

QUANTIFICATION OF CRYSTALLINE AND NONCRYSTALLINE MATERIAL IN GROUND KAOLINITE BY X-RAY POWDER DIFFRACTION, INFRARED, SOLID-STATE NUCLEAR MAGNETIC RESONANCE, AND CHEMICAL-DISSOLUTION ANALYSES¹

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Abstract—The capabilities of X-ray powder diffraction (XRD), infrared absorption (IR), solid-state magic-angle-spinning nuclear magnetic resonance (MAS-NMR), and chemical dissolution methods were assessed for estimating the amount of noncrystalline material in a ground kaolinite. The Georgia kaolinite was ground in a mechanical mortar for various lengths of time to produce a set of ground samples containing different amounts of the resulting noncrystalline material. In the XRD method, the intensities of characteristic reflections at 7.2 and 4.47 Å did not respond proportionally to the amount of crystalline kaolinite. Although a transmission-type X-ray diffraction method using the *hk* reflection gave a slightly better estimate than the reflection-type X-ray diffraction method using the basal reflection, both methods gave overestimated values for the amount of noncrystalline material. This overestimation may have been caused by a masking effect due to coaggregation. Using the characteristic IR absorption band at 3700 cm⁻¹ underestimated the amount of the noncrystalline material, if the proportion of this material <50%.

Extraction with NaOH gave estimations 15 to 20% greater than extraction with alkaline Tiron, except for the sample ground for 24 hr, for which both extractions indicated the presence of about 50% noncrystalline material. X-ray powder diffraction data of the residues after these extractions indicated that they consisted of crystalline kaolinite. ²⁹Si NMR spectra of samples ground for ≥30 hr suggested that SiO₄ tetrahedra were considerably distorted. ²⁷Al NMR spectra showed a signal for tetrahedral Al for the sample ground for 10 hr, which increased with an increase in grinding time. Plots of the Al(IV)/[Al(IV) + Al(VI)] ratios vs. time were similar to those of chemical extraction curves. Inasmuch as extraction with hot 0.5 M NaOH is a rather harsh treatment, the composition of the noncrystalline material must have been similar to that of the crystalline kaolinite. The chemical dissolution using alkaline Tiron appeared to be superior to other methods, such as XRD, IR, and NaOH extraction, for estimating the amount of noncrystalline material in kaolinite.

Key Words—Chemical dissolution, Dry grinding, Infrared spectroscopy, Kaolinite, Noncrystalline, Nuclear magnetic resonance, X-ray powder diffraction.

INTRODUCTION

Noncrystalline materials greatly influence the physical, chemical, and biological activities of soils. The identification and quantification of noncrystalline or short-range ordered materials in soils, however, are far more complicated than those used to identify and quantify crystalline materials. No well-established analytical methods have been developed for the former materials, in contrast to X-ray powder diffraction methods, which are commonly used for the latter. Selective chemical dissolution techniques have been widely used and provide useful results in the study of noncrystalline components. One major disadvantage is that the specific chemical composition of the noncrystalline material affects the cation selectivity of

chemical dissolution methods, as well as their extraction capacity (Wada, 1977; Kodama and Jaakkimainen, 1982). This problem may be partly overcome by comparing the results of two or more separate dissolution methods; however, even if similar data are obtained, this agreement may be fortuitous. Thus, another independent measurement is desirable to support the chemical dissolution results.

In the present investigation, X-ray powder diffraction, infrared absorption, and chemical dissolution methods were evaluated as a means of quantifying the noncrystalline material content of ground kaolinite samples. The samples were prepared from kaolinite by mechanical grinding and therefore represented mixtures of varying proportions of crystalline and noncrystalline phases, both of which have essentially the kaolinite composition. In recent years, high-resolution solid-state nuclear magnetic resonance (NMR) techniques using magic-angle spinning (MAS) have pro-

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vided a means of studying minerals (Lippmaa *et al.*, 1980, 1981; Kinsey *et al.*, 1985; Komaneni *et al.*, 1985). In the present study, ^{29}Si and ^{27}Al solid-state MAS-NMR techniques were also used to estimate the amount of noncrystalline material in these samples. The NMR data suggest that the chemical dissolution methods can provide reliable results for the systems of kaolinite composition.

EXPERIMENTAL

Sample preparation

The kaolinite sample used in this investigation was from Macon, Georgia, and was supplied by the Georgia Kaolin Company. The 2–5- μm fraction of the sample was separated by sedimentation and freeze-dried. The fractionated sample was mechanically ground in air in agate mortar under ambient conditions without adding water for various periods of time from 10 to 150 hr to prepare a set of samples containing different amounts of noncrystalline material (see Takahashi, 1959). Evidently the rate of the structural breakdown under such conditions is related to the grinding speed and the volume ratio of sample to an effective capacity of the mechanical mortar. Therefore, the grinding times and apparatus used in the present investigation should be considered as operational parameters.

Analytical methods

X-ray powder diffraction (XRD) analysis was carried out by three different techniques using $\text{CoK}\alpha$ radiation ($\lambda = 1.7902 \text{ \AA}$). XRD patterns of the original and the ground kaolinite samples were recorded on randomly oriented powders using a Scintag PAD V automated powder diffractometer equipped with a graphite monochromator. Residues after chemical extractions were analyzed with a Debye-Scherrer powder diffraction camera. For recording non-basal reflections, a Guinier-de Wolff focusing camera (transmission-type) was used, and XRD traces were obtained by means of a microdensitometer.

Selective chemical dissolution methods using 0.5 M NaOH (Hashimoto and Jackson, 1960) and alkaline Tiron, 1,2-dihydroxybenzene-3,5-disulfonic acid disodium salt (Biermans and Baert, 1977; Kodama and Jaakkimainen, 1982) were used to extract Si and Al and, thereby, to evaluate the amount of noncrystalline material that had been produced by grinding.

Infrared absorption spectra were recorded on a Beckman IR 4250 spectrophotometer and a Nicolet FT-IR spectrometer for samples pelleted with KBr. The recording on the latter spectrometer was available through the courtesy of R. S. Dean, ESSO Resources Canada Ltd, Calgary, Alberta. One-milligram and 0.7-mg air-dry and pre-heated (300°C) samples, respectively, were pelleted with 400 mg KBr.

^{29}Si MAS-NMR spectra were recorded at 59.62 MHz

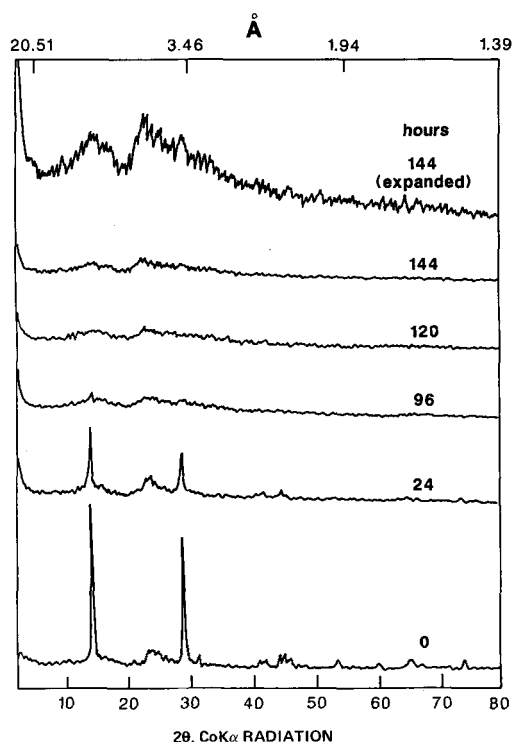


Figure 1. X-ray powder diffraction patterns of non-oriented specimens of original and ground kaolinite samples.

on a Bruker MSL-300 NMR spectrometer using a magnetic field of 7.1 T. The magic-angle spinning rates were ~ 3.5 kHz. About 8000 free-induction decays (FIDs) were accumulated with a repetition time of 2 s. In the cross polarization (CP) experiments, a Bruker CXP180 spectrometer operated at 35.6 MHz was employed with single 2–5-ms contacts, using the flip-back sequence with spin-temperature inversion. Chemical shifts were given in parts-per-million with respect to tetramethylsilane (TMS). ^{27}Al NMR spectra were recorded at a frequency of 78.17 MHz on a Bruker MSL-300 spectrometer with a magic-angle spinning rate of 8 kHz. One hundred FIDs were collected at a repetition time of 1 s using a 2- μs pulse length. Chemical shifts were expressed in ppm with respect to $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ used as an external reference. Background signals originated from the probe were subtracted when necessary.

RESULTS AND DISCUSSION

Estimates by X-ray powder diffraction

Figure 1 shows the degradation of the kaolinite crystallinity as a function of grinding time. In particular, the intensities of the basal reflections at 7.2 and 3.6 Å were greatly reduced. A drastic reduction in intensity took place during the first 96 hr of grinding; after that the distinct basal reflections could not be found. Instead, two broad humps having maxima at about 6 and 4.4 Å were present. The latter hump corresponded to

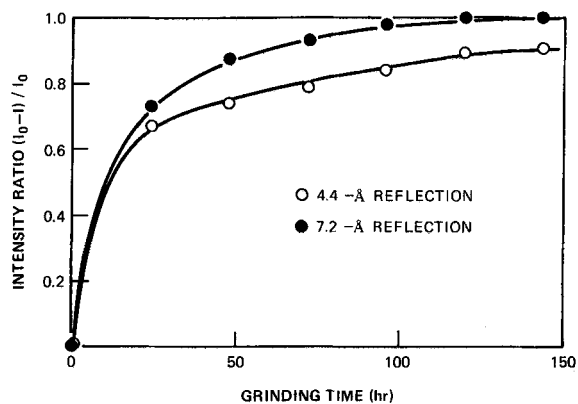


Figure 2. Intensity ratios expressed by $(I_0 - I)/I_0$ as an indicator of the quantity of noncrystalline fractions in ground kaolinite samples. I_0 = peak intensity of one of the reflections at 7.2 and 4.4 Å in the original sample; I = peak intensity of corresponding reflection in the ground sample.

a group of major hkl reflections at about 4.3–4.6 Å and were asymmetrically skewed toward higher angles, suggesting that after the disappearance of basal reflections the ground kaolinites still retained a two-dimensional crystallinity. After the observed peak intensities were corrected for the amount of sample, the degree of crystal breakdown can intuitively be expressed by the relation $(I_0 - I)/I_0$, where I_0 is the peak intensity of a specific reflection of the original kaolinite sample and I is the reduced peak intensity of the corresponding reflection of the ground sample.

In the present investigation, the basal reflection at 7.2 Å and the non-basal reflection at 4.4 Å were employed for the analysis. Intensity data were recorded by a reflection-type diffractometer (Scintag) and a transmission-type diffraction camera (Guinier-de Wolff) for the basal and non-basal reflections, respectively. Plots of $(I_0 - I)/I_0$ against grinding time are given in Figure 2. The curve for the 4.4-Å reflection was about 0.1–0.15 units lower than the curve for the 7.2-Å reflection except for the first 24 hr, in which the trends of both curves were similar. The curve of the basal reflection suggested a complete breakdown of the kaolinite crystals after grinding for 120 hr; however, as discussed below, small amounts of residue after chemical extraction were found even for the 120- and 144-hr ground samples. For example, the treatment with NaOH dissolved 86% (oven-dry weight basis) of the 120-hr ground sample. XRD examination of the residues showed that they consisted of kaolinite having a crystallinity nearly as high as that of the original kaolinite. Therefore, it was not appropriate to use the 7.2-Å reflection for determining the amount of the crystalline kaolinite, chiefly because the small residual 7.2-Å peak was masked by the broad hump at ~6 Å of the noncrystalline material formed by grinding (cf. Figure 1). This led to an underestimation for the amount

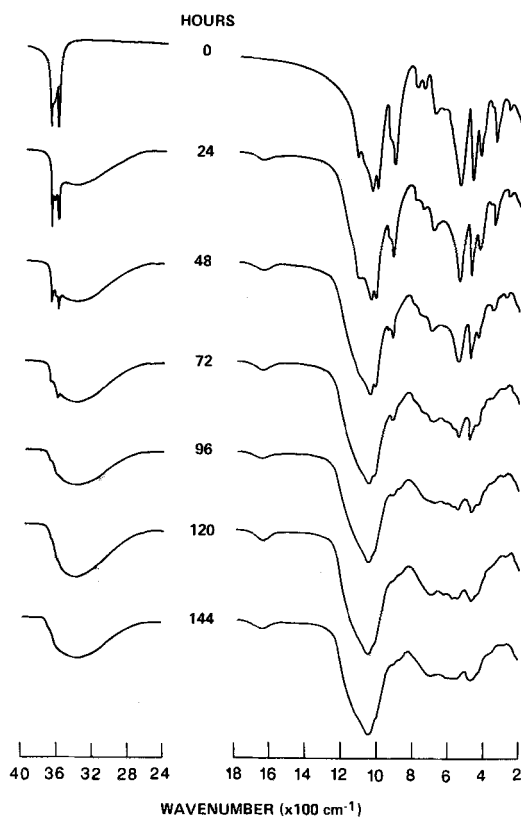


Figure 3. Infrared absorption spectra of original and ground kaolinite samples.

of the crystalline phase. Consequently, the amount of noncrystalline material was overestimated, as seen in Figure 2. The masking effect might have been caused by coaggregation, which is common in such dry-ground samples (Takahashi, 1959). The 4.4-Å peak gave a somewhat more satisfactory estimation, but as the amount of the noncrystalline component increased, the 4.4-Å peak of the crystalline phase became difficult to distinguish from the asymmetrically skewed diffraction band at ~4.2–4.6 Å, which was developed by grinding. In the present case, the value of I_0 was known, and the error in calculating $(I_0 - I)/I_0$ was therefore minimal. If the value of I_0 had not been known, as for most materials, the choice of I_0 would have been critical for the estimation, as well as for the determination of I .

Infrared analysis

Kaolinite has a characteristic absorption band at 3700 cm^{-1} due to its outer hydroxyl group. This band may be used to quantify kaolinite (Kodama and Oinuma, 1963). As the grinding time of the samples increased, well-defined absorption spectra, including the characteristic 3700- cm^{-1} band, became featureless spectra (Figure 3). Assuming that the spectra of the samples ground for different times between 24 and 120 hr were composed of two end-member spectra representing

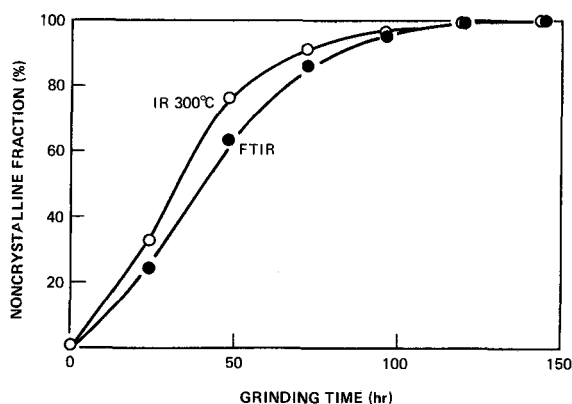


Figure 4. Amount of noncrystalline material in ground kaolinite samples estimated by infrared absorption methods, using the absorption band at 3700 cm^{-1} .

samples ground for 0 and 144 hr, the amount of residual crystalline phase may be estimated using the Fourier-transform infrared spectrophotometer. Composite absorption spectra between 4000 and 2400 cm^{-1} were graphically deconvoluted in terms of the corresponding spectra of the two end-member components. The resulting ratios were expressed as the fractional weight of the noncrystalline component (Figure 4).

The amount of noncrystalline material steadily increased as the grinding time increased to 72 hr, after which the increase became very small. The increase in the first 72 hr as estimated from the IR data was not as sharp as that estimated from the XRD data. This discrepancy is not surprising, because IR methods are relatively insensitive to crystallinity, compared with XRD methods. Because structural breakdown by dry grinding made powdery samples more hygroscopic, the presence of a broad IR band due to adsorbed water in the OH region may have contributed some error to the graphical deconvolution. To reduce this effect, samples were heated at 300°C for 16 hr prior to pelleting with oven-dry KBr. The amount of crystalline kaolinite in various samples was evaluated from observed absorption intensities of the band at 3700 cm^{-1} . As seen in Figure 4, the estimated amounts of noncrystalline material were similar, except for in the first 72 hr in which the estimated amounts of this material slightly increased.

Chemical dissolution

Both NaOH and alkaline Tiron dissolution methods showed little selectivity, inasmuch as the amounts of Si and Al extracted gave an Si/Al ratio close to unity (Figure 5), which was to be expected from the original kaolinite composition; Si, 21.0%; Al, 20.9%. The noncrystalline fraction (%) in Figure 5 is expressed by the ratio of the amount of Si or Al in extracts to that in the original kaolinite. The results verified the suitability of the two dissolution methods for compounds hav-

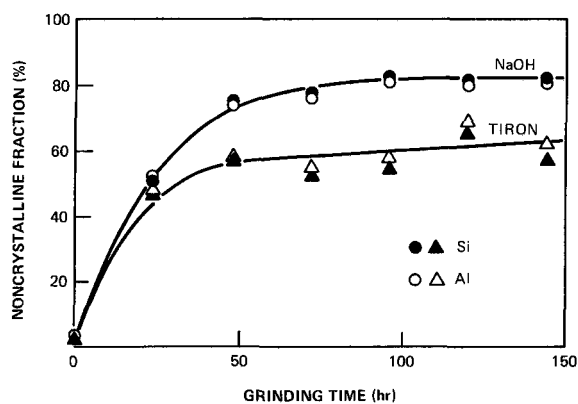


Figure 5. Amount of noncrystalline material in original and ground kaolinite samples estimated by two separate chemical dissolution methods.

ing kaolinite composition. As seen in Figure 5, the two dissolution methods suggest that the sample ground for 24 hr contained about 50% noncrystalline material. For samples ground for longer periods, however, NaOH extracted about 15–20% more than did alkaline Tiron. This difference may be explained by the greater harshness of the NaOH treatment (higher concentration and temperature). The latter treatment might more effectively have attacked a portion of still crystalline but poorly ordered kaolinite whose structural imperfection was introduced by the prolonged grinding (>24 hr). For this reason, the sample ground for 24 hr, for which nearly the same amount of noncrystalline material was estimated by the two sets of dissolution data ($\sim 50\%$, Figure 5), was considered to be most suitable as a reference sample to assess the results of other methods. Evidently the XRD methods tended to overestimate the quantity of noncrystalline material, and the IR method tended to underestimate the amount of this material.

Solid state ^{29}Si and ^{27}Al MAS-NMR

The ^{29}Si MAS-NMR spectrum of the unground kaolinite (Figure 6a) showed a sharp resonance at -91.8 ppm from TMS, which is attributable to the signal of Si in the Q^3 polymerization state, i.e., three Si atoms bonded to an SiO_4 tetrahedron. Dry-ground samples showed an increase in breadth of this resonance, especially samples ground for 30 hr or more (Figures 6c–6f), suggesting that as the grinding time increased structural disorder became more pronounced.

Compared with the spectrum of the original kaolinite, the spectra of ground samples showed, in addition to an increase in breadth, that all signals shifted gradually toward lower frequency. Cross polarization (CP) ^{29}Si NMR spectra (Figure 7) demonstrated that on grinding the corresponding resonance broadened and shifted to lower frequency as well, suggesting that residual hydroxyls in the ground samples were present

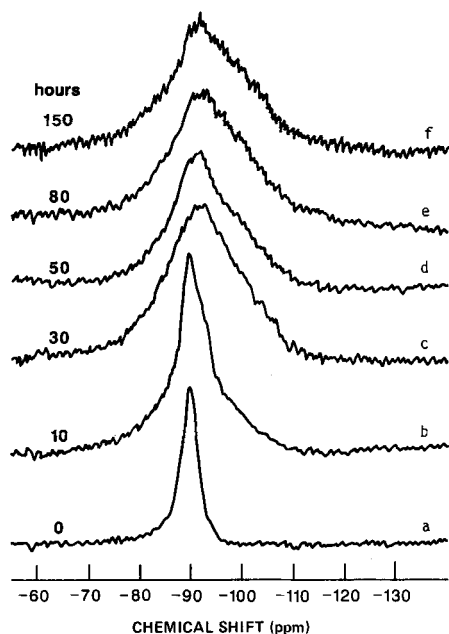


Figure 6. ^{29}Si magic-angle-spinning nuclear magnetic resonance spectra of original and ground kaolinite samples.

in several different Si environments. This behavior was similar to that observed by MacKenzie *et al.* (1985) for metakaolin. Heating the sample ground for 150 hr in water at 300°C in a sealed vessel returned the position of the spectrum to that of the sample ground for 30 hr and also resulted in a decrease in the breadth of the spectrum (Figure 7f), verifying the influence of hydroxyls on the signals due to Si polymerization.

The ^{27}Al MAS-NMR spectra of samples ground for various periods of time are shown in Figure 8. The spectrum of the original kaolinite (Figure 8a) displayed a single peak at -4.1 ppm, indicating that Al in the kaolinite structure was exclusively in the octahedral coordination. In the spectra of the ground samples (Figures 8b–8e), however, extra resonance peaks near 30 ppm (except for the sample ground for 10 hr) and near 56–60 ppm were present, characteristic of tetrahedral Al. The weak resonance at about 30 ppm corresponded to that previously observed in the spectra of metakaolin and, according to MacKenzie *et al.* (1985), may be due to a separate tetrahedral species. All spectra had wide and weak spinning side bands, which were minimized by applying high (8 kHz) spinning rate. As seen in Figure 8, the Al(VI) signals were shifted from -4.1 to 2.0 ppm, and the Al(IV) signals shifted from 56 to 60 ppm as grinding time increased. A similar tendency for ^{27}Al NMR spectra to shift to the low field has been observed for kaolinite samples heated at various temperatures (Watanabe *et al.*, 1987).

The intensity of the Al(VI) signal increased with an increase in the grinding time, suggesting that this signal may be used as a measure of the extent of structural

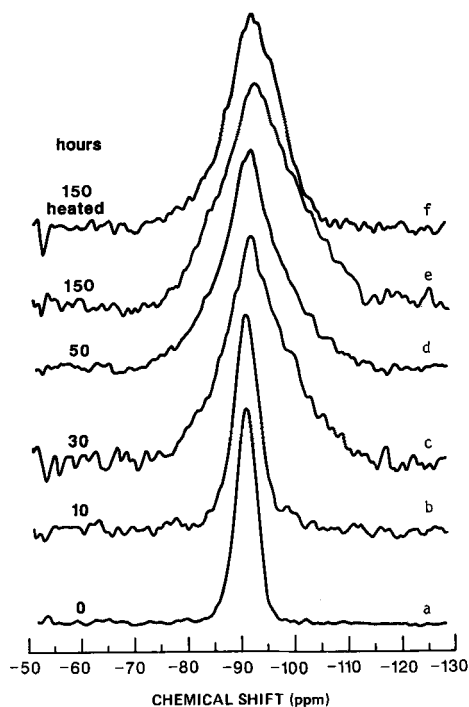


Figure 7. Cross polarization ^{29}Si magic-angle-spinning nuclear magnetic resonance spectra of original and ground kaolinite samples.

breakdown in the kaolinite sample. Both Al(IV) and Al(VI) signal intensities were expressed by areas under the corresponding peaks, and the proportions of Al(IV) to the sum of Al(IV) and Al(VI) nuclei were plotted against grinding time (Figure 9): The results clearly indicate that during the first 30 hr of grinding nearly 35% of the Al(VI) and the original kaolinite converted to Al(IV). After that, the increase in the ratio Al(IV)/[Al(VI) + Al(IV)] was gradual. The trend of the whole curve resembled the two extraction curves given in Figure 5. The signal intensity ratio, however, is not necessarily equivalent to the abundance ratio of Al(IV) and Al(VI) nuclei in the structure. Possibly some of the Al atoms were in sites that are much distorted from spherical symmetry for NMR detection (Watanabe *et al.*, 1987). This phenomenon could have been due to electric field gradients resulting from crystallographic distortions and/or defects that had been induced by grinding. Heating the sample ground for 150 hr in a sealed vessel at 300°C in the presence of water eliminated the Al(IV) signal in the spectrum, indicating that the conversion of Al(VI) to Al(IV) induced by dry-grinding was reversible by hydroxylation. The abundance of Al(IV) cannot directly be translated to the amount of noncrystalline material, unless the ratio of Al(IV) and Al(VI) in the noncrystalline material is known. The Tiron extraction curve (Figure 5) gave the amounts of the noncrystalline material, 56 and 60%, for the 80- and 150-hr ground samples, respectively.

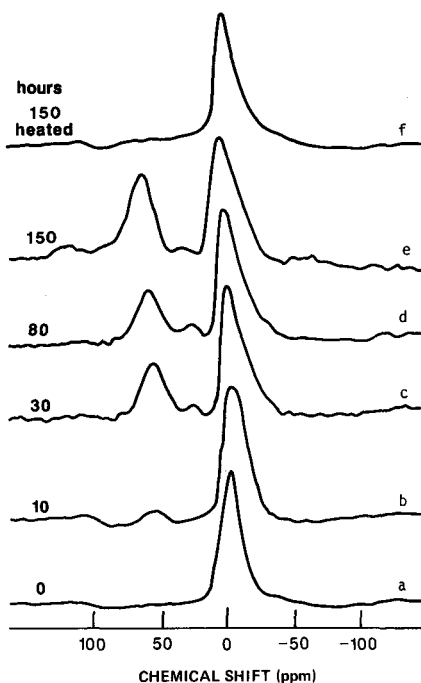


Figure 8. ^{27}Al magic-angle-spinning nuclear magnetic resonance spectra of original and ground kaolinite samples.

Using these amounts to convert the $\text{Al(IV)}/[\text{Al(IV)} + \text{Al(VI)}]$ ratio to amounts of the noncrystalline material gave rise to a common factor of 1.49, suggesting that the $\text{Al(IV)}/\text{Al(VI)}$ ratio in the noncrystalline material is about 2. If similar arguments are applied to the sample ground for 24 hr, the ratio of 0.26 in Figure 9 would correspond to 39%, which is lower than the 43% and 52% by the Tiron and NaOH extraction methods, respectively. Nevertheless, the NMR data appear to support the estimates by the chemical extraction methods.

^{27}Al and ^{29}Si MAS-NMR spectra of the ground kaolinite samples presented in Figures 6–8 bear a remarkable similarity to those reported for metakaolin (MacKenzie *et al.*, 1985; Watanabe *et al.*, 1987). The structural concepts proposed for metakaolin (Brindley and Nakahira, 1959; Freund, 1973) may therefore help explain the structural damage introduced by dry-grinding. Thus, like the formation of metakaolin by heating, the dry-grinding caused dehydroxylation which changed the original $\text{Al}^{\text{VI}}(\text{OH})_2\text{O}_2$ coordination to an $\text{Al}^{\text{IV}}\text{O}_4\text{□}$ coordination, where □ indicates a vacancy due to the loss of a ligand. The fact that prolonged grinding for > 30 hr produced no significant increase in the Al(IV) signal suggests that the remaining hydroxyls were difficult to eliminate. Thus, some remnant structure of kaolinite appears to have persisted even after prolonged grinding. Undoubtedly due to the loss of hydroxyl(s), the octahedral $\text{Al}-\text{O}(\text{OH})$ sheets appeared to be more directly affected than the tetrahedral SiO_4 sheets, as seen from the changes in the corresponding

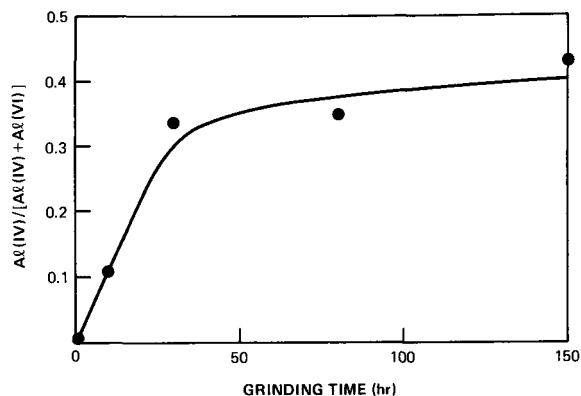


Figure 9. $\text{Al(IV)}/[\text{Al(IV)} + \text{Al(VI)}]$ ratios measured from ^{27}Al magic-angle-spinning nuclear magnetic resonance spectra as function of grinding time.

resonances given in Figures 6–8. Nevertheless, the $\text{Al(IV)}/[\text{Al(VI)} + \text{Al(IV)}]$ ratio and the chemical shift that appeared in the Si signal both gave near maximum values for the sample ground for 30 hr, corresponding to the dissolution curve obtained by the alkaline Tiron method. Thus, the foregoing solid-state NMR data gave reasonable support to the choice of the sample ground for 24 hr as a reference sample. From these results, we conclude that if the composition of the noncrystalline material is similar to that of the crystalline material, the chemical dissolution using alkaline Tiron appears to be superior to the other methods, such as XRD, IR, or chemical dissolution using NaOH, for estimating the amount of noncrystalline material in kaolinite.

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