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X-RAY VARIANCE METHOD TO DETERMINE THE DOMAIN SIZE AND LATTICE DISTORTION OF GROUND KAOLINITE SAMPLES

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ABSTRACT

The variance method [WILSON, 1963] was applied to determine the changes in domain size and lattice distortion along the 001 direction in dry grinding experiments of Sedlec (Zettlitz) kaolinite samples. Very short grinding (3 min) already resulted in considerable lattice distortion, while change in domain size is of minor extent. A grinding of 30—40 min converted the medium crystallized Sedlec (Zettlitz) kaolinite into a substance which had an X-ray diffraction pattern similar to that of poorly crystallized kaolinite$_d$.

INTRODUCTION

In an earlier paper I dealt with the changes in the crystallinity parameters of kaolinite on a sample series of artificially destructed structure (by means of dry grinding). I proposed to introduce a complex crystallinity index to characterize the state of crystallinity. This index proved to be appropriate to trace the changes due to the effect of grinding which affect the X-ray diffractogram pattern.

The complex crystallinity index (CCI) turned out to be very useful also for the comparison of natural state samples. However, it provided no numerical information on two very important parameters, grain size and lattice distortion. The components due to domain size and lattice distortion could not be distinguished in the distortion of the diffraction profile. (The effects of deformation and domain size appear superimposed).

It was necessary to undertake a more thorough analysis of the 001 reflections, in addition to the determination of half width, which does not provide sufficient information. In many cases, when kaolinites of rock samples are studied, as a consequence of coincidences only the 001 reflexions can be well measured, particularly well the 001 which is the strongest peak of kaolinite. In the experiments reported now, series of artificially destructed kaolinites was examined. A more exact mathematical procedure was applied than in the previous experiments, in order to complete the results obtained at the application of the CCI with the changes in determination of domain size and lattice distortion.

The variance method [WILSON, 1962, 1963] was used to calculate the coherently dispersed domain size resulted during grinding as well as the deformation of the lattice in the direction 001.

SAMPLE PREPARATION AND X-RAY TECHNIQUES

An amount of 2g of Sedlec (Zettlitz) kaolinite was submitted to dry grinding in a grinding mill of type Fritsch Pulverisette—2, for 3, 5, 10, 15, 20, 30 and 40 minutes. The powders obtained were kept in an exsiccator for 24 hours.

The X-ray tests were performed by means of a Philips X-ray diffractometer, as follows: radiation: CuK_α, monochromator: graphite, goniometer speed: 1/2°/min, divergency and detector slits: 1°, proportional counter, time constant: 2, recording speed: 1600 mm/h.

The line profiles were measured by 0,05° 2Θ steps intervals, usually in the range of 11,00° 2Θ—13,45° 2Θ.

MATHEMATICS USED

The variance, i. e. the reduced second moment of the line profile, was established in order to study the line widening of the 001 reflexions, to distinguish the effect of domain size and lattice distortion, making use of the results by WILSON [1962, 1963] and MITRA [1969].

The reduced second moment of the intensity function is, by definition

$$W(2\Theta) = \frac{\int (2\Theta - \langle 2\Theta \rangle)^2 \, I\,(2\Theta)\, d\,(2\Theta)}{\int I\,(2\Theta)\, d\,(2\Theta)}$$

where $\langle 2\Theta \rangle$ is the centroid of the line.

The variances being additive, the resulting variance of one line profile is

$$W(2\Theta) = W_0 + W^p + W^d$$

where W_0, W^p, W^d are the variance values due to instrumental error, domain size and lattice distortion, respectively.

If the tails of the line profiles show the Cauchy distribution, i. e. they are approaching asymptotically the background, then variance is a linear function of the chosen angle range [WILSON, 1963].

The domain size and lattice distortion can be deduced from the ordinate incept and slope of the following equation [WILSON, 1963]

$$W\,(2\Theta) \cos \Theta \,/\, \lambda\,(\Delta 2\Theta) = {}^1/\pi^2 p + 4 \sin \Theta \operatorname{tg} \Theta \,\langle \varepsilon^2 \rangle \,/\, \lambda\,(\Delta 2\Theta)$$

where p is the effective domain size, $\sqrt{\langle \varepsilon^2 \rangle}$ is the expected value of the lattice distortion.

RESULTS

Variance, centroid, 001 directional domain size and lattice distortion were determined by using a program written for EMG—666 type computer.

Variance is very sensitive of the background. This made indispensable certain background corrections. *Fig. 1* shows the variance as a function of range. It is to be seen that the variance is linear in function of the chosen angle range.

Table 1. contains the centroid and variance value. The lowest row represents the data of Cserszegtomaj kaolinite (Hungary) which is disordered along axis *b*.

The centroid values also have been determined to calculate the variance. As a result of grinding, the centroid values shifted towards smaller 2Θ angles. This reflects a lattice dilatation according to axis *c*. This is in harmony with the statement made by FIEDLER and STEINICKE [1967], namely, that the *d* value of the 001 reflexion of poorly crystallized kaolinite is higher. Even 3 minute of grinding had a considerable effect on the centroid value.

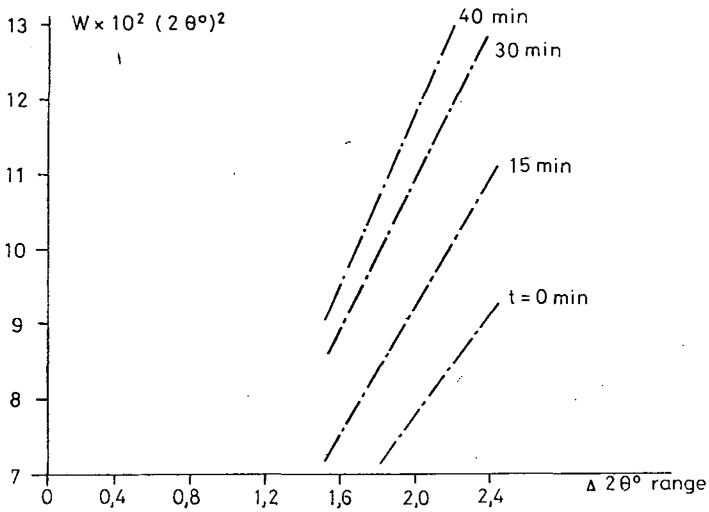

Fig. 1. Variance versus integration range

As mentioned before, the change in the half width of the 001 base reflexion is a result of line widening due to domain size and lattice distortion. In the experiment, the half width value of the 001 basal reflexion changed from 0,39° 2Θ to 0,42° 2Θ *(Fig. 2)*. Accordingly they belong to the range of poorly crystallized kaolinite, in harmony with the results published by BRINDLEY and KURTOSSY [1961], i. e. 0,3—0,4° 2Θ.

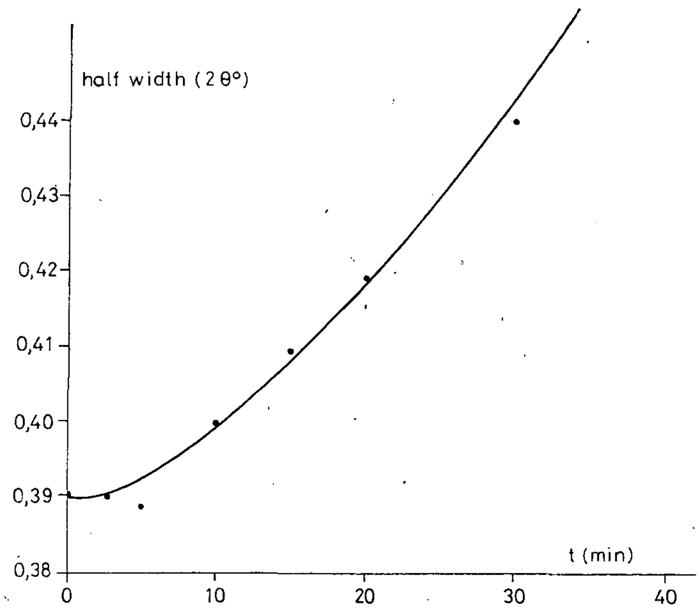

Fig. 2. The half width of 001 reflexion as a function of grinding time

TABLE 1

Variance analysis data

Grinding time (min)	Centroid (2Θ°)	Variance (2Θ°)	Range (2°Θ)
0	12,2691	0,09505	2,45
3	12,2264	0,09662	2,45
5	12,2223	0,10003	2,45
10	12,1942	0,10867	2,40
15	12,1869	0,11335	2,40
20	12,1610	0,12970	2,40
30	12,1493	0,13525	2,40
40	12,1142	0,12952	2,40
Cserszegtomaj	12,2134	0,12775	2,40

The changes in lattice distortion domain size provoked by grinding are illustrated in Table 2. Deformation changes at a higher rate in the early phase of grinding About 30—40 minutes of grinding brought the deformation values of the medium crystallized Sedlec (Zettlitz) kaolinite near to that of Cserszegtomaj kaolinite$_d$. (Table 2 and *Fig. 3*). Similar results have been obtained in the case of the CCI, too.

Domain size change is less important in case of short time grinding: in 30—40 minutes, however, the quasi-minimum values are obtained. It is very likely that

TABLE 2

Data of domain size and lattice distortion

Grinding time (min)	Domain size (Å)	Lattice distortion $\times 10^3$
0	120	6,34
3	122	6,68
5	117	7,10
10	110	7,63
15	104	8,22
20	88	9,01
30	91	10,34
40	87	11,30
Cserszegtomaj	100	12,90

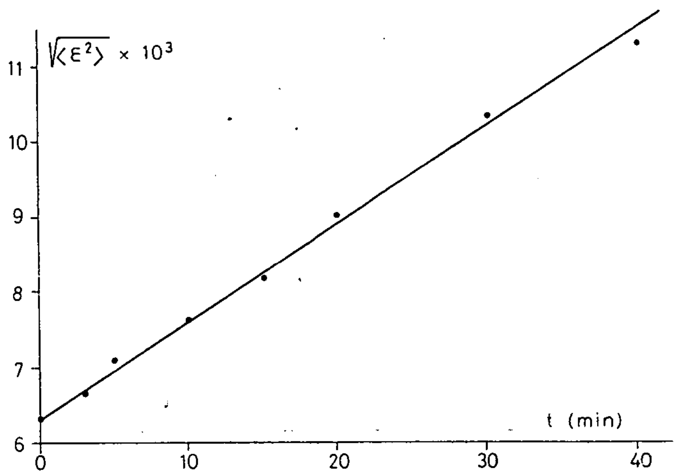

Fig. 3. Change of lattice distortion versus grinding time

amorphization begins in this phase *(Fig. 4)*. The trends of changes in domain size and lattice distortion show a fairly good agreement with the statement of KRANZE [1975] who pointed out that at the beginning of grinding lattice distortion is the morr important change.

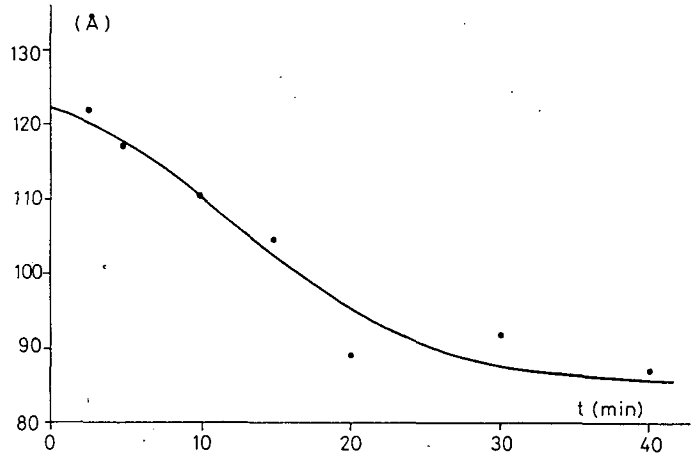

Fig. 4. Change of domain size versus grinding time

The present results emphasized once more the bearing of the proper choice of grinding time. The procedure of grinding affects two parameters, domain size and lattice distortion, which are also of genetical importance.

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