

X-RAY DIFFRACTION STUDIES ON THE TRANSFORMATION OF KAOLINITE INTO METAKAOLIN: I.  
VARIABILITY OF INTERLAYER SPACINGS

G. B. MITRA AND S. BHATTACHERJEE, *Department of Physics,  
Indian Institute of Technology, Kharagpur, India.*

ABSTRACT

Georgia kaolinite, untreated and dehydrated at temperatures ranging between 200°C and 600°C, have been studied for the X-ray line broadening of their basal reflections. It is observed that the interlayer spacing for the basal planes varies by a constant fraction of the mean value. The fractional change in the interlayer distance and the proportion of the planes so affected have been evaluated by Mitra's (1963) method for all stages of dehydration excepting the last two when only one reflection is available. A single line technique developed for this purpose, has been used for all the stages. The disorder originally present in the untreated sample, as variability of interlayer spacings, is increased only at earlier stages. At the next stage, the extent of the disorder remains the same but more planes are affected. Finally, the disorder increases leading to the collapse of the kaolin layer and formation of metakaolin. Two types of crystallites exist, one being more prone to disorder than the other.

INTRODUCTION

It is well known that kaolinite transforms into metakaolin at about 500°C due to loss of structural water. While kaolinite is crystalline, metakaolin has a highly disordered structure. Brindley and Nakahira (1959) on the basis of a detailed X-ray study, concluded that metakaolin has two-dimensional regularity in the kaolin layers which, however, are so stacked that three dimensional periodicity is lost.

An interesting question which remains unanswered is—through which process does this transformation take place and through which stages does it progress? It is well known that kaolinite contains structural defects. Brindley and Robinson (1946), Johns (1953) and Newnham (1961) have shown that stacking disorders exist in which one kaolin layer is shifted parallel to itself with respect to an adjacent layer. Mitra (1963) has observed another type of stacking disorder, namely, that the interlayer distance between the kaolin layers varies randomly by a constant fraction of the interlayer distance. Mitra (1963) has measured this fraction and the proportion of planes affected by such disorders and has suggested that this disorder is transmitted to the different stages of dehydration.

The present work was undertaken to investigate this hypothesis due to Mitra (1963) and hence to make a detailed study of the variation of 'g'—the mean fractional change in the interlayer spacing and of 'γ'—the proportion of planes affected by such disorder at different stages of dehydration.

## EXPERIMENTAL

*Description of the sample.* A sample of kaolinite from Georgia, U.S.A. was selected for investigation; its average chemical composition is  $\text{SiO}_2$  45.15,  $\text{Al}_2\text{O}_3$  35.92,  $\text{Fe}_2\text{O}_3$  0.02,  $\text{TiO}_2$  0.16,  $\text{MgO}$  0.59,  $\text{CaO}$  0.00,  $\text{Na}_2\text{O}$  2.10,  $\text{K}_2\text{O}$  0.03,  $\text{H}_2\text{O}(+)$  14.71,  $\text{H}_2\text{O}(-)$  0.27, total 98.95 weight percent. The sample was divided into several portions and each portion was heated in a platinum crucible for 10 hours each at temperatures of 200°C, 300°C, 400°C, 500°C and 600°C respectively in a muffle furnace. The samples were then cooled in a desiccator.

*Differential thermal analysis.* One hole of the specimen holder was packed with finely powdered kaolinite while the other was packed with powdered alumina as reference substance. Differential emfs' were recorded using a platinum and platinum-rhodium thermo-

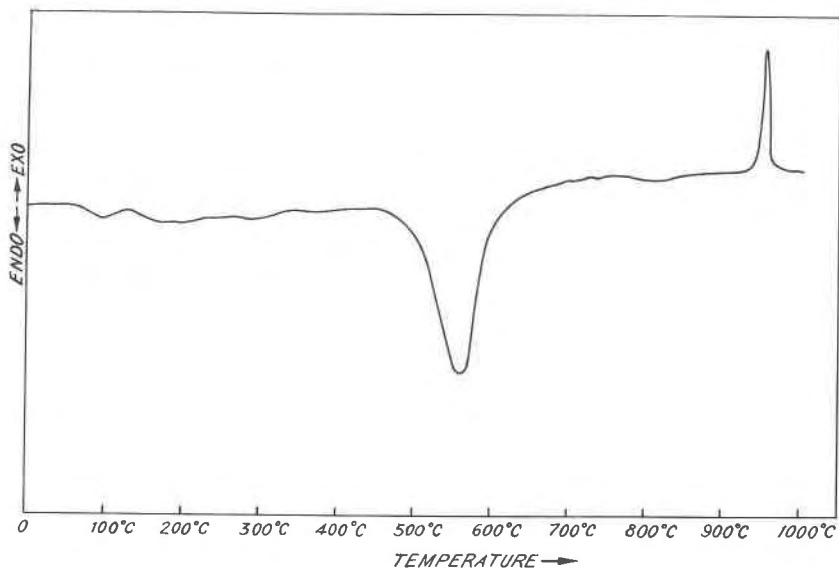


FIG. 1. Thermogram of the kaolinite sample.

couple and a galvanometer. The DTA curve (see Fig. 1) shows a broad and diffuse endothermic peak extending from about 150°C up to about 300°C, one sharp endothermic peak at 562°C, and one sharp exothermic peak at about 955°C.

*X-ray diffraction techniques.* For X-ray diffraction study, a Norelco diffractometer unit was used. A copper target and an aluminium-nickel balanced filter was used to get  $\text{CuK}\alpha$  radiation. For photographic technique a cylindrical rod about 0.3 mm in diameter, of the powdered sample mixed with collodion, was prepared. Each sample was exposed for 20 hours, using a 114.6 mm Debye Scherrer camera, for identification and determination of the peak positions.

For counter diffractometry, thin smooth rectangular cakes of the samples mixed with collodion were prepared so as to make the orientations of the crystallites highly random. X-ray diffraction profiles for different reflections from different samples were obtained with the help of the Norelco diffractometer fitted with a GM tube connected to a decade counter and an automatic chart recorder. Sharp reflections were recorded by the chart recorder at

a scanning speed of  $1/4^\circ (2\theta)$  per minute while the weak reflections were recorded by fixed-count technique. The goniometer was manually set at an interval of  $0.1^\circ$  to  $0.05^\circ$  and at each setting the time for 1000 counts was recorded thrice. The intensity profiles for various reflections were constructed with the average values of three consistent readings. Thus an accuracy of about 2%, which was sufficient for the present study, was achieved. Divergence and receiving slits used were of  $1^\circ$  and  $0.003''$  apertures respectively. Soller and antiscatter slits ( $1^\circ$ ) were used to render the beam highly directional so that air scattering was negligible and the rays could be treated as effectively monochromatic.

## RESULTS AND DISCUSSIONS

*Nature of the line profiles.* The observed line profiles for all reflections were corrected for geometrical aberrations by the Stokes (1948) deconvolution method. Geometrical line profiles for this purpose were obtained by using strain-free quartz of large particle size. Geometrical line profiles for those reflections of kaolinite, not in the immediate angular vicinity of any of the reflections of quartz, were constructed by applying Mitra's (1963) method.

Since the present study concerns only the interlayer distances, only the  $00l$  reflections were investigated. Basal reflections up to  $l=6$ , in the case of untreated sample, and  $l=4$  in all heat-treated samples up to and including  $400^\circ\text{C}$ , were present. For samples treated at  $500^\circ\text{C}$  and  $600^\circ\text{C}$ , only 001 and 002 reflections were present. The basal ( $00l$ ) reflections for all the samples untreated as well as treated up to  $400^\circ\text{C}$  were observed to be broad and asymmetrical. For samples dehydrated at  $500^\circ\text{C}$  and  $600^\circ\text{C}$  the 001 reflections were very broad and diffuse while the 002 were less so.

The asymmetry and the broadening for all reflections from different samples were observed to vary irregularly with the rise of dehydration temperature. Figures 2 and 3 plot  $\beta_d$  against  $l$  for the untreated as well as for samples treated up to  $400^\circ\text{C}$ , where  $h=2d \sin \theta/\lambda$ ,  $\beta_d$  is the integral breadth of the pure diffraction profile measured in units of  $h$ , and is calculated from Fourier coefficients of the different diffraction profiles corrected for geometrical effect,

$$\beta_h = \frac{F(0)}{F(0) + 2 \sum_{n=1}^{\infty} F(n)} \quad (1)$$

where  $F(n)$  is the Fourier coefficient of  $n$ th order,  $d$  is the interplaner distance,  $\theta$ -Bragg angle of reflections and  $\lambda$ -wave length of the radiation. The general features of the plots are as follows:

- (i) The plots are non-linear.
- (ii) Values of  $\beta_h$  increase with increasing  $l$  for all the samples.
- (iii) With rise of dehydration temperature the values of  $\beta_h$  corresponding to all  $l$  values increase though not in a regular way.

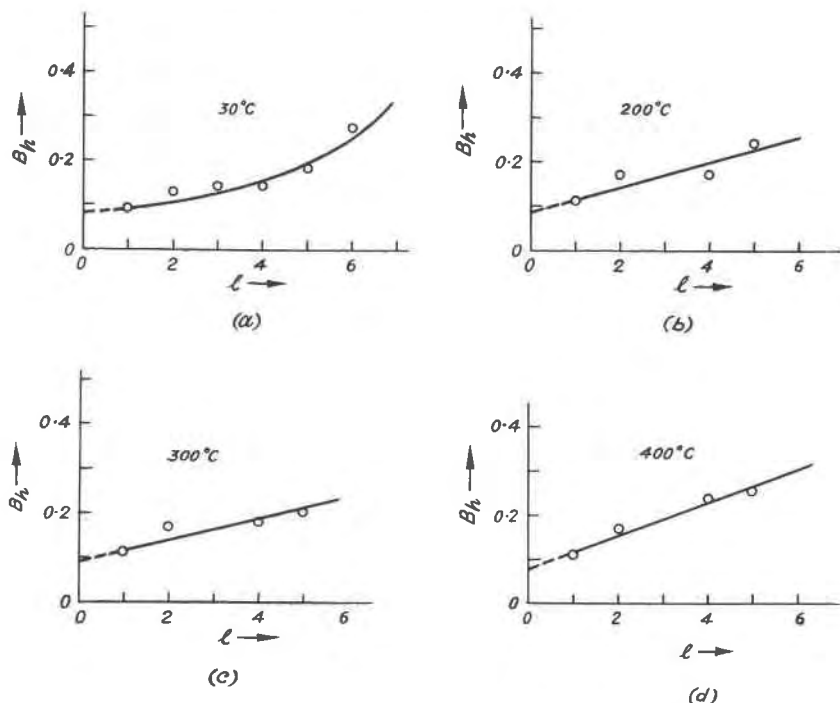


FIG. 2. Variation of integral width ( $\beta_h$ ) of the basal reflections with order ( $l$ ) of the reflections. (a), (b), (c), (d) Best fit curves used for extrapolation to find  $(\beta_h)_{l=0} = \beta_p$  for different samples.

These observations clearly show that the broadening can be attributed not only to particle size but also to other defects present in the samples. Mitra (1963) has shown that the defect affecting the  $(00l)$  reflections consists of variations in the interlayer distances and has described a method for the quantitative evaluation of the extent of the variability in the interlayer distance as well as the proportion of the planes affected by such defects. This method with some modifications has been adopted in the present work.

*Measurement of 'g' and 'γ'.* Values of  $g$ —the mean fractional change in the interlayer distance and  $\gamma$ —the proportion of planes affected by such disorder, for all basal reflections of these samples have been calculated by the method described by Mitra (1963) and determined from  $g = 1/\pi l \cot^{-1} \pi \Delta / \beta_D$  and  $\gamma = \beta_D / \sin^2 \pi l g$  where  $\Delta$  is the distance of the peak from the centroid of the diffraction profile and  $\beta_D = \gamma/2 (1 - \cos 2\pi l g)$ , the integral width of the defect profile.  $\Delta$  was determined by the method de-

scribed by Mitra (1963) and  $\beta_D$  from the relation

$$\beta_D = \beta_h - \beta_p$$

where  $\beta_p$  is the integral width due to particle size only. This equation is valid on the assumption that the particle size profile is of Cauchy type. Wilson (1962) has shown that the defect profile is also of the Cauchy type. Thus the additivity relation given above becomes valid.  $\beta_p$  has been determined by extrapolating the  $\beta_h$  vs.  $l$  curves for different samples to  $l=0$ , since, as has been shown later (equation 2) the defect broadening is zero at  $l=0$ . From the ordinates at  $l=0$ ,  $\beta_p = (\beta_h)_{l=0}$  was obtained. Determination of  $\beta_p$  by extrapolation of  $\beta_h$  to  $l=0$  is shown in Figures 2 and 3. Since  $\beta_h$  is a complicated function of  $l$ , various polynomial curves had to be tried to fit with the experimental data and the best fitting curve was used for purpose of extrapolation.

For samples treated at 500°C and 600°C respectively this could not be done because only 002 reflections could be considered. The  $g$  and  $\gamma$  values in these samples were determined by adopting a single line technique similar to that developed by Misra and Mitra (1967). The theoretical derivation of the method is as follows:

The Fourier transform  $Y(t)$  of the intensity line profile from a layered structure with variable interlayer spacing has been worked out by Wilson (1962) and is given by

$$Y(t) = NF^2e^{-2\beta D t}e^{-ibt} \tag{2}$$

where

$$b = Y \sin 2\pi lg$$

For

$$l = 0, \quad Y(t) = NF^2$$

which shows that at  $l=0$ , only particle size effect is present and defect is absent. This result has been used in determining particle size broadening of the 00 $l$  reflections.

The general expression for the variance of the defect profile developed by Wilson (1962) is given by

$$W_D = -\frac{1}{4\pi^2} \left[ 2(\sigma_1 + \sigma_2) \frac{J'(0)}{J(0)} + \frac{J''(0)}{J(0)} + \left\{ \frac{K'(0)}{J(0)} \right\}^2 \right] \tag{3}$$

where  $W_D$  is the variance of the line profile with mistake and  $\sigma_1$  and  $\sigma_2$  are the angular ranges over which integration is carried out.  $J(t)$  and  $K(t)$  are the real and imaginary parts of the  $t$ -th order Fourier transform  $Y(t)$  of the intensity profile given by

$$Y(t) = J(t) - iK(t) \quad (4)$$

Comparing equation (2) with equation (4) we get  $J(t) = NF^2 e^{-2\beta_D t} \cos bt$  and  $K(t) = NF^2 e^{-2\beta_D t} \sin bt$ . Using these expressions  $J(0)$ ,  $J'(0)$ ,  $J''(0)$  and  $K'(0)$  have been found out. On substitution of these values in equation (3) we get

$$W_D = \frac{1}{\pi^2} \{S\beta_D - \beta_D^2\} \quad (5)$$

where  $S = \sigma_1 + \sigma_2$  the range over which the integration for determination of  $W_D$  is carried out. The total variance of the line profile corrected for geometrical effect only can now be written as

$$W = W_P + W_D$$

where  $W_P$  is the variance due to particle size line profile. Proceeding as Mitra (1964) we have for  $W$  in  $2\theta$  unit.

$$\frac{W \cos \theta}{\lambda S} = \frac{1}{\pi^2 P'} - \frac{\beta_D^2}{\pi^2 d^2} \frac{\lambda}{S \cos \theta} \quad (6)$$

where  $1/P' = 1/P + \beta_D/d$ ;  $P$ , is the true particle size. Equation (6) shows that a plot of  $(W \cos \theta)/(\lambda S)$  against  $\lambda/(S \cos \theta)$  will be linear. This equation was used to find the values of  $\beta_D$  in the case of samples dehydrated at 500°C and 600°C. From the slope of the linear plots of  $(W \cos \theta)/(\lambda S)$  against  $\lambda/(S \cos \theta)$  (fig. 4) values of  $\beta_D$  for the 002 reflections were found out. This method was also extended to 002 reflec-

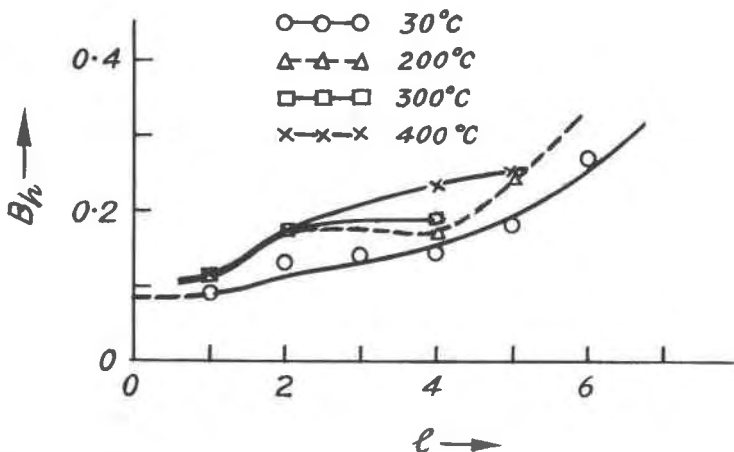


FIG. 3 Plots of  $\beta_h$  vs  $l$  for samples dehydrated at different temperatures.

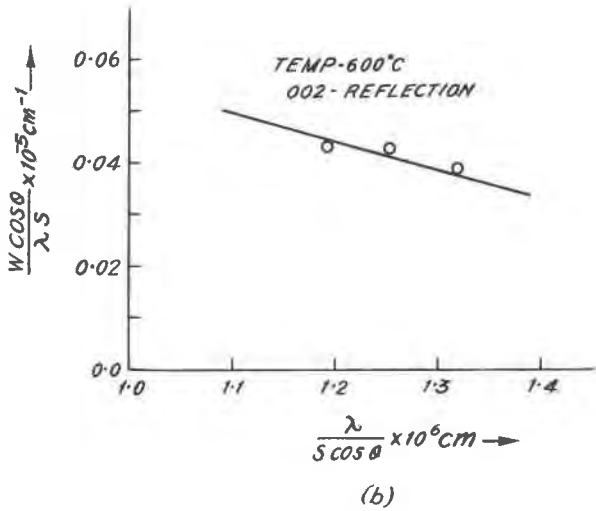
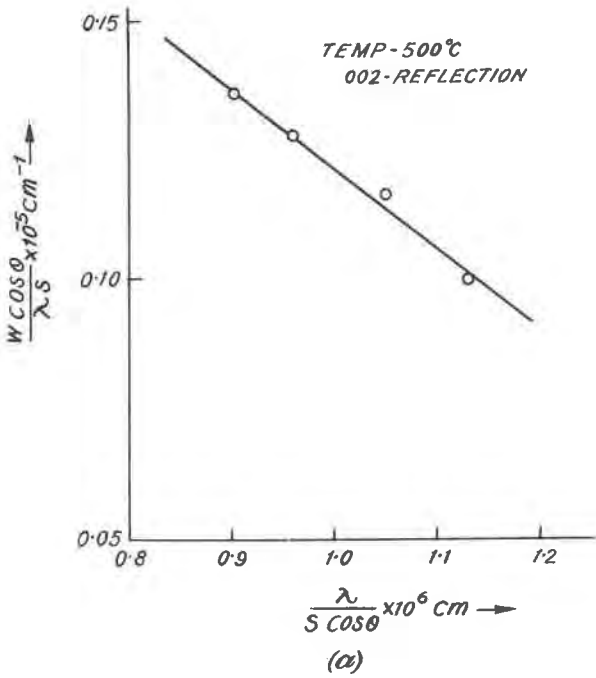


FIG. 4. Plots of  $W \cos \theta / \lambda S$  vs  $\lambda / S \cos \theta$  corresponding to 002 reflection for samples dehydrated at (a) 500°C (b) 600°C.

tions for all other samples as well. Comparison with particle size and  $\beta_D$  from  $\beta_h$  measurements described previously was found to give consistent results.

#### DISCUSSIONS

Table 1 shows that with dehydration the mean fractional change in the interlayer distances of the basal planes first increases from 0.148 to 0.171 at 200°C while  $\gamma$ , the proportion of such planes, changes from 0.063 to 0.065, a change which is practically insignificant. Then at 300°C, the  $g$ -value remains the same but more planes become affected as is shown by the increase of  $\gamma$  value from 0.065 to 0.080. At 400°C both  $g$  and  $\gamma$  remain almost unchanged. But at 500°C the value of  $g$  increases sharply to 0.210 while the value of  $\gamma$  decreases from 0.077 to 0.033. Thus in the

TABLE 1. VARIATION OF  $g$  AND  $\gamma$  WITH DEHYDRATION OF THE KAOLINITE SAMPLE

Temperature	$g$	$\gamma$
30°C	0.148	0.063
200°C	.171	.065
300°C	.171	.080
400°C	.173	.077
500°C	.210	.033
600°C	.218	.021

first stage of dehydration the planes which were originally affected by defects are further affected with the extent of defects in them increasing. At the next stage, *i.e.* above 200°C, the extent of the defects remains unchanged while number of planes so affected is increased. It is noteworthy that the fresh planes which are affected at this stage, have defects of extent equivalent to the maximum attained at the previous stage. This points to the existence of something like a "latent heat of transformation". On increasing the temperature to 400°C the conditions are not changed—thus indicating the existence of a dynamical equilibrium. At 500°C and beyond an unexpected phenomenon is met with. While the extent of the defects has increased, the proportion of planes affected by them has decreased.

This may be explained on the assumption that the specimen consists of two types of crystallites, which can be called type I and II. Type I is more prone to defect with dehydration while type II is less so. This difference may be due to several facts including the state of initial perfection of the crystallites. It is well known in the case of order-disorder phenomena in alloys that the existence of one misplaced atom induces



other atoms to occupy misplaced sites. In a similar way, the existence of variable interlayer distances in a kaolinite crystallite may induce other layers to follow suit in a cooperative way as and when interlayer forces are weakened by snapping of interlayer OH bonds due to removal of OH groups.

At 200°C due to expulsion of surface water which is evidenced by the weak endothermic band in this range of temperature in the DTA curve, the value of  $g$  increases while  $\gamma$  increases only very slightly. It is expected that in this low temperature range only a few crystallites of type I will be affected. Hence the value of  $\gamma$  is not increased so markedly. As the temperature is further increased more and more crystallites of type II get affected which is shown by an increase in the value of  $\gamma$  upto 400°C. At 400°C dynamical equilibrium is maintained by more crystals of type II and still more of type I being affected by the defects but a number of already affected crystals of type I suffer a collapse of the kaolin layers which go into amorphous or turbostratic states. It must be remembered that  $\gamma$  represents the proportion of crystalline planes affected by the defect and does not take into consideration any possible presence of an amorphous or turbostratic state. At 500°C the sharp increase in  $g$  value shows that collapse of the kaolinite structure has progressed, the larger proportion of the already affected planes of the type I having been converted to the amorphous metakaolin phase. Only a proportion of the planes in type II remain in the kaolinite structure with greater disorder. As the temperature is increased further to 600°C more and more planes from type II are affected showing an increase in the value of  $\gamma$  and the disorder also increases a little more. Thus it may be concluded that the transformation of kaolinite to metakaolin starts somewhere between 400°C and 500°C and the formation of the metakaolin phase is preceded by a gradual variation of the interlayer distances which increases sharply just when the collapse of the structure takes place. This process continues even at 600°C and beyond till the conversion is complete.

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