

CHARACTERIZATION OF THE PARTICLE SIZE AND THE CRYSTALLINITY OF CERTAIN MINERALS BY INFRARED SPECTROPHOTOMETRY AND OTHER INSTRUMENTAL METHODS—I. INVESTIGATIONS ON CLAY MINERALS

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Abstract—Effects of particle size, crystallinity and the amount of the structural water in kaolinites on their infrared spectra, were studied. The samples were ground in a vibrating ball-mill, and infrared and X-ray spectra, as well as thermal and specific surface area measurements, were taken on the initial and ground samples. Changes of the 3705-cm^{-1} infrared band intensity and of the absorbance ratio of the $A_{3630}/A_{3705\text{-cm}^{-1}}$ bands were determined as a function of the grinding time. Correlation functions between the absorption ratio, calculated from the infrared spectra, and the average particle size, as well as between the amorphism, calculated from the X-ray spectra, and the average particle size, were obtained.

INTRODUCTION

Recently, considerable attention has been given to the quantitative determination of the individual clay minerals. At present, X-ray powder diffraction is by far the most widely used method for quantitative determination. The determination, however, will be inaccurate if the samples studied have considerable X-ray amorphous parts. The advantages of infrared determinations compared to X-ray powder diffraction, in principle, are that with the infrared technique both the crystallized materials and the X-ray amorphous samples can be investigated. In spite of these advantages, the infrared methods are still less widespread for quantitative determination of clay minerals from soils and other silicates. The explanation lies in the fact that the pellet preparation involves many sources of error. Due to the effect of the crystal structure, some absorption bands of certain vibrations become wider, while others become sharper, and occasionally some are split into several components by the degenerate vibrations.

In most cases, the increasing irregularity of the crystal structure increases the local symmetry of the vibrating groups, e.g. SiO_4 , of the clay minerals resulting in a decrease of the number of the degenerate vibrations and a simplified spectra. The greatest problem is that the materials of equivalent chemical composition but of different particle size and crystalline state have considerably different spectra (Duyckaerts, 1959; Tuddenham and Lyon, 1960; Sato *et al.*, 1969).

It is well known that infrared spectra depend also on the orientation of the crystals, on the state of polymorphism, on the shape and size of the absorbing mineral particles and on the material in which the sample particles are imbedded. Complete optical homogeneity would be attainable only if the refractive

indices of the studied and embedding materials were equal. This refractive index difference affects the quantity of the light reflected from the particles, thereby changing the intensity of the light transmitted through the sample as well. The wavenumbers of the absorption bands are changed because of the anomalous dispersion caused by the refractive index difference (Steger, 1964; Duyckaerts, 1959). In the present work, changes of the infrared spectra with particle size and the crystalline state of kaolinite were investigated to obtain quantitative information.

All the spectra were recorded with the same embedding material (spectroquality potassium bromide) under strictly identical experimental conditions. Therefore, the intensity and wavenumber of the characteristic infrared bands depend only on the particle size, degree of crystallinity and the chemical composition of the sample. Infrared spectra were recorded on the original samples, and later, on samples subjected to grinding in order to reduce the particle size and the degree of crystallinity. Samples were taken after appropriate grinding and infrared as well as X-ray powder diffraction spectra were registered. Specific surface area and thermal measurements also were made.

EXPERIMENTAL

Two clay minerals of different origin with different physical characteristics and different degrees of crystallinity were studied: Zettlitz kaolin and Szegilong paper kaolin. According to the preliminary X-ray measurements, the Zettlitz kaolin contains about 90% kaolinite, 8% illite and 2% quartz; the Szegilong paper kaolin contains about 95% kaolinite and 5% amorphous materials.

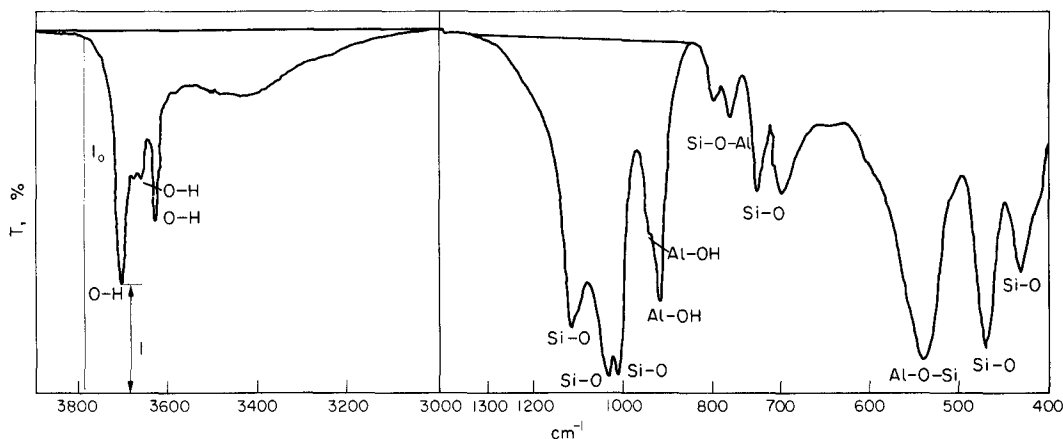


Figure 1. Infrared spectra of Zettlitz kaolin.

Grinding was carried out in a 1-liter vibration ball-mill on a 100-g air dry sample with 700-g, 10-mm dia. steel balls. One mg kaolin, 800 mg potassium bromide and the so-called dilution method were employed to record the infrared spectra. The infrared spectra were obtained using a Zeiss Model UR-10 double beam prism spectrophotometer. The X-ray powder diffraction spectra were obtained on a Model 1051 Philips diffractometer at 1.5405-Å wavelength ($\text{CuK}\alpha$). All of the diffraction spectra were recorded for 0.5-g samples and to avoid orientation, the samples were subjected to intensive vibration for long periods.

DTA measurements were carried out with a MOM Model J. Paulik-F. Paulik-L. Erdey derivatograph. Tests were made on 0.5-g samples.

The specific surface area of the samples were determined from the weight increase of the dried samples equilibrated over different sulfuric acid solutions for 30 days. The BET equation was employed for the calculations.

RESULTS AND DISCUSSION

The infrared spectra of Zettlitz kaolin is shown in Figure 1. Band assignments are listed in Table 1. Band intensities were determined by the baseline method and the characteristic absorption values were calculated.

One-hundred grams of Zettlitz kaolin was ground for 10 days. Samples were taken, initially hourly, and later on, daily. Infrared spectra of all of the samples were recorded. Changes of the band intensity at

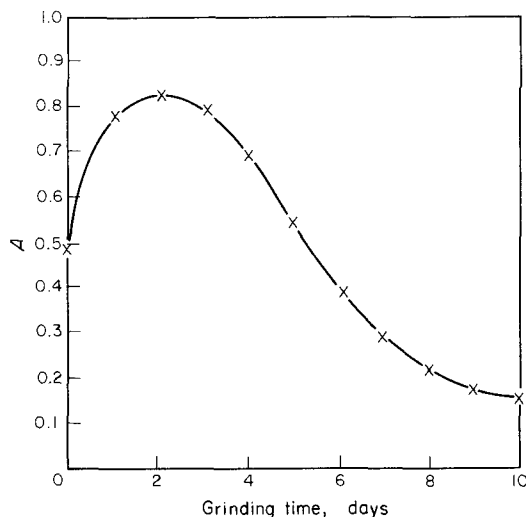
Table 1. Band assignments of Zettlitz kaolin

| Wavenumber (cm^{-1}) | Assignments |
|---------------------------------|---|
| 3705, 3660, 3630 | O-H stretching vibrations |
| 1120, 1040, 1020 | Si-O asymmetrical stretching vibrations |
| 700, 420, 432 | Si-O bending vibrations |
| 940, 920 | Al-OH bending vibrations |
| 795, 760 | Si-O-Al ^{IV} compounded vibrations |
| 540 | Si-O-Al ^{VI} compounded vibration |

3705 cm^{-1} (using the 1002- cm^{-1} band as reference standard) as a function of the grinding time is shown in Figure 2. Because the band maximum wavenumbers were not shifted, the band intensity changes were correlated with the effects of grinding.

It can be seen from Figure 2 that at first the infrared absorption values grow. Then after a certain grinding time, they pass a maximum and decline, even below the initial value corresponding to the unground sample. The explanation of this phenomenon is that in the early phase of the grinding there is an actual particle size decrease and the particles are broken into smaller pieces; thus an increase in the band intensities of the infrared spectra results. These little, but very numerous particles act as new light scattering sites and the energy loss caused by the scattering makes absorption readings higher than expected.

Continuing the grinding (in our case, over a period of 4-5 days), the primary particles tend to adhere to each other, due to the increased surface energy and the action of the amorphous surface layers formed during the grinding. Larger agglomerates form which behave like the original unground particles and yield

Figure 2. Changes of the band intensity at 3705 cm^{-1} .

decreasing absorption values. It is to be noted that, after 10 days of grinding, the absorption dropped even below the original value. This occurs because grinding affected not only the particle size, but also the regularity of the crystal structure, which decreases with increased grinding. Here mechanochemical reactions, e.g. loss of structural water, play an important part. It is well known that valuable conclusions can be obtained about the regularity of the structure and the degree of crystallinity of the clay minerals from the characteristic absorption ratios (Parker, 1969, 1972; Keyser *et al.*, 1965; Chukrov and Zvyagin, 1969). Van der Marel and Zwiers (1959) and Van der Marel (1960) pointed out that the two strongest (OH) bands of kaolinite are at 3705 and 3603 cm^{-1} . The absorption band at 3705 cm^{-1} was assigned to the stretching vibration of the O-H groups located between the layers, while the sharp absorption band at 3630 cm^{-1} was assigned to the stretching vibration of the O-H in the plane of the layer. Parker (1969, 1972) reported that the ratio of these absorption bands depends on the nature of the kaolinite and also on the shape of the particles, the regularity of the crystal structure, as well as the incidence angle of the ray passing the sample. Strictly identical experimental conditions were employed and the absorption ratio, $A_{3630} \text{ cm}^{-1} / A_{3705} \text{ cm}^{-1}$ was measured as a characteristic, shown in Figure 3.

As can be seen, at first the ratio increases only slightly, then, after a certain grinding time, considerable increase can be observed. The reason for this is that at the beginning of the grinding of layered clay minerals, the clay particles are delaminated, at first only along the double layers, and as grinding continues, layers are broken into smaller pieces. Decrease of the regularity of the structure in the direction of the *c* axis decreased the intensity of the 3705- cm^{-1} band and increased the 3630/3705- cm^{-1} absorption ratio.

Other measurements were taken to confirm the conclusions drawn from the infrared spectra. The

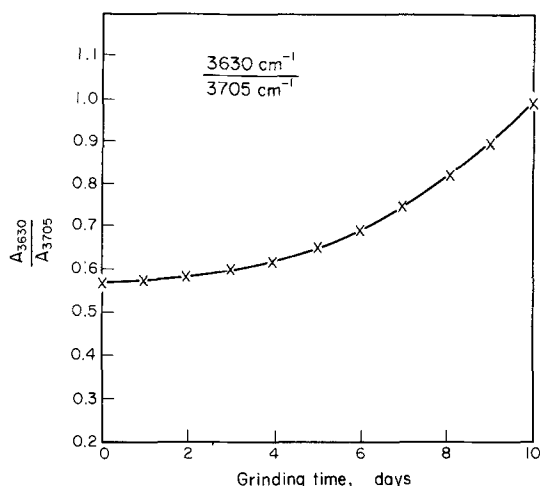


Figure 3. Changes of the absorption ratio as a function of the grinding time.

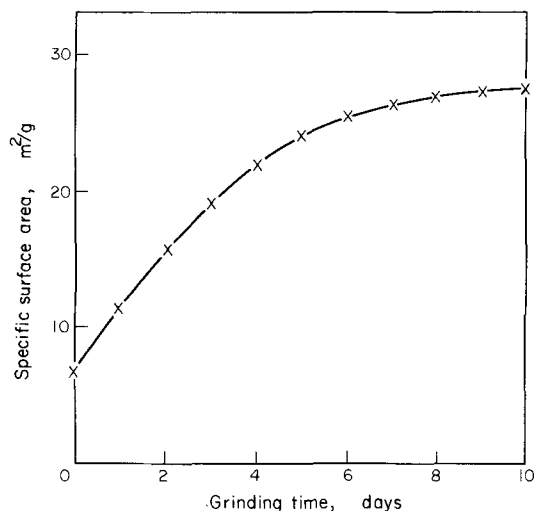


Figure 4. Specific surface area of the Zettlitz kaolin.

effect of fracturing caused by the grinding process was followed by determining the change in the specific surface area as measured by water vapor absorption (Figure 4). From the monotonously rising curve of the specific surface area, it can be concluded that, at the beginning of the grinding the particle size decreases, and at the same time the delamination of the layers also occur. Both phenomena result in an increase of the specific surface area. Further on, due to the aggregation of the adhering particles, a smaller increase of the specific surface area is observed but from the shape of the curve it is evident that grinding is still efficient. Considering the size and the mobility of the water vapor molecules, it can be assumed that it is possible to measure the total surface area, i.e. the sum of the surface area of the primary and of the secondary (agglomerate) particles, by the method used.

The degree of structural lattice irregularity and the degree to which the sample became amorphous, were followed by X-ray powder diffraction spectra of the ground samples. The two most significant basal reflections (7.16 and 3.57 Å) and a (*hkl*) reflection between 4.67 and 4.04 Å, were examined (Figure 5). At the beginning of the grinding the basal reflection peak areas increase. The area decrease caused by the irregularity of the crystal structure appeared only after a 1-day grinding period. It can be assumed, that a parallel orientation of the layers caused by the grinding resulted in an increase of the peak areas (Juhász, 1975). Particle orientation can occur in samples prepared for X-ray powder diffraction. To help eliminate this, X-ray spectra were obtained after an intensive shaking treatment of the preparation in an ultrasonic bath. Parallel measurements were made on each of the fractions and the average of the results are shown in Figure 5.

The greatest change was observed in the (001) reflection 7.16 Å, characterizing the successive kaolinite layers. From X-ray spectra, it is possible to study the phenomenon of delamination caused by grinding. The

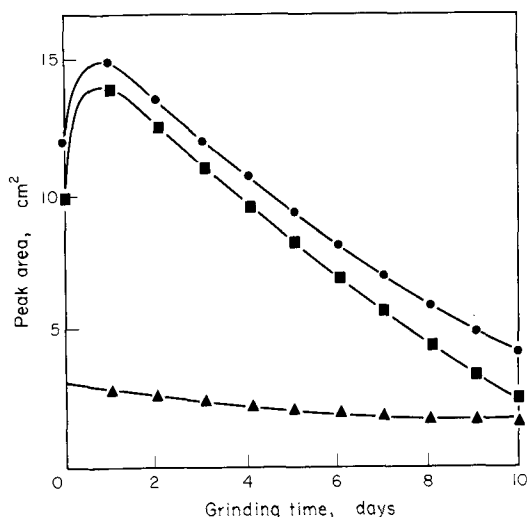


Figure 5. Changes of two basic reflections (at 7.16 and 3.57 Å) and an (*hkl*) reflection (4.767–4.04 Å) of Zettlitz kaolin as a function of the grinding time. ●, 7.16 Å; ■, 3.573 Å; ▲, 4.67–4.04 Å.

infrared method is not able to distinguish between the two most important processes, namely the change of the particle size and the delamination of the layers.

The overlap of certain closely spaced lines is also an important measure of the degree of crystallinity. The reflections at 4.18 and 4.13 Å are the most suitable to examine structure irregularity, because these bands appear as separate lines only in well-crystallized kaolinite and they overlap at once if the smallest irregularity is present (Murray and Lyons, 1955; Nemezc, 1973). Intensity changes of these reflections were quantitatively determined by measuring their overlapping total peak areas (see Figure 5). The peak areas of the (*hkl*) reflections change to a lesser extent than those of the basal reflections. The intensity changes of the X-ray reflections were also influenced by the particle size changes.

The effect of the grinding on the structure was followed also by thermal measurements. The maximum endotherm difference temperature of the endothermic peaks corresponding to the loss of structural water and surface adsorbed water were determined from the DTA curves. Water loss was determined from the TG curves. It was found that the temperature corresponding to the peak maximum of the structural water in the Zettlitz kaolin decreased from 570 to 545°C. The quantity of the structural water also decreased because of the action of the grinding (Figure 6). Both effects are due to the mechanochemical activation of the ground material (see the initial and 10-day ground sample, respectively). The temperature corresponding to the peak maximum of the adsorbed water, however, increased from 100 to 125°C during the same treatment. The quantity of the adsorbed water was increasing. The quantity of the structural water decreased from 130 to 90 mg per 1-g sample, while that of the adsorbed water increased from 20 to 80 mg as a function of the grinding time. The agglomeriza-

tion and the crushing process of the particles cannot be sharply distinguished by any of the methods used (Norton, 1939; Grimshaw and Roberts, 1945).

Quite similar infrared, X-ray and water vapor adsorption curves were obtained on the Szegilong paper kaolin which contains about 5% amorphous material. The absolute changes of these curves were less pronounced due to the originally smaller particle size and the lower degree of crystallinity.

The specific surface area, X-ray powder diffraction and thermal data back up the conclusions drawn from the infrared spectra about the particle size and structural changes occurring during the grinding process. We have attempted to establish correlations describing these relationships as functions of the grinding time, as well as the absorption vs decreasing crystallinity. An exponential equation, suggested by Aljavidin, was applied to calculate the parameters of the particle size vs grinding time relationship.

The parameters of the function:

$$d = d_0 e^{-at},$$

where d_0 is the average particle size in the original sample, d is the actual average particle size, t is grinding time, and a is constant, were calculated.

The d values were determined from the original sample and from the final sample (after 10 days of grinding). The particle size of the original and the ground samples were determined by an automatic particle counter (Classimat Leitz, Wetzlar, GFR) and from the electron-microscope photographs.

The extent to which the samples became amorphous and the irregularity of the samples were deduced from the X-ray spectra, as the peak height of the basic reflections decreased with decreasing particle size while the peak area remained constant. It was assumed that any decrease in the peak area is caused by an increase of amorphism. Therefore, the ratio of the peak areas of the original and the ground samples is a measure of the amorphism. Thus the

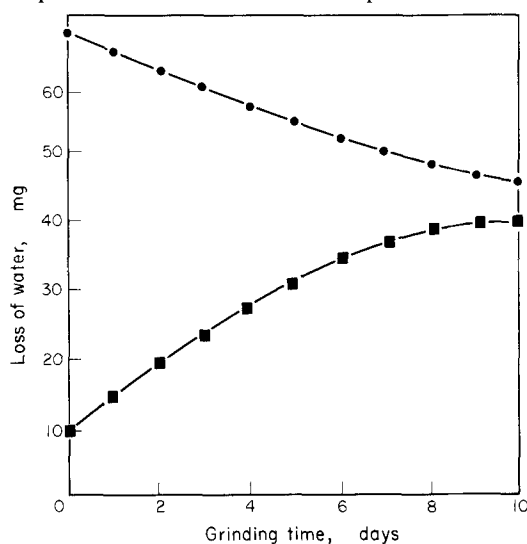


Figure 6. TG curves of Zettlitz kaolin. ●, Structural water; ■, adsorbed water.

Table 2. The correlation functions of the kaolins

| Samples | d vs t | y vs d | x vs d | y vs x |
|------------------------|--|-------------------------|--------------------------|---|
| Zettlitz kaolin | $d = d_0 e^{-0.187t}$ $a = 0.187$ $d_0 = 2.60 \mu\text{m}$ | $y = 0.20(1/d) + 0.48$ | $x = 2.6 d^{0.5} + 0.48$ | $y = 0.24(1/x) + 0.34$ |
| Szegilong paper kaolin | $d = d_0 e^{-0.1015t}$ $a = 0.1015$ $d_0 = 2.20 \mu\text{m}$ | $y = 0.225(1/d) + 0.64$ | $x = 0.128 d^2 + 0.36$ | No correlation was found to exist between y and x |

y is absorbances ratio calculated from infrared spectra ($A_{3630 \text{ cm}^{-1}}/A_{3705 \text{ cm}^{-1}}$).

x is degree of amorphism calculated from X-ray spectra.

7.16-Å basic reflection of the kaolins, characterizing the irregularity of the structure in the direction of the c axis, was measured. The increased amorphism of the ground samples results in a decreased quotient. The correlation functions obtained are listed in Table 2. The x vs d and y vs d functions of Zettlitz kaolin are shown in Figure 7.

Quantitative conclusions can be drawn from the shape of the particle size vs ratio of the stretching vibration bands of the structural O-H groups curves and the degree of the amorphism vs particle size curves respectively. The relationship between the absorption ratio calculated from the infrared spectra and the average particle size is hyperbolic.

The asymptote of the hyperbole of the Zettlitz kaolin is 0.48, and that of the Szegilong paper kaolin is 0.64. That is to say, intensive grinding induced changes can be measured for well-crystallized clay minerals better than for the poorly crystallized ones.

From these functions, the particle size of the sample can be calculated if the absorption ratios are known. It can be seen from Figure 7, that the absorption ratio of the Zettlitz kaolin did not change essentially above the 1.5- μm particle size.

The parameters of a square function relating to the amorphism (x) vs particle size (d) relationship of the

Zettlitz kaolin, and those of a parabolic function applied for the Szegilong paper kaolin, were calculated. From the shape of the x vs d function, it can be concluded that the irregularity of the structure in the direction of the c axis depends considerably on the particle size of the clay minerals.

No correlation was found to exist between the y and x values of the Szegilong paper kaolin because the original poorly crystallized sample rendered the determination of the x and y values rather uncertain.

In conclusion, it appears that if the particles are below the two micron limit, the infrared band intensities of clay minerals depend on the following factors: size distribution and average particles size of the primary particles, the crystalline state of the particles and chemical changes caused by dehydration and mechanochemical activation.

The quantitative determination of the clay minerals by infrared spectroscopy can be carried out only with samples of strictly identical particle size under strictly identical sample preparation methods.

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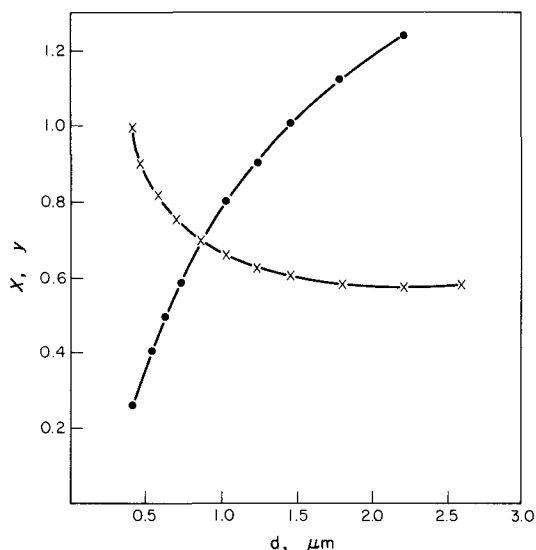


Figure 7. Absorbance ratio (y) vs particle size (d) and degree of amorphism vs particle size functions of Zettlitz kaolin. ●, $x \rightarrow d$; ×, $y \rightarrow d$.

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