

The Effect of Chemical Treatment on The Production of Active Silica from Rice Husk

H. Kurama

Osmangazi University, Mining Engineering Department, Batı -Meşelik, Eskişehir, Turkey

S. K. Kurama

Anadolu University, Department of Material Science and Engineering, Eskişehir, Turkey

ABSTRACT : In this study the effect of chemical treatment on the production of high purity silica from rice husk was investigated. Rice husk, supplied from Kastomonu region-Turkey, was used as a sources of silica. They were washed with water to remove the contaminants present in them then dried in an oven at 100°C for 24 h. The dried husks were then subjected to the chemical treatment before calcinations in order to increase silica contents of husk ash. In experiments, HCl was used as a leaching reagent for extracting inorganic impurities from the husk and the affect of leaching temperature, reactive concentration, leaching time and solid percent on the purity of silica ash were systematically investigated. The results of leaching test showed that high purity amorphous silica could be produced with a 99.74 %t grade. The surface properties of both rice hush and husk ashes were analyzed by Scanning Electron Microscope (SEM).

1 INTRODUCTION

Rice husk are the natural sheaths that form on the rice grains during their growth. Removed during the refining of rice, these husks have no commercial interest. When it burns, the silica rich ash (87-97 %) from 13-29 % by weight is produced depending on the variety, climate and geographic location (Amick 1982). The silica in husk is in hydrated amorphous form, either opal or silica gel. Due to the high silica content, rice husk has become a source for preparation of number of silicon compounds such as solar grade silicon (Ikram et al. 1988), silicon carbide (Sharma et al. 1984, Krishnarao et al. 1992, Romero et al. 1996), silicon nitride (Rahman 1994), zeolite and concrete and cements surfactant (Real et al. 1996).

Presently, the word production of rice is approximately 500 million tons a year containing 50-100 million tons of rice husks (Andreoli et al. 2000). In Turkey the annual rice production is about 240000 tons, equivalent to 2.4×10^4 tons of rice husk. These husks are mostly thrown away as waste.

The husk is mainly consisted of 70 - 75 % organic matters such as lignin, cellulose and sugar and remaining silica with small amount of alkali and other trace elements. Utilization of rice husk as a source of silica is based on removal of impurities with a low effort. Many authors (Riveros et al. 1986, Patel et al. 1987, Chakraverty et al. 1988, Krishnarao et al. 2001, Delia et al. 2002) have concluded that preliminary simple acid leaching of rice husk

before thermal treatment proved to be effective in substantially removing most of the metallic impurities and producing silica ash with a high specific surface area (<250 m²/g) and small particle sizes (<5µm). However, except for some studies on the thermal treatment of rice husk, few systematic work has been done to determine the optimum conditions for the acid leaching steps of silica ash production. The objective of the present work is to determine the effect of acid treatment parameters such as percent solid, leaching temperature, and reactive concentration and leaching time on the production of high purity silica ash from rice husk.

2 EXPERIMENTAL

2. / Material and Methods

The rice husk sample was supplied from Kastomonu region-Turkey. They were washed with water to remove the contaminants present in them then dried in an oven at 100°C for 24 h. The chemical composition of the sample is shown in Table 1. SiO₂ was found to be 13.66 %, the carbon and water content is 84%.

There are several leaching agent that can be used in the extraction of inorganic impurities from rice husk such as HCl, H₂SO₄ and HNO₃. However using H₂SO₄ leads to formation of metallic sulphates, some of which are not easily soluble in water. Again HCl

Table 1 Chemical composition of rice husk

Elements	Weight Percent * rice husk
SiO ₂	13.66
Al ₂ O ₃	0.76
Fe ₂ O ₃	0.02
CaO	1.08
MgO	0.56
K ₂ O	0.50
LOI	83.42

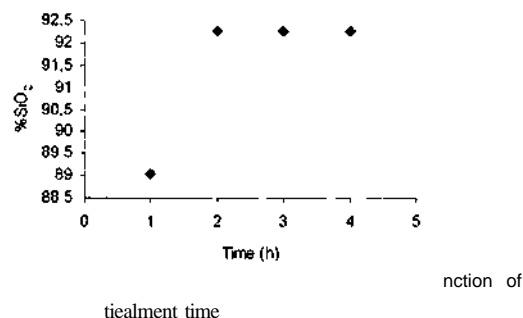
is cheaper and more effective than H₂SO₄, hence the choice of HCl as an extracting agent for leaching test in this study. A known weight (5 and 10 g) of dry husk was reacted with 100 ml of HCl acid solution in a 250 ml glass flask with mounted magnetic stirrer and topped with reflux condenser in the case of boiling point tests in order to prevent evaporation losses of the solution. The leaching test was performed with 1, 2, 3 M HCl solution at 25°C, 60°C and 90°C, in order to determine the effect of solution concentration and temperature on the product. After leaching tests, the husk was washed with distilled water and then dried. Acid treated husks were then subjected to the thermal treatment at 700°C which was determined as optimum temperature in previous study (Kula et al. 1996), in electric muffle furnace. The samples were thus kept in furnace for 2 hours until complete combustion took place.

Quantitative chemical analyses of ashes were done by X-ray fluorescence (XRF) and standard wet methods. The surface structure and distribution of silica and inorganic impurities were analyzed by using Jeol 5600 scanning electron microscope (SEM). SEM was also employed in combination with energy dispersive X-ray analysis (EDX) in order to investigate the chemistry of the un-treated and treated husk ash.

3 RESULTS AND DISCUSSION

3.1 Contacting Time

Figure 1 shows the leaching test results for 1 M HCl acid solution concentration, 10 % solid, (10 g of husk in 100 ml solution) at 25°C after the calcination process. It clearly indicates that, the dissolution of impurities continues up to 2 hours. In other words the silica contents of husk ash was increased from 88 % to 97 % with increasing contacting time up to 2 hours after this point no further change was observed.



3.2 Effect of Solid Percentage

The effect of solid percentage on the dissolution of inorganic impurities from rice husk was tested for 5 % 10 % solid with using 1 M HCl acid solution at 25°C for 2 hours contact time. It was found that the final SiO₂ content of husk ash increases with the decreasing solid content from 10 to 5 %. The SiO₂ content increased from 91.28 to 97.63 %. This can be explained by the better contact of solution with husk at lower solid content due to the low specific density of husk.

3.3 HCl Concentration

The leaching test results for HCl treatment (1-3 M) for 2 hours duration and 5% solid at 25°C are given in Table 2. It was found that, the silica percent of rice husk does not show any linear relationship with molarities of acid used during the treatment. However the silica content of ash is increased from 88.02 to 99.50 % for 2 M HCl concentration.

Table 2. Silica in husk ash for different acid concentration

Treatment	SiO ₂ %
Non-treated	88.02
1 M	97.63
2M	98.49
3M	97.95

3.4 Effect of leaching Temperature

The effect of the leaching temperature on the purity of the husk ash was tested with 1, 2 M HCl concentrations at 5% solid and 25, 60, 90°C. It was determined that increasing the leaching temperature from 25 to 60°C is resulted slightly higher product purity. However, further increase of temperature did not caused any positive effect on purity. This can be explained by the saturation of impurities extracted with HCl at 60°C.

Table 3 Effect of acid leaching temperature for the production of amorphous silica ash

Temperature (°C)	SiO ₂ %	
	1M HCl	2M HCl
25	97.63	99.50
60	98.44	99.74
90	98.44	99.74

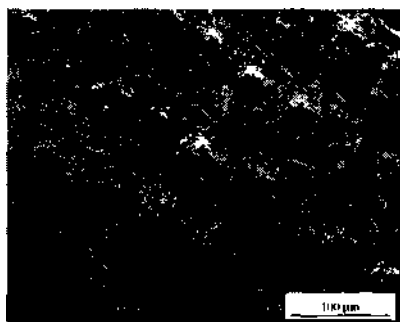
The analysis of the impurities and the effect of the chemical treatment on husk ash purity are given in Table 4. This indicates that, inorganic impurities present in husk are effectively removed by leaching with HCl before calcinations.

Table 4 Inorganic Oxides content of treated (2 M, 5% solid, 2 hours) and untreated silica ash

Sample	Impurities %				
	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	CaO	MgO
Un treated	3.65	0.10	4.60	2.60	0.73
Treated (2M)	0.04	0.04	0.17	0.09	0.08
Treated (90°C)	0.04	0.023	0.05	0.04	0.06

3.5 Microscopic studies

Rice husk and all products, both chemically treated (2M HCl, 5% solid at 25°C) and untreated husk ash were examined by scanning electron microscopy (SEM) in order to find out the effect of chemical treatment on silica ash. In Figure 2 the characteristic cob-shaped cellulose skeleton of the outer epidermis of husk and calcined products was clearly visible. It showed that chemical treatment did not cause any deleterious effect on ash structure.



(a)



(b)



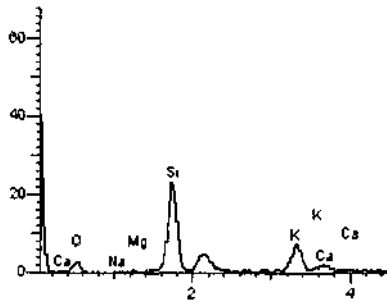
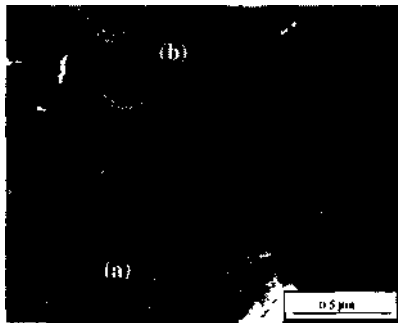
(c)

Figure 2. SEM micrographs of silica from rice husk (a), calcinated husk (b) and acid treated + calcinated husk (c).

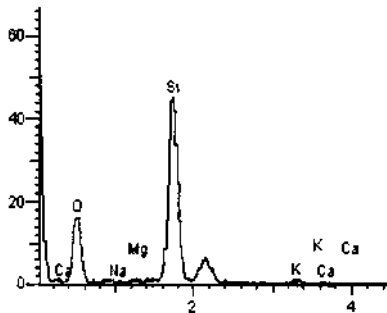
The micrograph of the natural rice husk is shown in Figure 1 a. The organic molecules appeared to be arranged over the skeleton. This caused the slightly smoothing of the protuberances and widening of parallel grooves between the protuberances. Although these organic molecules are partly removed from skeleton surface by calcination (Fig. 1b), acid treatment before calcinations is led to complete removing of the organic part and leaving behind the silica skeleton alone (Fig. 1c).

The silica and inorganic impurities distribution of both calcinated products were analyzed by using EDX and results are presented in Figure 3, 4. It was detected that, silica is more concentrated in the outer epidermis than inner epidermis for untreated husk ash (Fig. 3). The inorganic impurities, mainly potassium was also still present in ash and concentrated in the inner epidermis. Krisnaro et al. (1994) reported that the black particle in husk ash are due to the carbon fixed in them. This happens due to surface melting of silica in the presence of K₂O impurity causing the decreasing of the silica purity. But in the case of acid treated husk ash, however the silica

content of outer epidermis is slightly more than the inner epidermis, it can be concluded that, silica is distributed all over the husk ash (Fig. 4). The peak intensity of silica is higher than the untreated one. This can be attributed the complete removal of impurities by acid treatment.

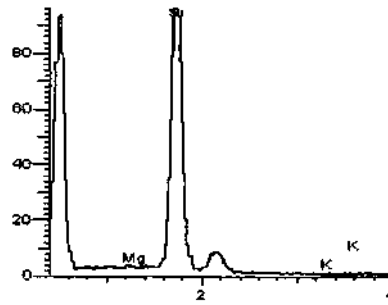
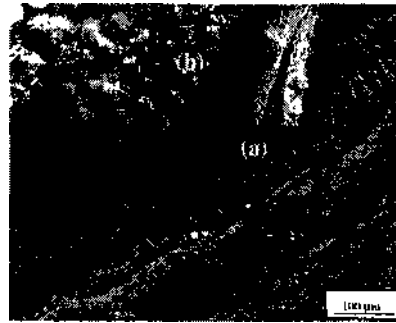


(a)

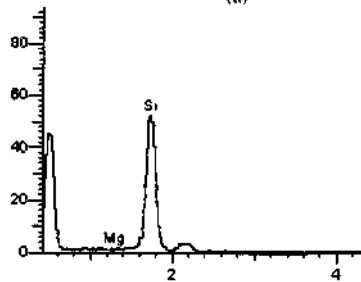


(b)

Figure 3 The SEM micrographs and EDX diffractograms of calcinated husk; (a) inner epidermis, (b) outer epidermis



(a)



(b)

Figure 4 The SEM micrographs and EDX diffractograms of acid Heated husk ash; (a) inner epidermis; (b) outer epidermis

4 CONCLUSIONS

Many interesting material preparation routes are burdened with high material cost. As an example the cost of the preparation of porous silica for the use of commercial products ranges \$US 2-10 per kg. (Conrad et al. 1992) For this reason, the production of porous and high-grade silica from rice husk as a competitive raw material is gaining interest. In this

study, it was found that purity of silica ash is greatly affected from chemical treatment and treatment parameters. From these experiments, the following conclusions can be drawn;

- The silica content of husk ash can be increased from 88.03% to 99.70% by HCl acid treatment before calcinations process.
- Although the amount of silica obtained from raw rice husk does not follow any linear relationship with the molarity of acid used during treatment, for 2 M HCl concentration the silica content of ash increased to 99.50 %.
- The highest silica content was obtained from 2 M HCl treatment at 60°C. However due to the extra cost of heating solution to 60°C, slightly less pure can also be obtained more cheaply at 25°C.
- The chemical and EDX analyses results showed that acid treatment with 2 M HCl, 5% solid at 25°C nearly complete treatment of impurities from husk ash.
- The cost of the treatment method used in this study is estimated to be around \$US 4 / kg. Given that silica production cost in the market ranged between \$US 2-10 / kg, the proposed method in this study may be commercially feasible.

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