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Studies on Decomposition of Ilmenite from Sri Lanka

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Abstract : Ilmenite and rutile deposits of Sri Lanka are found as beach sands in the East and North-West Coasts. Some 65,000 tons of ilmenite concentrates are currently exported from Sri Lanka each year, primarily to pigment manufacturers, without any beneficiation. This paper reviews some results of laboratory studies that have been carried out by the Ceylon Institute of Scientific and Industrial Research (CISIR) to prepare synthetic rutile from ilmenite using locally available raw materials. The main feature of this process is the use of saw dust for the first time in a beneficiation method as the reducing agent to reduce iron values in ilmenite to acid leachable form. In the process developed ilmenite is first oxidized and this is then reduced by using saw-dust. Reduced ilmenite is leached with hydrochloric acid to remove iron and the final concentrate is calcined to rutile having about 95 % TiO_2. The hydrochloric acid could be recovered from the leached liquor and iron oxide is obtained as a byproduct which could be used as a red pigment.

1. Introduction

Ilmenite and rutile are the only two naturally occurring titanium bearing minerals that have been seriously considered as suitable feedstock for either metal-producing or pigment industries. This is because only rutile and ilmenite are found in large enough commercial concentrations compared with other naturally occurring minerals containing titanium, so as to be suitable for industrial exploitation.

There has been a continuing growth in demand for titanium dioxide pigment, and this industry in the world has continued to expand to meet the spectacular growth in demand due to this inherent superior properties. The total titanium dioxide production capacity is more than 2 million tons a year and the growth rate of TiO_2 consumption averaged 5.5% during the period 1964 to 1972. The future growth is predicted to be about 5% a year.[22]

The existence of natural concentrates of titanium bearing mineral sands such as ilmenite and rutile in a high degree of purity in many places in the coasts of Sri Lanka has been known as far back as 1903. Over the last few decades systematic work on the beach sands of the islands referred to as "black sands" have been carried out by the Geological Survey Department of Sri Lanka, and at present the distribution of these deposits, and their mineralogy is known.[8,12]

2. Ilmenite and Rutile Deposits of Sri Lanka

These deposits in Sri Lanka are found as beach sands in the East and North-West Coast and occur in association with others namely, rutile, zircon and monazite. The largest and most important beach sand deposit occurs at Pulmoddai in the North-East Coast of the island, 34 miles North of Trincomalee. The deposit is approximately 4 miles in length with an average width of about 200 feet. The richest part of the deposit is in the Southern coast, where the percentage of heavy mineral amount to 95%. The approximate composition of the sand is as follows:

		w/w %
Ilmenite	($FeO.\ TiO_2$)	70-80
Rutile	(TiO_2)	8-12
Zircon	($ZrO_2.\ SiO_2$)	8-10

Besides the Pulmoddai deposit there are other deposits of mineral sands in several scattered points on the West Coast from Kundiramalai Bay on the North West Coast to Kirinda on the South of Sri Lanka. These deposits contain heavy minerals varying from 10-20% while occasionally the concentration rises over 80%. In all these deposits ilmenite is the main constituent with zircon next in order of importance.[18]

The Mineral Sands Corporation of Sri Lanka commenced commercial production of ilmenite from Pulmoddai sand in 1963 and rutile in 1968. About 65,000 tons of ilmenite concentrates are currently exported from Sri Lanka each year, primarily to pigment manufacturers, without any beneficiation.

The following Table gives the results of chemical analysis of ilmenite from Pulmoddai.

TABLE 1. Chemical Composition of Sri Lanka Ilmenite

SiO_2	—	0.38
TiO_2	—	53.61
Al_2O_3	—	0.54
Fe_2O_3	—	20.95
FeO	—	20.67
MnO	—	0.95
MgO	—	0.92
CaO	—	0.05
Cr_2O_3	—	0.05

The immense and expanding uses of high purity TiO_2 in the pigment and paper industries, combined with increasing demand for titanium metal, are expected to outstrip the production capacity of available sources of rutile. Therefore development of commercial processes for upgrading these ores is becoming increasingly important.

The traditional pigment-producing process is the "Sulphate Process", in which finely ground ilmenite is digested in sulphuric acid and titanium hydroxide precipitated by hydrolysis. This process creates large quantities of waste in the form of hydrated ferrous sulphate and sulphuric acid, and methods of disposal, such as discharge into rivers or sea, create pollution problems.[1,2]

The recently developed "Chloride Process" is becoming more attractive[1,7] to pigment producers because it produces less effluent and is cheaper to operate. However, the present economics of the chloride process are only favourable for feed materials containing at least 90% titanium dioxide (TiO_2) and with low proportions of metal oxide impurities, such as iron and manganese, which not only consume chlorine but also form troublesome liquid chlorides.

The preferred chloride process feedstock has always been natural rutile of which Sri Lanka currently exports about 16,000 metric tons per annum. Australia currently supplies more than 95% of the world demand of rutile. In recent years, however, the world production of rutile kept pace with demand and prices have been much inflated. Pigment producers have therefore been seeking alternative feeds, particularly high-grade slags and beneficiated ilmenite. Having considered these facts the Ceylon Institute of Scientific and Industrial Research (CISIR) carried out a series of laboratory experiments to upgrade Sri Lanka ilmenite to the more useful and more expensive rutile form by using locally available raw materials.

During the last two decades, many processes have been proposed for upgrading ilmenite, including high temperature smelting, direct and leaching, methods, and reduction processes in which the iron content is reduced either to ferrous oxide and extracted with acid or to metallic iron and removed by acid leaching or accelerated corrosion.[20,22]

The fundamental steps of the process that we have investigated in the CISIR laboratories are as follows—

> Ilmenite is first oxidized at a temperature range 900-1000°C for 3.00 hrs. This will facilitate the subsequent reduction stage. This oxidized ilmenite is then reduced in a closed vessel at 1100°C using sawdust which contains a high percentage of carbonaceous material as the reductant. Iron in reduced ilmenite is then leached with dilute hydrochloric acid. Hydrochloric acid leaching was investigated since Sri Lanka has a hydrochloric acid industry and also it was known that commercial units were available for converting ferrous chloride liquor to iron oxide pigment, the latter being recycled in the leaching stage.[3,4] The leached product obtained is calcined at 1000°C to get synthetic rutile having about 95% TiO_2.

3. Experimental

The ilmenite used through out the present work was obtained from the ilmenite separation plant at Pulmoddai. After each stage, chemical analysis and X-ray characterisation of all samples were carried out.

3.1 Chemical Analysis

The chemical analysis of treated samples was always carried out in duplicate. The titanium content of the treated samples was determined by a spectrophotometric method.[13] Atomic absorption methods were employed for the determination of other constituents except Al and Si. Ferrous iron determination was carried out according to the "Wilson" method.[13]

3.2 X-ray characterisation

Solid products were examined by means of a JEOL JD 8X X-ray powder diffractometer equipped with a graphite monochrometer using Cu K α radiation. XRD patterns were obtained at a scanning rate of 2°/min for qualitative study. The proportions of different phases present in the reaction products were determined by comparing the peak heights of most intense diffraction lines. Powder diffraction patterns were identified from patterns listed in the JCPDS Index.[17]

The differential thermal analysis of samples was carried out by using "MOM Q-Derivatograph". Scanning Electron Microscope microphotographs were taken using a JEOL Scanning Electron Microscope. Other experimental conditions that were used at each stage were as follows :-

3.3 Oxidation

Oxidation of ilmenite ore was carried out in temperature controlled electric furnaces. Calcined samples were quenched into water rapidly to study the phases present.

3.4 Reduction

Reduction of ilmenite was carried out in a sealed stainless steel vessel (Figure 1).

3.5 Dressing

Unreacted saw dust ash was separated out using a simple flotation technique without adding any activating agents or frothers. Running water was passed through a stirred aqueous mixture of reduced ilmenite in a flask and sawdust was collected from the overflowing water. Reduced ilmenite remained in the bottom of the flask.

3.6 Leaching

Leaching of reduced ilmenite was carried out under refluxing conditions at atmospheric pressure. Dilute hydrochloric acid (31 % w/v) was used as the leaching agent.

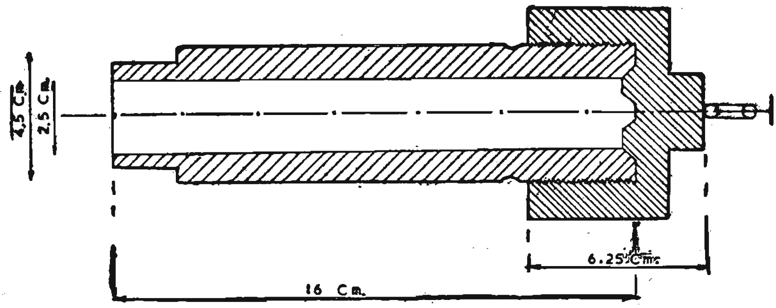


FIG I - AUTO CLAVE USED FOR ILMENITE REDUCTION

3.7 Calcining

Calcination of leached ilmenite was carried out in a temperatuie controlled furnace and the final product was quenched into water to study the phases present.

4. Results and Discussion

4.1 Preliminary Investigation

A sieve analysis was carried out on the beach sand ilmenite from the Pulmoddai plant and the results obtained are given in Table 2.

TABLE 2. Screen Analysis of Ilmenite Used

Screen size (BS mesh)	Percentage w/w
+ 60	0.4
—60 + 100	16.0
—100	83.6

A chemical analysis of the above fractions (Table 3) showed that ilmenite of particle size + 60 mesh had low TiO_2 and Fe_2O_3 content when compared with other fractions. X-ray powder diffraction analysis showed that this was due to the presence of other impurities such as α -quartz, zircon, etc.

TABLE 3. Variation of Ti and Fe Content of Different Particle Size of Ilmenite

Particle size	TiO_2	Total Fe as Fe_2O_3%
—100 mesh	48—57	45—48
100—60 mesh	52—59	38—42
+ 60 mesh	39—40	37—39
Raw Ilmenite	52—54	44—46

The XRD pattern of natural ilmenite is given in Figure 2. In addition to the peaks corresponding to the mineral ilmenite and rutile there are several peaks which resemble the compound Pseudorutile $Fe_2O_3.3TiO_2$ (or $Fe_2Ti_3O_9$).[19] This is a transition phase between ilmenite and rutile.

The identification of Pseudorutile depends solely on the two peaks at d = 3.82 and 1.375 Å, since the remaining lines in the powder patterns also characterize rutile.

Ilmenite of particle size-60 mesh was selected for further investigation since this fraction was comparatively free of impurities.

4.2 Oxidation Stage

Ilmenite samples were oxidized at different temperatures for the same duration and the change in composition observed.

The XRD patterns of the samples oxidized at 800°, 900°C and 1000°C for duration of 3 hrs are given in Figure 2.

The major products formed by oxidation of ilmenite at temperatures greater than 900°C are ferric pseudobrookite and rutile.[14]

This reaction proceeds according to the equation (1) and (2).

$$2Fe\,TiO_3 + \tfrac{1}{2}\,O_2 \longrightarrow Fe_2TiO_5 + TiO_2 \quad \text{.......(1)}$$

$$Fe_2Ti_3O_9 \longrightarrow Fe_2TiO_5 + 2TiO_2 \quad \text{.......(2)}$$

To study the optimum duration necessary for oxidation of ilmenite, samples were oxidised at 900°C for different durations. The Scanning Electron Micrographs of the samples oxidised at 900°C for 3 hrs 7 hrs and 24 hrs are given in Figure 3.

Formation of fine pores on the ilmenite particles was observed. With the increase of duration of oxidation the pores are more visible. The presence of micro cracks and pores on the ilmenite particles facilitates the reduction of ilmenite to rutile.

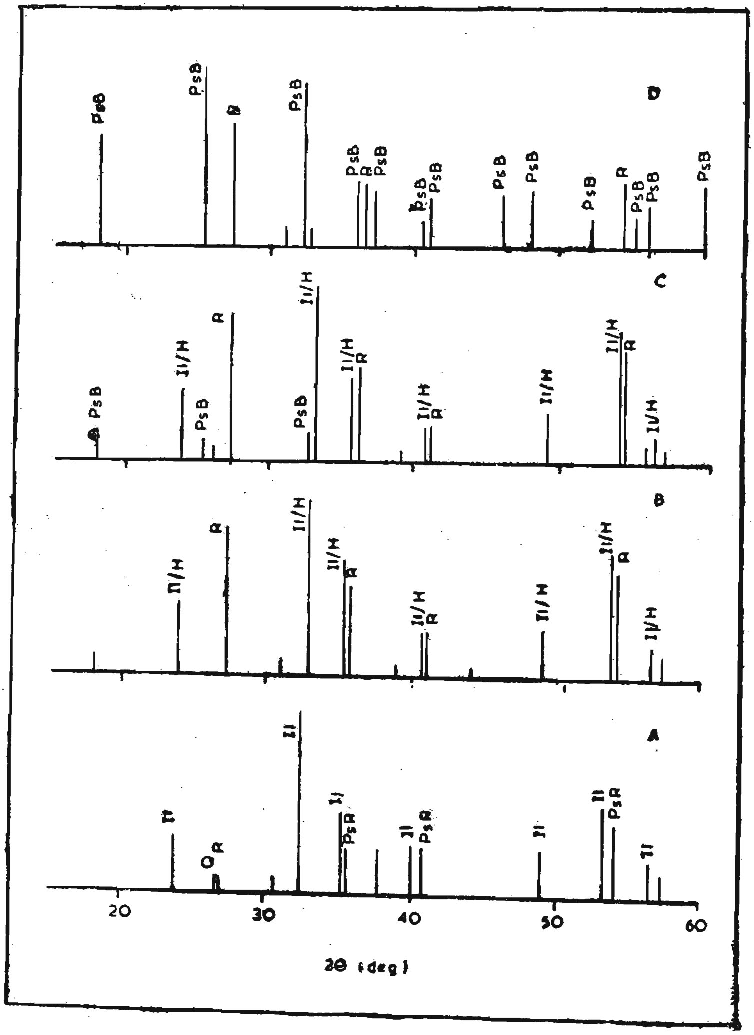


Figure 2. X-ray patterns of raw Ilmenite and oxidised Ilmenite

A — Raw Ilmenite
B — Oxidised Ilmenite 800°C 3 hrs.
C — Oxidised Ilmenite 900°C 3 hrs.
D — Oxidised Ilmenite 1000°C 3 hrs.
I1 — Ilmenite PsR — pseudorutile
R — Rutile Q — Quartz
PsB — Pseudobrookite H — Hematite

(A)

Figure 3. Scanning Electron Micrograph of Oxidised Ilmenite at 900°C

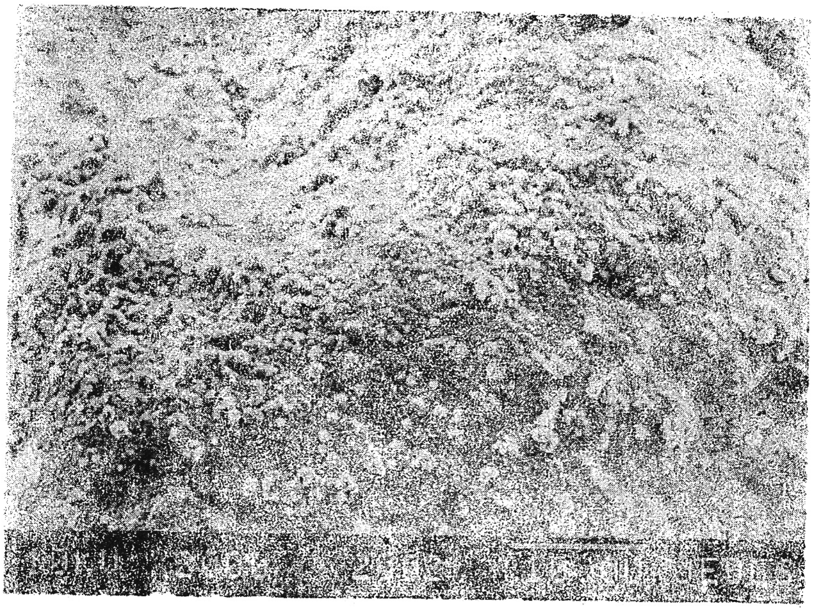
Conditions — Accelerating voltage — 10 Kv
Magnification — 2000
Micron value — 10 η

(A) Raw Ilmenite without Oxidizing

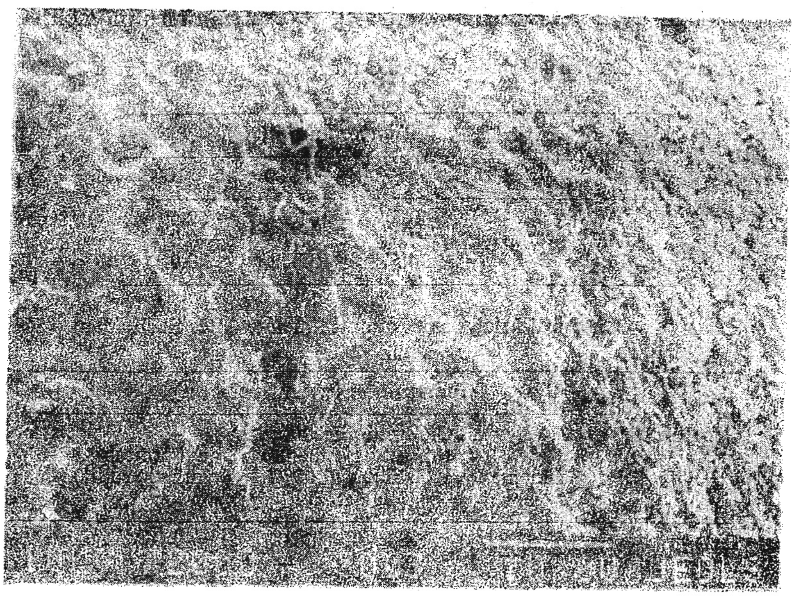
(B) Oxidized for 3.0 hrs.

(C) Oxidized for 7.0 hrs.

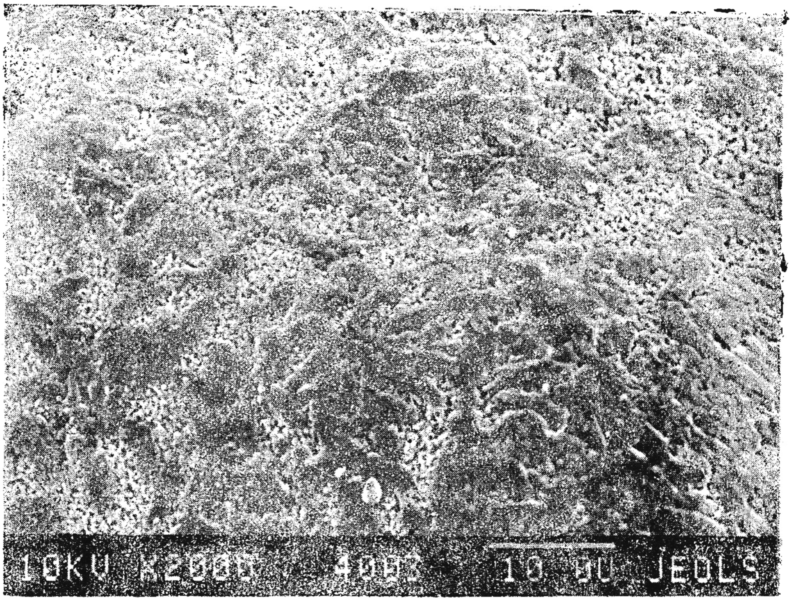
(D) Oxidized for 24.0 hrs.



(B)



(C)



(D)

Chemical analyses of oxidized ilmenite are given in Tables 4 and 5. These tables indicate the mean value obtained in analysing several samples in each stage.

TABLE IV — Chemical Composition of Oxidized Ilmenite at Different Temperatures

Component	Temperature (°C)		
	800	900	1000
TiO_2	60.5	61.2	68.5
FeO	2.64	1.19	0.0
Fe_2O_3	34.57	35.62	29.0

TABLE V — Chemical Analysis of Natural Ilmenite After Each Stage

Component	Composition (weight per cent)			
	Raw Ilmenite	Oxidized Ilmenite 1000°C; 3 h	Reduced Ilmenite 1100°C 3 h	Final product (synthetic rutile)
TiO_2	53.85	68.5	66.07	94.64
FeO	16.76	0.0	—	—
Fe_2O_3	26.35	29.0	—	1.50
Fe (total)	—	—	28.06	—

Figure 4 shows the diffraction patterns of unoxidized reduced ilmenite and also preoxidized reduced ilmenite of same time duration. It is clearly seen that unoxidized reduced ilmenite still contains unreacted ilmenite and we can conclude that for better reduction, ilmenite has to be preoxidized. The amount of iron in the final product is largely decreased if ilmenite is oxidized at a higher temperature (1000°C 3 hrs). Table 6 shows the variation of iron content of synthetic rutile with oxida ion temperature.

TABLE 6. Variation of Ti and Fe content of Synthetic Rutile on Preoxidation Temperature of Ilmenite

Oxidation Temperature (°C)	Synthetic Rutile	
	TiO_2 %	Total Fe as Fe_2O_3 %
700	79.53	12.85
800	89.78	4.79
900	84.89	3.85
1000	93.17	2.88

From the above observation it is clear that to get a higher TiO_2 percentage in in the final product oxidation has to be carried out around 1000°C. Hence, for further studies the oxidation stage was carried out at 1000°C for 3.00 hours duration.

4.3 Reduction Stage

Samples of preoxidized ilmenite were reduced in an autoclave (Figure 1) by using sawdust as the reducing agent, since this contained mainly carbonaceous material. Typical chemical analysis of the sawdust used is given in Table 7.

TABLE 7. Chemical Composition of Sawdust

	w/w %
Loss on ignition	99.44
SiO_2	0.21
CaO	0.21
MgO	0.03
Fe_2O_3	0.02
Al_2O_3	0.11
TiO_2	0.00
K_2O	0.01
Na_2O	0.01
Total	100.06

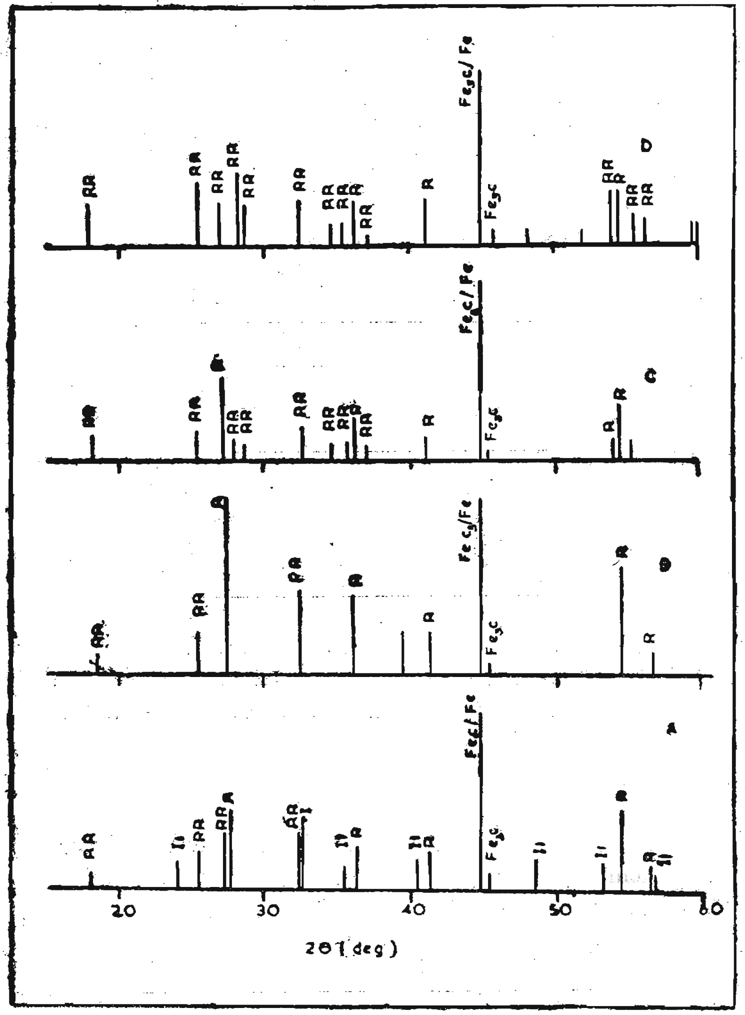


Figure 4. X-ray patterns of reduced ilmenite

A — Raw Ilmenite reduced at 1100°C 3 hrs.
B — Oxidized Ilmenite 800°C reduced at 1100°C 3 hrs.
C — Oxidized Ilmenite 900°C reduced at 1100°C 3 hrs.
D — Oxidized Ilmenite 1000°C reduced at 1100°C 3 hrs.

Il — Ilmenite
RR — Reduced rutile
Fe_3C — Cementite
R — Rutile
Fe — Iron

4.3.1 Effect of reduction temperature and duration

Initially a 1 : 1 mixture of sawdust (particle size - 44 BS mesh) mixture was used in the reduction stage for 3.00 hrs duration at different temperatures. Figure 4 shows the X-ray patterns of the reduced ilmenite. These observations reveal that sawdust could be used for successful reduction of iron values in ilmenite to metallic iron. In the reduction with sawdust, the reductant is ostensibly solid carbon, and much of the chemistry of carbon in the form of coke and CO has been found by several workers.[6,9,10,11,14] It is also clear that

(i) by keeping the duration of reduction for 3.00 hrs successful reduction occurs at temperatures around 1100°C.

(ii) the first stage of reduction is conversion of Fe^{3+} in pseudobrookite to Fe^{2+} in the form of ilmenite, (Figure 4). As a result the pseudo brookite concentration progressively decreases whereas that of ilmenite increases. This indicates that in the early stage of reduction ilmenite is reformed by a recombination reduction mechanism. The d - spacings of the reformed ilmenite were close to those for stoichiometric $FeTiO_3$.

$$Fe_2TiO_5 + TiO_2 + C \longrightarrow 2\,FeTiO_3 + CO \qquad (1)$$

(iii) the second stage of reduction is conversion of Fe^{2+} to metallic iron, as shown by XRD patterns. Hence, the ilmenite concentration progressively decreased and there was corresponding increase in the concentration of metallic iron and reduced rutile. The reduced rutile form (eq.3) was suboxides of titanium,[10] and no attempt was made to identify these oxides in this paper. (Figure 4).

$$FeTiO_3 + C \longrightarrow Fe + TiO_2 + CO \qquad (2)$$

$$nTiO_2 + C \longrightarrow Ti_n\,O_{2n-1} + CO \qquad (3)$$

Formation of cementite (Fe_3C) was also observed (reaction 4) in the reduced phases of ilmenite, as a result of the reaction between iron and carbon.

$$3\,Fe + C \longrightarrow Fe_3C \qquad (4)$$

Also it was clear from these results that, the optimum duration necessary for complete reduction of ilmenite at a temperature of 1100°C is 3.00 hrs. Figure 5 shows the reduction phases at different temperatures at different time durations.

Hence, for further studies a reduction temperature of 1100°C and a duration of 3 hrs was selected.

Chemical analyses of reduced phases are given in Table VI.

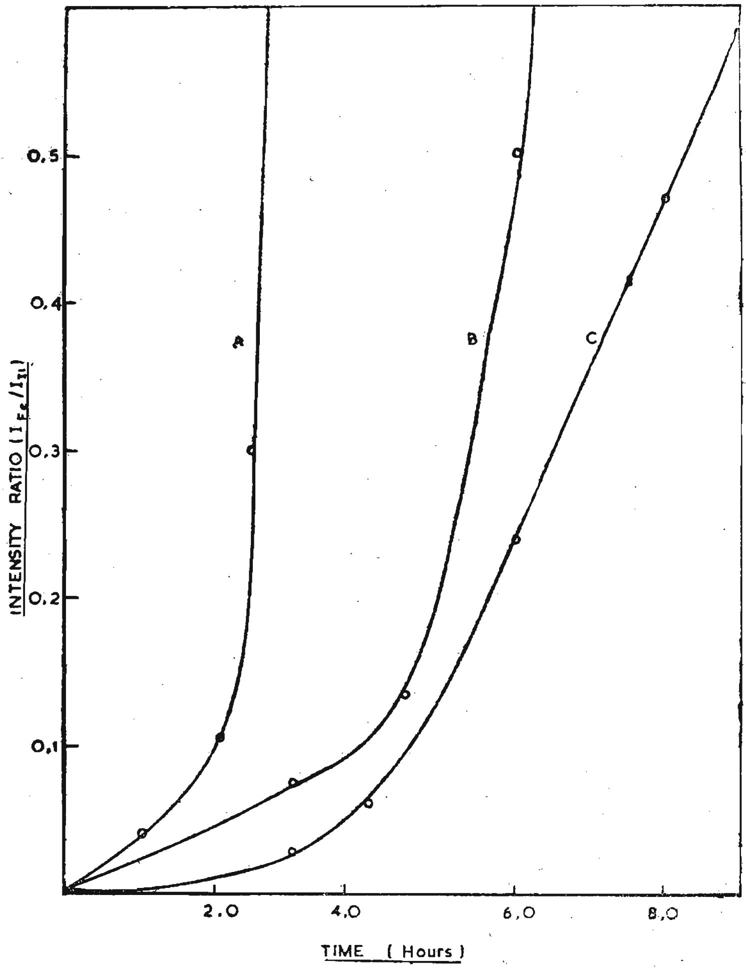


Figure 5. Effect of duration of reduction at different temperatures

$$\text{Intensity ratio} = \frac{\text{(Intensity of Fe line (110)}}{\text{(Intensity of Ilmenite line (104)}}$$

A — Preoxidized Ilmenite reduced at 1100°C
B — Preoxidized Ilmenite reduced at 1000°C
C — Preoxidized Ilmenite reduced at 900°C

4.3.2 Effect of amount of sawdust used for reduction

A series of experiments were carried out with varying amounts of sawdust and oxidized ilmenite at 1100°C for 3 hrs in an autoclave to study the effect of sawdust to ilmenite ratio on reduction. It was noted that sawdust to ilmenite ratio up to 1 : 4 could be used and with this ratio also a little amount of unreacted sawdust was left after reduction. This unreacted sawdust could be separated out and re-cycled. Therefore for further studies equal amounts of sawdust and ilmenite were used for the reduction.

4.3.3 Effect of particle size of sawdust

Sawdust of different particle sizes (-44, 44 - 30, 30 - 22, +22 BS mesh) was used for reduction and it was found that irrespective of the particle size of sawdust used, oxidized ilmenite is reduced at 1100°C. But it was noted that if the particle size is small the mixing before reduction with ilmenite and subsequent dressing of unreacted sawdust was easy.

4.3.4 Dressing

The purpose of this step is to separate unreacted burnt sawdust from reduced ilmenite. Since reduced ilmenite contains metallic iron, this separation could be easily carried out by using a magnetic separator. Also as the density of unburnt sawdust is comparatively low when compared to ilmenite, the separation also could be done by using a flotation technique. For our studies we used a simple gravity flotation technique. Separated unreacted burnt sawdust could be re-used in the reduction process.

5. Leaching Stage

The initial experiments were carried out by using laboratory grade hydrochloric acid (31% w/v) under refluxing conditions at normal atmospheric pressure.

5.1 Effect of Acid Concentration

Acids of different dilutions were used for leaching and each time the amount of metallic iron, TiO_2 and Mg dissolved in the solution were determined (Table 8).

TABLE 8

Strength of acid % v/v of 31% w/v acid	Weight loss in the sample % w/w	Amount dissolved (% w/w)		
		TiO_2	Mg	Fe
15	30.22	0.50	0.11	24.14
20	23.26	0.52	0.10	20.15
25	37.19	1.83	0.11	23.05
56	43.39	8.54	0.14	30.13

From these observations, it is clear that by increasing the concentration of acid the amount of iron leached out also increases. But accordingly the amount of TiO_2 dissolving also increases. Therefore, 20 - 15% v/v of 31% w/v HCl acid is good for the leaching stage.

5.2 Effect of Leaching Time Duration

15% and 20% v/v HCl acid was used for leaching and the amount of metallic iron dissolved in the solution at different time intervals was analysed to study the duration for complete leaching. Results obtained are given in Figure 6.

It is clear that for complete leaching of iron in reduced ilmenite at least 4.00 hrs is essential if 20% HCl of 31% w/v is used.

6. Calcination

XRD patterns of acid leached samples consisted of reduced rutile phases. Therefore, these samples were calcined to convert them to rutile. The DTA of acid leached sample was taken (Figure 7) and it was found to have an endothermic peak at about 550°C and an exothermic peak at about 970°C. The endothermic peak at 550°C indicates the oxidation of the leached sample. The exothermic peak at 970°C indicates the converson of titanium dioxide present in the sample to the rutile type of titanium dioxide.

6.1 Duration of Calcination

Acid leached reduced ilmenite samples were calcined at 1000°C for different time durations to study the optimum time duration required for conversion of reduced titanium dioxide to rutile. The XRD patterns of the oxidized samples were taken and it showed the presence of only the rutile phase.

From these observations the calcining temperature was selected as 1000°C and duration as 3.00 hrs to ensure good results.

6.2 Final Product

Figure 8 shows clearly that the final product is essentially pure rutile, and the mean value of chemical analysis of several samples obtained by this process is given in Table 9.

TABLE 9. Chemical Analysis of Synthetic Rutile Obtained

Component	%w/w
TiO_2	95.97
Fe_2O_3	1.57
MgO	0.86
Al_2O_3	0.80
MnO	1.21
SiO_2	0.69

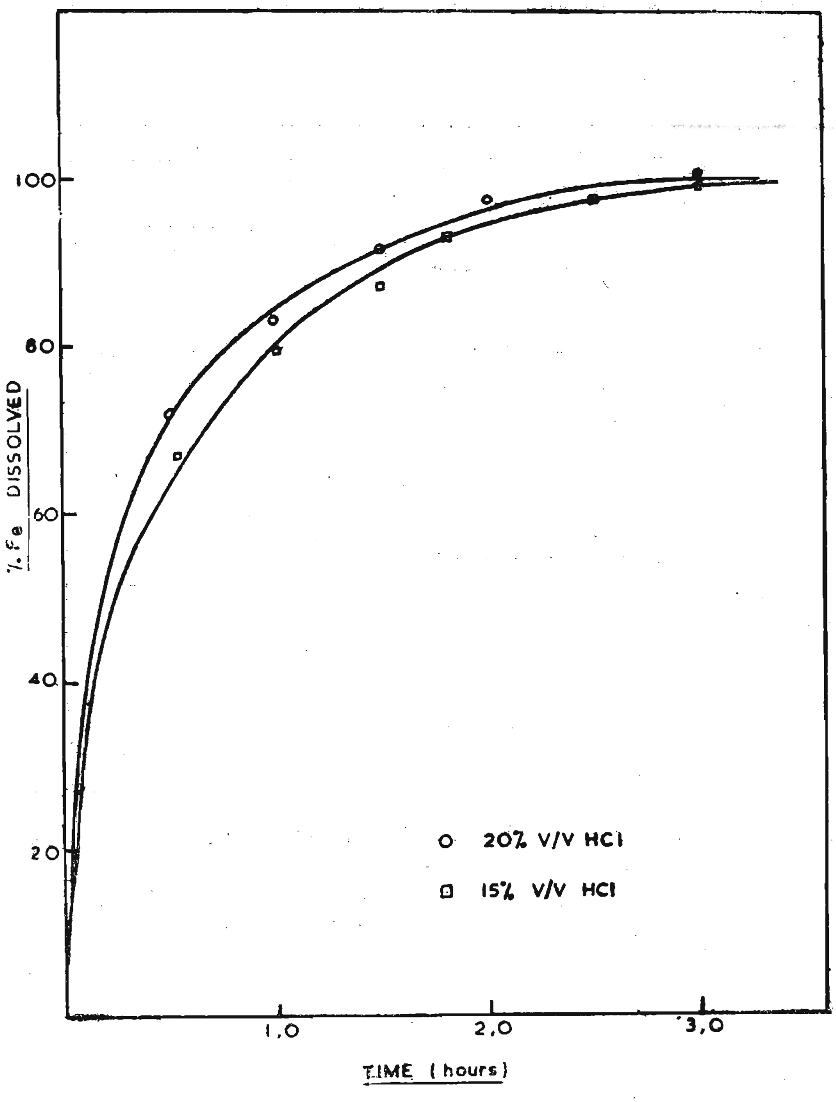


Figure 6. Effect of leaching time duration on the amount of iron leached out from the reduced sample in different acid solutions.

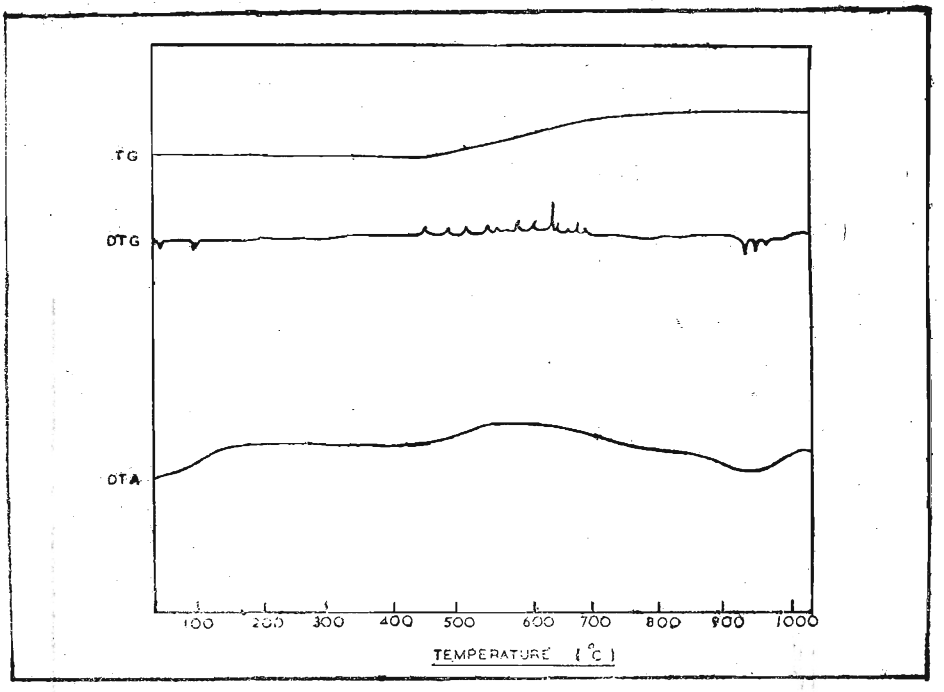


Figure 7. DTA of acid leached reduced ilmenite

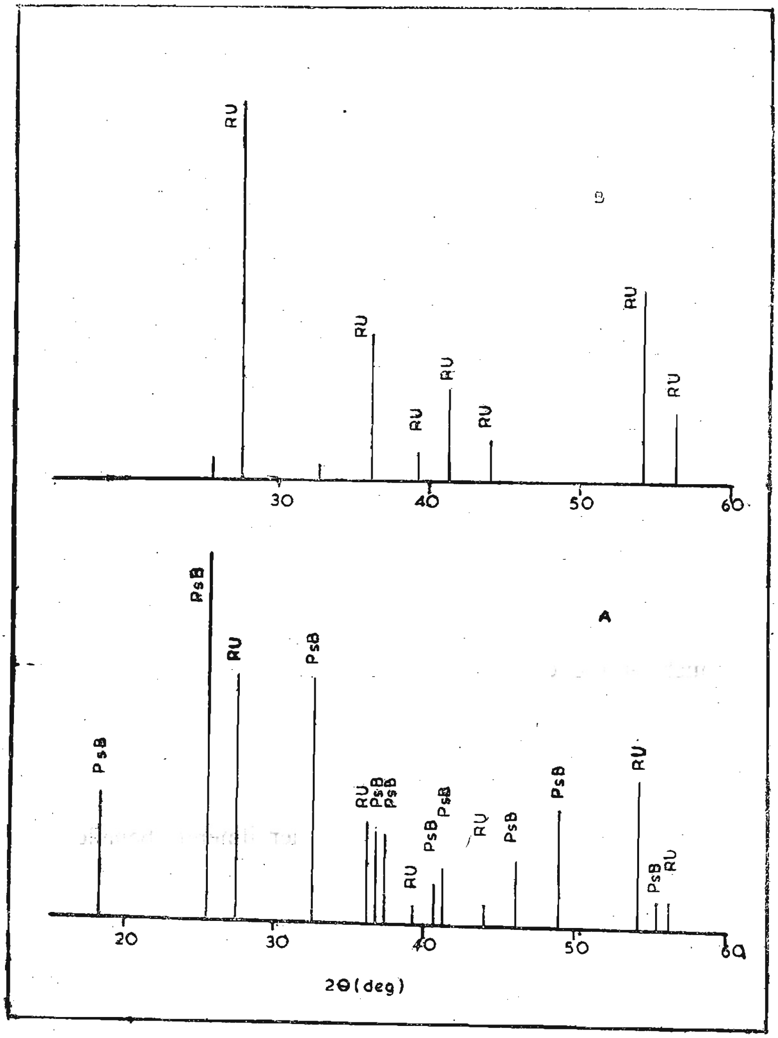


Figure 8. XRD patterns of synthetic rutile

A — from unoxidized ilmenite
B — from oxidized ilmenite

7. Conclusion

On the basis of above results it is clear that Pulmoddai ilmenite could be converted to synthetic rutile having a high titanium dioxide value (90 - 95%) using locally available raw materials.

Processes similar to this type of beneficiation of ilmenite on a large scale have been developed in several countries in the world successfully.[5,16,20,22]

The process developed has the following advantages :-

(*a*) The artificial rutile produced shows as high as 95 to 97% TiO_2 content, while the grain size of the product is almost the same as that of the starting one. The product has a good appearance and is free of fine powders, thus being suitable as the starting material for titanium tetrachloride manufacture.

(*b*) Saw dust which is at present a waste material is used as the reductant.

(*c*) The hydrochloric acid used in the leaching stage can be recovered and reused and the process is free of the pollution problem.

(*d*) The hydrogen gas evolved in leaching of iron in reduced ilmenite can be utilized in the reduction stage as it is a good reducing agent and also much of the chemistry of hydrogen reduction of ilmenite is already known. [6,21]

(*e*) The process can be applied to almost any kind of ilmenite ore having different ferrous to ferric ratios.

This synthetic rutile can compete with other ilmenite beneficiates obtained in similar types of processes in different countries (Table 10).

TABLE 10. Analysis of Ilmenite Beneficiate (WT %) [1]

Company	TiO_2	FeO	Fe_2O_3	Al_203	Mg0	Ca0	Mn0	Cr_2O_3	$Si0_2$
Western Titanium (Australia)	91.1	4.91	—	1.10	0.36	0.12	2.08	0.05	0.71
Gulf Chemical Metallurgical Corporation (USA)	90.0	—	5.86	—	—	—	—	—	—
Tiron Chemical Corporation (Canada)	92.6	2.71	—	1.65	0.28	0.43	1.57	0.08	0.67
Murphyores & CSIRO (Australia)	95.4	—	1.43	0.30	0.14	0.40	0.05	—	0.64
British Titan (U.K.)	92.1	2.62	1.17	—	—	—	—	—	0.86
Ishihara (Japan)	96.1	—	1.30	0.46	0.07	0.01	0.03	0.15	0.15
CISIR	95.97	—	1.57	0.80	0.86	—	1.21	—	0.69

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