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REDUCTION OF ORIENTATION EFFECTS IN THE QUANTITATIVE *X*-RAY DIFFRACTION ANALYSIS OF KAOLIN MINERALS

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ABSTRACT

Two simple methods for reducing preferential orientation of kaolinite and dickite in powder mounts for the *x*-ray diffractometer have been evaluated. Neither of these methods requires the use of diluents or any unusual amount of sample preparation. Grinding the powder in a high-speed vibratory mill is shown to reduce the orientation index to a satisfactory level, but not without severely reducing the crystallinity of the clay mineral. Packing −325 mesh powder into an end-loading specimen holder effectively reduces the orientation index to the predicted theoretical value. The latter method is recommended as a simple and effective method for controlling orientation effects during quantitative analysis of kaolin minerals when basal reflections must be used as analytical lines. However, it is shown that, provided no interfering lines are present, and line intensities are sufficiently high, the non-basal (060) reflection provides a more satisfactory analytical line.

INTRODUCTION

Quantitative mineralogical analysis of kaolin-bearing rocks by *x*-ray diffraction is seriously hindered by the tendency of clay mineral particles to assume a preferred orientation when normal techniques are used to prepare powder mounts for the diffractometer. This is especially true of the well-crystallized platy kaolin minerals, kaolinite and dickite, which tend to be aligned with their basal planes parallel to the specimen surface, greatly enhancing the intensity of the basal reflections. Quite often these basal reflections are the only ones suitable for quantitative intensity measurements.

To further complicate matters, the degree of preferred orientation achieved is not reproducible, depending on factors such as: the pressure applied, the degree of crystallinity of the kaolin mineral, the particle size of the powder, and the relative proportions of kaolin and non-platy minerals in the powder. The simplest method of obtaining reliable intensity measurements would appear to be the preparation of randomly oriented specimens, rather than specimens with a controlled degree of orientation. Basically, this can be achieved by either of two methods: by preventing the kaolin particles from laying flat on the sample surface, or by changing the shape of the particles.

Various methods have been described (Brindley, 1961) for minimizing preferred orientation, most of them falling into the first category. They generally depend on modifying the specimen holder and the technique of filling it, or on the addition of a foreign substance to the powder.

Engelhardt (1955) and later Gordon and Harris (1956) proposed the use of a specimen holder which is filled from the end. By this method no pressure is applied normal to the surface of the specimen, and a near approach to random orientation is probably achieved. However, very little detailed information as to the effectiveness of the method was presented. Some methods fall into both categories. Flörke and Saalfeld (1955) demonstrated a method whereby the individual clay particles are coated in order to form spherical particles. Brindley and Kurtossy (1961) proved the effectiveness of embedding the kaolin particles in an organic cement. They proposed measuring the intensity ratio between a (00l) and (hk0) reflection as an indicator of the degree of preferred orientation, and also calculated an approximate value for this ratio on theoretical grounds. While effectively reducing preferred orientation, this method suffers from the disadvantages common to all methods in which a foreign substance is added. Considerable time and work are involved. Also, the material is seriously diluted, an important factor when small amounts are to be determined.

The present work was undertaken to determine whether simple methods would effectively reduce preferred orientation without the need for diluents or other additions. Measurements of the intensity ratios as proposed by Brindley and Kurtossy (1961) were used to judge the degree of randomness achieved. After a preliminary survey, two methods which appeared to offer the best possibilities were chosen for study: 1) milling of the kaolin mineral in a high speed vibratory mill, in an attempt to change the particle shape, and 2) the method of specimen packing proposed by Engelhardt (1955).

Materials and Instrumentation

The clay minerals used for these experiments were obtained from Ward's Natural Science Establishment, and corresponded to those described in the A.P.I. Research Project 49 (Kerr *et al.*, 1951). They included kaolinite 4 from Macon, Georgia, dickite 16 from St. George, Utah, and halloysite 13 from Eureka, Utah. In addition, a sample of kaolin was obtained by sedimenting the clay fraction from a kaolinized rock from Northern Ontario. This sample still contained about 15% of finely divided quartz and other minor impurities. Each of these clay samples was carefully disaggregated by hand in a porcelain mortar, and brushed gently through a 325 mesh screen. Electron micrographs (Kerr *et al.*, 1951) have shown the kaolinite plates to have an average diameter of about one micron, while the dickite plates have an average diameter of about 5 microns.

Synthetic mixtures of kaolinite 4 in a matrix of quartz and calcite

were made up to contain 80, 60, 40 and 20% of kaolinite by weight. Both the quartz and calcite were obtained from large natural crystals which were pulverized sufficiently to pass a 325 mesh screen. The mixtures were thoroughly blended in plastic vials using a Spex model 5000 mixer-mill. The same instrument, with a tungsten-carbide grinding vial, was used in the milling experiments.

All diffraction patterns were obtained with a Philips diffractometer using: a copper-target tube operated normally at 30 Kv and 20 Ma, a nickel filter, 1° divergence and scatter slits, 0.006″ receiving slit, a Geiger tube detector operated at 1490 volts, a scan speed of 2°/min. for full scans and ½°/min. over lines for planimeter measurements, a chart speed of 30″/hr., and normally the following rate meter constants: scale factor 8, multiplier 1, time constant 4.

Experiments with High-Speed Milling

Attempts were made to fragment the clay particles by grinding in a high-speed vibratory mill, and, by so doing, reduce their tendency toward preferred orientation.

Experimental procedure and results. One gram samples of dickite were milled for 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15 and 20 minutes using only one grinding ball. Specimens for the diffraction measurements were prepared by laying the standard specimen holder face down on a glass plate, and pressing the powder into the opening with a spatula. Reasonable care was taken to press each sample with approximately the same pressure. A fast scan from 4° to 66° was made with the diffractometer on each sample after milling. It was seen that the basal intensities decreased with milling, although the reflections remained fairly sharp. The (hk0) reflections became diffuse and gradually diminished in intensity, merging after fifteen minutes into three broad bands. Background increased slightly as milling time increased, but there appeared to be no significant change in line positions. The end product, after twenty minutes of milling, resembled a poorly-crystallized halloysite.

Slow scans over the (001), (002) and (060) lines were made in duplicate after repacking each sample. (The basal reflections for the 1- and 2-minute samples were above the acceptable linear counting range of the geiger-counter detector, so they were re-run, along with the 10-minute sample, with reduced intensity to obtain an approximate correction factor for the counting losses.) The area under each peak after correcting for background was measured using a planimeter. The peak intensities and half-widths of the (001) lines were also measured (Table 1). The ratios of the peak areas $I_{(001)}/I_{(060)}$ and $I_{(002)}/I_{(060)}$ (taken as the average

TABLE 1. DIFFRACTED INTENSITIES FROM MILLED DICKITE

Milling Time (min.)	Integrated Intensities (cm^2)			(001) Peak Int. (c.p.s.)	(001) Half Width (° 2θ)
	$I_{(001)}$	$I_{(002)}$	$I_{(060)}$		
0	47.5	39.8	3.5	780	0.19
1	36.5	24.8	3.2	754	0.22
2	27.4	21.0	3.4	643	0.21
3	24.1	17.4	3.6	491	0.21
4	19.6	16.2	3.0	436	0.21
5	18.0	14.6	3.6	359	0.23
6	17.8	12.8	3.4	321	0.24
7	14.6	11.8	3.6	249	0.26
8	14.3	10.7	3.5	234	0.26
9	14.2	10.2	3.2	198	0.28
10	14.8	10.8	3.8	218	0.27
15	8.8	4.8	2.5	87	0.44
20	7.1	5.0	2.2	73	0.50

of the duplicate scans) were plotted (Fig. 1) as a function of milling time. It is seen that milling rapidly decreases the tendency toward preferential orientation, and after about ten minutes of milling, the orientation indices

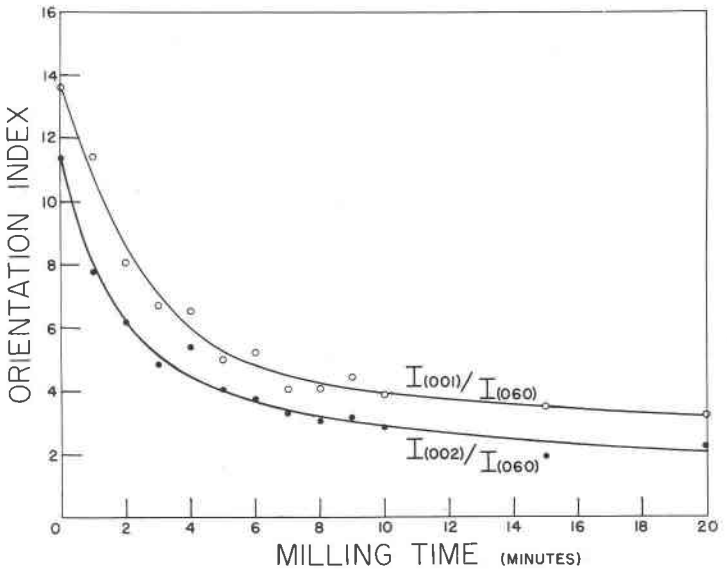

FIG. 1. Variation of the orientation indices of dickite 16 with milling. Integrated intensities were measured on samples packed into the normal holder.

approach the theoretical values for random orientation, which have been calculated (Brindley and Kurtossy, 1961) as 3.90 and 2.12 for the first and second order indices, respectively. It should be noted that while the basal intensities are drastically reduced, the (060) intensity remains practically constant until more than ten minutes of milling is applied. Also, it is only after ten minutes of milling that the (001) peak becomes significantly broadened. These observations suggest that there is an optimum milling time, beyond which continued milling only serves to degrade the sample toward an amorphous state.

As a check on the long-term reproducibility of the milling action, seven samples of a kaolin-bearing rock, which had previously been crushed finer than 325 mesh and homogenized, were milled under identical conditions on different occasions over a two month period. The samples were kept until all had been milled, and then the diffraction intensities from the (001) kaolin line and a quartz line at 50.13° were measured for each sample. The results showed a relative standard deviation of 15% for the kaolin intensity, but only 5.1% for the quartz intensity. Corresponding reproducibility tests on a single milled rock sample which was repacked and remeasured ten times showed a relative standard deviation of 5% for the kaolin intensity, and 4.3% for the quartz intensity. The kaolin appears to be particularly sensitive to any slight differences which may occur during normal use of the mill.

Experiments with End-Loading Specimen Holder

Measurements were made of the orientation index achieved with a specimen holder of the type proposed by Engelhardt (1955), which attempts to prevent the kaolin plates from being aligned parallel to the specimen surface.

Method and results. The specimen holder (Fig. 2) was constructed from a Philips holder by cutting away the end piece and cementing a glass plate onto the back. To fill the holder, the top surface is covered with a glass slide which is taped in place. The powder sample is poured in from the end and packed in by tapping the bottom of the holder on a solid surface. In order to administer a reproducible tap, a small frame was constructed in which the holder was allowed to drop onto the base from a constant height.

Two series of specimens were prepared from −325 mesh dickite and kaolinite by gradually increasing the number of taps administered. The (001), (002), and (060) lines were scanned slowly in duplicate, and the peak areas measured with a planimeter. It was found (Fig. 3) that the

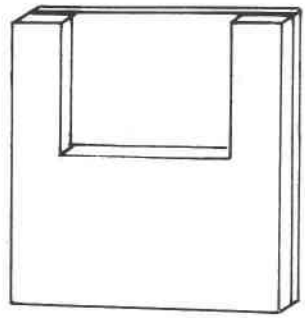

FIG. 2. Drawing (actual size) of the end-loading specimen holder with a glass plate cemented on the back. A second glass plate is taped on the front while the holder is being filled.

measured values of the orientation index $I_{(001)}/I_{(060)}$ were very close to the predicted value of 3.90, while the values obtained for $I_{(002)}/I_{(060)}$ were consistently somewhat higher than the predicted value of 2.12. Also, the indices were practically independent of the number of taps administered, once enough taps had been given to obtain a smooth, well-packed surface. Twenty-five taps was found to produce a good sample. Prolonged tapping tended to cause a layering effect in the powder.

In order to illustrate the large effect which preferred orientation can

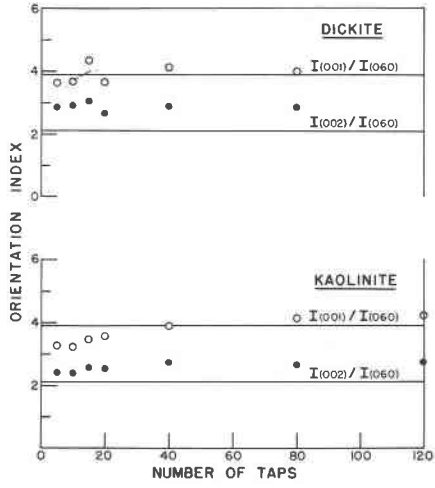

FIG. 3. Variation of the orientation indices of dickite 16 and kaolinite 4 with the number of taps given to pack the powder into the end-loading holder. Integrated intensities were measured on disaggregated (−325-mesh) samples. The straight lines at 3.90 and 2.12 are the calculated theoretical values for random orientation.

have on basal intensities, measurements were made on this series of four kaolin minerals: dickite 16, kaolinite 4, halloysite 13 and the Northern Ontario kaolin (sample A).

After being disaggregated, samples of each of these minerals were packed into both the end-loading holder and the normal holder, and scanned over the (001), (002), and (060) diffraction lines. Duplicate scans were made on each sample after repacking. Peak intensities and integrated intensities were obtained from the chart tracings, and orienta-

TABLE 2. COMPARISON OF DIFFRACTED INTENSITIES FROM VARIOUS KAOLIN MINERALS

Sample	Normal Holder Integrated Intensities (cm^2)			Normal Holder Peak Intensities (c.p.s.)		
	(001)	(060)	(001)/(060)	(001)	(060)	(001)/(060)
Dickite 16	56.5	3.5	16	1410	59	24
Kaolinite 4	28.0	4.1	6.8	469	57	8.3
Halloysite 13	16.1	5.7	2.8	74	28	2.8
Kaolin Sample A	63.3	1.0	62	1580	18	86
Sample	End-loading holder Integrated Intensities (cm^2)			End-loading holder Peak Intensities (c.p.s.)		
	(001)	(060)	(001)/(060)	(001)	(060)	(001)/(060)
Dickite 16	19.1	4.6	4.1	537	73	7.3
Kaolinite 4	14.9	4.4	3.4	242	57	4.2
Halloysite 13	18.2	5.4	3.3	77	30	2.6
Kaolin Sample A	14.2	4.2	3.4	328	48	6.8

tion indices calculated. Since kaolin sample A is only 85% kaolin, all intensity readings on this sample were multiplied by 100/85 to make them roughly comparable with the other, purer kaolin minerals. The results are shown in Table 2. It is seen that the least difference between the line intensities of the various materials, and the most consistent approach to random orientation, is achieved with the end-loading holder when integrated intensities are measured. The differences between the minerals are emphasized when preferred orientation is present and peak intensities are measured.

DETERMINATION OF KAOLINITE CONTENT OF SYNTHETIC MIXTURES

A series of four synthetic mixtures of kaolinite, as previously described, along with a sample of kaolin-bearing rock, were analysed for kaolinite using the diffraction-absorption technique (Leroux *et al.*, 1953). Pure

kaolinite 4 was used as the standard. Two methods of sample preparation were used: packing the −325 mesh material into the normal holder, and packing the same material into the end-loading holder with 25 taps. Integrated intensity and peak intensity measurements were made on slow scan recorder traces of the (001), (002) and (060) lines in each case.

TABLE 3. KAOLINITE CONTENT (WT. %) OF SYNTHETIC MIXTURES AND ONE UNKNOWN, DETERMINED EXPERIMENTALLY USING VARIOUS ANALYTICAL LINES

Actual % Kaolinite	Analytical Results Based on:					
	(001) Line		(002) Line		(060) Line	
	P	I	P	I	P	I
Normal Specimen Holder						
80	85.1	79.4	80.4	78.4	77.8	74.4
60	65.2	66.2	60.6	58.3	60.4	56.0
40	42.5	40.9	36.6	35.9	40.2	39.9
20	25.4	25.7	23.7	21.0	21.3	19.7
35.3[1]	—	—	97.8	91.6	29.2	35.6
End-Loading Specimen Holder						
80	85.2	85.5	84.1	80.7	82.0	76.5
60	74.2	70.0	66.1	65.1	66.1	59.3
40	50.7	46.2	54.0	43.0	41.7	38.9
20	31.3	21.1	30.0	24.6	25.6	19.4
35.3[1]	70.5	44.2	65.7	40.8	37.3	33.1
35.3[1]	—	34.4[2]	—	31.8[2]	—	30.4[2]

[1] Rock sample, which, by chemical analysis, contains 35.3% kaolin.
[2] Analysed using dickite as standard. (All other analyses used kaolinite as standard.)
P Results based on peak intensity.
I Results based on integrated intensity. High intensity copper tube was used for integrated intensities of (060) line with end-loading holder.

In addition, the (060) line with the end-loaded samples was rescanned using a high-intensity copper-target tube operated at 50 Kv and 40 Ma. The results, calculated as per cent kaolinite for each line, are presented in Table 3. In order to have an independent kaolinite determination on the rock sample, an alumina assay was made and the corresponding kaolinite content (35.2%) calculated. This particular rock sample was mainly a mixture of kaolinite, quartz, calcite and hematite, no other alumina-bearing components being present.

It can be seen that, provided the mixtures being analysed contain exactly the same type of kaolin mineral as the pure standard mineral, acceptable analytical results can be obtained by each method, whether preferred orientation is eliminated or reproducibly controlled. However, consistently better results are obtained with integrated intensity measurements of the non-basal (060) line. When "unknown" samples are being analysed, acceptable results are obtained when preferred orientation is eliminated, or when non-basal analytical lines are used. Again, the best results for the unknown, sample A, are obtained when the (060) line is measured using randomly oriented samples. When using the basal reflection to analyse sample A, better results were obtained using dickite, rather than kaolinite, as a standard, pointing out the need for a close match between standard and unknown, even when preferred orientation is eliminated.

Conclusions

While it was found that high-speed milling will effectively reduce preferred orientation of dickite in powder mounts prepared in the normal manner, the procedure has severe drawbacks. The most serious of these is the progressive destruction of the crystallinity of the clay mineral. In addition, under a given set of conditions, the milling action itself does not appear to be sufficiently reproducible from day to day, causing rather large variations to be observed in the diffracted intensity from a standard sample.

The modified end-loading sample holder, however, has been shown to achieve a reliable, random orientation using material which has only been disaggregated sufficiently to pass a 325-mesh screen. This method of specimen preparation is recommended when a basal reflection must be used as the analytical line in the quantitative determination of kaolin.

However, when serious interferences do not exist, the (060) kaolin line provides a more reliable analytical line, provided that the line intensity is sufficiently high for accurate integrated intensity measurements. To this end, a high intensity copper-target tube capable of 50 Kv–40 Ma operation was used to provide twice the maximum intensity obtainable from a conventional tube rated at 50 Kv–20 Ma.

Even when preferred orientation has been reduced to a minimum, the basal reflection intensities of different kaolin minerals are not sufficiently similar to allow the selection of one as a standard suitable for all kaolins. To achieve the best analytical results, a pure standard must be chosen which is as similar as possible to the mineral being analysed. Remaining differences can then be minimized using integrated line intensities obtained from randomly-oriented samples.

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