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Rutile from ilmenite using coconut pith as a reductant

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Rutile, the raw material needed for chloride route has to be prepared by removing iron from ilmenite, as rutile deposits are scarce in nature. In this study, the iron oxide present in ilmenite was reduced for different times and temperatures using coconut pith which is an agrowaste available in large quantities in Kerala. Pith has low *S*, *P* and ash contents and has a moderate calorific value. The reduction process was studied using chemical analysis, SEM, X-ray and EPMA. Reduction of iron oxide in the ilmenite reaches a maximum at 3 to 4 h at 1040° C containing 84% of iron in the metallic state and the rest in the ferrous state. Treatment with 20% hydrochloric acid at 80° C for 1 h with stirring, leaches out most of the iron from the reduced ilmenite leaving behind only 2% iron. The SEM and X-ray data show the gradual reduction and structural changes taking place during reduction of ilmenite with coconut pith.

1. Introduction

Ilmenite and rutile are the important source minerals of titanium. Ilmenite is available abundantly in nature, whereas the availability of rutile is very limited. The titanium extraction plants follow the chloride route, in which rutile is converted to $TiCl_4$. The Kerala beach sands contain ilmenite and rutile of the order of 130 and 7 million tonnes respectively [1].

Iron which is present in ilmenite has to be removed to obtain rutile. Many methods, such as reduction, smelting, reduction and leaching, etc., have been tried by various workers [2–6]. It has been found that reduction of the iron oxide using coal, or CO gas followed by acid leaching, is a fairly good method for the production of synthetic rutile. Jena *et al.* [7] have reported a study on the utilization of Indian ilmenite to produce rutile, whereas the ilmenite is subjected to reduction using coal, followed by leaching with hydrochloric acid which gave a product containing 92% TiO_2.

Coconut pith is the waste fluffy material discarded during the separation of coconut fibres from the coconut husk. The annual production of pith in Kerala, India, and the world are 0.5, 0.65 and 3.6 million tonnes respectively. Practically all the pith is going to waste at present. In fact, the discarding of pith in back-waters has led to the pollution of back-waters in Kerala.

This paper describes the results of our experiments on the preparation of synthetic rutile by the reduction of ilmenite using coconut pith as a reductant. The reduction process has been studied using chemical analysis, scanning electron microscopy, X-ray diffraction and electron microprobe analysis.

2. Experimental methods and materials

Chemical assay of the coconut pith and pith charcoal was carried out using standard methods and the results are shown in Table I. The average composition of Kerala ilmenite [8] is shown in Table II. Reduction experiments were carried out in static conditions using pith and ilmenite in the weight ratio 4:1. The reaction set-up (Fig. 1) consisted of a stainless steel tube of length 75 cm and outer diameter 6.25 cm. Ilmenite was put on a bed

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TABLE I Chemical assay data of coconut pith

	Retted pith	Retted pith char
Fixed carbon (%)	37.10	72.45
Ash content (%)	7.10	19.00
Moisture content (%)	9.80	8.00
Sulphur (%)	0.20	0.22
Phosphorus (%)	0.11	0.30

of pith in the reaction tube above which a layer of remaining pith was placed again. The bed height was about 50 cm and ilmenite was placed in the middle. The reaction tube was then closed with a lid, made airtight using "O" ring and flanges, and heated in a furnace to the required temperature and time, while cold water was run through the cooling tubes. After a specified time, the tube was taken out from the furnace and cooled to room temperature. The product was taken out and put into water. The floating carbon particles were removed and the reduced ilmenite in the settled portion was dried in an oven at 110° C for 2 h. Chemical analysis of the samples was carried out using standard analytical methods.

Scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) studies were carried out using a Jeol Model 35C scanning electron microscope. A Philips X-ray diffractometer was used for the X-ray analysis. For leaching, the reduced sample (about 3 g) of ilmenite was heated with 100 ml of 20% hydrochloric acid at 80° C and stirred for 1 h. It was then filtered, washed with water, dried in an oven at 110° C for 2 h and analysed for the iron content.

TABLE II Average composition of Kerala ilmenite

Constituent	(%)
TiO_2	60.3
FeO	9.7
Fe_2O_3	24.8
SiO_2	1.4
CaO	0.15
MgO	0.65
Al_2O_3	1.0
MnO_2	0.4
Cr_2O_3	0.14
V_2O_5	0.26
P_2O_5	0.17
ZrO_2	0.60

3. Results and discussion

Coconut pith is an agricultural waste containing low sulphur, low phosphorus and low ash (Table I) and is therefore ideally suited for reduction purposes.

The ilmenite sample which was used for the experiments contained no metallic iron and most of the iron was in the form of ferric, a fact that was confirmed from the X-ray and chemical analysis. The total iron content was 28.5%, out of which 28.24% was in the form of ferric iron.

During heating, the ferric oxide becomes reduced slowly as per the following reactions:

$$C + O_2 \rightarrow CO_2 \tag{1}$$

$$CO_2 + C \rightarrow 2CO \tag{2}$$

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 \tag{3}$$

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2 \tag{4}$$

$$FeO + CO \rightarrow Fe + CO_2 \tag{5}$$

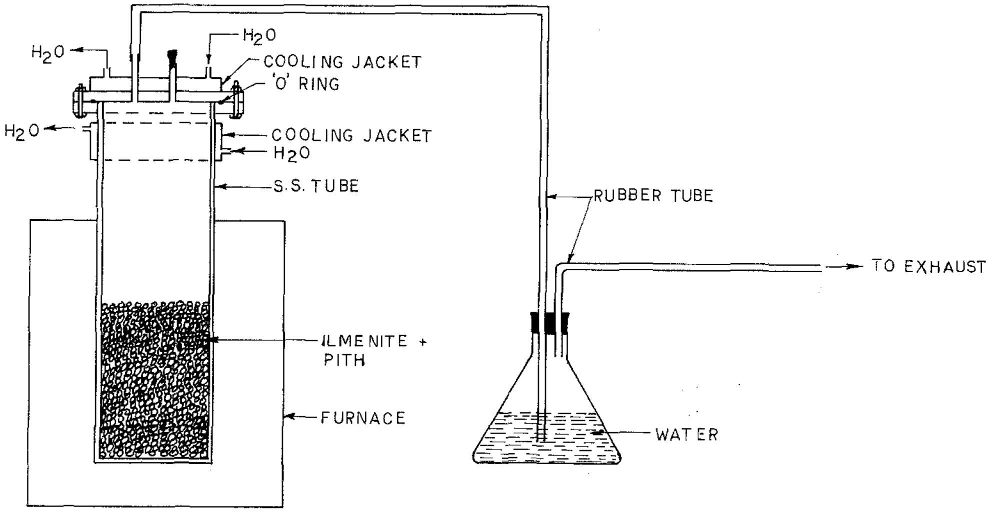

Figure 1 A schematic diagram of the reaction assembly.

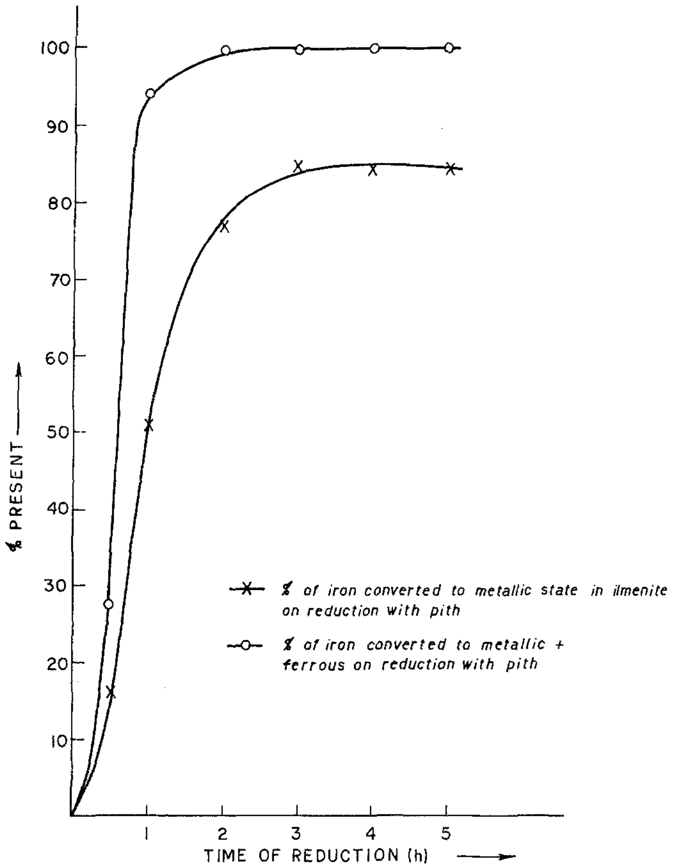

Figure 2 Reduction percentage against time of reduction.

Even though carbon was the reductant, it was shown by El-Guindy and Davenport [9] that above 1020° C the principal reduction takes place through CO gas. Hence, here also reduction of the ilmenite proceeded probably through the diffusion of gas into the interior of the particles. The reduction went on increasing with time at 1040° C as shown in Fig. 2. Fig. 2 is a plot of the quantities of metallic iron and metallic and ferrous iron on the basis of total iron present as a function of time. The reduction was fast and there was no induction period observed in the figure.

It was evident that in the first 3 h the reduction proceeded at a relatively rapid rate. In 1 h about 50% of the iron was already converted to metallic and only less than 10% was present in the ferric state. The total iron was converted to ferrous and metallic iron in 3 h. After 3 h about 77.2% of iron was in the form of metallic iron and the rest in the form of ferrous iron. After 4 h 84.7% of the iron was converted to metallic iron, after which there was no considerable effect of time on the reduction. It is clear that after 3 h there is no ferric iron present in the ilmenite. Fig. 3 is a plot of reduction temperature against percentage of metallic iron present, at constant time. It is evident from the figure that if the reduction time is reduced, the temperature is increased and vice versa, for achieving the same amount of reduction. After about 1050° C there is no considerable effect of time on reduction. As the metallic iron content at 2 h is only 21.5% at 1040° C, it is clear that at about 1040° C, the time required for maximum reduction is around 3 to 4 h.

The SEM pictures of the ilmenite samples are shown in Fig. 4. Fig. 4a shows the surface of the unreduced ilmenite particle, which shows a relatively smooth nonporous surface. In Fig. 4b, which is after reduction of 0.5 h at 1040° C, the appearance of cracks and minor pores is an indication that some reduction has taken place. As the reduction time increases, the size and number of pores increase, which is evident from the Figs. 4b to g. The CO gas formed from pith may be getting diffused into the particle causing more and more reduction with increase in time. Chemical analysis

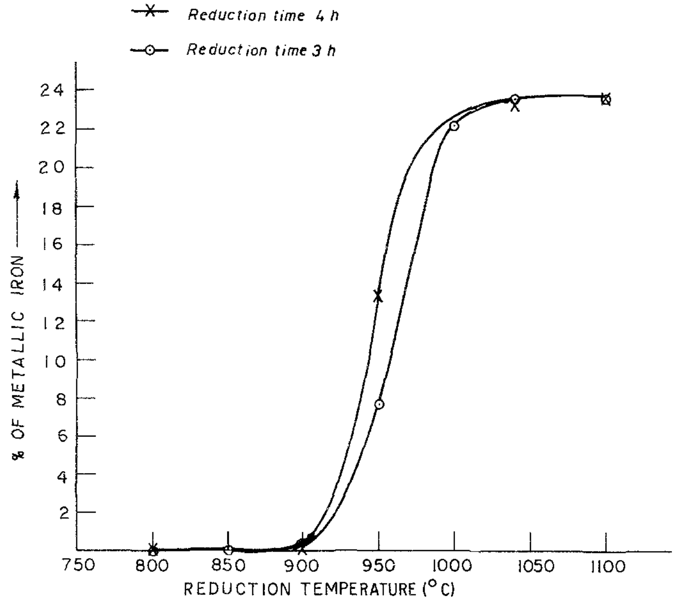

Figure 3 Reduction of ilmenite using pith at various temperatures.

data shows that the quantity of metallic iron goes on increasing with time. The electron microprobe studies (Figs. 5a and b) of the surface of the unreduced and reduced ilmenite particle shows that on the surface of the unreduced ilmenite particle there is very little iron. Probably, iron is present mainly inside the core of the particle. On reduction one obtains an increasing appearance of iron on the surface. In some of the experiments metallic iron globules are found separated from the ilmenite particles. This may be due to the volume change, which squeezes the particle due to the formation of rutile. Jones and Stephens [10] have also observed that on reduction of Australian ilmenite at 1200° C, agglomeration of the metallic iron occurred at the periphery of the grain.

The major peaks of the X-ray diffraction analysis of ilmenite at different stages of reduction are given in Table III. The maximum intensity peak in the 0.5 h reduced sample is that of ilmenite, while the metallic irion peak has only 27% relative intensity. As reduction proceeds the ilmenite peak slowly diminishes and disappears after 3 h, which may be due to the complete reduction of iron oxide to

TABLE III X-ray diffraction data (major peaks only)

Reduction time	Peak number	θ	d	Relative intensity (%)	Assignment
0.5 h	1	12.04, 16.37	3.69, 2.74	12.5, 100	Ilmenite
	2	13.83	3.23	33.33	Rutile
	3	23.31	1.95	27.08	Iron
1.5 h	1	13.80	3.23	38.78	Rutile
	2	16.30	2.75	55.10	Ilmenite
	3	22.43	2.02	100	Iron
2 h	1	12.04	3.69	26.47	Ilmenite
	2	13.76	3.24	40	Rutile
	3	22.38	2.02	100	Iron
3 h	1	11.97	3.72	26.47	Ilmenite
	2	13.78	3.24	44.12	Rutile
	3	22.08, 22.38	2.05, 2.02	26.47, 100	Iron
5 h	1	13.76	3.24	87.18	Rutile
	2	22.17, 22.41	2.04, 2.02	25.64, 100	Iron

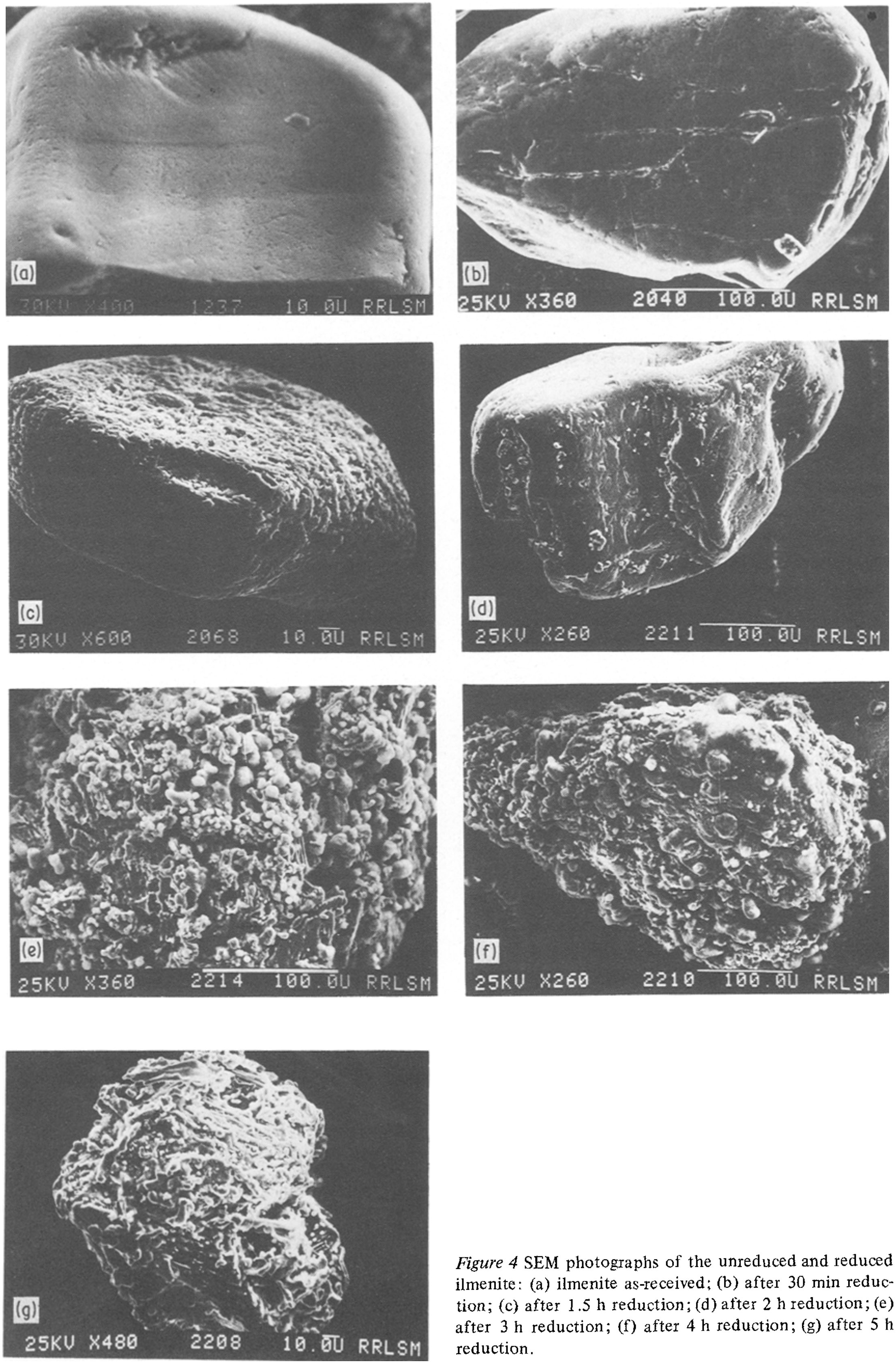

Figure 4 SEM photographs of the unreduced and reduced ilmenite: (a) ilmenite as-received; (b) after 30 min reduction; (c) after 1.5 h reduction; (d) after 2 h reduction; (e) after 3 h reduction; (f) after 4 h reduction; (g) after 5 h reduction.

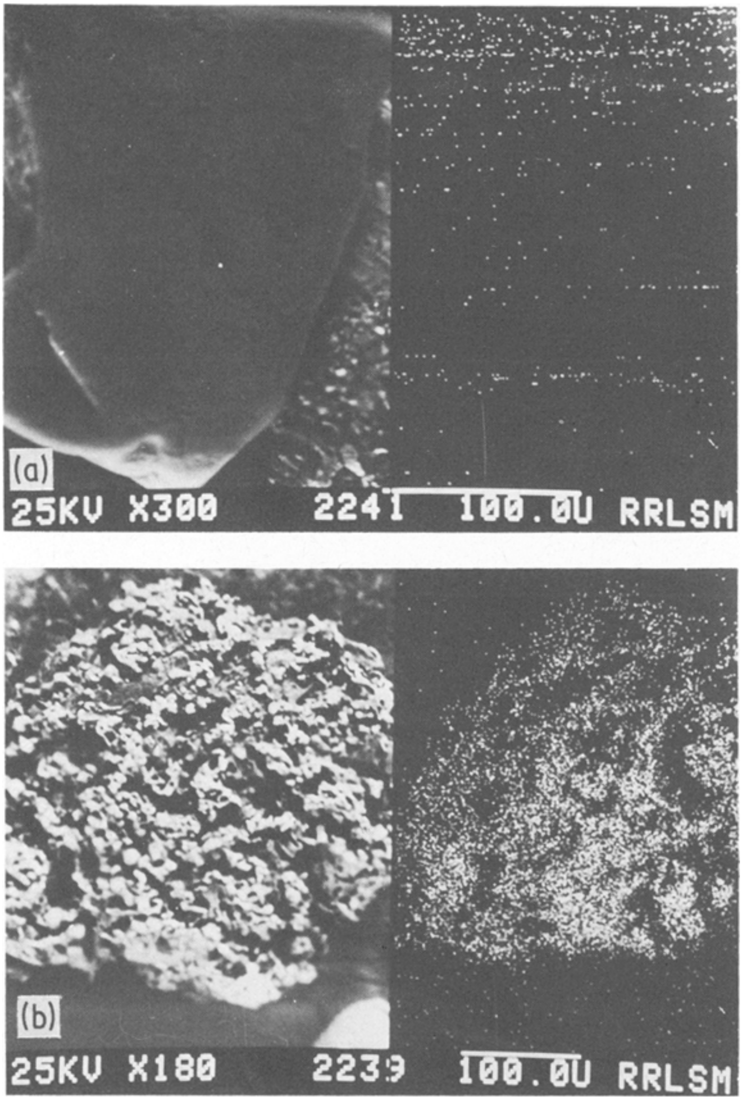

Figure 5 Electron microprobe of the surface of (a) unreduced ilmenite for iron, and (b) reduced ilmenite (1040° C, 4 h) for iron.

the metal or ferrous state, and hence decomposition of the ilmenite to give rutile. Consequently, rutile and metallic iron peaks become increasingly prominent. The X-ray data confirms the slow conversion of ilmenite to rutile and metallic iron. Decomposition of ilmenite is complete before 4 h.

The chemical analysis data of the reduced and leached ilmenite is given in Table IV. Leaching with dilute HCl removes iron from the sample. As reduction time increases, more iron is removed from the sample. The sample which was reduced for 1 h, contains about 21.5% iron after leaching while the one reduced for 4 h contains only 2.29% of iron. Fig. 6 shows a plot of percentage iron remaining after reduction and leaching against reduction temperature at constant time. It shows that the iron removed is directly proportional to the percentage of reduction. When reduction is higher, the iron removed by leaching is correspondingly high and hence iron remaining after leaching is lower. The trend is as seen in Fig. 3.

TABLE IV Chemical analysis data of the reduced and leached ilmenite

Number	Reduction time (h)	Iron present (%)
1	0.0	24.63
2	1.0	21.48
3	2.0	3.38
4	3.0	2.74
5	4.0	2.29
6	5.0	1.96

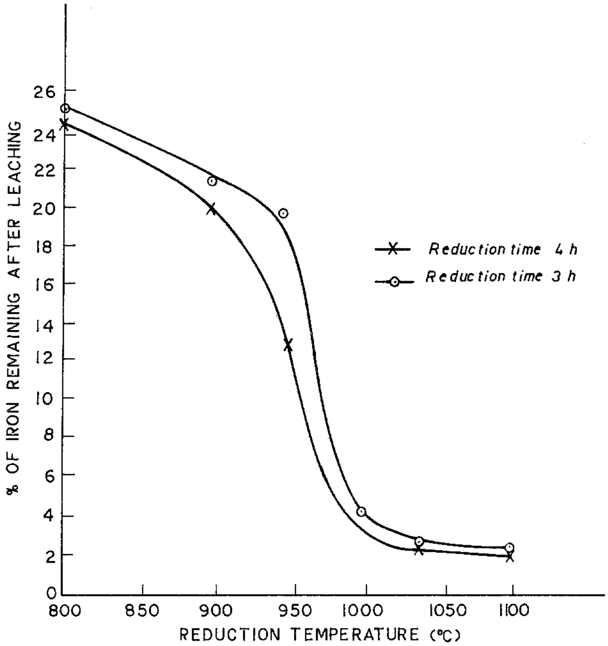

Figure 6 Plot of iron remaining against reduction temperature at constant time.

After about 1050° C, the effect of temperature is not very significant.

The data in Table IV shows the relation between time of reduction and the iron left after leaching at a reduction temperature of 1040° C. As the time of reduction increases, the quantity of iron left in rutile decreases. This decrease is prominent up to about 3 to 4 h, after which it is negligible. When reduction is higher, the quantity of iron leached will be higher and the quantity of iron left lower. The quantity of iron leached out increases up to about 4 h and then slowly stabilizes. Hence reduction at about 1050° C for about 3 h and leaching in dilute 20% HCl at 80° C gives a rutile sample which contains less than 3% iron.

4. Conclusions

The iron oxide present in ilmenite becomes reduced to iron on heating in presence of coconut pith. The study of the effect of time and temperature on the reduction process shows that the rate of reduction is directly proportional to time up to about 4 h and to temperature up to about 1050° C, after which there is no significant increase in reduction. At 4 h and 1040° C, about 84% of the iron is present as metallic iron and the rest as ferrous iron, which is confirmed by chemical analysis. SEM studies of the surface of the reduced ilmenite shows changes taking place on the surface due to reduction. X-ray diffraction data shows changes in the relative intensities of the peaks indicating gradual replacement of ilmenite by rutile and iron. Leaching out of iron from reduced particles is directly proportional to the percentage of reduction.

This study shows that the reduction of ilmenite at about 1050° C using pith as reductant for about 3 to 4 h converts all the iron in ilmenite to the metallic and ferrous state, which can be removed by leaching with 20% hydrochloric acid solution at 80° C for 1 h giving a rutile sample containing only about 2% iron.

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