# Effect of thermal and chemical treatments on carbon and silica contents in rice husk

M. PATEL, A. KARERA, P. PRASANNA
Regional Research Laboratory (CSIR), Bhopal 462 026, India

Thermal treatment of rice husk has been conducted up to 1000° C in air, oxygen, argon and non-oxidizing atmospheres. Chemical treatments consisted of HCl, H_2SO_4, HNO_3, NaOH and NH_4OH. Purity, particle size distribution and SEM micrographs of chemically treated samples are presented. Carbon and SiO_2 contents in rice husk, coked at different temperatures and time, have been determined to show that a $C:SiO_2$ ratio of 2:1, required for the production of solar grade silicon, can be achieved at low temperature. SiO_2 of 99% purity can be obtained by acid leaching. The results have been interpreted in terms of two types of bonding of silicon, a rigid structural framework, and selective sites for the preferential attack of acid and alkali in rice husk.

1. Introduction

For the production of solar grade silicon, the $C:SiO_2$ ratio is very important [1–5]. The ideal ratio is considered [2] to be 2:1 which can be varied by external additives or by the flow of CO_2. In the production of SiC and Si_3N_4 from rice husk, similarly, the amount of carbon and silica contents are to be controlled [6, 7]. The carbothermic reduction reaction in rice husk takes place as

$$2C + SiO_2 = Si + 2CO$$
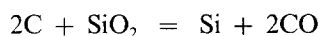
and the pyrolysed or coked rice husk [2] can have a $C:SiO_2$ ratio of 4:1 at 700 to 900° C. Chemical pretreatment of rice husk is also a requirement in the production of solar grade silicon in particular, and many other industrial products [1]. However, no systematic studies seem to have been made at lower temperatures in particular. The present paper deals with a systematic evaluation of carbon and SiO_2 in both thermally and chemically treated rice husks. The scope of the work has been extended to some basic findings on the nature of bonding between carbon and SiO_2.

The SiO_2 present in rice husk is described to be in a hydrated amorphous form like silica gel [8, 9]. Part of the silica may be tied up [10] with polysaccharides forming some sort of bonding [8] between silicon and the organic compounds. The location of SiO_2 is suggested to be in the epidermis portion of the rice hull and in the spaces between the epidermal tissues. The desilicified hulls [11] contains about 2.5% of SiO_2. No reports are, however, available to show the sites for the initiation of desilicification reactions and on crack propagation in rice husk.

2. Experimental procedure

The coking reaction was conducted in a 1 litre glass vessel with an outlet fitted in such a way that the environment surrounding the rice husk was non-oxidizing.

HCl, H_2SO_4 and HNO_3 used for acid treatment and NaOH and NH_4OH for alkali treatment were all of laboratory grade. All the reactions with alkali were conducted in polythene beakers.

For acid reactions, the rice husk was refluxed in a glass round-bottomed flask on a hotplate at about 100° C.

Thermogravimetric analysis (TGA) of samples was carried out in a Du Pont TGA equipment at a heating rate of 10 to 20° C min^{-1} in argon, air and O_2 atmospheres.

For optical microscopy a Leitz Metalloplan microscope was used. A Jeol JSM 35 CF SEM was used for SEM studies. All chemical analyses were carried out by standard wet chemical analysis methods.

3. Results and discussion

The composition of rice husk varies from place to place because of the soil conditions and the nature of the crops grown. The results presented here will be limited to rice husk obtained from suburb areas of Bhopal (Madhya Pradesh, India). The chemical analysis of this rice husk is shown in Table I. SiO_2 is found to be 22.12%; the carbon and water content is 74% and $(Al_2O_3 + Fe_2O_3 + CaO + MgO)$ constitute about 4%. The percentage of SiO_2 reported in the literature [3, 12, 13] varies from 15 to 22%. The

TABLE I Chemical analysis of raw rice husk

Constituent	Content (wt %)
Organic material and moisture	73.87
Al_2O_3	1.23
Fe_2O_3	1.28
CaO	1.24
MgO	0.21
SiO_2	22.12[†]
MnO_2*	0.074

*By atomic absorption spectrometry.
[†] Amounts of SiO_2 in the midrib and lamella of rice husk differ by 1%.

TABLE II Organic constituents of rice husk

Constituent	Content (wt %)	
	Organic material	Carbon
Cellulose	43.3	19.22
Lignin	22.00	17.93
D-Xylose	17.52	7.008
L-Arabinose	6.53	2.612
Methyl glucoronic acid	6.53	1.82
D-Galactose	2.37	0.846

organic part is composed [12] of cellulose, lignin and hemicellulose; the latter is a mixture of D-xylose, L-arabinose, methylglucoronic acid and D-galactose (Table II).

3.1. Thermal treatment
The volatile matter in rice husk contains organic matter as well as water. Elimination of the volatile matter is not spontaneous in a non-oxidizing atmosphere as it is in air or an oxidizing environment. Fig. 1 indicates the weight loss curves of rice husk at 200, 300 and 400° C at different durations in a non-oxidizing atmosphere. This atmosphere is composed of reducing gases coming from the rice husk. The maximum loss can be as much as 52.8%, which is at 400° C after 2 h of treatment. At 200 and 300° C, even after 6 h of coking, the loss does not attain 53%. It was presumed that heat treatment above 400° C or for a duration of more than 4 h may not be necessary as the loss had reached a constant value of 52 to 53% in 2 h of heating at 400° C.
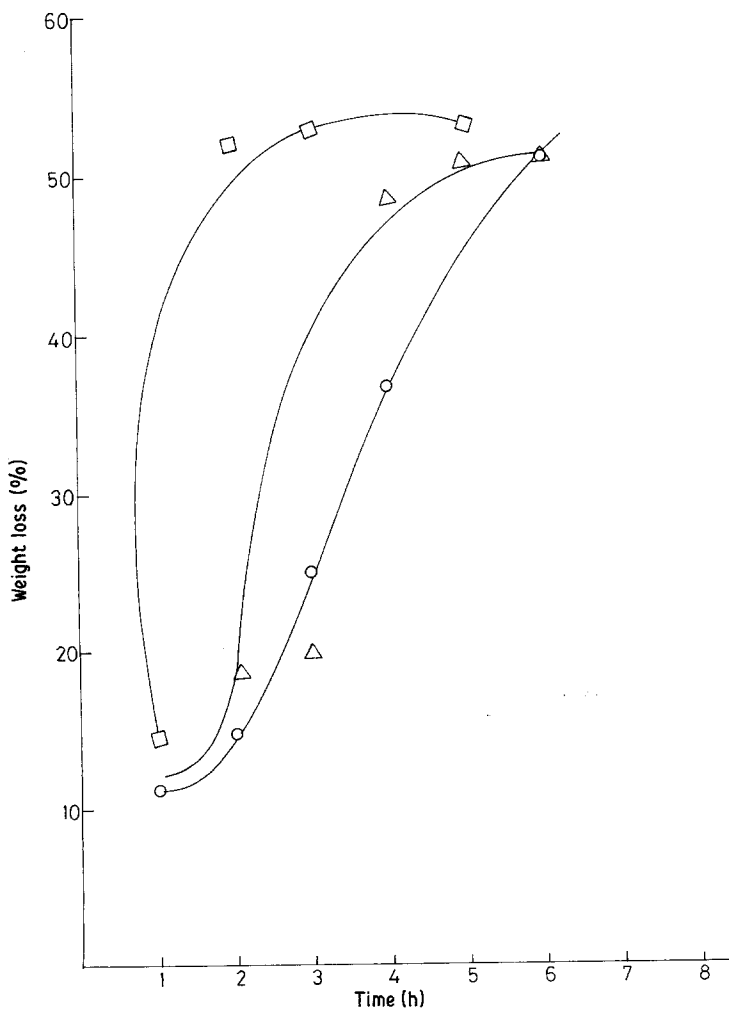
The coked rice husk samples were analysed for carbon and inorganic oxide contents at various temperatures. The values are calculated with respect to the weight of coked rice husk and not the raw rice husk (Table III). The percentage of carbon goes on decreasing with rise in temperature from 200 to 400° C in the heating durations of 1 to 6 h. Values of the inorganic oxide content increase correspondingly with increase in coking temperature and time. It can be seen that the inorganic oxide content reaches its maximum value of 45.9% at 400° C after 2 h of coking.

The percentage of volatile matter lost at 400° C is 52% after 2 to 3 h of heating in a non-oxidizing atmosphere. There is practically no further loss on increasing the heating period. The carbon to inorganic oxide ratios (C : I) are also calculated (Table III). The ratio varies from 3 : 1 to 1 : 1 and the requirement for solar grade silicon can be met within this range.

In the calculated values shown in Table II, 49% is the carbon content in rice husk. In the present sample, the experimental value is 54%. In fact, attainment of coked rice husk with 54% carbon is accomplished at 300° C after 5 h of heat treatment in a non-oxidizing atmosphere. These experimental conditions are very useful in the process of production of SiC from rice husk.

3.2. TGA studies
Thermogravimetric analyses of both raw and coked rice husks have been conducted in argon, oxygen and

Figure 1 Weight loss of rice husk with time at different temperatures: (O) 200, (△) 300, (□) 400° C.

TABLE III Carbon and inorganic oxides in rice husk coked at different temperatures for different periods

Duration (h)	200° C			300° C			400° C		
	Carbon (wt %)*	Inorganic oxides (wt %)†	C : I	Carbon (wt %)*	Inorganic oxides (wt %)†	C : I	Carbon (wt %)*	Inorganic oxides (wt %)†	C : I ratio
1	75.7	24.5	3.08 : 1	–	–	–	75.2	24.8	3.03 : 1
2	73.1	26.9	2.71 : 1	73.1	26.9	2.71	55.1	44.9	1.22 : 1
3	66.2	33.8	1.95 : 1	65.1	34.9	1.86	54.1	45.9	1.17 : 1
4	64.2	35.8	1.79 : 1	–	–	–	54.1	45.9	1.17 : 1
5	–	–	–	54.7	45.3	1.20	–	–	–
6	55.9	44.1	1.26 : 1	–	–	–	–	–	–

*Calculated with respect to coked rice husk.
†Inorganic oxides are estimated in Table I.

air up to 900° C. Fig. 2 indicates the percentage loss against temperature curves for raw rice husk in argon and air. It can be seen that the loss becomes significant above 200° C, and the trend continues up to 500 to 550° C in raw rice husk. It is surprising that the percentage loss is higher in argon atmosphere than in air. The air surrounding the sample is contaminated with a reducing atmosphere due to the burning of carbon, and therefore the loss in this case is less than in an argon atmosphere. Beyond 600° C, the loss becomes insignificant and is therefore not presented in this graph.

TGA curves of coked rice husk are presented in Fig. 3. As the reducing atmosphere caused by organic compounds is not emitted on the treatment of coked rice husk, the percentage loss in oxygen is much higher than that in argon in the present figure. An oxygen atmosphere causes immediate burning of the sample at 400° C and the loss takes place abruptly. The loss of volatile matter in an argon atmosphere, on the other hand, takes place slowly even up to a temperature of 800° C.

The percentage loss against temperature curves for NaOH- and HCl-treated rice husk samples are shown in Fig. 4. The weight loss follows rapidly on heat treatment at 200 to 300° C and reaches saturation at around 600° C. As the NaOH-treated rice husk contains mostly carbon, the percentage loss value is higher than for the HCl-treated rice husk. The later product contains, on the other hand, mostly SiO_2 and some amount of organic compounds. The atmosphere here is air in both cases. It can be seen that the NaOH-treated rice husk loses about 96% of its weight which is all carbon (see Table V) below.

3.3. Chemical treatment
Rice husk was subjected to both acid and alkali treatments: HCl, H_2SO_4 and HNO_3 as acid (Table IV) and NaOH and NH_4OH as alkalis (Tables V and VI). Table IV summarizes the results obtained with HCl
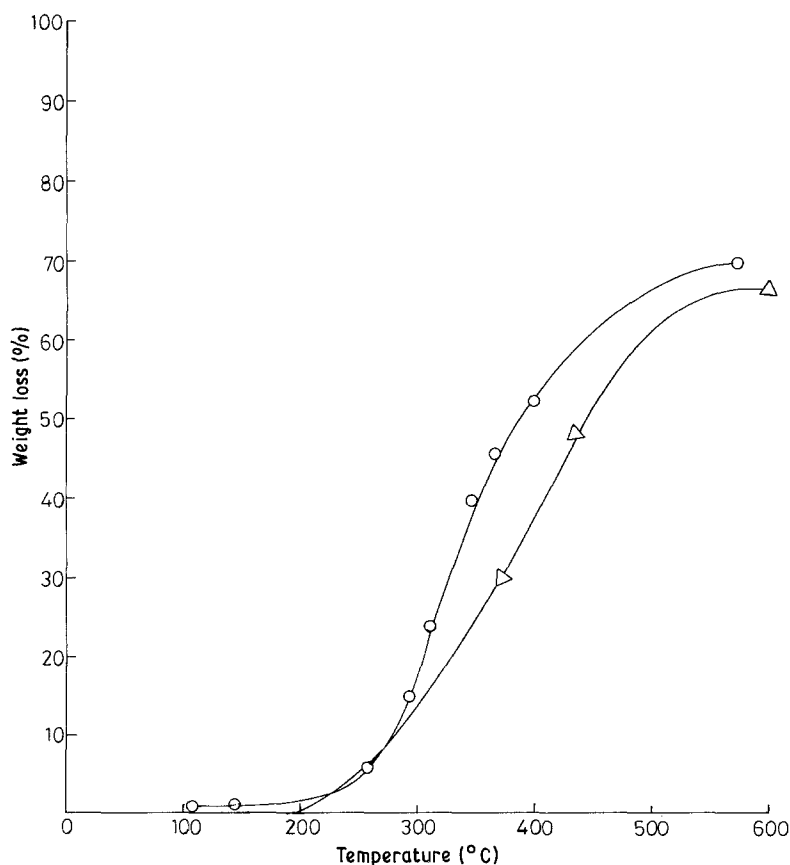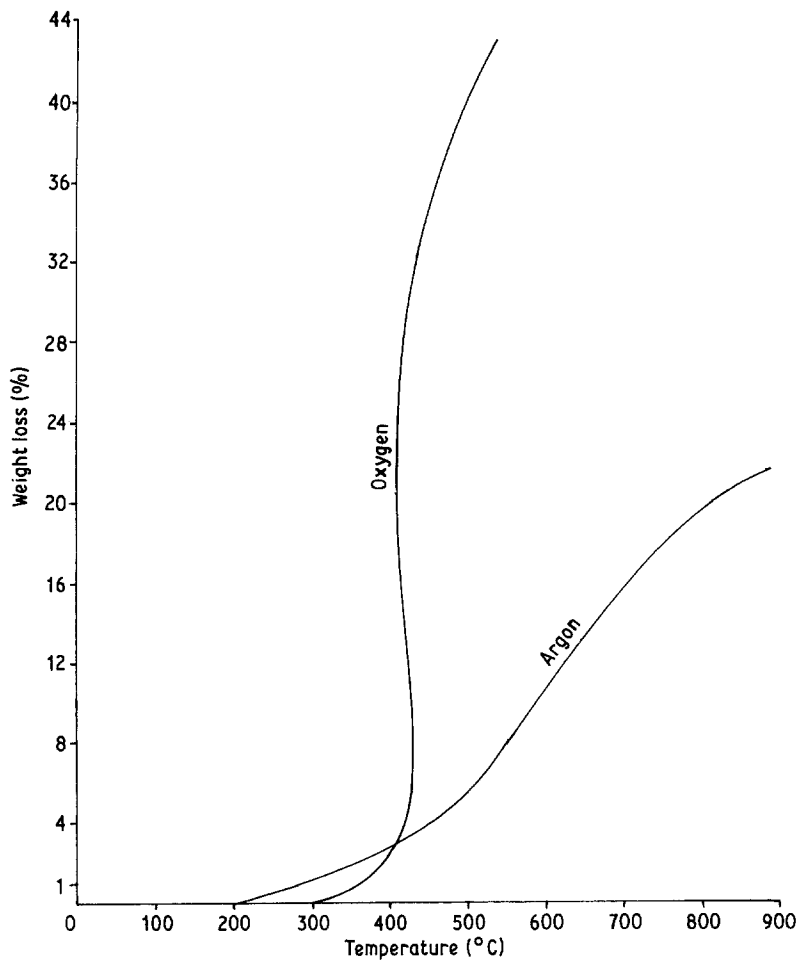

Figure 2 TGA curves of raw rice husks in (△) air and (○) argon atmospheres.

Figure 3 TGA curves of cooked rice husk in argon and O_2 atmospheres.

treatment (4 to 12 N), 2 N H_2SO_4 and 8 N HNO_3 for 2 to 6 hours duration. Acid treatment, except with HNO_3, causes charring of the cellulose part which separates out from the silica structural network.

The amount of silica obtained from raw rice husk does not follow any linear relationship with time and the normality of acid used during treatment. In HCl, the yield of SiO_2 varies from 31 to 34% with respect to this raw rice husk. In H_2SO_4 (2 N) the yield of SiO_2 obtained with respect to treated husk is 28.5%, whereas
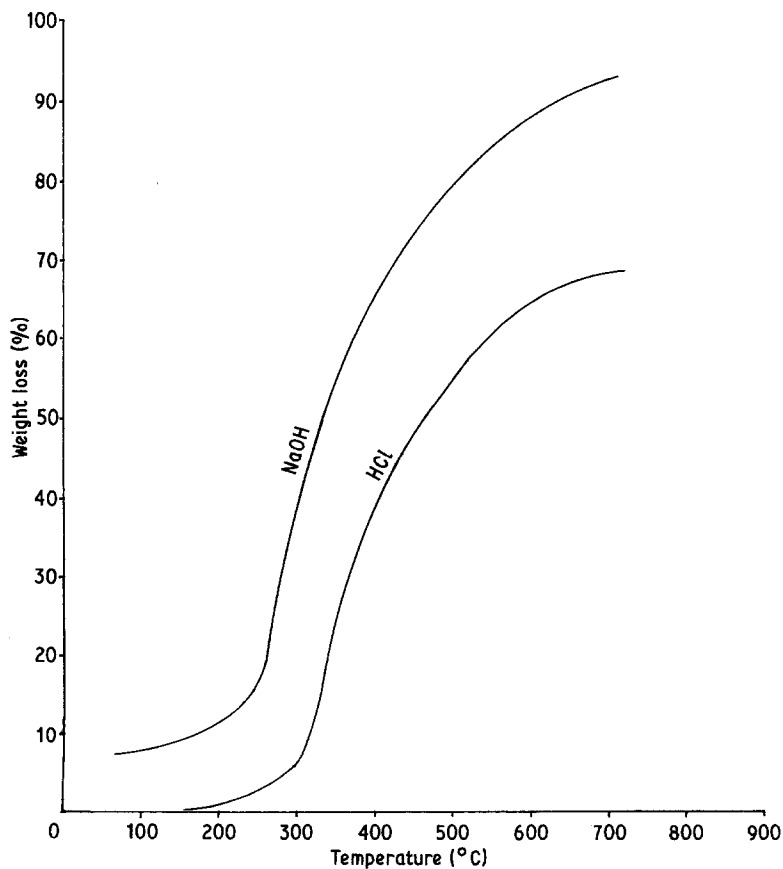
Figure 4 TGA curves of chemically treated rice husk.

TABLE IV Percentages of carbon and silica obtained on acid treatment of rice husk

Acid	Time of heating (h)	SiO_2 (wt %)*	SiO_2 (wt %)†
12 N HCl	2 to 5	32.37	19.70
10 N HCl	2 to 6	35.41	22.25
8 N HCl	2 to 6	34.77	22.07
4 N HCl	2 to 6	30.98	21.62
2 N H_2SO_4	2 to 6	28.47	18.09
8 N HNO_3	2 to 6	41.42	18.77

*With respect to treated rice husk.
†With respect to raw rice husk.

it is 41.4% in $HNO_3(8 N)$. Such variations are due partly to the solubility of SiO_2 as H_2SiO_3. In fact, the reflux reactions are difficult to carry out in H_2SO_4 or HNO_3, and therefore only limited experiments have been carried out (Table IV).

Treatment of rice husk in NaOH, on the other hand, dissolves SiO_2 as Na_2SiO_3 as follows:

$$SiO_2 + 2NaOH = Na_2SiO_3 + H_2O$$
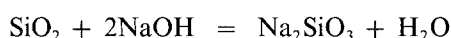
NH_4OH, being a very weak alkali, cannot dissolve out SiO_2 and all the SiO_2 remains intact (24%). This value is with respect to the treated rice husk. The amount of carbon is decreased from 95% in NaOH to 75 to 76% in NH_4OH. The percentage of silicon retained does not vary according to the strength of NH_4OH used (Table VI).

A little insight into the structure of the organic compounds present in rice husks (Fig. 5a) can support the concept of the bonding of silicon with organic molecules.

Cellulose, $(C_6H_{10}O_5)_n$, the main constituent of rice husk, being a polysaccharide, does not seem to posses considerable bonding property. Lignin, which exists with cellulose, is mosly inert and therefore it is also not expected to be suitable for bonding.

TABLE V Treatment of rice husk with NaOH

Normality	Carbon (wt %)	SiO_2 (wt %)*
3	97.903	2.097
6	96.885	3.115
9	93.330	6.670
12	94.930	5.070

*Average of 2 to 3 experiments, calculated with respect to raw rice husk.

TABLE VI Treatment of rice husk with NH_4OH

Normality	Carbon (wt %)	SiO_2 (wt %)*
3	76.96	23.04
6	76.52	23.49
9	75.99	24.01
12	76.61	23.39

The remaining four organic materials in rice husk are aldehydes (monosaccharides) which become polar due to an electromeric effect. In the aldehyde group, the electromeric effect operates as shown below:

$$\begin{array}{c} H \\ | \\ -C=O \rightarrow H\overset{+}{C}-O^- \end{array}$$
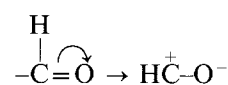
This type of electron transfer is brought into play only under the influence of an attacking reagent. It seems therefore that in rice husk, in addition to free SiO_2, silicon is bonded with monosaccharides only. The possible bonding of silicon with four aldehyde residues, as indicated above, is shown in Fig. 5b.

Based on the assumption that four monosaccharide molecules react with one atom of silicon (as silicon is tetravelent), the percentages of silicon that can remain bonded with different aldehyde compounds have been calculated (Table VII). A maximum of 2.88% Si, equivalent to 6.15% SiO_2, can be retained according to this calculation. The experimental result in Table V
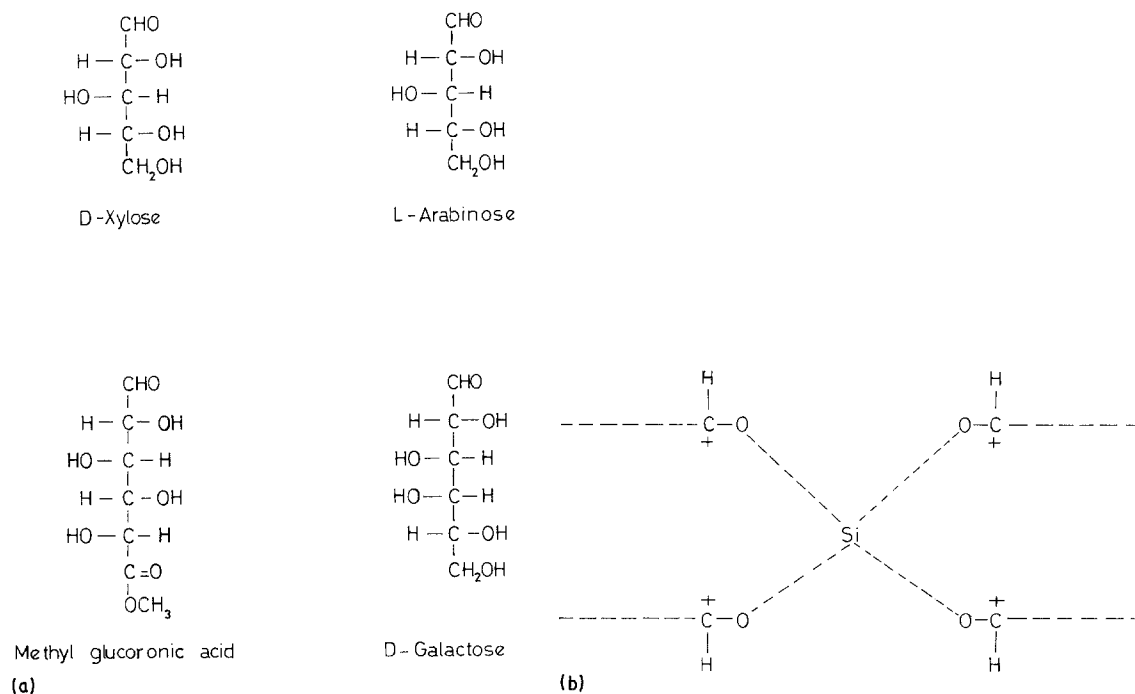

Figure 5 (a) Structural formulae of the carbohydrates present in rice husk. (b) Possible bonding of silicon with carbohydrate in rice husk.

2461

TABLE VII Calculated contents of silicon and SiO_2

Organic constituent	SiO_2 (wt %)	Silicon (wt %)
D-Xylose	5.179	2.421
L-Arabinose	0.225	0.225
Methyl glucoronic acid	0.3465	0.162
D-Gluctose	0.145	0.068
Total	6.1515	2.876

indicate that different percentages of SiO_2 can be retained by rice husk according to the normality of NaOH used. The calculated value of 6.15% tallies with the experimental value obtained at 9 N (Table V).

At lower concentrations below 9 N, some amount of silicon is also retained in rice husk (1 to 3% as SiO_2) which we assume to be bonded firmly with the mono-saccharides. Martin [11] has reported that 2.5 wt % SiO_2 is always retained on disilicification. This percentage varies, as the binding energies between silicon and the four monosaccharides are different; they are released in accordance with the concentration in NaOH.

3.4. Purity and particle size analysis

SiO_2 produced from rice husk by HCl treatment is of high purity (99%). It looks white and is free-flowing in nature, appearing to be in a fibrous or needle form.

The purity of the product hardly varies on increasing the acid concentration or the time of reflux reaction. The experiments were conducted in 4 to 12 N HCl and 1 to 12 h of reflux. Washing of the acid-treated rice husk mixtures containing silica and carbonaceous matter is continued until the filtrate is free from acid. The temperature of carbonization has preferably to be below 700° C to avoid any transformation of amorphous to crystalline form. The purity cannot, however, be increased above 99%; the remaining 1% may be metal oxides insoluble in acid.

Fig. 6 shows the cumulative mass percentage against the equivalent spherical diameter. 90% of the particles give values of less than 20 µm.

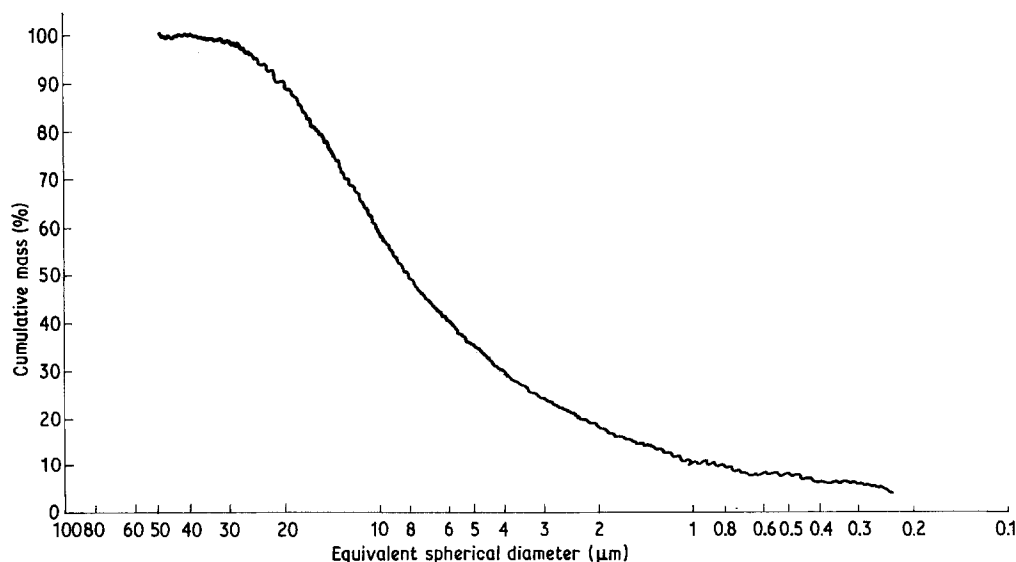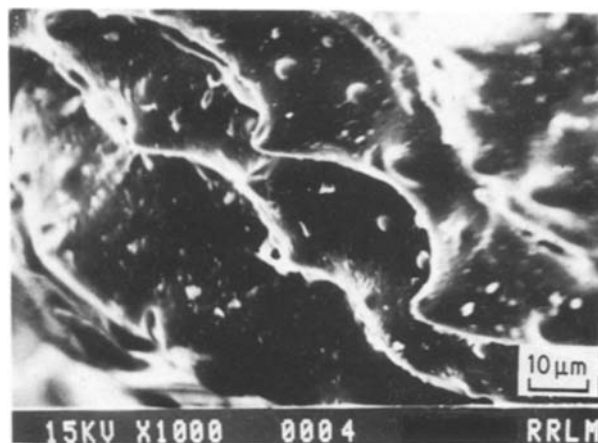As the SiO_2 obtained is of high purity, free-flowing

Figure 7 SEM micrograph of raw rice husk.

fine particle size and is resistant to thermal transformation up to 700° C, the product may be suitable as a dispersoid in metal–ceramic composite materials. This product may be better than when simply burnt in air.

3.5. Microscopic studies

All the products, both thermally and chemically treated, have been examined in optical microscopy. However, as SEM micrographs are presented, these will be omitted. The structural network typical of rice husk is observed clearly, even at magnifications of 25 or 50 × in all chemically treated samples, irrespective of the concentration of acids or alkali used.

Rice husk is represented by a regular well-defined layered structure (Fig. 7) as observed in vermiculite and other phyllosilicates [14]. SiO_2 obtained from acid treatment of rice husk continues to preserve the layered type of structural network (Fig. 8). Rice husk treated with HCl of strength as much as 12 N also produces SiO_2 retaining the structural framework. It appears that the organic molecules are arranged over the structural backbone in the natural state in a way similar to the bone and flesh arrangement in human beings. Acid takes away the organic part leaving behind the silica
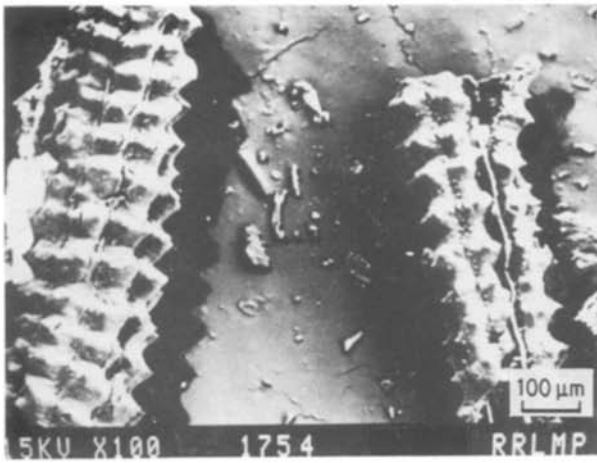

Figure 6 Particle size analyses of silica from rice husk (− 350 mesh particles used).

Figure 8 SEM micrograph of silica from rice husk.

Figure 11 SEM micrograph of outer epidermis of acid-treated rice husk.

skeleton. The SEM micrograph shows that the peak propagates along the Y-axis first and then the X-axis. This is evident especially in the right side of the micrograph (Fig. 8). In the inner surface the structure is plane, especially after acid treatment (Fig. 9). The silica backbone is probably grown over a plane surface. Some cracks occur around the summits also (Fig. 10). Fig. 11, taken at a higher magnification, shows the way in which the organic part has been etched out by acid, leaving behind the silica part in folds at the summit.

Alkali treatment of rice husk also cannot destroy the inherent structure of the husk. NaOH treatment removes the SiO_2, leaving behind the fibrous organic material (Fig. 12) which is supposed to be complementary to Fig. 8. Holes are observed in between which are probably formed as a result of alkali attack on the rice husk. As part of the SiO_2 is in intimate contact or bonded to the organic molecules, some silicon remains intact. It is observed that the lower the concentration of alkali, the lesser is the amount of silicon retained by
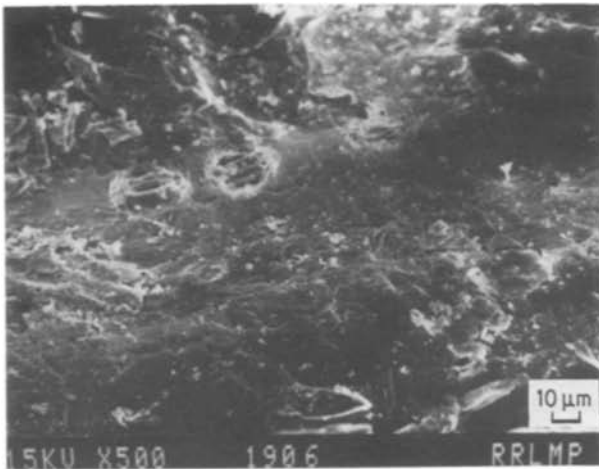

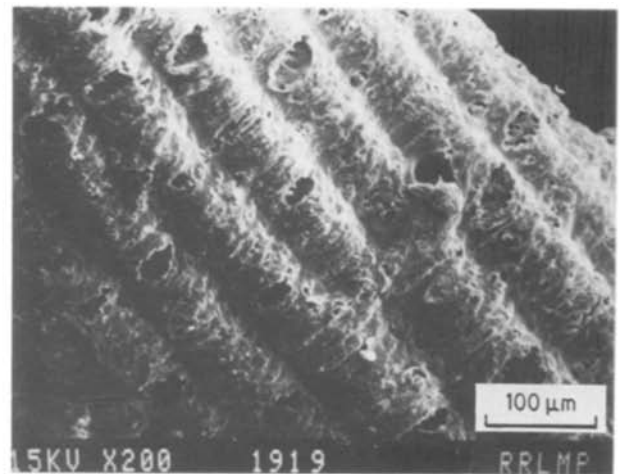*Figure 9* SEM micrograph of inner epidermis of acid-treated rice husk.

Figure 12 SEM micrograph of desilicified, alkali-treated (NaOH) rice husk.
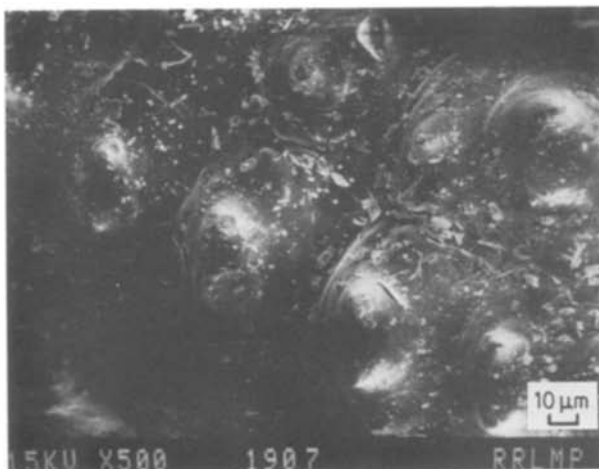

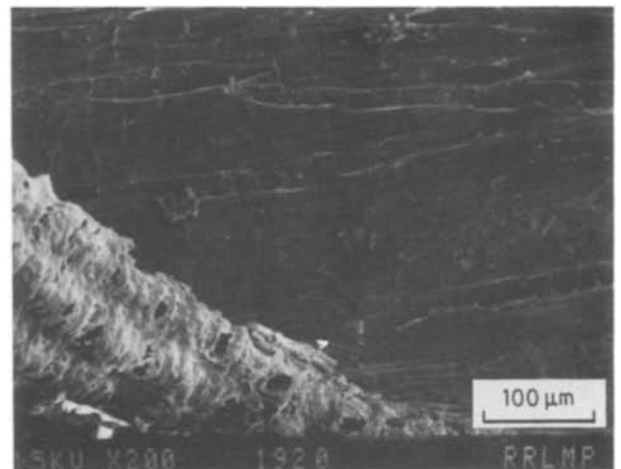*Figure 10* SEM micrograph of siliceous outer epidermis of acid-treated rice husk.

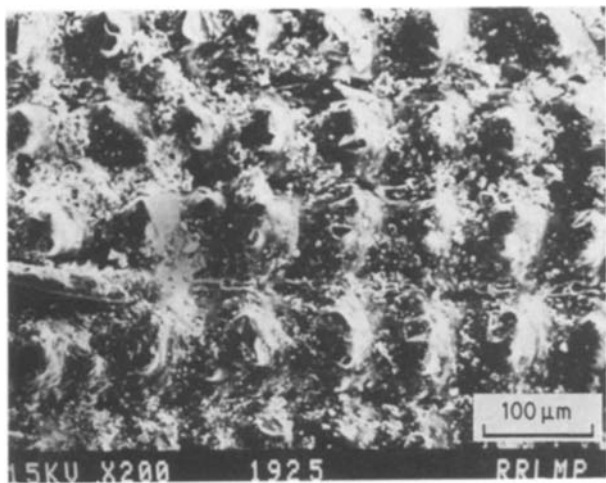*Figure 13* SEM micrograph of desilicified, alkali-treated (NaOH) rice husk.

2463

Figure 14 SEM micrograph of NH$_4$OH-treated rice husk.

the treated husk. The concentrated (> 9 N) NaOH solution cannot penetrate through the holes so easily as the relatively less concentrated 3 N NaOH solution. As with acid treatment, the inner surface of rice husk remains plane on NaOH treatment (Fig. 13). NH$_4$OH treatment is less effective than NaOH, as the micrograph in Fig. 14 indicates.

4. Conclusions

The C : SiO$_2$ ratio of 2 : 1 required in the production of solar grade silicon can be achieved at 200 to 400° C in the atmosphere given out during coking of the rice husk itself. This ratio varies according to the atmosphere. Acid leaching of rice husk can produce SiO$_2$ of 99% purity. Rice husk has a fairly rigid structural backbone formed by silicon to which the monosaccharides are bonded. Part of the silicon is also present in the free form.

References

1. A. KARERA, S. NARGIS, S. PATEL and M. PATEL, *J. Sci. Ind. Res.* **45** (1986) 441.
2. L. P. HUNT, J. P. DISMUKES and J. A. AMICK, *Proc. Electrochem. Soc.* (1981) 81.
3. J. A. AMICK, *J. Electrochem. Soc.* **129** (1982) 864.
4. H. D. BANERJEE, H. N. ACHARYA and S. K. DUTTA, *Mater. Lett.* **2** (4A) (1984) 265.
5. H. D. BANERJEE, S. SEN and H. N. ACHARYA, *Mater. Sci. Eng.* **52** (1982) 173.
6. M. PATEL, C. B. RAJU, A. K. RAY and A. KARERA, Indian Patent filed No. 1 NP/91/85/Pat. (1985).
7. S. B. HANA, N. A. L. MANSOUR, A. S. TAHA and H. M. A. ABDALLAH, *Br. Ceram. Trans. J.* **84** (1985) 18.
8. F. C. LANNING, *J. Agric. Food Chem.* **11** (1963) 435.
9. C. STERLING, *Amer. J. Bot.* **54** (1967) 840.
10. S. L. LIU and C. H. HO, *J. Chin. Chem. Soc.* **6** (1960) 41.
11. J. I. MARTIN, MS thesis, Louisiana State University (1938).
12. N. K. SHARMA, S. WILLIAMS and A. ZANGWIL, *J. Amer. Ceram. Soc.* **67** (1984) 715.
13. J. H. CHENG and LUNGWEI, in Proceedings of CIMME Annual Convention, Miaoli, Taiwan, December 1979 p. 105.
14. M. PATEL, *X-ray Spectrometry* **10** (2) (1981) 82.