

RICE HUSKS AS A SOURCE OF HIGH PURITY SILICA

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Silica originating from rice husks has been proposed for use in the manufacture of solar cells. By measuring the concentration of impurities (Fe, Zn, Ca, Mn) found in the washing solutions, the conditions necessary for achieving high purity, including the optimum time, number of washing cycles and the temperature and concentration of the washing solutions (HCl + H₂O), were chosen. Following this procedure, 99.98% pure silica was obtained. The major impurity was Ca with a concentration of 100 ppm.

1. Introduction

Rice husks, an agricultural waste-product, are known to have a high silica content (approximately 18%). The major impurities are Na, K, Mn, Mg, Ca and Fe. The amount of deleterious contaminants affecting solar cell performance, such as B, As and F, are generally very low compared to other cheap sources of silica such as sand, bentonite and diatomaceous earth [1]. Rice husks, therefore, may be an important source of solar grade silicon.

Basu et al. [2] have reported on a process for the conversion of ash, obtained by burning rice husks, into silicon tetrachloride by chlorination. Singh and Dhindaw [1] described the structure and crystallization of silica obtained by burning rice husks at different temperatures. This silica was subsequently reduced to silicon. Amick [3] reported on the leaching of rice husks, as well as techniques to adjust the carbon to silica ratio in coked materials in an effort to use carbon reduction of the ash to silicon. Rice husk ashes have also been reduced to silicon using magnesium [4,5].

Rice husks heated in an oxidizing atmosphere can be transformed into a white ash which is almost pure SiO₂ and has a granular shape and high specific surface area.

The procedure followed by Amick [3] began with a water rinse, which did not change significantly the amount of impurities found in the rice

husks (10,000–40,000 ppm). Next, he kept the husks in a boiling solution of 1:3 HCl:H₂O for 1 h, followed by 20 min in a boiling solution of 1:1 HCl:H₂O. Finally he dried the husks in hot air. After this process, there was a significant decrease in the amount of impurities remaining (approximately 300 ppm). Pyrolysis, using a flowing gas containing 1% anhydrous HCl in argon, reduced the impurities even more, to a level of 75 ppm.

Banerjee et al. [5] began with water rinses, followed by sun drying and burning at 400°C to get white ash (SiO₂). This ash was leached with concentrated HCl for 2 h, rinsed with water and dried. Finally it was reduced with magnesium to produce silicon with 100–1000 ppm of impurities (Mg, Al, B).

The above procedures showed that rice husks can be purified in a very simple way, and with very low energy consumption. While Amick [3] and Banerjee et al. [5] analyzed the rice husks at the end of each step, they did not give details about how they chose the washing time and concentration of their washing time and concentration of their washing solutions. In this paper we describe how the amount of impurities dissolved in the washing solutions varied as a function of time and how the most convenient washing time was chosen. The procedure was repeated several times in order to find the number of cycles required. The purpose of this investigation was to optimize the process for obtaining SiO₂ from rice husks. The

purification process developed has the following steps:

- (a) Water rinses. Distilled water was used to get rid of the dust and other particles of foreign matter present in the rice husks.
- (b) Leaching with an acid solution. To extract the metals by forming soluble compounds in a solution of HCl and deionized water.
- (c) Drying. The great amount of gas needed to desiccate the rice husks makes it necessary to employ a filter to reduce the contamination by particles carried by the gas, or to desiccate the husks in a closed system with an absorber inside.
- (d) Pyrolysis or burning. To evaporate or to oxidize the organic components of the rice husks.
- (e) Leaching the ashes. Convenient, but necessary only if the amount of metals extracted is larger than the contaminants introduced by the reagents and the drying procedure.

2. Results

(a) Water rinsing. The rice husks were rinsed with distilled water at room temperature, and de-

canted to separate the solid and liquid phases. The liquid phase was then evaporated to measure the percentage of total solids extracted by the water. This procedure was applied to the same sample of rice husks five times, with the following results for the percentage of solids extracted: 0.30, 0.28, 0.17, 0.13 and 0.11.

(b) Leaching with acid solution. HCl was used because it is inexpensive and comes in a reasonable purity. We used a 3% HCl solution, boiling with a reflux to reduce the evaporation losses of the solution. To measure the rate of dissolution we took small samples of solution at fixed intervals and measured the percentage of solids extracted. Fig. 1 shows the results obtained with three samples of rice husks rinsed twice and boiled in a 3% HCl solution in Mexico City ($T = 94^{\circ}\text{C}$).

From fig. 1 we can see that the amount of impurities extracted with the water rinses at room temperature was very small in comparison with the purification attained when leaching with acid. We also can see that after 6 h of boiling the solution became nearly saturated, or exhibited a very slow dissolution rate. Applying a 6 h leaching procedure to the same sample several times showed that

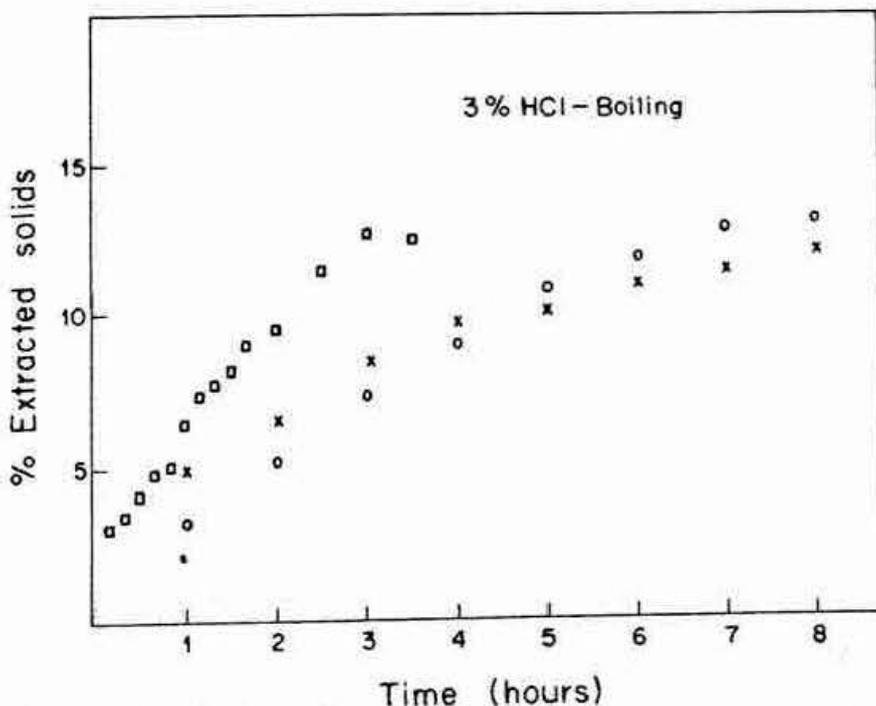


Fig. 1. Percentage of solids in solution as a function of time, for three samples of rice husks boiling in 3% HCl solution.

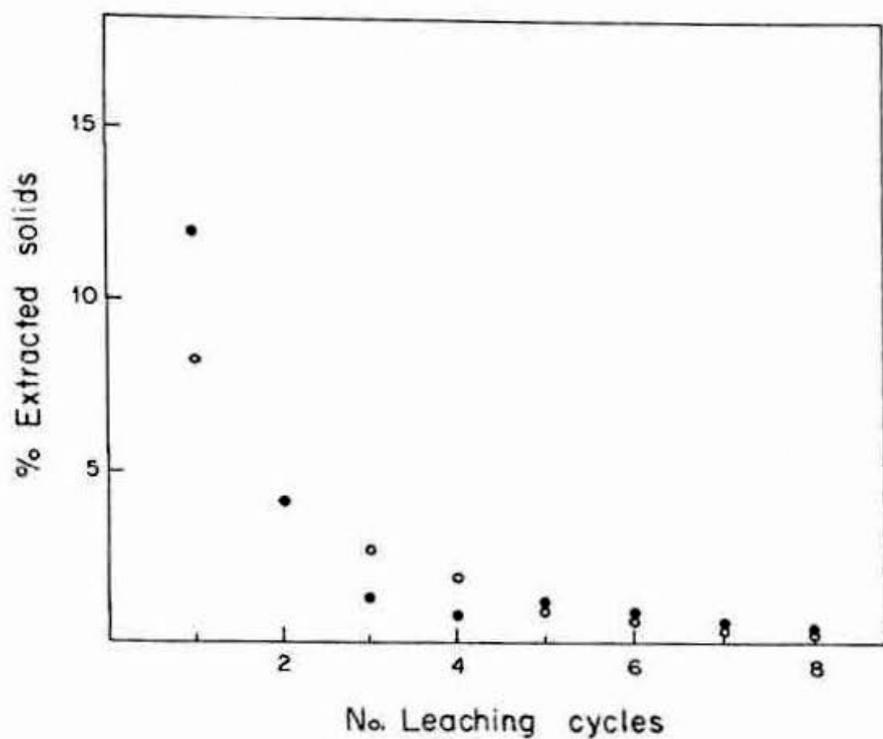


Fig. 2. Comparison of the percentage of dissolved solids at the end of each leaching process at the boiling point (●), and below the boiling point (○).

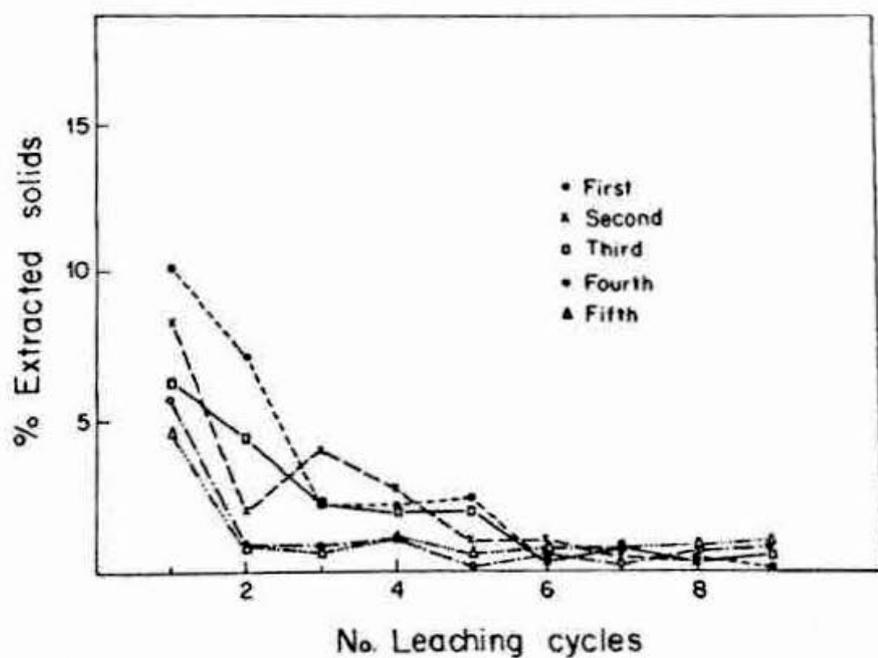


Fig. 3. Percentage of dissolved solids at the end of each leaching process (3% HCl, temperature = 90°C and elapsed time = 6 h), for five different samples of rice husks.

the amount of extracted solids decayed rapidly. Doubling the amount of HCl gave about the same extraction rate. A violent movement of the rice husks was observed during boiling and the temperature was therefore reduced to 90°C (below the boiling point), to avoid the grinding action between grains. The extraction rate was about the same, as can be observed in fig. 2.

Fig. 3 shows the percentage of solids extracted for five different samples leached up to nine times. The initial mass of each sample was 50 g. The volume of the 3% HCl solution was 600 ml, the temperature was 90°C and the time of leaching (before using a new solution) was 6 h. The general trend indicated that the amount of extracted solids decayed very fast in the beginning, reaching a constant amount after several leaching cycles. The elements detected in the extracted solids by a qualitative analysis (X-ray fluorescence) were: Fe, Zn, Cu, Br, Rb, Mn, Ti, As or Pb.

Fig. 4 shows the concentration of some elements in the solution at the end of the successive leaching processes, measured by atomic absorption spectroscopy. Most of the elements reached a con-

stant concentration after 4-7 leaching processes. We also found that the amount of silicon in solution is small compared with that in the solid phase.

(c) Drying. In order to avoid contamination by particles carried by the gas flow, we choose to desiccate the wet husks in a closed system, using silica gel as an absorber and drying for 4 days. Table 1 shows the concentration of impurities remaining in the rice husk after six leaching cycles. The spark source mass spectrometric analysis was made by Northern Analytical Laboratory. Table 1 also shows the values measured by Amick.

(d) Pyrolysis or burning. We chose burning because it is a cheaper process. Using filtered air (0.22 μm) we heated the rice husks in a quartz tube furnace, measuring simultaneously their weight and temperature (DTA measurements). The results shown in fig. 5 confirmed the exothermic nature of the fast weight loss. By adjusting the temperature and the elapsed time it was possible to control the amount of carbon in the SiO_2 . Given enough time, air and temperature, it was possible to control the amount of carbon in the SiO_2 . Given enough time, air and temperature, it

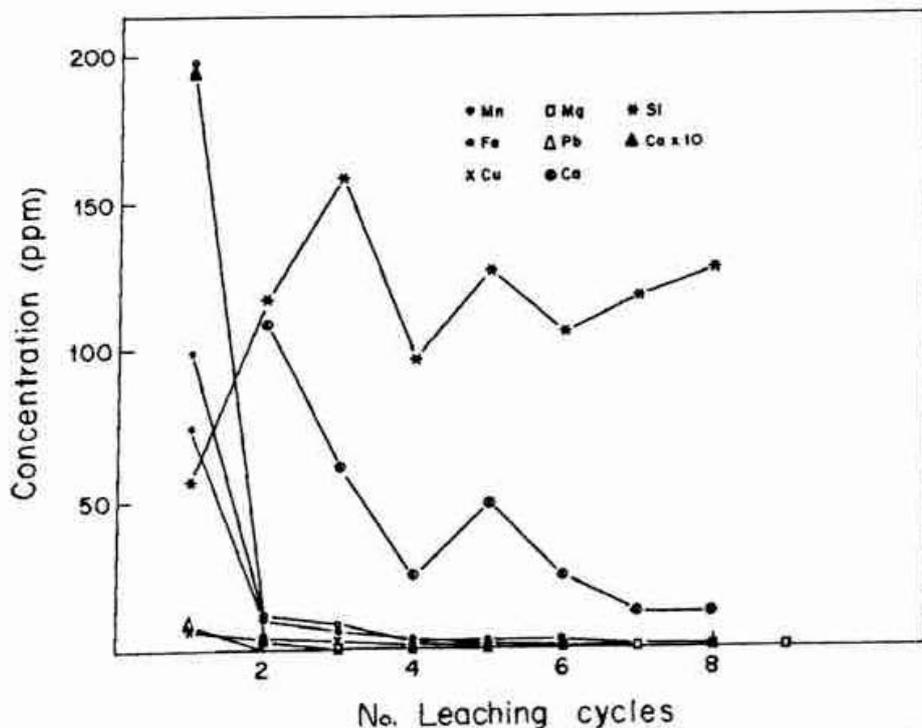


Fig. 4. Concentration of some elements in the 3% HCl solution at the end of each 6 h leaching process at 90°C.

Table 1
Analysis by mass spectrometry of the rice husk (ppm)

Impurities	Rice hulls acid leached		HCl coked	Burned
	Amick	Riveros and Garza	Amick	Riveros and Garza
B	10	7	5	5
Al	60	Major	10	15
P	ND	0.8	ND	3
Cr	ND	1	ND	ND
Mn	30	7	10	ND
Fe	40	140	10	10
Cu	ND	0.8	ND	2
Ni	ND	2	ND	6
Ti	60	155	ND	ND
Zn	ND	0.6	ND	ND
Na	10	15	10	1
K	10	Major	10	10
Mg	60	10	20	4
Ca	50	Major	ND	100
Pb	ND	0.1	ND	ND

ND means not detected.

was possible to get white ash of almost pure SiO_2 , as can be seen from the results shown in table 1.

(e) Leaching the ashes. Because of the high

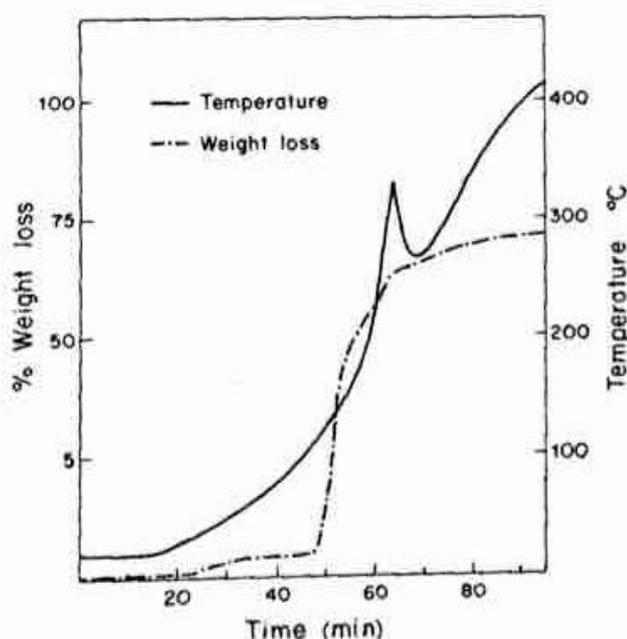


Fig. 5. Weight loss of the leached rice husk, heated in a quartz tube furnace, measuring simultaneously its temperature. The maximum slope in the weight loss corresponds to an exothermic process (burning).

purity reached in the last step, and considering that each process introduces some contamination, we decided not to apply it until we have the pertinent information about the reduction needed to obtain silicon from the SiO_2 .

3. Conclusion

Using the procedure described above, high purity silica was obtained from rice husks using small amounts of inexpensive reagents, very simple equipment, and a minimum of manipulation. The silica obtained was 99.98% pure. The major impurity remaining was Ca, having a concentration of 100 ppm.

It was found that the performance of this procedure was optimum under the following conditions:

- Number of water rinses: 3;
- Time of leaching with a HCl solution: 6 h;
- Number of leaching cycles: 6;
- Solution temperature: 90°C;
- HCl concentration: 3%.

It remains to study the optimum conditions (i.e. temperature and time) for the burning of the rice husks. Also more experimental work must be done to reduce the Ca concentration found in the ashes.

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