

Utilization of Silica in Rice Hulls as Raw Materials for Silicon Semiconductors

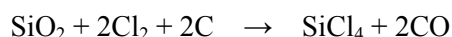
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Abstract

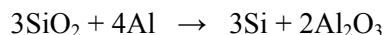
Highly pure silicon and silicon compounds are required in high technology products such as semiconductors and solar cells. Rice hulls consist of 71 to 87wt% organic components such as cellulose and 13 to 29wt% inorganic components. In rice hulls, 87 to 97wt% of the inorganic components are silica (SiO₂). Rice plants absorb water-soluble siliceous ions via the roots. These ions are transported to stems, leaves and rice hulls by sap flow. In rice hulls, siliceous ions accumulate at the cuticle outside of the epidermis.

The production of pure silicon compound (SiCl₄) and of silicon metal as the starting material for purification from rice hull ash is proposed to utilize rice hull SiO₂ in high technology industries. In one process, SiO₂ in rice hull ash reacts with Cl₂ on the presence of C and is converted to SiCl₄.



The SiCl₄ is purified by distillation. The production of SiCl₄ from rice hull ash is much more efficient than that from mineral SiO₂.

In another process, SiO₂ in rice hull ash reacts with aluminum (Al) to synthesize Si and Al₂O₃.



The reactivity of rice hull SiO₂ is higher than that of mineral SiO₂.

Although rice hulls are now utilized for agricultural materials and fuel, rice hull SiO₂ also has high potential for use as industrial raw materials.

Key words: Rice hull silica, Silicon metal, Silicon tetrachloride, Silicon solar cell, Silicon semiconductor

Introduction

Silica (SiO₂) is contained in siliceous plants such as rice, wheat and scouring rush. Rice plants absorb water-soluble siliceous ions via their root. The ions are transported to stems, leaves and rice hulls by sap flow. In rice hulls, siliceous ions accumulate at the cuticle outside of the epidermis. In 2007, 628 million tons of paddy were produced worldwide, 11.5 million tons in Japan and 28.0 million tons in Thailand (Table 1).⁽¹⁾ Rice hulls are agricultural by-products with 13 to 29wt% inorganic components and 71 to 87wt% organic components such as cellulose depending on the species, climate and geographic location of growth. The inorganic

components contain 87 to 97% SiO₂ in hydrated amorphous form with small amounts of alkali and other trace elements. The SiO₂ accumulates between the epidermis and the cuticle of the rice hull as hydrated SiO₂. This SiO₂ appears in the cell wall of the epidermis even if the organic components in rice hulls are removed by combustion. Hara (1986) reported on the chemical composition of rice hull ash worldwide and determined that their SiO₂ content exceeds 90wt%.⁽²⁾ More than 25 million tons of SiO₂ can be reproduced by rice production annually. The SiO₂ produced from siliceous ions (e.g., SiO₃²⁻) is assumed to be highly reactive because of its fine particles, large porosity, good grindability and large surface area.

Table 1 Production of paddy, rice hull and rice hull ash in 2007.

Country	Paddy (x10 ⁶ tons)	Rice hull (x10 ⁶ tons)	Silica (x10 ³ tons)
China	188.19	37.64	7.528
India	140.13	28.03	5.606
Indonesia	53.62	10.72	2.144
Vietnam	35.33	7.07	1.414
Thailand	27.97	5.59	1.118
Myanmar	15.55	3.11	622
Philippines	15.19	3.04	608
Brasil	11.88	2.38	476
Japan	11.49	2.30	460
USA	9.19	1.84	368
Pakistan	8.26	1.65	330
S. Korea	6.39	1.28	256
World	628.09	125.62	25.124

It is assumed that 20wt% of paddy is rice hull and 20wt% of rice hull is SiO₂.

It is possible to produce raw materials of silicon semiconductors, highly pure silicon compounds, or silicon metal from the active SiO₂ in rice hulls. If the active SiO₂ in rice hulls reacts with chlorine gas in the presence of carbon, the SiO₂ can easily and efficiently change to SiCl₄ at a lower temperature, even though silica sands react with chlorine gas in the presence of carbon at 1070°C and the conversion of SiO₂ to SiCl₄ is 3 to 40% varying with mining locations.⁽³⁾

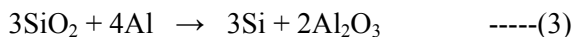


SiCl₄ is purified by distillation because of its boiling point of 57.6°C, and the highly pure SiCl₄ is changed to highly pure Si metal by reaction with Zn metal.⁽⁴⁾ Silicon metal is commercially prepared by reaction of high-purity silica with wood, charcoal, and coal in an electric arc furnace using carbon electrodes. At temperatures over 1900°C, carbon reduces silica to silicon according to the following chemical reaction,



The silicon produced via this process is called metallurgical grade silicon and is at least 98% pure.

Si metal can be produced by several processes. One of these processes is the reaction of SiO₂ with aluminum (Al) metal as shown below.



Wang, *et al.* (1993) reported that the adiabatic combustion temperature of this reaction is 1760K, and the product Si (melting point, 1683K) is melted.⁽⁵⁾ If the active SiO₂ in rice hulls reacts with

Al, it can be easily and efficiently changed to Si at a lower temperature.

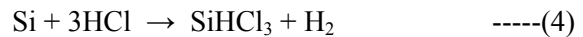
This paper discusses efficient SiCl₄ production by chlorination and efficient Si metal production by reaction with Al metal of active SiO₂ in rice hull ash.

Materials and Experimental Procedures

SiCl₄ Production by Chlorination of SiO₂ in Rice Hulls

Purification of Silicon and Silicon Compounds

Silicon and silicon compounds are utilized in semiconductors, advanced ceramics, optical fiber, and so on. These products require highly pure silicon metal or silicon compounds as raw materials. In the modern industrial purification process, metallic silicon with 98.5% purity is chlorinated by HCl to produce trichlorosilane (SiHCl₃, B.P. 31.8°C) at 300°C with Cu catalyst, and the SiHCl₃ is purified by distillation.



Highly pure SiHCl₃ is converted to highly pure polycrystalline silicon by hydrogenation and/or disproportionation. Metallic silicon is produced from electric smelting of silica stone and carbon such as charcoal. The smelting process needs silica stone with more than 99.0% purity and electricity of 16MW/ton-Si.

In another purification process, SiO₂ reacts directly with Cl₂ in the presence of carbon to produce silicon tetrachloride (SiCl₄) that can be purified by distillation because of its boiling point of 57.6°C. In contrast to the conventional purification process using SiHCl₃, the SiCl₄ production process does not require smelting of Si and pure silica stone as a raw material of Si metal. This process is suitable for countries lacking highly pure silica stone resources and sufficient electricity. However, the chlorination of mineral SiO₂ (amorphous, opal) proceeds at a temperature above 1300°C, and the chlorination process is not industrialized because of the corrosion of reactor materials by chlorine gas at a reaction temperature above 1300°C. The modern chlorination process is utilized for smelting Ti metal at temperatures below 1000°C. We developed a process for producing SiCl₄ from SiO₂ in rice hulls with high efficiency at temperatures below 1000°C.^(4, 6, 7, 8, 9)

Purification of SiO₂ in Rice Hulls

In 1973, Basu, *et al.* (1973) reported on efficient SiCl₄ production from active SiO₂ in rice hulls.⁽³⁾ According to their results, a mixture of SiO₂ and C that was prepared by pyrolysis of rice hulls in N₂ could be chlorinated at 1000°C to produce a nearly quantitative yield of SiCl₄.

We also examined the chlorination of pyrolyzed rice hulls^(4, 6) by conducting chlorination experiments using a chlorination reactor (Figure 1). Pyrolyzed rice hull samples that contained 45.3wt% SiO₂ and 53.6wt% C were prepared by pyrolysis of rice hulls in Ar at 700°C. A 1g sample in an alumina boat was set in the center of the quartz reactor with a 30mm inner diameter and was heated to the prescribed temperature from 600 to 1000°C in Ar flowing at 100mL/min by a horizontal electric furnace. After 30min at the prescribed temperature, the gas stream of 100mL/min was changed from argon to chlorine and chlorination was started and the reaction time was the contact period of chlorine gas. The conversion of SiO₂ to SiCl₄ was estimated from the loss of SiO₂ by treating reaction residue by HF and the amount of SiCl₄ in the effluent gas after the reactor was produced from the loss of SiO₂ by chlorination. Figure 2 presents the chlorination rate curves from 600 to 900°C for the pyrolyzed rice hulls and from 900 to 950°C for the mixture of SiO₂ (reagent grade, amorphous)-activated carbon with a SiO₂/C weight ratio of 0.85 (the same ratio as that of the pyrolyzed rice hulls) as a comparison. Eighty percent of the SiO₂ in the pyrolyzed rice hulls were converted to SiCl₄ by chlorination at 900°C for 1hr. However, the conversions of the mixture of amorphous SiO₂ and activated carbon were 3% at 950°C for 1hr. and 0.5% at 900°C for 1hr. These results indicated that the pyrolyzed rice hulls were very reactive and that the SiO₂ in rice hulls could be efficiently converted to SiCl₄.

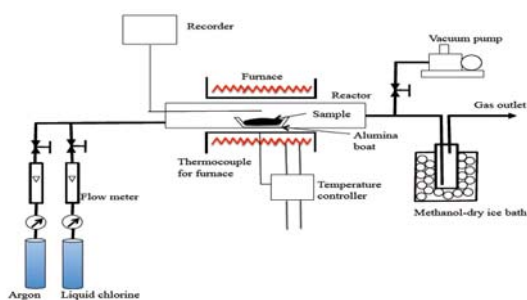


Figure 1. Schematic of the 30mm chlorination reactor system.

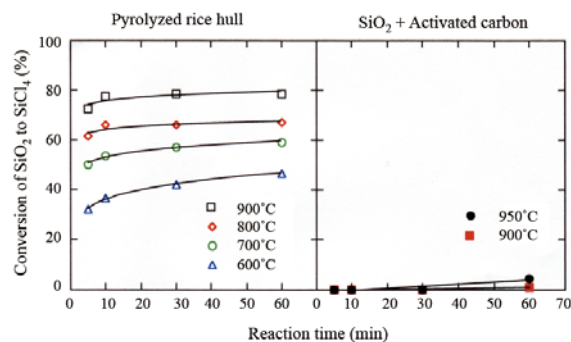


Figure 2. Conversion of SiO₂ to SiCl₄ vs. reaction time for chlorination of pyrolyzed rice hull and SiO₂ + activated carbon.

Purification of SiO₂ in Rice Hull Ash

The use of rice hulls as a raw material for producing SiCl₄ could lead to lower operating costs, due to the cheapness of rice hulls at a mill site. However, with mass production of SiCl₄ from rice hulls, economical collection and transportation of raw rice hulls is difficult because the specific gravity of rice hulls is 0.1 and rice fields are very broad.

In several countries, rice hulls are an important biomass. Rice hulls are utilized as fuel for electric power generation because the heat of combustion is 16,318kJkg⁻¹, and a large amount of dense rice hull ash is produced as a by-product. Rice hull ash is almost unutilized, although a small amount is utilized as a component of cement. The utilization of rice hull ash as a SiO₂ source for chlorination is more advantageous than collecting and transporting rice hulls. The chlorination of SiO₂ in rice hull ash needs the addition of C and is assumed to have less reactivity than pyrolyzed rice hulls because the SiO₂ and C in pyrolyzed rice hulls are prepared from rice hulls and are very finely dispersed.⁽³⁾

Two different rice hull ash samples, Ash-1 and -2 (Table 2), were prepared with a circulating fluidized bed furnace (made by Hokuto Engineering Co., Ltd.). For Ash-1, a WHB-80-D furnace was used, the feed rate of rice hulls was 80kg/hr, the combustion temperature was 800±80°C, and the residence time was 4 hrs. For Ash-2, a WHB-450-M furnace was used, the feed rate of rice hulls was 450kg/hr, the combustion temperature was 900±100°C, and residence time was 4 hrs. Ash-3 was obtained by burning 20g of dried rice hulls in a quartz reactor tube with an inner diameter of 55mm at 800°C in air flowing at 2L/min. Table 2 compares the compositions of SiO₂, Na₂O, K₂O, MgO, CaO, and carbon; crystalline phases and surface areas for

Ash-1, -2 and -3; and those for silica sand and SiO₂ reagent as a comparison. The rice hull ash was mixed with oil coke to a C/SiO₂ mole ratio of 2.5, using a mortar agitator for the chlorination experiments. These experiments were carried out with the same apparatus and procedure as those of pyrolyzed rice hulls. The results of chlorination at 900°C for 1hr are summarized in Table 3. The conversions for Ash-1+C, Ash-2+C and Ash-3+C were higher than those for silica sand + C and SiO₂ reagent + C; additionally, the SiO₂ in rice hulls is more reactive for chlorination than that in minerals and reagent. The conversion of 81.0% for Ash-1+C was higher than those for Ash-2+C and Ash-3+C (47.9% for Ash-2+C and 49.2% for Ash-3+C) and was similar to that of 80% for pyrolyzed rice hulls (Figure 2). This result indicated that the carbon of 21.3 wt% and SiO₂ in Ash-1 prepared from rice hulls had good dispersiveness and contact of SiO₂ with C.

Table 2. Chemical compositions, crystalline phases and surface areas of rice hull ashes, silica sand and SiO₂ reagent.

	Composition (wt%)						SiO ₂ (wt/wt)	Crystalline phase	Surface area (m ² /g)
	SiO ₂	Na ₂ O	K ₂ O	MgO	CaO	C			
Ash-1	74.1	0.34	0.89	0.19	0.91	21.3	0.031	Cristobalite	76
Ash-2	96.5	0.07	0.75	0.06	0.10	2.1	0.010	"	4
Ash-3	97.2	0.16	0.43	0.16	0.20	0	0.010	Amorphous	44
Silica sand	97.7	0.16	0.21	0.01	0.07	0	0.005	α-Quartz	2
SiO ₂ reagent	99.999	0	0	0	0	0	0	Amorphous	13

To improve the low reactivity of SiO₂ for the chlorination of rice hull ash in comparison with pyrolyzed rice hulls, alkaline and alkaline earth metal salts, which break Si-O bonds, were added to the mixture of rice hull ash and carbon, in order to accelerate the chlorination of SiO₂ to SiCl₄. Table 3 summarizes the effect of alkaline and alkaline earth metal salt additives on the chlorination of rice hull ash at 900°C for 1hr. The conversion of chlorination was 60.4% for Ash-1, with 21.3% of unburned carbon. Potassium salts of 10wt% for SiO₂ in Ash-1 were added to Ash-1, and accelerated the reaction of chlorination (Exp. No. 1 to 7). However, the addition of sodium salts (Exp. No. 8 and 9), a magnesium salt (Exp. No. 10) and a calcium salt (Exp. No. 11) inhibited the reaction. The conversion of Ash-1+C after adding carbon (C/SiO₂=2.5 compound (mole/mole)) was 81.0%, although the conversion of Ash-1+C+10wt%KHSO₄ was 87.9%. The conversions of Ash-2+C (47.9%) and Ash-3+C (49.2%) were lower than that of Ash-1, even though the addition of potassium salts to Ash-2+C

and Ash-3+C remarkably increased the conversion (70.2% to 82.1%). However, the addition of lithium, sodium, magnesium and calcium salts to Ash-2+C and Ash-3+C inhibited the reaction, similar to the results for Ash-1.

Table 3. Effect of alkaline and alkaline earth metal salt additives on chlorination of rice hull ashes at 900°C for 1 hr.

Exp. No.	Rice hull ash	Additive (10wt% for SiO ₂)	Conversion (wt% for SiO ₂)
1	Ash-1	-	60.4
2	"	K ₂ CO ₃	66.3
3	"	KCl	72.0
4	"	KHSO ₄	70.4
5	"	KOH	69.2
6	"	KNO ₃	67.8
7	"	K ₂ SO ₄	69.1
8	"	Na ₂ CO ₃	44.0
9	"	NaCl	56.7
10	"	MgCl ₂	55.3
11	"	CaCl ₂	45.8
12	Ash-1+C	-	81.0
13	"	KHSO ₄	87.9
14	Ash-2	K ₂ CO ₃	1.3
15	Ash-2+C	-	47.9
16	"	KHSO ₄	82.1
17	Ash-3+C	-	49.2
18	"	KHSO ₄	70.2
19	Silica sand+C	-	8.7
20	"	KHSO ₄	26.2
21	SiO ₂ reagent+C	-	7.4
22	"	KHSO ₄	53.8

X-ray diffraction with samples after chlorination at 600 to 1000°C indicated that samples containing alkali and alkaline earth metal salts were entirely changed into chlorides.

The mechanism of chlorination acceleration by K and that of chlorination inhibition by Na, Ca and Mg were analyzed as follows. The melting point of KCl is 776°C, that of LiCl is 614°C, that of NaCl is 800.4°C, that of CaCl₂ is 774°C, and that of MgCl₂ is 714°C. These chlorides were brought into contact with SiO₂ in the molten state above 800°C. SiO₂ glass containing alkaline metal ions such as Li⁺, Na⁺ and K⁺ is ion-conductive at high temperatures. Part of the molten salts is expected to diffuse in SiO₂ as K⁺ or Na⁺. The chlorination of SiO₂ may accelerate by breaking the Si-O bond and distorting the Si-O lattice by alkaline metal ions such as K⁺ and Na⁺. The interatomic distance of the Si-O in SiO₂ (solid) is 1.609Å. As stated in an earlier report,⁽⁶⁾ Cl₂ is assumed to react with C to form gaseous carbon chlorides that react with SiO₂. At present, the details of carbon chloride structures are not known, while the interatomic distance

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between C and Cl is in the range of 1.67 to 1.77Å with various bonding states, including Cl-C-, Cl-C=, Cl-C (benzene nucleus), and Cl-C. Carbon chlorides having an interatomic distance of 1.67 to 1.77Å cannot diffuse into a Si-O lattice. The ionic radius of 6-coordinated K^+ is 1.52Å, that of Li^+ is 0.90Å, that of Na^+ is 1.16Å, that of Mg^{2+} is 0.86 and that of Ca^{2+} is 1.14Å. These ions are assumed to diffuse into the SiO_2 lattice, and the ionic radius of K^+ is the greatest in the alkaline and alkaline earth metal ions, so that it probably distorts the Si-O lattice at the highest level. As a consequence, carbon chlorides are able to diffuse into the Si-O lattice, and chlorination is accelerated. The ionic radii of Li^+ , Na^+ , Mg^{2+} , and Ca^{2+} are not sufficient to distort the Si-O lattice, and chlorination is not accelerated. The melts of their chlorides cover SiO_2 and C and prevent the contact with Cl_2 , hindering chlorination. The above consideration is supported by the fact that the addition of K, Na, Ca and Mg salts did not affect chlorination below the melting point of each chloride, and the conversion of SiO_2 to $SiCl_4$ was almost the same as for those without the addition.

Figure 3 presents the reaction rate curves of Ash-2+C and Ash-2+C+KHSO₄ during chlorination at 600 to 1000°C. The melting point of KCl is 776°C and the effect of the addition is positive at chlorination temperatures over 800°C but not at 600 and 700°C.

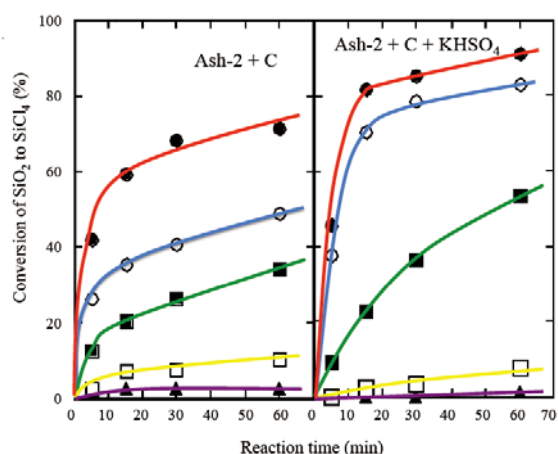


Figure 3. Reaction rate curves of chlorination of Ash-2 + C and Ash-2 + C + KHSO₄ samples at various temperature from 600 to 1000°C.

Chlorination temperatures:

●: 1000°C, ○: 900°C, ■: 800°C, □: 700°C, ▲: 600°C

Figure 4 plots the conversion of the Ash-2+C mixture containing KHSO₄ from 0.1 to 15wt% for SiO_2 (potassium metal equivalence: 0.02 to 3 wt%) at 900°C for 1hr. The accelerating effect for chlorination was observed for only the 0.1wt% addition of KHSO₄ and was constant over 10wt% of KHSO₄.

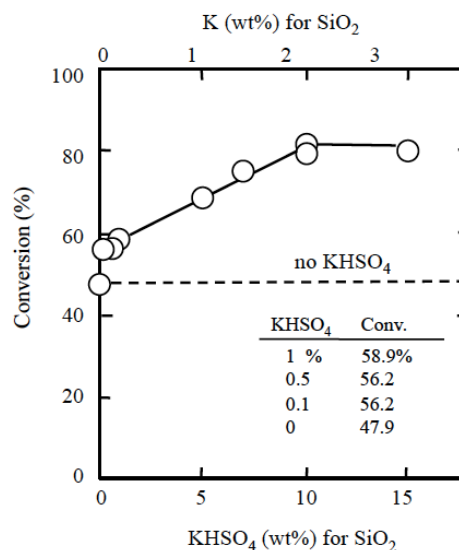


Figure 4. Effect of amount of KHSO₄ added to Ash-2 + C + KHSO₄ at 900°C for 1 hr.

Impurities in the distillate with single-stage distillation of $SiCl_4$ produced by chlorination of Ash-2 are listed in Table 4. Highly pure $SiCl_4$ is obtained by multi-stage distillation, even though the phosphor content is quite high.

Table 4. Impurities in distillate with single-stage of $SiCl_4$ produced by chlorination of Ash-2.

Element	Concentration(ppm)	Element	Concentration(ppm)
Na	1.04	Mg	0.19
Fe	0.90	K	0.77
Ti	<0.1	Cu	<0.1
Cr	0.29	P	650
Al	0.99	Zn	1.18
Ca	0.66	V	<0.1

Utilization of Highly Pure $SiCl_4$

Figure 5 presents the products from highly pure $SiCl_4$ and this utilization. AEROGIL (fine SiO_2 particles) and synthetic quartz glass such as optical fiber are being manufactured on an industrial scale from highly pure $SiCl_4$. Recently,

interest in the production of solar-grade silicon by the reaction of SiCl_4 with Zn has increased.

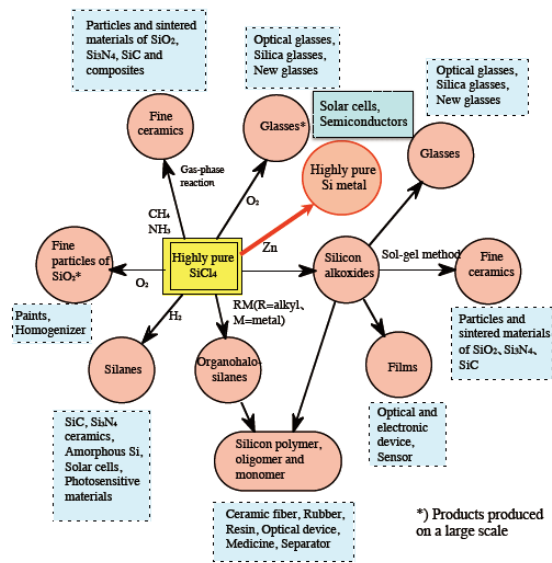


Figure 5. Products from highly pure SiCl_4 and this utilization.

Si Production From SiO_2 in Rice Hulls

Si production by the Reaction of SiO_2 in Rice Hulls with Carbon

Si metal is presently produced industrially with arc heating of highly pure silica stone (more than 99.0%) in the presence of carbon such as charcoal and coke near 2000°C . The reaction is known as a carbothermal process (reaction (2)).



Regarding Si production from rice hulls, Amick, *et al.* (1982) reported that rice hulls washed with diluted hydrochloric acid solutions have a low concentration of impurities, with especially low concentrations (10 to 20 ppmw) of Al and iron, which are the major impurities in conventional raw materials used to prepare metallurgical grade silicon.^(10,11) The SiO_2 in rice hulls is active and easily to produced by the reaction (5)



near 1100°C . However, they reported that rice hull pellets containing carbon and silica were preheated at 1500°C in a graphite cylinder purged with argon, and the preheating was stopped when carbon monoxide evolved due to the reaction (6)



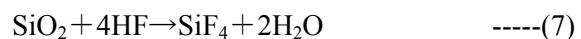
and the evolution of SiO was very low. They demonstrated that acid leaching of rice hulls produced much purer coked (pyrolyzed) materials than that used in the furnace test; however, sufficient raw materials were not available to conduct a smelting test.

In the experiments reported here, rice hulls were washed with distilled water to remove dust and soil and then subjected to acid leaching by reflux boiling in 3%(v/v) HCl for 2 hrs. at a ratio of 50g hull/L to decrease impurities such as K_2O , Al_2O_3 and Fe_2O_3 . After leaching, the rice hulls were washed with distilled water to pH7.0 and dried at 100°C for 24 hrs. in vacuo. Table 5 indicates the chemical components of non-leached rice hulls that were washed with distilled water only, and leached rice hulls analyzed by ICP. Acid leaching efficiently removed impurities except CaO.

Table 5. Chemical components of non-leached rice hulls (NLRH) and leached rice hulls (LRH).

	Al_2O_3 [%]	Fe_2O_3 [%]	K_2O [%]	MgO [%]	MnO [%]	Na_2O [%]	CaO [%]
NLRH	0	0.164	0.197	0.047	0.049	0.005	0.158
LRH	0	0.004	0	0.001	0	0.006	0.079

Pyrolyzed rice hulls that were a mixture of SiO_2 and C were prepared by heat-treating of the leached rice hulls at 600°C for 1hr. in flowing N_2 at 100mL/min. The ratio of the pyrolyzed rice hulls was $\text{C}/\text{SiO}_2 = 1.0(\text{w/w})$ and $= 5.01(\text{mole/mole})$. The amount of carbon was obtained from the ignition loss of pyrolyzed rice hulls in air, and the amount of SiO_2 was obtained from the weight loss due to the reaction (7).



Rice hull ash was prepared by burning the pyrolyzed rice hulls at 600°C . The rice hull ash was of white color, had no carbon, and had a surface area of $311.1\text{m}^2/\text{g}$ (very large compared with the surface area of SiO_2 reagent ($0.2\text{m}^2/\text{g}$)). The pyrolyzed rice hulls and the rice hull ash were weighed to a ratio of $\text{C}/\text{SiO}_2 = 2$ (mole/mole) and mixed with a mortar. The mixtures were tempered with sucrose to shape the pellets and heated at 400°C for 1 hr. in N_2 . The pellets were set in a graphite crucible and heated at 1600 to 2000°C for 10 min in Ar flowing at 50mL/min in a high-frequency furnace (Figure 6). After reaction, the sample was weighed, and the Si content was measured by an X-ray internal standard method.

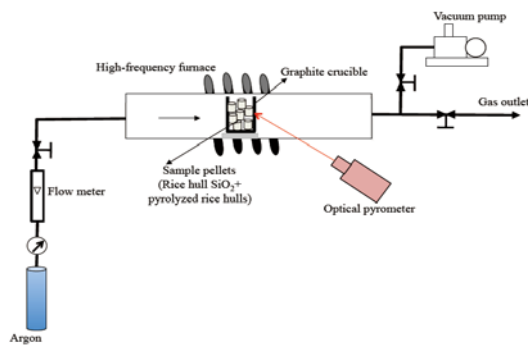
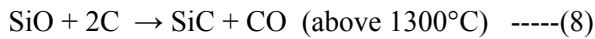
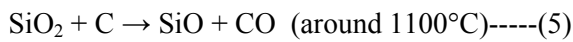


Figure 6. Schematic of the high-frequency furnace reactor system of Si production from rice hulls.

No Si metal was produced in the reaction (2) in the temperature range of 1600 to 2000°C. A white deposit of SiO was deposited inside of reactor downstream of sample crucible. The reactions of $2C + SiO_2$ may occur as shown below.



The SiC formation (6) occurs through reactions (5) and (8). Estimation of ΔG indicates that reaction (2) takes place above 1665°C, but ΔG of reaction (6) is lower than that of reaction (2). If SiO_2 and C exist in the reaction system, reaction (6) takes place preferentially. Table 6 presents the results of crystalline phase detected in products and weight loss of reaction. No Si metal is found at any reaction temperature. The weight loss is derived from SiO formation because the vapor pressure of SiO is quite high and SiO is discharged from reaction zone by flowing Ar.

Table 6. Weight loss of sample (mixture of rice hull SiO_2 and pyrolyzed rice hulls ($C/SiO_2 = 2.0$ (mole ratio))) after reaction and XRD peaks detected in products.

Temperature [°C]	Weight loss [%]	XRD peaks		
		SiO_2	SiC	Si
1600	22.6	○	-	-
1800	45.4	○	○	-
1900	72	-	○	-
2000	100	-	-	-

Si Production by the Reaction of SiO_2 in Rice Hulls with Aluminum

Si-O has a binding energy of 423KJ/mole and is very stable. To break Si-O bonds, Banerjee, *et al.* (1982) reported Si production from rice hulls by the reactions (9)⁽¹²⁾



and (10).⁽¹³⁾



Banerjee, *et al.* (1982) used Mg and Ca reduction to produce Si metal, instead of heat generated by the reaction, ΔH . Thus, their reactions are not thermite reactions.⁽⁵⁾

In the experiments reported here, Si metal was produced by the reaction of SiO_2 in rice hulls with Al. SiO_2 is reduced to Si metal with Al. The heat generated by the oxidation of Al is not used to drive the reaction (3). Thus, the reaction is not a thermite reaction. The SiO_2 in rice hulls was prepared that the leached rice hulls were treated at 600°C for 1 hr. in flowing N_2 to obtain the pyrolyzed rice hulls, and then the pyrolyzed rice hulls were burned at 600°C to get the rice hull SiO_2 . Rice hull SiO_2 and Al powders were weighed to achieve an SiO_2/Al mole ratio of 3/4 and were mixed by a planetary ball mill. A 3gr mixture was set in the graphite vessel with 14 mm outer diameter, 20 mm height, and 1.5 mm thickness, and heated to 1000 to 1300°C in Ar flowing in a high-frequency furnace (Figure 6). Amorphous SiO_2 reagent was used as a reference. The conversion of SiO_2 to Si was estimated from the content of SiO_2 in the products analyzed by an X-ray internal standard method.

Figure 7 plots the conversion of SiO_2 to Si for rice hull $SiO_2 + Al$, and SiO_2 reagent + Al samples at reaction temperatures from 1000 to 1300°C for 10 min. The SiO_2 reagent sample exhibited a higher conversion at temperatures below 1200°C than rice hull SiO_2 . The reaction of SiO_2 with Al progresses where SiO_2 contacts the melted Al (melting point of Al is 660.4°C). The specific surface areas are 311.1m²/g for rice hull SiO_2 and 0.2m²/g for SiO_2 reagent, and the bulk specific gravities are 0.9g/cm³ for rice hull SiO_2 and 2.2g/cm³ for SiO_2 reagent. From these results, the contact density (ratio of SiO_2 molecules per unit of contact of liquid Al molecules) of the mixture of rice hull SiO_2 and Al is less than that of

the mixture of SiO_2 reagent and Al. Therefore, the conversion of rice hull $\text{SiO}_2 + \text{Al}$ was low. At 1300°C , the vapor pressure of Al becomes 0.032 Torr, even though the vapor pressures of Al are 10^{-3} Torr at 1100°C and 10^{-2} Torr at 1200°C . The reaction of SiO_2 and Al proceeds between solid SiO_2 and gaseous Al, and thus the conversion of the reaction of rice hull SiO_2 with a larger surface area and gaseous Al became higher than that of SiO_2 reagent with a smaller surface area and Al. We found that the additives to rice hull SiO_2 improved the contact density of SiO_2 and Al and yielded higher conversion at lower reaction temperatures. After reaction, the products were in the powder state. This means that the temperature was less than the melting point of Si (1410°C), and no thermite reaction developed.

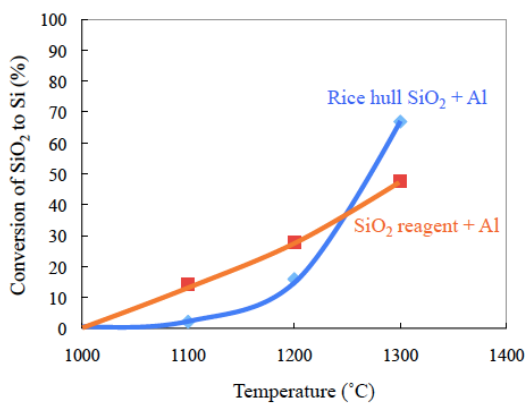


Figure 7. Conversion of SiO_2 to Si for rice hull $\text{SiO}_2 + \text{Al}$, and SiO_2 reagent+Al samples reacted at reaction temperatures from 1000 to 1300°C for 10 min.

Figure 8 plots the reaction rate curves at 1300°C . The reaction of rice hull SiO_2 and Al results in a rapid increase of the conversion in the initial reaction stage. Thus, rice hull SiO_2 is more reactive than amorphous SiO_2 reagent.

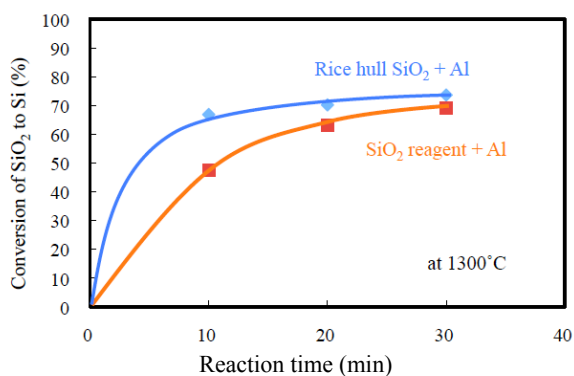


Figure 8. Reaction rate curves of Al reduction of rice hull SiO_2 and SiO_2 reagent at 1300°C .

Si metal powder can be produced by the process described above. Si metal should be purified for the use of solar cells and semiconductors. The present purification process is the chlorination of Si metal by HCl at around 300°C in the presence of Cu catalyst. If powder Si metal is used in this process, a more economical and efficient process can be established. Purification is not hindered by Al_2O_3 , a by-product of this process.

Conclusions

Rice hulls contain unique SiO_2 with a large surface area and high reactivity. The most unique point of SiO_2 in rice hulls is the resources produced by rice crops every year. We developed a technology to produce highly pure SiCl_4 by chlorination of rice hull ash, a by-product of heat recovery by the combustion of rice hulls. We also demonstrated that Si metal could be effectively produced from rice hull SiO_2 by the reaction with aluminum. Not only food but also industrial raw material such as highly pure SiCl_4 and Si metal, which are used to produce solar cells and semiconductors, is provided by rice plant.

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