

## CRYSTALLITE GROWTH OF RICE HUSK ASH SILICA

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### ABSTRACT

The effect of temperature of firing and time of annealing on crystallite size of silica obtained by burning boiled rice husk was studied by the X-ray broadening technique. The results showed that nuclei of disordered cristobalite were present in ash silica, and crystallite growth was governed by two processes, namely nucleation and growth taking place simultaneously with a rate varying with the temperature of treatment. The nucleation process manifested itself in the low temperature range of 800–900°C, while growth was more pronounced in the temperature range 1000–1100°C, occurring with different activation energies of 81.3 and 52.4 cal mole<sup>-1</sup>, respectively. Both processes occurred with the same intensity at 964°C. A growth process and crystal perfection followed with an activation energy of 36.8 cal mole<sup>-1</sup>.

### INTRODUCTION

The stability range of the three predominant crystalline modifications of silica are considered by Fenner [1] to be as follows

quartz  $\xrightarrow{870^{\circ}\text{C}}$  tridymite  $\xrightarrow{1470^{\circ}\text{C}}$  cristobalite

According to the view suggested by Flörke [2] and supported by other authors [3–6] the conversion from quartz to cristobalite does not proceed through the intermediate form tridymite. The presence of impurities favours the formation of tridymite.

The nature of rice husk ash silica was intensively studied by Bartha and Huppertz [7]. They showed that silica in the pulverized husk ash is a disordered cristobalite, as indicated by the position of the main peak in its X-ray diffraction pattern. This phase exists up to 600°C and at 725°C crystallization occurs. About 70% of the silica is transformed into cristobalite. A previous study [8] showed that silica in ash exists in two forms, Si–O and Si–OH. Cristobalite is the crystalline phase identified at 800°C onwards. Impurities favour tridymite formation at 1200°C [9]. A change in the crystallite size was seen to occur abruptly at 1000°C which was accompanied by a small change in the specific surface area [10].

The kinetics of crystallite growth of cristobalite developed by heating rice

husk ash silica is therefore studied here for samples fired between 500 and 1200°C for various time intervals ranging from 5 min to 24 h depending on the temperature of annealing. Crystallite size was followed by the X-ray broadening technique.

## EXPERIMENTAL WORK

### *Sample preparation*

White rice husk ash was prepared by burning boiled husk in an atmosphere of air at 500°C for 3 h [9]. Samples from the ash were placed in platinum crucibles and introduced into an electric muffle furnace adjusted at the required annealing temperature between 500 and 1200°C, and were left at the temperature of the furnace for different time intervals ranging between 5 min and 24 h.

Specific gravity was carried out for samples fired between 500 and 1200°C and soaked for 3 h at the required temperature according to ASTM [C329-56 (1970)]. The results are represented in Fig. 1. The percent of cristobalite formed was calculated at each temperature from the equation [11]

$$\frac{1-x}{b'} + \frac{x}{b''} = 1/B$$

where,  $x$  = amount of cristobalite transformed,  $b'$  = specific gravity of rice husk ash silica fired at 500°C,  $b''$  = specific gravity of cristobalite: 2.32 g cm<sup>-3</sup>,  $B$  = specific gravity determined for the ash samples fired between 500 and 1200°C. The results obtained are shown in Fig. 2.

### *Determination of crystallite size*

Crystallite size was measured by the X-ray broadening technique. Scanning by X-ray was carried out for powder samples at a slow rate of 1/40 min<sup>-1</sup> in the position of maximum peak characteristic of silica forms between 2θ 19° and 2θ 24°. The maximum peak was found to occur at 2θ 21–22°, equivalent to a lattice spacing of  $d = 4.05 \text{ \AA}$  and (111) crystallographic plane. The apparatus used was a Philips type of Goniometer PW 1050/

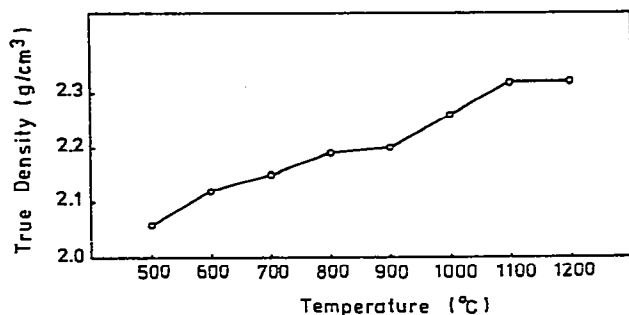


Fig. 1. Specific gravity of rice husk ash silica fired at different temperatures.

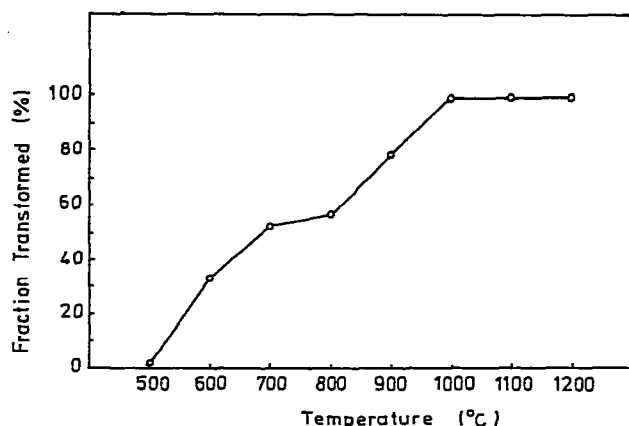


Fig. 2. Percent of ash silica transformed at each firing temperature.

25, using copper radiation  $K = 1.54 \text{ \AA}$  and a Ni filter. The crystallite size was measured from the width of the diffraction curve, which is usually measured in radians, at an intensity equal to half the maximum intensity. The size of the crystallite was calculated from the Scherrer formula [12]

$$t = \frac{K}{B \cos \theta} = \frac{0.9}{B \cos \theta}$$

where,  $K$  was found by Bragg to be equal to 0.9, and  $B$  is the width of half maximum intensity.

## RESULTS AND DISCUSSION

Ash silica fired at  $500^\circ\text{C}$  gave the low specific gravity value of  $2.06 \text{ g cm}^{-3}$  which is different from those characteristic of the allotropic forms of silica: quartz  $2.65 \text{ g cm}^{-3}$ , tridymite  $2.26 \text{ g cm}^{-3}$ , cristobalite  $2.32 \text{ g cm}^{-3}$  and flint  $2.21 \text{ g cm}^{-3}$ . This is mainly attributed to the nature and the mode of stacking of the different silica groups Si—O and Si—OH [8], as well as the presence of carbon in the ash (ignition loss at  $1000^\circ\text{C} = 0.98\%$ ). Firing of the ash above  $800^\circ\text{C}$  gives cristobalite [7–9]. Therefore, the specific gravity of cristobalite was taken as the base for the calculation of the degree of transformation of the ash silica from the amorphous state to the crystalline state. More than 80% of the ash was readily transformed into cristobalite at  $800^\circ\text{C}$  (Fig. 2). No correction was made for the possible presence of glass in the values obtained.

X-Ray peaks of ash silica fired between  $500$  and  $800^\circ\text{C}$  were widened with low intensities. The X-ray peak was present in the position of cristobalite but the value of  $2\theta$  was shifted. This behaviour indicates that the siloxane groups, Si—O, present in the ash silica may be forming nuclei of disordered cristobalite. These findings are confirmed by the view of Bartha and Hupertz [7] that cristobalite is the form of silica present in rice husk. The shift in the value of  $2\theta$  was also seen to occur with increase of the period of

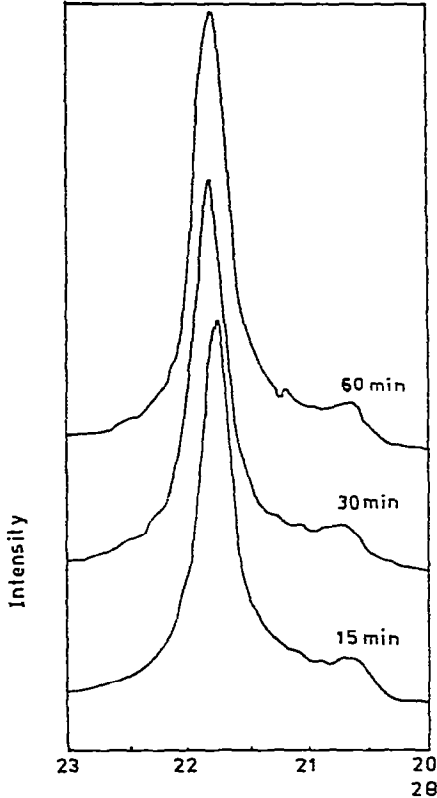


Fig. 3. Value of  $2\theta$  for rice husk ash silica fired at  $1000^{\circ}\text{C}$  for different time intervals.

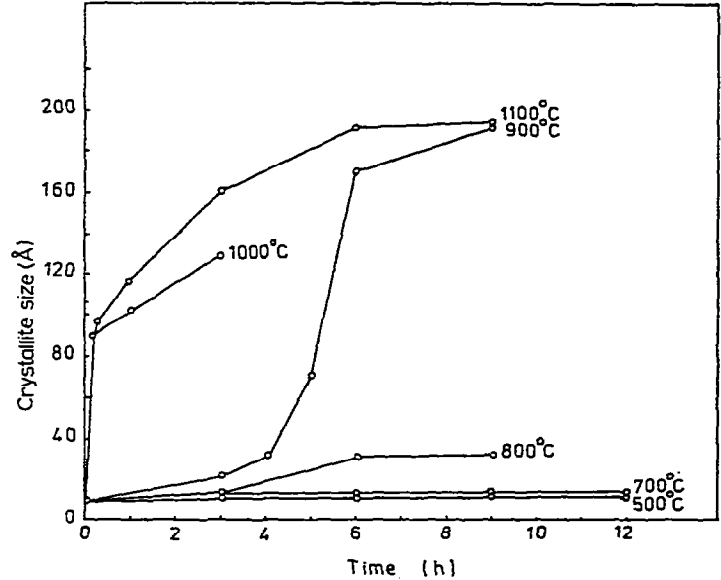


Fig. 4. Effect of temperature and time of annealing on crystallite size of rice husk ash silica.

annealing. This is better visualized by the curves of ash samples fired at  $1000^{\circ}\text{C}$  for 15, 30 and 60 min (Fig. 3), i.e. a crystal perfection is taking place from disordered to ordered cristobalite with increase of time of annealing. The value of  $2\theta$  remained constant for samples annealed for longer periods.

The crystallite size of ash silica fired between  $500$  and  $700^{\circ}\text{C}$  remained nearly constant even after a soaking period of 24 h (Fig. 4). Firing the ash at  $900^{\circ}\text{C}$  for 4 h, however, favoured the crystallites growth, while firing at  $1000^{\circ}\text{C}$  or  $1100^{\circ}\text{C}$  gave well crystalline material after a few minutes, the size of which did not develop much with time of soaking, i.e. time did not favour crystallite growth of ash silica at both low and high treatment temperatures.

The rate of grain growth, like the rate of reaction, should increase exponentially with temperature. Usually the growth rate is inversely proportional to crystallite size and is represented by the relation [13]

$$\frac{dD}{dt} = \frac{K}{D}$$

where  $D$  = grain size,  $t$  = time,  $K$  = rate constant. It gives, by integration, the

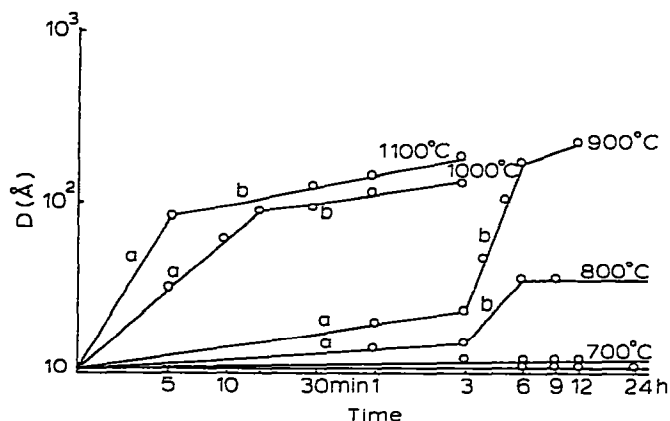


Fig. 5. Log plot of crystallite size against time.

following relation

$$(D^2 - D_0^2) = K(t - t_0)$$

The log plot of  $D$  against  $\log t$  (Fig. 5) shows that the curves of ash fired at different temperatures could be represented by more than one straight line intersecting with slopes varying between 0.19 and 1.0, usually a slope approaching 0.5 is accepted for the above relation. Plotting  $\log(D^2 - D_0^2)$  against  $\log(t - t_0)$  gave curves that could be represented by two lines intersecting a and b (Fig. 6). This behaviour indicates that more than one process is taking place, namely nucleation, crystallite growth and crystal perfection. The slopes of the lines a and b representing the rate reaction constant  $K$  at each temperature are plotted on a logarithmic scale against  $1/T$  (Fig. 7). Line a is represented by two parts intersecting at a temperature of  $964^\circ\text{C}$ . This indicates that the process taking place is not a simple one. It is therefore

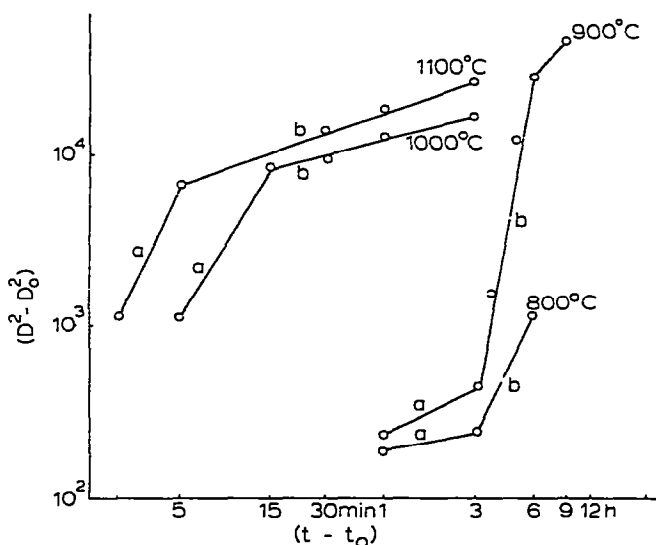


Fig. 6. Log plot of  $(D^2 - D_0^2)$  against time  $(t - t_0)$ .

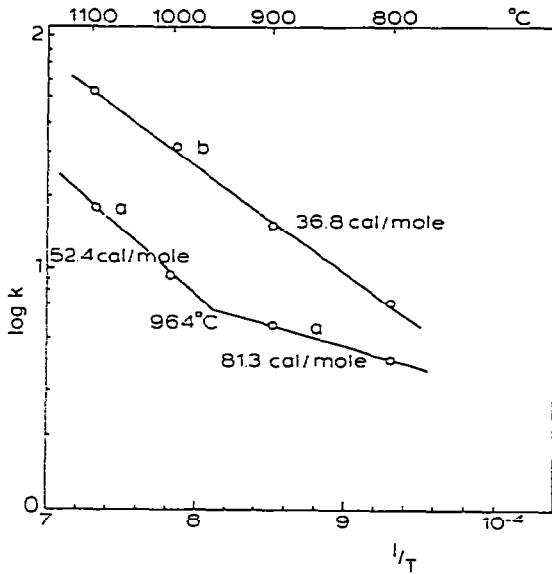


Fig. 7. Log  $K$  against  $1/T$ .

believed that the nucleation and crystallite growth processes are taking place simultaneously during annealing. The temperature of annealing governs the process predominating. The activation energy for the different processes is calculated from the Arrhenius equation as follows

$$K = A e^{-Q/RT}$$

Multiplying the slope of the plot of  $\log K$  against  $1/T$  by 4.575 gives the corresponding activation energy. Thus, in the temperature range 800–900°C the nucleation process manifests itself during the first 3 h with an activation energy of 81.3 cal mole<sup>-1</sup>. This view is supported by the slight change in crystallite size with increase of time of annealing during this period. In the temperature range 1000–1100°C, on the other hand, crystallite growth is the predominating process, with an activation energy of 52.4 cal mole<sup>-1</sup>. The point of intersection, 964°C, represents the temperature at which both processes occur with the same intensity. Line b represents one process, mainly crystallite growth and crystal perfection, with an activation energy of 36.8 cal mole<sup>-1</sup>.

Verduch [14] investigated the kinetics of the formation of cristobalite from amorphous silica in the temperature range 945–1085°C. He recognized a definite nucleation period which is a temperature function that delivered an activation energy of 102 cal mole<sup>-1</sup> followed by a growth and perfection of cristobalite crystals with an activation energy of 50.9 cal mole<sup>-1</sup>. These results support the view that in ash silica there exist nuclei of disordered cristobalite that readily grow with rise of temperature. This growth process occurs simultaneously with the nucleation process, a case different from amorphous silica. As a result the activation energy required for the nucleation and growth processes for ash silica is comparatively low and varies with the temperature of annealing according to the process predominating. Mean-

while, the activation energy needed for the growth and crystal perfection is also lower than that needed for other types of amorphous silica.

## CONCLUSIONS

Ash silica fired at 500°C gave a low specific gravity of 2.06 g cm<sup>-3</sup> due to the nature of stacking of Si—O and Si—OH groups as well as the presence of carbon (ignition loss at 1000°C = 0.98%).

The position of maximum X-ray peak of ash silica fired between 500 and 800°C occurs in the region of cristobalite, indicating the presence of nuclei of cristobalite. However, the value of  $2\theta$  is slightly shifted, denoting a disordered form.

Nucleation and growth processes occur simultaneously during the first period of annealing. The temperature of treatment governs the predominating process, accordingly activation energy varies being 81.3 and 52.4 cal mole<sup>-1</sup> for the temperature ranges 800–900°C and 1000–1100°C, respectively. At 964°C both processes occur with the same intensity. Growth and crystal perfection then follow with an activation energy of 36.8 cal mole<sup>-1</sup>.

Activation energies required for the different processes are comparatively lower than those required for other types of amorphous silica.

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