnetite from ilmenite. After gravity separation the heavy fraction of the sand and gravel in Oregon and Washington has been subjected to the low and high intensity magnetic, high tension, and heavy medium separation techniques to get zircon, ilmenite,

chromite, magnetite and gold fractions corresponding to 67-90% recoveries⁴³. A review with 10 references on methods for beneficiation of the Baltic region marine sand containing ilmenite, rutile, zircon, monazite and other minerals has been reported by Luszczikiewicz⁴⁴. Several other reports on the fractionation of Baltic sand have been appeared⁴⁵⁻⁴⁷. In these works, gravity separation, magnetic separation (high & low intensity), high voltage electrical separation, flotation methods have been used. Skripko *et al.*⁴⁸ have used screw separator instead of cone separators for beneficiation of a washed sand. The concentrate containing 59.2% ilmenite with ~95% recovery has been obtained. Ayranci^{49,50} has reported the fractionation of coastal sands of Turkey using the seiving, tabling, gravity concentration by Wilfley table, magnetic and electrostatic method. The beach sand of Pakistan coastal area has been separated by applying gravity, electrostatic and magnetic separation methods⁵¹. There are also reports on the fractionation of heavy and light minerals in beach sand of the coastal area of Bangladesh by the use of bromoform (sp.gr. 2.9) and subsequent fractionation of the heavy part by the electromagnetic method³²⁻³⁵.

In this paragraph, the reports on the dissolution of ilmenite (partial or complete) with sulphuric acid have been assembled. There are many papers⁵²⁻⁶⁷ in literature describing the leaching of non-pretreated ilmenite with sulphuric acid of different concentrations to get either partial dissolution for enrichment of ilmenite or complete dissolution for further precipitation, hydrolysis or solvent extraction treatments to produce pigment grade titanium dioxide. Beside these works, the leaching of ilmenite with a mixture of sulphuric acid and ferrous sulphate solution⁶⁸, with sulphuric

acid in presence of the constant supply of air⁶⁹, with a mixture of sulphuric acid and sodium chloride⁷⁰, with a mixture of sulphuric acid and potassium sulphate solution at 350°C⁷¹ and with dilute sulphuric acid (~10%) at high temperature (~160° and pressure ~200 PSI)^{72,73} have been carried out. A mechanistic work on the leaching of ilmenite with sulphuric acid in which the effects of temperature, particles size, stirring speed and concentration of sulphuric acid on the rate of dissolution of ilmenite have been reported by Han *et al.*⁷⁴. The Arrhenius activation energy is 64.4 kJ mol⁻¹. The rate of dissolution is increased with increasing concentration of sulphuric acid (upto 28 g mol dm⁻³). The maximum leaching at 28 g mol dm⁻³ sulphuric acid is explained partially by the H⁺ concentration peaks at about this concentration, and also the reaction products TiOSO₄ and ferrous sulphate covered the surface of ilmenite when high concentration of sulphuric acid used, but dissolved in water and are removed from the surface when dilute acid involved. The overall leaching has been described best by surface chemical reaction limiting with an order of 0.55 with respect to acid concentration. Rieck *et al.*⁷⁵ have patented a work on the dissolution of slag-ilmenite mixture by the waste sulphuric acid obtained from the titanium dioxide manufacturing plant based on the sulphate process. Another paper⁷⁶ describing the regeneration of sulphuric acid from the effluent of sulphate process, its use to produce synthetic rutile from ilmenite and the manufacture of sulphuric acid by Bayer process from ferrous sulphate produced in different stages has been published. From phosphorous containing minerals of titanium, phosphorous could be removed by leaching with dilute sulphuric acid (75 g dm⁻³) at 30°C stage-wise (2 h/stage)⁷⁷ or

with 40% sulphuric acid solution at 120°C for 10 hours at solid to liquid ratio of 1 : 7⁷⁸. For dissolution of ilmenite, the prior digestion with concentrated sulphuric acid (88%) at 200°C for 3 hours and subsequent leaching with water has been reported⁷⁹. A study on the leaching with sulphuric acid has been recommended for vanadium and chromium removal from ilmenite⁸⁰.

A large number of works⁸¹⁻⁸⁷ has been reported on the leaching of non-pretreated ilmenite with hydrochloric acid of different concentrations to achieve either partial dissolution in preparing synthetic rutile or complete dissolution with an aim to prepare pigment grade titanium dioxide. Sinha⁸⁸ and Yoshikoshi *et al.*⁸⁹ have reported that the reactivity of ilmenite for leaching with (20 wt. %) HCl at high temperature (108-110°C) is increased by prior oxidation at 950°C and reduction at 850°C of ilmenite. According to Hussein *et al.*⁹⁰, the iron removal from ilmenite by hydrochloric acid at 50-90°C is the lowest after pre-oxidation, ~35% from powdered ilmenite and ~95% from pre reduced ilmenite (by hydrogen at 700°C). Tolley⁹¹ has patented a work on the leaching of pre-roasted (600-900°C) ilmenite with hydrochloric acid solution at 80-110°C. Rutile has been prepared⁹² from ilmenite by pre-oxidation at 1000°C for 30 minutes, pre-reduction with charcoal at 950°C for 1 hour and subsequent leaching with 20% hydrochloric acid. The same procedure has been followed by Sinha⁹³ to remove iron from ilmenite, excepting that he used 900°C for oxidation and 800-900°C for reduction in fluidized bed reactors. Non aqueous hydrochloric acid (HCl-CH₃OH and HCl-C₂H₅OH) solution have been used to leach iron from ilmenite at room temperate and compared with the leaching by aqueous hydrochloric acid⁹⁴.

Farup⁹⁵ has dissolved iron from ilmenite by heating it with three times its weight of 20% hydrochloric acid at 70–80°C for 12 hours and the titanium dioxide residue has then converted into soluble form by digestion with concentrated sulphuric acid. Prior oxidation and reduction of ilmenite with subsequent leaching by hydrochloric acid are shown to be useful for chromium removal⁹⁶ from ilmenite.

This paragraph is devoted to the works done on the direct leaching of ilmenite with acid leaching agents excluding sulphuric and hydrochloric acids. For titanium dioxide recovery from ilmenite, Nagasubramonian and Liu⁹⁷ digested ilmenite with aqueous hydrofluoric acid. The leaching of ilmenite in hydrofluoric acid as regards to the contact time, acid concentration, solid to liquid phase ratio, number of leaching-stages and temperature has been investigated by Biswas and Mondal⁹⁸. About 81% titanium is dissolved within 5 hours by 6.5 g eq dm⁻³ hydrofluoric acid at boiling point. Multi-stage leaching is not advantageous, but the leaching is too much temperature dependent. The kinetics of this process has been investigated by Hansen and Traut⁹⁹. They have reported that the leaching rates of titanium and iron from ilmenite are increased with increasing temperature (23–65°C) and hydrofluoric acid concentration (4.64–29 g eq dm⁻³) but decreased with increasing the particle size (20–74µm). The activation energy of titanium and iron leaching from ilmenite are 52.6 and 48.4 kJ mol⁻¹ respectively. The recovery of titanium and iron in leach solution is 100 and 99% respectively by leaching with 19.33 g eq dm⁻³ hydrofluoric acid for 40 minutes. The nitrofluoro process (leaching with the azeotrope non-aqueous hydrofluoric-nitric acid boiling at 52°C) has been reported by Kigoshi *et al.*¹⁰⁰. According to this work, the most of titanium from ilmenite is dissolved in solvent and iron can be precipitated selectively. Vicintinn¹⁰¹

has mixed 88 (wt.%) titanium dioxide (rutile) with twice its weight of sodium fluosilicate and heated to 700–800°C in a fluidized bed reactor and dissolved the resulted mass in dilute hydrofluoric acid at 60–90°C. A patent¹⁰² on the alkali leaching (NaOH) of ilmenite to remove aluminium oxide, silicon dioxide and arsenic has been appeared to produce raw material for chlorination process.

In the following few paragraphs, the works on the oxidation, reduction, roasting and fusion of ilmenite (or synthetic rutile) have been summarized. There are many studies^{103–112} on the reduction of ilmenite with carbon in the form of charcoal, coal, coke, graphite etc. in the temperature range 700–1100°C. In these studies iron in ilmenite has been reduced to metallic iron and/or iron carbide which are either leached out with dilute acid^{105,107} (sulphuric or hydrochloric) or separated magnetically^{104–110}. Leaching with concentrated sulphuric acid resulted in the dissolution of titanium dioxide but not of iron probably due to the fact that iron becomes passive in contact with concentrated sulphuric acid^{105–108}. It is also reported that the leaching in presence of added iron filings with sulphuric acid of the reduced mass (graphite) gives better results than that of unreduced mass¹⁰³. Carbon reduction followed by impurity dissolution and electrolysis has also been investigated to get metal free titanium dioxide¹¹². The carbon reduction of ilmenite has been studied in electric arc^{113,114} (temperature over 1700°C) and plasma arc¹¹⁵ (temperature 2300–2400°C) generated between a thoriated tungsten cathode of a plasma torch and the sample in the crucible serving as anode.

Excepting carbon and carbonaceous solid materials as reducing agent, carbon monoxide^{111,116,117}, mixture of carbon monoxide and carbon dioxide¹¹⁸, hydrogen^{111,117,119,120}, methane^{121,122}, coke oven gas¹²³, sowdust¹²⁴ etc. have been used in the temperature range from about 700°C

to about 1100°C to investigate the partial reduction of ilmenite. The kinetics of hydrogen reduction of ilmenite has been reported by Kurihara *et al.*¹²⁵. Ilmenite is transformed into metallic iron and rutile at 700°C and at higher temperature, the rutile is reduced to lower oxides. The reduction rate data are represented by equation: $kt = [1-(1-R)^{1/3}]$, where R is the weight loss ratio of oxygen in ilmenite due to reduction. At 1000°C, the pseudo-brookite (Fe_2TiO_5) and free rutile are identified as oxidation product of ilmenite. The reduction rate of pseudo-brookite is higher than that of ilmenite. From this work, the workers concluded that pseudo-brookite and rutile are produced by complete roasting of ilmenite ore, and its products are more easily reduced than unroasted ore. The kinetics of reduction of ilmenite with hydrogen and carbon monoxide have been reported by Daguang *et al.*¹²⁶. Below and above 1000°C diffusion and phase boundary reaction respectively are the rate controlling factor. The relation between the two controlling processes and the reduction process has been discussed. At high temperature, ilmenite is reduced to metallic iron. The kinetics of reduction by carbon monoxide has also been reported by Merk and Pickles¹²⁷. The rate and the degree of reduction are increased linearly with increasing temperature to 1000°C. The addition of magnesium oxide, manganous oxide, calcium oxide and silicon dioxide lowered the reduction rate of iron oxide in ilmenite. Pre-oxidation at 700-800°C forms pseudo-brookite, which exhibits higher reduction rate. The results obtained have been explained in terms of the physical and chemical changes.

The reduction kinetics of a mixture of synthetic ilmenite and graphite powder have been investigated in the temperature range 980-1100°C with

various graphite contents under nitrogen and carbon dioxide atmosphere by Kang and Yoon¹²⁸. DTA data of the reaction are obtained simultaneously with the measurement of the weight loss. The initial rate of reduction of ilmenite has been explained in terms of solid-solid reaction between ilmenite and graphite, and the latter stage of the reduction has been applied to the Rao's physicochemical model for reaction between solids through gaseous intermediates. The activation energy of reduction by gaseous intermediates is $282 \pm 8 \text{ kJ mol}^{-1}$. In carbon dioxide little reduction of ilmenite is found due to the infiltration of carbon dioxide into the pellet. The same system has also been investigated by Gupta *et al.*¹²⁹ but in argon atmosphere. No measurable reaction is obtained at 1000°C , but the rate is high at 1100°C . An inflection in the reduction curve at ~2% weight loss at 1050 and 1100°C is thought due to the difficulty in nucleating iron. The rate is increased significantly by the addition of ferric chloride which promotes the nucleation of iron. The addition of rutile decreases the reduction rate and addition of manganous oxide stabilizes a pseudo-brookite phase.

The kinetics of reduction of ilmenite with lignite coal have been investigated by Sucre *et al.*¹³⁰ using an inductively heated rotary kiln. The influences of temperature (948 – 1115°C), pre-oxidation, char-to-ore ratio and the rotational speed on the kinetics are examined by gas analysis and flow measurements. Gupta *et al.*¹³¹ investigated the same system monitored by TGA, x-ray diffraction, optical microscopy and electron-probe micro-analysis of the products. The rate of reduction and the size of iron particles decrease with increasing degree of weathering of the concentrate. Stoichiometric ilmenite is reduced faster than pseudo-rutile ($\text{Fe}_2\text{O}_3\text{TiO}_3$),

which is a weathering product. The addition of ferric chloride, which promoted the nucleation of iron, increases the rate of reduction and significant coarsening of the iron is obtained at 1000°C. In general, the products of reaction are iron, rutile, reduced rutile, unreacted ilmenite and pseudo-brookite solid solution. A small amount of manganese (1.2-1.6% MnO) in the concentrates stabilizes a pseudo-brookite phase which retains a significant amount of iron. Manganese also forms an α -oxide phase, (Fe, Mn)TiO₃, which is mainly a manganese titanate and concentrates toward the centre of the reducing particles.

The metallo-thermic reduction of ilmenite has been investigated by few workers¹³²⁻¹³⁴. Behra and Mohanty¹³² reduced an ilmenite concentrate with aluminium-silicon mixture in presence of barium peroxide, potassium chlorate, magnesium oxide, fluorspar and lime to yield ferro-titanium alloy. Maximum titanium recovery (59.24%) and alloy yield (84.34%) are achieved with 12.5% silicon (related to aluminum) and addition of potassium chlorate. Ferro-titanate has been prepared by thermite reaction with powdered aluminium and calcium^{133,134}. Ilmenite 137 kg, powdered aluminium 8 kg and calcium 80 kg are mixed and ignited with barium peroxide to yield 60.8 kg metal containing 38.90% titanium (61.26% yield), 50.5% iron, 3% aluminium and 2.5% silicon, and 162 kg slag. Addition of calcium oxide to make the ratio CaO/SiO₂ (in ore) within 0.8-2.0 instead of using powdered calcium improves the yield (62.5%) slightly.

Roasting in presence of alkali metal compounds has been investigated by several works. Titanium dioxide (scattering coefficient 8900 cm² g⁻¹ and brightness 91%) has been prepared from beneficiated ilmenite¹³⁵. The raw

material (10 μm) has been mixed with alkali metal hydroxide, oxide or carbonate, roasted at 700–900°C for 2.5 hours, digested in 12 g eq dm^{-3} hydrochloric acid twice to form suspension and calcined the suspension at 900°C for one hour to get the product. Jebsen *et al.*¹³⁶ have fused ilmenite with an alkali metal compound, the melt is subjected to an oxidizing roasting, heated with sulphuric acid to dissolve the soluble salts, iron is reduced to ferrous state by sulphur dioxide and the insoluble residue of crude titanic oxide is purified by repeated treatment with sulphuric acid, and the ferrous sulphate liquor is evaporated for the recovery of sulphuric acid. Similar studies have also been made by Jebsen *et al.*¹³⁶ and others¹³⁷. Barton¹³⁸ has heated ilmenite with sodium sulphide to ferrous sulphide and electrolyzed the product in aqueous sodium chloride so that the liberated chlorine effected the decomposition and solution of the sulphides. The residue is relatively pure titanium dioxide. On the otherhand, the workers of titanium alloy manufacturing company¹³⁹ have fused ilmenite with sodium sulphide and the melt boiled with dilute sulphuric acid of such strength as to dissolve only the iron. The residue is washed and heated with stronger sulphuric acid to form titanium sulphate, which is dissolved in water, iron is reduced to ferrous state, clarified and boiled to precipitate the titanium as hydrous oxide.

Several other fusion methods followed by different physical and chemical methods of separation have been investigated. Shiah¹⁴⁰ has fused ilmenite and calcium sulphate (1:10: to 10:1) in presence of hydrogen at 1500–1800°F to reduce iron in ilmenite to metallic iron and calcium sulphate to calcium sulphide which is separated magnetically. The magnetic fraction

is leached with ferric chloride solution to dissolve metallic iron and left a titanium dioxide residue. Fratila *et al.*¹⁴¹ have fused ilmenite with sodium carbonate to remove chromium (chromite, FeCr_2O_4) from ilmenite. Ilmenite (0.1 mm) is mixed with sodium carbonate [1:(0.5-1)], calcined for 1.5-2 hours at 850-900°C and the resulting sodium chromate is washed out by hot water. The chromium content of ilmenite is reduced from 0.7-0.9% to 0.047-0.049% by this treatment. Fusion of ilmenite below 1100°C with a mixture of sodium carbonate and sulphite, magnetic separation of the calcine to titanium dioxide and iron oxide from the non-magnetic gangue and partial leaching with dilute sulphuric acid gives ~90% titanium dioxide for pigment manufacture¹⁴². On heating ilmenite with a mixture of calcium oxide and sodium carbonate at 900°C, Saklatwalla *et al.*¹⁴³ have prepared calcium titanate which is purified by washing with water and then leaching iron with 10% sulphuric acid. Calcium titanate is decomposed by concentrated sulphuric acid (165°C) to produce calcium sulphate, and soluble titanium sulphate. A combined fusion (sodium carbonate) and reduction (anthracite dust, 800°C) process has been used by Pellereau *et al.*¹⁴⁴. Water leaching and carbonation of the resulted mass, separates sodium carbonate, leaching with dilute sulphuric acid removes iron, heating of residue at 150°C and subsequent leaching with concentrated sulphuric acid makes a titanyl sulphate solution. Readily soluble titanium sulphate has been prepared¹⁴⁵ by heating ilmenite with sulphuric acid and alkali metal sulphate at 200-350°C.

Buckman¹⁴⁶ heated a mixture of ilmenite, sulphur, barium sulphate and coke in a Blast Furnace and dissolved the melt in strong hydrochloric acid. A product composed of sodium titanate and metallic iron is obtained by

smelting titaniferrous ore with coke and sodium hydroxide, which is lixiviated with hot water and with 50-60% sulphuric acid to dissolve titanium¹⁴⁷. Titanium dioxide concentrate has been obtained by oxidation and reduction of ilmenite in presence of sodium sulphite at 500-900°C in 3 stages, quenching in water, and by magnetic separation¹⁴⁸. Sulphatization of ilmenite with ammonium sulphate has been investigated by Lee and Sohn¹⁴⁹. The optimum sulphation condition are temperature 400°C, time 3 hours, salt to ilmenite ratio 11:1, ilmenite particle size ~200 mesh. Water leaching recovered 94.5% titanium and 99.8% iron.

Many reports on the chlorination of non-treated or treated ilmenite are available in literature¹⁵⁹⁻¹⁶¹. Kinetics of the selective chlorination of ilmenite has been investigated by Deventer¹⁶². Ilmenite has been beneficiated by selective chlorination in which the iron is selectively chlorinated as volatile iron chloride, leaving behind an enriched residue of titanium dioxide. Relatively high partial pressure of chlorine and low oxygen partial pressures required for chlorination of iron. Under equilibrium condition at 1200°K and 1 atm, selective chlorination of ilmenite is not thermodynamically possible in the presence of carbon, since the chlorination occurs practically in non equilibrium condition. Batch experiments conducted at 915-970°C in a horizontal tube furnace have showed that the kinetics of selective chlorination are limited by diffusion of iron through a product layer of titanium dioxide formed from the outside of a particle. The iron content has been used to follow the kinetics of chlorination. Only about 4% of titanium is lost as volatiles during chlorination. Vanadium, silicon, calcium and manganese are removed partially, whereas chromium, aluminium, niobium and magnesium are not removed at all.

There are hundreds of papers on the extraction behavior of Fe^{3+} and Ti^{4+} from aqueous solutions by varieties of solvents. In most cases, it is found that the selectivity of the extractants towards the separation of Fe^{3+} from Ti^{4+} is poor. The following paragraph summarizes the conditions at which these metal ions are extracted from aqueous solutions.

Both the metal ions under consideration are extracted by acetylacetone^{163,164} and benzoylacetone¹⁶⁴. With acetylacetone as an extractant, the extraction is quantitative for Fe^{3+} in the pH range 2.5-7, whereas it is 30% for Ti^{4+} in the pH range 3-5. But with benzylacetone as an extractant, both the metal ions are extracted quantitatively at pH ~3. The complete extraction of Fe^{3+} by thenoyltrifluoacetone has been reported from various aqueous media by several workers¹⁶⁵⁻¹⁶⁹. The titanium (IV) extraction by thenoyltrifluoacetone is also quantitative from 10-11 g mol dm⁻³ aqueous acid solution¹⁷⁰. Another common extractant, oxine or 8-hydroxyquinoline extracts both iron (III)¹⁷¹⁻¹⁷³ and titanium (IV)^{174,175} quantitatively from aqueous solution of pH ~2. With cupferron (N-nitrosophenylhydroxylamine), Fe^{3+} is extracted quantitatively from concentrated hydrochloric acid solution¹⁷⁶⁻¹⁸¹, whereas Ti^{4+} is extractable in the pH range 0-5^{177,182,183} depending on diluent and the synergistic agents in organic phase. The partial extractions of Fe^{3+} by amines have been reported from aqueous solution containing fluoride¹⁸⁴, bromide¹⁸⁵, sulphate¹⁸⁶, thiocyanate¹⁸⁷, phosphate¹⁸⁸, cyanide¹⁸⁹, oxalate¹⁹⁰, tartrate¹⁹¹ and citrate¹⁹² ions. Only the thiocyanate-amine extraction system is quantitative for Fe^{3+} and is used for the colorimetric determination of iron¹⁹³. With quaternary amines, Fe^{3+} as anionic complex is extractable as ion-pairs^{194,195}. In presence of anions like citrate and thiocyanate, Ti^{4+} is extracted by low molecular weight secondary and tertiary amines^{196,197}. The

organophosphoric acids have been extensively used to make investigation on the extraction behaviors of Ti^{4+} . Dibutylphosphoric acid^{198,199}, mono-(2-ethylhexyl)-phosphoric acid²⁰⁰, di-(2-ethylhexyl) phosphoric acid²⁰¹, di-isoamylphosphoric acid²⁰² and di-tolyl phosphoric acid²⁰³ have been used for the extraction of Ti^{4+} . Likewise, there are many reports on the extraction of Fe^{3+} by alkyl phosphoric acid²⁰⁴⁻²⁰⁷ and arylphosphoric acid^{208,209}. With most of the organophosphoric acids, the clear-cut separations of Ti^{4+} from Fe^{3+} in single-stage is not possible for co-extraction of the species²¹⁰⁻²¹³. The neutral organophosphorous ester, e.g. tri-butyl phosphate extracts both titanium(IV)²¹⁴⁻²¹⁷ and iron(III)²¹⁸⁻²²³. Carboxylic acids also extracts both titanium(IV)²²⁴ and iron(III)²²⁵⁻²³¹ but poorly. N-benzoyl-N-phenyl-hydroxyl amine (BPHA) extracts Ti^{4+} from strong acid^{232,233} whereas it extracts Fe^{3+} in the pH range 0.6 to 10²³⁴⁻²³⁶ and in both cases the method has been used for the colorimetric determination of the elements. The quantitative extraction of Fe^{3+} by β -isopropyltropolone (IPT) from weak acid solution (pH)²³⁷⁻²³⁹ and by methylisobutylketone (MIBK) from strong hydrochloric acid solution (>7 g eq. dm^{-3})²⁴⁰⁻²⁵¹ have been reported. Titanium is not reported to be extracted by MIBK.

OBJECT OF THE PRESENT INVESTIGATION

Ilmenite is the most important ore mineral of titanium. It is the compound oxide of titanium and iron. The production of titanium by hydrometallurgical process has appeared to be easier than pyrometallurgical processes. Titanium is generally extracted as dioxide from ilmenite fraction by conventional sulphuric acid leaching and precipitation route. However in the conventional process a large fraction of ilmenite is being rejected undissolved and the co-dissolved associated transition elements such as Cr, Ni, V etc. may be co-precipitated with titanium which may seriously discolour the white pigment colour of titanium dioxide. The ilmenite found in Bangladesh contains the transition metals such as Cr, Ni, Mn etc. so the product obtained by the conventional method is coloured. To improve the product quality, other ways are to be searched to utilize the ilmenite found in our country. Consequently, studies have been undertaken to find out an easy leaching route for ilmenite with highest possible dissolution of titanium (with mineral acids) and then for the recovery methods of titanium and iron as their oxides from the leach solution. For this purpose the following experiments were proposed to be carried out stepwise :

1. THERMAL TREATMENT (ROASTING) OF ILMENITE POWDER WITH LPG PYROLYSED PRODUCT AND SUBSEQUENT LEACHING :

Roasting has been proposed to be investigated as functions of time, temperature, LPG flow rate and particle size. The X-ray diffraction data have to be taken. Leaching of the roasted mass will be investigated as

functions of acid concentration, temperature, solid to liquid ratio and agitation speed in hydrochloric and sulphuric acid to elucidate the optimum conditions for roasting and leaching.

2. THERMAL TREATMENT (ROASTING) OF ILMENITE POWDER BY THE REFORMED PRODUCT OF THE LPG-H₂O MIXTURE IN PRESENCE OF NICKEL POWDER AND SUBSEQUENT LEACHING :

Roasting has been proposed to be investigated as functions of time, temperature, gas flow rate and water vapour content in LPG to elucidate an optimum condition for roasting. To examine the effect of roasting treatment, the XRD pattern of the product will be taken. The leaching of the roasted mass obtained at optimum condition are proposed to be investigated as functions of acid concentration, temperature, solid to liquid ratio and agitation speed to find out an optimum condition for leaching.

3. SALT-WATER VAPOUR ROASTING OF ILMENITE :

The studies on the salt roasting using NaCl, Na₂SO₄, NaNO₃ and Na₂CO₃ as salts have been proposed to be investigated as functions of ilmenite powder to salt ratio, time of roasting, temperature of roasting, carrier gas flow rate and water vapour pressure to find out the conditions for the best roasting. The XRD patterns have to be taken to obtain ideas on the composition of the roasted products. To obtain the optimum condition for leaching of the salt roasted products, the leaching studies have been proposed to be investigated as functions of acid concentration, temperature, agitation speed, solid to liquid ratio and the leaching-stages in hydrochloric acid only.

4. KINETICS OF LEACHING OF THE ROASTED MASS ($\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ VAPOUR ROASTING) GIVING THE BEST DISSOLUTION (IN HYDROCHLORIC ACID) :

Kinetics of leaching of the roasted mass ($\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ vapour roasting) giving the best dissolution (in hydrochloric acid) have been proposed to be studied as functions of hydrochloric acid concentration, temperature and the phase mixing rate (r.p.m). From this study the rate constants for dissolution processes and the exponents in the rate equation are to be evaluated.

5. LEACH SOLUTION TREATMENT :

From the best leached solution, the methods for the isolation of titanium and iron as pure compounds are to be developed using liquid-liquid extraction and precipitation techniques.

EXPERIMENTAL

4.1 CHEMICALS USED, THEIR SOURCES AND SPECIFICATIONS

All the chemicals used in this investigation excepting ilmenite sand, LPG and Kerosin were of analar grade. Ilmenite used in all experiments was collected in single lot from Bangladesh Atomic Energy Commission's Pilot Plant for separation of heavy minerals from beach sands at Cox's Bazar. According to the information provided by the BAEC's Pilot Plant, the composition of their supplied sand was : TiO_2 38.5%, Fe_2O_3 25.62%, FeO 29.75%, SiO_2 1.2%, P_2O_5 0.03%, MnO 1.3% and Cr_2O_3 1.08%. However, our laboratory analysis showed that the percentages of titanium and iron were 27.8% (corresponding to 46.4% TiO_2) and 32.4% respectively. If we consider 50% iron exist as FeO and the rest as Fe_2O_3 , then 90% of the supplied sample was comprised of titanium and iron oxides. A residue amounting to about 5% of the total mass was obtained, so that the rest 5% of total mass dissolved was comprised of various metals oxide, viz. MgO , Al_2O_3 , MnO , Cr_2O_3 etc. The composition of the residue was not known to us. The supplied sample was dry-ground in a ball mill and sieved to collect powder of different particle sizes.

The liquified petroleum gas (LPG) in cylinder was collected from local market. It was composed mainly of butane - cut of the Bangladesh Oil Refineries. The cylinder was provided with a gas regulator. The diluent, Kerosin used in liquid-liquid extraction was purchased locally and distilled

to collect a white fraction below 180°C. Specification for all other chemicals are given below.

Chemicals	Producers	Purity
1. Titanium dioxide	E. Merck	99.0%
2. Ferric ammonium sulphate	do	99.0%
3. Sodium sulphate	do	99.0%
4. Methyl isobutyl Ketone (MIBK)	do	99.0%
5. Potassium thiocyanate	BDH	98.0%
6. Orthophosphoric acid	do	85.0%
7. Hydrochloric acid	do	36.0%
8. Nitric acid	do	69-72%
9. Sulphuric acid	do	98.0%
10. Hydrogen peroxide	do	30.0%
11. Oxalic acid	do	99.8%
12. Sodium carbonate	do	99.9%
13. Sodium hydroxide	do	96.0%
14. Sodium nitrate	do	99.5%
15. Sodium chloride	do	99.9%
16. Hexane-1-ol	do	98.0%
17. Nickel powder	RIEDEL-DE-HAEN AG SEELZE-HANNOVER	99.8%
18. Bis-2-(ethyl hexyl) phosphate (HDEHP)	Tokyo Kasei Industry	95.0%
19. Phenolphthalein	Matheson Coleman & Bell	Pure
20. Nitrogen gas cylinder	Bangladesh Oxygen Limited	-
21. Ethyl alcohol	Carew & Co., Bangladesh	95.0%
22. Potassium bisulfate	E. Merck	Pure
23. Benzene	BDH	99.0%
24. Ethylene glycol	E. Merck	99.0%
25. n-Hexane	BDH	99.0%
26. Toluene	Hopkin & William	Pure
27. Chloroform	BDH	99.0%
28. Carbontetrachloride	BDH	99.8%

4.2 PREPARATION OF DIFFERENT STANDARD SOLUTIONS

a) PREPARATION OF ACID SOLUTIONS :

The acid solutions of different concentrations were prepared by proper dilutions of 16 g eq dm^{-3} HNO_3 , 12 g eq dm^{-3} HCl and 36 g eq dm^{-3} H_2SO_4 with distilled water. 15% H_2SO_4 solution was prepared by diluting 98% H_2SO_4 .

b) PREPARATION OF POTASSIUM THIOCYANATE SOLUTION :

About 100 g of A.R. potassium thiocyanate was dissolved in water in a 250 cm^3 volumetric flask, and the solution made upto the mark with distilled water. The solution was calculated as 2 g eq dm^{-3} . This solution was used in iron estimation.

c) PREPARATION OF OXALIC ACID SOLUTION :

As the molecular weight $[(\text{COOH})_2 \cdot 2\text{H}_2\text{O}]$ and basicity of oxalic acid are 126 & 2 respectively, 15.75g of oxalic acid in 250 cm^3 solution made 1 g eq dm^{-3} solution. This solution was used for the standardization of sodium hydroxide solution.

d) PREPARATION OF SODIUM HYDROXIDE SOLUTION :

The caustic soda solution was prepared by dissolving the (~40g) carbonate washed out sodium hydroxide pellets and the actual strength determined by titrating with the standard oxalic acid solution using phenolphthalein as indicator. The standard sodium hydroxide solution was used to standardise the acidity of leached solutions.

e) PREPARATION OF PHENOLPHTHALEIN SOLUTION :

As phenolphthalein is insoluble in water but soluble in alcohol (ethyl), to 250 cm³ alcohol about 10g of phenolphthalein was dissolved. This was used as indicator in the acid-base titrations.

f) PURIFICATION AND PREPARATION OF HDEHP SOLUTION :

The commercial grade bis-(2-ethylhexyl) phosphoric acid has a purity of about 95%. It was purified to about 99% by scrubbing its benzene solution with aqueous ethylene glycol solution several times and finally with fresh water to remove any ethylene glycol in the organic phase²⁵². It was then dehydrated by using high vacuum pump. The purified HDEHP was found to be about 99% on its mono-acid content.

Preparation of HDEHP solution : HDEHP is dimeric in kerosin. On this basis 1 g mol dm⁻³ solution of HDEHP was prepared by dissolving 329 cm³ of the purified HDEHP (specific gravity 0.98) in a dry 500 cm³ volumetric flask and then made upto the mark with kerosin. This solution represented the stock solution of HDEHP (stock-1).

Then 0.25g mol dm⁻³ HDEHP solution was made by taking out appropriate amount of stock-1 into appropriate flask and diluting upto the mark by kerosin after adding an appropriate amount of hexane-1-ol as de-emulsifier. This solution was used to purify the leach solution for titanium dioxide preparation.

g) PREPARATION OF STANDARD TITANIUM (IV) SOLUTION :

0.2g of commercially pure TiO₂ was fused with about 20 times of its weight of KHSO₄ in a suitable platinum crucible, keeping at fusion heat until

the oxide dissolved (~1h). The fused mass was cooled at room temperature and dissolved in 15% H_2SO_4 by gentle heating. The solution was washed into a 250 cm^3 volumetric flask and made upto the mark with 15% H_2SO_4 solution.

Then

$$\begin{aligned} 1\text{ cm}^3 &\equiv 0.0008\text{ g of TiO}_2 \\ &\equiv 0.0048\text{ g of Ti} \end{aligned}$$

h) PREPARATION OF STANDARD IRON (III) SOLUTION :

0.864g of A.R. ferric ammonium sulphate $[\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$ was weighed out into a 1 dm^3 volumetric flask, dissolved in water, and made upto the mark after adding 10 cm^3 of concentrated hydrochloric acid. Then

$$1\text{ cm}^3 \equiv 0.0001\text{ g of Fe}$$

i) PREPARATION OF MIBK SOLUTION :

The molecular weight (100.16) and the specific gravity (0.8) indicate that the undiluted methylisobutyl ketone (99%) is about 8 g mol dm^{-3} in strength. Whenever necessary, it was diluted with distilled kerosin to get the solutions of different concentrations. This solution was used in the separation of Fe^{3+} from Ti^{4+} in leach solution.

j) PREPARATION OF 1 g mol dm^{-3} SODIUM CARBONATE SOLUTION :

1 dm^{-3} amount of 1 g mol dm^{-3} sodium carbonate solution was prepared by dissolving 106g anhydrous sodium carbonate. This solution was used in stripping and precipitation of Ti^{4+} from the HDEHP extract.

4.3 EXPERIMENTAL TECHNIQUES

4.3a) ANALYTICAL TECHNIQUE : SPECTROPHOTOMETER

Spectrophotometry is concerned with the determination of the concentration of a substance by measurement of the relative absorption of light with respect to a known concentration of the substance.

A Bausch and Lomb spectronic-20 spectrophotometer has been used to estimate the amount of Ti^{4+} and Fe^{3+} in solutions. It operates from a 115 volt, 60 Hz main. The wavelength is from 375 to 650 nm, and can be extended to 950 nm by addition of a red filter and exchange of photo-tubes. The effective band width is 20 nm. The instrument consists of a diffraction grating monochromator and an electronic detector : amplification and measuring system. Special small test tubes (1 cm width) are used as containers for the sample.

For spectrophotometric work, the wavelength control is rotated until the desired wavelength in nm is indicated on the wavelength scale. The amplifier control is adjusted to bring the meter needle to zero on the "Percent Transmittance Scale" or ∞ on the "Absorbance Scale". The test tube containing water or blank solution is then inserted in the sample holder. The light control is then rotated until the meter reads "100" or "0". The unknown sample is then inserted in place of the blank and the percent transmittance or Absorbance read directly from the meter.

The chief advantages of spectrophotometric analysis are that they provide the sample, easier and prompt means for determining minute quantities of the substances more accurately in comparison to the other methods such as volumetric, gravimetric etc. methods.

The spectrophotometry is based on the Beer-Lambert's law

$$\log \frac{I_0}{I_t} = \epsilon ct \dots\dots\dots (3)$$

where, I_0 and I_t represent the intensity of incident and transmitted light, and ϵ , c and t represent the molar extinction co-efficient, concentration in g mol dm^{-3} and thickness of solution medium respectively. The term in the L.H.S is called absorbance (A) or optical density (O.D), whereas (I_t/I_0) is the transmittance (T).

The equation (3) represents that the absorbance is proportional to the concentration. Hence by plotting 'A' (ordinate) against concentration (abscissa), a straight line passing through the origin is usually obtained. Thus if the absorbances for a number of solutions of known concentrations are determined with a spectrophotometer and a calibration curve is constructed, then the unknown concentration of the same substance can be read off from the calibration curve after measuring its absorbance.

Discrepancies in spectrophotometric analysis are usually found when the coloured solute ionises, dissociates or associates in solution. Discrepancies may also occur when monochromatic light is not used. Throughout the whole investigation, the concentrations of titanium and iron in leach solutions were determined by spectrophotometric method in order to calculate the percentages of Ti and Fe present in solution.

i) SPECTROPHOTOMETRIC ESTIMATION OF TITANIUM (IV) :

The addition of H_2O_2 to an acidic Ti^{4+} solution produces a yellow colour²⁵³ due to the formation of $\text{TiO}_2(\text{SO}_4)_2^{2-}$ on $\text{Ti}(\text{H}_2\text{O}_2)^{4+}$. Upto 0.5 mg of TiO_2 per cm^3 , the intensity of colour is proportional to the amount of the element present. The final solution should be 3 to 6 g eq dm^{-3} in H_2SO_4 .

Construction of calibration curve for titanium (IV) : 1.0 cm^3 , 2.0 cm^3 , 3.0 cm^3 , 4.0 cm^3 , 5.0 cm^3 , 6.0 cm^3 portions of the standard solution (vide, sec, 4.2g) of titanium were taken in six different 100 cm^3 volumetric flasks. To each flask 1.0 cm^3 of 30% H_2O_2 was added. The flasks were then made upto the mark with 15% H_2SO_4 . A blank solution was prepared and used to calibrate the spectro-photometer. The absorbances of the samples were measured at 415 nm. A straight line was obtained by plotting absorbances against concentration. The calibration plot is shown in the Fig. 2.

Estimation of titanium (IV) in the leach solutions : The concentration of Ti^{4+} in the non-fluoride leach solution was measured by comparing the absorbance reading, obtained on proper dilution ($A < 0.3$) of leach solution with 15% H_2SO_4 , after addition of 1 cm^3 H_2PO_4 (to eliminate the effect of co-existing Fe^{3+} in leach solution) and 1 cm^3 30% H_2O_2 with the standards in the calibration curve.

ii) SPECTROPHOMETRIC ESTIMATION OF IRON (III) :

Depending upon the concentration of thiocyanate ion, ferric ion reacts²⁵³ with thiocyanate to give a series of red-coloured compounds, at low thiocyanate concentration the predominant coloured species is $[\text{Fe}(\text{SCN})]^{2+}$, whereas at 0.1 g eq dm^{-3} thiocyanate concentration it is largely $[\text{Fe}(\text{SCN})_6]^{-3}$. In the spectrophometric determination, a large excess of thiocyanate should be used, since this increases the intensity and also the stability of colour. Strong acid such as hydrochloric acid of concentration $0.05\text{--}0.5 \text{ g eq dm}^{-3}$ should be present to suppress the hydrolysis of Fe^{3+} .

Construction of calibration curve for iron (III) : 1.0 cm^3 , 2.0 cm^3 , 3.0

cm^3 , 4.0 cm^3 , 5.0 cm^3 portions of the standard solution of iron (vide sec. 4.2h) were taken in five different 100 cm^3 volumetric flasks. To each flask 5 cm^3 5 g eq dm^{-3} nitric acid and 10 cm^3 2 g eq dm^{-3} potassium thiocyanate solutions were added. The flasks were then made upto the mark with distilled water. A blank solution was prepared to calibrate the spectrophotometer. The absorbances of the samples were measured at 480 nm . By plotting the absorbances against their respective concentrations, a straight line was obtained. The calibration curve is given in the Fig. 3 as absorbance versus Fe^{3+} concentration in mg cm^{-3} .

Estimation of iron (III) in the leach solution : Aliquot of properly diluted leach solution was oxidized by 5 cm^3 5 g eq dm^{-3} nitric acid on heating. To it 10 cm^3 2 g eq dm^{-3} KSCN solution was added and diluted upto the mark with water. The absorbance ($A < 0.3$) of resulting solution was determined against blank solution. This method is suitable for determination of Fe^{3+} in hydrochloric acid leach solution. The concentration of Fe^{3+} in ion in leach solution could be obtained by the difference of the estimated amounts obtained with and without HNO_3 oxidation.

In case of sulphate leach solutions, the absorbance of the solution was not constant but varied with time. So after the solution preparation a definite time (30 mins) was allowed prior to the measurement of the absorbance values.

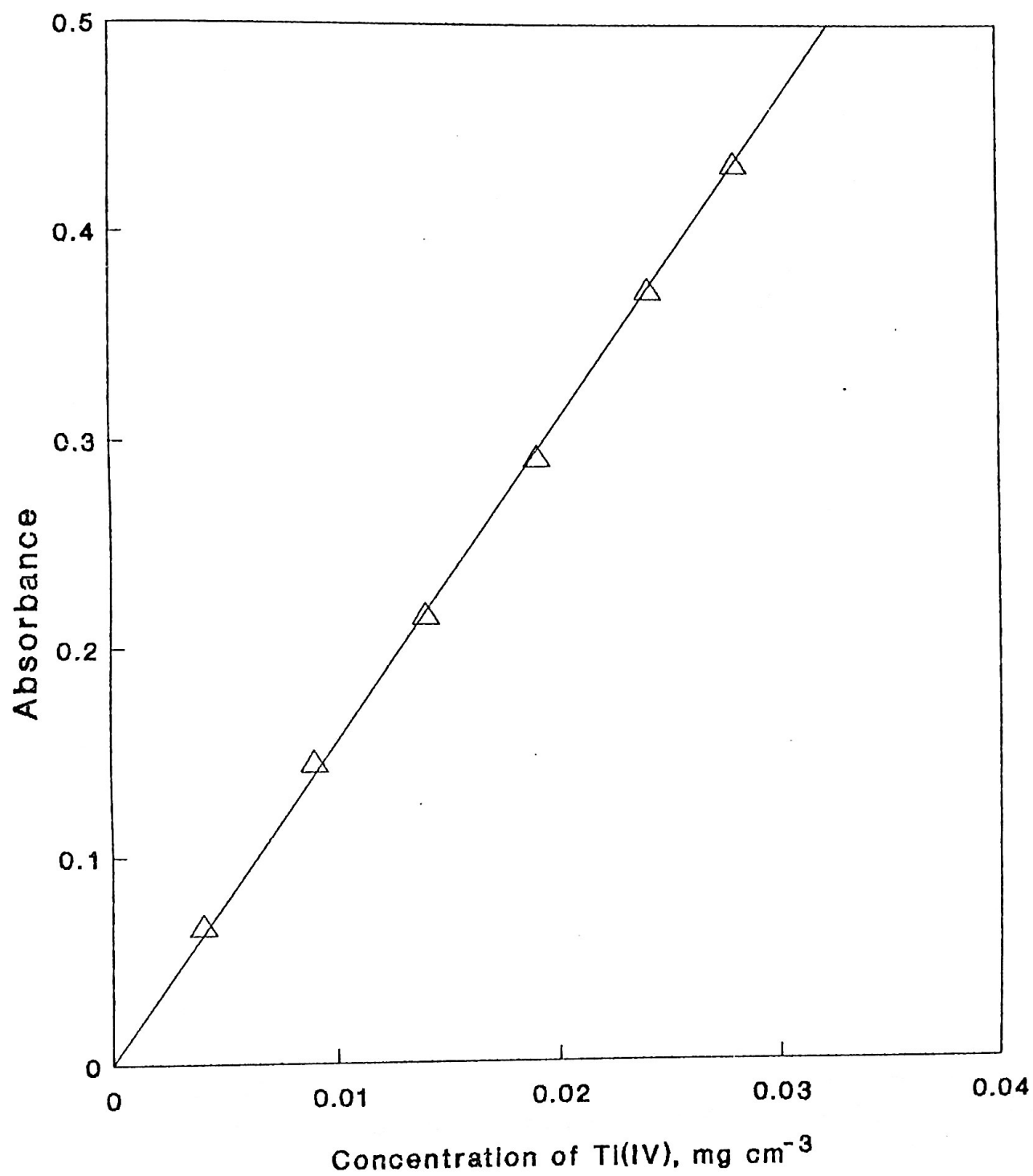


Fig. 2. Calibration curve for the spectrophotometric estimation of Ti(IV) at 415 nm wavelength.

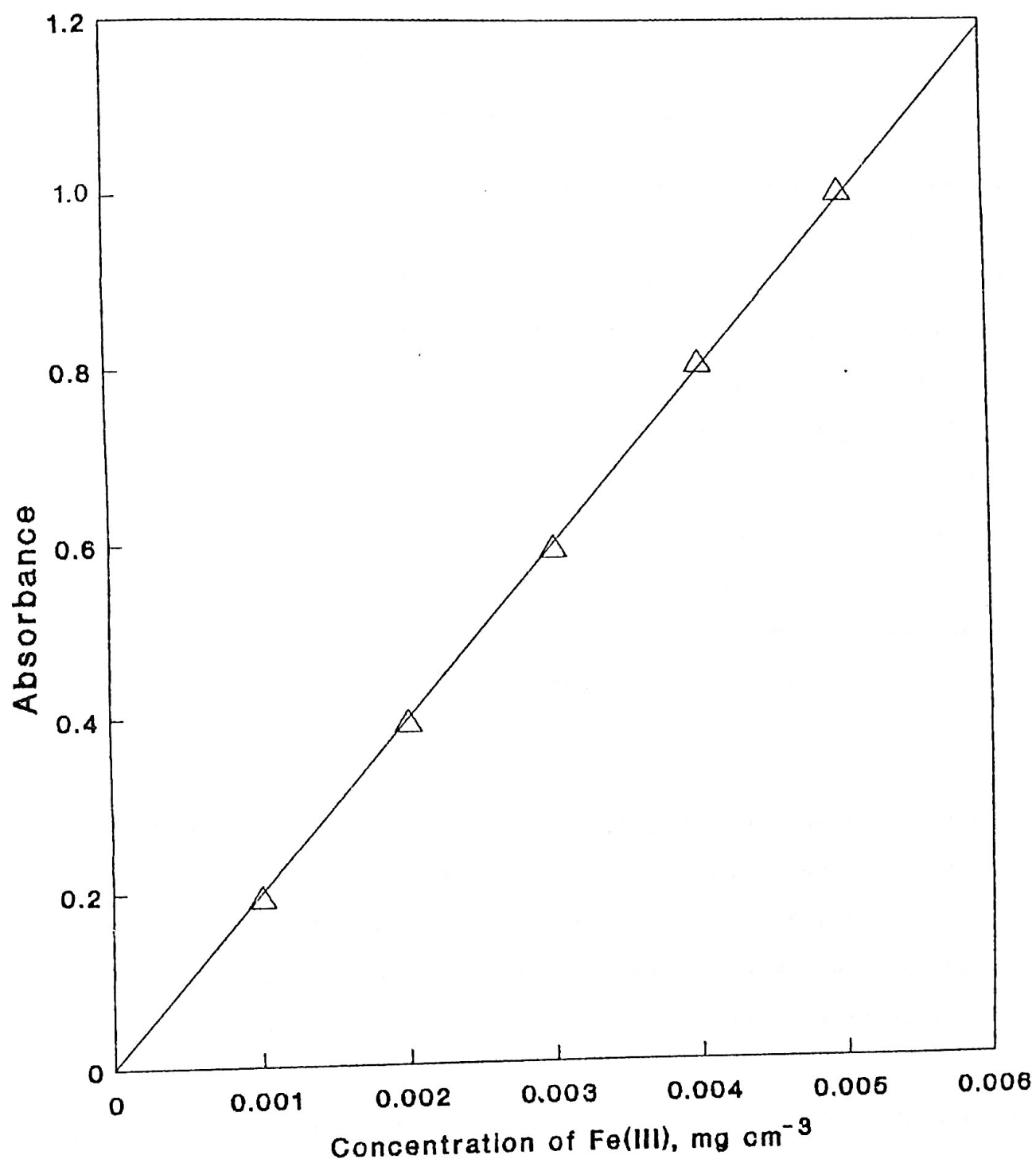


Fig. 3. Calibration curve for the spectrophotometric estimation of Fe(III) at 480 nm wavelength.

4.3b) PHASE MIXING :

i) *IN SOLID-LIQUID SYSTEM : MAGNETIC STIRRER :*

The heating and the stirring of ilmenite sand during leaching in HCl and H_2SO_4 has been done by a magnetic hot plate (MM-1 Magnetic stirrer). A rotating field of magnetic force is employed to induce variable speed stirring action with in either closed or open vessels. The stirring is accomplished with the aid of a small magnet sealed in polythene which is caused to rotate by the rotating magnet. The voltage on the armature of the motor is controlled by an auto-transformer with multiple tapping, while the field windings are supplied with a constant high voltage. This arrangement gives a range of very stable speeds and high torque at low speed. The control of speed is for superior to that obtained with a rheostat. The usual model has a 1/30 H.P motor and the speed attainable is 50-700 r.p.m.

ii) *IN LIQUID-LIQUID SYSTEM : SHAKING MACHINE :*

For small scale or preliminary liquid-liquid extraction studies, shaking machine has been used. It is an electrically driven Zencon's Stuart Flask Shaker with eight arms (220 V, 50 Hz). For phase mixing, the aliquots of aqueous and organic phase are taken in reagent bottle and agitated for a definite time in a thermostated water bath. After phase separation the heavier aqueous layer can be separated from the organic layer by pipetting. The shaking speed could be controlled by a regulator. For bulk phase mixings, 1 dm^3 separating funnels have been used and the phase mixings are affected by a multidirectional flask shaker (Gallenkamp SD-250), 220 V, 50 Hz, $36 \times 63 \times 36\text{ cm}$ (overall) $11.5 \times 38 \times 18\text{ cm}$ carrier internal, motor power = 1/20 H.P, 170 Mev/min in ambient condition.

4.3c) HIGH TEMPERATURE APPARATUS : ELECTRIC TUBE FURNACE :

For various thermal treatments of ilmenite, a Griffin 1450°C Tube Furnace has been used. The furnace has two tube-holes and a close temperature control. Metallic or refractory tubes upto 32 mm O.D. can be accommodated. It has a well ventilated enamelled sheet metal case. Heating chamber is constructed of high quality insulating blocks and heated by silicon carbide elements. The furnace temperature is controlled by a Pt/13% Rh-Pt thermocouple connected to a non-indicating potentiometric proportional controller. The temperature setting dial has a range 0-1500°C and an effective length of 15 cm. The over-all size is 45 cm x 33 cm x 48 cm. It can be operated by 220v, 50 Hz supplies.

4.3d) GAS FLOW REGULATION :

As the liquified petroleum gas in cylinder is used only for the cooking purposes in urban areas in Bangladesh, the cylinder has a special type of regulator which only opens and closes the passage of gas and consequently, it could not be used to control the gas flow rate properly. The laboratory gas-regulators could not be fitted with the LPG cylinder. To regulate the LPG flow from the cylinder, we adopted the following technique :

In this technique, a screwed gas flow regulating clip was used across the gas-exiting plastic tube. At a certain screwed condition of the clip, the gas flow rate was determined by water displacement. When the flow rate became known, the gas was allowed to burn in a Bunsen Burner with a tall flame whose height was measured corresponding to several gas flow rates (varied by the screw of the clip), the flame heights were determined, and plotted as flame height (in inch) versus gas flow rate (in $\text{cm}^3 \text{min}^{-1}$) in Fig. 4. During the whole experiment, the gas flow rate was then regulated by the screw of the clip until the flame height for the desired flow rate was obtained. In all the experiments, the gas flow rate refers to that at ambient temperature.

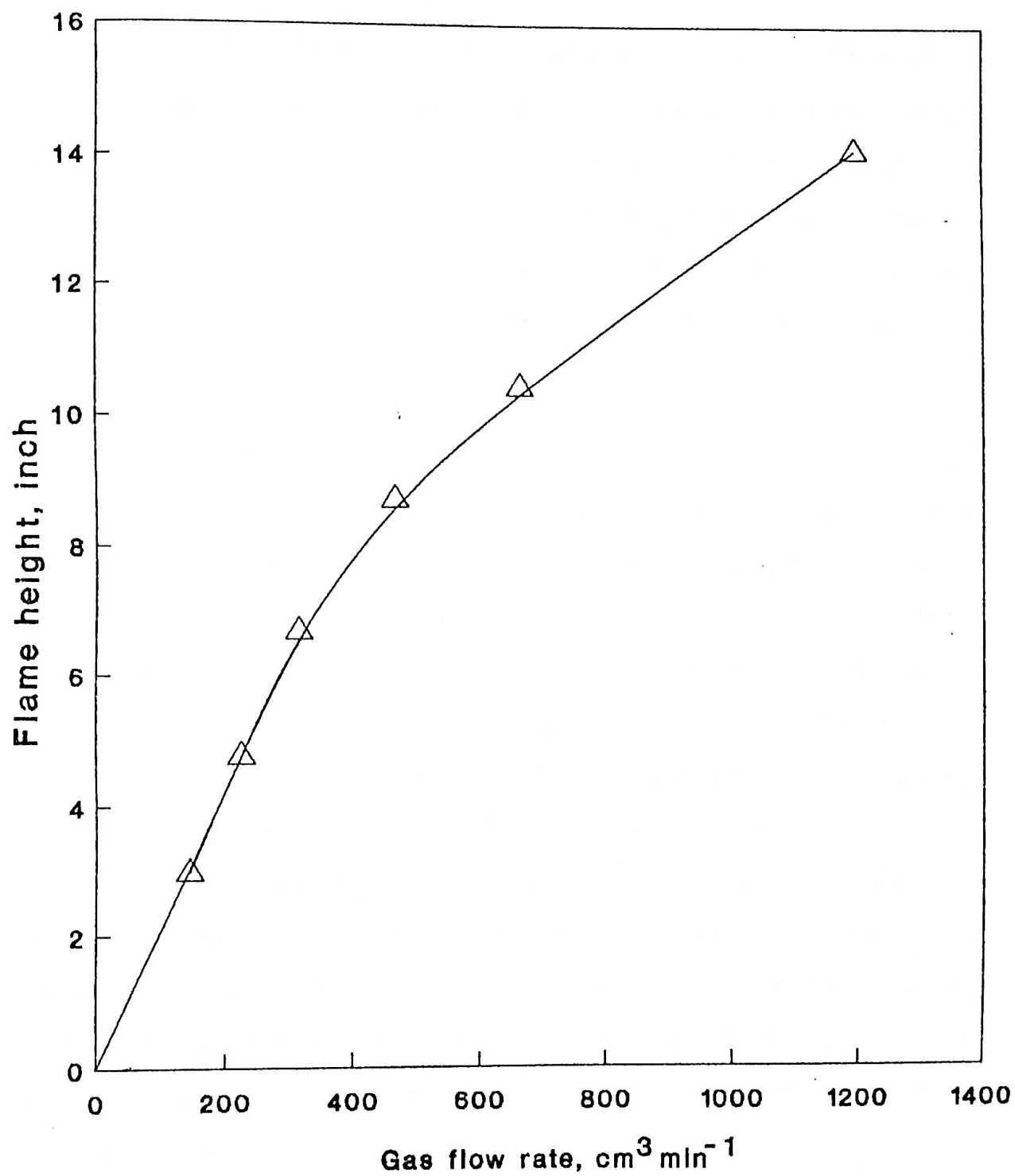


Fig. 4. Calibration of gas flow rate : flame height versus gas flow rate plot.

4.3e) THERMOSTATS : TEMPERATURE CONTROL IN LIQUID-LIQUID EXTRACTION:

In order to investigate the liquid-liquid extraction studies at constant desired temperature, a water bath has been used, whose temperature is controlled by a thermostat-regulator, a heater and a stirrer. When a temperature lower than the ambient temperature has been needed, ice is added time to time. An accurate thermometer has been used to check the actual temperature of the bath.

4.3f) ACIDITY MEASUREMENT : PH METER :

A "Corning-7" model pH meter (assembled with a glass and a colomel reference electrode) has been used for the measurement or for the adjustment of acidity and alkalinity (more accurately hydrogen ion activity) of the aqueous solutions. The operating procedure is simple. The temperature compensator is first set. The glass electrode is cleaned and dipped into the distilled water for a short time, and then inserted into a buffer solution of known pH (pH 0.65-5). After giving power to the instrument, the galvanometer reading is adjusted to the known pH of the solution by adjusting the amplifier control. The electrodes are washed several times with distilled water and the residual water present on the surface of the electrodes is removed by touching a filter paper. The test solution is taken in a beaker and electrodes are dipped into the solution to read the pH of the solution.

4.3g) SIZE REDUCTION : THE BALL MILL :

A Ball Mill (Norton, Chemical Process Products Division, SL. No. CV-75138) has been used for dry-grinding of ilmenite. It consists of bowl

containing about thirty porcelain balls of different sizes and two slow rotating rolls on which the bowl can rotate. The grinding action is achieved by impact of the balls in the bowl.

4.3h) SIZE SORTING : THE SIEVE SHAKER :

During the grinding operation in Ball Mill, the particles of different size of the ground ilmenite have been separated from time to time by a Kurl Kolb Sieve Shaker (220 v, 50 Hz) to avoid over-grinding. Three sieves, viz. 200 μm , 125 μm and 65 μm sieves have been used. The fractions collected over 200 μm and 125 μm sieves are charged to the Ball mill for regrinding, whereas the fraction collected over 65 μm sieve is stored in a dry bottle for use in the experiment. The under-size from the 65 μm sieve has been rejected. The sieving is affected by the simultaneous circular and vertical vibratory motions on the sieve.

4.3i) X-RAY DIFFRACTOMETER :

The X-ray powder diffraction patterns of the samples were recorded according to the step scanning procedure (step size, 0.03°) using a computerized Philips PW 1710 Diffractometer using Nickel filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$) at 40 K $\bar{\text{v}}$ and 20 mA. The X-ray patterns were taken with complements from the laboratory of Inorganic Chemistry, Department of Chemistry, Perugia University, Perugia, Italy. The interlayer spacings ("d" values) were calculated from the 2 θ values of maximum inflections as given in the chart in Appendix-I.

4.4 EXPERIMENTAL PROCEDURES

4.4a) EXPERIMENTAL SET-UP AND PROCEDURES FOR DIFFERENT THERMAL TREATMENTS OF ILMENITE PRIOR TO LEACHING :

The following experimental set-up (Fig. 5) was used for thermal treatment of ilmenite in presence of liquified petroleum gas (LPG). A definite amount of ilmenite (5 g $<125 >63 \mu\text{m}$) was taken on a stainless steel boat (17.5 cm long, O.D 2.05 and ID 1.96 cm). The boat was placed inside a steel pipe, which was 92 cm long, 2.73 cm in OD and 2.18 cm in ID. To facilitate the placement and removal of boat, a steel wire (30 cm) was connected to the boat. The steel pipe was put in a horizontal position in one of the two tube-holes of an electric tube furnace. One end of the pipe was connected to a LPG cylinder through a high temperature cork and polypropylene tube. Within the cork and main stopper of the cylinder, the polypropylene tube was provided with a screwed gas flow regulating clip. The screwed regulating clip was used instead of a common regulator as indicated previously (Vide Sec. 4.3d). The other end of the steel pipe was connected to a Bunsen Burner through a high temperature cork and polypropylene tube. Bunsen Burner was used to burn off the out coming gases such as non-pyrolysed LPG and hydrogen.

For carrying out a roasting experiment, the boat containing the ilmenite was placed inside the steel pipe and all the connections were made air tight. The gas flow rate was then fixed by opening the cylinder cork completely and adjusting the flow stopper to get a certain flame height corresponding to a definite flow rate. After this adjustment, the gas flow

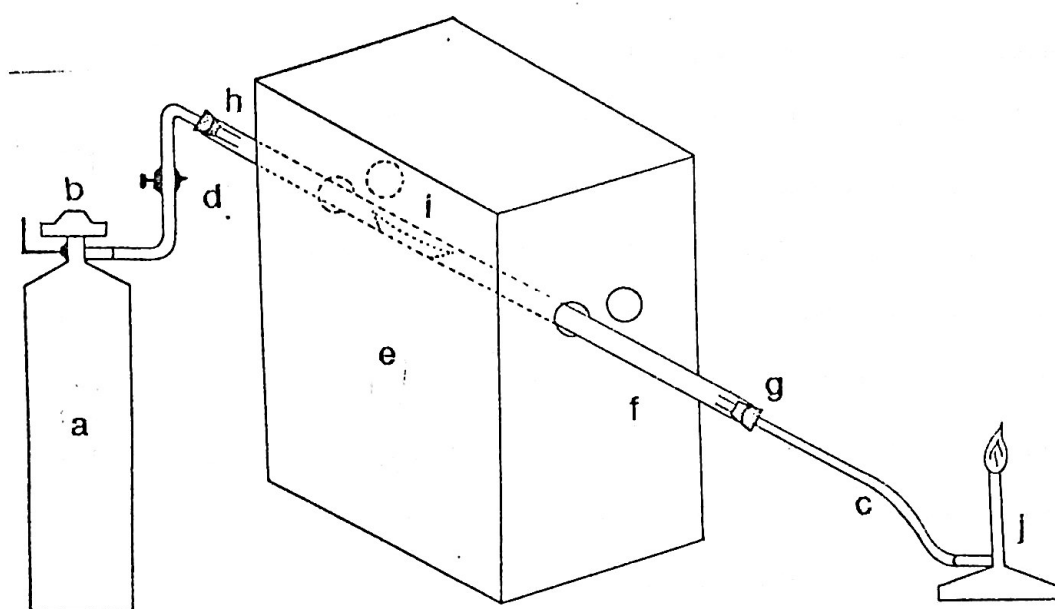


Fig. 5. *Experimental set-up for thermal treatment of ilmenite in presence of liquified petroleum gas.* a, LPG cylinder; b, regulator of the cylinder; c, rubber connecting tube; d, gas flow regulating clip; e, electric tube furnace; f, GI steel pipe; g, rubber cork; h, glass tube; i, steel boat containing ilmenite and j, gas burner.

was stopped by the cylinder cork only. The ilmenite inside the steel pipe was pre-heated to a desired temperature by the electric furnace. The temperature of the furnace was thermostated within $\pm 15^{\circ}\text{C}$, and occasionally verified by a pyrometer (Alnor instrument company, upto 2500°C).

On attainment of the desired temperature, the gas was allowed to flow through steel pipe at the pre-fixed flow rate just by operating the cylinder cork and the out coming gases was burnt off. After passing the gas for a definite time, the temperature was allowed to fall to $\sim 150^{\circ}\text{C}$. The material on the steel-boat was then taken out with the aid of the attached wire. It was cooled to room temperature over P_4O_{10} in a desiccator and then weighed.

As it was not possible to measure the extent of roasting by the analysis of the out coming gases for laboratory facility limitations, any change obtained from this treatment was realised by comparing the percentages of metals dissolved on leaching of the treated product in 6 g eq dm^{-3} HCl and H_2SO_4 with those obtained for the non-treated ilmenite leached with the same acid concentrations. The treated material was also analysed by the powder X-ray diffraction and compared with that for non-treated ilmenite.

The experimental set-up used for treatment of ilmenite powder with LPG-water vapour mixture in presence of nickel powder as catalyst was essentially the same as described above. However, there were some differences, which are described below :

1. Here two steel pipes were used; one (pipe I) containing the ilmenite powder and the other containing the nickel powder (pipe II) on steel boats.

2. Pipe II was connected air-tightly to the LPG cylinder through a water-bubbling device which was immersed upto its neck in a thermostatic water bath ($\pm 0.5^\circ\text{C}$). The LPG flow rate was adjusted as described earlier. The gas was then allowed to be saturated with the water vapour at a desired temperature by bubbling and finally the LPG-water vapour mixture was passed through the pipe II containing the catalyst at a desired high temperature.
3. The outcoming gas-mixture from the pipe II was allowed to enter the pipe I containing the ilmenite powder.

Here also the course of the thermal treatment was followed by leaching and X-ray powder diffraction measurements.

A similar experimental set-up using only one steel pipe was used for the salt (NaCl , Na_2SO_4 , NaNO_3 , Na_2CO_3)- H_2O vapour roasting. In these cases, nitrogen as carrier gas was used. Nitrogen at a given flow rate was saturated with water vapour at a given thermostated temperature and was allowed to pass through the steel pipe containing ilmenite powder and the salt at a given ratio on a ceramic or fired earthen boat. Steel boat was not suitable for its attack by the liberated acid during the thermal hydrolysis of the salts. The acid attack was also encountered with the steel pipe. As we could not replace the steel pipe with an acid resistance pipe, the normal procedure^{254,255} for studying the salt-water vapour roasting was not followed. Consequently, the courses of the salt-water vapour roasting were again determined by leaching and X-ray powder diffraction.

4.4b) EXPERIMENTAL SET-UP AND PROCEDURE FOR LEACHING :

Most of the leaching experiments were done at the boiling points of the leaching agents. For boiling temperature leaching, 50 cm³ leaching agent (e.g. 6 g eq dm⁻³ HCl or H₂SO₄) was taken in a pyrex made 250 cm³ flat bottomed distilling flask. It was agitated and heated under reflux with the help of a magnetic hot plate. The rotating speed of the stirring plastic coated steel capsule was kept at 300 r.p.m. in most of the cases, otherwise stated. When the leaching agent started to boil, the refluxing device (a pyrex tube of length 1.5 m with a rubber cork) was opened and a weighed amount (1 g) of the material to be leached was introduced. To effect proper refluxing, the lower part of the refluxing tube was cooled by wet cloth wrapping. As soon as the material to be leached was added to the leaching agent, the time of leaching was counted. After certain intervals, aliquots of the leaching solution (0.5 cm³) were withdrawn from the flask twice, one for titanium (IV) and other for iron (total) estimations in leach solution.

When the leachings were to be done at lower temperature, the leaching flask was placed inside a beaker containing water at a thermostated temperature, which itself was placed on the magnetic hot plate. The water in the beaker and the leaching agent in the leaching flask were agitated magnetically by the same equipment but with different stirring capsules.

4.4c) PROCEDURES FOR LIQUID-LIQUID EXTRACTION AND STRIPPING :

In order to separate Fe³⁺ from Ti⁴⁺ in leach solution, the method of liquid-liquid extraction and stripping have been applied to the leach solution. In preliminary experiments, the extraction characteristics of Fe³⁺

and Ti^{4+} were found out with methylisobutyl ketone and di-2-ethylhexyl-phosphoric acid. Since it will be seen later that the best leaching was obtained with hydrochloric acid, the extraction characteristics was also investigated from the hydrochloric acid medium. In small scale preliminary experiments, aliquots of aqueous and organic phases (20 cm^3 each) were taken in 125 cm^3 reagent bottle, shaken for a pre-determined time period in a thermostatic water bath, settled and the aqueous phase was pipetted out for analysis of Fe^{3+} and Ti^{4+} . Sometimes, the organic phase was also analysed after back washings.

In relatively large-scale operations, about 500 cm^3 portion of aqueous phase was contacted with the extractant of definite concentration at an organic to aqueous phase ratio (O/A) of 1.

Stripping was also done in a similar way to liquid-liquid extraction. Aliquots of a suitable stripping agent (simply water for stripping of Fe^{3+} from loaded MIBK phase, and 1 g mol dm^{-3} sodium carbonate or 6 g eq dm^{-3} hydrochloric acid solution for stripping of Ti^{4+} from loaded HDEHP phase) and the loaded organic phase (O/A = 1) were taken in a 1 dm^3 separating funnel, shaken for about 5 minutes, settled and separated. In the case of stripping of Ti(IV) from HDEHP solution with hydrochloric acid solution (6 g eq dm^{-3}) the O/A ratio was kept at 10 to increase the concentration of Ti(IV) in the stripped solution.

4.4d) PROCEDURES FOR REGENERATION OF EXTRACTANTS AND PRECIPITATION OF METALS :

During the stripping operations of metal-loaded organic phase, the metals transferred to the aqueous phase and the organic phase became

almost free from metals, which could be used further for extraction. So, the procedures for regeneration of extractant and the stripping were not different.

The precipitation of Fe^{3+} from the aqueous stripped solution could be easily done by the addition of a small amount of an alkali solution. The precipitate could be filtered as $\text{Fe}(\text{OH})_3$ and ignited to Fe_2O_3 . Titanium (IV) in the stripped sodium carbonate solution was precipitated as metatitanic acid, H_2TiO_3 spontaneously as the stripping proceeded. The precipitate could be easily filtered, room-dried and ignited at 900°C to get TiO_2 powder.

EXPERIMENTS, RESULTS AND DISCUSSION

5.1 LEACHING OF NON-TREATED ILMENITE POWDER BY DIFFERENT MINERAL ACIDS

The amounts of titanium and iron dissolved on leaching of non-treated ilmenite powder ($<125\ \mu\text{m}$) by different acid ($2\ \text{g eq dm}^{-3}\ \text{H}_2\text{SO}_4$, HCl , HNO_3 , HClO_4 and HF) at their boiling temperatures have been determined at a solid to liquid ratio (S/L) of $0.05\ \text{kg dm}^{-3}$. The results are given in Table E at three different leaching times.

Table E. *Amounts of titanium and iron dissolved on leaching of non-treated ilmenite sand by different acids.*

Temperature = boiling temperature ($\sim 110^\circ\text{C}$),

S/L = $0.05\ \text{kg dm}^{-3}$,

Particle size = $<125\ \mu\text{m}$,

Acid concentration = $2\ \text{g eq dm}^{-3}$,

Weight of ilmenite = $5\ \text{g}$ ($\equiv 1.39\ \text{g}$ titanium and $1.62\ \text{g}$ iron).

Acid	Wt % of metals dissolved (± 0.05)					
	5h		15h		30h	
	Ti	Fe	Ti	Fe	Ti	Fe
HF	41.0	3.8	45.0	6.2	45.0	10.0
HCl	2.5	0.7	3.6	1.2	3.6	1.8
HNO_3	1.4	1.6	1.8	3.6	2.1	6.2
H_2SO_4	2.5	2.6	3.1	9.0	3.1	11.9
HClO_4	1.6	0.2	2.0	0.3	2.1	0.4

It is apparent from Table E that excepting hydrofluoric acid, the investigated most common mineral acids in diluted conditions are not at all effective for acceptable extent of leaching of the non-treated ilmenite. A thorough study on the direct leaching of ilmenite powder with hydrofluoric acid was carried out in our laboratories by other workers and reported⁹⁸. The methods for the purification of hydrofluoric acid leach solution (separation of $\text{Fe}^{3+}/\text{Fe}^{2+}$ from Ti^{4+}) were encountered with some special types of problems, e.g. $\text{Fe}^{3+}/\text{Fe}^{2+}$ could not be separated efficiently from Ti^{4+} in presence of fluoride ion by the most common acidic, basic or neutral extractants²¹³. Consequently, we realised that the hydrofluoric acid leaching route for processing ilmenite should be avoided and a more common acid should be applied technically, so that the post-leaching processes become simple.

With hydrochloric and sulphuric acids the percentages of titanium and iron dissolved have been found to be increased with increasing their concentrations. Table I in the Experimental Data Section and Fig. 6 shows the percentages of titanium and iron dissolved at different time intervals with 6 g eq dm^{-3} hydrochloric and sulphuric acids at their boiling points. It is found that the percentages of titanium and iron dissolution are increased with increasing the leaching time (upto 4h) in hydrochloric acid medium with maximum dissolutions of ~53.5% Ti and 60.0% Fe, in comparison to 3.6% Ti and 1% Fe dissolutions in 2 g eq dm^{-3} HCl medium. With further increasing the concentration of hydrochloric acid, the dissolution percentages are not so increased further. With 6 g eq dm^{-3} sulphuric acid as leaching agent, the maximum dissolutions have not been obtained even

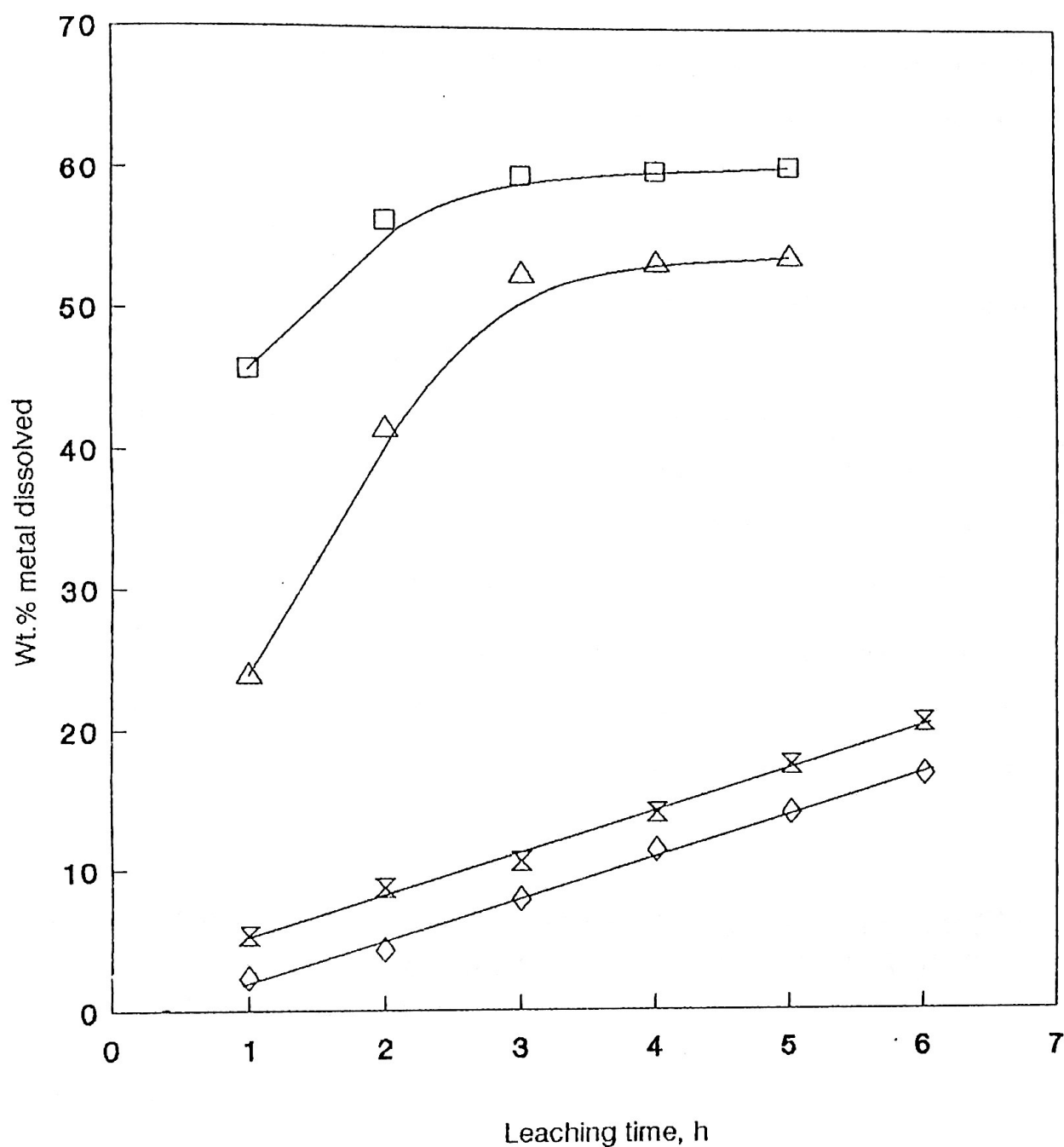


Fig. 6. Plot of weight percentage of metals dissolved versus leaching time of non-treated powdered ilmenite. (Δ): Ti, HCl; ($\square$): Fe, HCl; ($\diamond$): Ti, H₂SO₄ and ($\times$): Fe, H₂SO₄. Leaching conditions : [Acid]=6 g eq dm⁻³, temp=boiling point, S/L ratio=0.02 kg dm⁻³, S=1 gm, agitation speed=292 rpm (HCl) and 372 rpm (H₂SO₄).

after 6 h's leaching. After 6 h, the percentages of titanium and iron dissolved are ~17% and 20.5%, in comparison to ~2.6% and ~3% respectively in 2 g eq dm⁻³ sulphuric acid solution.

From these studies, it is concluded that

- 1) the hydrochloric acid is a better leaching agent than sulphuric acid having identical concentrations,
- 2) The equilibrium is reached rapidly with hydrochloric acid (4 h) in comparison to that obtained with sulphuric acid (>6 h);
- and 3) The hydrochloric acid leaching is much more concentration dependent (upto 6 g eq dm⁻³) than the sulphuric acid leaching.

In all subsequent experiments, the progress of any pre-treatment of powdered ilmenite will be followed up by the leaching characteristics of the treated ilmenite with 6 g eq dm⁻³ HCl and H₂SO₄ solutions which are given in Fig. 6 or in Table I.

5.2 THERMAL TREATMENT (ROASTING) OF ILMENITE POWDER WITH LPG-PYROLYSED PRODUCTS AND SUBSEQUENT LEACHING

a) ROASTING :

The thermal decomposition of hydrocarbon is known as pyrolysis. Above 1000°C, methane is pyrolysed to carbon and hydrogen²⁵⁶. Other hydrocarbons decompose rapidly at considerably lower temperatures, 500-800°C. In presence of silica-alumina catalyst, pyrolysis occurs at still lower temperature.

Propane at 600°C decomposes to give four products : propylene, ethylene, methane and hydrogen²⁵⁷. Similarly, butane at such a temperature gives butalene, propylene, ethylene, methane and hydrogen. So with higher hydrocarbons, like butane in LPG could produce at least hydrogen at a temperature around 600°C. It is therefore expected that hydrogen in the pyrolysed product of butane/propane in LPG at a temperature around 600°C can react with ilmenite to do some changes.

The effects of the following parameters have been investigated for roasting of ilmenite with liquified petroleum gas pyrolysed products :

i) *EFFECT OF ROASTING TIME :*

A definite amount of ilmenite (5 g) have been roasted with LPG-pyrolysed product (flow rate, $230 \text{ cm}^3 \text{ min}^{-1}$) at $650 \pm 15^\circ\text{C}$ for various times of roasting such as 30, 45, 60, 75 and 90 min. The extents of roasting at various roasting times have been determined by the subsequent leaching of the roasted mass (1 g ilmenite $\equiv$ 1.014, 1.053; 1.23, 1.212 and 1.142 g roasted mass after 30, 45, 60, 75 and 90 min's roasting respectively).

The percentages of titanium and iron dissolved, on leaching of the roasted masses equivalent to 1 g ilmenite, in 50 cm^3 6 g eq dm^{-3} HCl and H_2SO_4 at different leaching times are given in Table II and plotted in Figs. 7-9, as the percentages of metals dissolved against leaching times. From these figures or Table II, the maximum percentages of titanium and iron dissolved in the acids at different roasting times have been tabulated in Table III and plotted in Fig. 10, as the maximum percentages of metals dissolved versus the roasting time.

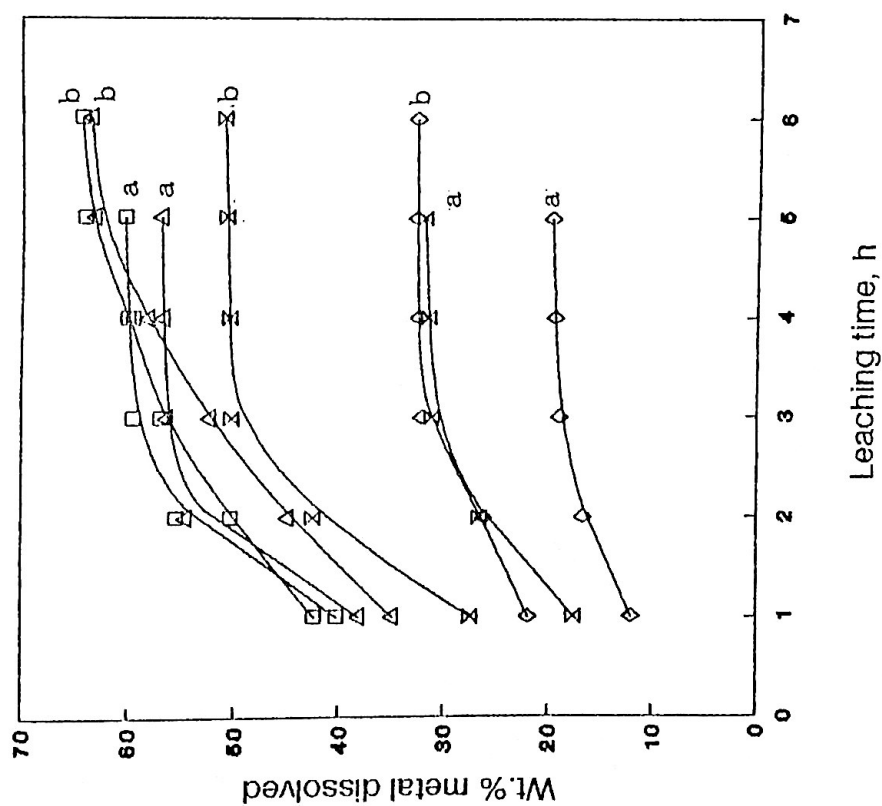


Fig. 7. Plot of weight percentage of metals dissolved versus leaching time of the roasted product of ilmenite in presence of LPG. (Δ): Ti, HCl; (□): Fe, HCl; (◇): Ti, H₂SO₄ and (Σ): Fe, H₂SO₄. Roasting conditions: temp. = $650 \pm 15^\circ\text{C}$, LPG flow rate = $230 \text{ cm}^3 \text{ min}^{-1}$. leaching conditions: temp. = boiling point, [Acid] = 6 g eq dm^{-3} , S/L ratio = 0.02 kg dm^{-3} , agitation speed = 292 rpm (HCl)/ 372 rpm (H₂SO₄). Roasting time, (a) = 30 min., (b) = 45 min.

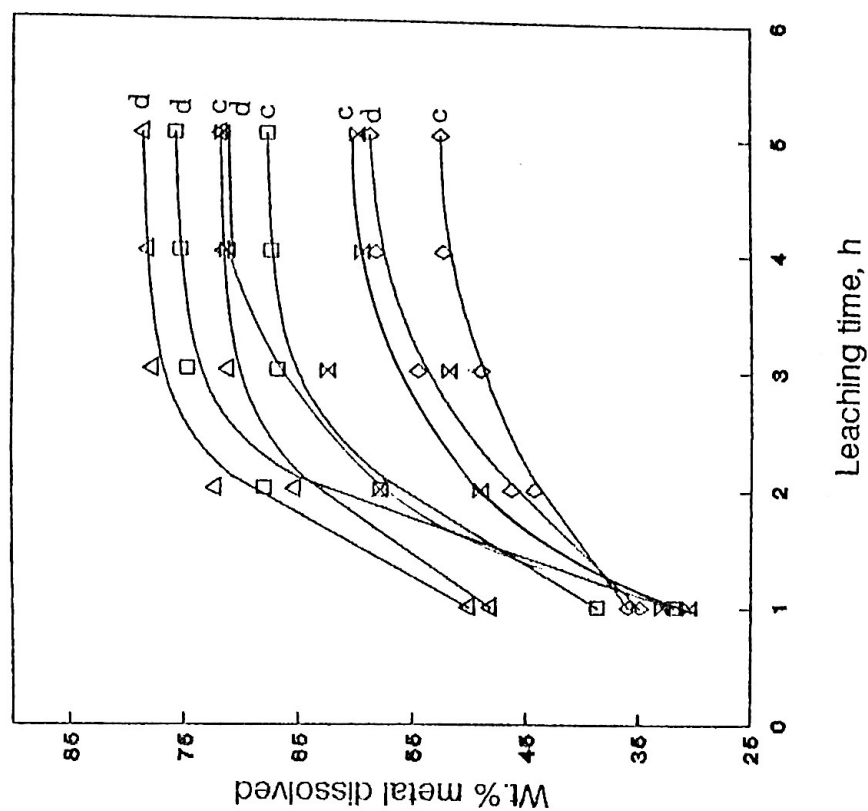


Fig. 8. Plot of weight percentage of metals dissolved versus leaching time of the roasted product of ilmenite in presence of LPG. (Δ): Ti, HCl; (□): Fe, HCl; (◇): Ti, H₂SO₄ and (Σ): Fe, H₂SO₄. Roasting and leaching conditions are as in Fig. 7. Roasting time, (c) = 60 min, (d) = 75 min.

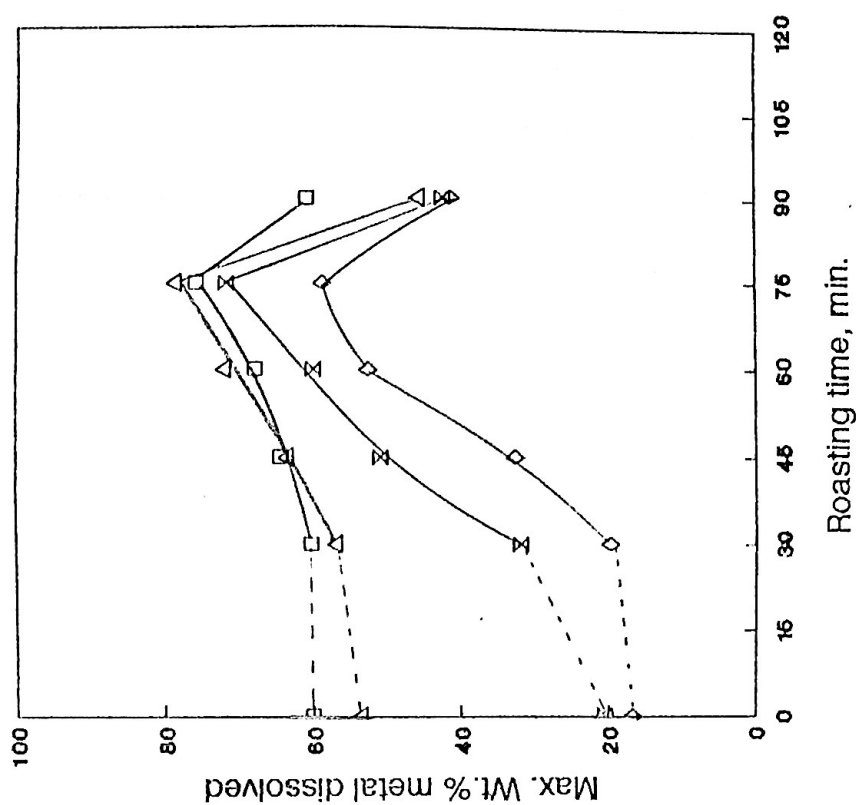


Fig. 10. Plot of maximum weight percentage of metals dissolved in 5 h versus roasting time of the roasted product of ilmenite in presence of LPG. (Δ): Ti, HCl; (□): Fe, HCl; (◇): Ti, H₂SO₄ and (Σ): H₂SO₄. Roasting and leaching conditions are as in Fig. 7.

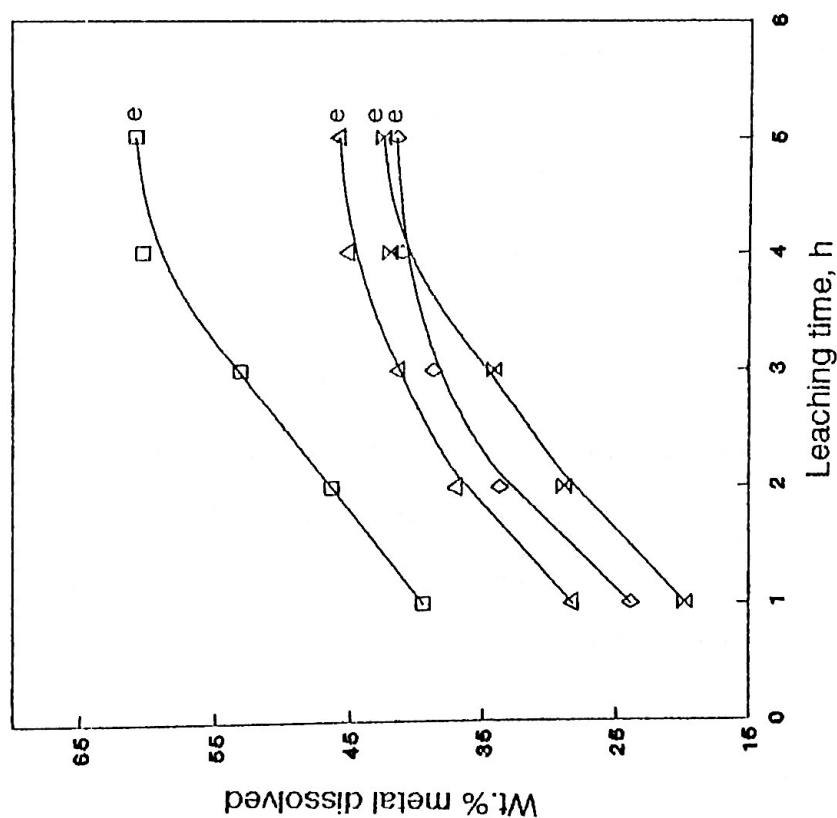


Fig. 9. Plot of weight percentage of metals dissolved versus leaching time of the roasted product of ilmenite in presence of LPG. (Δ): Ti, HCl; (□): Fe, HCl; (◇): Ti, H₂SO₄ and (Σ): Fe, H₂SO₄. Roasting and leaching conditions are as in Fig. 7. Roasting time (e) = 90 min.

It is found that the maximum percentages of titanium and iron dissolved in both leaching agents are increased with increasing the roasting time upto 75 min and then decreased sharply. The effect of the LPG-roasting time could be easily followed up by the maximum percentages of titanium and iron dissolved in 6 g eq dm^{-3} sulphuric acid. The percentages of titanium and iron dissolved in 6 h's leaching time in sulphuric acid are ~17% and 20.5% respectively for the non-treated ilmenite; and these values are increased to ~59% and 71.5% respectively in 4h's leachings for the LPG-roasting time of 75 min. Similarly, when hydrochloric acid (6 g eq dm^{-3}) is used as leaching agent, the maximum percentages of titanium and iron dissolved are increased from 53.5% and 60% for the non-treated ilmenite to 78.4% and 75.6% respectively for roasted ilmenite obtained after 75 min's roasting.

In our opinion, on heating ilmenite in presence of LPG at $\sim 650^\circ\text{C}$, the ferric oxide or the pseudo-brookite phase is converted gradually into ferrous oxide or ilmenite phase by reduction with hydrogen on carbon produced from the decomposition of liquified petroleum gas at the temperature used. Possibly, ilmenite phase is more easily dissolved in sulphuric and hydrochloric acid solutions. This phase transition is completed possibly with 75 min at the roasting conditions stated. If the roasting is prolonged after this time, the ilmenite phase is converted into another phase (may be the mixture of TiO_2 and metallic Fe) which is less susceptible to leaching with the acids under investigations. A thorough study on the different phases obtained at different roasting conditions in presence of LPG is needed to give the mechanisms of leaching. But, such a study need at

least a X-ray diffractometer and a thermal analyser for routine work. Due to the lack of such facilities in our laboratories, such attempts have not undertaken. Nevertheless as we are particularly interested on the conditions at which a maximum dissolution of titanium and iron from our source ilmenite can be obtained; the study have been continued to find out a roasting process and its condition which may give the best leaching in the said acids. Even then, some attempts have been taken to identify the phases giving the best dissolutions by X-ray analysis which will be discussed later at the end of each section.

ii) EFFECT OF ROASTING TEMPERATURE :

5 g ilmenite have been roasted with LPG pyrolysed product (flow rate, $230 \text{ cm}^3 \text{ min}^{-1}$) for 75 min at various temperatures such as (600 ± 15) , (650 ± 15) , (700 ± 15) , (750 ± 15) and $(800 \pm 15)^\circ\text{C}$. The extents of roasting at various roasting temperatures have been determined by the subsequent leaching of the roasted mass equivalent to 1 g ilmenite ($\approx 1.085, 1.212, 1.292, 1.951$ and 3.78g roasted mass at $600, 650, 700, 750$ and 800°C respectively). Around and above 700°C , the amount of carbon deposited is very high; and it appears that the carbon deposition is increased with increasing temperature which could easily be followed up by the weight gain of the roasted mass.

The percentages of titanium and iron dissolved on leaching of the roasted masses obtained at different roasting temperatures at different leaching times are given in Table IV. The plots similar to these given in Figs. 7-9 could be drawn to find out the maximum percentages of metals

dissolved on roasting at different temperatures. However, such plots have not been included for simplicity; and the maximum percentages of titanium and iron dissolved at different parameters could easily be evaluated from the Table IV.

The maximum percentages of titanium and iron dissolved in 6 g eq dm⁻³ hydrochloric and sulphuric acids are given in Table V for different roasting temperatures; and these data have been plotted in Fig. 11, as the maximum weight percentages of metals dissolved against the roasting temperatures in °C.

With both leaching agents, it is found that the maximum weight percentages of titanium and iron dissolved pass through maxima at a roasting temperature of 700°C. The roasting at 700°C for 75 min gives a product which on dissolution gives 82.8% titanium and 79.1% iron dissolutions in 6 g eq dm⁻³ hydrochloric acid, whereas in 6 g eq dm⁻³ sulphuric acid medium, the maximum dissolutions of 65% titanium and 72.9% iron are obtained. With further increase in the roasting temperature, say to 800°C, the maximum percentages of metals dissolved are decreased sharply. The roasted mass at 800°C for 75 min gives 28.7% titanium and 51.7% iron dissolutions in 6 g eq dm⁻³ hydrochloric acid and 17.5% titanium and 48.7% iron dissolutions in 6 g eq dm⁻³ sulphuric acid. From these results, it is concluded that the optimum LPG-roasting temperature is 700°C and the roasting over 700°C will greatly decrease in the dissolution characteristics of the roasted mass together with the associated high carbon deposition on roasted mass.

The pyrolysis of butane or propane in LPG at a temperature 800°C,

should give only hydrogen, methane, other lower molecular weight saturated and unsaturated hydrocarbons but not carbon. However, in our experiments, we found the carbon deposition on ilmenite even at 600°C. Exact reason for this is not known to us. It is likely however that the constituents of the used ilmenite may anyhow act as catalyst for the decomposition to carbon from methane produced on pyrolysis. This proposition has been suggested on the ground that the carbon deposition takes place only over the ilmenite powder, but not on the edges of the boat or on any other places within the tube. Since roasting time is quite long (over 1h), to perform the roasting at higher temperature is not possible due to the enormous quantities of carbon deposition.

iii) EFFECT OF LPG-FLOW RATE :

To study the effect of LPG-flow rate on roasting, 5 g ilmenite has been roasted at $(700 \pm 15)^{\circ}\text{C}$ for 75 min at various LPG flow rates of 150, 190, 230, 270 and $310 \text{ cm}^3 \text{ min}^{-1}$. The extents of roasting at different gas flow rates have been understood from the leaching results of the roasted masses (1 g ilmenite $\equiv$ 1.471, 1.375, 1.292, 2.641 and 3.99 g at gas flow rates of 150, 190, 230, 270 and $310 \text{ cm}^3 \text{ min}^{-1}$ respectively). Above and below the gas flow rates of $230 \text{ cm}^3 \text{ min}^{-1}$, the weights of the roasted masses indicate that the amount of deposited carbon is very high.

The percentages (wt) of titanium and iron dissolved on leaching of the roasted masses equivalent to 1 g ilmenite with $50 \text{ cm}^3 \text{ 6 g eq dm}^{-3}$ hydrochloric and sulphuric acids are given in Table V. From this Table, the maximum weight percentages of titanium and iron dissolved on leaching with

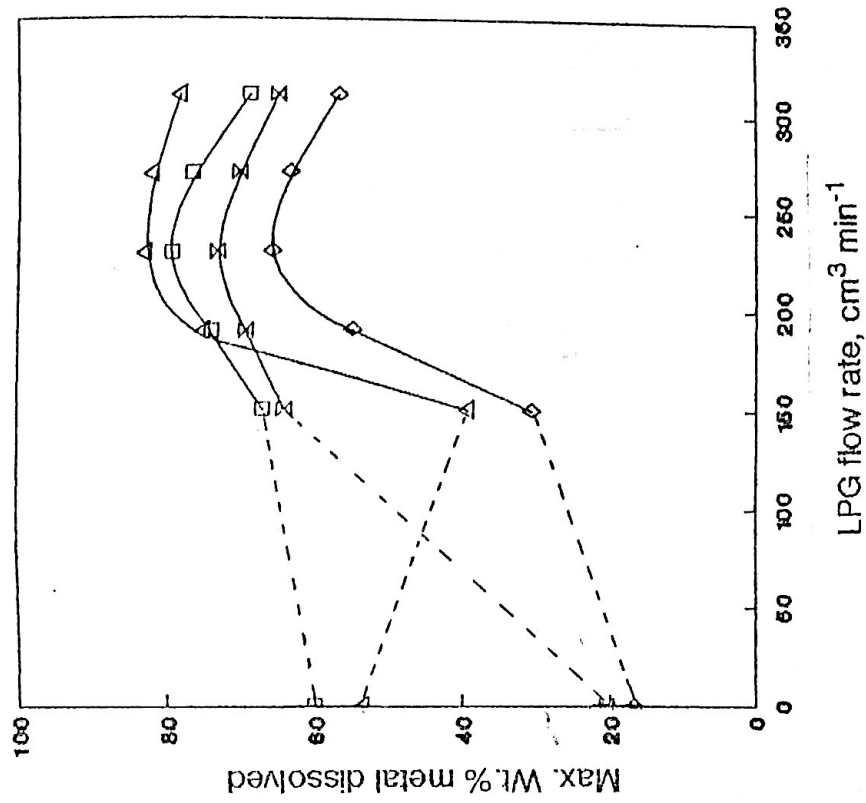


Fig. 11. Plot of maximum weight percentage of metals dissolved in 5 h versus roasting temperature of the roasted product of ilmenite in presence of LPG. (Δ): Ti, HCl; (□): Fe, HCl; (◇): Ti, H₂SO₄ and (Σ): Fe, H₂SO₄. Roasting conditions: time=75 min. LPG flow rate=230 cm³ min⁻¹, leaching conditions are as in Fig. 7.

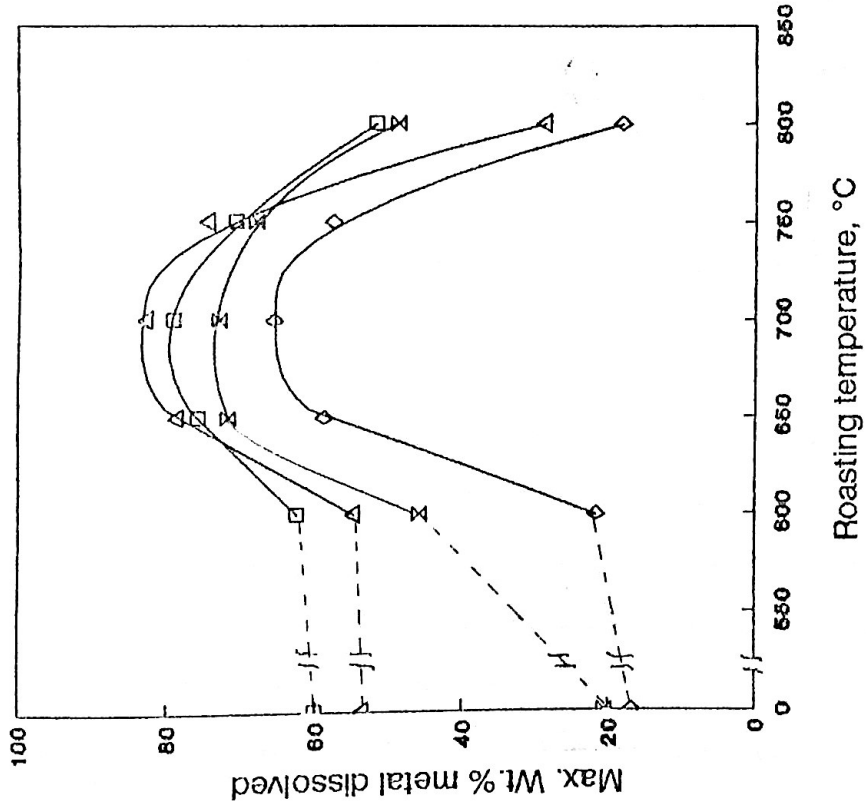


Fig. 12. Plot of maximum weight percentage of metals dissolved in 5 h versus roasting LPG flow rate of the roasted product of ilmenite in presence of LPG. (Δ): Ti, HCl; (□): Fe, HCl; (◇): Ti, H₂SO₄ and (Σ): Fe, H₂SO₄. Roasting conditions: time=75 min, temp=(700±15)°C. Leaching conditions are as in Fig. 7.

both leaching agents are given in Table VII for different gas flow rates. Figure 12 represents the data in Table VII graphically as the maximum wt.% metals dissolved versus roasting gas flow rate in $\text{cm}^3 \text{min}^{-1}$.

It is seen from the figure that the maximum wt. percentages of both titanium and iron in either of the leaching agents are increased with increasing the gas flow rate sharply upto $230 \text{ cm}^3 \text{min}^{-1}$ and then gradually decreased, particularly in the case of titanium dissolution. For example about 83% titanium dissolution from the roasted mass obtained in presence of gas flow rate of $230 \text{ cm}^3 \text{min}^{-1}$ is decreased to only ~39%, 74%, 81.7% and 78% titanium dissolution from the roasted masses obtained in presence of gas flow rate of $150 \text{ cm}^3 \text{min}^{-1}$, $190 \text{ cm}^3 \text{min}^{-1}$, $270 \text{ cm}^3 \text{min}^{-1}$ and $310 \text{ cm}^3 \text{min}^{-1}$ respectively. It may therefore be concluded that the optimum LPG flow rate should be about $230 \text{ cm}^3 \text{min}^{-1}$ and the roasting in presence of a lower gas flow rate will greatly decrease the dissolution percentage of titanium associated with higher amounts of carbon deposition on the roasted mass. However, the reason why the higher amounts of carbon deposition takes place below the gas flow rate of $230 \text{ cm}^3 \text{min}^{-1}$ is not clear to us.

iv) EFFECT OF PARTICLE SIZE :

In all the above experiments, the ilmenite powder fraction having particle size $>63 \mu\text{m}$ $<125 \mu\text{m}$ has been used. In order to find out the effect of particle size of ilmenite on roasting, 5 g ilmenite of different particle size such as $<63 \mu\text{m}$, $>63 \mu\text{m}$ $<125 \mu\text{m}$ and $>125 \mu\text{m}$ has been roasted at $(700 \pm 15)^\circ\text{C}$ for 75 min at a gas flow rate of $230 \text{ cm}^3 \text{min}^{-1}$. After roasting, the roasted masses corresponding to 1 g ilmenite have been leached with 6 g eq dm^{-3} hydrochloric and sulphuric acids, to estimate the maximum percentages of

titanium and iron dissolved for different size fractions. The results are given in Table F.

The results given in the Table indicate that the roasting and subsequent leaching with hydrochloric acid is little affected by the particle size of ilmenite used in roasting. However, for sulphuric acid as leaching agent, the roasting or more probably the subsequent dissolution of titanium and iron is decreased with decreasing the particle size. The cause of this behaviour is not known to us. Nevertheless it should be pointed out here that during leaching, as the particle size decreases, the particles covered with deposited carbon are floated out of the level of the leaching agent and adheres to the side of the vessel, which may influence the dissolution characteristics.

Table F. *Effect of particle size on roasting.*

Roasting time = 75 min

Roasting temperature = $(700 \pm 15)^{\circ}\text{C}$

Roasting LPG flow rate = $230 \text{ cm}^3 \text{ min}^{-1}$

Leaching temperature = boiling temperature

Acid concentrations = 6 g eq dm^{-3}

Solid to liquid (S/L) ratio = 0.02 kg dm^{-3}

Leaching agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Particle size, μm	Max. wt. % metals dissolved in 6 g eq dm^{-3} HCl		Max. wt. % metals dissolved in 6 g eq dm^{-3} H_2SO_4	
	Ti	Fe	Ti	Fe
<63	82.8	80.6	44.7	36.5
>63<125	85.0	82.1	52.3	60.8
<125	82.8	79.1	65.0	77.8

Roasted Product :

Knowing the best conditions for the LPG-roasting of ilmenite, about 60 g ilmenite (in 12 sets) have been roasted at $(700 \pm 15)^{\circ}\text{C}$ for 75 min at LPG flow rate of $230 \text{ cm}^3 \text{ min}^{-1}$. To verify any change occurring in ilmenite during the roasting process, the X-ray diffraction patterns of the pre-treated and roasted ilmenite obtained under the above condition have been taken for comparison. The diffraction patterns of the two samples are given in Fig. 13. The 'd' spacings of the two samples are also given in Table G, which also includes the 'd' values of synthetic ilmenite (pure) collected from the ASTM cards.

It is seen from the table and the figure that the X-ray pattern of pure ilmenite with high intensities also appeared in non-treated and the LPG-roasted ilmenite samples. Low intensity peaks disappear. Some additional peaks with moderate intensities appeared in our source ilmenite sample, indicating the presence of other crystalline phase in the sample as expected. These additional peaks disappear in the LPG-roasted mass to give another new set of peak pattern. High value of the 'd' spacing in the roasted mass ($d = 9.923 \text{ \AA} \text{ \& } 8.310 \text{ \AA}$) suggests the formation of a clay like phase from the impurities in ilmenite. This clay like phase probably catalyses the carbon deposition on ilmenite.

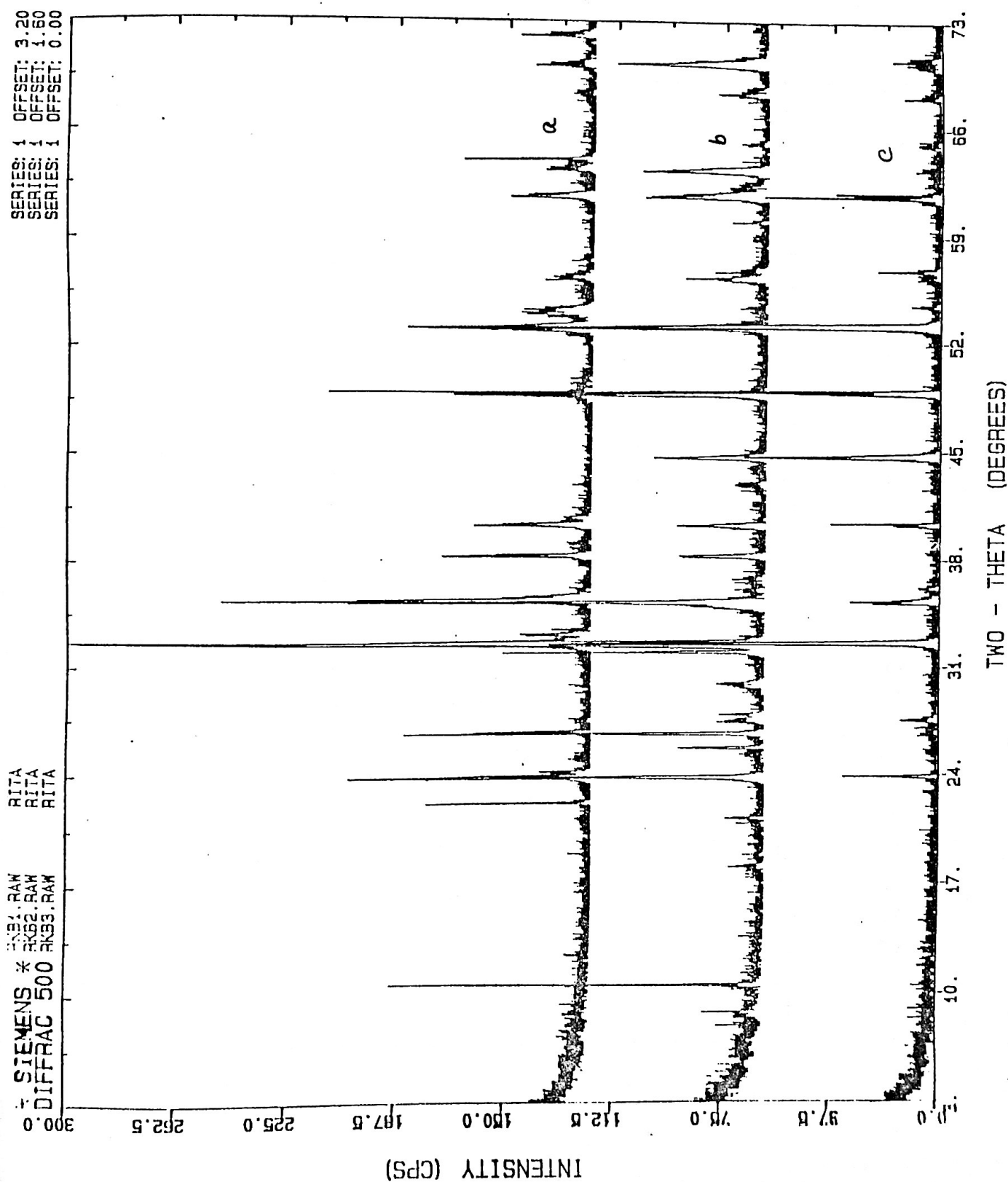


Fig. 13. X-ray diffraction patterns of (a) Non treated ilmenite (b) LPG roasted ilmenite product (c) LPG water vapour roasted ilmenite product in presence of nickel catalyst.

Table G. *X-ray diffraction patterns of ilmenite and the LPG-roasted ilmenite (at 700°C, for 75 min, in presence of LPG flow rate of 230 cm³ min⁻¹).*

Ilmenite our sample		Ilmenite from ASTM card		LPG-roasted Ilmenite	
d, °A	RI	d, °A	RI	d, °A	RI

a) Common peaks

3.723	41.4	3.737	30.0	3.723	34.9
2.745	100.0	2.754	100.0	2.745	100.0
2.534	70.0	2.544	70.0	2.539	57.2
2.344	34.1	2.349	2.0	2.347	11.3
2.231	22.4	2.237	30.0	2.231	10.8
1.865	30.3	1.868	40.0	1.865	35.1
1.725	33.7	1.726	55.0	1.723	29.1
1.503	18.6	1.506	30.0	1.505	17.2
1.467	10.3	1.468	35.0	1.469	17.3

b) Additional peaks

4.000	38.7	2.177	2.0	9.923	6.4
3.329	23.4	2.103	2.0	8.310	44.1
2.693	12.6	1.831	1.0	4.177	4.2
1.694	13.6	1.653	2.0	3.454	11.8
1.688	11.5	1.635	9.0	3.336	51.9
1.454	30.1	1.621	3.0	3.236	5.1
		1.434	1.0	2.789	38.9
				2.514	5.3
				2.436	4.2
				2.023	14.4
				1.632	10.1
				1.621	7.6
				1.541	5.3

b) LEACHING :

To investigate the effect of various parameters on leaching characteristics of roasted mass, the material prepared under the best conditions has been used. The effects of the following parameters have been studied :

i) EFFECT OF ACID CONCENTRATION :

A selected amount of ilmenite roast equivalent to 1 g ilmenite has been leached with HCl and H_2SO_4 of different concentration such as 2, 4, 5, 6 and 8 g eq dm^{-3} at a solid to liquid phase ratio (S/L) 0.02 g dm^{-3} and at boiling temperatures. The weight percentages of titanium and iron dissolved at various leaching intervals (1-5h) are given in Table VIII. However, the weight percents of metals dissolved against various acid concentrations are not shown graphically for simplicity. The maximum percentages of titanium and iron dissolved in both acids of different concentration are evaluated from the above table, and tabulated in Table IX and represented graphically in Fig. 14.

It is seen from the above figure that the maximum weight percentages of titanium dissolutions are very much decreased in both acids at concentrations below 6 g eq dm^{-3} particularly. The iron dissolutions are also decreased similarly. In the acid concentration region above 6 g eq dm^{-3} , the maximum dissolution percentages are little increased with increasing concentration. The effect of acid concentration on the titanium and iron dissolutions from the roasted mass is very sharp in the acid concentration range of 4 to 6 g eq dm^{-3} for both acids. It is therefore concluded that the

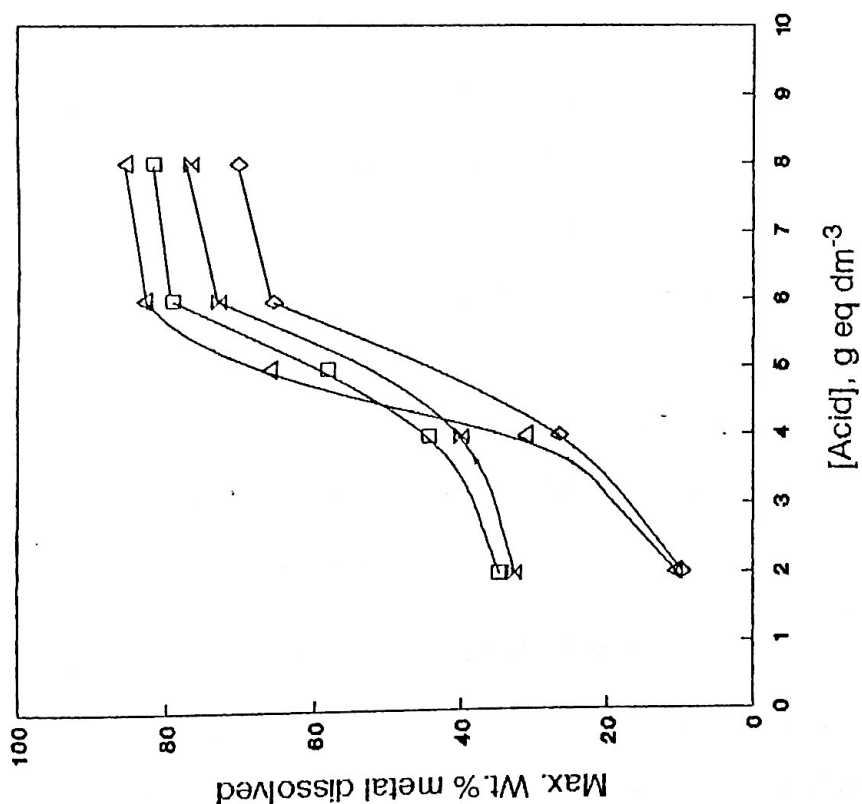


Fig. 14. Plot of maximum weight percentage of metals dissolved in 5 h versus the concentrations of leaching acids on the leaching of the LPG roasted ilmenite product. (Δ): Ti, HCl; ($\square$): Fe, HCl; ($\diamond$): Ti, H₂SO₄ and ($\times$): Fe, H₂SO₄. Roasting conditions: time=75 min, temp.= (700±15)°C, LPG flow rate=420 cm³ min⁻¹. Leaching conditions: temp.=boiling point, agitation speed=292 rpm (HCl)/372 rpm (H₂SO₄), S/L=0.02 kg dm⁻³, S=1 g.

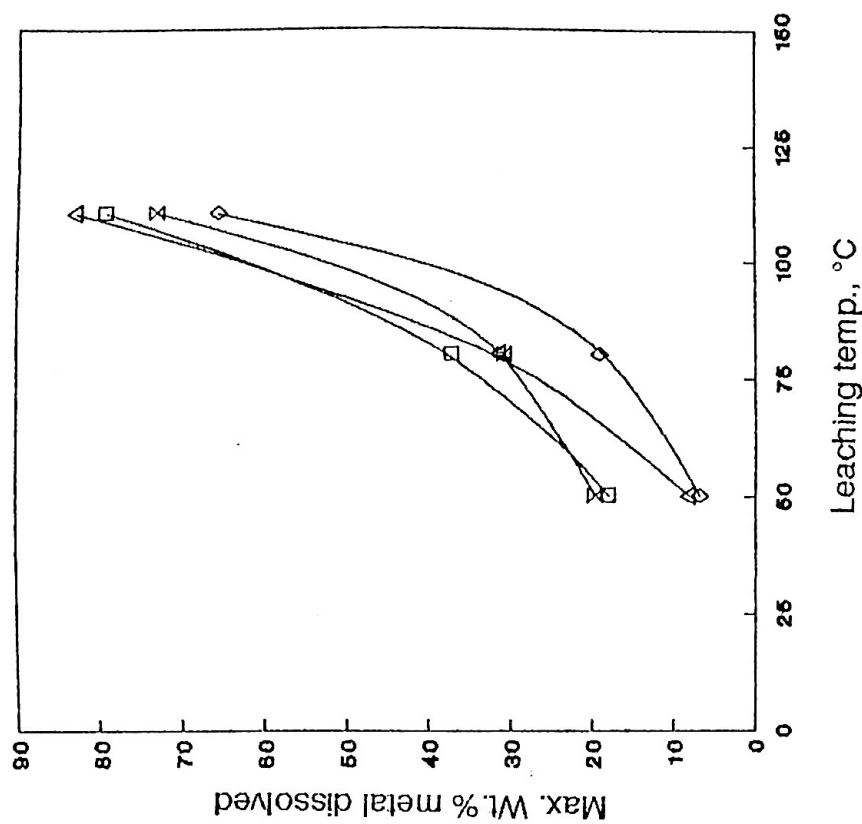


Fig. 15. Plot of maximum weight percentage of metals dissolved in 5 h versus leaching temperature on the leaching of the LPG roasted ilmenite product. (Δ): Ti, HCl; ($\square$): Fe, HCl; ($\diamond$): Ti, H₂SO₄ and ($\times$): Fe, H₂SO₄. Roasting conditions are as in Fig. 14. Leaching conditions: [Acid]=6 g eq dm⁻³, agitation speed=292 rpm (HCl)/372 rpm (H₂SO₄), S/L=0.02 kg dm⁻³, S=1 g.

hydrochloric or sulphuric acid concentration of 6 g eq dm^{-3} is quite effective for the efficient leaching of the LPG roasted ilmenite.

ii) *EFFECT OF TEMPERATURE :*

The roasted ilmenite equivalent to 1 g ilmenite has been leached with 6 g eq dm^{-3} hydrochloric and sulphuric acids at S/L ratio 0.02 kg dm^{-3} and at various leaching temperatures such as 50 ± 2 , 80 ± 2 and $110 \pm 2^\circ\text{C}$ (boiling temperature). Table X shows the experimental results. From this table, the maximum weight percentages of titanium and iron dissolved in both acids obtained at different leaching temperatures are given in Table XI. The data given in table have been plotted as maximum weight percentages of metals dissolved versus the temperature of leaching in degree centigrade and are shown in Fig. 15.

The effect of temperature on the dissolution of titanium and iron from the roasted mass are similar. The dissolution of both titanium and iron are increased with the increasing the leaching temperature. The effect is very sharp in between the temperature range 80 to 110°C . The high temperature dependence of the leaching of the roasted mass indicates the high activation energies for titanium and iron dissolutions. Moreover, since the dependence of temperature on titanium and iron dissolutions are almost identical, it is thought that the dissolution of both metals in both acids occur by the same mechanism of chemical control.

iii) *EFFECT OF SOLID TO LIQUID RATIO :*

The effect of the solid to liquid ratio on leaching has been investigated by measuring the concentration of titanium and iron dissolved at

various time intervals in leached solutions obtained by the leaching of roasted masses equivalent to 1, 1.5, 2, 3 and 5 g ilmenite with 50 cm³ 6 g eq dm⁻³ hydrochloric and sulphuric acid solutions. The experimental results are given in Table XII. From this table the maximum weight percentage of both metals at various S/L ratio are given in Table XIII and plotted in Fig. 16.

It is evident from the figure 16 that the percentages of both the metals are considerably decreased on increasing the S/L ratio as expected from any leaching study. With hydrochloric acid as leaching agent, it is observed that iron is leached preferentially. The titanium dissolution of 82.8% at S/L ratio of 0.02 kg dm⁻³ is decreased to only about 5% dissolution at S/L ratio of 0.10 kg dm⁻³, whereas under identical conditions 79% dissolution of iron is decreased to only about 43% at 0.10 kg dm⁻³. Similar behaviour is also encountered for leaching with sulphuric acid. About 65% titanium and 71% iron dissolutions at 0.02 kg dm⁻³ are decreased to only about 17% titanium dissolution and 35.5% iron dissolution at 0.10 kg dm⁻³.

Table XIII also contains the column for the maximum concentrations of titanium and iron in both acid leach solutions at various S/L ratios. The maximum concentration of metals in leach solution (g dm⁻³) have been plotted against the solid to liquid phase ratio (S/L in kg dm⁻³) in Fig. 17. It is found that the concentrations of iron in both acids are increased substantially with increasing the S/L ratio. For example, 5 g dm⁻³ iron in leach solution for S/L ratio of 0.02 kg dm⁻³ is increased to about 14 g dm⁻³ iron in hydrochloric acid (or about 12 g dm⁻³ iron in sulphuric acid solution) for S/L phase ratio of 0.10 kg dm⁻³. On the otherhand the

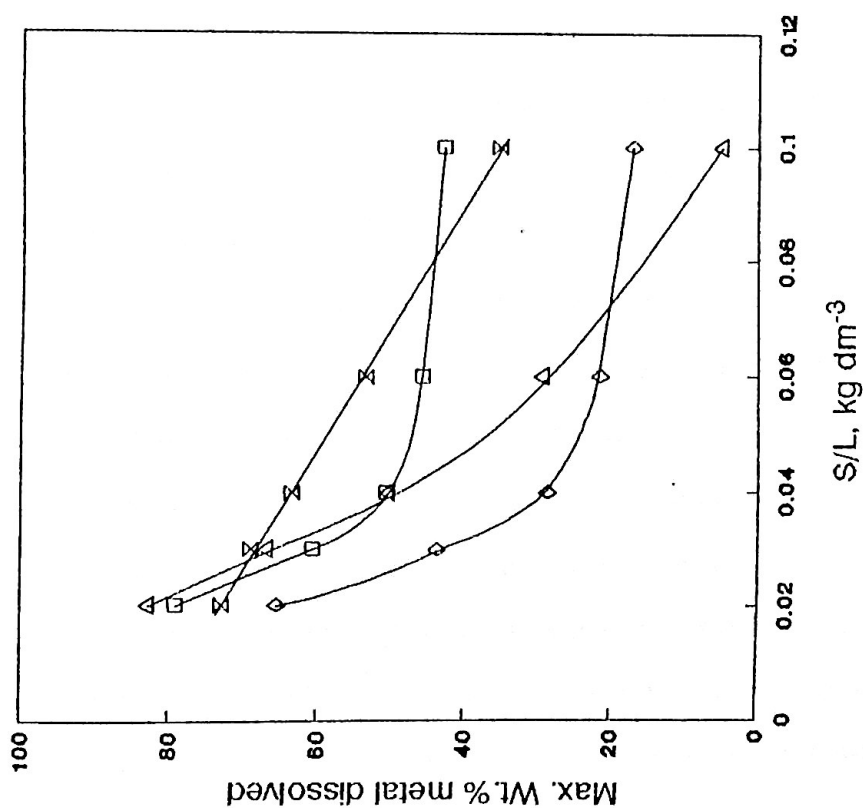


Fig. 16. Plot of maximum weight percentage of metals dissolved on 5 h versus solid to liquid phase ratio for leaching of LPG roasted ilmenite. (Δ): Ti, HCl; (□): Fe, HCl; (◇): Ti, H₂SO₄ and (Σ): Fe, H₂SO₄. Roasting conditions are as in Fig. 14. Leaching conditions: [Acid] = 6 g eq dm⁻³, temp = boiling point and agitation speed = 292 rpm (HCl)/372 rpm (H₂SO₄).

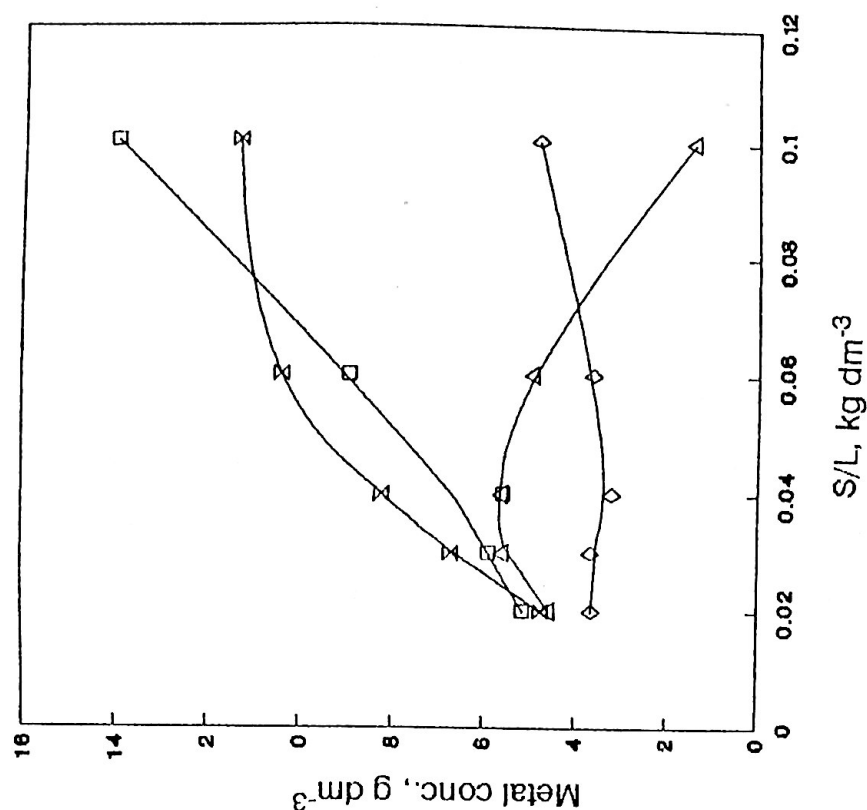


Fig. 17. Plot of the concentration of metal ions in leach solution in 5 h versus solid to liquid phase ratio for leaching of LPG roasted ilmenite. (Δ): Ti, HCl; (□): Fe, HCl; (◇): Ti, H₂SO₄ and (Σ): Fe, H₂SO₄. Roasting and leaching conditions are as in Figs. 14 and 16 respectively.

concentration of titanium in hydrochloric acid leach solution is decreased with the increase in the S/L values particularly above 0.04 kg dm^{-3} . With sulphuric acid as leaching agent the maximum concentration of titanium in leach solution is little varied with the change of S/L values.

The above information indicates that the leaching at high solid to liquid ratio cannot be practiced for lower metal dissolution and non-appreciable increment of titanium concentration in the leach solutions. Due to lower concentration of titanium in leached solution at higher solid to liquid phase ratio the stage wise leaching would appear to be inconvenient too.

iv) EFFECT OF AGITATION SPEED :

In the above studies the agitation speeds of 292 rpm for hydrochloric acid system and 372 rpm for sulphuric acid system were used. Lastly, the effect of the agitation speed on the leaching of the roasted mass in hydrochloric acid (6 g eq dm^{-3}) at its boiling temperatures and at a S/L value of 0.02 kg dm^{-3} has been investigated. The maximum percentages of titanium and iron dissolved at various agitation speeds (calibrated rotating speed of magnetic stirrer) during leaching are given in Table H. For hydrochloric acid as leaching agent, percentages of both titanium and iron dissolved are increased substantially with increasing the agitation speed particularly in its lower regions. This result indicates that in the investigated lower regions of agitation speed, the dissolution process is diffusion controlled as it is well known that for the diffusion controlling processes, the extent of dissolution is affected by agitation speed (increased

with increasing rpm of the agitating capsule). But in the upper regions of the agitation speed, the almost independence of metal dissolution percentages with increase in the rpm value indicates that the process of leaching should be chemically controlling over 292 rpm which was also predicted from the leaching agent concentration dependence study.

TABLE II. *Effect of agitation speed on leaching.*

Roasting temperature = $(700 \pm 15)^\circ\text{C}$

Roasting time = 75 min

Roasting LPG flow rate = $230 \text{ cm}^3 \text{ min}^{-1}$

Particle size = $>63 \mu\text{m} < 125 \mu\text{m}$

Leaching temperature = boiling temperature

Acid concentration = 6 g eq dm^{-3}

Solid to liquid ratio = 0.02 kg dm^{-3}

Leaching agent	Agitation speed, rpm (calibrated)	Percentage of titanium dissolved	Percentage of iron dissolved
HCl	198	54.4	54.8
	220	71.9	58.0
	292	82.8	79.0
	350	83.5	80.0

5.3 THERMAL TREATMENT (ROASTING) OF ILMENITE POWDER BY THE REFORMED PRODUCTS OF THE LPG-H₂O MIXTURE IN PRESENCE OF NICKEL POWDER AND SUBSEQUENT LEACHING

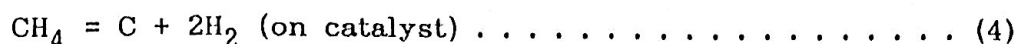
a) ROASTING :

Although the roasting of ilmenite in presence of the pyrolysed product of LPG at ~700°C for ~75 min gives a product which on leaching with 6 g eq dm⁻³ hydrochloric acid for ~5 h at its boiling point results in ~84% titanium dissolution, our aim to dissolve ilmenite quantitatively (at least ~100% titanium dissolution) has not yet been achieved. The preceding study gives the leaching result comparable to leaching with hydrofluoric acid^{98,99} of same concentrations. The difficulties encountered in the treatment of the hydrofluoric acid leach liquor²¹³ could be avoided by following the LPG-roasting hydrochloric acid leaching route.

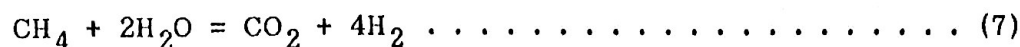
However, before going to the treatment of hydrochloric acid leach solution, we have searched for a still better roasting process which could facilitate the dissolution of more titanium on leaching with 6 g eq dm⁻³ hydrochloric and sulphuric acids. Consequently in this sub-chapter, we have discussed the results obtained on roasting of ilmenite powder with the reformed LPG-H₂O mixture in presence of nickel catalyst and subsequent leaching of the product mass with hydrochloric and sulphuric acids of concentrations 6 g eq dm⁻³.

On passing hydrocarbon (mainly methane) - steam mixture at ~700°C (1300°F) through a furnace containing supported nickel catalyst, a mixture of gasses consisting of CO, H₂, little CO₂, O₂ and N₂ and some unconverted

hydrocarbon is produced. This process is called reforming²⁵⁸. For methane reforming, the conversion takes place in two steps.



During reforming, little CO_2 is also formed for the following equilibria :



The higher hydrocarbons can be used in place of methane and in these cases, the equilibria are slightly more favourable. Higher CO to H_2 ratio is obtained with the increasing chain length of hydrocarbon.

Therefore, we reformed the LPG- H_2O mixture by passing it through a tube containing metallic nickel powder on a steel boat around 700°C and passed the reformed gas through another tube containing ilmenite powder or another boat at the same temperature (same reforming and roasting temperature) for studying the system. Several preliminary experiments were carried out to find out the possible reforming and roasting temperature and time of roasting. The effects of the following factors have been investigated for the roasting of ilmenite with the LPG-reformed products.

i) EFFECT OF ROASTING TIME :

5 g ilmenite powder has been roasted with the LPG-reformed product (LPG flow rate $110 \text{ cm}^3 \text{ min}^{-1}$, water vapour pressure 31.5 mm Hg, reforming and roasting temperature at $(750 \pm 15)^\circ\text{C}$ for various roasting times of 30, 40, 45, 50 and 60 min. The progress of reforming and/or roasting has been

followed up by the percentages of titanium and iron dissolved on leaching the roasted products at S/L ratio of 0.02 kg dm^{-3} with 6 g eq dm^{-3} hydrochloric and sulphuric acids at their boiling points. Table XIV represents the data obtained on leaching the roasted products at various leaching times. The leaching results are also shown graphically in Figs. 18-20 as the percentages of titanium or iron dissolved versus leaching time in hours. These figures show that the leaching is completed within 3 h in all cases. For these figures or from the data in Table XIV, the maximum percentages of titanium and iron dissolved on leaching of the product masses obtained on roasting for different time intervals are given in Table XV and shown graphically in Fig. 21 as maximum weight percentages of metals dissolved versus roasting time in minutes.

It is evident from figure 21 that the maximum weight percentages of titanium in both acids increase with increasing the roasting time upto 40 min and on further increasing the roasting time, the maximum dissolution percentage of titanium is decreased considerably particularly with hydrochloric acid. For example, the 53.5% titanium dissolution of ilmenite could be increased to ~83% dissolution by roasting for 40 min, which is decreased to only 37% dissolution by roasting for 60 min. On the otherhand, the iron dissolution is increased with increasing the roasting time upto 50 min which is slightly decreased with further prolonging of the roasting time upto 60 min.

Since we are particularly interested on the titanium dissolution, it is concluded from the above results that the optimum roasting time is 40 min and the roasting over 40 min will greatly decrease the dissolution percentages of metals, particularly of titanium with hydrochloric acid.

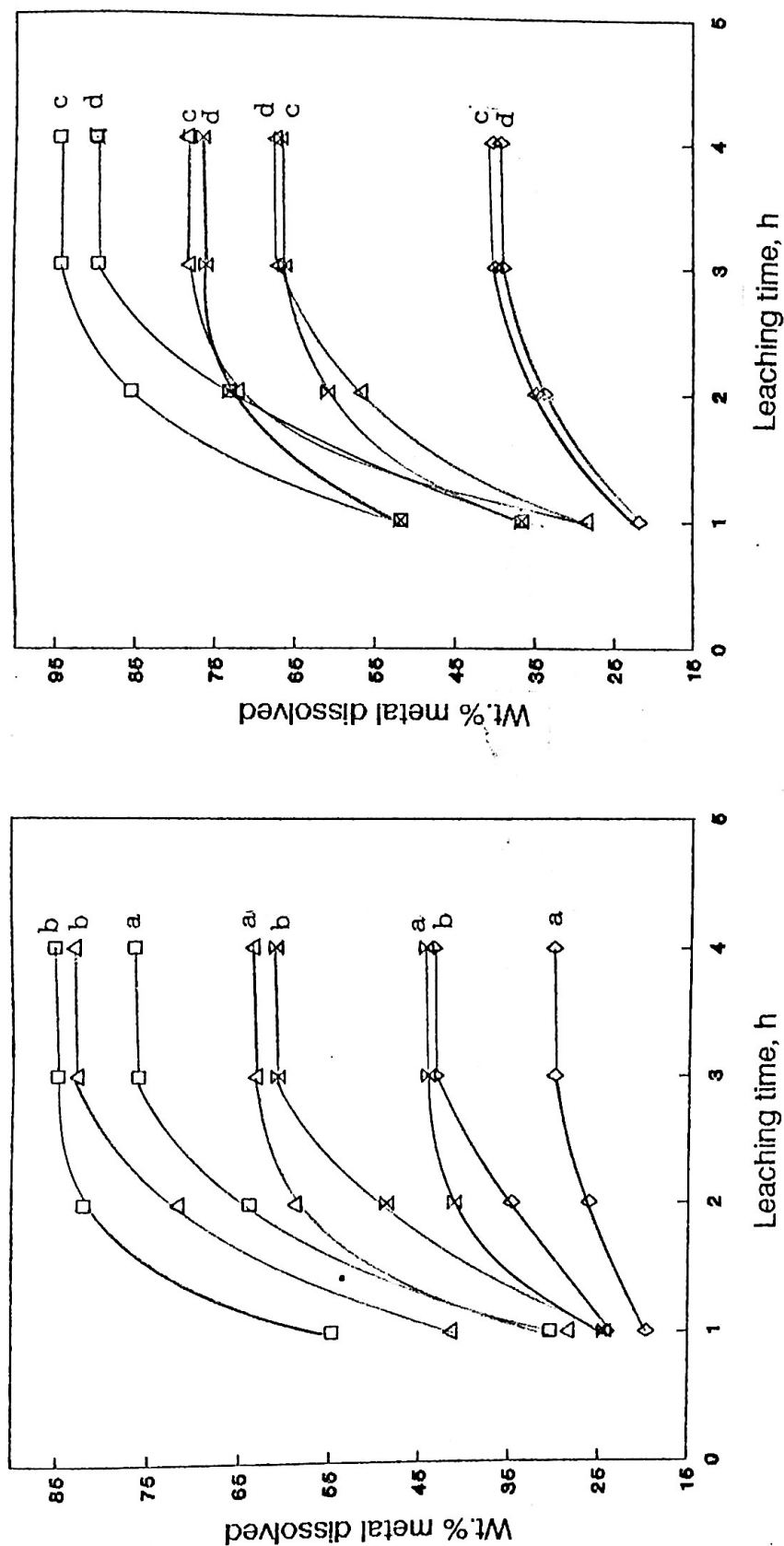


Fig. 18. Plot of weight percentage of metals dissolved versus leaching time of the roasted product of ilmenite obtained by the LPG-water vapour roasting in presence of nickel catalyst. (Δ): Ti, HCl; ($\square$): Fe, HCl; ($\diamond$): Ti, H_2SO_4 and ($\times$): Fe, H_2SO_4 . Roasting conditions: temp. = $(750 \pm 15)^\circ\text{C}$, LPG flow rate = $110 \text{ cm}^3 \text{ min}^{-1}$, W.V.P ($\text{P}_{\text{H}_2\text{O}}$) = 31.5 mm Hg . Leaching conditions: temp. = boiling point, $[\text{Acid}] = 6 \text{ g eq dm}^{-3}$, agitation speed = 292 rpm (HCl)/ 372 rpm (H_2SO_4). Roasting time (a) = 30 min, (b) = 40 min.

Fig. 19. Plot of weight percentage of metals dissolved versus leaching time of the roasted product of ilmenite obtained by the LPG-water vapour roasting in presence of nickel catalyst. (Δ): Ti, HCl; ($\square$): Fe, HCl; ($\diamond$): Ti, H_2SO_4 and ($\times$): Fe, H_2SO_4 . Roasting and leaching conditions are as in Fig. 18. Roasting time: (c) = 45 min, (d) = 50 min.

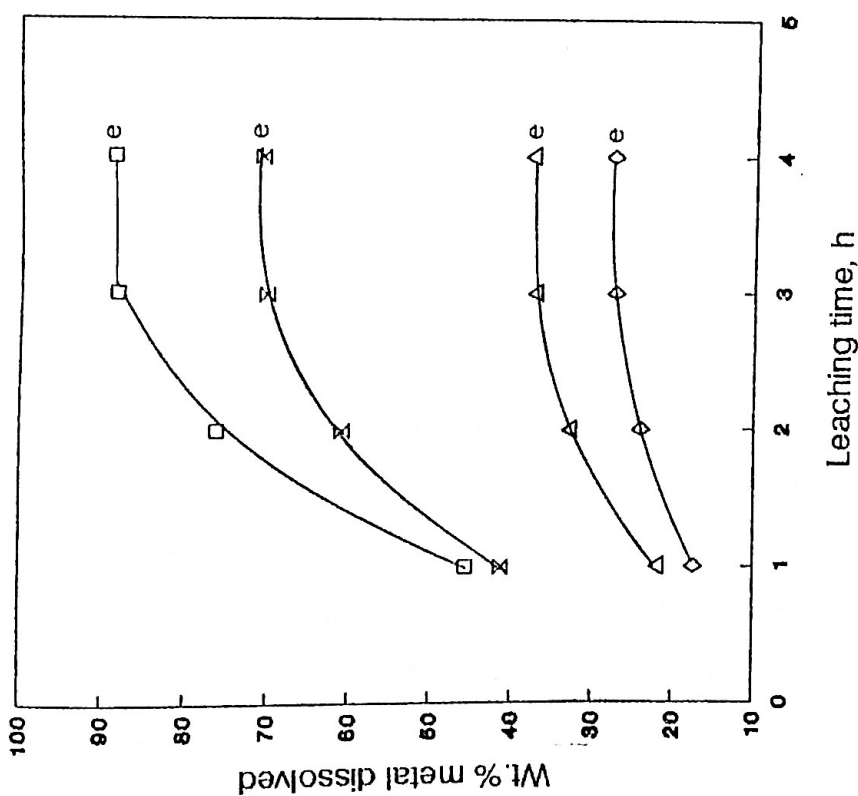


Fig. 20. Plot of weight percentage of metals dissolved versus leaching time of the roasted product of ilmenite obtained by the LPG-water vapour roasting in presence of nickel catalyst. (Δ): Ti, HCl; (□): Fe, HCl; (◇): Ti, H₂SO₄ and (⋈): Fe, H₂SO₄. Roasting and leaching conditions are as in Fig. 18. Roasting time: (e) = 60 min.

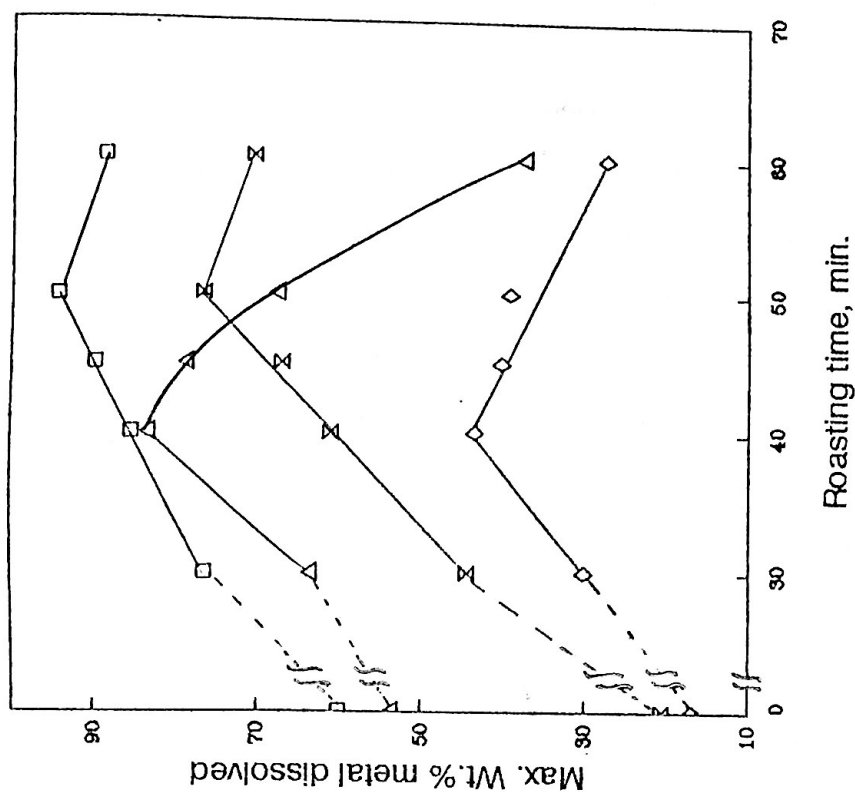


Fig. 21. Plot of maximum weight percentage of metals dissolved versus roasting time of the roasted product of ilmenite obtained by the LPG-water vapour roasting in presence of nickel catalyst. (Δ): Ti, HCl; (□): Fe, HCl; (◇): Ti, H₂SO₄ and (⋈): Fe, H₂SO₄. Roasting and leaching conditions are as in Fig. 18.

ii) EFFECT OF ROASTING TEMPERATURE :

5 g ilmenite powder has been roasted in presence of reformed LPG-products for 40 min at temperature of (600 ± 15) , (650 ± 15) , (700 ± 15) , (750 ± 15) and $(800\pm15)^{\circ}\text{C}$. The percentages of titanium and iron dissolved on leaching of the roasted masses obtained from each 1 g ilmenite with 6g eq dm^{-3} hydrochloric and sulphuric acids at different leaching time intervals are given in Table XVI. Using these data, the plots similar to these given in Fig. 18-20 could be drawn to estimate the maximum percentages of metals dissolved at different roasting temperatures. But such plots are not shown for simplicity.

The maximum weight percentages of titanium and iron dissolved at various conditions could however be easily read from the data given in Table XVI; these values are given in a tabular form in Table XVII, which are also shown graphically in Fig. 22 as the maximum weight percentages metals dissolved versus the roasting temperature (in $^{\circ}\text{C}$) plots.

It is found that the maximum percentages of both the metals of interest in both leaching agents are increased with increasing the roasting (also reforming) temperature upto $(700\pm15)^{\circ}\text{C}$ and then decreased considerably. For example, the titanium dissolution of ~54% in 6h from the non-treated ilmenite is increased to ~92% in 3h from the roasted mass obtained on roasting in presence of LPG-reformed gases at $(700\pm15)^{\circ}\text{C}$ for 40 min, and this value is decreased to ~81% from the roasted mass obtained at $(800\pm15)^{\circ}\text{C}$.

It is therefore concluded that the most favourable roasting temperature is $(700\pm15)^{\circ}\text{C}$ and the roasting over this temperature decreases the dissolution percentages of metals from ilmenite.

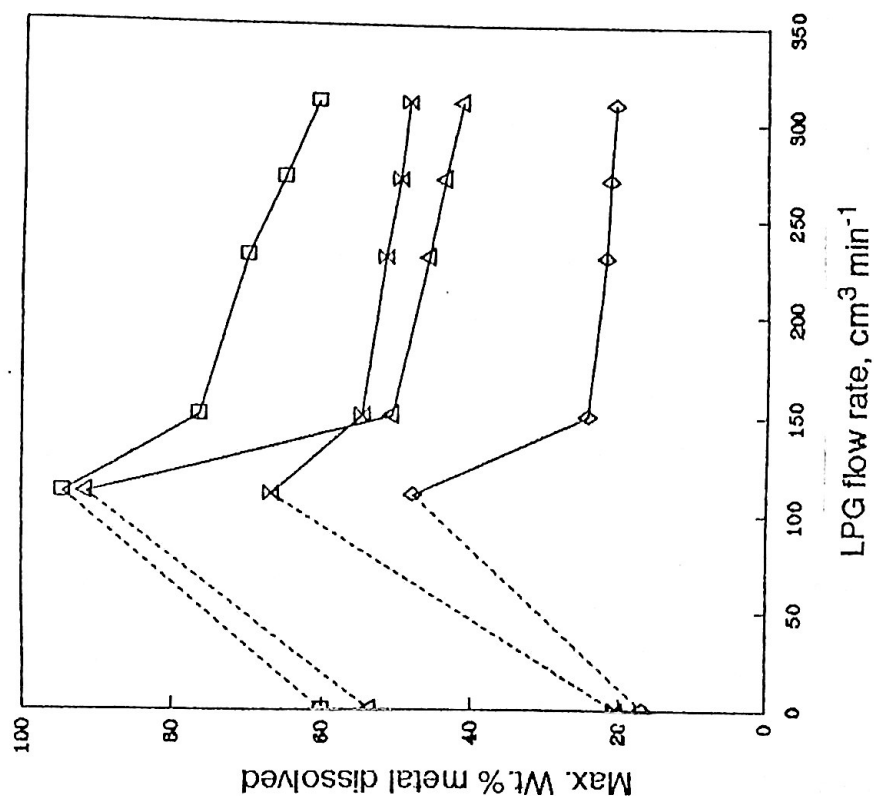


Fig. 22. Plot of maximum weight percentage of metals dissolved versus roasting temperature of the roasted product of ilmenite obtained by the LPG-water vapour roasting in presence of nickel catalyst (Δ): Ti, HCl; (◇): Fe, HCl; (□): Ti, H₂SO₄ and (X): Fe, H₂SO₄. Roasting conditions: time=40 min, LPG flow rate=110 cm³ min⁻¹. P_{H₂O}=31.5 mm Hg. Leaching conditions are as in Fig. 18.

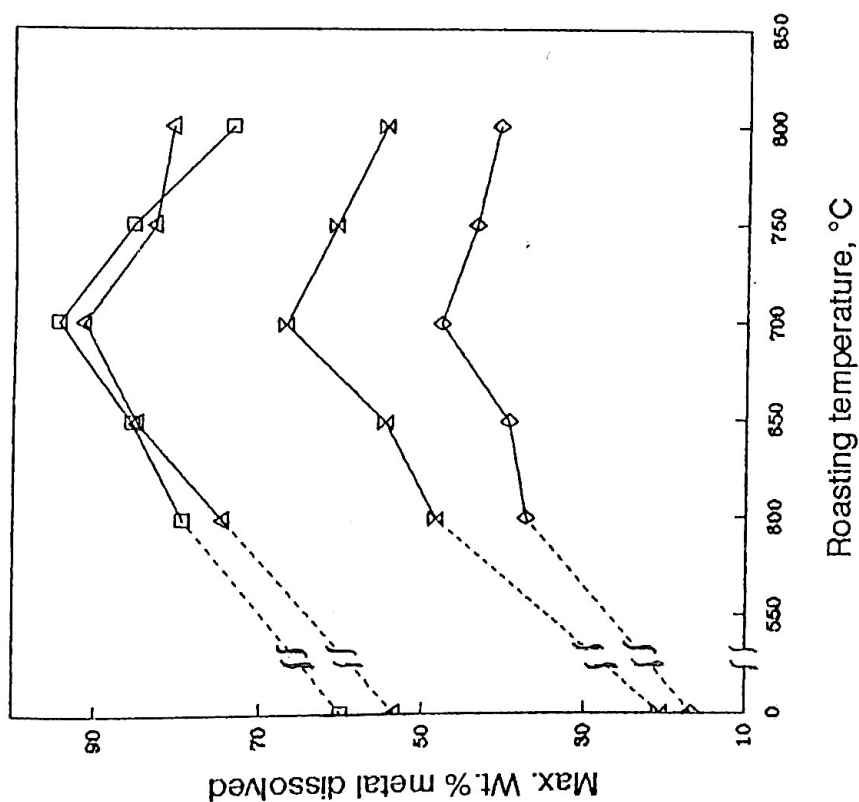


Fig. 23. Plot of maximum weight percentage of metals dissolved versus LPG flow rate of the roasted product of ilmenite obtained by the LPG-H₂O vapour roasting in presence of nickel catalyst. (Δ): Ti, HCl; (◇): Fe, HCl; (□): Ti, H₂SO₄ and (X): Fe, H₂SO₄. Roasting conditions: time=40 min, P_{H₂O}=31.5 mm Hg. temp=(700±15)°C. Leaching conditions are as in Fig. 18.

iii) EFFECT OF GAS FLOW RATE :

5 g ilmenite has been roasted each time at the most favourable temperature of $(700 \pm 15)^{\circ}\text{C}$ for 40 minutes but at different LPG flow rates of 110, 150, 230, 270 and $310 \text{ cm}^3 \text{ min}^{-1}$. In these experiments, the water vapour pressure in the gas mixture has been kept constant at 0.041 atm. The weight percentages of titanium and iron dissolved on leaching the 1 g ilmenite equivalent roasted masses obtained at different conditions with $50 \text{ cm}^3 \text{ 6 g eq dm}^{-3}$ in both acid are given in Table XVIII. The maximum weight percentages of titanium and iron dissolved on leaching the roasted masses obtained after roasting at various LPG flow rates have been read off from the data given in the above table and tabulated in Table XIX. The maximum weight percentage metal dissolved versus the LPG flow rate ($\text{cm}^3 \text{ min}^{-1}$) plots are shown in Fig. 23.

It is found that the maximum weight percentages of titanium and iron dissolved in both acids are largely increased for the roasted mass at $110 \text{ cm}^3 \text{ min}^{-1}$ LPG flow rate, in comparison to the results obtained from the non-treated ilmenite. Below this LPG flow rate, due to the limitation of bubbling the gas through the thermostated water reservoir, the experiments could not be done. Above this flow rate, the dissolution percentages of both metals in both acids are considerably decreased. For example, the titanium dissolution of 91.5% in hydrochloric acid obtained from the roasted mass at LPG flow rate of $110 \text{ cm}^3 \text{ min}^{-1}$ is reduced to only ~41% titanium dissolution from the product obtained at LPG flow rate of $310 \text{ cm}^3 \text{ min}^{-1}$.

The reason why the dissolution percentages of metals decrease with increasing the LPG flow rate above $110 \text{ cm}^3 \text{ min}^{-1}$ is not clear to us.

However, it may be due to the lowering of the partial pressure of reducing gases (CO and H₂) at higher gas flow rate for shorter residence time over nickel catalyst per volume of flow gas, resulting in poorer decomposition of LPG.

Nevertheless, it is concluded that the optimum LPG flow rate should be around 110 cm³ min⁻¹ in the LPG-water vapour roasting of ilmenite and the roasting in higher gas flow rate will extensively decrease the dissolution percentages of the metals from ilmenite.

iv) EFFECT OF THE WATER VAPOUR CONTENT IN LPG :

Lastly, the effect of the water vapour content in the LPG flow gas has been studied. 5 g ilmenite has been roasted at (700±15)°C, for 40 min and in presence of LPG flow rate of 110 cm³ min⁻¹ mixed up with different water vapour contents corresponding to the pressure of 31.5, 55.5 92.6 and 149.4 mm Hg (0.041, 0.073, 0.122 and 0.196 atm). The leaching results obtained from the roasted massed obtained at different water contents are given in Table XX. The maximum weight percentages of titanium and iron dissolved in both acids at different water vapour pressure are given in Table XXI and plotted in Fig. 24.

The maximum weight percentages of both metals in both acids are decreased considerably with increase in the water content in the flow gas. The reason for this type of behaviour may be due to the higher partial pressure of water vapour at higher water content in the flow gas, which hinders the reduction of the ilmenite into other phases which are susceptible to acid leaching due to back oxidation by excess water vapour.

In this case, lower roasting time is expected to give better results. But such studies have not been carried out. It is however concluded that the optimum water vapour pressure in the flow gas is 0.041 atm and the roasting in higher water vapour pressure, under the experimental condition cited, will greatly decrease the leaching percentages of metals from ilmenite.

Since the particle size of ilmenite used in the roasting showed only a little effect (Table E) on the LPG pyrolysed product roasting of ilmenite, we have not conducted such experiments here.

Roasted product :

Based on the above experimental results, about 55 g ilmenite (in 11 sets) has been roasted at $(700 \pm 15)^{\circ}\text{C}$, $110 \text{ cm}^3 \text{ min}^{-1}$ LPG flow rate and 0.041 atm water vapour pressure for 40 minutes. To observe any change occurring in ilmenite during the LPG-H₂O vapour roasting process, the X-ray powder diffractogram of the mass has been taken and shown in Fig. 13. From this diffractogram, the "d"-spacings of the sample are given in Table I. Although the "d" spacing of the LPG-H₂O vapour roasted product have some common values to those for pure ilmenite or non-treated ilmenite (Table G), many peaks of ilmenite have been disappeared after the roasting. Moreover, the relative intensities of the peaks have been changed remarkably. For example, the intensity of the (100% R.I) peak at 2.743 Å in ilmenite is reduced to 61% R.I. in the roasted product. On the contrary to this, the R.I. value at 1.86 Å is changed from 40% in ilmenite to 100% in roasted mass. Comparison of the data given in Table F and H clearly indicates that some modifications have certainly occurred during the roasting process and the product

obtained from the LPG-roasted mass differs from that obtained from the LPG-water vapour roasted mass. However, due to the presence of more than one phases in the roasted mass, it seems to be very difficult to identify the phases with the help of the ASTM cards.

Table I. *X-ray powder diffraction pattern of the LPG-water vapour roasted ilmenite (at 700°C, 110 cm³ min⁻¹ LPG flow rate, 0.041 atm water vapour pressure for 40 min).*

d, Å	3.711	2.743	2.546	2.022	1.885	1.849	1.840	1.722	1.713
	*(3.737)	(2.754)	(2.544)		(1.868)			(1.726)	
R.I, %	14	61	11	28	100	17	3	91	5
	(30)	(100)	(70)		(40)			(55)	
d, Å	1.618	1.503	1.375						
		(1.506)							
R.I, %	10	30	6						
		(30)							

* Figures in the parentheses indicate values for synthetic ilmenite (pure) obtained from the ASTM card No. 29-7334.

b) LEACHING :

The materials prepared under best conditions have been used to investigate the leaching characteristics of the roasted mass. The effects of the following parameters have been studied.

i) EFFECT OF ACID CONCENTRATION :

A selected amount of ilmenite roast (0.96g) equivalent to 1g ilmenite has been leached with HCl and H₂SO₄ of different concentrations such as 2, 4, 6 and 8 g eq dm⁻³ at a solid to liquid ratio (S/L) of 0.02 kg dm⁻³ at their boiling temperatures. The weight percentages of titanium and iron

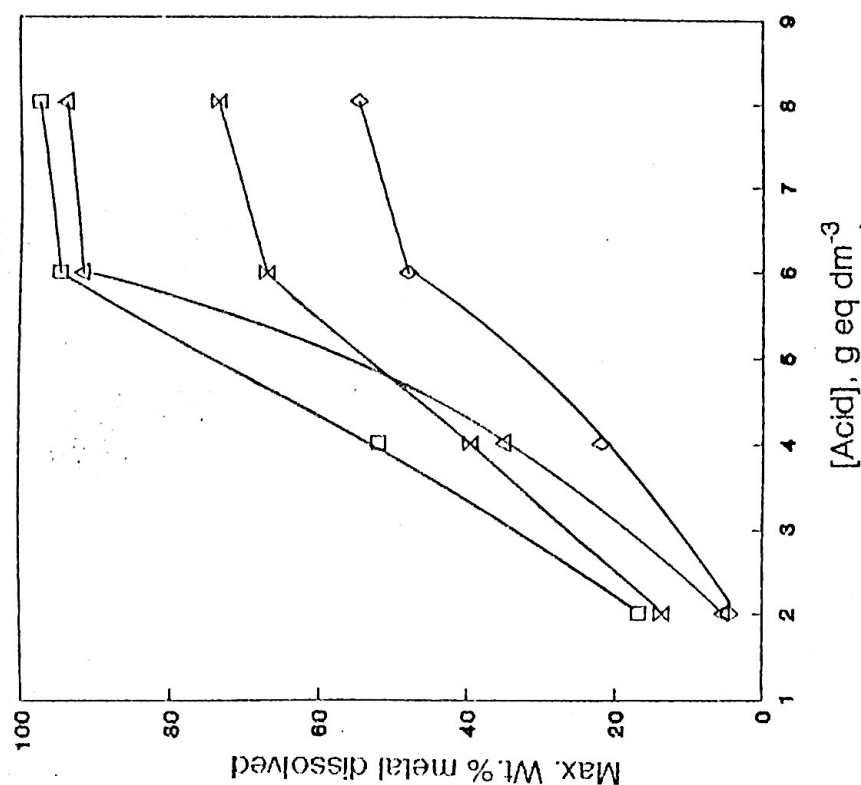


Fig. 25. Plot of maximum weight percentage of metals dissolved versus the concentrations of leaching acids on the leaching of the roasted product of ilmenite obtained by the LPG-H₂O vapour roasting in presence of nickel catalyst. (Δ): Ti, HCl; (□): Fe, HCl; (◇): Ti, H₂SO₄ and (⋈): Fe, H₂SO₄. Roasting conditions: time=40 min, temp=(700±15)°C, LPG flow rate=110 cm³ min⁻¹, (P_{H₂O})=31.5 mm Hg. Leaching conditions: temp.=boiling point, agitation speed=292 rpm (HCl)/372 rpm (H₂SO₄), S/L=0.02 kg dm⁻³, S=1 g.

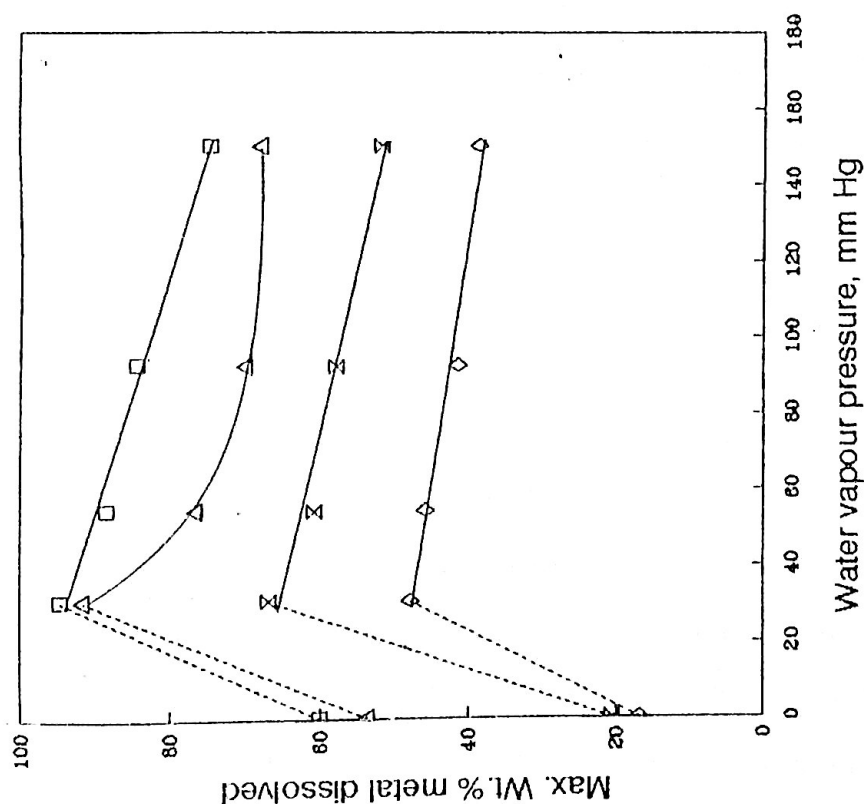


Fig. 24. Plot of maximum weight percentage of metals dissolved versus roasting water-vapour pressure of the roasted product of ilmenite obtained by the LPG-H₂O vapour roasting in presence of nickel catalyst. (Δ): Ti, HCl; (□): Fe, HCl; (◇): Ti, H₂SO₄ and (⋈): Fe, H₂SO₄. Roasting conditions: time=40 min, temp=(700±15)°C, LPG flow rate=110 cm³ min⁻¹. Leaching conditions are as in Fig. 18.

dissolved at various leaching intervals (1-4 h) are given in Table XXII. However, the weight percentages of metals dissolved against leaching time at different acid concentrations have not shown graphically to avoid the complexity. The maximum weight percentages of titanium and iron dissolved in both acids of different concentrations have been evaluated from the above table, which have been given in Table XXIII and represented graphically in Fig. 25.

It is seen from the above figure that the maximum weight percentages of titanium dissolution are vary much decreased, in both acids, with decreasing concentrations, particularly below 6 g eq dm^{-3} . The iron dissolution varies similarly. Above 6 g eq dm^{-3} acid concentrations, the maximum dissolution percentages are little increased. The effect of the acid concentrations on the titanium and iron dissolutions from the roasted mass is very sharp in the acid concentration range of 2 to 6 g eq dm^{-3} for both acids. It is therefore concluded that the hydrochloric or sulphuric acid concentration of 6 g eq dm^{-3} is quite effective for leaching of the LPG-H₂O vapour roasted ilmenite.

ii) EFFECT OF TEMPERATURE :

The roasted ilmenite (0.96g) equivalent to 1g ilmenite has been leached separately with 6 g eq dm^{-3} hydrochloric and sulphuric acids at S/L ratio of 0.02 kg dm^{-3} but at different leaching temperatures, such as (50 ± 2) , (80 ± 2) and $(110 \pm 2)^{\circ}\text{C}$ (boiling temperature). Table XXIV shows the experimental results. From this table the maximum weight percentages of titanium and iron dissolved in both acids have been found at different

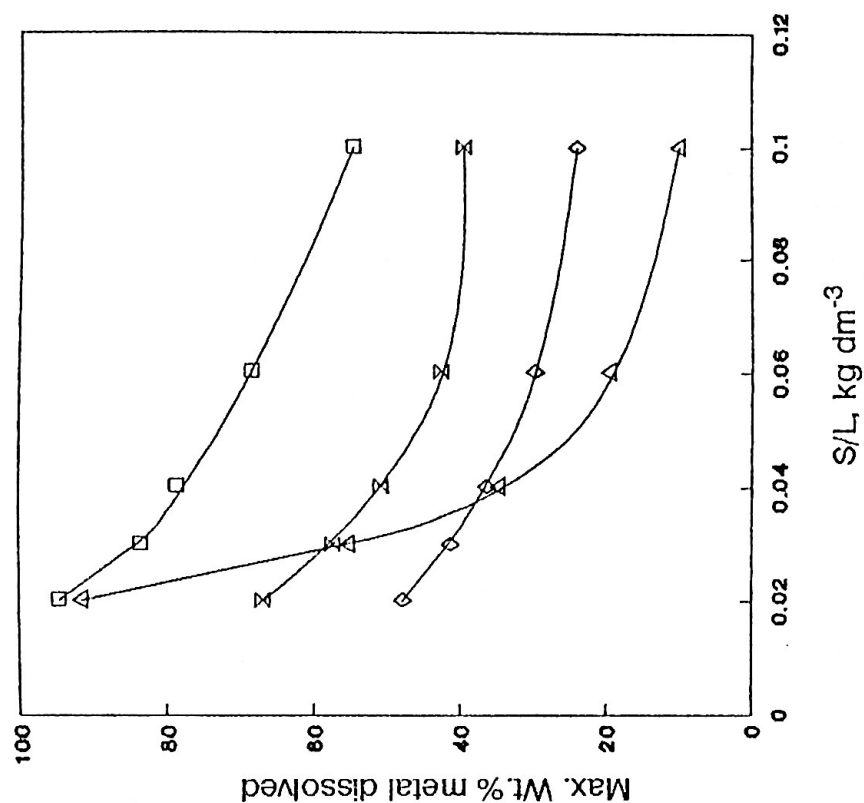


Fig. 27. Plot of maximum weight percentage of metals dissolved versus solid to liquid phase ratio on the leaching of the roasted product of ilmenite obtained by the LPG-H₂O vapour roasting in presence of nickel catalyst (Δ): Ti, HCl; (□): Fe, HCl; (◇): Ti, H₂SO₄ and (x): Fe, H₂SO₄. Roasting conditions are as in Fig. 25. Leaching conditions: temp = boiling point, [Acid] = 6 g eq dm⁻³, agitation speed = 292 rpm (HCl)/372 rpm H₂SO₄.

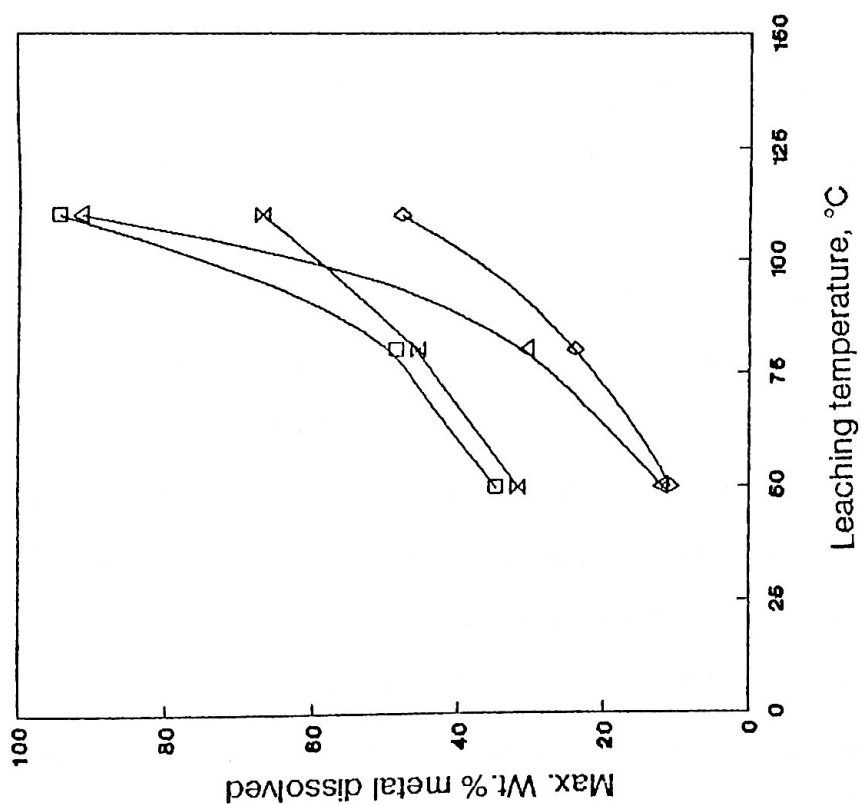


Fig. 26. Plot of maximum weight percentage of metals dissolved versus leaching temperature on the leaching of the roasted product of ilmenite obtained by the LPG-H₂O vapour roasting in presence of nickel catalyst (Δ): Ti, HCl; (□): Fe, HCl; (◇): Ti, H₂SO₄ and (x): Fe, H₂SO₄. Roasting conditions are as in Fig. 25. Leaching conditions: [Acid] = 6 g eq dm⁻³, agitation speed = 292 rpm (HCl)/372 rpm (H₂SO₄), S/L = 0.02 kg dm⁻³ S = 1 g.

leaching temperatures and are given in Table XXV. The data given in this table have been plotted as maximum weight percentages of metals dissolved versus the temperature of leaching in °C and are shown in Fig. 26.

The effects of the leaching temperature on the dissolution of titanium and iron from the roasted mass are similar. The dissolutions of both titanium and iron are increased with increasing the leaching temperature. The effect is very sharp in between the temperature range 80 to 110°C. The high temperature dependence of the leaching of the roasted mass indicates the high activation energies for titanium and iron dissolutions. Moreover, since the dependences of temperature on titanium and iron dissolution are almost identical, it is thought that the dissolution of both metals in both acids occurs by the same mechanism of chemical control in nature.

iii) EFFECT OF SOLID TO LIQUID RATIO :

The effect of the solid to liquid phase ratio (S/L) on leaching has been investigated by measuring the concentrations of titanium and iron dissolved at various time intervals in leached solutions obtained by the leaching of roasted masses equivalent to 1, 1.5, 2, 3 and 5 g ilmenite with $50 \text{ cm}^3 \text{ } 6 \text{ g eq dm}^{-3}$ hydrochloric and sulphuric acid solutions. The experimental result are given in Table XXVI from which the maximum weight percentages of both metals at various S/L ratio are calculated and given in Table XXVII. The data in Table XXVII have been plotted in Fig. 27.

It is evident from figure 27 that the percentages of both the metals are considerably decreased on increasing the S/L ratio as expected for any leaching study. With hydrochloric acid as leaching agent, it is observed that

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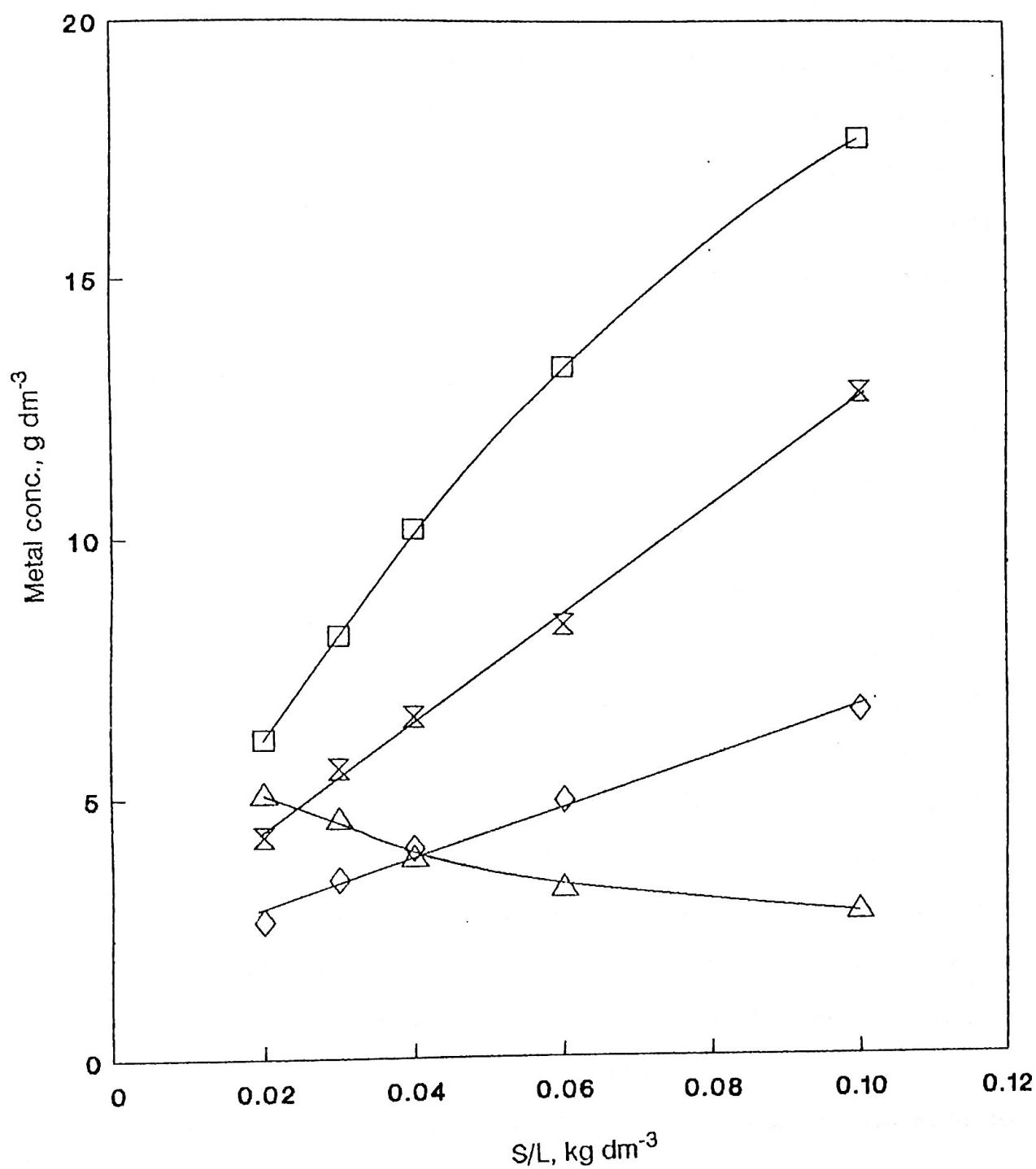


Fig.28. Plot of the concentration of metal ions in leach solution versus solid to liquid phase ratio on the leaching of the roasted product of ilmenite obtained by the LPG- H₂O vapour roasting in presence of nickel catalyst (Δ) : Ti, HCl; (□): Fe, HCl; (◇) :Ti, H₂SO₄ and (X):Fe, H₂SO₄. Roasting and leaching conditions are as in Figs. 25 and 27 respectively.

iron is leached preferentially. The titanium dissolution of 91.5% at S/L ratio of 0.02 kg dm^{-3} is decreased to only about 10% dissolution at S/L ratio of 0.10 kg dm^{-3} ; whereas under identical condition, 94.3% dissolution of iron is decreased to only about 54.7%. Similar behaviour is also encountered for leaching with sulphuric acid. About 47.9% titanium and 66.9% iron dissolution at 0.02 kg dm^{-3} are decreased to only about 24% titanium dissolution and 39.6% iron dissolution at 0.10 kg dm^{-3} .

Table XXVIII also contains the columns for the maximum concentrations of titanium and iron in both acid leach solutions at various S/L ratios. The maximum concentrations of metals in leach solutions (1 g dm^{-3}) have been plotted against the solid to liquid phase ratio (S/L in kg dm^{-3}) in Fig. 28. It is found that the concentrations of iron in both acids are increased substantially with increasing the S/L ratio. For example, 6.11 g dm^{-3} iron in leach solution for S/L ratio of 0.02 kg is increased to about 18 g dm^{-3} iron in hydrochloric acid for S/L ratio of 0.10 kg dm^{-3} . Similarly in sulphuric acid the iron concentration of $\sim 4.3 \text{ g dm}^{-3}$ at 0.02 kg dm^{-3} is increased to 12.8 g dm^{-3} at 0.1 kg dm^{-3} . On the otherhand, the concentration of titanium in hydrochloric acid solution is decreased with the increase in the S/L value particularly upto 0.04 kg dm^{-3} , and with sulphuric acid as leaching agent the maximum concentration of titanium in solution is increased with the increase in the S/L values.

The above information indicates that the leaching at high solid to liquid ratio is not useful for lesser extents of metal dissolutions and non-appreciable increment of the titanium concentrations in the leach solutions. Due to the lowering concentration of titanium in hydrochloric acid leach

solution at higher solid to liquid phase ratios, the stage-wise leaching would appear to be inconvenient, too.

iv) *EFFECT OF AGITATION SPEED :*

In all the above studies the agitation speed of 292 rpm for hydrochloric acid system and 372 rpm for sulphuric acid system were used. Lastly the effect of the agitation speed on the leaching of the roasted mass in hydrochloric acid (6 g eq dm^{-3}) at its boiling temperature and at a S/L value of 0.02 kg dm^{-3} has been investigated. The maximum percentages of titanium and iron dissolved at various agitation speed (calibrated rotating speed of capsules), during leaching are given in Table J. For hydrochloric acid as leaching agent, percentages of both titanium and iron are increased substantially with increasing the agitation speed. The result indicates that in the investigated lower agitation speed regions, the dissolution process is diffusion controlled as it is well known that for the diffusion controlling processes, the extent of dissolution is affected by agitation speed (increased with increasing rpm of the agitation capsule). But in higher agitation speed region ($>220 \text{ rpm}$), the dissolution is almost independent of agitation speed which indicates that the process is chemically controlled. The acid concentration dependence studies at 292 rpm have also suggested the same.

The identical study with sulphuric acid has also been done and the results are shown in Table I. Leaching characteristics with sulphuric acid are similar to those with hydrochloric acid.

TABLE J. Effect of agitation speed on leaching of the LPG-H₂O vapour roasted mass.

Roasting time = 40 min

Roasting temperature = (700±15)°C

Roasting LPG flow rate = 110 cm³ min⁻¹

Water vapour pressure = 31.5 mm Hg

Particle size = >63 µm<125 µm

Leaching temperature = boiling temperature

Acid concentration = 6 g eq dm⁻³Solid to liquid ratio = 0.02 kg dm⁻³

Leaching agent	Agitation speed, rpm (calibrated)	Maximum percentage of dissolution	
		Ti	Fe
HCl	198	69.7	73.0
	220	87.7	91.2
	292	91.5	94.3
	350	92.8	95.2
H ₂ SO ₄	170	39.2	54.7
	300	45.2	65.4
	372	47.9	66.9
	490	46.5	66.3
	690	45.7	63.8

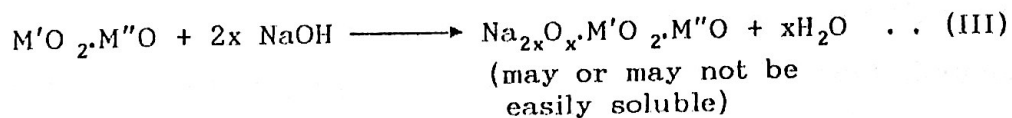
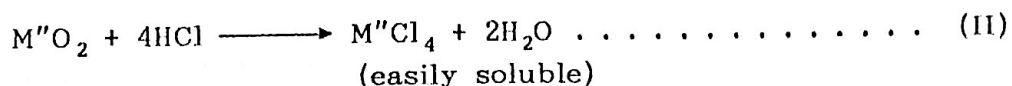
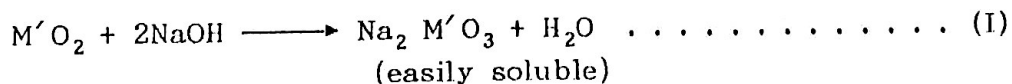
5.4 SALT-WATER VAPOUR ROASTING OF ILMENITE

(a) ROASTING :

It is well known that the metal salt at elevated temperature (near their melting points) react with water vapour to metal hydroxide and an acid corresponding to the anion of the salt^{254,255,259}. For example, sodium chloride reacts with water vapour above 800°C (near m.p) to form sodium hydroxide and hydrochloric acid according to the following reaction :



At such a high temperature, sodium hydroxide remains in the molten state, whereas, the produced acid comes out of the reaction site. Sodium hydroxide may then react in-situ with acidic oxides to form sodium salts according to reaction scheme-I, which are expected to be dissolved in water or dilute acidic solution. Moreover, as shown in the reaction scheme-II, the acids produced may react with basic oxides in-situ before being driven off the reaction tube. Mixed insoluble oxides may often be conveniently salt-water vapour roasted to a product as given in the reaction scheme (III) which may be susceptible to easy leaching in hot water or hot weak acid or basic solution.



As ilmenite is a mixed oxide of titanium (IV) and iron (II), the salt-water vapour roasting should follow up the reaction scheme (III) and the roasted product should be tested for its leaching characteristics. It is also mentionable that the phase of the type $\text{Na}_{2x}\text{O}_x \cdot \text{M}'_y\text{O}_{2y} \cdot \text{M}''_z\text{O}_z$ (x, y, z having any value) may also be formed depending on reaction conditions and phase stability.

Furthermore, at different roasting conditions, the value of "x" in the reaction product may vary to give different phases of different characteristics. The identification of the product phases again needs extensive study, which has been avoided and we are interested only on the leaching characteristics of the roasted products in an aim to get condition for the centpercent dissolution of titanium from ilmenite.

These type of studies can easily be followed up by estimating the amount of the expelled hydrochloric acid produced if quartz tubes and boats are used. Due to the lack of facilities in getting quartz materials, we used steel pipe and ceramic boat. Although ceramic boat was not found to be attacked by the acid, the hydrochloric acid reacted significantly to corrode the steel tube. So we were unable to follow up the progress of the reaction by the usual hydrochloric acid analysis.

In the following few paragraphs, the results of the $\text{NaCl}/\text{Na}_2\text{SO}_4/\text{NaNO}_3/\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ vapour roasting of ilmenite have been discussed.

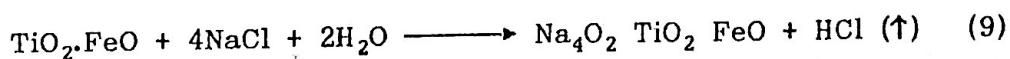
i) EFFECT OF ILMENITE POWDER TO SALT RATIO :

The portion of 1 g ilmenite has been mixed homogeneously with different amount of NaCl , Na_2SO_4 , NaNO_3 or Na_2CO_3 to get different ilmenite to salt ratios. These mixtures have been water vapour [passed with nitrogen

as carrier gas at $420 \text{ cm}^3 \text{ min}^{-1}$ ($515 \text{ cm}^3 \text{ min}^{-1}$ for Na_2SO_4 system) having vapour pressure of 31.5 mm Hg] roasted at 800°C (850°C for Na_2CO_3 and 885°C for Na_2SO_4) for 60 min (90 min for NaNO_3). The whole of the reaction products have been leached with 50 cm^3 2 g eq dm^{-3} hydrochloric acid at its boiling points with a pulp agitation speed of 292 rpm. In most of the cases, the leaching is completed within 90 minutes for NaCl and Na_2SO_4 roasted product whereas NaNO_3 and Na_2CO_3 roasted products need 60 and 45 minutes respectively.

The leaching results at different time intervals are given in Table XXVIII. From this table, the maximum weight percentages of titanium and iron dissolved in a definite time at different reaction conditions are given in Table XXIX and plotted in Figs. 29 and 30 for titanium and iron respectively.

In the case of NaCl -water vapour roasting the maximum weight percentages of both the metals of our interest pass through maxima at ilmenite to NaCl ratio of 0.67. The enhancement of the titanium and iron dissolution with lowering the ilmenite to salt ratio is possibly due to the stoichiometric factor; whereas the decreases in dissolution percentages below ilmenite NaCl ratio of 0.67 are possible due to the presence of unreacted sodium hydroxide associated with the roasted mass, which eventually decreases the concentration of leaching agent. The ilmenite to NaCl ratio of 0.67 (theoretical 0.65) corresponds to the following stoichiometric equation;



The progress of roasting can be realised by comparing this result with the results given for nontreated ilmenite with 2 g eq dm^{-3} HCl in reference⁹⁸ (1.5% titanium and 0.6% iron dissolved in 2 h).

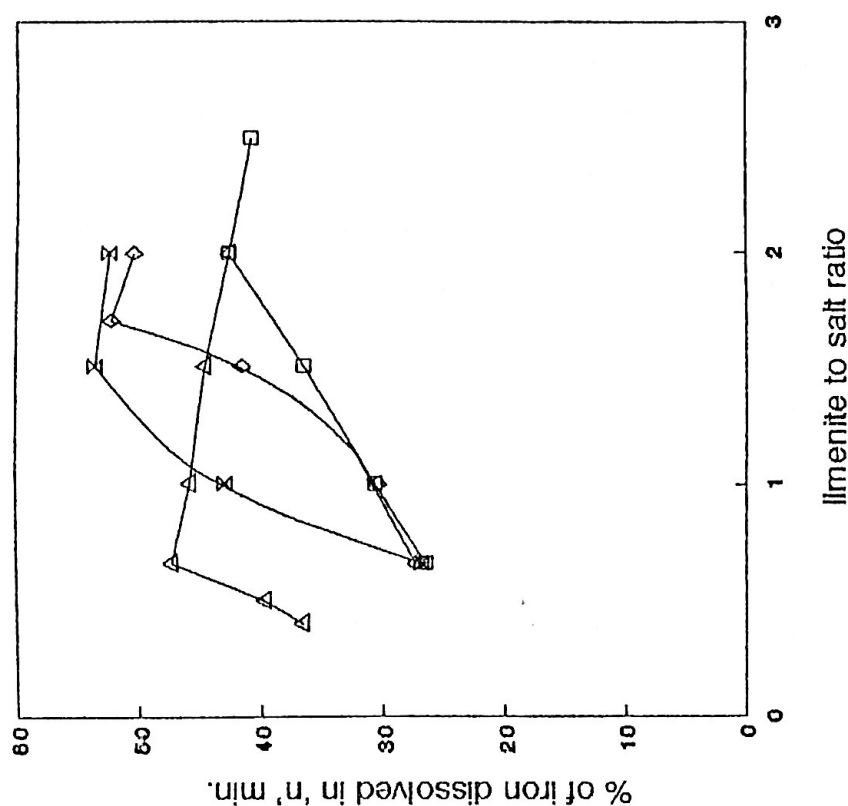


Fig. 29. Plot of weight percentage of titanium dissolved in 'n' min. versus roasting ilmenite to salt ratio. (Δ): NaCl, $n = 120$; (□): Na₂SO₄, $n = 120$; (◇): NaNO₃, $n = 90$ and (⋈): Na₂CO₃, $n = 45$. Roasting conditions: temp = 800°C (885°C for Na₂SO₄ & 850°C for Na₂CO₃; time = 60 min. (90 min. for NaNO₃); N₂ flow rate = 420 cm³ min⁻¹ (515 cm³ min⁻¹ for Na₂SO₄); W.V.P (P_{H_2O}) = 31.5 mm Hg. Leaching conditions: [HCl] = 2 g eq dm⁻³; agitation speed = 292 rpm; temp = b.p.; S/L = 0.02 kg dm⁻³, S = 1 g.

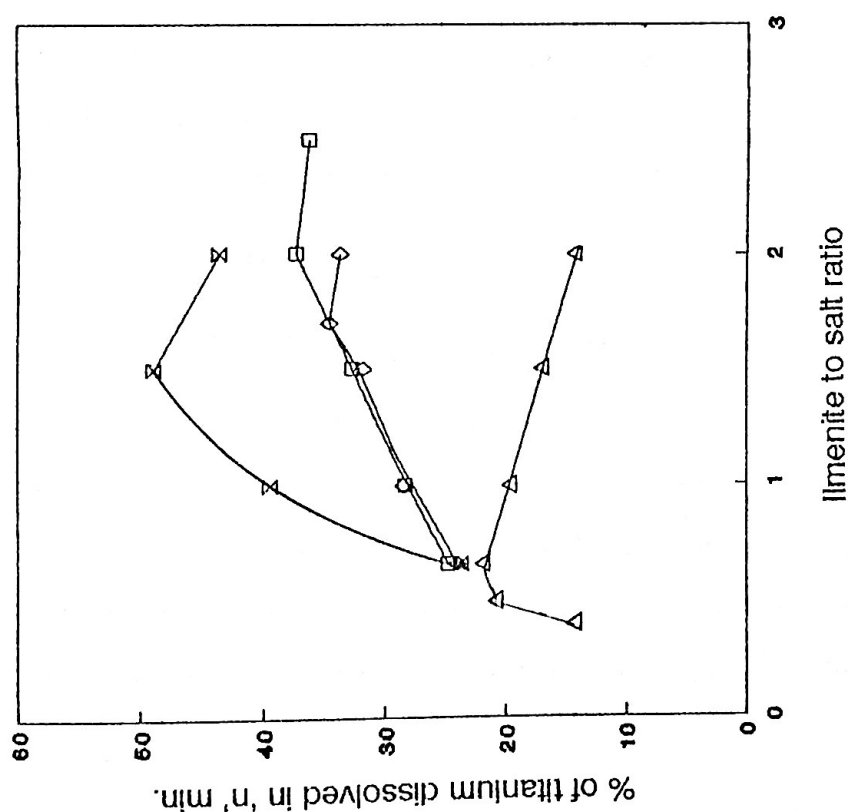
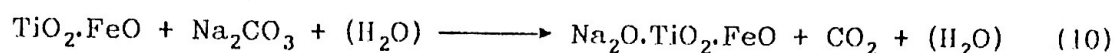
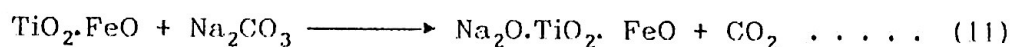


Fig. 30. Plot of weight percentage of iron dissolved in 'n' min. versus roasting ilmenite to salt ratio. (Δ): NaCl, $n = 120$; (□): Na₂SO₄, $n = 120$ (◇): NaNO₃, $n = 90$ and (⋈): Na₂CO₃, $n = 45$. Roasting and leaching conditions are as in Fig. 29.

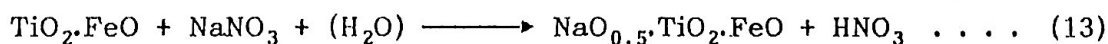
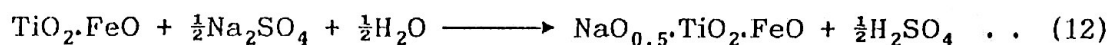
Similar behaviour has been observed with sodium carbonate roasting. The maximum weight percentages of titanium and iron in leach solution vary with the ilmenite to Na_2CO_3 ratio passing through maxima at a ratio of 1.5. The decrease in the dissolution percentages at lower ilmenite to salt ratio is again due to the presence of unreacted NaOH associated with the roasted mass. The ilmenite to salt ratio of 1.5 indicates the following stoichiometric reaction during Na_2CO_3 - water vapour roasting;



Following alternative roasting reaction can be ruled out since the decomposition of sodium carbonate takes place well above (above 1050°C) the roasting temperature :



The roasting results with sodium sulphate and sodium nitrate in presence of H_2O -vapour indicate the formation of a phase $\text{Na}_{2x} \text{O}_x \cdot \text{TiO}_2 \cdot \text{FeO}$ with x value close to 0.5 for which the maxima should be obtained at ilmenite to salt ratio of 2.14 (for Na_2SO_4) and 1.78 for (NaNO_3).



The formation of same phase with later two reagents could be verified by the X-ray diffractograms of two products, which will be discussed later.

It is therefore concluded from the above results for the salt- H_2O vapour roasting of ilmenite that the optimum ilmenite to salt ratio should be 0.67, 2.12, 1.78 and 1.48 for NaCl , Na_2SO_4 , NaNO_3 and Na_2CO_3 systems respectively.

(ii) *EFFECT OF ROASTING TIME :*

The ilmenite (1 g)-salt mixtures at their optimum ratios (2,1.7,1.5 and 0.67 for Na_2SO_4 , NaNO_3 , Na_2CO_3 and NaCl respectively) have been roasted at constant temperatures (800°C for NaCl and NaNO_3 , 850°C for Na_2CO_3 and 885°C for Na_2SO_4) for different time intervals from 40 to 150 minutes. Each of the roasted product has been subjected to leaching with 50 cm^3 2 g eq dm^{-3} hydrochloric acid at its boiling temperature. The percentages of titanium and iron dissolved in the leach solutions at different leaching time are given in Table XXX. From this table the maximum weight percentages of titanium and iron dissolved in a definite time from the roasted masses obtained at different roasting times are given in Table XXXI and plotted in Figs. 31 & 32 for titanium and iron respectively.

In all the salt-systems, the maximum percentages of titanium and iron pass through maxima. For NaCl -roasted system, the maximum weight percents of titanium and iron dissolutions are increased to 25% and 62% respectively at roasting time 75 minutes, which are decreased to 20.7% and 53.6% respectively when the roasting is allowed for 90 minutes. The optimum roasting time for Na_2CO_3 and Na_2SO_4 systems are 45 and 90 minutes respectively. In Na_2CO_3 roasted system, 56.5% titanium and 61.7% iron dissolutions from the product obtained at the roasting time of 45 minutes are extensively decreased to 12.5% titanium and 18.7% iron dissolutions from the product obtained at 75 minutes' roasting. Likewise for Na_2SO_4 roasted system, 39.2% titanium and 45.6% iron dissolutions from 90 minutes' roasted mass are decreased to only 13.3% titanium and 13.9% iron dissolutions from 150 minutes' roasted products. Although the behaviours of NaNO_3 system is

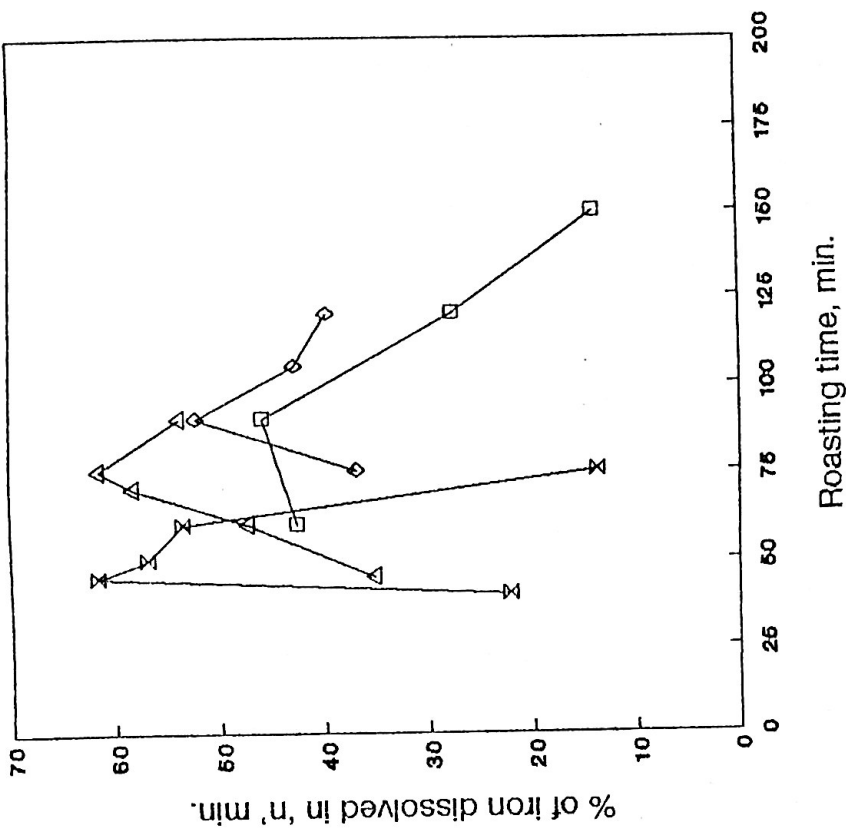


Fig. 31. Plot of weight percentage of titanium dissolved in 'n' min. versus roasting time. (Δ): NaCl, $n=120$; (□): Na₂SO₄, $n=120$; (◇): NaNO₃, $n=90$ and (⋈): Na₂CO₃, $n=45$. Ilmenite to salt ratio=2 for NaNO₃, 0.67 for NaCl & 1.5 for Na₂CO₃. Roasting and leaching conditions are as in Fig. 29.

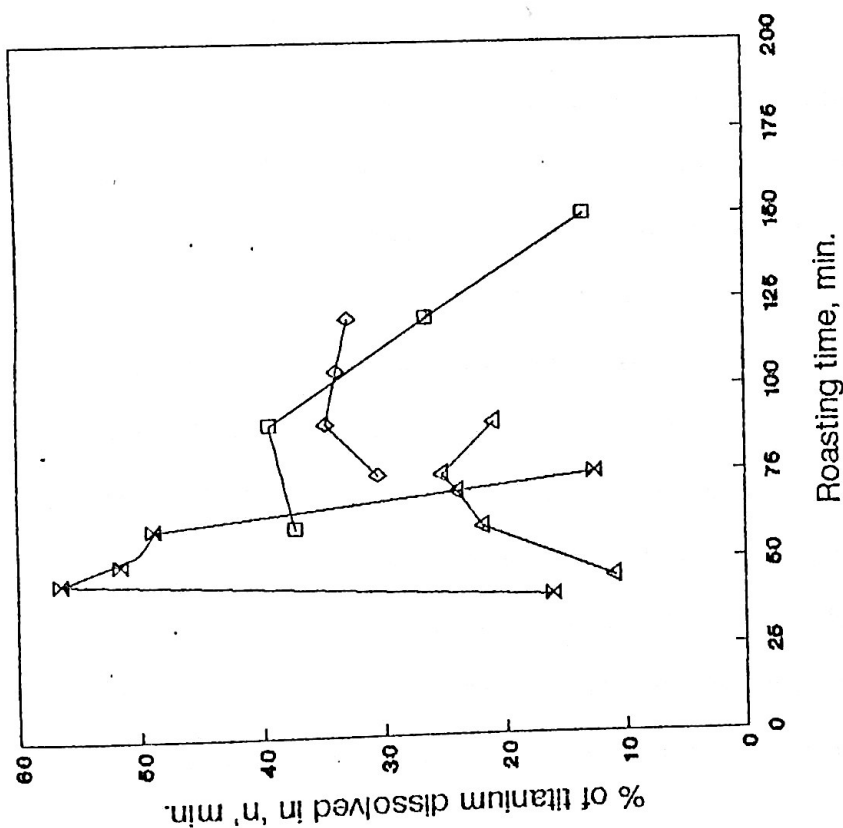


Fig. 32. Plot of weight percentage of iron dissolved in 'n' min. versus roasting time. (Δ): NaCl, $n=120$; (□): Na₂SO₄, $n=120$; (◇): NaNO₃, $n=90$ and (⋈): Na₂CO₃, $n=45$. Ilmenite to salt ratio=2 (1.7 for NaNO₃, 0.67 for NaCl & 1.5 for Na₂CO₃). Roasting and leaching conditions are as in Fig. 29.

similar to the other systems, the effect of roasting time is not so large. The maximum dissolutions of titanium (34.8%) and iron (52.2%) are obtained at 90 minutes' roasting, which are little decreased to 32.9% titanium and 39.7% iron dissolutions, when the roasting is continued for 120 minutes.

The decreasing leaching behaviours of titanium and iron from salt-roasted masses are difficult to explain. Possibly, the prolonged roasting time facilitates some sorts of phase transitions, which are less susceptible to acid leaching. It is, however, concluded from these study that the optimum roasting times are 75, 90, 90 and 45 minutes for NaCl, Na₂SO₄, NaNO₃ and Na₂CO₃ systems respectively at their optimum ilmenite to salt ratios and the long time roasting decreases the solubility of the metals significantly, particularly in the cases of Na₂SO₄ and Na₂CO₃ systems.

iii) EFFECT OF ROASTING TEMPERATURE :

The effect of the roasting temperature has been monitored by leaching of the roasted products obtained at different temperatures but at constant optimum ilmenite to salt ratios and roasting times. The leaching results at S/L ratio of 0.02 kg dm⁻³ (based on ilmenite content) are given in Table XXXII. The maximum weight percentages of titanium and iron which have been read off from the data given in the above table are collectively shown in Table XXXIII. Figures 33 and 34 represent the variations of maximum weight percentages of titanium and iron respectively dissolved in 'n' minutes' leaching of the roasted product with the variations of roasting temperatures in °C. In all cases, the maximum weight percentages of titanium and iron dissolved vary with roasting temperatures and pass through

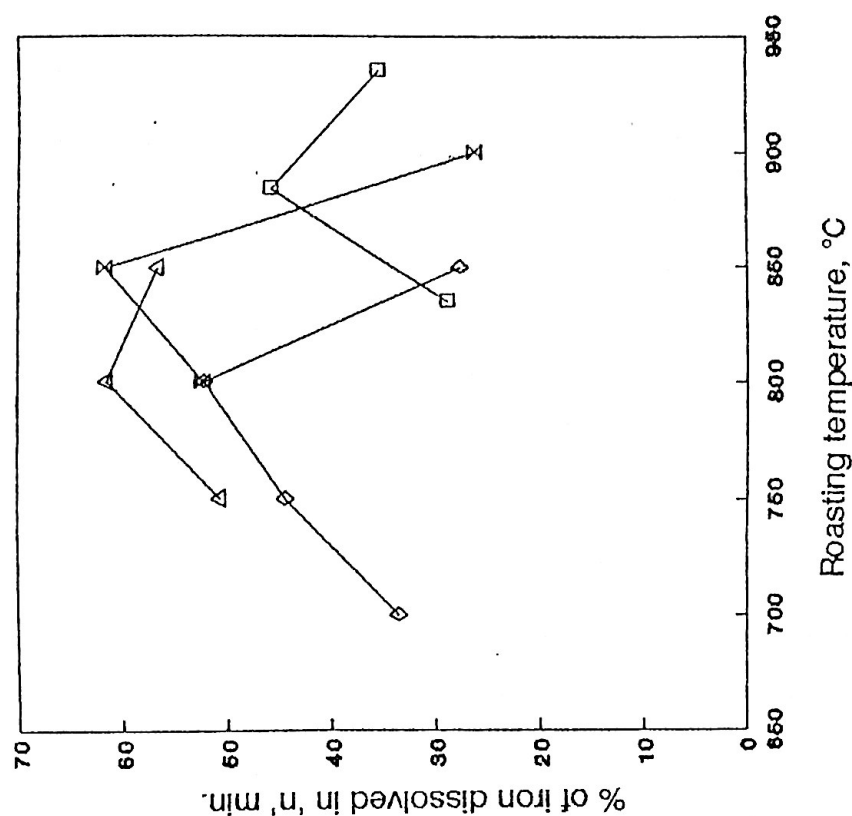


Fig. 33. Plot of weight percentage of titanium dissolved in 'n' min. versus roasting temperature. (Δ): NaCl, n = 120; (□): Na₂SO₄, n = 120; (◇): NaNO₃, n = 90 and (⋈): Na₂CO₃, n = 45. Roasting time = 90 min. (45 min. for Na₂CO₃ & 75 min. for NaCl). The other roasting and leaching conditions are as in Figs. 29 & 32.

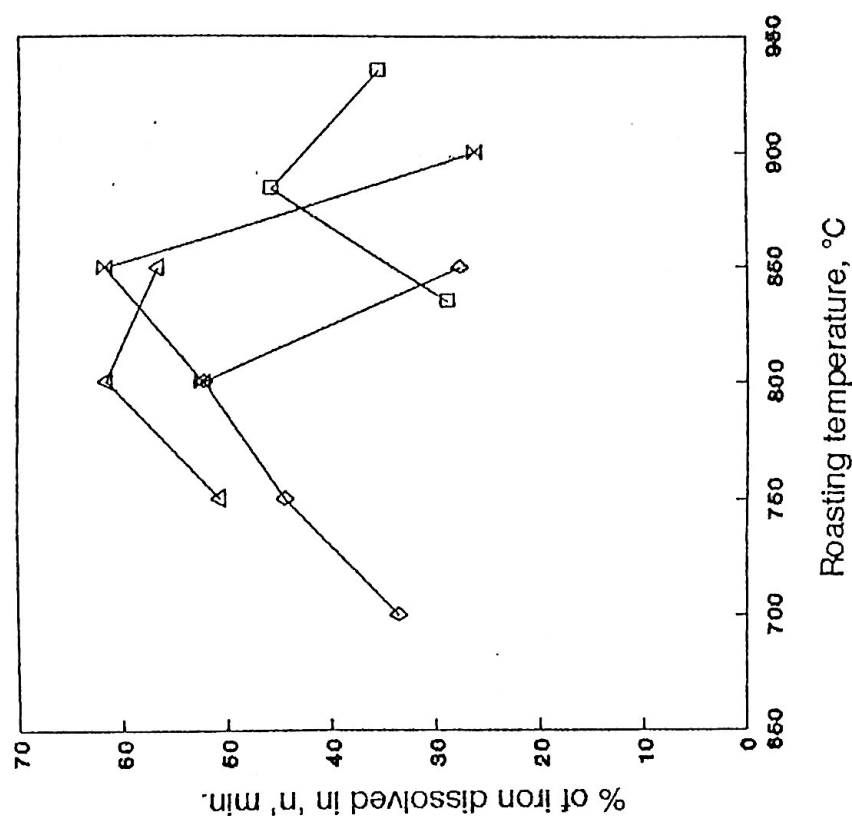


Fig. 34. Plot of weight percentage of iron dissolved in 'n' min. versus roasting temperature. (Δ): NaCl, n = 120; (□): Na₂SO₄, n = 120; (◇): NaNO₃, n = 90 and (⋈): Na₂CO₃, n = 45. Roasting time = 90 min. (45 min. for Na₂CO₃ & 75 min. for NaCl). The other roasting and leaching conditions are as in Figs. 29 & 32.

maxima. The optimum roasting temperatures for the best leachings are determined to be 800, 885, 800 and 850°C for NaCl Na₂SO₄, NaNO₃ and Na₂CO₃ systems respectively. The roasting over the optimum temperatures has possibly the same effect as those encountered with the increased roasting time over optimum values.

iv) *EFFECT OF CARRIER GAS (NITROGEN) FLOW RATE :*

Usually in the salt-water vapour roasting, the flow rate of the carrier gas exhibits some effect on the extent of roasting at a certain roasting temperature and time. This is due to the fact that the carrier gas carries more water vapour at it higher flow rate which eventually affect the rate and extent of roasting. Consequently, the effect of the carrier gas flow rate on the salt-water-vapour roasting of ilmenite has been investigated.

This investigation has again been monitored by the leaching behaviour of the roasted product obtained from different roasting processes carried out at different gas flow rates but at constant temperature, time and ilmenite to salt ratios. The experimental results are given in Table XXXIV. The maximum weight percentages of titanium and iron dissolved after 'n' minutes' at different carrier gas flow rates have been calculated from above table and are given in Table XXXV, which have been plotted in Figures 35 and 36 for titanium and iron respectively.

In all salt roasting systems, it is evident from the results given in Figs. 35 and 36 that the dissolution percentages of both metals from the roasted masses are increased with increasing the carrier gas flow rate upto 420 cm³ min⁻¹ and on further increase in the carrier gas flow rate the

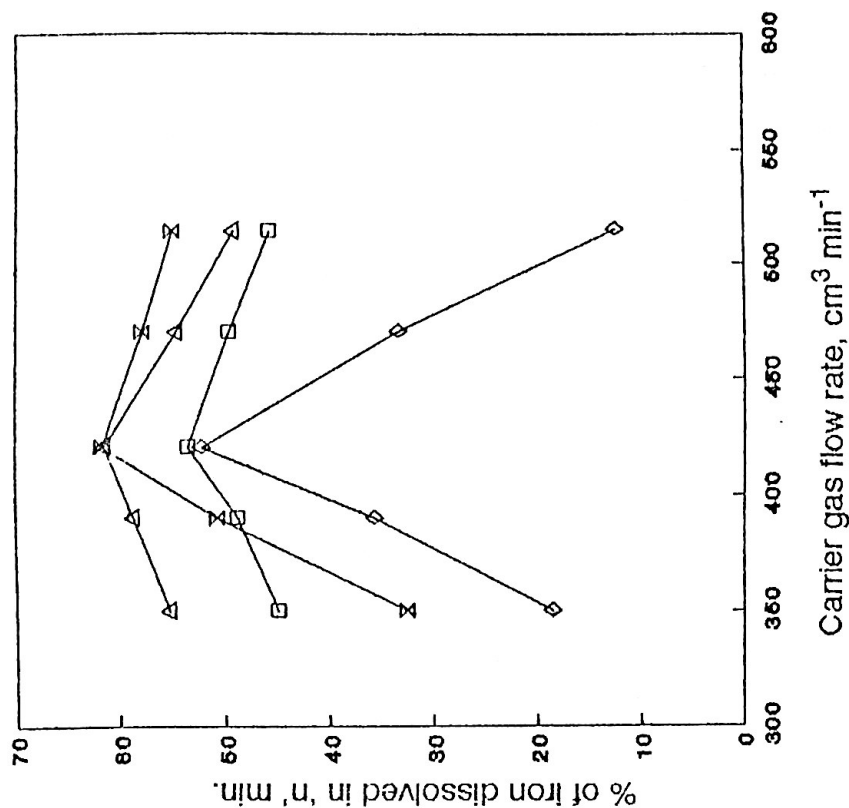


Fig. 35. Plot of weight percentage of titanium dissolved in 'n' min. versus roasting carrier gas flow rate. (Δ): NaCl, n = 120; (□): Na₂SO₄, n = 120; (◇): NaNO₃, n = 90 and (⋈): Na₂CO₃, n = 45. Ilmenite to salt ratio = 2 (1.7 for NaNO₃, 0.67 for NaCl & 1.5 for Na₂CO₃). Roasting time = 90 min. (45 min. for Na₂CO₃ & 75 min. for NaNO₃). The other roasting and leaching conditions are as in Fig. 29.

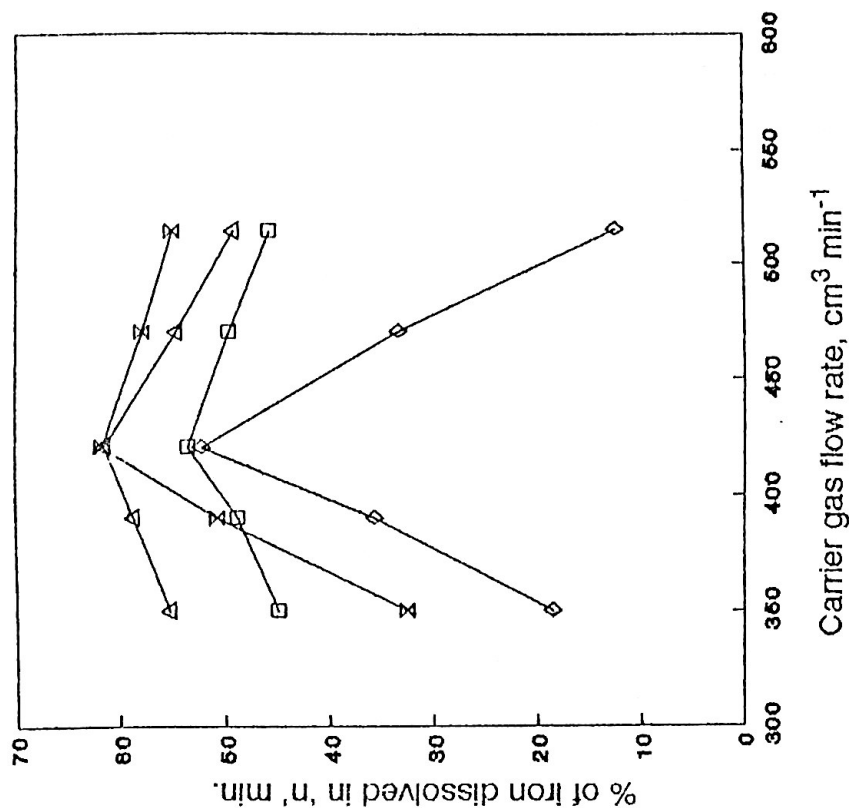


Fig. 36. Plot of weight percentage of iron dissolved in 'n' min. versus roasting carrier gas flow rate. (Δ): NaCl, n = 120; (□): Na₂SO₄, n = 120; (◇): NaNO₃, n = 90 and (⋈): Na₂CO₃, n = 45. Ilmenite to salt ratio = 2 (for NaNO₃, 0.67 for NaCl & 1.5 for Na₂CO₃). Roasting time = 90 min. (45 min. for Na₂CO₃ & 75 min. for NaNO₃). The other roasting and leaching conditions are as in Fig. 29.

adversative leaching results are obtained. The rates of the salt-roasting processes are usually increased with increase in the carrier gas (inert) flow rate due to the fact that the amount of water vapour entering into the reaction tube is increased with increasing the gas flow rate^{254,255,259}. The unfavorable leaching results obtained at higher gas flow rate are due possibly to the phase transition of the first formed easily leachable roasted product to a phase resistant to leaching.

v) EFFECT OF WATER VAPOUR PRESSURE :

In all the above salt roasting studies, a constant water vapour pressure of 31.5 mm Hg was used. Since water is a reactant in this type of roasting process, the effects of water vapour pressure on different salt-roasting processes under investigation have been found out.

The leaching results of the salt-water vapour roasted masses obtained at constant optimum temperature, time, ilmenite to salt ratio and carrier gas flow rate but at different water vapour pressures are given in Table XXXVI. The Table XXXVII represents the maximum weight percentages of titanium and iron dissolved in 'n' minutes from the roasted masses obtained at various water-vapour pressures. The results are also shown graphically in Figs. 37 and 38 for titanium and iron respectively.

The shape of the curves in Figs 37 and 38 indicates that the optimum water vapour pressure is 31.5 mm Hg for all systems under investigation. The maximum percentages of metals dissolved are extensively decreased with increasing the water vapour pressure. For example, the increase in the water vapour pressure from 31.5 mm Hg to 55.5 mm Hg, decreases the

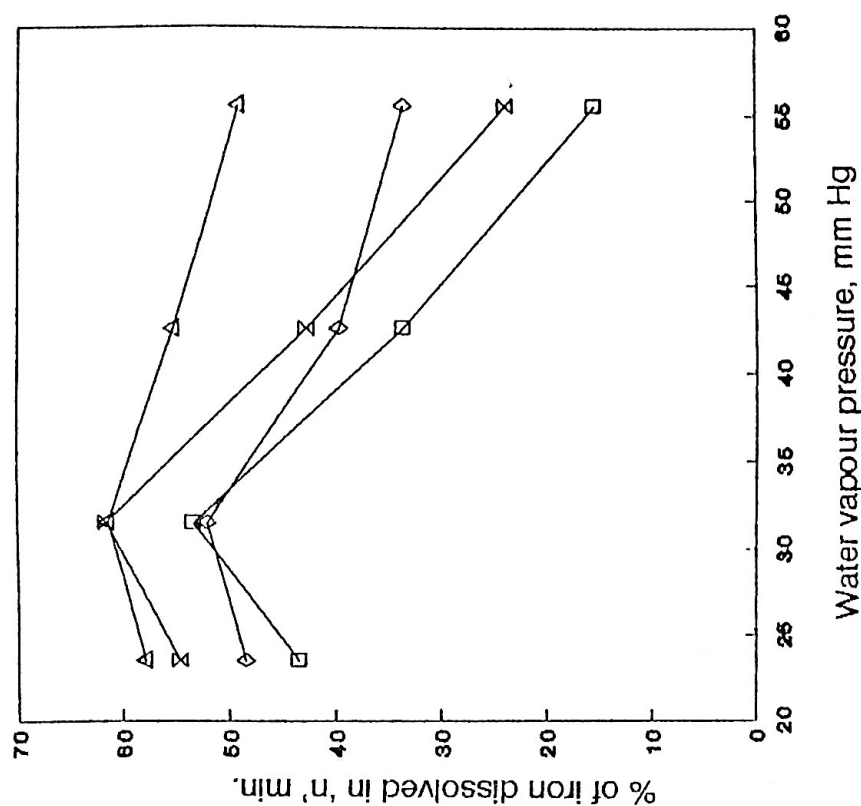


Fig. 37. Plot weight percentage of titanium dissolved in 'n' min. versus roasting water vapour pressure. (Δ): NaCl, n=120; (□): Na₂SO₄, n=120; (◇): NaNO₃ n=90 and (⋈): Na₂CO₃, n=45. Ilmenite to salt ratio=2 (1.7 for NaNO₃, 0.67 for NaCl & 1.5 for Na₂CO₃). Roasting conditions: time=90 min. (45 min. for Na₂CO₃ & 75 min. for NaCl) carrier gas flow rate=420 cm³ min⁻¹. Leaching conditions are as in Fig. 29.

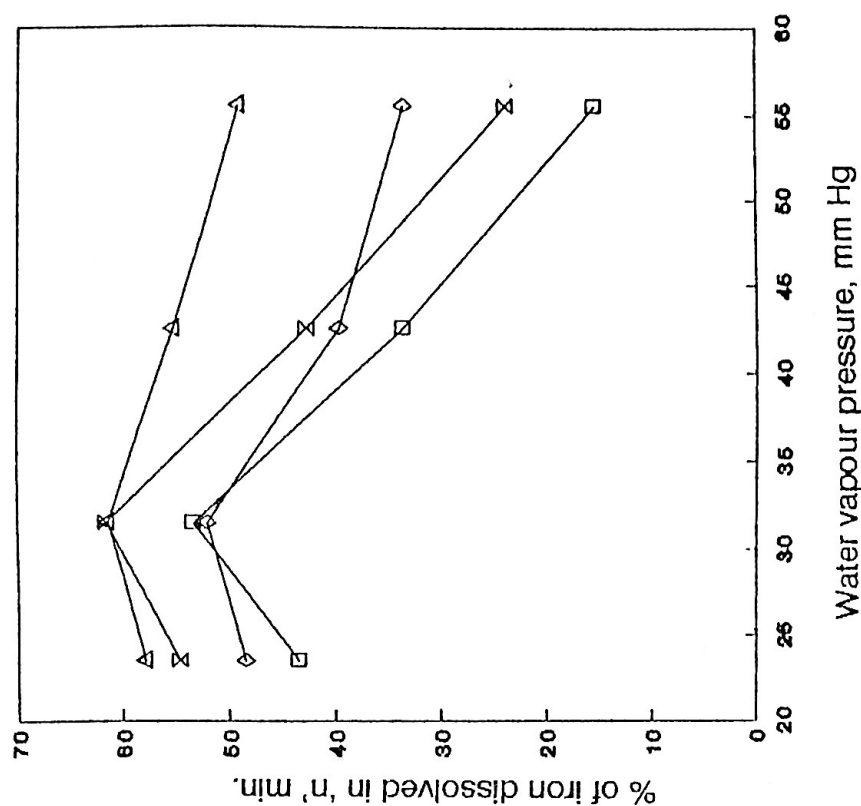


Fig. 38. Plot of weight percentage of iron dissolved in 'n' min. versus roasting water vapour pressure. (Δ): NaCl, n=120; (□): Na₂SO₄, n=120; (◇): NaNO₃ n=90 and (⋈): Na₂CO₃, n=45. Ilmenite to salt ratio=2 (1.7 for NaNO₃, 0.67 for NaCl & 1.5 for Na₂CO₃). Roasting conditions: time=90 min. (45 min. for Na₂CO₃ & 75 min. for NaCl) carrier gas flow rate=420 cm³ min⁻¹. The leaching conditions are as in Fig. 29.

titanium dissolutions from 25.2, 43.5, 34.8 and 56.5% to 13.3, 13.3, 12.8 and 20.2% for NaCl, Na₂SO₄, NaNO₃ and Na₂CO₃ systems respectively.

The decrease in the solubilities of the reaction products at higher water vapour pressure is possibly due to the same reason as mentioned in the case of the effect of carrier gas flow rate.

b) LEACHING :

The leaching characteristics of the salt water vapour roasted ilmenite products obtained at their respective optimum conditions have been thoroughly investigated as functions of leaching agent concentration, temperature and pulp agitation speed. The effect of solid to liquid phase ratio and stage-wise leaching of the sodium carbonate-water vapour roasted product of ilmenite have also been investigated.

i) EFFECT OF LEACHING ACID CONCENTRATION :

The aliquots of salt-water vapour roasted product equivalent to 1 g ilmenite have been leached with 50 cm³ HCl solution of various acid concentrations ranging from 1 to 6 g eq dm⁻³ at their bolting points and at the pulp agitation speed of 292 rpm to calculate the percentages of titanium and iron dissolved at various leaching times. The results are given in Table XXXVIII. In all acid concentrations, the leaching is completed within a definite time interval for each of the roasted systems. This time is below 90, 60, 90 and 30 minutes for NaCl, NaNO₃, Na₂SO₄ and Na₂CO₃ systems respectively, which were observed in all previous leaching studies of the salt-water vapour roasted mass.

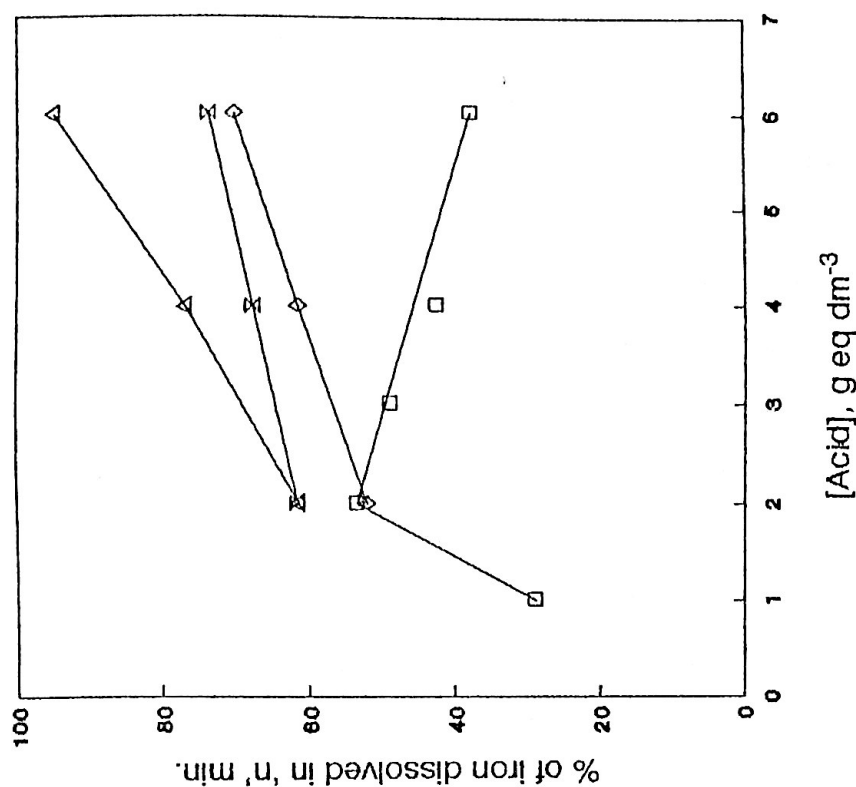


Fig. 40. Plot of weight percentage of iron dissolved in 'n' min. versus acid conc. on the leaching of the salt-water vapour roasted ilmenite. (Δ): NaCl, $n=120$; (□): Na₂SO₄, $n=120$; (◇): NaNO₃, $n=90$ and (⋈): Na₂CO₃, $n=45$. The roasting and leaching conditions are as in Fig. 39.

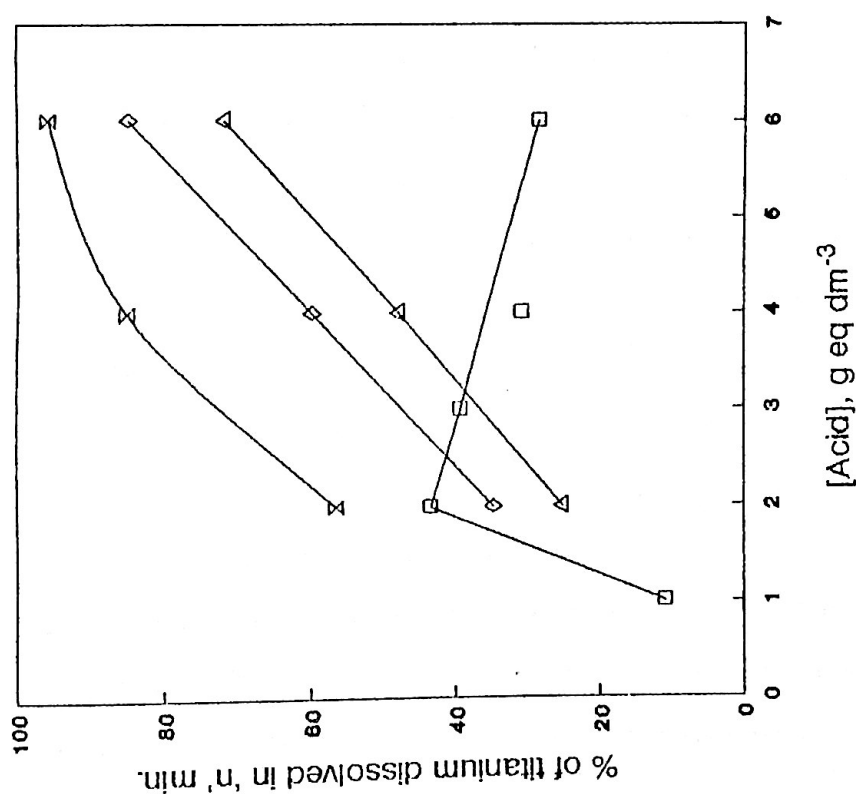


Fig. 39. Plot of weight percentage of titanium dissolved in 'n' min. versus acid conc. on the leaching of the salt-water vapour roasted ilmenite. (Δ): NaCl, $n=120$; (□): Na₂SO₄, $n=120$; (◇): NaNO₃, $n=90$ and (⋈): Na₂CO₃, $n=45$. Roasting conditions: Ilmenite to salt ratio=2, 1.7 0.67 and 1.5 for Na₂SO₄, NaNO₃, NaCl and Na₂CO₃ systems respectively; time=90 min. (45 min. for Na₂CO₃ & 75 min. for NaCl); temp=800°C (885°C for Na₂SO₄ & 850°C for Na₂CO₃); N₂ flow rate=420 cm³ min⁻¹; W.V.P (P_{H_2O})=31.5 mm Hg. Leaching conditions: temp=boiling point; agitation speed=292 rpm; pulp ratio=0.02 kg dm⁻³; $S=1$ g.

The maximum weight percentages of titanium and iron dissolved in hydrochloric acid solutions of different concentration are given in Table IXI. These result are also shown as the maximum weight percentages of titanium and iron dissolved in 'n' minutes versus the acid concentration in g eq dm^{-3} plots in Figs. 39 and 40 respectively. The results obtained with the NaCl, NaNO_3 and Na_2CO_3 roasted products show the usual leaching behaviour, the extents of titanium and iron dissolved are increased with increasing the acid concentration. The best titanium dissolution of about 96% together with about 74% iron has been obtained from the leaching of the Na_2CO_3 roasted product with 6 g eq dm^{-3} hydrochloric acid for only 30 minutes. On the otherhand, the best iron dissolution of about 95% together with about 72% titanium dissolution has been obtained from the leaching of the NaCl roasted mass with 6 g eq dm^{-3} hydrochloric acid for 90 minutes.

The leaching results obtained from Na_2SO_4 roasted mass are seemed to be unusual and difficult to explain. Here the percentages of titanium and iron dissolved show peaks at 2 g eq dm^{-3} hydrochloric acid. Below this concentration, the maximum percentages of both metals are decreased extensively, where as, in acid solutions having concentration grater than 2 g eq dm^{-3} , the maximum dissolution percentages are decreased slowly but significantly.

The comparison of these results with those obtained for the LPG and LPG-water vapour roasted ilmenite products shows that the Na_2CO_3 -water vapour roasting is the best way of pre-treating ilmenite for easy and almost quantilative dissolution (96%) of titanium in 6 g eq dm^{-3} hydrochloric acid within only 30 minutes leaching. The Na_2CO_3 -water vapour roasting (45 min) is also faster than the other roasting processes.

ii) EFFECT OF LEACHING TEMPERATURE :

The aliquots of salt-water vapour roasted products equivalent to 1 g ilmenite have been leached with 50 cm³ 6 g eq dm⁻³ hydrochloric acid (2 g eq dm⁻³ hydrochloric acid for (Na₂SO₄) at various leaching temperatures ranging from 50°C to boiling temperature and at the pulp agitation speed of 292 rpm, to calculate the percentages of titanium and iron dissolved at various leaching times. The results are given in Table XL. The maximum weight percentages of titanium and iron dissolved in hydrochloric acid solution at different leaching temperatures are given in Table XLI. The results are also shown graphically as the maximum weight percentages of titanium and iron dissolved versus the leaching temperature in °C plots in Figs. 41 and 42 respectively. The results obtained with the salt roasted products show the usual leaching behaviour; the extents of titanium and iron dissolved are increased with increasing the leaching temperature upto the boiling point of the reagent at ambient pressure.

iii) EFFECT OF AGITATION SPEED :

The selected amounts of salt-water vapour roasted products equivalent to 1 g ilmenite have been leached with 50 cm³ hydrochloric acid solution of 6 g eq dm⁻³ (2 g eq dm⁻³ for Na₂SO₄) at their boiling temperature but at different pulp agitation speed ranging from 194 rpm to 480 rpm to calculate the percentages of titanium and iron dissolved at various leaching time. The maximum weight percentages of titanium and iron dissolved in 'n' minutes' at different pulp agitation speed for the investigated salt roasting systems are given in Table K.

The effect of the pulp agitation speed on the leaching behaviours of the investigated salt-water vapour roasted products are not different.

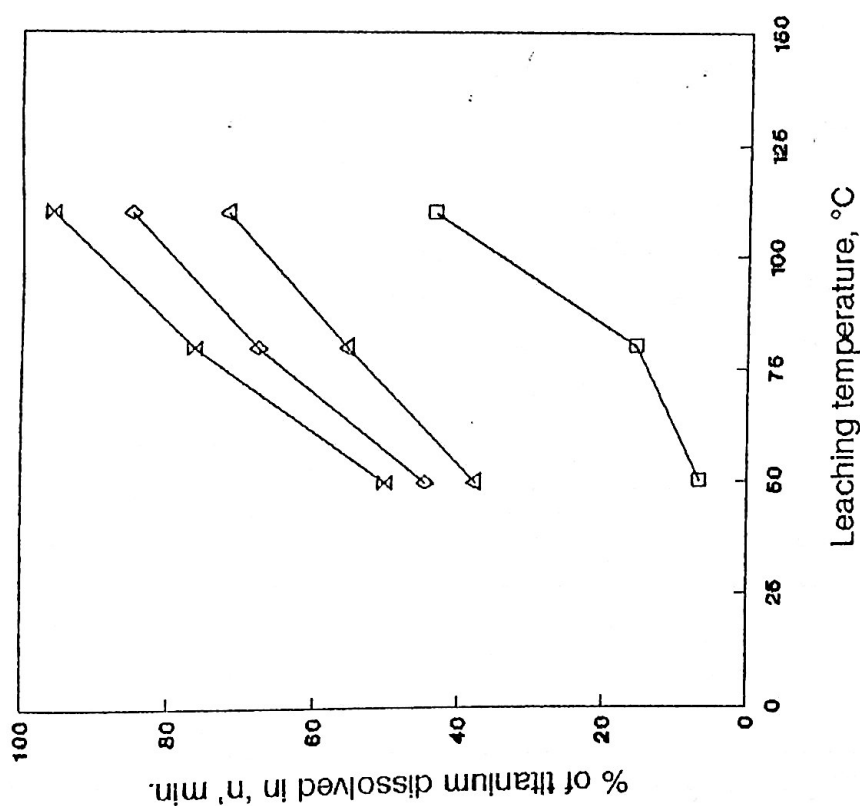


Fig. 41. Plot of weight percentage of titanium dissolved in 'n' min. versus temperature on leaching of the salt water vapour roasted ilmenite. (Δ): NaCl, n=120, (□): Na₂SO₄, n=120, (◇): NaNO₃, n=90 and (⊗): Na₂CO₃, n=45. The roasting conditions are as in Fig. 39. Leaching conditions: [HCl]=6 g eq dm⁻³ (2 g eq dm⁻³ for NO₂SO₄); agitation speed=292 rpm; pulp ratio=0.02 kg dm⁻³, S=1 g.

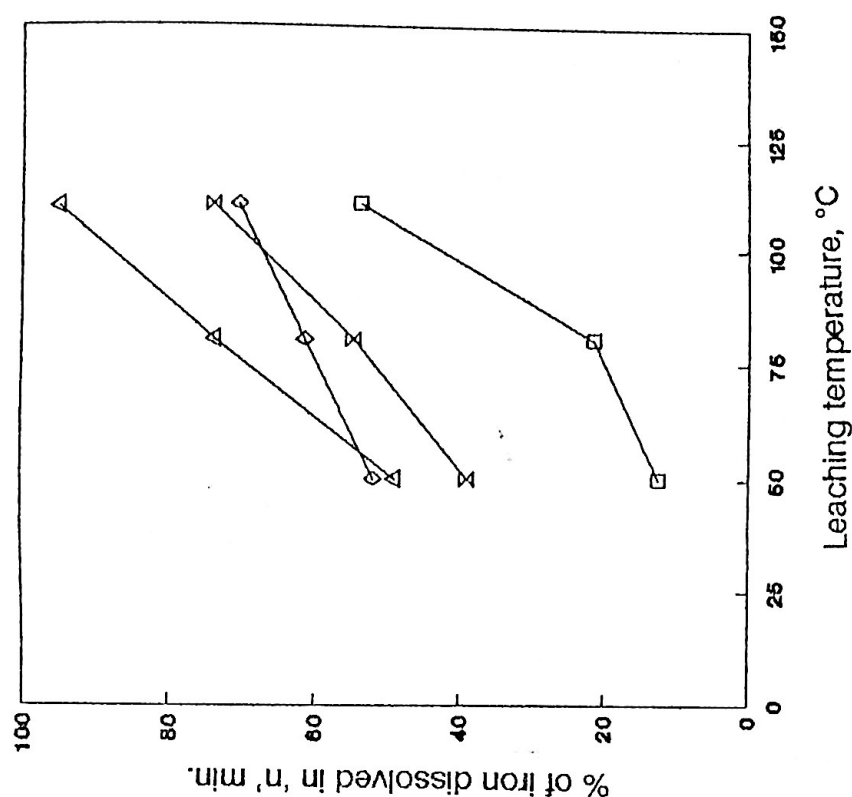


Fig. 42. Plot of weight percentage of iron dissolved in 'n' min. versus temperature on leaching of the salt water vapour roasted ilmenite. (Δ): NaCl, n=120; (□): Na₂SO₄, n=120; (◇): NaNO₃, n=90 and (⊗): Na₂CO₃, n=45. The roasting and leaching conditions are as in Fig. 39 and Fig. 41 respectively.

Although the variation of solubilities of metals from the roasted masses is considerably large at the lower pulp agitation speed region, the variations at higher pulp agitation speed region are insignificant. Possibly, this behaviour is due to the change in the mechanism of dissolution.

At lower agitation speed, say at 200 rpm the diffusion is the rate controlling for greater interfacial film thickness. As the agitation speed increases, the film thickness decreases resulting in an increase in the diffusion rate. Consequently, at higher speed (where the rate of dissolution becomes independent of agitation speed), the diffusion of reagent or product through the film remains no longer rate controlling and so the process becomes chemically controlling.

Table K. *Effect of agitation speed on the leaching of the salt-water vapour roasted ilmenite.*

Roasting temperature = 800°C (885°C for Na₂SO₄ & 850°C for Na₂CO₃)

Roasting time = 90 min (45 min for Na₂CO₃ and 75 min for NaCl)

Ilmenite to salt ratio = 1.7 for NaNO₃, 2 for Na₂SO₄, 0.67 for NaCl & 1.5 for Na₂CO₃

Carrier gas flow rate = 420 cm³ min⁻¹

Water vapour pressure = 31.5 mm Hg

Leaching acid concentration = 6 g eq dm⁻³ (2 g eq dm⁻³ for Na₂SO₄)

Leaching temperature = boiling temperature

Pulp ratio = 0.02 kg dm⁻³ (based on ilmenite content)

Agitation (calibra- ted) speed, rpm	Max. wt. % metals dissolved in n* min. for							
	NaCl roast		Na ₂ SO ₄ roast		NaNO ₃ roast		Na ₂ CO ₃ roast	
	Ti	Fe	Ti	Fe	Ti	Fe	Ti	Fe
194	58.8	82.7	30.5	36.5	61.0	61.1	65.5	50.1
240	65.2	92.3	40.0	48.5	76.1	66.0	84.9	66.0
292	71.8	94.9	43.5	53.5	84.9	70.2	95.8	73.7
350	72.5	96.0	44.5	55.9	86.5	71.0	96.5	74.0
480	74.1	96.5	45.7	57.8	87.1	73.3	96.9	74.4

* n = 120, 120, 90 and 45 for NaCl, Na₂SO₄, NaNO₃ and Na₂CO₃ systems respectively.

iv) EFFECT OF SOLID TO LIQUID PHASE RATIO :

The effect of solid to liquid phase ratio on the dissolution of the sodium carbonate-water vapour roast have been investigated by estimating the amount of titanium and iron dissolved on leaching the roasted product (equivalent to 1 g ilmenite) with 50, 25, 16.7, 12.5 and 10 cm³ 4 g eq dm⁻³ hydrochloric acid at its boiling temperature. From the percentage dissolutions, the concentrations of titanium and iron in leach solutions have been calculated. The results are given in Table XLII.

Figures 43a and 43b show the variations of the percentages of titanium and iron dissolved in 45 minutes, leaching with the variation of solid to liquid phase ratio. It is found that the percentage of titanium dissolved in 45 minutes leaching is decreased extensively with increasing the solid to liquid phase ratio. The percentage of iron dissolved in 45 minutes' leaching is also found to decrease slightly with increasing the S/L ratio.

A simple calculation shows the presence of 40 meq hydrochloric acid for 5.8 meq titanium and 5.8 meq iron each at the highest investigated S/L value of 0.1 kg dm⁻³; these values definitely indicate the sufficiency of the reagent for dissolution even at this S/L ratio. It is therefore, concluded that the decrease in the percentage dissolution of metal ions (particularly of titanium) at higher S/L ratios is not for the scarcity of the reagent. The reason for this behaviour may be due to the following two possibilities :

- (a) Saturation of leach solution with titanium above a certain S/L ratio;
and
- (b) Precipitation of a titanium compound from titanium in leached solution.

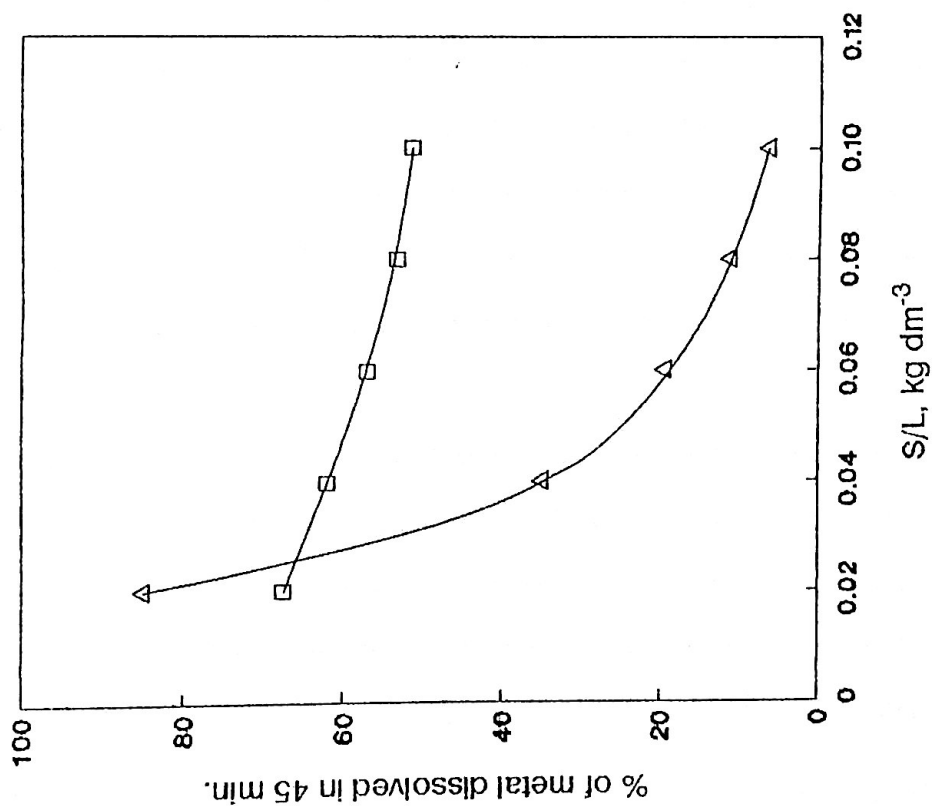


Fig. 43a. Plot of weight percentages of titanium and iron dissolved in 45 min. versus solid to liquid phase ratio (S/L) for leaching of sodium carbonate-water vapour roasted mass. (Δ): Ti; (□): Fe.

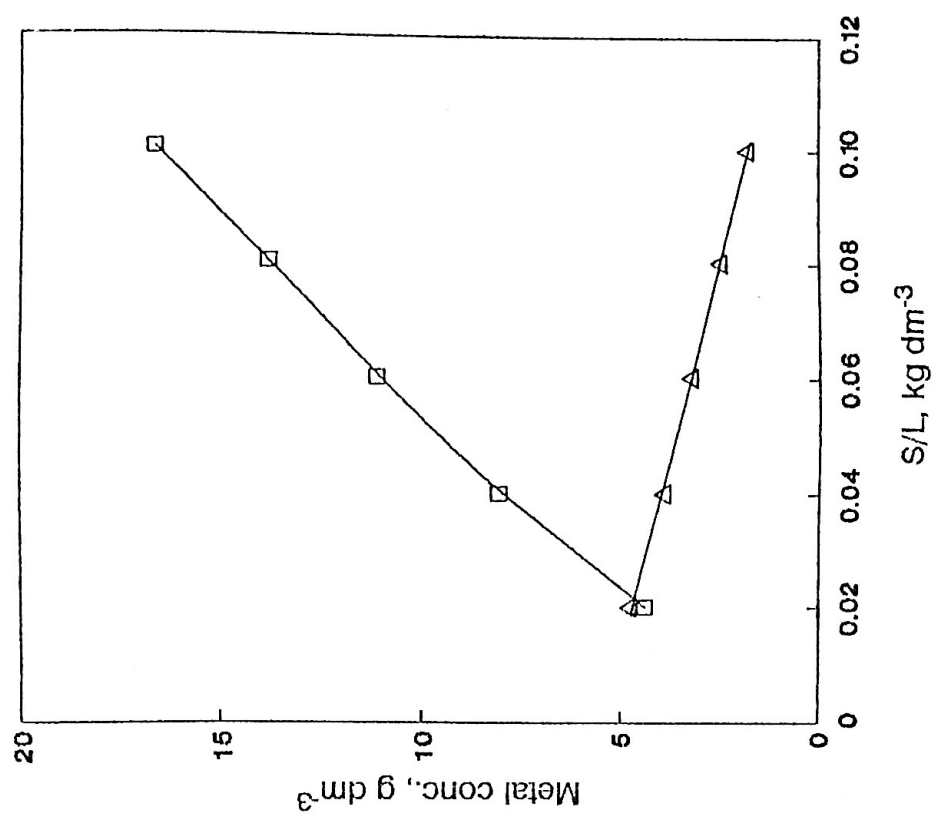


Fig. 43b. Plot of the concentration of metal ions in leach solution versus solid to liquid phase ratio (S/L) for leaching of sodium carbonate-water vapour reacted mass. (Δ): Ti; (□): Fe.

The first possibility has been ruled out from an examination of the plots in Fig 43, where concentrations of metal ions in leached solution have been plotted against the S/L ratio. Since the concentration of titanium in leach solution decreases significantly with increasing S/L ratio, the saturation of leach solution with titanium is not the reason for this behavior.

The second possibility has been predicted from the percentages of titanium dissolved in various time intervals at higher S/L ratios. During leaching at S/L ratio of 0.08 kg dm^{-3} , 35.72% titanium dissolution in 12 min has been reduced to 11.3% titanium dissolution in 45 min. The decrease of the titanium concentration in leached solution with time is due to the thermal hydrolysis of dissolved titanium. It is well known that the precipitation of metatitanic acid, $\text{TiO}_2 \cdot x\text{H}_2\text{O}$ takes place on heating an acidic solution (HCl, H_2SO_4 etc, but not the complex forming acid) of a titanium salt²⁶⁰. The thermal hydrolysis of titanium taking place during leaching at higher S/L ratio has been demonstrated by heating a leach solution containing $\sim 5 \text{ g dm}^{-3}$ titanium which results in a decrease in titanium concentration to $\sim 1 \text{ g dm}^{-3}$ and a precipitate is found to be suspended in solution.

It is therefore concluded that the leaching of the sodium carbonate-water vapour roasted product at a high S/L ratio can not be used to get a highly concentrated solution of titanium and iron in leach solution. It could however be used for enrichment of ilmenite by getting a residue containing mainly the hydrated titanium dioxide leaving almost all iron in leach solution.

Experiments have shown that the thermal hydrolysis of titanium (titanyl) chloride apparently takes place, when the titanium concentration in 4 g eq dm^{-3} hydrochloric acid solution exceeds about 5 g dm^{-3} . If the quantitative co-leaching of titanium and iron are desired with a maximum concentration of titanium in leach solution, the leaching should be carried out at a S/L ratio of 0.02 kg dm^{-3} for about 40 min. Longer time and higher S/L ratio will result in a decrease of titanium concentration in leach solution.

v) STAGE-WISE LEACHING :

During the investigation on the effect of solid to liquid phase ratio on dissolution of metal ions by 4 g eq dm^{-3} hydrochloric acid at its boiling point from the sodium-carbonate-water vapour roasted product, it has been found that only 6.5% titanium and 51.4% iron are present in the leach solution when the S/L ratio is 0.1 kg dm^{-3} and the leaching time is 45 min. This result inspired us to make a study on the stage-wise leaching for the system mentioned above. In this study, the residue left after a certain stage has been subjected to further leaching with an equal volume of the fresh leachant.

The stage-wise leaching results are given in Table XLIII and shown graphically in Fig. 44 as cumulative titanium and iron concentration versus stage-number plots. The results show that the cumulative percentage dissolution of iron is only ~62% in the fourth stage when 51.4% dissolution of iron occurs in the first stage. The cumulative percentage dissolution of titanium is also not so much increased with the number of stages. This

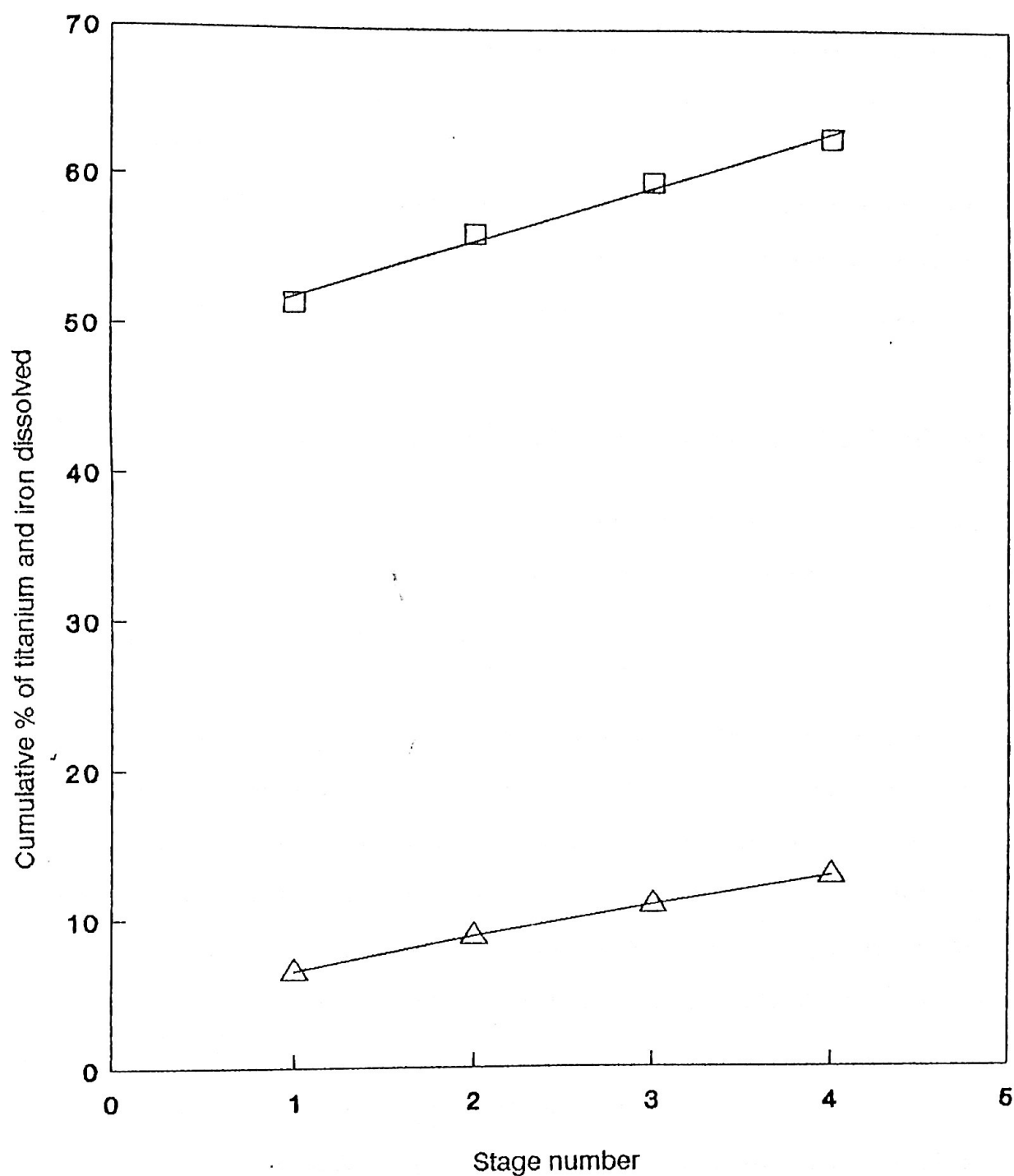


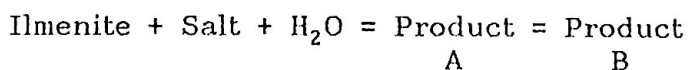
Fig. 44. Plot of cumulative percentages of titanium and iron dissolved in 45 min. versus stage number. (Δ): Ti and ($\square$): Fe.

result suggests that the partial leaching of iron from the roasted product by stage-wise leaching using a high S/L ratio is not recommendable to enrich ilmenite.

The reason for this behaviour is possibly due to the formation of a film of hydrated titanium dioxide on the roasted mass, which slows down the diffusion rate of reagent to and the products from the reaction site.

5.5 CHARACTERIZATION OF SALT-ROASTED PRODUCTS

The salt-water vapour roasting results of ilmenite are best explained, in all cases, if we consider the following scheme for roasting:



Product A produced first is easily leachable. On increasing either reaction time, temperature, salt to ilmenite ratio, gas flow rate or water vapour pressure from their optimum values will facilitate the formation of product B, which is resistant to acid leaching. It is however very difficult to identify the product A and B phases due to the complexities of the $\text{Na}_2\text{O}-\text{TiO}_2-\text{FeO}$ system. Many phases of compositions $\text{Na}_{2x}\text{O}_x \cdot \text{Ti}_y \cdot \text{O}_{2y} \cdot \text{Fe}_z\text{O}_z$ having a large number of x , y and z values are possible as experienced from an examination of the ASTM X-ray diffraction cards.

A thorough X-ray diffraction study of the roasted products at various experimental roasting parameters is needed to identify the product A and product B. Such a complicated study has not been undertaken, nevertheless, we have tried to observe any change in the X-ray diffraction pattern of

ilmenite occurred in the salt roasted masses obtained at optimum conditions in forming largely the phase product A.

The possible phases (product A) obtained at the optimum condition as predicted from the study of the effect of ilmenite to salt ratio are $\text{Na}_4\text{O}_2 \cdot \text{TiO}_2 \cdot \text{FeO}$, $\text{NaO}_{0.5} \cdot \text{TiO}_2 \cdot \text{FeO}$, $\text{NaO}_{0.5} \cdot \text{TiO}_2 \cdot \text{FeO}$ and $\text{Na}_2\text{O} \cdot \text{TiO}_2 \cdot \text{FeO}$ for the NaCl, Na_2SO_4 , NaNO_3 and Na_2CO_3 systems respectively. It is expected therefore that the X-ray diffractograms of the Na_2SO_4 and NaNO_3 roasted products obtained at optimum conditions should be more or less identical, whereas those of NaCl and Na_2CO_3 roasted products obtained at optimum conditions should be different.

The X-ray diffraction patterns of Na_2SO_4 and NaNO_3 roasts, as shown in the fifth and seventh columns in Table L, are almost identical with a few underlined "d" values uncommon. Most of the deflections coincided with the X-ray diffraction pattern of NaFeTiO_4 (Appendix-2). However, due to the presence of certain uncommon deflections, the products contain at least another phase uncommon together with NaFeTiO_4 . These phases are probably responsible for getting different leaching results from the Na_2SO_4 and NaNO_3 roasts. These additional phases could not however be identified easily. Comparisons of the X-ray patterns of ilmenite (first column) with those of Na_2SO_4 (fifth column) and of NaNO_3 (seventh column) roasted products clearly indicate that the salt-water vapour roastings took place during the treatment and the whole amounts of ilmenite have been converted. One point of interest to note here that a composition of $\text{NaO}_{0.5} \cdot \text{FeO} \cdot \text{TiO}_2$ was predicted from the optimum ilmenite-salt ratio, but the X-ray analysis suggests the composition $\text{NaO}_{0.5} \cdot \text{FeO}_{1.5} \cdot \text{TiO}_2$. Possibly the first phase is thermodynamically

unstable and is not formed; whereas the second phase is thermodynamically stable and is formed only in the oxidizing atmosphere. In the experiments, we used nitrogen as carrier gas, so the oxidation of FeO to Fe₂O₃ takes place via the oxidizing action of Na₂SO₄ and NaNO₃ prior to or during the roasting operation. It could however be concluded here that the salt-roasted ilmenite product should have a composition NaO_{0.5}·FeO_{1.5}·TiO₂ (optimum ilmenite-salt ratio being such that the ilmenite to Na₂O ratio becomes 2) provided the salt possesses an oxidizing power. In these two particular cases, it is expected that the oxidation of FeO takes place by the reaction of N₂O₅ and SO₃ gases produced by the dehydration of HNO₃ and H₂SO₄, which in turns are produced by the thermal hydrolysis of NaNO₃ and Na₂SO₄ respectively at high temperature.

The X-ray diffraction pattern of the sodium chloride-water vapour-ilmenite roasted product is given in the third column in Table L. A comparison of its diffraction pattern with the pattern of ilmenite shows that some of the "d" values are common, but their relative intensities are varied. Since the diffraction due to all "d" values for ilmenite are not found in the X-ray pattern of NaCl-roasted product, it is concluded that a salt roasted product is produced whose X-ray pattern is almost similar to ilmenite. The optimum ilmenite to sodium chloride ratio has suggested a composition of Na₄O₂·FeO·TiO₂. Unfortunately, we did not obtain any ASTM X-ray diffraction pattern card for such a composition for confirmation. The X-ray pattern of the roasted product did not coincided with the X-ray pattern of related compounds available in ASTM cards (Appendix-1).

We are particularly interested in the phases obtained by the sodium

carbonate-water vapour roasting of ilmenite because of the fact that the best leaching is obtained from this product. The X-ray diffraction pattern of this product ($\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ vapour roast) is given in the ninth column with the corresponding intensities in the tenth column in Table L. The under lined seven 'd' values correspond to the compound $\text{Na}_{0.75}\text{Fe}_{0.75}\text{Ti}_{0.25}\text{O}_2$ i.e., $\text{Na}_3\text{Fe}_3\text{TiO}_8$. The comparison of the X-ray powder diffraction pattern of ilmenite (first column in Table L with that of $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ vapour roasted product indicate that the whole amounts of ilmenite have been transferred to new phases on roasting. The 'd' values in column nine suggest the presence of another (second) phase in addition to $\text{Na}_3\text{Fe}_3\text{TiO}_8$. Unfortunately, we were unable to identify this phase by searching the ASTM X-ray diffraction cards of the related compounds. However, if we assume that all iron present in ilmenite is used to form $\text{Na}_3\text{Fe}_3\text{TiO}_8$, then by stoichiometry, about two-third of titanium forms the second phase without any iron. The second phase may or may not contain sodium. To confirm this, we have analysed the roasted product for its sodium content. The percentage of sodium in the water washed roasted sample (washing is done to remove any adhered Na_2CO_3 or NaOH) is found to be ~12.5% which suggests that the second phase does not contain any sodium. The second phase should be a oxide of titanium, TiO_x .

Otherwise, if the second phase also contains sodium, then it should also contain iron and titanium in ratio 1:1:3, so that the percentage of sodium in the roasted mass remains at 12.5. The relative proportions of $\text{Na}_3\text{TiFe}_3\text{O}_8$ and $\text{NaTi}_3\text{FeO}_8$ in the roasted mass may vary on roasting conditions. The rate study may ultimately solve this problem as it is predicted that two types of

rates for each metal ion dissolution are expected for dissolution from a mixture of $\text{Na}_3\text{TiFe}_3\text{O}_8$ and $\text{NaTi}_3\text{FeO}_8$. On the otherhand, if two types of rates for titanium and uniform rate for iron dissolution are observed, than the roasted product should be comprised of $\text{Na}_3\text{TiFe}_3\text{O}_8$ and an oxide of titanium.

In either of the above possible phases containing iron, titanium and sodium; iron exists in ferric state. Since the Na_2CO_3 -water vapour roasting studies have been carried out in an inert atmosphere, the ferrous iron in ilmenite must be oxidize by CO_2 produced from decomposition H_2CO_3 which in turn is produced by the reaction of Na_2CO_3 with H_2O at the roasting temperature.

It should be pointed out here that the phase $\text{Na}_2\text{TiFeO}_4$ resulting from this roasting study was predicted from the optimum ilmenite to carbonate ratio used in roasting. The estimated percentage of sodium in the roasted product does not support this composition (should contain ~22% sodium) for the roasted mass. The lower percentage of sodium in the product may be due to the volatilization of sodium hydroxide (mp. 318°C) at the roasting temperature, formed by the thermal hydrolysis of sodium carbonate prior to its reaction with ilmenite. Since the roasting has been carried out at 850°C , the vapour pressure of sodium hydroxide should be of considerably high value at the temperature of its formation and consequently, a significant amount of it is lost by vaporization resulting in a lower experimental optimum ilmenite to sodium carbonate ratio.

5.6 KINETICS OF DISSOLUTION OF THE SODIUM CARBONATE-WATER VAPOUR ROASTED ILMENITE BY HYDROCHLORIC ACID SOLUTION

The forgoing studies show that the best leaching of both titanium and iron from ilmenite by hydrochloric acid solution is obtained by the prior sodium carbonate-water vapour roasting of ilmenite. The optimum roasting condition as determined is : ilmenite to Na_2CO_3 ratio = 1.5, roasting time = 45 min, roasting temperature = 850°C , carrier gas (N_2) flow rate = $420\text{ cm}^3\text{ min}^{-1}$ and water vapour pressure = 31.5 mm Hg ; whereas, the best leaching conditions for extraction of titanium and iron from the roasted mass are: leaching time = 30 min, S/L = 0.02 kg dm^{-3} pulp agitation speed = 292 rpm, leaching temperature = 110°C and reagent concentration = $6\text{ g eq dm}^{-3}\text{ HCl}$. Under the above conditions, ~96% titanium and ~74% iron are leached into the solution.

As pointed out in the earlier section, the x-ray diffraction study of the roasted product indicates the presence of more than one phase, it is likely that the rate study on the dissolution of the roasted mass may lead to the identification of the another phase in conjunction with $\text{Na}_3\text{Fe}_3\text{TiO}_8$.

As the leaching processes are heterogeneous in character, the kinetics of the process will depend on the shape and size or surface area of the solid material at any time during leaching.

TREATMENT OF RATE DATA :

At a constant temperature and phase mixing rate and solid to liquid ratio (S/L), the rate of dissolution of a solid by a liquid reagent may be expressed as :

$$-(dW/dt) = k.A.C^a \dots\dots\dots (14)$$

where, W is the weight of the unreacted solid at a time t, A its surface

area, C the reagent concentration, 'a' the reaction order with respect to reagent concentration and k is the rate constant. If W is expressed in g, A in dm^2 , C in mol dm^{-3} and t in sec, then the k will be in $\text{g dm s}^{-1} \text{mol}^{-1}$ provided 'a' is unity.

In order to get an integrated form of the rate equation from Eq (14), the consideration must be given to the variation of the surface area with time. In an attempt to have a fruitful solution to this problem, we must have to consider that the roasted mass used in the leaching experiments is of spherical in shape with uniform particle size.

If we use a very closely sieved fraction (narrow mesh number difference), then a definite amount of powder will contain approximately the same number of particles. Let us suppose that 1 g of the sample of particle size $>63 \text{ mp} < 125 \text{ mp}$ contains 'n' number particles. Then, the area occupied by 1 g powder (A) is approximately given by :

$$A = n4\pi r^2 \quad \dots \dots \dots (15)$$

where, r is the radius of each particle. As the radius of each particle (r) decreases with time of leaching, the weight at any instance can be calculated from the following relation;

$$W = n(4/3)\pi r^3 \rho \quad \dots \dots \dots (16)$$

where, ρ is the density of the material.

Now, if we define the fraction reacted, R at any time as :

$$R = \frac{W_o - W}{W_o} \quad \dots \dots \dots (17)$$

where W_o and W are the initial weight and weight after certain time, then from Eqns. (14-17), we can get the following equations :

From eqn. (16) :

$$-(dw/dt) = -n4\pi\rho r^2(dr/dt) \dots\dots\dots (18)$$

or, from eqns. (14, 15 & 18) :

$$-4\pi n\rho r^2(dr/dt) = k4\pi n r^2 C^a \dots\dots\dots (19)$$

$$\text{or, } -\frac{dr}{dt} = \frac{kC^a}{\rho} \dots\dots\dots (20)$$

Now, on integrations within the limits $r = r_0$, when $t = 0$ and $r = r$, when $t = t$, we get :

$$\int_{r_0}^r dr = \frac{kC^a}{\rho} \int_0^t dt \dots\dots\dots (21)$$

$$\text{or, } r_0 - r = \frac{kC^a}{\rho} t \dots\dots\dots (22)$$

Now, for spheres, the fraction reacted (Eq. 17) may be presented as follow :

$$R = \frac{(4/3) \pi r_0^3 \rho - (4/3) \pi r^3 \rho}{(4/3) \pi r_0^3 \rho}$$

$$R = 1 - r^3/r_0^3 \dots\dots\dots (23)$$

$$\text{or, } 1 - R = r^3/r_0^3 \dots\dots\dots (24)$$

$$\text{or, } r = r_0 (1 - R)^{1/3} \dots\dots\dots (25)$$

By Eq. (25), the Eq. (22) takes the form;

$$r_0 \left\{ 1 - (1 - R)^{1/3} \right\} = \frac{kC^a}{\rho} t \dots\dots\dots (26)$$

$$\text{or, } 1 - (1 - R)^{1/3} = \frac{kC^a}{\rho r_0} t \dots\dots\dots (27)$$

$$\text{or, } 1 - (1 - R)^{1/3} = qt \dots\dots\dots (28)$$

where, q = pseudo rate constant = $(kC^a/\rho r_0)$. It is important to note here that the final rate equation is independent of number of particles but dependent on the radius of each particle on which the rate is varies inversely with radius of particles.

The Eq. (28) follows that at a certain fixed reagent concentration, the plots of $1-(1-R)^{1/3}$ versus time, t will yield straight lines with slopes equalling to q .

Now, for a definite powder of closely related mesh member, the terms ρ and r_0 in 'q' are constants. So, the value of 'q' will apparently vary on the reagent concentration, C . If the values of ' q_{HCl} ' are determined by the slopes of $1-(1-R)^{1/3}$ versus time, t plots at various reagent concentrations, C_{HCl} ; then

$$\log q_{HCl} = \log (kC^a/\rho r_0) + a \log C_{HCl} \dots \dots \dots (29)$$

Equation (29) indicates that the plot of $\log q_{HCl}$ versus $\log C_{HCl}$ will give straight lines with slope equalling to 'a', the reaction order with respect to the reagent concentration and the intercept (I) equalling to $\log (K/\rho r_0)$. It is apparent that the value of the dissolution rate constant, k can be evaluated from the intercept (I) provided ρ and r_0 are known for the powder under investigation.

To make a study on the effect of temperature on the rate of dissolution, q_T values are to be determined at different temperatures, T (in absolute scale) and the data should be plotted according to the Arrhenius equation^{99,262,263}.

$$\log k \text{ or } \log q_T = \log (\text{constant}) - E_a/2.303RT \dots \dots \dots (30)$$

where, the symbols have their usual significances.

Equation (30) indicates that the plot of $\log R$ or $\log q_r$ against inverse of absolute temperature ($1/T$) should give straight line with slope equalling to $-E_a/2.303RT$, from which the value of the apparent activation energy, E_a can be evaluated.

Since, the dissolution process is heterogeneous in nature, it is expected that the rate of dissolution should be dependent on the pulp agitation speed. The effect of pulp agitation speed on the rate of dissolution can be represented by the following Eq. (31) :

$$\log q_{rpm} = \log \frac{k C^a}{\rho r_o} + b \log (rpm) \quad \dots \dots \dots (31)$$

where, C is the constant reagent concentration and 'b' the exponent of the pulp agitation speed in the rate equation. The value of 'b' can be easily evaluated from the slope of the $\log q_{rpm}$ versus $\log (rpm)$ plot at a fixed reagent concentration.

Consequently, on evaluating the values of the exponents 'a' 'b' and R the empirical rate equation at a constant temperature and S/L equal to 0.02 kg dm^{-3} for the dissolution process may be written as :

$$1 - (1 - R)^{1/3} = \frac{k}{\rho r_o} C^a (rpm)^b \quad \dots \dots \dots (32)$$

EXPERIMENTAL :

About 80 g of ilmenite has been subjected to sodium carbonate-water vapour roasting at its optimum conditions in 40 batches. All products have been mixed together, reground (agglomerated during roasting) in a ball-mill and sieved time to time to collect materials of $<125 \text{ }\mu\text{m}> 63 \text{ }\mu\text{m}$ in particle

size so that r_o of the collected fraction varies within 62.5×10^{-6} m to 31.5×10^{-6} m. This sample is used in all kinetic experiments and in determining the density of the product.

All of the kinetics experiments have been carried out by leaching the powdered sample equivalent to 1 g ilmenite with 50 cm^3 leachant under reflux. After each 3 minutes interval, 0.5 cm^3 portions of leachant are taken out twice, one for titanium and other for iron estimations. From the concentration of titanium and iron dissolved at a certain interval (t), the percentages (f) dissolved and the fraction reacted (R) for both metal ions are calculated ($R = f/100$).

RESULTS AND DISCUSSION :

Density, ρ of the powdered sample has been determined to be 3.58 g cm^{-3} pycnometrically (10 cm^3) using the formula.

$$\rho = \frac{W_3 d}{W_1 + W_3 - W_2} \quad \dots \dots \dots (33)$$

where, W_1, W_2 and W_3 are the weights of pycnometer plus water, pycnometer plus samples plus water and of sample respectively and d is the density of water at the ambient temperature. On salt roasting of ilmenite, the density of ilmenite is decreased from 4.72 g cm^{-3} to 3.58 g cm^{-3} for the roasted mass, which indirectly suggests the association of Na_2O with ilmenite in the product.

a) EFFECT OF HYDROCHLORIC ACID CONCENTRATION ON RATE OF DISSOLUTION

The kinetic data obtained at various hydrochloric acid concentrations but at constant temperature (110°C), pulp mixing speed (200 rpm) and S/L ratio (0.02 kg dm⁻³) are given in Table XLIV. The plots of $1-(1-R)^{1/3}$ versus time (t) in minutes for titanium and iron are given in Figs. 45 and 46 respectively.

It appears from Fig. 45 that the dissolution of titanium from the roasted mass by hydrochloric acid solutions of various concentrations (1-6 g eq dm⁻³) follows well the rate law given by Eq. (28). From the slopes of the lines, the values of q_{HCl} , min⁻¹ at various hydrochloric acid concentration can be estimated.

On the other hand, Fig. 46 for iron dissolution indicates that the 'q' value in min⁻¹ i.e. The slope of $1-(1-R)^{1/3}$ versus time (t) in minute plots is dependent on time of leaching. The $q_{HCl(ini)}$ value (min⁻¹) obtained by studying the leaching upto 10 min is decreased to $q_{HCl>12}$ on studying the leaching above 12 min. The 'q' and log q values for dissolution of both metal ions from the roasted mass at various hydrochloric acid concentrations are given in Table XLV and plotted as log q_{HCl} versus log [HCl] in Fig. 47.

The slopes of the plots in Fig. 47 for both metal ions vary with hydrochloric acid concentration. The slopes in low hydrochloric acid concentration region (<2 g eq dm⁻³) are ~3 and ~1.5 for titanium and iron dissolution respectively. In higher hydrochloric acid concentration region (>2 g eq dm⁻³) the slopes are ~1, and ~0.5 for titanium and iron respectively. It is therefore concluded that the exponent 'a' of the reagent concentration term in rate Eq. (32) depends the concentration of the reagent used.

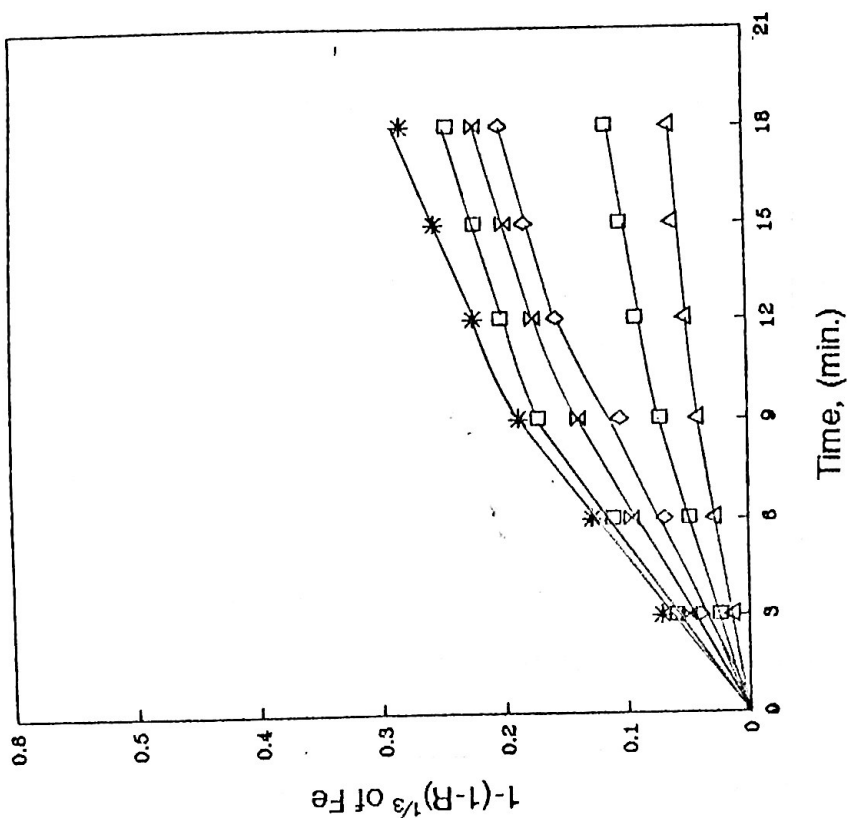


Fig. 46. Plot of $1-(1-R)^{1/3}$ versus time (min.) for iron dissolution for the effect of conc of HCl on the rate of dissolution of $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ vapour roasted ilmenite product. (Δ): 1 g eq dm^{-3} HCl; (◇): 1.5 g eq dm^{-3} HCl; (□): 2 g eq dm^{-3} HCl; (⋈): 3 g eq dm^{-3} HCl; (□): 4 g eq dm^{-3} HCl and (*): 6 g eq dm^{-3} HCl. Leaching conditions are as in Fig. 45.

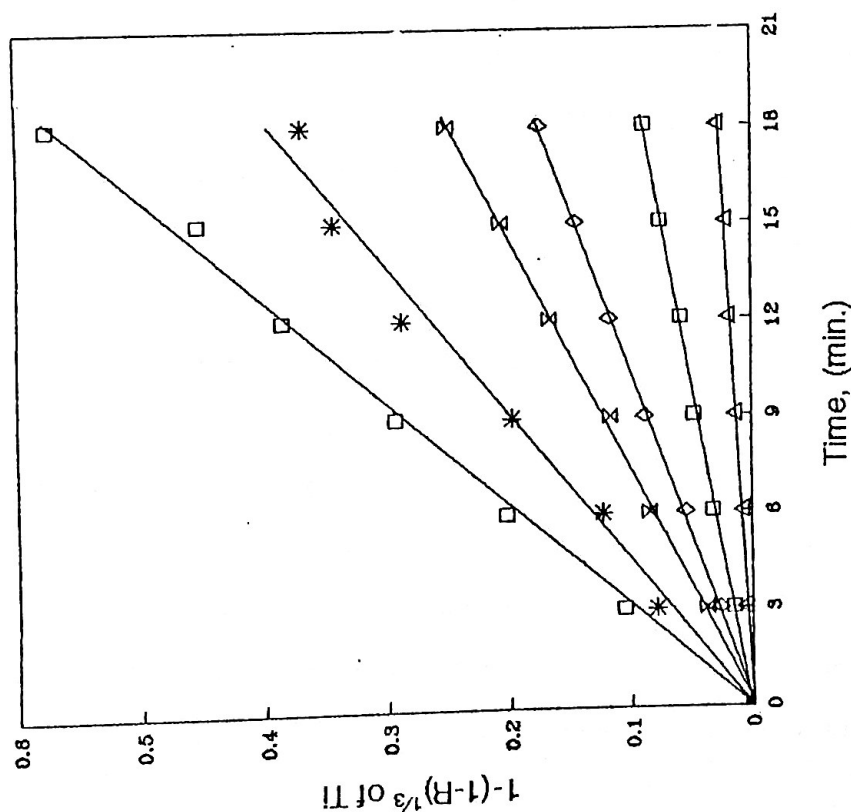


Fig. 45. Plot of $1-(1-R)^{1/3}$ versus time (min.) for titanium for the effect of conc of HCl on the rate of dissolution of $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ vapour roasted ilmenite product. (Δ): 1 g eq dm^{-3} HCl; (◇): 1.5 g eq dm^{-3} HCl; (□): 2 g eq dm^{-3} HCl; (⋈): 3 g eq dm^{-3} HCl; (□): 4 g eq dm^{-3} HCl and (*): 6 g eq dm^{-3} HCl. Leaching conditions: S/L ratio=0.02 kg dm^{-3} ; Stirring speed=200 rpm; temp=110°C and Vol. of liquid=50 cm^3 .

The change in the value of exponent 'a' in the rate equation with the variation of hydrochloric acid concentration for both metal ions clearly indicates the change in the dissolution mechanism from diffusion control to chemical control with increasing concentration of the leachant. This change in mechanism from diffusion-control to chemical-control is due to the fact that at low reagent concentration, the rate of diffusion is very slow and therefore it governs the whole process. With increasing reagent concentration, the rate of diffusion increases to such an extent that it superseeds the rate of chemical reaction and consequent the process shifts from diffusion control to chemical control. In dissolutions of metals and metal oxides by acids it is the general trend^{264,265}. From the nature of the plots in Fig. 47, it is clear that the process is intermediate-control when the concentration of hydrochloric acid is kept around 2 g eq dm⁻³.

It is interesting to point out here that the variation of $q_{\text{HCl(Fe)}}$ with time of leaching (Fig. 46) does not change in the mechanism of dissolution. The only reason for the variation of $q_{\text{HCl(Fe)}}$ value above about 12 min could be the variation of the density and/or initial radius of the leachable component in the roasted phase (cf. Eq. 27). The density of the leachable component may be altered due to the transformation of the constituents of the roasted mass by reaction with hydrochloric acid in the first step to a iron compound from which leaching of iron takes place after ~12 minutes. If the density of the iron compound produced is twice the density of roasted mass, then the value of 'q' after 12 minutes will be about half of the 'q' value before ~10 minutes.

From the intercept of the lines in fig. 47, the values of the constant for titanium and for iron dissolution at <10 min and >12 min in lower and

higher concentration regions can be evaluated. $\log(t)$ c_l and c_h prefixes represent the lower and higher concentration ranges of hydrochloric acid under investigation respectively, I the intercept and Fe_l and Fe_h the subscripts for iron dissolution at <10 min and >12 min respectively, then the values of the intercepts are :

$$\begin{aligned} I_{Ti}^{c_l} &= -2.75, & I_{Fe_l}^{c_l} &= -2.37, & I_{Fe_h}^{c_l} &= -2.65 \\ I_{Ti}^{c_h} &= -2.38, & I_{Fe_l}^{c_h} &= -2.03 \text{ and } I_{Fe_h}^{c_h} &= -2.32 \end{aligned}$$

Assuming the value of $\rho = 3.58 \text{ g cm}^{-3}$ (experimentally determined) and $r_o = 5 \times 10^{-3} \text{ cm}$ (varies within $3.15 \times 10^{-3} \text{ cm}$ to $6.3 \times 10^{-3} \text{ cm}$); the value of ρr_o becomes equal to 0.0179 g cm^{-2} . Since the intercept (m^{-1}) equals to $\log(k/\rho r_o)$, the value of the rate constant can be easily evaluated to be:

$$k_{Ti}^{c_l} = 3.19 \times 10^{-5} \text{ cm}^2 \text{ g}^{-1} \text{ mol}^{-3} \text{ m}^{-1}$$

$$k_{Fe_l}^{c_l} = 7.64 \times 10^{-5} \text{ cm}^2 \text{ g}^{-1} \text{ mol}^{-1.5} \text{ m}^{-1}$$

$$k_{Fe_h}^{c_l} = 4.01 \times 10^{-5} \text{ cm}^2 \text{ g}^{-1} \text{ mol}^{-1.5} \text{ m}^{-1}$$

$$k_{Ti}^{c_h} = 7.34 \times 10^{-5} \text{ cm}^2 \text{ g}^{-1} \text{ mol}^{-1} \text{ m}^{-1}$$

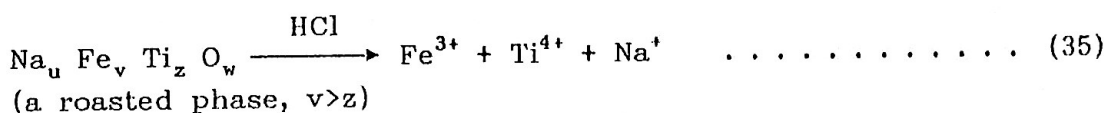
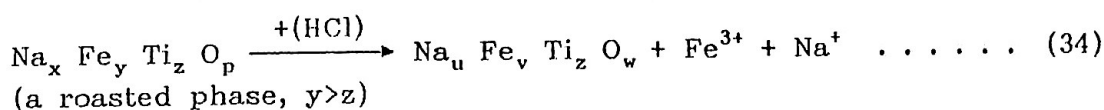
$$k_{Fe_l}^{c_h} = 1.67 \times 10^{-4} \text{ cm}^2 \text{ g}^{-1} \text{ mol}^{-0.5} \text{ m}^{-1}$$

$$k_{Fe_h}^{c_h} = 8.93 \times 10^{-5} \text{ cm}^2 \text{ g}^{-1} \text{ mol}^{-0.5} \text{ m}^{-1}$$

The above values of the constant are only valid at 110°C , 200 rpm and 0.02 kg dm^{-3} S/L ratio. The variation of any one of these parameters, will result in the variation of the value of rate constant.

It is interesting to note here, that the values of the rate constant for titanium dissolution and iron after 12 min's dissolution are almost identical in both concentration regions of hydrochloric acid. Moreover, the above values for titanium dissolution and iron after 12 min's dissolution are almost half of the rate constant for iron dissolution upto ~10 min in both concentration regions of hydrochloric acid.

The kinetic results also suggest the presence of a more than one phase in the roasted product. One of the roasted phase, containing more iron than titanium, leached to dissolve iron and a phase which already existed in the roasted mass. It is thought that initial rate of iron dissolution is due to two parallel reactions as suggested bellow :



In our opinion, the rate of reaction represented by Eq. (34) is almost ceases within about 12 min and after this time the dissolution takes place only through Eq. (35). As the reaction (34) proceeds, the amount of reactant in Eq. (35) is produced gradually and subsequently leached to dissolve Fe^{3+} in a slower rate and titanium in a rate identical to the initial rate. However, the stoichiometric equations can not be given for the inadequate knowledge of the components of roasted product.

It is concluded from this study that

- (1) The initial rate of dissolution of iron is a combination of two parallel reactions;

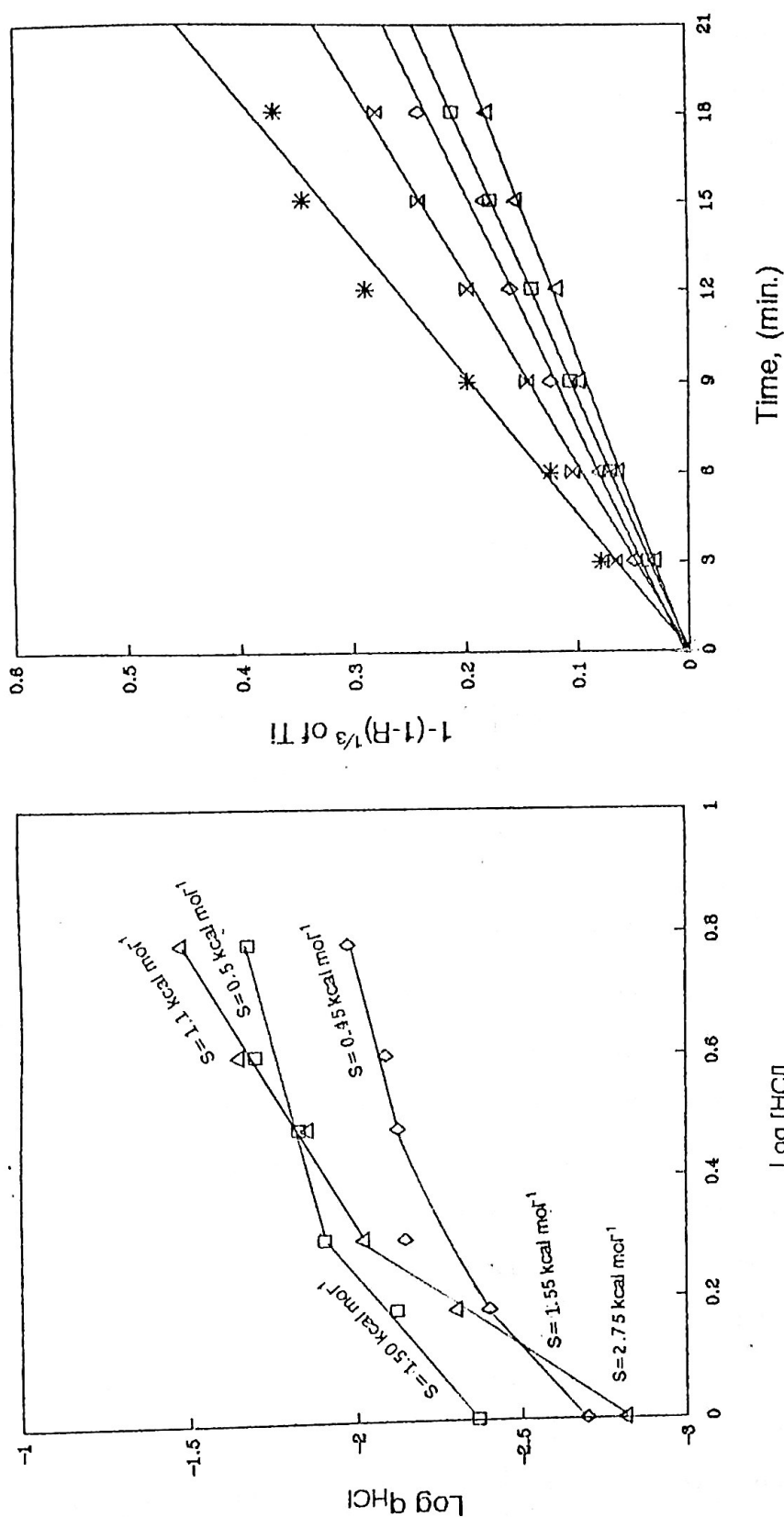


Fig. 47. Plot of $\log q_{\text{HCl}}$ versus $\log [\text{HCl}]$ for titanium and iron dissolution from the $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ vapour roasted ilmenite product (based on Table XLIV and Figs. 45 and 46). (Δ): $\log q_{\text{HCl}}(\text{Ti})$; ($\square$): $\log q_{\text{HCl}}(\text{Fe})$ and ($\diamond$): $\log q_{\text{HCl}}(\text{Fe})$; 12

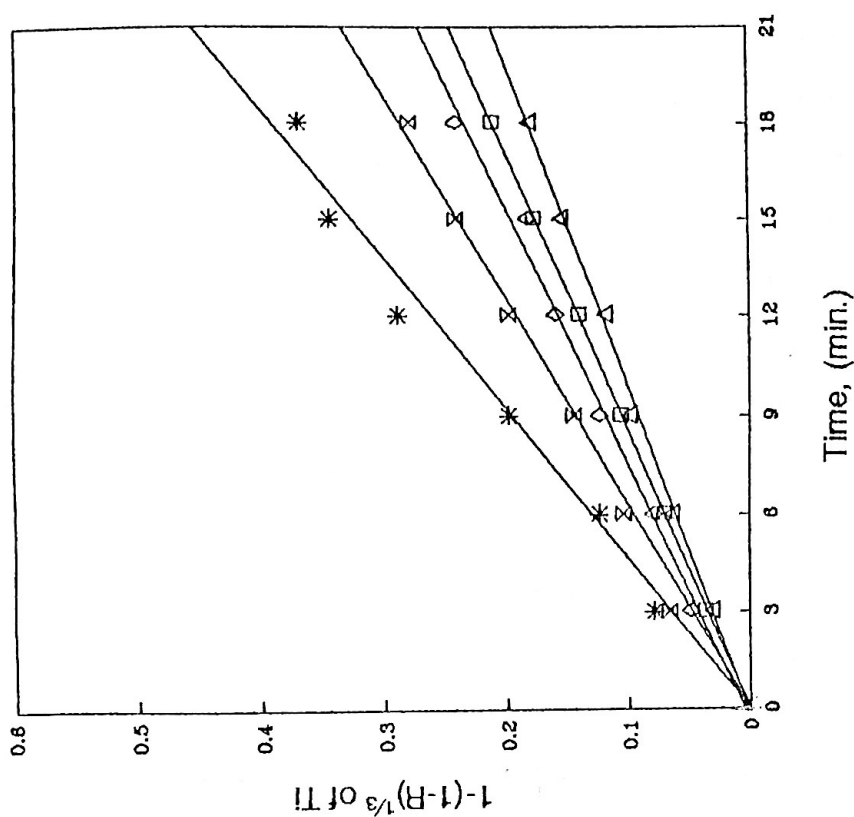


Fig. 48. Plot of $1-(1-R)^{1/3}$ versus time (min.) for titanium: Effect of temperature on the rate of dissolution of $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ vapour roasted ilmenite product. (Δ): 313°K ; ($\square$): 333°K ; ($\diamond$): 353°K ; ($*$): 373°K and $\times$: 383°K . Leaching condition: S/L ratio = 0.02 kg dm^{-3} , stirring speed = 200 rpm. Acid conc. = 4 g eq dm^{-3} and vol. of liquid = 50 cm^3 .

- (2) The mechanism of leaching is changed; a diffusion control at lower hydrochloric acid concentration region ($< 2 \text{ g eq dm}^{-3}$) to a chemically control at higher hydrochloric acid concentration region;
- (3) The exponent of concentration terms for titanium and iron are ~ 3 and ~ 1.5 in the diffusion controlling region and are ~ 1 and ~ 0.5 in the chemically controlling region;
- (4) The numerical values of the rate constants for titanium and iron (after 12 min's dissolution) are of same value in both concentration regions. The values are $\sim 4 \times 10^{-5} \text{ cm}^2 \text{ g}^{-1} (\text{mol}^{-a}) \text{ m}^{-1}$ and $\sim 8 \times 10^{-5} \text{ cm}^2 \text{ g}^{-1} (\text{mol}^{-a}) \text{ m}^{-1}$ for low and high concentration regions of hydrochloric acid respectively (value of 'a' is ~ 3 and ~ 1 for titanium and, ~ 1.5 and ~ 0.5 for iron in low and high concentration regions) and that
- (5) The value of the rate constant for initial dissolution of iron is almost twice the rate constant after 12 mins dissolution. This suggests that the initial rate of iron is due to two parallel reactions.

b) EFFECT OF TEMPERATURE ON RATE OF DISSOLUTION :

The kinetic data for the rate of dissolution of the roasted mass by 4 g eq dm^{-3} hydrochloric acid (chemically controlling region) at different temperature ($40\text{--}110^\circ\text{C}$) are given in Table XLVI and the $[1-(1-R)^{1/3}]$ versus T (min) plots are given in Figs. 48 and 49 for titanium and iron respectively. From the slopes of the lines, the values of the pseudo-rate constant q_T for titanium and iron at < 12 min's and > 12 min's dissolutions are calculated; and reported in Table XLVII and are plotted in Fig. 50, as $\log q_T$ versus $(1/TK) \times 10^3$ plots.

The experimental points in all cases under consideration in Fig 50 do not fall on straight lines, but curves are obtained having a higher

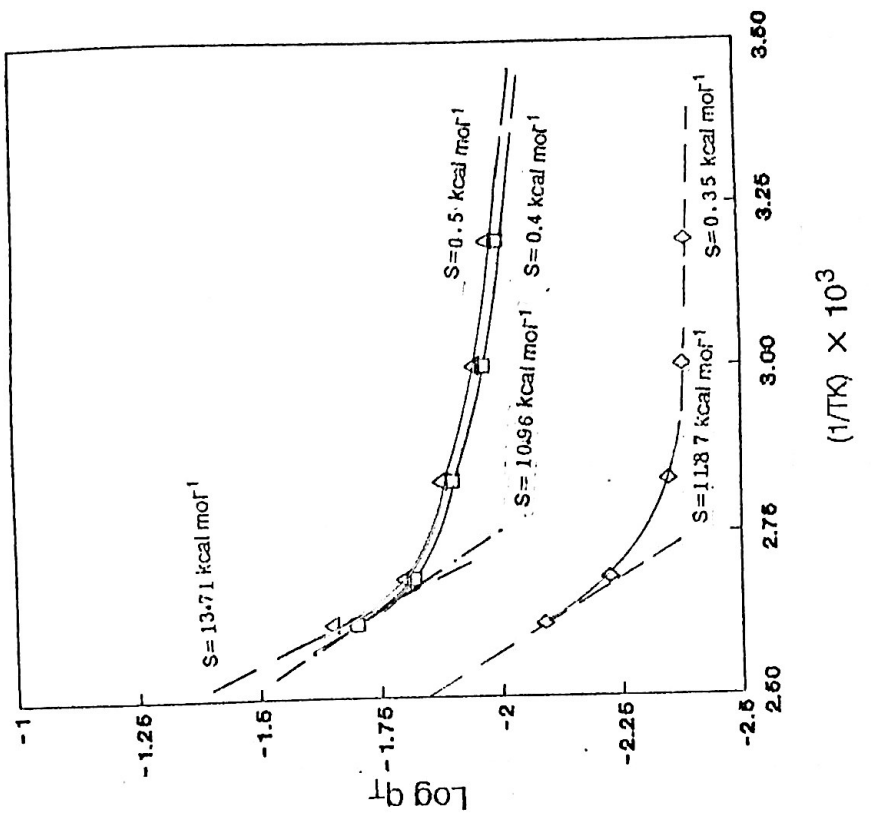


Fig. 50. Plot of $\log q_T$ versus $(1/TK) \times 10^3$ for titanium and iron dissolution from the $Na_2CO_3-H_2O$ vapour roasted ilmenite product (based on Table XLVI and Figs. 48 and 49). (Δ): $\log q_T (Ti)$; ($\square$): $\log q_T (Fe)$; ($\diamond$): $\log q_T (Fe)$; ($\circ$): $\log q_T (Fe)$.

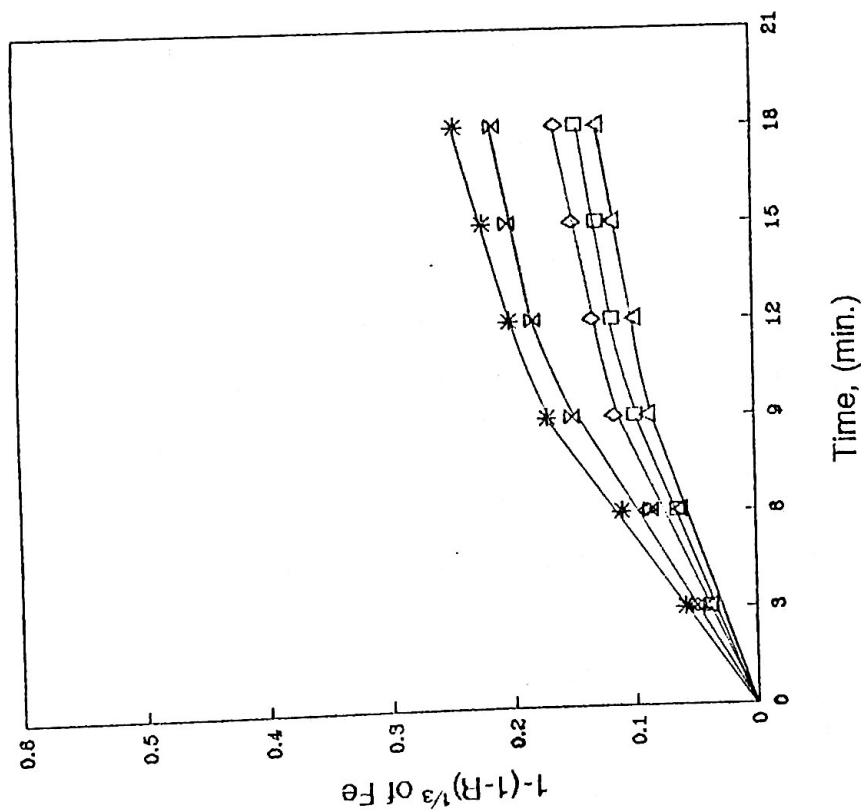


Fig. 49. Plot of $1-(1-R)^{1/3}$ versus time (min.) for iron: Effect of temperature on the rate of dissolution of $Na_2CO_3-H_2O$ vapour roasted ilmenite product. (Δ): 313°K; ($\square$): 333°K; ($\diamond$): 353°K; ($\circ$): 373°K and ($*$): 383°K. Leaching conditions are as in Fig. 48.

asymptotic slope at higher temperature region and a lower asymptotic slope at lower temperature regions under investigation. From the slope of the asymptotic lines, the apparent activation energies, E_a for the systems have been evaluated by considering the Arrhenius' equation (cf. Eq. 30). The values are ~ 13.7 kcal mol $^{-1}$ and 0.5 kcal mol $^{-1}$ for titanium dissolution at higher and lower temperature regions respectively. The corresponding value for iron dissolution are little lower (~ 12 kcal mol $^{-1}$ and ~ 0.4 kcal mol $^{-1}$).

The values of the activation energies at higher temperature region support our prediction made earlier that the dissolution process is chemically controlled when more than 2 g eq dm $^{-3}$ hydrochloric acid solution is used in leaching. The low value of activation energy at low temperature region suggests the diffusion controlled mechanism. So the statement "the dissolution process is chemically control when more than 2 g eq dm $^{-3}$ hydrochloric acid solution is used in leaching" is strictly true provided the leaching is done at boiling temperature of the leachant. Even with 4 g eq dm $^{-3}$ hydrochloric acid concentration, the dissolution process becomes purely diffusion control at $\sim 50^\circ\text{C}$. These conclusion are drawn based on the following theoretical backgrounds.

A diffusion-controlled process is characterized by being slightly dependent on temperature (low activation energy), while the chemically-controlled process is strongly temperature dependent (high activation energy). The reason is that the diffusion coefficient, α (rate constant for a diffusion-controlled process, k is nothing but (α/δ) where δ is the thickness of diffusion layer) is linearly dependent on temperature by the Stokes-Einstein equation.

$$\alpha = \frac{RT}{N} \cdot \frac{I}{2 \pi r \eta} \dots \dots \dots (36)$$

While the chemical rate constant k is exponentially dependent on temperature by Arrhenius' Equation.

$$k = A. e^{E_a/RT} \dots \dots \dots (37)$$

where the symbols have their usual significances. These two equations suggest that if the temperature is doubled, the diffusion coefficient α or diffusion controlling rate constant, $k = \alpha/\delta$ is nearly doubled; where as the chemical reaction rate constant, k is increased nearly hundredfold.

The activation energy of the diffusion-controlled process is characterized as being $1-3 \text{ kcal mol}^{-1}$, while for a chemically reaction controlled process it is usually greater than 10 kcal mol^{-1} . An intermediate controlled reaction has an activation energy in the range of $5-8 \text{ kcal mol}^{-1}$.

Usually, a process may change its mechanism from chemical control at lower temperature to diffusion control at higher temperature. The reason is that at low temperature the rate of chemical reaction is so slow that it is much less than the rate of diffusion i.e. the rate is chemically controlled. At high temperature the rate of chemical reaction is accelerated with the rise in temperature and it becomes much faster than the rate of diffusion i.e. it becomes diffusion controlled.

The above discussion points out that the activation energies obtained at low and high temperature regions are opposite to those should be obtained theoretically. In our opinion, this is due to a change in the reaction mechanism for the dissolution process, i.e. the chemical reaction leading to the dissolution of the roasted mass changes with the temperature. At high temperature region, the high activation energy suggests that one of the chemical reaction step causing the dissolution is a slow process with

respect to the diffusion of the hydrogen ion or the product ions through the surface film. On the otherhand, the low activation energy at low temperature region suggests that the chemical reaction steps (different from the above) resulting the dissolution are fast processes with respect to the diffusion of the reactant leachant and the products through the surface film.

The above statements are supported by the hydrochloric acid concentration dependence study on rate. In low concentration region of hydrochloric acid, the exponent of its concentration term varies from its value in the higher concentration region. Now, we thought that the reaction leading to the dissolutions of titanium and iron at lower concentration region differs from that at higher concentration regions. This study on the effect of temperature on rate suggests that the reaction taking place at lower concentration region is favoured to occur in lower temperature regions under investigation.

It is however, very difficult to predict the actual reaction taking place at two different conditions. To get further informations on the effect of temperature, the rate studies have also been carried out with leachant (HCl) of low concentration. With 1 g eq dm^{-3} hydrochloric acid, the rate data at different temperature are given in Table XLVIII and plotted as $1-(1-R)^{1/3}$ versus time (t , min) in Fig. 51 for both titanium and iron. From the slopes of the lines, the values at different temperatures are calculated at different temperatures (Table XLIX). The Arrhenius plots are given in Fig. 52. In all cases, straight lines are obtained. From the slopes of the lines the activation anergy has been calculated for each system. The value of the activation

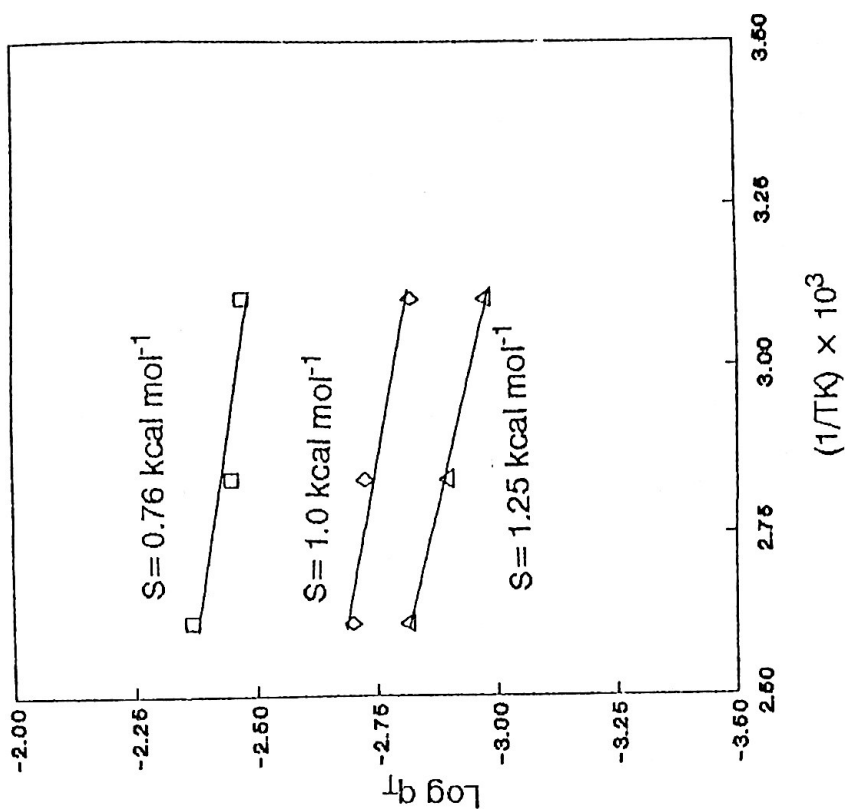


Fig. 52. Plots of $\log q_T$ versus $(1/TK) \times 10^3$ for titanium and iron dissolution from the $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ vapour roasted ilmenite product. ($\square$): $\log q_T$ (τ); ($\diamond$): $\log q_{T(\text{Fe})}$; (Δ): $\log q_{T(\text{Fe})}$. Leaching conditions are as in Fig. 51.

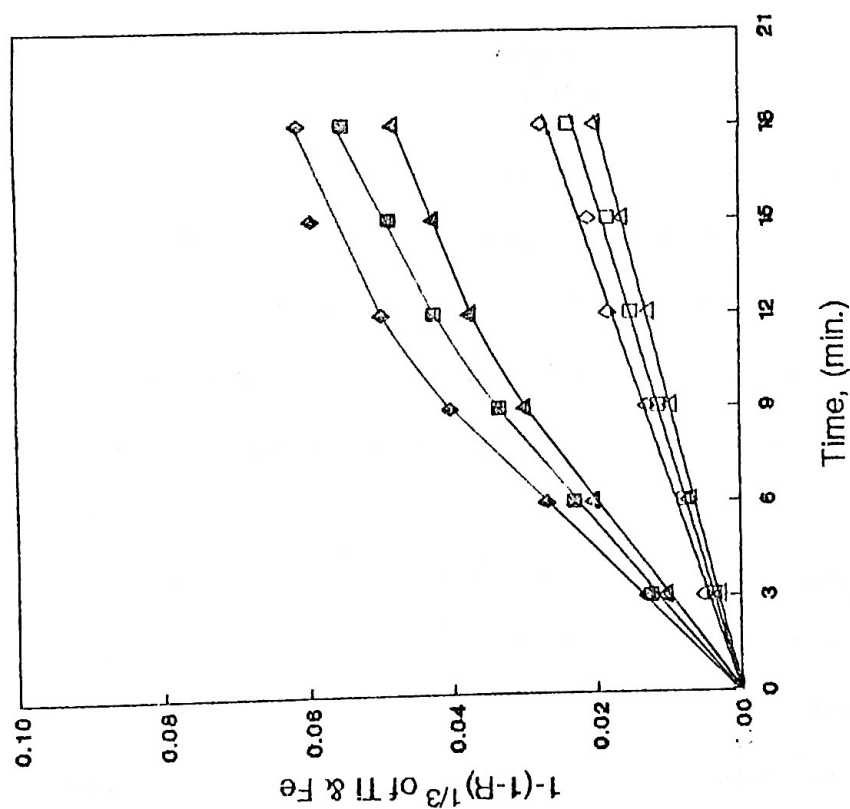


Fig. 51. Plot of $1-(1-R)^{1/3}$ versus time (min.) for titanium and iron: Effect of temperature on the rate of dissolution of $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ vapour roasted ilmenite product. (Δ): 323°K, Ti; ($\square$): 353°K, Ti; ($\diamond$): 383°K, Ti and (Δ): 323°K, Fe; ($\square$): 353°K, Fe; ($\diamond$): 383°K, Fe. Leaching conditions: $[\text{HCl}] = 1 \text{ g eq dm}^{-3}$; stirring speed = 200 rpm; $S/L = 0.02 \text{ kg dm}^{-3}$ and vol. of liquid = 50 cm^3 .

energy of titanium and iron dissolutions are again of low value (~ 1 kcal mol⁻¹), but now over the entire temperature range under investigation. This concludes that at low hydrochloric acid concentration, one chemical reaction (very fast reaction steps) leads to the dissolution over the whole studied temperature range.

c) *EFFECT OF PHASE MIXING RATE (R.P.M) ON THE RATE OF DISSOLUTION :*

The effects of phase mixing rate on the rate of dissolution at 110°C have been studied at two distinct different conditions, one for 4 g eq dm⁻³ hydrochloric acid and other for 1 g eq dm⁻³ hydrochloric acid. With 4 g eq. dm⁻³ hydrochloric acid, the data for the rate measurements are given in Table L. The Table L indicates that the rate of dissolution is almost independent of the phase mixing rate. The $1-(1-R)^{1/3}$ versus t (min) plots coincide each other (not shown graphically) and the q_r values at different phase mixing rate obtained by the least square analysis are given in Table LI. The $\log q_{rpm}$ versus $\log (rpm)$ plots are shown in Fig 53. The lines in this figure have almost zero slope ('b' = 0, cf. eq. 31) supporting our previous suggestion, "the dissolution reaction taking place at high hydrochloric acid concentration and at 110°C is chemically controlled," Since the chemically controlled reactions are independent of the phase mixing rate²⁶⁴.

The experimental rate data obtained for 1 g eq dm⁻³ hydrochloric acid at 110°C are given in Table LII. The $1-(1-R)^{1/3}$ versus time (min) plots are given in Fig. 54 for both titanium and iron dissolution. From the slope of this lines, the 'q' values at different rpm are given in Table LIII and shown

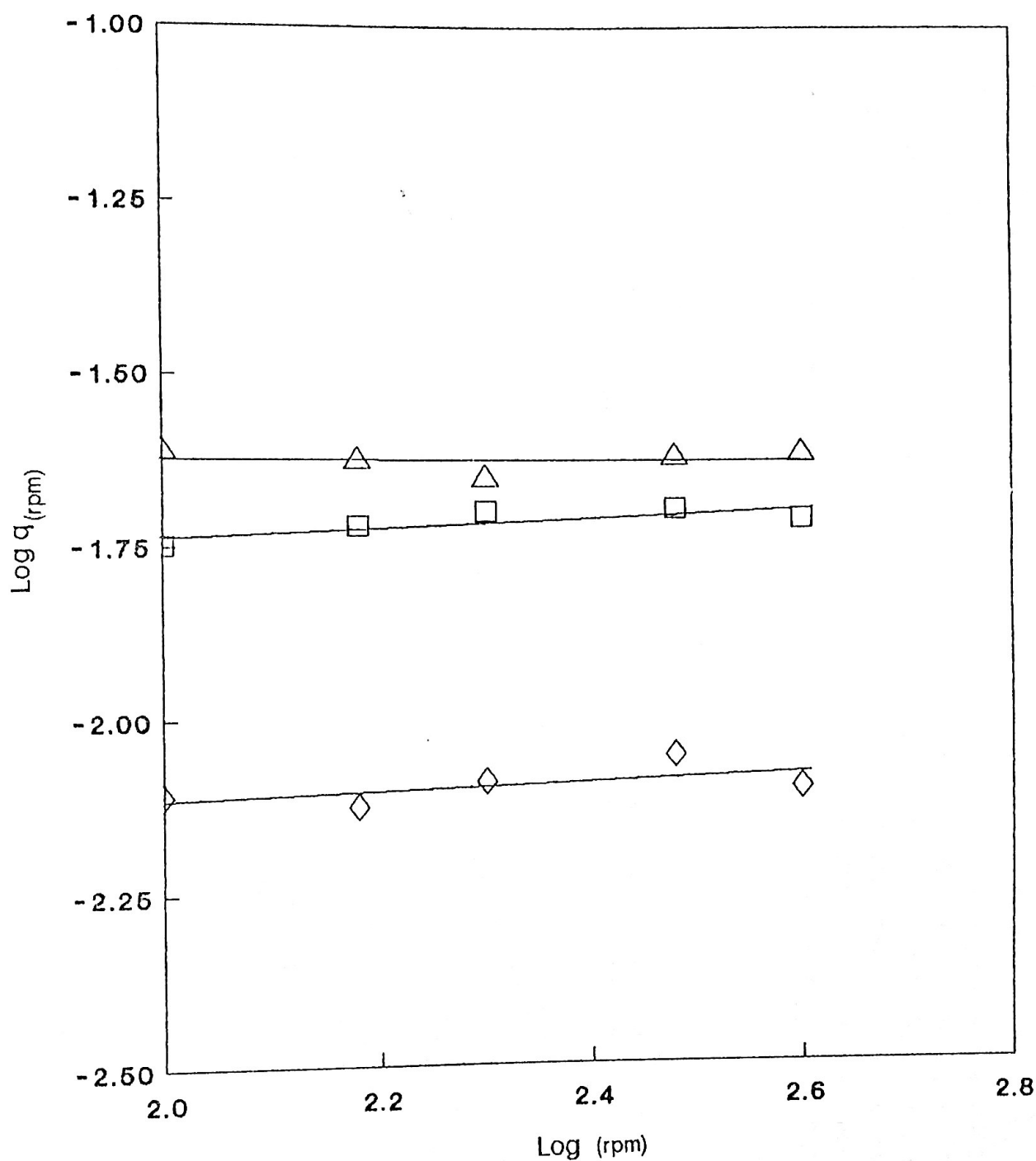


Fig. 53. Plot of $\log q_{rpm}$ versus $\log (rpm)$ for titanium and iron dissolution from $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ vapour roasted ilmenite product. (Δ): $\log q_{rpm \text{ Ti}}$; ($\square$): $\log q_{rpm \text{ Fe (ln)}}$ and ($\diamond$): $\log q_{rpm \text{ Fe} > 12\%}$. Leaching conditions: $[\text{HCl}] = 4 \text{ g eq dm}^{-3}$; temp. = 110°C ; $\text{S/L} = 0.02 \text{ kg dm}^{-3}$ and vol. of liquid = 50 cm^3 .

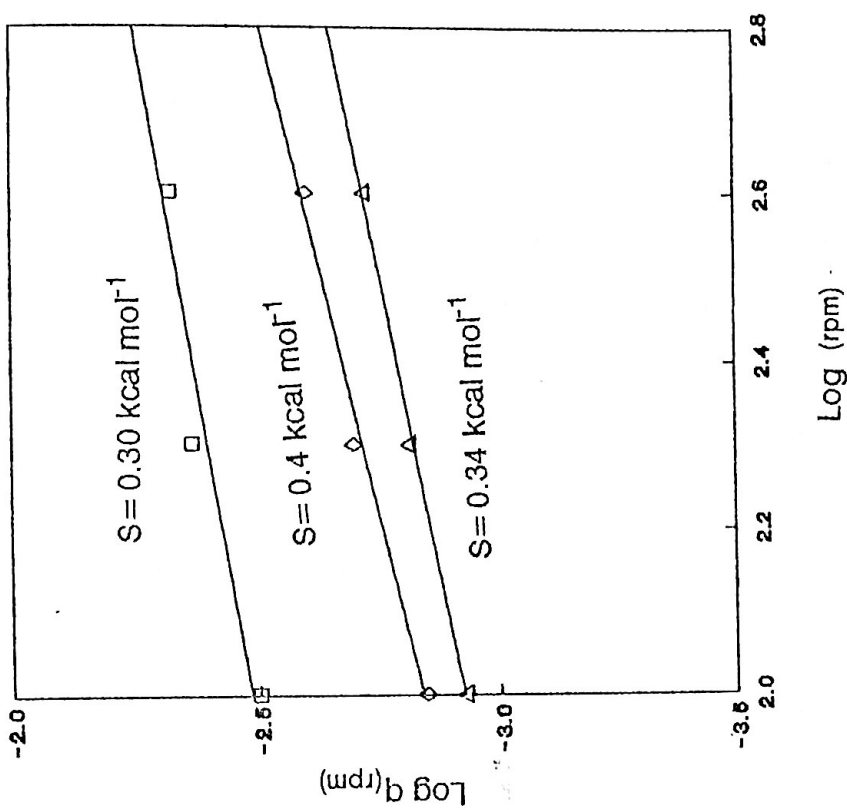


Fig. 55. Plot of $\log q_{\text{rpm}}$ of versus $\log (rpm)$ for titanium and iron dissolution from $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ vapour roasted ilmenite product. (Δ): $\log q_{\text{rpm Ti}}$; ($\square$): $\log q_{\text{rpm Fe (In)}}$ and ($\diamond$): $\log q_{\text{rpm Fe}} > 12$. Leaching conditions are as in Fig. 54.

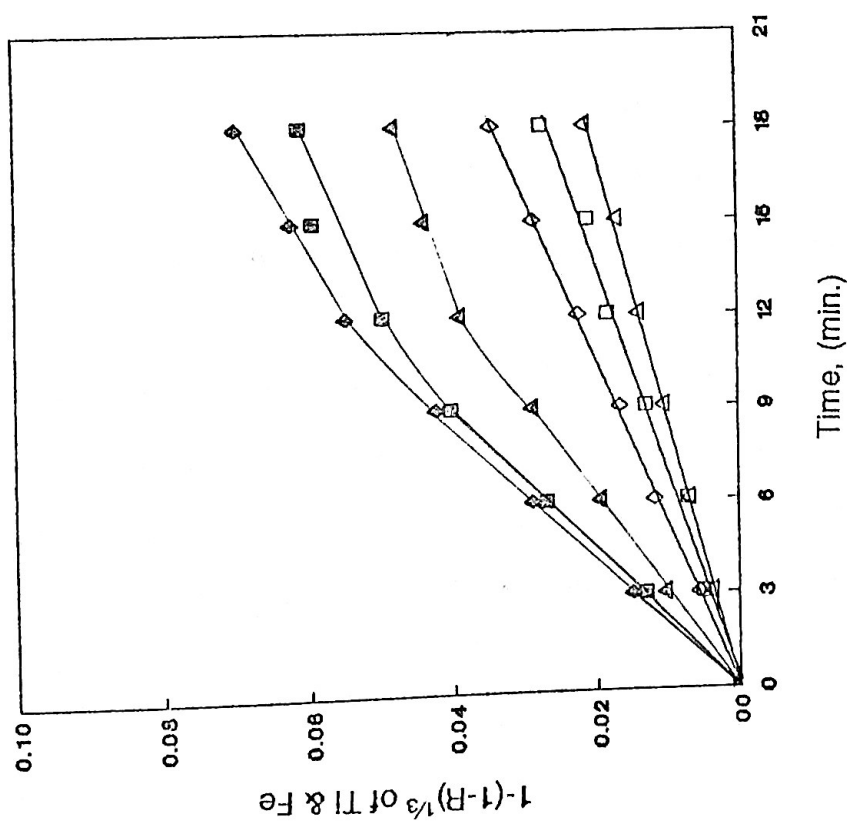


Fig. 54. Plot of $1-(1-R)^{1/3}$ versus time (min.) for titanium and iron: Effect of agitation speed on the rate of dissolution of $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ vapour roasted ilmenite product. (Δ): 100 rpm, Ti; ($\square$): 200 rpm, Ti; ($\diamond$): 400 rpm, Ti; ($\blacktriangle$): 100 rpm, Fe; ($\boxtimes$): 200 rpm, Fe and ($\blacklozenge$): 400 rpm, Fe; Leaching conditions: $[\text{HCl}] = 1 \text{ g eq dm}^{-3}$; temp = 110°C ; $\text{S/L} = 0.02 \text{ kg dm}^{-3}$ and vol. of liquid = 50 cm^3 .

graphically in Fig. 55, as $\log q_{\text{rpm}}$ versus $\log (\text{rpm})$ plots. The straight lines having slopes of ~ 0.35 are obtained. The result also supports our previous statement, "the dissolution process taking place at low hydrochloric acid concentration and at 110°C is diffusion controlled," since for a diffusion controlled process, the increased speed of phase mixing increases the rate of reaction²⁶⁶. One consideration must be undertaken to use these data that the rpm values given are not absolute because an additional phase mixing effect is present there for boiling action of the pulp. But this effect is invariably associated with all data.

5.7 RECOVERY OF TITANIUM FROM LEACH SOLUTION

From the leaching study, we have concluded that the enrichment of ilmenite, containing only about 40% of total iron present, can be prepared by leaching the $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ vapor roasted ilmenite by 6 g eq dm^{-3} hydrochloric acid at high S/L (kg dm^{-3}). The removal of remaining iron is not possible due to the passiveness of the residue. Consequently, almost complete dissolution of the roasted mass at low S/L ratio and the subsequent separation of Fe^{3+} from Ti^{4+} are deserved. Literature survey²¹⁰⁻²¹³ suggests that the separation of the ions under consideration from hydrochloric acid medium is possible by liquid-liquid extraction by MIBK. The following paragraphs report our findings towards the extraction of Fe^{3+} by MIBK.

1) DEPENDENCE OF EXTRACTION RATIO ON CONTACT TIME FROM IRON (III) EXTRACTION WITH METHYLISOBUTYL KETONE (MIBK) :

Table LIV represents the values of extraction ratio at various time intervals for extraction of Fe^{3+} from 6 g eq dm^{-3} hydrochloric acid medium ($5 \text{ g dm}^{-3} \text{ Fe}^{3+}$) by undiluted MIBK at organic to aqueous phase ratio of 1 and at a temperature of $(30 \pm 1)^\circ\text{C}$. Figure 56 shows the extraction ratio versus time of contact plot. It is found that the extraction ratio of iron is increased with increasing the time of contact upto about 30 sec, and the curve is levelled off above this time. From this result, it is concluded that the extraction of iron (III) from concentrated hydrochloric acid medium by MIBK is very fast and takes only about 30 seconds for equilibration. However, it is important to note here that the shaking has been performed at an optimum rate and since the rate of extraction depends on the extraction parameters, longer times e.g. about 2 minutes have been allowed subsequently to ensure the attainment of equilibrium at different experimental parameters.

2) DEPENDENCE OF EXTRACTION RATIO ON CONCENTRATION OF IRON (III) FOR EXTRACTION BY MIBK :

The variation of extraction ratio on the initial aqueous concentration of iron (III) ($1\text{--}15 \text{ g dm}^{-3}$) is given in Table-LV and Fig. 57. It is seen that the extraction ratio decreases with the increment in concentration of iron (III) in the aqueous phase. However, the variation of extraction ratio is less pronounced at lower concentration region. This may be due to the loading of iron in MIBK which results in the decrease of the free MIBK concentration in the organic phase.

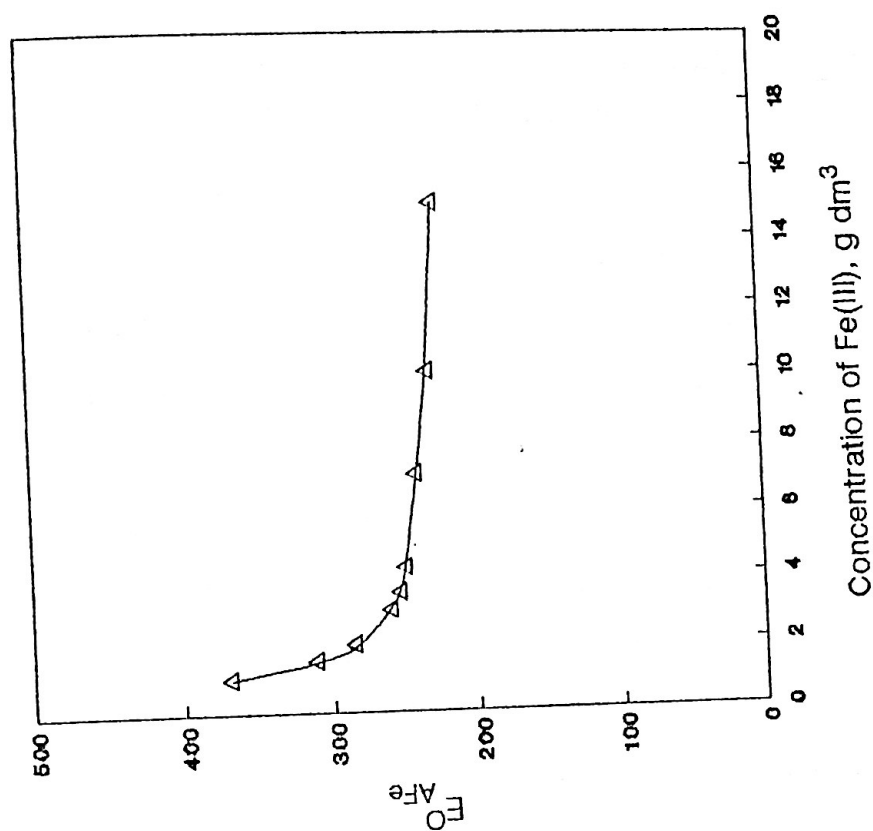


Fig. 57. E_{AFe}^O as a function of iron concentration in the case of extraction with MIBK. $HCl = 5 \text{ g eq dm}^{-3}$, $MIBK = 8 \text{ mol dm}^{-3}$.

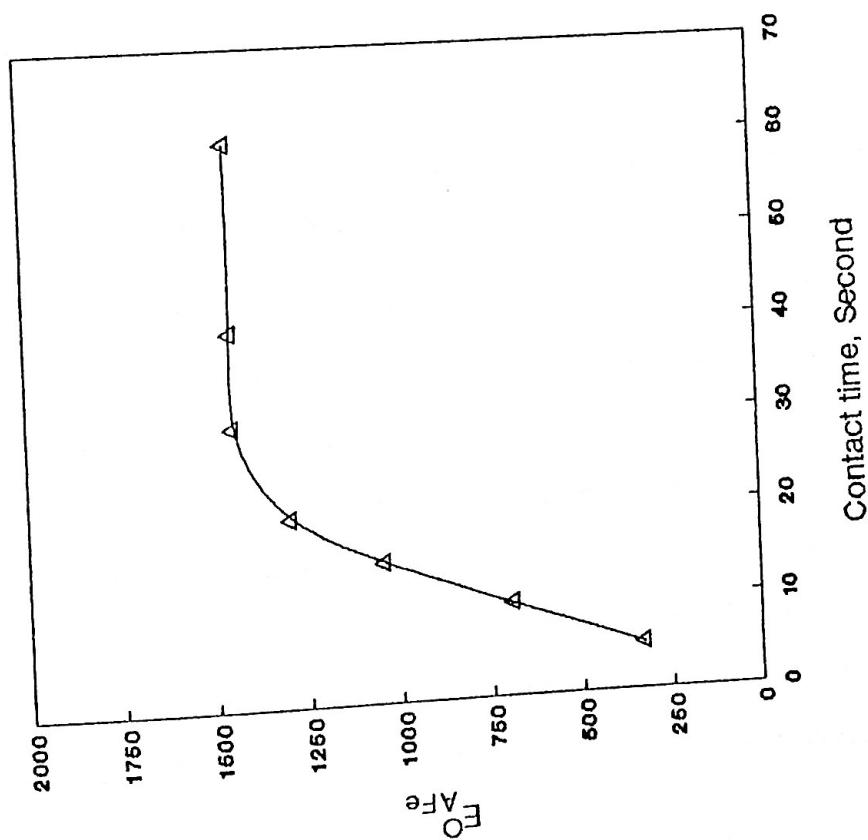


Fig. 56. Determination of the time required to reach the equilibrium in iron (III) extraction with MIBK: extraction ratio, E_{AFe}^O vs. time curves. $C_{Fe(III)}^A = 5.0 \text{ g dm}^{-3}$, $MIBK = 8 \text{ mol dm}^{-3}$, Aqueous $HCl = 6 \text{ g eq dm}^{-3}$.

3) DEPENDENCE OF EXTRACTION RATIO ON AQUEOUS ACIDITY (HYDROCHLORIC ACID CONCENTRATION) FOR THE EXTRACTION OF IRON (III) BY MIBK :

The values of the experimentally determined extraction ratio at several hydrochloric acid concentrations, ranging from 2 to 7 g eq dm⁻³ are given in Table-LVI and plotted in Fig. 58 as log-log plot. From the figure it is evident that the extraction of Fe³⁺ by MIBK is extensively dependent on the hydrochloric acid concentration in the aqueous phase; increases with increasing the hydrochloric acid concentration but not linearly. The slope of the curve at lower concentration region (S₁) is about 6 whereas, at higher concentration region (S_h) is about 16. The increase in the extraction ratio with increasing hydrochloric acid suggests the extraction of it by MIBK²⁶¹. It is believed that a certain portion of hydrochloric acid is extracted by forming the extractable Fe³⁺ species and the rest being extracted by MIBK alone.

4. DEPENDENCE OF EXTRACTION RATIO ON EXTRACTANT (MIBK) CONCENTRATION :

The experimental results are shown in Table-LVII and Fig. 59. The dilution of MIBK was done by kerosin. The log-log plot is not a straight line. A curve having slope of ~0.5 in the lower concentration and of ~8 in the higher concentration region is obtained. It is generally known that MIBK is used undiluted in the extraction process. Addition of nonpolar diluent to a metal loaded MIBK solution results in the back extraction of metal²⁶¹. The sharp decrease in the extraction ratio with decrease in the concentration of MIBK in kerosin is believed to be resulted from the same cause. Due to this

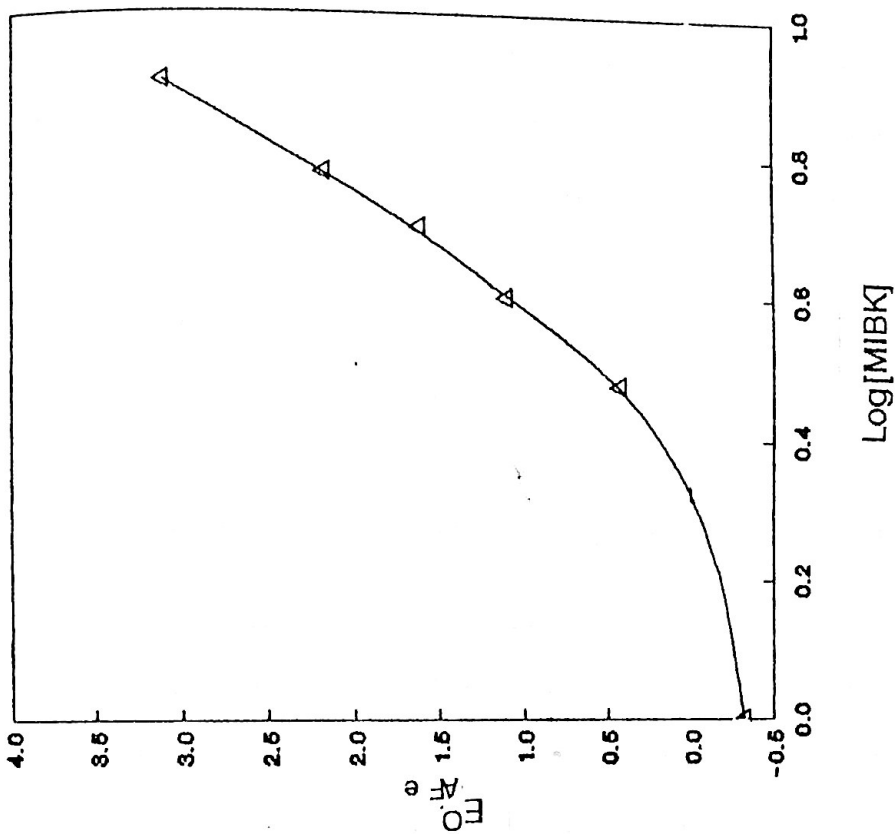


Fig. 59. $\log E_{AF_e}^O$ vs. a function of $\log [MIBK]$ in the organic phase at fixed acidity of aqueous phase. Aqueous $HCl = 6 \text{ g eq dm}^{-3}$; Slope = 0.5 (S) and slope = 8(S_n). Diluent is kerosin.

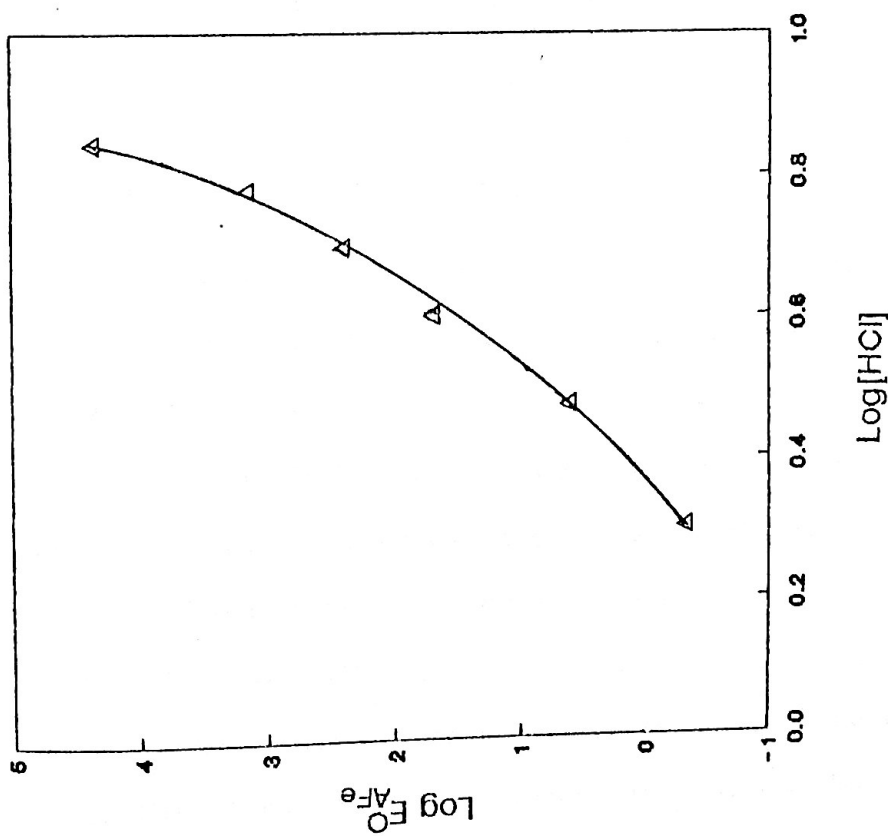
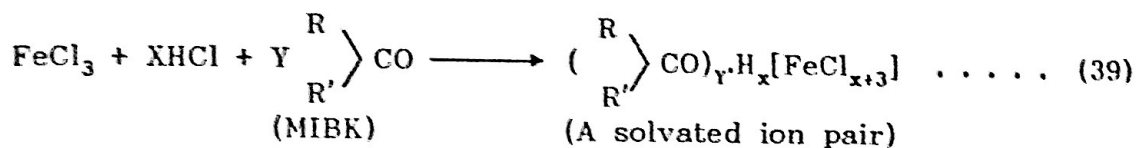


Fig. 58. $\log E_{AF_e}^O$ as a function of $\log [HCl]$ at fixed MIBK concentration. MIBK = 8 mol dm^{-3} ; slope = 6 (S) and slope = 16 (S_n).

known behaviour and the extraction of hydrochloric acid by MIBK, the reaction involving the extraction cannot be suggested. However, it is probable that Fe^{3+} is extracted by the following type of reaction.



5. DEPENDENCE OF EXTRACTION RATIO ON TEMPERATURE :

The Table-LVIII and Fig. 60 ($\log E_{\text{AFe}}^0$ versus $1/\text{TK}$) show that the extraction of iron (III) with MIBK is decreased with increase in temperature under investigation. The extraction process is therefore exothermic. The apparent enthalpy change for the extraction of Fe(III) by MIBK has been calculated to be $\Delta H = -13.40 \text{ kJ mol}^{-1}$. The low enthalpy change supports the extraction via solvation mechanism.

6. LOADING EFFECT OF ORGANIC PHASE :

The cumulative amount of Fe^{3+} extracted in organic phase (8 M in MIBK) at various stages (aqueous phase renewed) are given in Table-LIX and Fig. 61. It is evident from the table and figure that the organic phase is loaded to its full capacity with iron (III) within about 7 contacts under the experimental conditions stated. During the first five contacts almost all the metal-ion in fresh aqueous solutions is extracted into the organic phase, indicating a high affinity of the extractant towards Fe^{3+} .

The loading capacity of MIBK is found to be only 3.754 g Fe^{3+} per 100 g MIBK. Moreover, a simple calculation shows that the Fe^{3+} to MIBK ratio

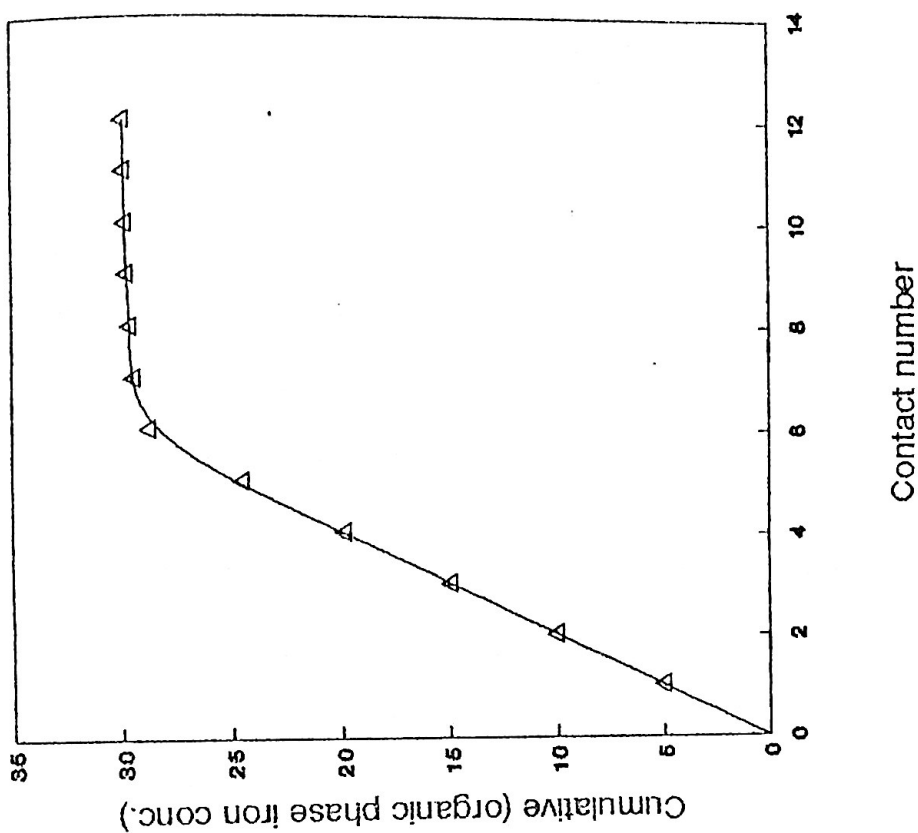


Fig. 61. Loading effect of organic phase in the extraction of iron (III) with MIBK. $\text{HCl} = 6 \text{ g eq dm}^{-3}$, $\text{MIBK} = 8 \text{ mol dm}^{-3}$, $C_{\text{Fe(III)}}^A = 5.0 \text{ g dm}^{-3}$.

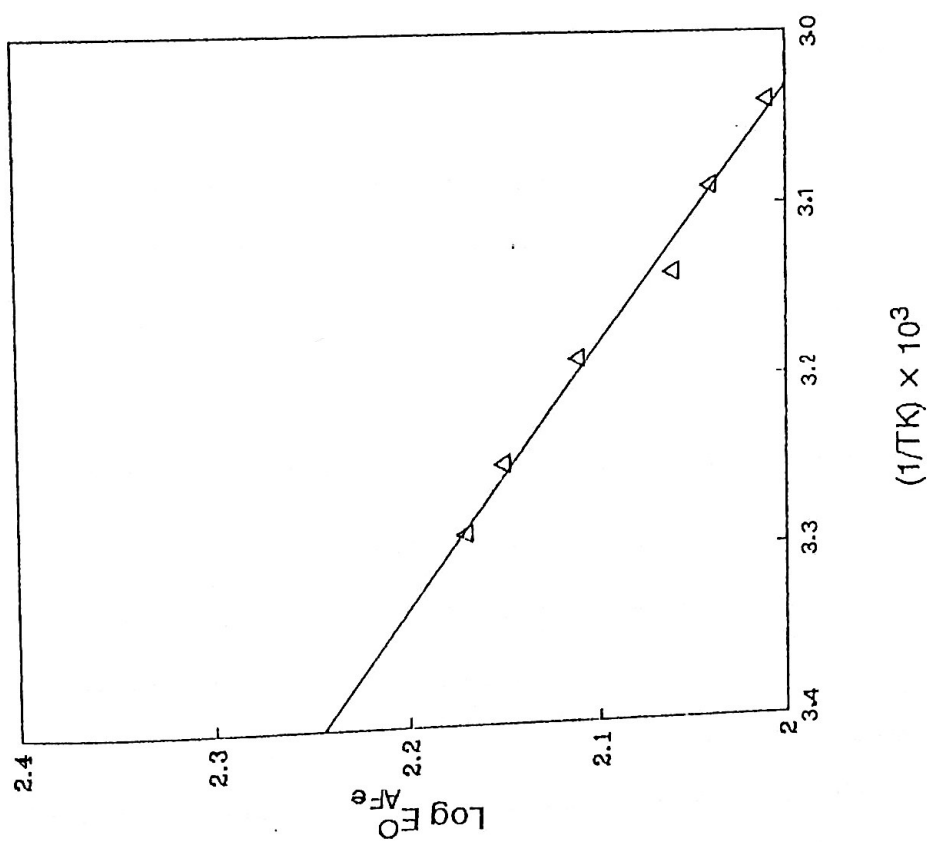


Fig. 60. $\text{Log } E_{A\text{Fe}}^O$ vs. $(1/TK) \times 10^3$ plots in the case of extraction with MIBK. $C_{\text{Fe(III)}}^A = 5.0 \text{ g dm}^{-3}$, $\text{HCl} = 6 \text{ g eq dm}^{-3}$, $\text{MIBK} = 8 \text{ mol dm}^{-3}$.

is about 1 to 15 from the loading study. The involvement of 16 MIBK molecules per Fe(III) was obtained from the extractant dependence study. Therefore, the solvation number is around 15, when pure MIBK is used as extractant. Of course, due to the absence of diluent in the system, a certain fraction of MIBK acts as the solvent for the extracted species. The solvation number determined by the extractant dependence study agrees well with that obtained from the loading study.

7. EFFECTS OF VARIOUS DILUENTS ON THE EXTRACTION OF Fe^{3+} BY MIBK :

The aliquots of 10 cm^3 of extractant in different diluents such as benzene, kerosin, n-hexane, toluene, chloroform and carbontetrachloride have been added to the same volumes of aqueous solution in six different 250 cm^3 reagent bottles; and the phases are contacted for three minutes. After allowing the phases to settle, the aqueous layers are taken out and analysed.

From the experimental data (Table-XL), it is found that the extraction ratio is high for diluent benzene and low for carbontetrachloride.

The diluents can be arranged in their decreasing extents of extraction as follows :

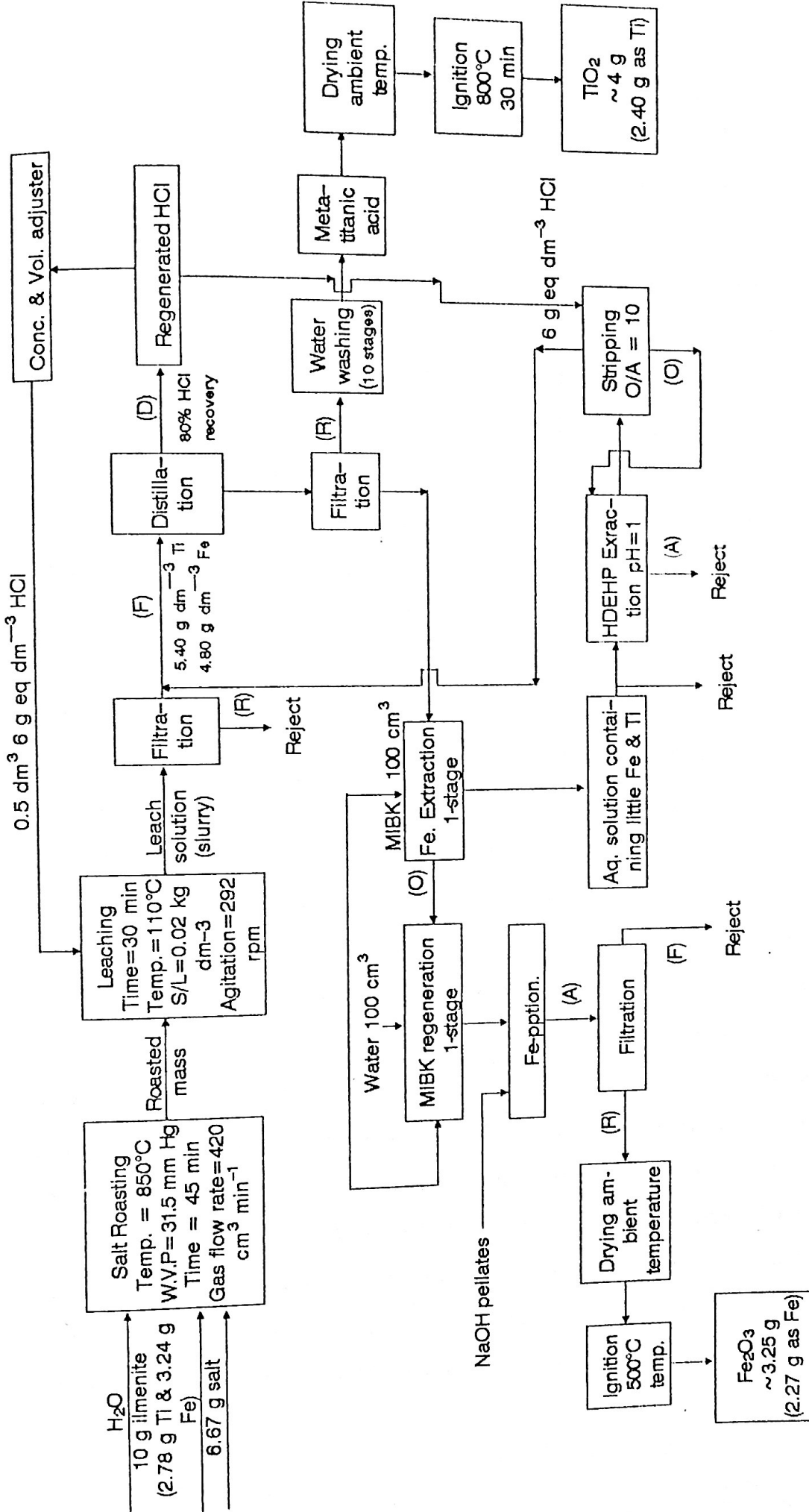
Benzene > Kerosin > n-Hexane > Toluene > Chloroform > Carbontetrachloride

The extents of extraction in different diluents indicate that if MIBK is used as an extractant for Fe^{3+} extraction, benzene or kerosin will give better results than n-hexane, toluene, chloroform or carbontetrachloride.

The above results clearly indicate that Fe^{3+} from the leach solution obtained at low S/L ratios could be separated almost quantitatively by

single-stage extraction with undiluted MIBK. The iron extracted MIBK can be stripped simply by distilled water in only two to three steps. The iron in the MIBK phase comes into the water phase and is precipitated as oxide or hydrated oxide on addition of NaOH pellets from which pigment grade iron oxide (black) can be prepared by heating the dried oxide or hydroxide at about 500°C. The almost iron free titanium in hydrochloric acid solution can be distilled off to regenerate hydrochloric acid of about 6 g eq dm⁻³ concentration. During this operation, as the concentration of hydrochloric acid is decreased and as the time of heating is increased, a very pure precipitate of hydrated titanium dioxide, TiO₂.xH₂O is separated out almost quantitatively. The trace amount of Fe³⁺ in the MIBK extracted aqueous raffinate does not contaminate the precipitate. The precipitate can be easily filtered, washed, dried and ignited at about 800°C to get pigment grade titanium dioxide. The filtrate containing some Ti⁴⁺ after separation of precipitated hydrated titanium dioxide, may be rejected or subjected to HDEHP extraction (pH-1) HCl (6 g eq dm⁻³, O/A = 10) stripping steps to recover the residual titanium. The stripped solution containing more than 10 g dm⁻³ titanium can be recycled to the distillation unit for hydrochloric acid regeneration.

Further study suggests, a more simplified method. The leach solution containing titanium and iron can be distilled off to regenerate hydrochloric acid with subsequent precipitation of hydrated titanium dioxide in which a considerable amount of iron is absorbed. The precipitate can be easily separated, washed with distilled water several times (about ten times) to remove absorbed iron, dried and ignited to prepare pigment grade titanium dioxide.

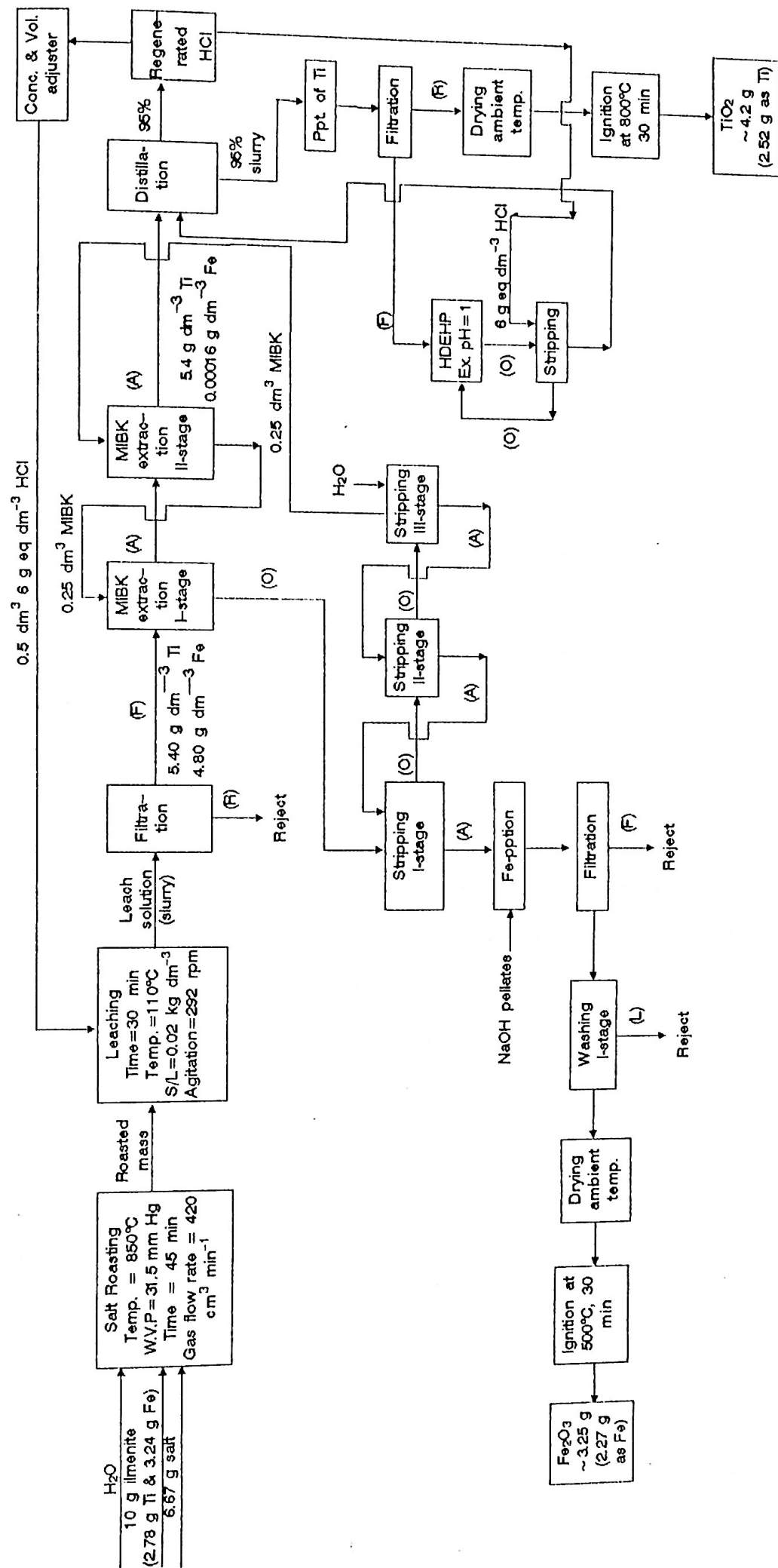


FLOW SHEET — A

Thus, 10 g ilmenite has been mixed intimately with 6.67 g Na_2CO_3 and roasted at 850°C for 45 minutes, carrier gas flow rate $420\text{ cm}^3\text{ min}^{-1}$ and water vapour pressure 31.5 mm Hg. On leaching with 0.50 dm^{-3} 6 g eq dm^{-3} hydrochloric acid, the roasted mass yields a solution containing $\sim 5.40\text{ g dm}^{-3}$ titanium and $\sim 4.80\text{ g dm}^{-3}$ iron corresponding to $\sim 96\%$ titanium and $\sim 74\%$ iron dissolutions. The solution is then subjected to distillation for recovery of hydrochloric acid (about 80% recovery).

As distillation proceeds, a precipitate of metatitanic acid or hydrated titanium dioxide, absorbing some quantity of iron appears gradually (precipitation yield is about 90%). It is filtered and the residue is washed eight to ten times with distilled water, dried in ambient temperature and ignited at about 800°C for half an hour to produce 4 g titanium dioxide of very white-in-colour. The analysis of the product shows that it does not contain chromium but contains less than 0.01% iron. The filtrate containing most of the iron and non-precipitated titanium could be rejected or recycled after separating iron by MIBK extraction as indicated in the Flowsheet A.

Alternatively, the leach solution can be treated as follows : the leach solution is contacted with 250 cm^3 undiluted MIBK twice to extract most of the iron present. The first extract is stripped with equal volume of distilled water thrice. On stripping, iron comes into the water phase and is precipitated by the addition of NaOH pellets in the stripped solution of the first stage only. The aqueous solution obtained in the second and third stripping stages are recycled or rejected. The precipitate of iron obtained in the first-stripping stage is filtered, dried and ignited at 500°C for half an hour to get $\sim 3.25\text{ g Fe}_2\text{O}_3$ (pigment grade, iron-black). The stripped MIBK phase may be recycled in the subsequent second-extraction-stage, whereas



the extracted phase obtained in the second-extraction-stage can be recycled as the extractant in the subsequent first-extraction-stage. The raffinate from the extraction step is subjected to distillation for hydrochloric acid recovery (~95%) and for the concurrent precipitation of very pure metatitanic acid. The precipitate is filtered, dried and ignited to get 4.12 g titanium dioxide. The precipitation yield is ~95%. The product is very white and pure (contains only 0.005% Fe). The steps are shown in Flowsheet B.

The economics of the process will however be greatly depend on the energy involvement in the salt-roasting, leaching and distillation steps. These should be estimated on a pilot-plant scale basis. Regarding the reagents, sodium carbonate is very cheap (Tk. 20 per kg; Tk. 1 = £0.015), hydrochloric acid is recoverable (~85%) and cheap (Tk. 15 per kg, commercial) and the extractant MIBK is also recoverable to a great extent (2% loss due to water miscibility). The loss of hydrochloric acid results from its extraction into the MIBK (4% of acid in aqueous phase is extracted into the MIBK phase). Since the products are relatively of high price (Tk. 3600/kg TiO_2 and Tk. 400/kg Fe_2O_3 for Aldrich qualities) and the recoveries are very high, the process is expected to demand a commercial application.

SUMMARY

The work described in the dissertation can be summarized in the following few paragraphs.

(A)

The comparison of the leaching characteristics of ilmenite in various inorganic acids shows that excepting in hydrofluoric acid, negligible amounts of titanium and iron are dissolved in 2 g eq dm^{-3} acids at their boiling points for 30 h. However, the dissolution increases with increasing acid concentrations, particularly upto 6 g eq dm^{-3} . Under similar condition, hydrochloric acid dissolves more ilmenite than does sulphuric acid. With 6 g eq dm^{-3} hydrochloric acid, ~53.5% titanium and 60% iron dissolutions occur within 4 h, longer leaching time does not increase the percentage dissolutions.

(B)

Ilmenite has been roasted prior to leaching by heating with liquified petroleum gas (LPG). The ilmenite has been subjected subsequently to leach with 6 g eq dm^{-3} hydrochloric and sulphuric acid solution to follow up the progress of heat treatment at different parameters. The optimum roasting conditions with LPG-pyrolysed products are at $(700 \pm 15)^{\circ}\text{C}$ for 75 min at LPG flow rate $230 \text{ cm}^3 \text{ min}^{-1}$ and $>63 < 125 \text{ }\mu\text{m}$ particle size. The maximum weight percentages of metals dissolved from the roasted mass are ~85% titanium and 82.1% iron with 6 g eq dm^{-3} hydrochloric acid, whereas it is 52.3% titanium and 60.8% iron with 6 g eq dm^{-3} sulphuric acid system. The weight

percentages of metals dissolved increase with increasing the roasting temperature, time, gas flow rate and with decreasing particle size upto their optimum values mentioned above. On further increase in roasting time, temperature and gas flow rate, the roasted mass gives poorer dissolutions of titanium and iron.

The optimum leaching conditions with hydrochloric acid solutions are greater than 6 g eq dm^{-3} acid concentration, temperature at boiling point, solid to liquid phase ratio (S/L) of 0.02 kg dm^{-3} and at pulp agitation speed of 350 rpm for 5 h. Identical concentration of sulphuric acid gives poorer dissolution. Comparison of the X-ray powder diffraction patterns (XRD) of ilmenite and roasted mass suggest the chemical/physical change occurring during roasting treatment.

(C)

A different method of thermal treatment applied to ilmenite is to react with the reformed products of the LPG- H_2O vapour mixture in presence of nickel catalyst. The roasted mass has been subjected subsequently to leaching with 6 g eq dm^{-3} hydrochloric acid sulphuric acid solutions to follow up the progress of heat treatment at different parameters.

The optimum roasting conditions are :

- i) The maximum percentages of titanium dissolved by both acids increase with increasing the roasting time upto 40 min; and on further increasing the roasting time, the maximum dissolution percentage of titanium is decreased. On the otherhand, the iron dissolution is increased with increasing the roasting time upto 50 min which is slightly decreased with further increase in the roasting time upto 60 min.

- ii) The maximum percentages of both the metals dissolved in both the acids are increased with increasing roasting temperature upto $(700 \pm 15)^{\circ}\text{C}$ and then decreased considerably.
- iii) The optimum LPG flow rate should be around $110 \text{ cm}^3 \text{ min}^{-1}$ and the roasting in higher gas flow rate will extensively decrease the dissolution percentages of the metals from ilmenite roasted product.
- iv) The optimum water vapour pressure in the flow gas is 0.041 atm and the roasting at higher water vapour pressure will greatly decrease the percentages of metals dissolved from ilmenite roasted product.

A comparison of X-ray powder diffraction pattern (XRD) of ilmenite and the roasted mass suggest the chemical/physical change occurring during roasting but the composition of phases present in roasted mass could not be identified.

The optimum leaching conditions are :

- i) Titanium and iron dissolution from the roasted mass is very sharp in the acid concentration range of 2 to 6 g eq dm^{-3} for both acids and above 6 g eq dm^{-3} acid concentration, the maximum percentages are little increased. Therefore the optimum leaching acid concentration can be taken as 6 g eq dm^{-3} .
- ii) The dissolution of both metals are increased with increasing the leaching temperature and the variation is very sharp between 80° to 110°C . The high temperature dependence of the leaching of the roasted mass indicates the high activation energies for

dissolution of both metals and the dissolution occurs by the mechanism of chemical controlling in nature for both the metal ions.

iii) The percentages of both the metals are considerably decreased on increasing the S/L ratio as expected for any leaching study. The titanium and iron dissolutions of 91.5% and 94.3% are decreased to about 10% and 54.7% respectively on increasing S/L ratio from 0.02 kg dm^{-3} to 0.10 kg dm^{-3} . Similar behaviour is also encountered for leaching with sulphuric acid. The concentration of iron in both acids are increased substantially with increasing S/L ratio. On the otherhand, the concentration of titanium in hydrochloric acid solution is decreased with increasing the S/L ratio; and with sulphuric acid, the concentration of titanium in solution is increased with increase in the S/L values.

iv) The percentage of metals dissolved are increased considerably with increasing the pulp agitation speed for both acids.

At optimum condition, the maximum weight percentages of titanium and iron dissolved are 91.5% and 94.3% respectively in hydrochloric acid; whereas these are 47.9% and 66.9% respectively in sulphuric acid.

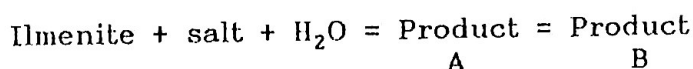
(D)

The advantage of the thermal hydrolysis of Na salts (NaCl , Na_2SO_4 , NaNO_3 and Na_2CO_3) at around 800°C has been exploited. The alkali produced in-situ has been reacted with ilmenite to give easily soluble roasted masses. Although from all the salts used, the hydrolysed product is NaOH , different roasted masses with different leaching characteristics are obtained due to

the existence of different atmospheres (oxidising, non-oxidising, inert etc.) in the furnace. The optimum roasting conditions with NaCl, Na₂SO₄, NaNO₃ and Na₂CO₃ are ilmenite (1 g) to salt (wt) ratios of 0.67, 2.00, 1.70 and 1.50; time 75, 90, 90 and 45 min; temperature 800°C, 885°C, 800°C and 850°C respectively; carrier gas (N₂) flow rate 420 cm³ min⁻¹ and water vapour pressure 31.5 mm Hg; whereas the optimum leaching conditions are 6 g eq dm⁻³ (2 g eq dm⁻³ for Na₂SO₄) hydrochloric acid at boiling point, S/L ratio of 0.02 kg dm⁻³, pulp agitation speed of 292 rpm and 120, 120, 90 and 45 min leaching time for NaCl, Na₂SO₄, NaNO₃ and Na₂CO₃ system respectively. Under these conditions 71.8, 43.5, 84.9 and 95.8% titanium and 94.9, 53.5, 70.2 and 73.7% iron are dissolved for NaCl, Na₂SO₄, NaNO₃ and Na₂CO₃ systems respectively. The best leaching has been obtained from the Na₂CO₃-H₂O vapour roasted mass.

(E)

The salt-water vapour roasting results of ilmenite are best explained, in all cases, if we consider the following scheme for roasting.



Product A produced first is easily leachable. On increasing either reaction time, temperature, salt to ilmenite ratio, gas flow rate or water vapour pressure from their optimum values will facilitate the formation of product B, which is resistant to acid leaching.

A thorough X-ray diffraction study of the roasted products at various experimental roasting parameters is needed to identify the product A and product B. Such a complicated study has not been undertaken, nevertheless, we have tried to observe any change in the X-ray diffraction pattern of

ilmenite occurred in the salt roasted masses obtained at optimum condition in forming largely the phase product A.

The XRD pattern of Na_2SO_4 and NaNO_3 roasted products are almost similar to each other, but differ widely with the XRD pattern of ilmenite. Most of the diffraction peaks coincide with the XRD pattern of NaFeTiO_4 . Presence of some uncommon peaks suggest the presence of another phase together with NaFeTiO_4 . Original peaks for ilmenite disappears on salt-water vapour roasting with these two reagents. The XRD pattern of $\text{NaCl-H}_2\text{O}$ vapour roasted product indicates a change occurring during roasting operation, but the product phase could not be identified.

The most of the diffractions of the $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ vapour roasted product confirm the formation of the phase, $\text{Na}_3\text{Fe}_3\text{TiO}_8$. However, the product does not contain only this phase. From the rest of the diffraction patterns, the co-existing phase could not be identified. From stiochiometric relationship, a phase of composition $\text{NaTi}_3\text{FeO}_8$ could be suggested, but there exists no ASTM card for such a compound.

(F)

The rates of dissolution of titanium and iron from the $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ vapour roasted product (powder) have been investigated as function of hydrochloric acid concentration, temperature and pulp agitation speed. The plots of $1-(1-R)^{1/3}$ versus time (t) in min for titanium give straight lines of uniform slope but in the case of iron the slop changes after 10 min's dissolution. The actual cause of such behaviour is not known to us.

The following conclusions are drawn from the dependence of the rate on hydrochloric acid concentration :

- 1) the initial rate of dissolution of iron is a combination of two parallel reactions;

- 2) the mechanism of leaching is changed; a diffusion control at lower hydrochloric acid concentration region ($< 2 \text{ g eq dm}^{-3}$) to a chemically control at higher hydrochloric acid concentration region;
- 3) the exponent of concentration terms for titanium and iron are ~ 3 and ~ 1.5 in the diffusion controlling region; and are ~ 1 and ~ 0.5 in the chemically controlling region;
- 4) the numerical values of the rate constants for titanium and iron (after 12 min dissolution) are of same value in both concentration regions. The values are $\sim 4 \times 10^{-5} \text{ cm}^2 \text{ g}^{-1} (\text{mol})^{-a} \text{ m}^{-1}$ and $\sim 8 \times 10^{-5} \text{ cm}^2 \text{ g}^{-1} (\text{mol})^{-a} \text{ m}^{-1}$ for low and high concentration regions of hydrochloric acid respectively (values of 'a' are ~ 3 and ~ 1 for titanium and ~ 1.5 and ~ 0.5 for iron in low and high concentration regions) and that
- 5) the value of the rate constant for initial dissolution of iron is almost twice the rate constant after 12 min's dissolution. This suggests that the initial rate of iron is due to two parallel reactions.

The plots of the logarithm of pseudo-rate constant, q_T versus $(1/TK) \times 10^3$ are not linear. The curves having a higher and lower asymptotic slopes at higher and lower temperature regions respectively are obtained. From the slopes of the asymptotic lines, the apparent activation energies, E_a for the systems have been evaluated by considering the Arrhenius equation. The values are $\sim 13.7 \text{ kcal mol}^{-1}$ and $0.5 \text{ kcal mol}^{-1}$ for titanium dissolution at higher and lower temperature regions respectively. The corresponding values for iron dissolution are little lower ($\sim 12 \text{ kcal mol}^{-1}$ and $\sim 0.4 \text{ kcal mol}^{-1}$).

The effect of phase mixing rate on the rate of dissolution at 110°C have been studied at two distinct different condition, one for 4 g eq dm^{-3}

and other for 1 g eq dm⁻³ hydrochloric acid. At 110°C, the zero slope at 4 g eq dm⁻³ hydrochloric acid and 0.35 slope value at 1 g eq dm⁻³ hydrochloric acid suggests that the dissolution reactions at high and low hydrochloric acid concentration are chemically and diffusion controlled respectively.

(G)

For separation of Fe³⁺ from Ti⁴⁺ in leach solution, liquid-liquid extraction method has been applied. From a concentrated hydrochloric acid solution, iron (III) can be quantitatively extracted with undiluted methylisobutylketone (MIBK). The extraction characteristics of Fe³⁺ by MIBK have been thoroughly investigated :

- i) The extraction is very fast taking only 30 seconds for extraction.
- ii) The extraction ratio decreases with increase in initial iron (III) concentration in aqueous phase.
- iii) The extraction increases extensively with increase in aqueous acidity.
- iv) The extraction is increased with increasing MIBK concentration. The extractant dependence is 0.5 and 8 at lower and higher extractant concentration regions.
- v) The extraction is decreased with increasing temperature of extraction. The apparent enthalpy change is about -13.4 kJ mol⁻¹. The low enthalpy change suggests the extraction via solvation mechanism.
- vi) The loading capacity of MIBK is 3.754 g Fe per 100 g MIBK and the Fe³⁺ to MIBK ratio is about 1 to 15 in saturated extracted phase.

The organic phase is saturated with Fe^{3+} within 10 contacts and in the first five contacts almost all the iron (III) in the aqueous phase is extracted into the organic phase.

- vii) The extraction ratio is very high for diluent benzene and low for carbontetrachloride. The diluents for MIBK can be arranged in the following order of extractibility :

Benzene > Kerosin > n-Hexane > Toluene > Chloroform > Carbontetrachloride

The condition under which Fe^{3+} is extensively extracted, Ti^{4+} is not extracted at all.

From the iron (III) free solutions, titanium (IV) can be thermally hydrolysed during the recovery of hydrochloric acid by distillation. During distillation (upto ~80%), most of titanium (IV) is precipitated as $\text{TiO}_2 \cdot n\text{H}_2\text{O}$, leaving a mother liquor containing about $1\text{--}2 \text{ g dm}^{-3}$ titanium. The titanium (IV) concentration in the mother liquor may be easily increased by adjusting the pH of solution to about 1 and extracting with 0.4 g eq dm^{-3} (0.2 M) di-(2-ethylhexyl) phosphoric acid in kerosin at O/A ratio 1 and subsequent stripping with 6 g eq dm^{-3} hydrochloric acid at O/A ratio 10. The stripped solution containing more than 10 g dm^{-3} Ti^{4+} is recycled to the distillation unit for hydrochloric acid regeneration.

(H)

The isolation of titanium and iron as their oxides from ilmenite are as follows : 10 g ilmenite on roasting with 6.67 g Na_2CO_3 at the optimum conditions yields a solution, with 0.50 dm^{-3} 6 g eq dm^{-3} hydrochloric acid solution, containing $\sim 5.40 \text{ g dm}^{-3}$ titanium and $\sim 4.80 \text{ g dm}^{-3}$ iron. The leach solution is contacted with 250 cm^3 undiluted MIBK twice to extract most of

the iron present. The first extract is stripped with equal volume of distilled water thrice. Iron in the water phase is precipitated by the addition of NaOH pellets in the stripped solution from first stage only. The precipitate is filtered, dried and ignited at 500°C (30 min) to get ~3.25 g Fe_2O_3 (iron black). The stripped MIBK phase is recycled.

The raffinate from the extraction step is subjected to distillation for hydrochloric acid recovery (~95%) and for the concurrent precipitation of very pure metatitanic acid. The precipitate is filtered, dried and ignited to get 4.12 g titanium dioxide. Overall titanium recovery from ilmenite is over 91%.

EXPERIMENTAL DATA

Table I. *Leaching of non-treated powdered ilmenite with 6 g eq dm⁻³ hydrochloric and sulphuric acids. (Fig. 6)*

Leaching temperature = boiling temperature

Solid to liquid ratio (S/L) = 0.02 kg dm⁻³

Particle size = >63 μ m <125 μ m

Weight of ilmenite = 1 g.

Acid	Agitation speed, rpm	Time, h	Wt. % metal dissolved	
			Ti	Fe
HCl	292	1	23.9	45.6
		2	41.4	56.0
		3	52.2	59.2
		4	53.0	59.6
		5	53.5	60.0
H ₂ SO ₄	372	1	2.3	5.3
		2	4.3	8.7
		3	7.9	10.6
		4	11.4	14.1
		5	14.1	17.5
		6	16.8	20.5

Table II. Data for the effect of roasting time on the subsequent leaching of the roasted product in presence of LPG (For figure - 7-9).

Roasting temperature = $650 \pm 15^\circ \text{C}$

LPG flow rate = $230 \text{ cm}^3 \text{ min}^{-1}$

Particle size = $>63 \text{ } \mu\text{m}$ $<125 \text{ } \mu\text{m}$

Leaching temperature = boiling temperature

Solid to liquid (S/L) ratio = 0.02 kg dm^{-3}

Concentration of acids = 6 g eq dm^{-3}

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Roasting time, min.	Leaching time, h	Wt. % metals dissolved in			
		HCl		H_2SO_4	
		Ti	Fe	Ti	Fe
30	1	38.1	40.2	12.0	17.5
	2	54.5	55.4	16.7	26.6
	3	56.3	59.5	19.0	31.2
	4	56.7	60.0	19.4	31.5
	5	56.9	60.3	19.8	31.9
45	1	34.9	42.4	21.9	27.4
	2	44.9	50.3	26.2	42.5
	3	52.3	56.9	32.2	50.2
	4	58.1	59.5	32.5	50.4
	5	63.2	64.1	32.7	50.7
	6	63.5	64.4	32.7	50.9
60	1	48.1	38.6	35.9	32.8
	2	65.4	57.8	44.2	48.9
	3	71.2	66.8	48.9	51.7
	4	71.6	67.4	52.3	59.4
	5	71.9	67.8	52.6	59.9
75	1	50.1	31.9	34.9	30.4
	2	72.3	68.0	46.2	57.8
	3	77.8	74.7	54.5	62.4
	4	78.2	75.3	58.2	71.2
	5	78.5	75.8	58.8	71.7
90	1	28.3	39.5	23.9	19.8
	2	37.1	46.4	33.8	28.9
	3	41.4	53.2	38.8	34.2
	4	45.2	60.4	41.1	42.0
	5	45.8	60.9	41.5	42.5

Table III. *Effect of LPG roasting time of powdered ilmenite on the maximum percentages of metals dissolved in 5h by 6 g eq dm⁻³ acids. Data for the plot of maximum percentages of metals dissolved in 5 h versus roasting time (based on Table II and figure 7-9; for Fig. 10).*

Roasting temperature = $650 \pm 15^\circ \text{C}$

LPG flow rate = $230 \text{ cm}^3 \text{ min}^{-1}$

Particle size = $>63 \text{ } \mu\text{m}$ $<125 \text{ } \mu\text{m}$

Leaching temperature = boiling temperature

Solid to liquid (S/L) ratio = 0.02 kg dm^{-3}

Concentration of acids = 6 g eq dm^{-3}

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Roasting time, min.	Max. Wt. % metals dissolved in 5h			
	HCl		H_2SO_4	
	Ti	Fe	Ti	Fe
0	53.5	60.0	16.8	20.5
30	56.9	60.3	19.8	31.9
45	63.5*	64.4*	32.7	50.9*
60	71.9	67.8	52.6	59.9
75	78.6	75.8	58.8	71.7
90	45.8	60.9	41.5	42.5

* Max. Wt. % metal dissolved in 6h.

Table IV. Data for the effect of roasting temperature on the subsequent leaching of the roasted product in presence of LPG.

Roasting time = 75 min.

LPG flow rate = $230 \text{ cm}^3 \text{ min}^{-1}$

Particle size = $>63 \text{ } \mu\text{m}$ $<125 \text{ } \mu\text{m}$

Leaching temperature = boiling temperature

Solid to liquid (S/L) ratio = 0.02 kg dm^{-3}

Concentration of acids = 6 g eq dm^{-3}

Leaching pulp agitation speed = 293 rpm (HCl)/373 rpm (H_2SO_4)

Roasting temperature, $^{\circ}\text{C}, \pm 15^{\circ}\text{C}$	Leaching time, h	Wt. % metals dissolved in			
		HCl		H_2SO_4	
		Ti	Fe	Ti	Fe
600	1	32.7	40.4	8.7	23.4
	2	50.1	50.6	17.4	30.5
	3	54.2	58.2	21.3	37.6
	4	54.5	62.0	21.5	45.8
	5	54.8	62.5	21.8	45.8
650	1	50.1	31.9	34.9	30.4
	2	72.3	68.0	46.2	57.8
	3	77.8	74.7	54.5	62.4
	4	78.2	75.3	58.2	71.2
	5	78.6	75.8	58.8	71.7
700	1	37.0	30.4	28.3	21.3
	2	71.9	66.4	51.8	48.6
	3	81.7	73.0	60.6	64.8
	4	82.3	78.6	65.0	72.3
	5	82.8	79.1	65.5	72.9
750	1	60.9	30.4	34.9	21.3
	2	67.5	56.9	44.8	36.5
	3	73.5	68.9	53.9	51.7
	4	74.1	70.2	57.0	67.3
	5	74.5	70.7	57.5	67.9
800	1	15.3	39.5	12.1	34.9
	2	20.1	45.6	14.8	42.6
	3	24.9	48.7	17.2	47.2
	4	28.2	50.9	17.7	47.8
	5	28.7	51.7	18.2	48.7

Table V. Effect of LPG roasting temperature of powdered ilmenite on the maximum percentage of metal dissolved in 5h by 6g eq dm^{-3} acids. Data for the plot of maximum percentages of metals dissolved in 5h versus roasting temperature (based on Table IV for figure 11).

Roasting time = 75 min.

LPG flow rate = $230 \text{ cm}^3 \text{ min}^{-1}$

Particle size = $>63 \mu\text{m} <125 \mu\text{m}$

Leaching temperature = boiling temperature

Solid to liquid (S/L) ratio = 0.02 kg dm^{-3}

Concentration of acids = 6 g eq dm^{-3}

Leaching pulp agitation speed = 293 rpm (HCl)/373 rpm (H_2SO_4)

Roasting temperature, $^{\circ}\text{C}$, $\pm 15^{\circ}\text{C}$	Max. Wt. % metal dissolved in 5h			
	HCl		H_2SO_4	
	Ti	Fe	Ti	Fe
0	53.5	60.0	16.8	20.5
600	54.8	62.5	21.8	45.8
650	78.6	75.8	58.8	71.7
700	82.8	79.1	65.5	72.9
750	74.5	70.7	57.5	67.9
800	28.7	51.7	18.2	48.7

Table VI. Data for the effect of roasting gas flow rate on the subsequent leaching of the roasted product in presence of LPG.

Roasting time = 75 min.

Roasting temperature = $(700 \pm 15)^\circ\text{C}$

Particle size = $>63 \mu\text{m} < 125 \mu\text{m}$

Leaching temperature = boiling temperature

Solid to liquid (S/L) ratio = 0.02 kg dm^{-3}

Concentration of acids = 6 g eq dm^{-3}

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Roasting gas flow rate, $\text{cm}^3 \text{ min}^{-1}$	Leaching time, h	Wt. % metals dissolved in			
		HCl		H_2SO_4	
		Ti	Fe	Ti	Fe
150	1	22.9	37.9	15.2	35.0
	2	30.3	60.8	26.1	54.8
	3	34.9	63.9	28.3	60.8
	4	38.7	66.3	30.0	63.5
	5	39.2	66.9	30.5	63.9
230	1	37.0	30.4	28.3	21.3
	2	71.9	66.4	51.8	48.6
	3	81.7	73.0	60.6	64.8
	4	82.3	78.6	65.0	72.3
	5	82.8	79.1	65.5	72.9
190	1	33.4	27.6	23.6	19.9
	2	60.8	62.0	41.2	45.7
	3	69.2	68.4	49.4	61.3
	4	74.0	73.2	54.2	68.5
	5	74.5	73.8	54.7	69.1
270	1	34.1	28.7	26.1	18.5
	2	68.5	63.2	48.2	46.2
	3	77.3	71.8	56.8	62.3
	4	81.2	75.8	62.5	69.3
	5	81.7	76.2	63.1	69.8
310	1	28.3	38.0	14.2	19.8
	2	61.0	54.8	34.9	45.6
	3	70.2	60.8	47.9	54.0
	4	75.4	63.9	50.1	59.1
	5	77.3	68.0	56.0	64.2
	6	77.9	68.5	56.6	64.7

Table VII. *Effect of LPG roasting gas flow of powdered ilmenite on the maximum percentages of metals dissolved in 5h by 6 g eq dm⁻³ acids. Data for the plot of maximum percentages of metals dissolved in 5h versus roasting gas flow rate (based on Table VI for Fig. 12).*

Roasting time = 75 min.

Roasting temperature = (700±15)°C

Particle size = >63 µm <125 µm

Leaching temperature = boiling temperature

Solid to liquid (S/L) ratio = 0.02 kg dm⁻³

Concentration of acids = 6 g eq dm⁻³

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H₂SO₄)

Roasting gas flow rate, cm ³ min ⁻¹	Max. Wt. % metals dissolved in 5h			
	HCl		H ₂ SO ₄	
	Ti	Fe	Ti	Fe
0	53.5	60.0	16.8	20.5
150	39.2	66.9	30.5	63.9
190	74.5	73.8	54.7	69.1
230	82.8	79.1	65.5	72.9
270	81.7	76.2	63.1	69.8
310	77.9	68.5	56.6	64.7

Table VIII. *Effect of acid concentrations on the leaching characteristics of the LPG-roasted ilmenite : Data for plotting weight percent of metals dissolved against leaching time (h) at different acid concentrations.*

Roasting temperature = $(700 \pm 15)^{\circ}\text{C}$

Roasting time = 75 min.

Roasting gas flow rate = $230 \text{ cm}^3 \text{ min}^{-1}$

Particle size = $>63 \text{ } \mu\text{m}$ $<125 \text{ } \mu\text{m}$

Leaching temperature = boiling temperature

Leaching solid to liquid (S/L) ratio = 0.02 kg dm^{-3}

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Acid concentration, g eq dm^{-3}	Leaching time, h	Wt. % metals dissolved in			
		HCl		H_2SO_4	
		Ti	Fe	Ti	Fe
2	1	5.5	15.2	4.4	14.5
	2	7.1	30.4	7.6	25.1
	3	8.7	32.7	8.2	28.9
	4	10.0	34.3	8.7	32.2
	5	10.5	34.9	9.1	32.7
4	1	14.2	12.2	12.0	18.3
	2	22.9	38.0	21.8	30.4
	3	27.2	41.1	23.9	36.5
	4	30.5	44.1	26.1	39.5
	5	31.1	44.5	26.7	40.0
5	1	34.8	32.5	—	—
	2	50.1	42.6	—	—
	3	60.9	54.8	—	—
	4	65.3	57.8	—	—
	5	65.9	58.2	—	—
6	1	37.0	30.4	28.3	21.3
	2	71.9	66.4	51.8	48.6
	3	81.7	73.0	60.6	64.8
	4	82.3	78.6	65.0	72.3
	5	82.8	79.1	65.5	72.9
8	1	52.3	48.7	28.3	21.3
	2	76.2	66.8	54.5	55.6
	3	80.6	73.8	64.0	67.8
	4	84.9	80.9	69.7	75.9
	5	85.3	81.6	70.2	76.5

Table IX. *Effect of acid concentrations on the leaching of the LPG-roasted ilmenite : Data for the plot of maximum weight percentages of metals dissolved in 5h (based on Table VIII) versus the concentrations of leaching acid (for figure 14).*

Roasting temperature = $(700 \pm 15)^{\circ}\text{C}$

Roasting time = 75 min.

Roasting gas flow rate = $230 \text{ cm}^3 \text{ min}^{-1}$

Particle size = $>63 \text{ }\mu\text{m}$ $<125 \text{ }\mu\text{m}$

Leaching temperature = boiling temperature

Leaching solid to liquid (S/L) ratio = 0.02 kg dm^{-3}

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Acid concentration, g eq dm^{-3}	Max. Wt. % metals dissolved in 5h			
	HCl		H_2SO_4	
	Ti	Fe	Ti	Fe
2	10.5	34.9	9.7	32.7
4	31.1	44.5	26.7	40.0
5	65.9	58.2	-	-
6	82.8	79.1	65.5	72.9
8	85.3	81.6	70.2	76.5

Table X. *Effect of temperature on the leaching characteristics of the LPG-roasted ilmenite : Data for plotting weight percent of metals dissolved against time (h) at various temperatures.*

Roasting temperature = $(700 \pm 15)^{\circ}\text{C}$

Roasting time = 75 min.

Roasting gas flow rate = $230 \text{ cm}^3 \text{ min}^{-1}$

Particle size = $>63 \text{ }\mu\text{m} <125 \text{ }\mu\text{m}$

Acid concentration = 6 g eq dm^{-3}

Leaching solid to liquid (S/L) ratio = 0.02 kg dm^{-3}

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Leaching temperature, $^{\circ}\text{C}$	Leaching time, h	Wt. % metals dissolved in			
		HCl		H_2SO_4	
		Ti	Fe	Ti	Fe
50	1	3.3	14.2	2.2	15.9
	2	5.5	15.6	4.4	17.5
	3	6.5	16.7	5.4	18.3
	4	7.6	17.5	6.5	19.0
	5	8.1	18.0	6.9	19.6
80	1	10.9	10.7	10.5	17.8
	2	28.3	33.6	17.4	26.1
	3	30.2	36.1	18.0	29.3
	4	30.8	36.7	18.5	30.2
	5	31.3	37.2	19.1	30.7
110	1	37.0	30.4	28.3	21.3
	2	71.9	66.4	51.8	48.6
	3	81.7	73.0	60.6	64.8
	4	82.3	78.6	65.0	72.3
	5	82.8	79.1	65.5	72.9

Table XI. *Effect of temperature on the leaching of the LPG-roasted ilmenite :
Data for the plot of maximum percentages of metals dissolved in 5h
(based on Table X, for figure 15) versus the temperature of leaching.*

Roasting temperature = $(700 \pm 15)^{\circ}\text{C}$

Roasting time = 75 min.

Roasting gas flow rate = $230 \text{ cm}^3 \text{ min}^{-1}$

Particle size = $>63 \mu\text{m} <125 \mu\text{m}$

Acid concentration = 6 g eq dm^{-3}

Leaching solid to liquid (S/L) ratio = 0.02 kg dm^{-3}

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Leaching temperature, $^{\circ}\text{C}$	Max. Wt. % metals dissolved in 5h			
	HCl		H_2SO_4	
	Ti	Fe	Ti	Fe
50	8.1	18.0	6.9	19.6
80	31.3	37.2	19.1	30.7
110	82.8	79.1	65.5	72.9

Table XII. *Effect of solid to liquid ratio on the leaching characteristics of the LPG-roasted ilmenite : Data for plotting weight percent metals dissolved against time (h) of various solid to liquid ratio.*

Roasting temperature = $(700 \pm 15)^{\circ}\text{C}$

Roasting time = 75 min.

Roasting gas flow rate = $230 \text{ cm}^3 \text{ min}^{-1}$

Particle size = $>63 \mu\text{m}$ $>125 \mu\text{m}$

Acid concentration = 6 g eq dm^{-3}

Leaching temperature = boiling temperature

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Solid to liquid ratio, kg dm^{-3}	Leaching time, h	Wt. % metals dissolved in			
		HCl		H_2SO_4	
		Ti	Fe	Ti	Fe
0.02	1	37.0	30.4	28.3	21.3
	2	71.9	66.4	51.8	48.6
	3	81.7	73.0	60.6	64.8
	4	82.3	78.6	65.0	72.3
	5	82.8	79.1	65.5	72.9
0.03	1	29.3	22.8	20.3	19.2
	2	57.9	51.0	37.5	45.0
	3	65.5	59.6	42.8	67.9
	4	66.2	60.1	43.3	68.3
	5	66.8	60.6	43.8	68.9
0.04	1	27.0	21.6	13.5	48.2
	2	44.0	43.1	26.1	55.8
	3	49.4	49.7	27.8	62.4
	4	49.9	50.2	28.2	62.9
	5	50.4	50.7	28.8	63.4
0.06	1	16.2	19.5	10.6	39.7
	2	24.8	39.4	19.7	46.3
	3	28.5	44.9	20.5	52.6
	4	29.0	45.4	21.1	53.1
	5	29.5	45.9	21.7	53.5
0.10	1	15.8	28.4	6.5	13.2
	2	20.9	35.9	15.1	24.3
	3	15.1	41.6	16.3	29.4
	4	7.9	42.6	16.9	35.0
	5	5.1	43.1	17.3	35.5

Table XIII. *Effect of solid to liquid ratio on the leaching of the LPG-roasted ilmenite : Data for the plot of maximum percentages of metals dissolved and the maximum concentration of metals in leach solution in 5h (based on Table XII, for figures 16 & 17) versus the solid to liquid ratio.*

Roasting temperature = $(700 \pm 15)^{\circ}\text{C}$

Roasting time = 75 min.

Roasting gas flow rate = $230 \text{ cm}^3 \text{ min}^{-1}$

Particle size = $>63 \mu\text{m}$ $>125 \mu\text{m}$

Acid concentration = 6 g eq dm^{-3}

Leaching temperature = boiling temperature

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Solid to liquid ratio kg dm^{-3}	Max. wt. % metals dissolved in 5h				Max. concentration of metals in leach solution in 5h, g dm^{-3}			
	HCl		H_2SO_4		HCl		H_2SO_4	
	Ti	Fe	Ti	Fe	Ti	Fe	Ti	Fe
0.02	82.8	79.1	65.5	72.9	4.56	5.13	3.63	4.72
0.03	66.8	60.6	43.8	68.9	5.57	5.88	3.65	6.62
0.04	50.4	50.7	28.8	63.4	5.60	5.57	3.20	8.22
0.06	29.5	45.9	21.7	53.5	4.92	8.92	3.62	10.39
0.10	5.1*	43.1	17.3	35.5	1.42	13.96	4.81	11.32

* Max. value is 20.9% at 2h; on further leaching concentration of titanium is decreased to 5.1% dissolutions in 5h.

Table XIV. *Data for the effect of roasting time on the subsequent leaching of the product obtained by the LPG-water vapour roasting in presence of nickel catalyst (for figures 18-20).*

Roasting temperature = $(750 \pm 15)^{\circ}\text{C}$

Particle size = $>63 \mu\text{m} < 125 \mu\text{m}$

LPG flow rate = $110 \text{ cm}^3 \text{ min}^{-1}$

Water vapour pressure = 31.5 mm Hg

Leaching temperature = boiling temperature

Solid to liquid (S/L) ratio = 0.02 kg dm^{-3}

Leaching acids concentration = 6 g eq dm^{-3}

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Roasting time, min	Leaching time, h	Wt. % metals dissolved in			
		HCl		H_2SO_4	
		Ti	Fe	Ti	Fe
30	1	28.3	30.4	19.6	24.3
	2	58.8	63.9	26.1	41.1
	3	63.2	76.1	30.0	44.1
	4	63.5	76.5	30.2	44.4
40	1	41.4	54.8	24.0	24.3
	2	71.7	82.1	34.8	48.7
	3	82.8	85.0	43.4	60.8
	4	83.0	85.2	43.6	61.0
45	1	28.3	36.5	21.8	36.5
	2	71.9	73.0	33.7	60.8
	3	78.1	89.4	40.0	66.3
	4	78.4	89.7	40.3	66.9
50	1	28.3	51.7	21.8	51.7
	2	56.6	85.2	34.8	73.0
	3	67.1	94.0	39.0	76.1
	4	67.5	94.3	39.3	76.5
60	1	21.8	45.6	17.4	41.1
	2	32.7	76.0	24.0	60.8
	3	37.0	88.2	27.2	70.0
	4	37.4	88.5	27.5	70.5

Table XV. Data for the plot of maximum weight percentages of metals dissolved in 4h versus roasting time in min (based on Table XIV for Fig. 21).

Roasting temperature = $(750 \pm 15)^{\circ}\text{C}$

Particle size = $>63 \mu\text{m} < 125 \mu\text{m}$

LPG flow rate = $110 \text{ cm}^3 \text{ min}^{-1}$

Water vapour pressure = 31.5 mm Hg

Leaching temperature = boiling temperature

Solid to liquid (S/L) ratio = 0.02 kg dm^{-3}

Leaching acids concentration = 6 g eq dm^{-3}

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Roasting time, min.	Max. Wt. % metals dissolved in 4h			
	HCl		H_2SO_4	
	Ti	Fe	Ti	Fe
0	53.6	60.0	16.8	20.5
30	63.5	76.5	30.2	44.4
40	83.0	85.2	43.6	61.0
45	78.4	89.7	40.3	66.9
50	67.5	94.3	39.3	76.5
60	37.4	88.5	27.5	70.5

Table XVI. *The effect of roasting temperature on the subsequent dissolution characteristics of the product obtained by the LPG-water vapour roasting in presence of nickel catalyst.*

Roasting time = 40 min.

Particle size = $>63 \mu\text{m}$ $<125 \mu\text{m}$

LPG flow rate = $110 \text{ cm}^3 \text{ min}^{-1}$

Water vapour pressure = 31.5 mm Hg

Leaching temperature = boiling temperature

Solid to liquid (S/L) ratio = 0.02 kg dm^{-3}

Leaching acids concentration = 6 g eq dm^{-3}

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Roasting temperature, $^{\circ}\text{C}$, $\pm 5^{\circ}\text{C}$	Leaching time, h	Wt. % metals dissolved in			
		HCl		H_2SO_4	
		Ti	Fe	Ti	Fe
600	1	47.9	39.5	24.0	27.4
	2	61.0	54.8	32.7	42.6
	3	74.1	79.1	37.0	48.2
	4	74.5	79.4	37.3	48.5
650	1	52.3	51.7	26.1	30.4
	2	76.2	74.5	34.8	47.1
	3	84.5	85.2	39.2	54.2
	4	84.9	85.5	39.5	54.7
700	1	56.6	66.9	32.7	42.6
	2	78.4	82.1	41.4	54.8
	3	91.0	94.1	47.5	66.4
	4	91.5	94.6	47.9	66.9
750	1	41.4	54.8	24.0	24.3
	2	71.7	82.1	34.8	48.7
	3	82.3	85.2	43.2	60.3
	4	82.8	85.5	43.6	60.8
800	1	50.1	39.5	21.8	21.3
	2	67.5	60.8	32.7	42.6
	3	80.2	73.0	40.3	54.3
	4	80.6	73.4	40.7	54.7

Table XVII. Data for the maximum weight percentages of metals dissolved in 4h from the products obtained at different roasting temperature (based on Table XVI, for Figure 22).

Roasting time = 40 min.

Particle size = $>63 \mu\text{m}$ $<125 \mu\text{m}$

LPG flow rate = $110 \text{ cm}^3 \text{ min}^{-1}$

Water vapour pressure = 31.5 mm Hg

Leaching temperature = boiling temperature

Solid to liquid (S/L) ratio = 0.02 kg dm^{-3}

Leaching acids concentration = 6 g eq dm^{-3}

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Roasting temperature, $^{\circ}\text{C}$, $\pm 15^{\circ}\text{C}$	Max. Wt. % metals dissolved in 4h			
	HCl		H_2SO_4	
	Ti	Fe	Ti	Fe
30	53.5	60.0	16.8	20.5
600	74.5	79.4	37.3	48.5
650	84.9	85.5	39.5	54.7
700	91.5	94.6	47.9	66.9
750	82.8	85.5	43.6	60.8
800	80.6	73.4	40.7	54.7

Table XVIII. Data showing the effect of roasting LPG flow rate on the subsequent dissolution characteristics of the product obtained by the LPG-water vapour roasting in presence of nickel catalyst.

Roasting time = 40 min.

Particle size = $>63 \mu\text{m} < 125 \mu\text{m}$

Roasting temperature = $(700 \pm 15)^\circ\text{C}$

Water vapour pressure = 31.5 mm Hg

Leaching temperature = boiling temperature

Solid to liquid (S/L) ratio = 0.02 kg dm^{-3}

Leaching acids concentration = 6 g eq dm^{-3}

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Roasting gas flow rate, $\text{cm}^3 \text{ min}^{-1}$	Leaching time, h	Wt. % metals dissolved in			
		HCl		H_2SO_4	
		Ti	Fe	Ti	Fe
110	1	56.6	66.9	32.7	42.6
	2	78.4	82.1	41.4	54.8
	3	91.0	94.1	47.5	66.4
	4	91.5	94.6	47.9	66.9
150	1	37.2	57.8	15.3	45.6
	2	45.2	70.0	21.9	51.7
	3	50.3	76.1	24.1	54.5
	4	50.7	76.5	24.4	54.8
250	1	28.4	48.7	11.0	42.6
	2	38.3	60.8	16.4	48.7
	3	45.5	69.6	21.5	51.2
	4	45.9	70.0	21.9	51.7
270	1	27.1	47.8	9.5	37.6
	2	36.5	56.4	16.8	43.9
	3	43.4	64.8	21.0	49.5
	4	43.8	65.2	21.3	49.8
310	1	26.2	45.6	8.3	36.5
	2	37.1	54.7	15.3	42.6
	3	41.1	60.5	20.4	48.3
	4	41.5	60.8	20.7	48.7

Table XIX. *Data for the effect of roasting LPG-flow rate on the maximum weight percentages of metals dissolved in 4h from the product obtained by the LPG-water vapour in presence of nickel catalyst (based on Table XVIII, for Figure 23).*

Roasting time = 40 min.

Particle size = $>63\ \mu\text{m}$ $<125\ \mu\text{m}$

Roasting temperature = $(700 \pm 15)^{\circ}\text{C}$

Water vapour pressure = 31.5 mm Hg

Leaching temperature = boiling temperature

Solid to liquid (S/L) ratio = $0.02\ \text{kg dm}^{-3}$

Leaching acids concentration = $6\ \text{g eq dm}^{-3}$

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Roasting gas flow rate, $\text{cm}^3\ \text{min}^{-1}$	Max. Wt. % metals dissolved in 4h			
	HCl		H_2SO_4	
	Ti	Fe	Ti	Fe
0	53.5	60.0	16.8	20.5
110	91.5	94.6	47.9	66.9
150	50.7	76.5	24.4	54.8
230	45.9	70.0	21.9	51.7
270	43.8	65.2	21.3	49.8
310	41.5	60.8	20.7	48.7

Table XX. *Data for the effect of roasting water vapour pressure on the subsequent leaching of the product obtained by the LPG-water vapour roasting in presence of nickel catalyst.*

Roasting time = 40 min.

Particle size = $>63\ \mu\text{m}$ $<125\ \mu\text{m}$

Roasting temperature = $(700 \pm 15)^\circ\text{C}$

LPG flow rate = $110\ \text{cm}^3\ \text{min}^{-1}$

Leaching temperature = boiling temperature

Solid to liquid (S/L) ratio = $0.02\ \text{kg}\ \text{dm}^{-3}$

Leaching acids concentration = $6\ \text{g eq}\ \text{dm}^{-3}$

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Roasting water vapour pressure, mm Hg	Leaching time, h	Wt. % metals dissolved in			
		HCl		H_2SO_4	
		Ti	Fe	Ti	Fe
31.5	1	56.6	66.9	32.7	42.6
	2	78.4	82.1	41.4	54.8
	3	91.0	94.1	47.5	66.4
	4	91.5	94.6	47.9	66.9
55.5	1	56.8	63.9	30.6	39.5
	2	69.9	76.0	38.2	48.7
	3	76.1	88.1	45.4	60.5
	4	76.5	88.4	45.9	60.8
92.6	1	50.3	57.8	24.0	41.1
	2	61.2	73.0	32.8	48.7
	3	69.5	84.1	41.1	57.3
	4	69.9	84.4	41.5	57.8
149.4	1	48.1	42.6	22.9	33.4
	2	59.0	63.8	30.6	42.6
	3	67.4	74.1	38.2	51.2
	4	67.7	74.5	38.5	51.7

Table XXI. Data for the plot of maximum weight percentages of metals dissolved in 4h versus water vapour pressure in mm Hg (based on Table XX, for figure 24).

Roasting time = 40 min.

Particle size = $>63 \mu\text{m}$ $<125 \mu\text{m}$

Roasting temperature = $(700 \pm 15)^\circ\text{C}$

LPG flow rate = $110 \text{ cm}^3 \text{ min}^{-1}$

Leaching temperature = boiling temperature

Solid to liquid (S/L) ratio = 0.02 kg dm^{-3}

Leaching acids concentration = 6 g eq dm^{-3}

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Roasting water vapour pressure, mm Hg	Max. Wt. % metals dissolved in 4h			
	HCl		H_2SO_4	
	Ti	Fe	Ti	Fe
0	53.5	60.0	16.8	20.5
31.5	91.5	94.6	47.9	66.9
55.5	76.5	88.4	45.9	60.8
92.7	69.9	84.4	41.5	57.8
149.4	67.7	74.5	38.5	51.7

Table XXII. *Effect of acid concentration on the leaching of the LPG-water vapour roasted ilmenite; Data for plotting weight percent of metals dissolved against leaching time (h) at different acid concentration (not shown graphically).*

Roasting time = 40 min.

Roasting temperature = $(700 \pm 15)^{\circ}\text{C}$

Roasting gas flow rate = $110 \text{ cm}^3 \text{ min}^{-1}$

Water vapour pressure = 31.5 mm Hg

Particle size = $>63 \mu\text{m}$ $<125 \mu\text{m}$

Leaching temperature = boiling temperature

Leaching solid to liquid (S/L) ratio = 0.02 kg dm^{-3}

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Acid concentration, g eq dm^{-3}	Leaching time, h	Wt. % metals dissolved in			
		HCl		H_2SO_4	
		Ti	Fe	Ti	Fe
2	1	3.8	10.6	1.6	8.4
	2	4.4	13.7	2.7	10.6
	3	5.0	16.3	4.2	13.4
	4	5.2	16.7	4.4	13.7
4	1	10.9	18.3	4.4	12.2
	2	22.1	36.5	14.7	24.3
	3	34.5	51.5	21.4	39.1
	4	34.9	51.8	21.8	39.5
6	1	56.6	66.9	32.7	42.6
	2	78.4	82.1	41.4	54.8
	3	91.0	94.1	47.5	66.4
	4	91.5	94.6	47.9	66.9
8	1	69.7	71.5	30.5	51.7
	2	82.8	85.2	43.4	63.9
	3	93.4	97.0	54.2	73.0
	4	93.7	97.3	54.6	73.4

Table XXIII. *Effect of acid concentration on the leaching of the LPG-water vapour roasted ilmenite : Data for the plot of maximum percentages of metals dissolved in 4h (based on Table XXII) versus the concentration of leaching acids (for Figure 25).*

Roasting time = 40 min.

Roasting temperature = $(700 \pm 15)^{\circ}\text{C}$

Roasting gas flow rate = $110 \text{ cm}^3 \text{ min}^{-1}$

Water vapour pressure = 31.5 mm Hg

Particle size = $>63 \mu\text{m} <125 \mu\text{m}$

Leaching temperature = boiling temperature

Leaching solid to liquid (S/L) ratio = 0.02 kg dm^{-3}

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Acid concentration, g eq dm^{-3}	Max. Wt. % metals dissolved in 4h			
	HCl		H_2SO_4	
	Ti	Fe	Ti	Fe
2	5.2	16.7	4.4	13.7
4	34.9	51.8	21.8	39.5
6	91.5	94.6	47.9	66.9
8	93.7	97.3	54.6	73.4

Table XXIV. *Effect of temperature on the leaching characteristics of the LPG-water vapour roasted ilmenite; Data for plotting weight percent of metals dissolved against leaching time (h) at different leaching temperatures (not shown graphically).*

Roasting time = 40 min.

Roasting temperature = $(700 \pm 15)^{\circ}\text{C}$

Roasting gas flow rate = $110 \text{ cm}^3 \text{ min}^{-1}$

Water vapour pressure = 31.5 mm Hg

Particle size = $>63 \mu\text{m} <125 \mu\text{m}$

Leaching acids concentration = 6 g eq dm^{-3}

Leaching solid to liquid (S/L) ratio = 0.02 kg dm^{-3}

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Leaching temperature, $^{\circ}\text{C}$	Leaching time, h	Wt. % metals dissolved in			
		HCl		H_2SO_4	
		Ti	Fe	Ti	Fe
50	1	8.3	28.9	5.5	22.8
	2	11.4	31.9	8.7	27.4
	3	11.8	34.7	10.5	31.5
	4	12.0	35.0	10.9	31.9
80	1	17.5	33.5	10.9	31.5
	2	24.0	42.6	17.5	36.5
	3	30.2	48.3	23.8	45.1
	4	30.6	48.7	24.0	45.6
110	1	56.6	66.9	32.7	42.6
	2	78.4	82.1	41.4	54.8
	3	91.0	94.1	47.5	66.4
	4	91.5	94.6	47.9	66.9

Table XXV. *Effect of temperature on the leaching of the LPG-water vapour roasted ilmenite : Data for the plot of maximum percentage of metals dissolved in 4h (based on Table XXIV) versus the temperature of leaching (for Figure 26).*

Roasting time = 40 min.

Roasting temperature = $(700 \pm 15)^{\circ}\text{C}$

Roasting gas flow rate = $110 \text{ cm}^3 \text{ min}^{-1}$

Water vapour pressure = 31.5 mm Hg

Particle size = $>63 \mu\text{m} <125 \mu\text{m}$

Leaching acids concentration = 6 g eq dm^{-3}

Leaching solid to liquid (S/L) ratio = 0.02 kg dm^{-3}

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Leaching temperature, $^{\circ}\text{C}$	Max. Wt. % metals dissolved in 4h			
	HCl		H_2SO_4	
	Ti	Fe	Ti	Fe
50	12.0	35.0	10.9	31.9
80	30.6	48.7	24.0	45.6
110	91.5	94.6	47.9	66.9

Table XXVI. *Effect of solid to liquid ratio on the leaching characteristics of the LGP-water vapour roasted ilmenite : Data for plotting weight percent of metal dissolved against leaching time (h) at different solid to liquid ratio (not shown graphically).*

Roasting time = 40 min.

Roasting temperature $(700 \pm 15)^{\circ}\text{C}$

Roasting gas flow rate = $110 \text{ cm}^3 \text{ min}^{-1}$

Water vapour pressure = 31.5 mm Hg

Particle size = $>63 \mu\text{m} <125 \mu\text{m}$

Leaching temperature = boiling temperature

Leaching acids concentration = 6 g eq dm^{-3}

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Solid to liquid (S/L) ratio, kg dm^{-3}	Leaching time, h	Wt. % metals dissolved in			
		HCl		H_2SO_4	
		Ti	Fe	Ti	Fe
0.02	1	56.6	66.9	32.7	42.6
	2	78.4	82.1	41.4	54.8
	3	91.0	94.1	47.5	66.4
	4	91.5	94.6	47.9	66.9
0.03	1	60.7	50.2	28.7	33.4
	2	68.6	55.3	33.9	47.5
	3	64.1	74.1	36.0	53.1
	4	55.2	83.5	41.3	57.4
0.04	1	43.7	43.1	23.7	25.4
	2	47.3	48.2	28.2	40.6
	3	43.7	68.4	30.0	45.6
	4	34.6	78.6	36.4	50.7
0.06	1	40.8	36.8	19.4	24.1
	2	34.7	46.1	24.7	27.2
	3	32.4	51.9	26.2	38.5
	4	19.5	68.4	29.8	42.5
0.10	1	22.9	34.5	14.2	20.3
	2	20.2	43.6	20.8	24.3
	3	19.1	48.7	21.8	36.5
	4	10.0	54.7	24.0	39.6

Table XXVII. *Effect of solid to liquid ratio on the leaching of the LPG-water vapour roasted ilmenite : Data for the plot of weight percentage of metals dissolved in 4h (based on Table XXVI) versus the solid to liquid ratio (for Figure 27 & 28).*

Roasting time = 40 min.

Roasting temperature $(700 \pm 15)^{\circ}\text{C}$

Roasting gas flow rate = $110 \text{ cm}^3 \text{ min}^{-1}$

Water vapour pressure = 31.5 mm Hg

Particle size = $>63 \mu\text{m}$ $<125 \mu\text{m}$

Leaching temperature = boiling temperature

Leaching acids concentration = 6 g eq dm^{-3}

Leaching pulp agitation speed = 292 rpm (HCl)/372 rpm (H_2SO_4)

Solid to liquid ratio, kg dm^{-3}	Wt. % metals dissolved in 4h				Concentration of metals on leaching for 4h, g dm^{-3}			
	HCl		H_2SO_4		HCl		H_2SO_4	
	Ti	Fe	Ti	Fe	Ti	Fe	Ti	Fe
0.02	91.5	94.6	47.9	66.9	4.08	6.12	2.66	4.27
0.03	55.2	83.5	41.3	57.4	4.60	8.11	3.44	5.57
0.04	34.6	78.6	36.4	50.7	3.86	10.18	4.04	6.57
0.06	19.5	68.4	29.8	42.5	3.25	13.30	4.97	8.33
0.10	10.0	54.7	24.0	39.6	2.78	17.72	6.67	12.83

Table XXVIII. Data for the effect of ilmenite powder to salt ratio on the subsequent leaching of the salt-water vapour roasted ilmenite.

Roasting temperature = 800°C (885°C for Na₂SO₄ & 850°C for Na₂CO₃)
 Roasting time = 60 min. (90 min. for NaNO₃)
 Gas flow rate = 420 cm³ min⁻¹ (515 cm³ min⁻¹ for Na₂SO₄)
 Water vapour pressure = 31.5 mm Hg
 Leaching acid concentration = 2 g eq dm⁻³
 Leaching pulp agitation speed = 292 rpm
 Leaching temperature = boiling temperature
 Pulp ratio = 0.02 kg dm⁻³ (based on ilmenite content)

Ilmenite powder to salt ratio, (w/w)	Leaching time, min.	Wt. % metals dissolved in HCl for							
		NaCl roast		Na ₂ SO ₄ roast		NaNO ₃ roast		Na ₂ CO ₃ roast	
		Ti	Fe	Ti	Fe	Ti	Fe	Ti	Fe
2.5	30	-	-	22.3	28.7	-	-	-	-
	60	-	-	33.9	37.2	-	-	-	-
	90	-	-	36.0	40.6	-	-	-	-
	120	-	-	36.2	40.8	-	-	-	-
2.0	30(15)	8.7	30.5	23.9	30.4	29.8	46.5	30.1	38.3
	60(30)	12.0	39.7	34.8	36.5	33.5	50.2	43.5	52.1
	90(45)	14.0	42.8	37.0	42.4	33.7	50.4	43.6	52.4
	120	14.2	42.6	37.3	42.6	-	-	-	-
1.7	30	-	-	-	-	30.5	48.9	-	-
	60	-	-	-	-	34.8	52.0	-	-
	90	-	-	-	-	34.6	52.2	-	-
	120	-	-	-	-	-	-	-	-
1.5	30(15)	12.0	32.1	19.6	24.8	27.5	36.7	33.4	39.8
	60(30)	14.7	41.2	29.2	31.3	31.6	41.3	48.7	53.3
	90(45)	16.6	44.3	32.5	36.5	31.8	41.5	48.9	53.5
	120	16.9	44.5	32.7	36.4	-	-	-	-
1.0	30(15)	15.2	33.6	15.2	19.2	24.0	24.4	26.7	30.7
	60(30)	17.4	42.8	23.5	24.6	28.3	30.6	39.2	42.6
	90(45)	19.6	45.6	28.5	30.4	28.5	30.4	39.4	42.9
	120	19.6	45.8	28.3	30.6	-	-	-	-
0.67	30(15)	17.4	35.1	12.3	16.2	17.4	24.4	17.4	18.4
	60(30)	19.6	44.3	18.7	20.7	24.0	27.5	23.9	27.6
	90(45)	21.6	47.1	24.6	26.3	24.0	27.3	23.7	26.8
	120	21.8	47.3	24.8	26.5	-	-	-	-
0.5	30	17.4	27.5	-	-	-	-	-	-
	60	18.5	35.1	-	-	-	-	-	-
	90	20.5	39.4	-	-	-	-	-	-
	120	20.7	39.7	-	-	-	-	-	-
0.4	30	8.7	22.9	-	-	-	-	-	-
	60	12.9	29.0	-	-	-	-	-	-
	90	14.0	36.4	-	-	-	-	-	-
	120	14.2	36.6	-	-	-	-	-	-

Figures in the parentheses indicate the leaching time in minute for Na₂CO₃ system.

Table XXIX. Data for the plot of weight percentages of metals dissolved in n^* min versus roasting ilmenite sand to salt ratio (based on Table XXVIII for Figure 29 & 30).

Roasting temperature = 800°C (885°C for Na_2SO_4 & 850°C for Na_2CO_3)

Roasting time = 60 min. (90 min. for NaNO_3)

Gas flow rate = 420 $\text{cm}^3 \text{min}^{-1}$ (515 $\text{cm}^3 \text{min}^{-1}$ for Na_2SO_4)

Water vapour pressure = 31.5 mm Hg

Leaching acid concentration = 2 g eq dm^{-3}

Leaching pulp agitation speed = 292 rpm

Leaching temperature = boiling temperature

Pulp ratio = 0.02 kg dm^{-3} (based on ilmenite content)

Ilmenite powder to salt ratio, (w/w)	Max. wt. % metals dissolved in n^* min for							
	NaCl roast		Na_2SO_4 roast		NaNO_3 roast		Na_2CO_3 roast	
	Ti	Fe	Ti	Fe	Ti	Fe	Ti	Fe
2.50	-	-	36.2	40.8	-	-	-	-
2.00	14.2	42.6	37.3	42.6	33.7	50.4	43.6	52.6
1.70	-	-	-	-	34.6	52.2	-	-
1.50	16.9	44.5	32.7	36.4	31.8	41.5	48.9	53.5
1.00	19.6	45.8	28.3	30.6	28.5	30.4	39.4	42.9
0.67	21.8	47.3	24.8	26.5	24.0	27.3	23.7	26.8
0.50	20.7	39.7	-	-	-	-	-	-
0.40	14.2	36.6	-	-	-	-	-	-

* $n = 120, 120, 90$ and 45 for NaCl , Na_2SO_4 , NaNO_3 and Na_2CO_3 systems respectively.

Table XXX. Data for the effect of roasting time on the subsequent leaching of the salt-water vapour roasted ilmenite.

Ilmenite powder to salt ratio = 2 (1.7 for NaNO_3 , 0.67 for NaCl & 1.5 for Na_2CO_3)Roasting temperature = 800°C (885°C for Na_2SO_4 & 850°C for Na_2CO_3)Gas flow rate = $420\text{ cm}^3\text{ min}^{-1}$ ($515\text{ cm}^3\text{ min}^{-1}$ for Na_2SO_4)

Water vapour pressure = 31.5 mm Hg

Leaching acid concentration = 2 g eq dm^{-3}

Leaching pulp agitation speed = 292 rpm

Leaching temperature = boiling temperature

Pulp ratio = 0.02 kg dm^{-3} (based on ilmenite content)

Roasting time, min.	Leaching time, min.	Wt. % metals dissolved in n* min for							
		NaCl roast		Na_2SO_4 roast		NaNO_3 roast		Na_2CO_3 roast	
		Ti	Fe	Ti	Fe	Ti	Fe	Ti	Fe
40	30(15)	-	-	-	-	-	-	9.8	14.2
	60(30)	-	-	-	-	-	-	15.9	22.1
	90(45)	-	-	-	-	-	-	16.0	22.1
	120	-	-	-	-	-	-	-	-
45	30(15)	7.6	19.1	-	-	-	-	37.5	45.0
	60(30)	8.7	29.9	-	-	-	-	56.3	61.5
	90(45)	10.7	35.0	-	-	-	-	56.5	61.7
	120	10.9	35.2	-	-	-	-	-	-
50	30(15)	-	-	-	-	-	-	31.9	40.7
	60(30)	-	-	-	-	-	-	51.4	56.8
	90(45)	-	-	-	-	-	-	51.6	56.9
	120	-	-	-	-	-	-	-	-
60	30(15)	17.4	35.1	23.9	30.4	-	-	33.4	39.8
	60(30)	19.6	44.3	34.8	36.5	-	-	48.7	53.3
	90(45)	21.6	47.1	37.0	42.4	-	-	48.9	53.5
	120	21.8	47.3	37.3	42.6	-	-	-	-
70	30(15)	17.4	45.9	-	-	-	-	-	-
	60(30)	19.6	53.6	-	-	-	-	-	-
	90(45)	23.7	58.2	-	-	-	-	-	-
	120	23.9	58.2	-	-	-	-	-	-
75	30(15)	21.8	49.0	-	-	28.3	30.5	9.8	11.0
	60(30)	22.9	55.1	-	-	30.5	36.7	12.3	18.9
	90(45)	25.0	61.3	-	-	30.5	36.9	12.5	18.7
	120	25.2	61.5	-	-	-	-	-	-
90	30(15)	15.2	43.6	25.8	32.4	30.5	48.9	-	-
	60(30)	17.4	45.9	36.7	39.8	34.6	52.0	-	-
	90(45)	20.7	53.6	39.2	45.6	34.8	52.2	-	-
	120	20.9	53.8	39.4	45.8	-	-	-	-
105	30	-	-	-	-	38.3	38.2	-	-
	60	-	-	-	-	33.7	42.6	-	-
	90	-	-	-	-	33.9	42.8	-	-
	120	-	-	-	-	-	-	-	-
120	30	-	-	11.8	13.5	30.5	33.5	-	-
	60	-	-	22.9	18.7	32.7	39.5	-	-
	90	-	-	26.1	27.4	32.9	39.7	-	-
	120	-	-	26.4	27.6	-	-	-	-
150	30	-	-	8.5	9.7	-	-	-	-
	60	-	-	10.3	11.2	-	-	-	-
	90	-	-	13.1	13.7	-	-	-	-
	120	-	-	13.3	13.9	-	-	-	-

Figures in the parenthesis indicate the leaching time in minute for Na_2CO_3 system.

Table XXXI. Data for the plot of maximum weight percentages of metals dissolved in n^* min versus roasting time in min (based on Table XXX, for Fig. 31 & 32).

Ilmenite powder to salt ratio = 2 (1.7 for NaNO_3 , 0.67 for NaCl and 1.5 for Na_2CO_3)

Roasting temperature = 800°C (885°C for Na_2SO_4 & 850°C for Na_2CO_3)

Gas flow rate = $420\text{ cm}^3\text{ min}^{-1}$ ($515\text{ cm}^3\text{ min}^{-1}$ for Na_2SO_4)

Water vapor pressure = 31.5 mm Hg

Leaching acid concentration = 2 g eq dm^{-3}

Leaching pulp agitation speed = 292 rpm

Leaching temperature = boiling temperature

Pulp ratio = 0.02 kg dm^{-3} (based on ilmenite content)

Roasting time, min.	Max. wt. % metals dissolved in n^* min for							
	NaCl roast		Na_2SO_4 roast		NaNO_3 roast		Na_2CO_3 roast	
	Ti	Fe	Ti	Fe	Ti	Fe	Ti	Fe
40	-	-	-	-	-	-	16.0	22.1
45	10.9	35.2	-	-	-	-	56.5	61.7
50	-	-	-	-	-	-	51.6	56.9
60	21.8	47.3	37.3	42.6	-	-	48.9	53.5
70	23.9	58.2	-	-	-	-	-	-
75	25.2	61.5	-	-	30.5	36.9	12.5	13.7
90	20.9	53.8	39.4	45.8	34.8	52.2	-	-
105	-	-	-	-	32.9	42.8	-	-
120	-	-	26.4	27.6	32.9	39.7	-	-
150	-	-	13.3	13.9	-	-	-	-

* $n = 120, 120, 90$ and 45 for NaCl , Na_2SO_4 , NaNO_3 and Na_2CO_3 systems respectively.

Table XXXII. *Data for the effect of roasting temperature on the subsequent leaching of the salt-water vapour roasted ilmenite.*

Ilmenite powder to salt ratio = 1.7 for NaNO_3 , 2 for Na_2SO_4 ,
0.67 for NaCl and 1.5 for Na_2CO_3

Roasting time = 90 min. (45 min. for Na_2CO_3 & 75 min. for NaCl)

Gas flow rate = $420 \text{ cm}^3 \text{ min}^{-1}$ ($515 \text{ cm}^3 \text{ min}^{-1}$ for Na_2SO_4)

Water vapour pressure = 31.5 mm Hg

Leaching acid concentration = 2 g eq dm^{-3}

Leaching pulp agitation speed = 292 rpm

Leaching temperature = boiling temperature

Pulp ratio = 0.02 kg dm^{-3} (based on ilmenite content)

Roasting temperature, °C	Leaching time, min.	Wt. % metals dissolved in n* min for							
		NaCl roast		Na_2SO_4 roast		NaNO_3 roast		Na_2CO_3 roast	
		Ti	Fe	Ti	Fe	Ti	Fe	Ti	Fe
700	30	-	-	-	-	25.0	27.5	-	-
	60	-	-	-	-	30.3	33.4	-	-
	90	-	-	-	-	30.5	33.6	-	-
	120	-	-	-	-	-	-	-	-
750	30	10.9	34.5	-	-	23.9	36.7	-	-
	60	13.1	43.6	-	-	32.7	44.3	-	-
	90	15.2	50.5	-	-	32.9	44.5	-	-
	120	15.4	50.7	-	-	-	-	-	-
800	30(15)	21.8	49.0	-	-	30.5	48.9	30.2	38.3
	60(30)	22.9	55.1	-	-	34.6	52.0	47.7	52.1
	90(45)	25.0	61.3	-	-	34.8	52.2	47.9	52.3
	120	25.2	61.5	-	-	-	-	-	-
835	30	-	-	19.6	15.2	-	-	-	-
	60	-	-	27.2	24.3	-	-	-	-
	90	-	-	31.4	28.6	-	-	-	-
	120	-	-	31.6	28.9	-	-	-	-
850	30(15)	17.4	47.5	-	-	17.4	18.3	37.5	45.0
	60(30)	20.7	50.5	-	-	20.7	27.5	56.3	61.5
	90(45)	22.6	56.5	-	-	20.9	27.7	56.5	61.7
	120	22.9	56.7	-	-	-	-	-	-
885	30	-	-	25.8	32.4	-	-	-	-
	60	-	-	36.7	39.8	-	-	-	-
	90	-	-	39.2	45.6	-	-	-	-
	120	-	-	39.4	45.8	-	-	-	-
900	30(15)	-	-	-	-	-	-	15.2	18.4
	40(30)	-	-	-	-	-	-	23.6	26.0
	60(45)	-	-	-	-	-	-	23.9	26.2
	120	-	-	-	-	-	-	-	-
935	30	-	-	6.5	18.3	-	-	-	-
	60	-	-	8.7	30.4	-	-	-	-
	90	-	-	10.6	35.3	-	-	-	-
	120	-	-	10.9	35.5	-	-	-	-

Figure in the parenthesis indicate the leaching time in minute for Na_2CO_3 system.

Table XXXIII. Data for the plot of maximum weight percentage of the metals dissolved in n^* min versus roasting temperature (based on the table XXXII for Fig. 33 & 34).

Ilmenite powder to salt ratio = 1.7 for NaNO_3 , 2 for Na_2SO_4 ,
0.67 for NaCl and 1.5 for Na_2CO_3

Roasting time = 90 min. (45 min. for Na_2CO_3 & 75 min. for NaCl)

Gas flow rate = $420 \text{ cm}^3 \text{ min}^{-1}$ ($515 \text{ cm}^3 \text{ min}^{-1}$ for Na_2SO_4)

Water vapour pressure = 31.5 mm Hg

Leaching acid concentration = 2 g eq dm^{-3}

Leaching pulp agitation speed = 292 rpm

Leaching temperature = boiling temperature

Pulp ratio = 0.02 kg dm^{-3} (based on ilmenite content)

Roasting temperature, °C	Max. wt. % metals dissolved in n^* min for							
	NaCl roast		Na_2SO_4 roast		NaNO_3 roast		Na_2CO_3 roast	
	Ti	Fe	Ti	Fe	Ti	Fe	Ti	Fe
700	-	-	-	-	30.5	33.6	-	-
750	15.4	50.7	-	-	32.9	44.5	-	-
800	25.2	61.5	-	-	34.8	52.2	47.9	52.3
835	-	-	31.6	28.9	-	-	-	-
850	22.9	56.7	-	-	20.9	27.7	56.5	61.7
885	-	-	39.4	45.8	-	-	-	-
900	-	-	-	-	-	-	23.9	26.2
935	-	-	10.9	35.5	-	-	-	-

* $n = 120, 120, 90$ and 45 for NaCl , Na_2SO_4 , NaNO_3 and Na_2CO_3 systems respectively.

Table XXXIV. Data for the effect of roasting carrier gas flow rate on the subsequent leaching of the salt-water vapour roasted ilmenite.

Ilmenite powder to salt ratio = 1.7 for NaNO_3 , 2 for Na_2SO_4 , 0.67 for

NaCl & 1.5 for Na_2CO_3

Roasting time = 90 min. (45 min. for Na_2CO_3 & 75 min. NaCl)

Roasting temperature = 800°C (850°C for Na_2CO_3 & 885°C for Na_2SO_4)

Water vapour pressure = 31.5 mm Hg

Leaching acid concentration = 2 g eq dm^{-3}

Leaching pulp agitation speed = 292 rpm

Leaching temperature = boiling temperature

Pulp ratio = 0.02 kg dm^{-3} (based on ilmenite content)

Carrier gas flow rate, $\text{cm}^3 \text{min}^{-1}$	Leaching time, min.	Wt. % metals dissolved in n* min for							
		NaCl roast		Na_2SO_4 roast		NaNO_3 roast		Na_2CO_3 roast	
		Ti	Fe	Ti	Fe	Ti	Fe	Ti	Fe
350	30(15)	15.2	39.8	24.2	32.4	10.9	15.3	13.1	23.0
	60(30)	17.4	45.9	33.5	38.5	15.2	18.3	18.5	32.2
	90(45)	19.4	55.1	37.0	44.6	15.5	18.5	18.8	32.5
	120	19.6	55.3	37.3	44.9	-	-	-	-
390	30(15)	17.2	41.2	25.5	37.2	23.9	31.5	29.1	37.8
	60(30)	19.6	46.8	36.2	42.5	28.2	35.4	46.2	50.5
	90(45)	22.6	58.6	40.5	48.6	28.5	35.7	46.4	50.8
	120	22.9	58.8	40.8	48.8	-	-	-	-
420	30(15)	21.8	49.0	26.1	33.6	30.5	48.9	37.5	45.0
	60(30)	22.9	55.1	38.1	43.2	34.6	52.0	56.3	61.5
	90(45)	25.0	61.3	43.3	53.2	34.8	52.2	56.5	61.7
	120	25.2	61.5	43.5	53.5	-	-	-	-
470	30(15)	9.8	32.3	25.5	31.5	20.3	29.8	34.3	41.2
	60(30)	14.5	48.9	36.2	40.8	24.5	33.1	52.4	57.6
	90(45)	19.2	54.5	41.5	49.4	24.8	33.4	52.6	57.9
	120	19.4	54.7	41.7	49.6	-	-	-	-
515	30(15)	4.4	21.4	25.8	32.4	6.5	6.1	30.8	37.9
	60(30)	8.7	39.8	36.7	39.8	13.5	12.2	46.5	55.1
	90(45)	13.1	49.0	39.2	45.6	13.5	12.5	46.8	55.1
	120	13.1	49.3	39.4	45.8	-	-	-	-

Figure in the parenthesis indicate the leaching time in minute for Na_2CO_3 system.

Table XXXV. Data for the plot of maximum weight percentages of the metals dissolved in n^* min versus roasting carrier gas flow rate (based on Table XXXIV for Fig. 35 & 36).

Ilmenite powder to salt ratio = 1.7 for NaNO_3 , 2 for Na_2SO_4 , 0.67 for NaCl & 1.5 for Na_2CO_3

Roasting time = 90 min. (45 min. for Na_2CO_3 & 75 min. NaCl)

Roasting temperature = 800°C (850°C for Na_2CO_3 & 885°C for Na_2SO_4)

Water vapour pressure = 31.5 mm Hg

Leaching acid concentration = 2 g eq dm^{-3}

Leaching pulp agitation speed = 292 rpm

Leaching temperature = boiling temperature

Pulp ratio = 0.02 kg dm^{-3} (based on ilmenite content)

Carrier gas flow rate, $\text{cm}^3 \text{ min}^{-1}$	Max. wt. % metals dissolved in n^* min for							
	NaCl roast		Na_2SO_4 roast		NaNO_3 roast		Na_2CO_3 roast	
	Ti	Fe	Ti	Fe	Ti	Fe	Ti	Fe
350	19.6	55.3	37.3	44.9	15.5	18.5	18.8	32.5
390	22.9	58.8	40.8	48.8	28.5	35.7	46.4	50.8
420	25.2	61.5	43.5	53.5	34.8	52.2	56.5	61.7
470	19.4	54.7	41.7	49.6	24.8	33.4	52.6	57.9
515	13.1	49.3	39.4	45.8	13.5	12.5	46.8	55.1

* $n = 120, 120, 90$ and 45 for NaCl , Na_2SO_4 , NaNO_3 and Na_2CO_3 systems respectively.

Table XXXVI. *Data for the effect of roasting water vapour pressure on the subsequent leaching of the salt-water vapour roasted ilmenite.*

Ilmenite powder to salt ratio = 1.7 for NaNO_3 , 2 for Na_2SO_4 , 0.67 for NaCl & 1.5 for Na_2CO_3

Roasting temperature = 800°C (885° for Na_2SO_4 & 850°C Na_2CO_3)

Roasting time = 90 min. (45 min. for Na_2CO_3 & 75 min. for NaCl)

Carrier gas flow rate = $420\text{ cm}^3\text{ min}^{-1}$

Acid concentration = 2 g eq dm^{-3}

Leaching temperature = boiling temperature

Leaching pulp agitation speed = 292 rpm

Pulp ratio = 3.02 kg dm^{-3} (based on ilmenite content)

Water vapour pressure, mm Hg	Leaching time, min.	Wt. % metals dissolved in n* min for							
		NaCl roast		Na_2SO_4 roast		NaNO_3 roast		Na_2CO_3 roast	
		Ti	Fe	Ti	Fe	Ti	Fe	Ti	Fe
23.5	30(15)	17.4	42.9	25.4	27.8	24.7	35.1	35.6	41.2
	60(30)	19.2	50.5	33.2	36.5	28.6	48.2	53.8	54.5
	90(45)	21.6	57.7	38.2	43.3	28.8	48.5	53.8	54.7
	120	21.8	57.9	38.5	43.5				
31.5	30(15)	21.8	49.0	26.1	33.6	30.5	48.9	37.5	45.0
	60(30)	22.9	55.1	38.1	43.2	34.6	52.0	56.3	61.5
	90(45)	25.0	61.3	43.3	53.2	34.8	52.2	56.5	61.7
	120	25.2	61.5	43.5	53.5	-	-	-	-
42.5	30(15)	13.1	36.8	23.9	21.3	18.9	21.4	26.9	26.8
	60(30)	15.2	45.9	28.3	30.4	25.2	39.7	36.7	42.6
	90(45)	18.3	55.1	32.7	33.4	25.4	39.7	36.9	42.8
	120	18.5	55.3	32.9	33.6	-	-	-	-
55.5	30(15)	4.4	21.4	8.7	9.1	8.7	21.4	14.6	17.4
	60(30)	8.7	39.8	10.9	12.2	12.6	33.4	20.0	23.7
	90(45)	13.1	49.0	13.1	15.2	12.8	33.6	20.2	23.9
	120	13.3	49.2	13.3	15.4	-	-	-	-

Figures in the parenthesis indicate the leaching time in minute for Na_2CO_3 .

Table XXXVII. Data for the plot of maximum weight percentages of the metals dissolved in n^* min versus roasting water vapour pressure (based on Table XXXVI for Fig. 37 & 38).

Ilmenite powder to salt ratio = 1.7 for NaNO_3 , 2 for Na_2SO_4 , 0.67 for NaCl & 1.5 for Na_2CO_3

Roasting temperature = 800°C (885° for Na_2SO_4 & 850°C Na_2CO_3)

Roasting time = 90 min. (45 min. for Na_2CO_3 & 75 min. for NaCl)

Carrier gas flow rate = $420\text{ cm}^3\text{ min}^{-1}$

Acid concentration = 2 g eq dm^{-3}

Leaching temperature = boiling temperature

Leaching pulp agitation speed = 292 rpm

Pulp ratio = 3.02 kg dm^{-3} (based on ilmenite content)

Water vapour pressure, mm Hg	Max. wt. % metals dissolved in n^* min for							
	NaCl roast		Na_2SO_4 roast		NaNO_3 roast		Na_2CO_3 roast	
	Ti	Fe	Ti	Fe	Ti	Fe	Ti	Fe
23.5	21.8	57.9	38.5	43.5	28.8	48.5	53.8	54.7
31.5	25.2	61.5	43.5	53.5	34.8	52.2	56.5	61.7
42.5	18.5	55.3	32.9	33.6	25.4	39.7	36.9	42.8
55.5	13.3	49.2	13.3	15.4	12.8	33.6	20.2	23.9

* $n = 120, 120, 90$ and 45 for NaCl , Na_2SO_4 , NaNO_3 and Na_2CO_3 systems respectively.

Table XXXVIII. Data for the effect of acid concentration on the leaching of the salt-water vapour roasted ilmenite.

Ilmenite powder to salt ratio = 1.7 for NaNO_3 , 2 for Na_2SO_4 , 0.67 for

NaCl & 1.5 for Na_2CO_3

Roasting temperature = 800°C (885°C for Na_2SO_4 & 850°C for Na_2CO_3)

Roasting time = 90 min. (45 min. for Na_2CO_3 & 75 min. for NaCl)

Carrier gas flow rate = $420\text{ cm}^3\text{ min}^{-1}$

Water vapour pressure = 31.5 mm Hg

Leaching temperature = boiling temperature

Leaching pulp agitation speed = 292 rpm

Pulp ratio = 0.02 kg dm^{-3} (based on ilmenite content)

Acid concentration, g eq dm^{-3}	Leaching time, min.	Wt. % metals dissolved in HCl for							
		NaCl roast		Na_2SO_4 roast		NaNO_3 roast		Na_2CO_3 roast	
		Ti	Fe	Ti	Fe	Ti	Fe	Ti	Fe
1	30	-	-	4.4	12.2	-	-	-	-
	60	-	-	8.7	18.2	-	-	-	-
	90	-	-	10.7	28.6	-	-	-	-
	120	-	-	10.9	28.9	-	-	-	-
2	30(15)	21.8	49.0	26.1	33.6	30.5	48.9	37.5	45.0
	60(30)	22.9	55.1	38.1	43.2	34.6	52.0	56.3	61.5
	90(45)	25.0	61.3	43.3	53.2	34.8	52.2	56.5	61.7
	120	25.2	61.5	43.5	53.5	-	-	-	-
3	30	-	-	30.5	36.5	-	-	-	-
	60	-	-	37.0	45.6	-	-	-	-
	90	-	-	39.2	48.7	-	-	-	-
	120	-	-	39.4	48.9	-	-	-	-
4	30(15)	34.8	45.9	18.4	30.4	43.4	51.9	72.4	53.1
	60(30)	41.4	61.3	26.9	36.8	59.6	61.1	84.4	67.4
	90(45)	47.6	76.5	30.5	42.6	59.8	61.5	84.9	67.6
	120	47.9	76.8	30.8	42.6	-	-	-	-
6	30(15)	47.9	67.4	21.8	21.3	67.5	58.0	87.1	61.3
	60(30)	58.8	82.7	25.0	27.4	84.7	70.2	95.8	73.5
	90(45)	71.6	94.5	28.3	35.5	84.9	70.2	95.8	73.7
	120	71.8	94.9	28.5	37.8	-	-	-	-

Figures in the parenthesis indicate the leaching time in minute for Na_2CO_3 system.

Table XXXIX. Data for the plot of maximum weight percentages of the metals dissolved in n^* min versus acid concentration on the leaching of the salt-water vapour roasted ilmenite (based on Table XXXVIII for Fig. 39 & 40).

Ilmenite powder to salt ratio = 1.7 for NaNO_3 , 2 for Na_2SO_4 , 0.67 for NaCl & 1.5 for Na_2CO_3

Roasting temperature = 800°C (885°C for Na_2SO_4 & 850°C for Na_2CO_3)

Roasting time = 90 min. (45 min. for Na_2CO_3 & 75 min. for NaCl)

Carrier gas flow rate = $420\text{ cm}^3\text{ min}^{-1}$

Water vapour pressure = 31.5 mm Hg

Leaching temperature = boiling temperature

Leaching pulp agitation speed = 292 rpm

Pulp ratio = 0.02 kg dm^{-3} (based on ilmenite content)

Acid concentration g eq dm^{-3}	Max. wt. % metals dissolved in n^* min for							
	NaCl roast		Na_2SO_4 roast		NaNO_3 roast		Na_2CO_3 roast	
	Ti	Fe	Ti	Fe	Ti	Fe	Ti	Fe
1	-	-	10.9	28.9	-	-	-	-
2	25.2	61.5	43.5	53.5	34.8	52.2	56.5	61.7
3	-	-	39.4	48.9	-	-	-	-
4	47.9	76.8	30.8	42.6	59.8	61.5	84.9	67.6
6	71.8	94.9	28.5	37.8	84.9	70.2	95.8	73.7

* $n = 120, 120, 90$ and 45 for NaCl , Na_2SO_4 , NaNO_3 and Na_2CO_3 systems respectively.

Table XI. Data for the effect of temperature on the leaching of the salt-water vapour roasted ilmenite.

Ilmenite powder to salt ratio = 1.7 for NaNO_3 , 2 for Na_2SO_4 , 0.67 for NaCl & 1.5 for Na_2CO_3

Roasting temperature = 800°C (885°C for Na_2SO_4 & 850°C for Na_2CO_3)

Roasting time = 90 min. (45 min. for Na_2CO_3 & 75 min. for NaCl)

Carrier gas flow rate = $420\text{ cm}^3\text{ min}^{-1}$

Water vapour pressure = 31.5 mm Hg

Leaching acid concentration = 6 g eq dm^{-3} (2 g eq dm^{-3} for Na_2SO_4)

Leaching pulp agitation speed = 292 rpm

Pulp ratio = 0.02 kg dm^{-3} (based on ilmenite content)

Leaching temperature, $^\circ\text{C}$	Leaching time, min.	Wt. % metals dissolved in HCl for							
		NaCl roast		Na_2SO_4 roast		NaNO_3 roast		Na_2CO_3 roast	
		Ti	Fe	Ti	Fe	Ti	Fe	Ti	Fe
50	30(15)	24.7	34.7	2.2	3.0	34.8	45.8	46.1	31.5
	60(30)	30.9	42.6	4.4	6.1	44.6	51.7	50.0	38.7
	90(45)	37.5	48.9	6.4	12.2	44.8	51.9	50.3	38.9
	120	37.8	48.9	6.6	12.5	-	-	-	-
80	30(15)	40.5	57.6	6.5	6.1	58.8	55.0	60.1	47.9
	60(30)	50.3	64.3	12.0	15.2	67.5	61.0	76.1	54.1
	90(45)	55.3	73.5	21.3	21.3	67.7	61.2	76.3	54.5
	120	55.5	73.5	15.5	21.5	-	-	-	-
110	30(15)	47.9	69.4	26.1	33.6	67.5	58.0	87.1	61.3
	60(30)	58.8	82.7	38.1	43.2	84.7	70.2	95.8	73.5
	90(45)	71.6	94.5	43.3	53.2	84.9	70.2	95.8	73.7
	120	71.8	94.9	43.5	53.5	-	-	-	-

Figures in the parenthesis indicate the leaching time in minute for Na_2CO_3 system.

Table XLI. Data for the plot of maximum weight percentages of the metals dissolved in n^* min versus temperature on leaching of the salt water vapour roasted ilmenite (based on Table XL for Figure 41 & 42).

Ilmenite powder to salt ratio = 1.7 for NaNO_3 , 2 for Na_2SO_4 , 0.67 for NaCl & 1.5 for Na_2CO_3

Roasting temperature = 800°C (885°C for Na_2SO_4 & 850°C for Na_2CO_3)

Roasting time = 90 min. (45 min. for Na_2CO_3 & 75 min. for NaCl)

Carrier gas flow rate = $420\text{ cm}^3\text{ min}^{-1}$

Water vapour pressure = 31.5 mm Hg

Leaching acid concentration = 6 g eq dm^{-3} (2 g eq dm^{-3} for Na_2SO_4)

Leaching pulp agitation speed = 292 rpm

Pulp ratio = 0.02 kg dm^{-3} (based on ilmenite content)

Leaching temperature, $^\circ\text{C}$	Max. wt. % metals dissolved in n^* min for							
	NaCl roast		Na_2SO_4 roast		NaNO_3 roast		Na_2CO_3 roast	
	Ti	Fe	Ti	Fe	Ti	Fe	Ti	Fe
50	37.8	48.9	6.6	12.5	44.8	51.9	50.3	38.9
80	55.5	73.5	15.5	21.5	67.7	61.2	76.3	54.5
110	71.8	94.9	43.5	53.5	84.9	70.2	95.8	73.7

* n = 120, 120, 90 and 45 for NaCl , Na_2SO_4 , NaNO_3 and Na_2CO_3 systems respectively.

Table XLII. Data for the plot of maximum weight percentages of titanium and iron dissolved from sodium carbonate-water vapour roasted product in 45 min. versus solid to liquid phase ratio (S/L). (Fig. 43a and 43b).

Roasting temperature = 850°C

Roasting time = 45 min.

Ilmenite to salt ratio = 1.5

Carrier gas flow rate = 420 cm³ min⁻¹

Water vapour pressure = 31.5 mm Hg

Leaching acid concentration = 4 g eq dm⁻³

Leaching temperature = boiling temperature

Leaching pulp agitation speed = 292 rpm

S/L ratio, kg dm ⁻³	% dissolution in 45 min of		Conc. (g dm ⁻³) in leached solution of	
	Ti	Fe	Ti	Fe
0.02	85.0	67.4	4.75	4.37
0.04	35.0	62.0	3.90	8.05
0.06	19.5	57.0	3.25	11.12
0.08	11.3	53.3	2.51	13.82
0.10	6.5	51.4	1.81	16.65

Table XLIII. *Data for stage-wise leaching of the sodium carbonate-water vapour roasted product of ilmenite (Fig. 44).*

Roasting temperature = 850°C

Roasting time = 45 min.

Ilmenite to salt ratio = 1.5

Carrier gas flow rate = 420 cm³ min⁻¹

Water vapour pressure = 31.5 mm Hg

Leaching temperature = boiling temperature

Leaching pulp agitation speed = 292 rpm

Leaching acid concentration = 4 g eq dm⁻³

S/L ratio = 0.10 kg dm⁻³

L = 10 cm³

Stage number	% dissolution in 45 min of		Dissolved cumulative % of	
	Ti	Fe	Ti	Fe
1	6.5	51.4	6.5	51.4
2	2.4	4.6	8.9	56.0
3	2.2	3.6	11.1	59.6
4	2.0	3.0	13.1	62.6

Table XLIV. *Effect of concentration of hydrochloric acid concentration on the rate of dissolution of $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ vapour roasted ilmenite product : Data for the plots of $1-(1-R)^{1/3}$ versus time (min) for titanium and iron (for Figs. 45 and 46).*

S/L = 0.02 kg dm⁻³
Temp. = 110°C

Stirring speed = 200 rpm
Vol. of liquid = 50 cm³

Concentration of HCl, g eq dm ⁻³	Time, min.	% metal dissolved		$[1-(1-R)^{1/3}]_{\text{Ti}}$	$[1-(1-R)^{1/3}]_{\text{Fe}}$
		Titanium	Iron		
1.0	3	1.55	3.88	0.0051	0.0131
	6	2.32	7.88	0.0071	0.0270
	9	3.87	11.64	0.0130	0.0404
	12	5.42	14.23	0.0184	0.0498
	15	6.20	16.82	0.0211	0.0595
	18	8.02	17.25	0.0275	0.0612
1.5	3	4.43	6.97	0.0150	0.0238
	6	9.32	13.66	0.0321	0.0478
	9	13.50	19.87	0.0472	0.0712
	12	16.44	24.71	0.0581	0.0903
	15	20.80	27.58	0.0748	0.1020
	18	24.14	30.21	0.0880	0.1130
2.0	3	7.79	11.64	0.0267	0.0404
	6	15.58	19.28	0.0549	0.0685
	9	24.16	28.28	0.0881	0.1045
	12	31.17	39.85	0.1171	0.1556
	15	37.41	44.99	0.1446	0.1801
	18	43.64	48.85	0.1740	0.2000
3.0	3	10.91	14.15	0.0377	0.0445
	6	23.38	26.03	0.0849	0.0956
	9	31.17	36.00	0.1170	0.1382
	12	42.08	43.72	0.1664	0.1743
	15	49.88	48.20	0.2056	0.1967
	18	57.67	52.72	0.2491	0.2209
4.0	3	21.82	16.71	0.0787	0.0591
	6	32.73	29.55	0.1237	0.1102
	9	48.32	42.88	0.1975	0.1703
	12	63.90	48.86	0.2879	0.2003
	15	71.70	52.72	0.3434	0.2209
	18	74.82	56.58	0.3685	0.2427
6.0	3	28.35	20.08	0.1052	0.0720
	6	49.18	33.69	0.2020	0.1280
	9	64.66	46.26	0.2930	0.1870
	12	76.73	53.09	0.3850	0.2230
	15	85.93	58.48	0.4530	0.2540
	18	92.32	62.83	0.5750	0.2810

Table XLV. Data for the plot of $\log q_{\text{HCl}}$ versus $\log[\text{HCl}]$ for titanium and iron dissolution from the $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ vapour roasted ilmenite product (based on Table XLIV and Figs. 45 and 46, for Fig. 47).

$\frac{[\text{HCl}]}{\text{g eq dm}^{-3}}$	$\log[\text{HCl}]$	Slopes of $1-(1-R)^{1/3}$ vs time plots			Log $q_{\text{HCl}}(\text{Ti})$	Log $q_{\text{HCl}}(\text{Fe})_{\text{ini}}$	Log $q_{\text{HCl}}(\text{Fe})_{>12}$
		For Ti $q_{\text{HCl}}(\text{Ti})$	For Fe				
			$q_{\text{HCl}}(\text{Fe})_{\text{ini}}$	$q_{\text{HCl}}(\text{Fe})_{>12}$			
1.0	0	0.00153	0.0043	0.0020	-2.815	-2.367	-2.698
1.5	0.176	0.0050	0.00758	0.0039	-2.301	-2.120	-2.400
2.0	0.301	0.0095	0.0125	0.0071	-2.020	-1.903	-2.146
3.0	0.477	0.0140	0.0149	0.0075	-1.853	-1.825	-2.124
4.0	0.602	0.0223	0.0199	0.00812	-1.650	-1.700	-2.090
6.0	0.778	0.033	0.0208	0.0107	-1.481	-1.680	-1.980

Table XLVI. *Effect of temperature on the rate of dissolution of $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ vapour roasted ilmenite product : Data for the plots of $1-(1-R)^{1/3}$ versus time (min) for titanium and iron (for Figs. 48 and 49).*

S/L = 0.02 kg dm⁻³

Stirring speed = 200 rpm

Acid concentration = 4 g eq dm⁻³

Vol. of liquid = 50 cm³

Temperature, °K	Time, min.	% metal dissolved		$[1-(1-R)^{1/3}]_{\text{Ti}}$	$[1-(1-R)^{1/3}]_{\text{Fe}}$
		Titanium	Iron		
313	3	8.73	10.58	0.0300	0.0365
	6	17.60	17.19	0.0625	0.0609
	9	26.48	23.80	0.0974	0.0866
	12	31.16	26.45	0.1170	0.0973
	15	39.08	30.41	0.1523	0.1138
	18	44.56	33.06	0.1785	0.1252
333	3	10.47	11.08	0.0362	0.0384
	6	19.51	18.05	0.0698	0.0642
	9	28.38	26.68	0.1053	0.0983
	12	36.32	30.80	0.1397	0.1155
	15	44.01	33.35	0.1758	0.1274
	18	50.60	37.10	0.2095	0.1432
353	3	14.01	14.15	0.0491	0.0495
	6	21.80	24.43	0.0787	0.0891
	9	32.70	30.86	0.1237	0.1157
	12	40.50	34.72	0.1589	0.1325
	15	45.16	38.08	0.1815	0.1476
	18	56.08	40.83	0.2399	0.1606
373	3	18.67	14.12	0.0666	0.0495
	6	28.04	23.79	0.1039	0.0866
	9	37.38	38.56	0.1445	0.1499
	12	48.20	45.01	0.1973	0.1807
	15	56.08	48.86	0.2399	0.2003
	18	62.34	50.08	0.2779	0.2109
383	3	21.82	16.71	0.0787	0.0591
	6	32.73	29.55	0.1237	0.1102
	9	48.32	42.88	0.1975	0.1703
	12	63.90	48.86	0.2879	0.2003
	15	71.70	52.72	0.3434	0.2209
	18	74.82	56.58	0.3685	0.2427

Table XLVIII. *Effect of temperature on the rate of dissolution of $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ vapour roasted ilmenite product : Data for the plots of $1-(1-R)^{1/3}$ versus time (min.) for titanium and iron (for Fig. 51).*

S/L = 0.02 kg dm⁻³

Stirring speed = 200 rpm

[HCl] = 1 g eq dm⁻³ (HCl)

Vol. of liquid = 50 cm³

Temperature, °K	Time, min.	% metal dissolved		$[1-(1-R)^{1/3}]_{\text{Ti}}$	$[1-(1-R)^{1/3}]_{\text{Fe}}$
		Titanium	Iron		
323	3	0.85	3.07	0.00287	0.01037
	6	2.04	6.02	0.00687	0.02050
	9	2.85	8.73	0.00960	0.03000
	12	3.75	10.83	0.01266	0.03750
	15	4.79	12.21	0.01625	0.04250
	18	5.88	13.72	0.02000	0.04800
353	3	1.12	3.70	0.00375	0.01250
	6	2.34	6.79	0.00787	0.02320
	9	3.39	9.71	0.01144	0.03350
	12	4.48	12.21	0.01517	0.04250
	15	5.48	13.91	0.01863	0.04870
	18	6.95	15.60	0.02375	0.05500
383	3	1.55	3.88	0.00510	0.01310
	6	2.32	7.88	0.00710	0.02700
	9	3.87	11.64	0.01300	0.04040
	12	5.42	14.23	0.01840	0.04980
	15	6.20	16.82	0.02110	0.05950
	18	8.02	17.25	0.02750	0.06120

Table XLIX. Data for the plot of $\log q_t$ versus $(1/TK) \times 10^3$ for titanium and iron dissolution from the $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ vapour roasted ilmenite product (based on Table XLVIII and Fig. 51 for Fig. 52).

Temperature, K	(1/TK) × 10 ³	Slop of 1-(1-R) ^{1/3} vs time plot			log q _{Ti}	log q _{[Fe]ini}	log q _{[Fe]12}
		For Ti q _{Ti}	For Fe				
			q _{[Fe]ini}	q _{[Fe]12}			
323	3.095	0.00105	0.00334	0.001503	-2.978	-2.477	-2.823
353	2.832	0.001264	0.00388	0.00188	-2.898	-2.450	-2.725
383	2.611	0.00153	0.0043	0.00200	-2.815	-2.367	-2.698

Table L. *Effect of agitation speed on the rate of dissolution of $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ vapour roasted ilmenite product : Data for the plots of $1-(1-R)^{1/3}$ versus time (min.) for titanium and iron.*

S/L = 0.02 kg dm^{-3}

Temperature = 110°C

Acid concentration = 4 g eq dm^{-3}

Vol. of liquid = 50 cm^3

Agitation speed, rpm	Time, min.	% metal dissolved		$[1-(1-R)^{1/3}]_{\text{Ti}}$	$[1-(1-R)^{1/3}]_{\text{Fe}}$
		Titanium	Iron		
100	3	21.62	12.84	0.078	0.0448
	6	38.15	27.14	0.1480	0.1002
	9	51.25	40.32	0.2130	0.1581
	12	64.43	46.28	0.2915	0.1871
	15	73.10	50.86	0.3545	0.2109
	18	77.86	55.17	0.3951	0.2347
150	3	20.02	16.09	0.0725	0.0568
	6	37.49	29.38	0.1450	0.1095
	9	51.10	41.38	0.2120	0.1631
	12	64.17	47.81	0.2898	0.1949
	15	72.72	52.05	0.3515	0.2173
	18	78.34	56.53	0.3995	0.2425
200	3	21.82	16.71	0.0787	0.0591
	6	32.73	29.55	0.1237	0.1102
	9	48.32	42.88	0.1975	0.1703
	12	63.90	48.86	0.2879	0.2003
	15	71.70	52.72	0.3434	0.2209
	18	74.82	56.58	0.3685	0.2427
300	3	22.38	16.91	0.0810	0.0599
	6	38.37	30.02	0.1490	0.1122
	9	51.62	44.58	0.2150	0.1786
	12	64.81	49.92	0.2940	0.2059
	15	73.22	54.64	0.3555	0.2517
	18	78.01	59.23	0.3965	0.2585
400	3	25.80	18.07	0.0947	0.0643
	6	38.47	31.82	0.1495	0.1199
	9	52.27	46.26	0.2185	0.1870
	12	65.47	51.99	0.2985	0.2170
	15	73.90	57.99	0.3610	0.2411
	18	78.99	59.62	0.4056	0.2609

Table LI. Data for the plot of $\log q_{(rpm)}$ versus $\log (rpm)$ for titanium and iron dissolution from $Na_2CO_3-H_2O$ vapour roasted ilmenite product (based on Table L for Fig. 53).

Agitation speed, rpm	log[rpm]	Slopes of $1-(1-R)^{1/3}$ VS time plot			Log $q_{rpm}(Ti)$	Log $q_{rpm}(Fe)_{int}$	Log $q_{rpm}(Fe)_{>12}$
		For Ti $q_{rpm}(Ti)$	For Fe				
			$q_{rpm}(Fe)_{int}$	$q_{rpm}(Fe)_{>12}$			
100	2.000	0.0245	0.01778	0.00778	-1.610	-1.750	-2.109
150	2.176	0.0237	0.01905	0.00751	-1.625	-1.720	-2.124
200	2.301	0.0223	0.01995	0.00812	-1.650	-1.700	-2.090
300	2.477	0.0239	0.02018	0.00883	-1.620	-1.695	-2.054
400	2.602	0.0242	0.01949	0.00794	-1.615	-1.710	-2.100

Table LII. Effect of agitation speed on the rate of dissolution of $Na_2CO_3-H_2O$ vapour roasted ilmenite product : Data for the plots of $1-(1-R)^{1/3}$ versus time (min.) for titanium and iron (for Fig. 54).

S/L = 0.02 kg dm⁻³
[HCl] = 1 g eq dm⁻³

Temperature = 110°C
Vol. of liquid = 50 cm³

Agitation speed, rpm	Time, min.	% metal dissolved		$[1-(1-R)^{1/3}]_{Ti}$	$[1-(1-R)^{1/3}]_{Fe}$
		Titanium	Iron		
100	3	1.12	2.97	0.00375	0.01000
	6	2.08	5.73	0.00700	0.01950
	9	3.11	8.45	0.01050	0.02900
	12	4.14	11.30	0.01400	0.03920
	15	5.01	12.65	0.01700	0.04410
	18	6.31	13.78	0.02150	0.04825
200	3	1.55	3.88	0.00510	0.01310
	6	2.32	7.88	0.00710	0.02700
	9	3.87	11.64	0.01300	0.04040
	12	5.42	14.23	0.01840	0.04980
	15	6.20	16.82	0.02110	0.05950
	18	8.02	17.25	0.02750	0.06120
400	3	1.67	4.43	0.00560	0.01500
	6	3.49	8.45	0.01180	0.02900
	9	4.94	12.21	0.01675	0.04250
	12	6.59	15.60	0.02250	0.05500
	15	8.37	17.60	0.02875	0.06250
	18	9.99	19.56	0.03450	0.07000

Table LIII. Data for the plot of $\log q_{[\text{rpm}]}$ versus $\log (\text{rpm})$ for titanium and iron dissolution from $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ vapour roasted ilmenite product (based on Table LII and Fig. 54 for Fig. 55).

Agitation speed, rpm	log[rpm]	Slope of $1-(1-R)^{1/3}$ VS time plot			Log $q_{rpm}(Ti)$	Log $q_{rpm}(Fe)_{inl}$	Log $q_{rpm}(Fe)_{>12}$
		For Ti $q_{rpm}Ti$	For Fe				
			$q_{rpm}(Fe)_{inl}$	$q_{rpm}(Fe)_{>12}$			
100	2.000	0.00117	0.00316	0.00147	-2.929	-2.500	-2.847
200	2.301	0.00153	0.00430	0.00206	-2.815	-2.367	-2.698
400	2.602	0.00188	0.00476	0.00250	-2.725	-2.325	-2.602

Table LIV. Data for the plot of concentration of iron in aqueous phase $C_{\text{Fe(III)}}^A$ VS time to determine the time required to reach the equilibria in the case of extraction with MIBK (Fig. 56).

$C_{\text{Fe(III)}}^A$ initial = 5 g dm⁻³

Acidity = 6 g eq dm⁻³

Extractant concentration = 8 mol dm⁻³ MIBK

Phase ratio = A : O = 1 : 1

Temperature = (30±1)°C

Metal ion	Initial metal ion conc., g dm ⁻³	Contact time in seconds	$C_{\text{Fe(III)}}^A$ g dm ⁻³	$C_{\text{Fe(III)}}^O$ g dm ⁻³	$E_{\text{Fe(III)}}^O = \frac{C_{\text{Fe(III)}}^O}{C_{\text{Fe(III)}}^A}$
Fe(III)	5.00	5	0.01400	4.98500	332
		10	0.00720	4.99280	693
		15	0.00478	4.99520	1045
	5.00	20	0.00385	4.99615	1298
		30	0.00345	4.99655	1448
		40	0.00345	4.99655	1448
	5.00	50	0.00345	4.99655	1448
		60	0.00345	4.99655	1448
	5.00				

Table LV. Data for the dependence of Extraction ratio on the concentration of iron (III) in the case of extraction with MIBK (Fig. 57).

Extraction concentration = 8 mol dm⁻³ MIBK

Acidity = 5 g eq dm⁻³

Phase ratio = A : O = 1 : 1

Contact time = 2 min.

Temperature = (30±1)°C

Metal ion	Initial metal ion conc., g dm ⁻³	C _{Fe(III)} ^A g dm ⁻³	C _{Fe(III)} ^O g dm ⁻³	$E_{Fe(III)}^0 = \frac{C_{Fe(III)}^O}{C_{Fe(III)}^A}$
Fe(III)	1.00	0.0027	0.9973	369
	1.50	0.0048	1.4952	311
	2.00	0.0070	1.9930	285
	3.00	0.0115	2.9885	260
	3.50	0.0138	3.4862	253
	4.25	0.0170	4.2330	249
	7.00	0.0290	6.9710	240
	10.00	0.0432	9.9567	230
	15.00	0.0670	14.9330	223

Table LVI. Data for the dependence of extraction ratio of iron (III) on aqueous acidity in the case of extraction with MIBK (Fig. 58).

C_{Fe(III)}^A initial = 5.00 g dm⁻³

Extractant concentration = 8 mol dm⁻³ MIBK

Phase ratio = A : O = 1 : 1

Contact time = 2 minute

Temperature = (30±1)°C

Aqueous Fe(III) conc. g dm ⁻³	Initial aqueous acidity, g eq dm ⁻³	log[HCl]	C _{Fe(III)} ^A g dm ⁻³	C _{Fe(III)} ^O g dm ⁻³	E _{Fe(III)} ^O	log E _{Fe(III)} ^O
					0.46	-0.33
5.00	2	0.301	3.413000	1.58700	4.01	0.60
5.00	3	0.477	0.998500	4.00150	49.51	1.69
5.00	4	0.602	0.099000	4.90100	249.25	2.40
5.00	5	0.699	0.019980	4.98002	1400.34	3.15
5.00	6	0.778	0.003568	4.99643	22221.22	4.35
5.00	7	0.845	0.000225	4.99977		

Table LVII. Data for the dependence of extraction ratio of iron (III) on extractant concentration in the case of extraction with MIBK. (Fig. 59).

$C_{\text{Fe(III)}}^{\text{A}}$ initial = 5 g dm⁻³

Acidity = 6 g eq dm⁻³

Extractant = MIBK

Phase ratio = A : O = 1 : 1

Contact time = 2 minutes

Temperature = (30±1)°C

Initial acidity, g eq dm ⁻³	MIBK, mol dm ⁻³	log[MIBK]	Aqueous Fe(III) conc. before shaking, g dm ⁻³	$C_{\text{Fe(III)}}^{\text{A}}$ g dm ⁻³	$C_{\text{Fe(III)}}^{\text{O}}$ g dm ⁻³	$E_{\text{Fe(III)}}^{\text{O}}$	log $E_{\text{Fe(III)}}^{\text{O}}$
6	1	0.000	5.00	3.38930	1.61070	0.4752	-0.32
6	3	0.477	5.00	1.36290	3.63710	2.6686	0.43
6	4	0.600	5.00	0.36705	4.63295	12.6220	1.10
6	5	0.699	5.00	0.11853	4.88147	41.1837	1.61
6	6	0.778	5.00	0.03376	4.96624	147.1042	2.17
6	8	0.903	5.00	0.00397	4.99603	1258.2872	3.10

Table LVIII. Data for the dependence of extraction ratio of iron (III) on temperature in the case of extraction with MIBK. (Fig. 60).

$C_{\text{Fe(III)}}^{\text{A}}$ (initial) = 5.00 g dm⁻³

Acidity = 6 g eq dm⁻³

Extractant concentration = 8 mol dm⁻³ MIBK

Phase ratio = A : O = 1 : 1

Contact time = 2 minutes

Initial acidity, g eq dm ⁻³	Temp. in °C	$\frac{1}{T_A} \times 10^3$	Aqueous Fe(III) conc. before shaking, g dm ⁻³	$C_{\text{Fe(III)}}^{\text{A}}$ g dm ⁻³	$C_{\text{Fe(III)}}^{\text{O}}$ g dm ⁻³	$E_{\text{Fe(III)}}^{\text{O}}$	log $E_{\text{Fe(III)}}^{\text{O}}$
6	31	3.29	5.00	0.033190	4.966810	149.6400	2.17
6	35	3.25	5.00	0.034764	4.965236	142.8200	2.15
6	40	3.19	5.00	0.038194	4.961806	129.9160	2.11
6	45	3.14	5.00	0.042910	4.957090	115.5229	2.06
6	50	3.09	5.00	0.044950	4.955050	110.2347	2.04
6	55	3.04	5.00	0.048923	4.951077	101.2010	2.01

Table LVIX. Data for the loading effect of organic phase in the extraction of iron (III) with MIBK (Fig. 61).

$C_{\text{Fe(III)}}^{\text{A}}$ initial = 5 g dm⁻³

Acidity = 6 g eq dm⁻³

Extractant concentration = 8 mol dm⁻³ MIBK

Phase ratio = A : O = 1 : 1

Contact time = 2 minutes (in each stage)

Temperature = (30±1)°C

MIBK mol dm ⁻³	Contact number	Acidity of aqueous phase g eq dm ⁻³	$C_{\text{Fe(III)}}^{\text{A}}(\text{ini})$ g dm ⁻³	$C_{\text{Fe(III)}}^{\text{A}}(\text{final})$ g dm ⁻³	$C_{\text{Fe(III)}}^{\text{O}}(\text{total})$ g dm ⁻³ (cumulative)
8	1	6	5.00	0.00360	4.99640
8	2	6	5.00	0.01465	9.98175
8	3	6	5.00	0.04657	14.93510
8	4	6	5.00	0.10539	19.82970
8	5	6	5.00	0.37539	24.45430
8	6	6	5.00	0.77068	28.68362
8	7	6	5.00	4.34120	29.34240
8	8	6	5.00	4.82350	29.51890
8	9	6	5.00	4.88230	29.63650
8	10	6	5.00	4.94110	29.69530
8	11	6	5.00	4.96000	29.73530
8	12	6	5.00	4.98000	29.75530

Table LX. Data for the dependence of extraction ratio of iron (III) on various diluents in the case of extraction with MIBK.

$$C_{\text{Fe(III)}}^{\text{A initial}} = 5 \text{ g dm}^{-3}$$

$$\text{Acidity} = 5 \text{ g eq dm}^{-3}$$

$$\text{Extractant concentration} = 1 \text{ mol dm}^{-3} \text{ MIBK}$$

$$\text{Phase ratio} = \text{A} : \text{O} = 1 : 1$$

$$\text{Contact time} = 3 \text{ minutes}$$

$$\text{Temperature} = (30 \pm 1)^\circ\text{C}$$

No. of Expt.	Diluent	Initial aqueous Fe(III) conc. g dm^{-3}	$C_{\text{Fe(III)}}^{\text{A}}$ g dm^{-3}	$C_{\text{Fe(III)}}^{\text{O}}$ g dm^{-3}	$E_{\text{AFe(III)}}^{\text{O}} = \frac{C_{\text{Fe(III)}}^{\text{O}}}{C_{\text{Fe(III)}}^{\text{A}}}$
1	Benzene	5.00	4.1480	0.8520	0.21
2	Kerosin	5.00	4.2657	0.7343	0.17
3	n-Hexane	5.00	4.3833	0.6167	0.14
4	Toluene	5.00	4.4715	0.5285	0.12
5	Chloroform	5.00	4.5598	0.4402	0.10
6	Carbontetra chloride	5.00	4.7362	0.2638	0.065

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APPENDICES

Appendix 1. Interlayer spacings ('d' values) at different 2θ values ($\lambda = 1.5405\text{\AA}$).

2θ	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0	—	882.63	441.32	294.21	220.66	176.53	147.11	126.09	110.33	98.076	88.263
1	88.263	80.243	73.555	67.897	63.047	58.845	55.167	51.922	49.038	46.457	44.135
2	44.135	42.033	40.122	38.370	36.779	35.308	33.950	32.693	31.526	30.440	29.425
3	29.425	28.476	27.587	26.751	25.964	25.223	24.522	23.859	23.232	22.636	22.071
4	22.071	21.532	21.020	20.531	20.065	19.619	19.193	18.785	18.394	18.018	17.659
5	17.659	17.312	16.979	16.660	16.352	16.054	15.768	15.491	15.225	14.967	14.717
6	14.717	14.476	14.243	14.017	13.798	13.586	13.381	13.181	12.988	12.800	12.617
7	12.617	12.440	12.267	12.099	11.936	11.777	11.622	11.471	11.325	11.182	11.042
8	11.042	10.906	10.773	10.643	10.517	10.394	10.273	10.155	10.040	9.927	9.8168
9	9.8168	9.7098	9.6042	9.5010	9.4001	9.3015	9.2053	9.1105	9.0173	8.9264	8.8378
10	8.8378	8.7500	8.6645	8.5806	8.4989	8.4181	8.3387	8.2609	8.1847	8.1100	8.0360
11	8.0360	7.9644	7.8935	7.8234	7.7549	7.6880	7.6220	7.5571	7.4932	7.4305	7.3688
12	7.3688	7.3081	7.2484	7.1897	7.1320	7.0751	7.0192	6.9642	6.9100	6.8567	6.8042
13	6.8042	6.7524	6.7015	6.6513	6.6019	6.5532	6.5053	6.4580	6.4114	6.3655	6.3203
14	6.3203	6.2757	6.2317	6.1883	6.1456	6.1035	6.0619	6.0209	5.9804	5.9405	5.9011
15	5.9011	5.8623	5.8239	5.7860	5.7488	5.7119	5.6755	5.6395	5.6041	5.5691	5.5345
16	5.5345	5.5004	5.4666	5.4333	5.4004	5.3679	5.3358	5.3040	5.2727	5.2417	5.2111
17	5.2111	5.1809	5.1510	5.1214	5.0922	5.0633	5.0348	5.0065	4.9787	4.9511	4.9238
18	4.9230	4.8968	4.8701	4.8437	4.8176	4.7918	4.7663	4.7410	4.7160	4.6913	4.6668
19	4.6669	4.6426	4.6187	4.5950	4.5715	4.5482	4.5253	4.5026	4.4801	4.4577	4.4357
20	4.4357	4.4138	4.3922	4.3708	4.3496	4.3287	4.3049	4.2872	4.2669	4.2467	4.2267
21	4.2257	4.2069	4.1872	4.1678	4.1486	4.1295	4.1106	4.0919	4.0733	4.0550	4.0357
22	4.0367	4.0187	4.0008	3.9831	3.9656	3.9481	3.9309	3.9139	3.8969	3.8801	3.8635
23	3.8535	3.8469	3.8306	3.8144	3.7983	3.7824	3.7666	3.7509	3.7354	3.7200	3.7047
24	3.7047	3.6896	3.6746	3.6596	3.6449	3.6302	3.6157	3.6013	3.5870	3.5728	3.5587
25	3.5587	3.5448	3.5309	3.5172	3.5036	3.4901	3.4767	3.4634	3.4502	3.4371	3.4241
26	3.4241	3.4112	3.3984	3.3857	3.3731	3.3606	3.3482	3.3359	3.3236	3.3115	3.2995
27	3.2995	3.2875	3.2756	3.2639	3.2522	3.2406	3.2291	3.2176	3.2063	3.1951	3.1839
28	3.1839	3.1727	3.1617	3.1508	3.1399	3.1291	3.1184	3.1078	3.0973	3.0868	3.0763
29	3.0763	3.0660	3.0657	3.0455	3.0354	3.0253	3.0153	3.0054	2.9955	2.9857	2.9760
30	2.9760	2.9664	2.9568	2.9472	2.9377	2.9283	2.9190	2.9098	2.9005	2.8914	2.8823
31	2.8823	2.8732	2.8643	2.8553	2.8465	2.8376	2.8289	2.8202	2.8116	2.8023	2.7945
32	2.7945	2.7859	2.7775	2.7691	2.7608	2.7526	2.7443	2.7362	2.7201	2.7200	2.7120
33	2.7120	2.7040	2.6961	2.6882	2.6804	2.6727	2.6649	2.6573	2.6496	2.6420	2.6345
34	2.6345	2.6270	2.6195	2.6121	2.6048	2.5974	2.5902	2.5830	2.5757	2.5686	2.5615

20	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
35	2.5615	2.5544	2.5474	2.5404	2.5334	2.5265	2.5196	2.5129	2.5060	2.4993	2.4926
36	2.4926	2.4859	2.4793	2.4727	2.4661	2.4596	2.4531	2.4466	2.4402	2.4338	2.4274
37	2.4244	2.4211	2.4149	2.4086	2.4024	2.3962	2.3901	2.3840	2.3779	2.3719	2.3650
38	2.3650	2.3599	2.3540	2.3480	2.3421	2.3362	2.3305	2.3247	2.3189	2.3131	2.3074
39	2.3047	2.3018	2.2962	2.2906	2.2849	2.2794	2.2739	2.2684	2.2629	2.2574	2.2521
40	2.2521	2.2467	2.2414	2.2360	2.2306	2.2254	2.2202	2.2149	2.2097	2.2045	2.1994
41	2.1994	2.1943	2.1892	2.1841	2.1791	2.1740	1.1691	2.1641	2.1592	2.1542	2.1493
42	2.1493	2.1445	2.1396	2.1347	2.1300	2.1225	2.1204	2.1157	2.1110	2.1063	2.1016
43	2.1016	2.0970	2.0924	2.0878	2.0832	2.0786	2.0741	2.0696	2.0651	2.0606	2.0562
44	2.0562	2.0517	2.0473	2.0429	2.0385	2.0342	2.0299	2.0256	2.0213	2.0170	2.0127
45	2.0127	2.0085	2.0043	2.0001	1.9959	1.9918	1.9876	1.9835	1.9795	1.9754	1.9713
46	1.9713	1.9673	1.9632	1.9592	1.9552	1.9513	1.9473	1.9433	1.9395	1.9356	1.9316
47	1.9316	1.9278	1.9239	1.9201	1.9163	1.9125	1.9087	1.9049	1.9012	1.8974	1.8937
48	1.8937	1.8900	1.8863	1.8826	1.8790	1.8754	1.8717	1.8682	1.8645	1.8609	1.8574
49	1.8574	1.8538	1.8503	1.8468	1.8433	1.8398	1.8364	1.8329	1.8294	1.8260	1.8226
50	1.8226	1.8192	1.8158	1.8124	1.8090	1.8057	1.8024	1.7990	1.7958	1.7924	1.7891
51	1.7891	1.7859	1.7827	1.7794	1.7762	1.7730	1.7657	1.7666	1.7634	1.7603	1.7571
52	1.7571	1.7539	1.7508	1.7477	1.7446	1.7415	1.7385	1.7354	1.7323	1.7293	1.7263
53	1.7263	1.7232	1.7202	1.7173	1.7143	1.7113	1.7083	1.7054	1.7025	1.6996	1.6966
54	1.6966	1.6937	1.6909	1.6879	1.6851	1.6822	1.6794	1.6765	1.6738	1.6709	1.6680

Appendix 2. X-ray diffraction patterns of some of the compounds of our interests taken from the ASTM cards (only the characteristic deflections are noted).

Compound	ASTM card No.	d, Å $\xrightarrow{\hspace{1cm}}$				
		(R.I., %) $\xrightarrow{\hspace{1cm}}$				
TiO ₂ (anatase)	21-1272	3.52 (100)	1.89 (35)	2.38 (20)	1.67 (20)	2.43 (10)
TiO ₂ (rutile)	21-1276	3.25 (100)	1.69 (60)	2.47 (50)	2.19 (25)	-
Fe _{0.94} O (iron oxide)	39-1088	2.08 (100)	2.52 (80)	1.51 (50)	1.29 (20)	-
FeO (iron oxide)	6-0615	2.15 (100)	2.49 (80)	1.52 (60)	-	1.24 (15)
FeO (ironous oxide)	6-0711	1.52 (100)	1.51 (100)	1.29 (60)	1.25 (20)	-
Fe ₃ O ₄ (iron oxide)	26-1136	2.44 (100)	1.43 (50)	1.56 (40)	4.67 (10)	-
γ-Fe ₂ O ₃ (iron oxide)	25-1402	2.51 (100)	1.47 (40)	2.95 (30)	7.91 (10)	-
Fe ₂ O ₃ (iron oxide)	39-1346	2.52 (100)	2.95 (35)	1.61 (24)	1.48 (34)	-
β-Fe ₂ O ₃ (iron oxide)	39-238	2.71 (100)	2.35 (16)	1.66 (40)	1.417 (19)	-
Fe ₃ O ₄ [iron (II,III) oxide]	19-629	2.53 (100)	1.49 (40)	2.97 (30)	4.85 (8)	-
Fe ₃ O ₄ (iron oxide)	28-491	2.60 (100)	1.40 (50)	2.03 (40)	1.40 (50)	-
Na ₂ TiO ₃	28-1152	2.25 (100)	1.59 (80)	2.60 (60)	1.36 (60)	1.30 (60)
2Na ₂ O·3TiO ₂	28-1153	2.71 (100)	2.51 (100)	2.50 (100)	9.45 (40)	6.63 (60)
Na ₆ Ti ₃ O ₇	28-1154	3.23 (100)	5.23 (80)	2.20 (80)	5.25 (80)	4.48 (60)

Compound	ASTM card No.	d, Å $\longrightarrow$				
		(R.I., %) $\longrightarrow$				
$4\text{Na}_2\text{O}_{0.5}\text{TiO}_2$	28-1155	2.30 (100)	2.22 (100)	2.20 (100)	9.65 (60)	7.30 (80)
$\text{Na}_{0.75}\text{Fe}_{0.75}\text{Ti}_{0.25}\text{O}_2$	25-877	2.20 (100)	5.48 (85)	1.61 (25)	2.74 (15)	2.57 (15)
$\text{Na}_{0.4}\text{Fe}_{0.53}\text{Ti}_{1.55}\text{O}_{3.99}$	32-1104	4.66 (100)	4.56 (100)	2.70 (100)	5.11 (40)	2.65 (100)
$\alpha\text{-NaFeTiO}_4$	32-1103	7.12 (100)	4.81 (70)	2.96 (40)	2.43 (50)	2.28 (30)
$\text{NaFeTi}_3\text{O}_8$	21-1130	3.63 (100)	3.10 (75)	2.71 (75)	2.53 (16)	2.39 (20)
$\text{Na}_{0.9}\text{Fe}_{0.9}\text{Ti}_{1.1}\text{O}_4$	21-1128	7.17 (100)	4.84 (40)	2.71 (35)	3.58 (25)	-
$\text{Na}_2\text{Fe}_2\text{Ti}_3\text{O}_{10}$	21-1129	7.30 (100)	2.71 (80)	2.44 (75)	4.84 (65)	2.89 (65)
NaFeTiO_4	33-1255	2.50 (100)	2.66 (85)	4.59 (65)	5.38 (10)	2.69 (50)

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