THE EFFECT OF GRINDING ON THE STRUCTURE AND BEHAVIOR OF BENTONITES*

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Abstract—The structure and behavior of homoionic bentonites was markedly affected by a grinding procedure often applied to clays. The main changes observed on clay powders were the breakage of weakly bound large aggregates, the reduction in the tactoids' thickness by delamination, the reduction in the plates' area, and the formation of colloidal matter. The tendency of clays to form secondary aggregates in aqueous suspensions is probably due to the exposure of active broken edges following grinding.

The mild mechanical stress applied increased both the rate and the amounts of parathion sorbed by clays from an apolar solvent. The effect of grinding on parathion adsorption in aqueous clay suspensions seems to be a rate effect.

Key Words—Bentonite, Delamination, Grinding, Montmorillonite, Structure.

INTRODUCTION

In many processes involving clays, both in research and industry, grinding or some other procedures which impose some mechanical stress on the clay particles are employed. Kaolinites have been studied rather extensively with regard to the effect of various mechanical stresses on them (Black, 1942; McKyes and Yong, 1971; Martin and Ladd, 1975; Yariv, 1975). For example, grinding kaolinite in a ball mill for 10 days was found to affect phosphate adsorption (Black, 1942). Little is known about the effect of grinding on bentonites despite their great importance as soil constituents and wide use in both research and industry. The reason for this is the dominance of kaolinite in industry and the assumption that in the soil and aqueous systems in which bentonite was most extensively studied, mild mechanical stress of this expandable clay will not affect its behavior. This assumption will be shown here to be untrue in a number of instances. The effect of the stress occurring during freeze-drying, for example, was demonstrated by Bowman (1975).

The purpose of this work was to examine the effect of the sort of grinding often applied to clays on the structure and behavior of bentonites. The effect on the character of the resulting ground powder, the adsorption of an organic molecule from a nonpolar solvent, the properties of the aqueous clay suspensions, and the behavior of the suspended clay upon drying (e.g., the ability to form self-supporting film), were investigated. X-ray powder diffraction, IR and UV-visible spectroscopy, and SEM and TEM microscopy were used.

MATERIALS AND METHODS

Homoionic clays saturated with Al, Cu, Fe, Zn, Mg, Ca and Na were prepared from Wyoming Bentonite (B-235, Fisher Scientific Co., Fair Lawn, N.J., U.S.A.) by a procedure described by Shainberg and Otoh (1968). The homoionic clays were freeze-dried and then ground in a ball mill for 1, 2, 5 and 25 min. The grinding of 3-g clay portions was done in a circular agate container of 5 cm i.d. with two agate balls of 12 g each, and five agate balls of 1.5 g each, at high speed. Stock aqueous clay suspensions at 1% concentration were prepared by shaking for 48 hr.

The ground clay powders were studied as follows: For the X-ray powder diffraction study the air-dried clay was placed in the instrument's sample holder and its surface was smoothed lightly with a glass bar. The thickness of the sample was infinite with respect to the X-ray powder diffraction. A measurement of a homoionic bentonite at all grinding times was completed within approximately half an hour. It was ensured that the relative humidity during consecutive runs of all the homoionic bentonites investigated did not vary significantly. Although the precision of the measurements with regard to the intensity and half-widths of the lines was not very high, the results obtained repeated themselves in all triplicate runs of each sample.

The kinetics of parathion adsorption from n-hexane was studied by shaking 0.1 g of ground clay powder which was oven-dried at 105°C with 10 cc of ^{14}C-labeled parathion solutions for various periods, from 1 hr to 10 days, in sealed vessels. Initial parathion concentrations from 50 to 2500 ppm were tested. Pure parathion (Analabs Inc.) mixed with ^{14}C-labeled parathion (obtained from Amersham Radiochemicals Centre) was used.

The behavior of the aqueous suspensions prepared from the ground clays was studied by measuring the light absorbance of diluted stock clay suspensions (500 ppm) at 530 nm, and by determining the precipitation rate of these suspensions. Precipitation was determined from the rate of change of the absorbance (at 530 nm) of the undisturbed suspensions with time. Adsorption of parathion in aqueous clay suspensions was deter-

mined by adding a 7 ppm aqueous solution of parathion to the oven-dried ground clay powder as well as by adding a 12 ppm aqueous parathion solution to presuspended clays, to a final parathion concentration of 7 ppm.

The following observations were made on the deposits obtained upon drying the aqueous suspensions of the ground clays: Self-supporting films were prepared from the 1% clay suspensions as described by Russell and Farmer (1964), and the nature of the resulting films was observed. IR spectra of thin films prepared by evaporating 1-cc portions of 0.16% aqueous clay suspensions on a polyethylene support were recorded. A clayless polyethylene blank was put in the reference beam. TEM observations were made on the following preparations: the 1% stock suspensions were diluted to 50 ppm and shaken for 3 days; a 0.05-cc portion of the diluted suspension was then applied to a 200-mesh copper grid covered with a collodium membrane and air-dried. The following preparations were observed through an SEM: 0.15-cc portions of the 1% stock suspensions were applied to a glass-covered stub, air-dried, and coated with a gold layer.

Apparatus

Grinding was done by the Fritsch Pulverasette type 501 planetary mill system. A Philips X-ray diffractometer type 1030 with a cobalt target was used for the X-ray diffraction measurements. Transmission electron micrographs were made with a Jem No. 7A TEM. Scanning electron micrographs were made with a Cambridge stereoscan-180 SEM. IR spectra were taken on a Perkin-Elmer 257 infrared spectrophotometer. Turbidity measurements were made on a Unicam Sp 500 UV and visible spectrophotometer with an Sp 505 program controller; all other UV-visible spectra were taken on a Varian Techtron UV-visible spectrophotometer Model 635.

RESULTS AND DISCUSSION

The type of grinding employed in this work is often used with clays (e.g., Davey and Low, 1971). The short grinding times employed justify the use of the term "mild grinding." The use of a planetary mill means that various modes of mechanical stress were applied and not predominantly shearing. Therefore, the results obtained are an indication of what mechanical stress can do but do not define the nature of the stresses responsible for a given effect.

Observation on ground clay powders

The X-ray powder diffraction spectra of Na-, Ca-, and Zn-bentonites were taken. The effect of the time of grinding is shown in Figure 1. As the grinding time was increased, the c-spacing peaks of Ca-bentonite gradually became more diffuse. In addition, a slight increase in intensity after 1 min and a decrease at longer
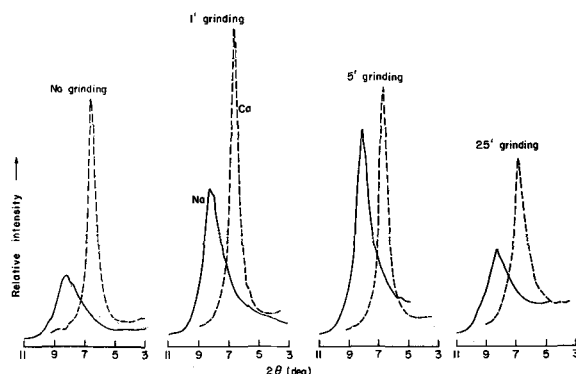

Fig. 1.   X-ray powder diffraction spectra of Na- and Ca-bentonite as affected by grinding. (Dry powder; 2000 × 4 × 2°.)

grinding times were observed. In the case of Na-bentonite a maximum in the intensity of the c-spacing peak occurs at 5 min of grinding. As in the case of Ca-bentonite there is a widening of the c-spacing peak with grinding. This widening, however, was observed only after 5 min of grinding. There might even have been a slight narrowing after 1 min of grinding.

The proposed interpretation of the above observations is that at the shorter grinding times the imperfectly oriented, weakly bound aggregates are broken, thus allowing a better alignment in the powder, which increases the peak intensity. With further grinding, distortions in the plate stacking and delamination processes may account for the reduction in the c-spacing peak's intensity, as well as in its widening. With Ca, the c-spacing peak intensity is reduced after shorter grinding times than with Na-bentonite. This does not indicate a stronger bonding between plates in Na-bentonite, but rather the presence of large aggregates with a smaller number of well-aligned plates (smaller tactoids) in that clay. Accordingly, upon freeze-drying, the Na-clay forms larger aggregates with less well aligned plates than Ca-bentonite.

The background diffraction indicates that the colloidal matter content increased upon grinding in both Ca- and Na-bentonites. The marked widening and reduction in intensity of the c-spacing peak upon grinding for 25 min, as compared with no grinding, was also observed in the case of Zn-bentonite.

A striking effect of mild grinding of several homoionic bentonites on the adsorption of parathion from n-hexane was observed (Figure 2 and Table 1). Table 2 shows the relatively negligible effect of grinding kaolinite clays on the adsorption of parathion. It is possible that the effect of grinding on parathion adsorption is a rate effect (Figure 2). However, it may be considered as at least a quasi-equilibrium effect, in view of the large differences in adsorption observed even after several days of contact. In general, adsorption studies of a similar nature assume equilibrium after periods of up
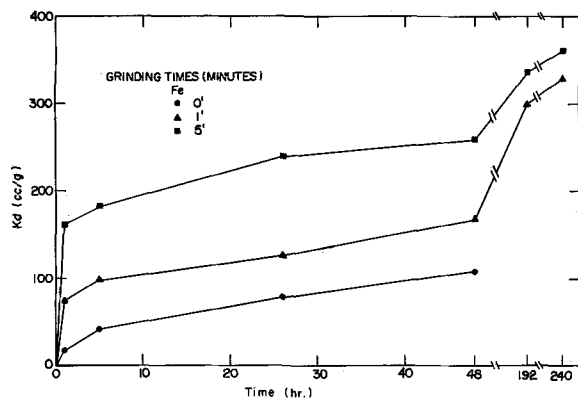
Fig. 2. Adsorption kinetics of parathion from n-hexane on Fe-bentonite as affected by grinding. (1% clay suspension, 250 ppm initial parathion concentration.)

Fig. 3. Precipitation curves of ground and unground Na-bentonite. (500 ppm suspension.)

to 2 or 3 days (e.g., Mills and Biggar, 1969). After 2 days there was still a significant difference in adsorption on clays ground for various periods, and even after 8 days some difference was still observed. Figure 2 presents this for the case of Fe-bentonite. There is a period of about 1 hr of fast adsorption, at the end of which there is a significant difference in the amount adsorbed between the various grinding times. This period may be followed by a slow equilibration to the same final state. Such equilibration was actually observed with Fe- and Cu-bentonite.

As might be expected, the effect of grinding on parathion adsorption depends strongly on the nature of the exchangeable cation. The strongest effect of grinding was observed in the case of the Cu- and Na-clays. Saltzman and Yariv (1976) demonstrated that oven-drying prevents penetration of parathion into the interlayer space of Na-bentonite, but not into the interlayer space of Ca-bentonite. Hence, the fact that the Na-clay is more sensitive to grinding than polyvalent clays suggests that one important effect of grinding on the rate of adsorption of parathion may be associated with de-
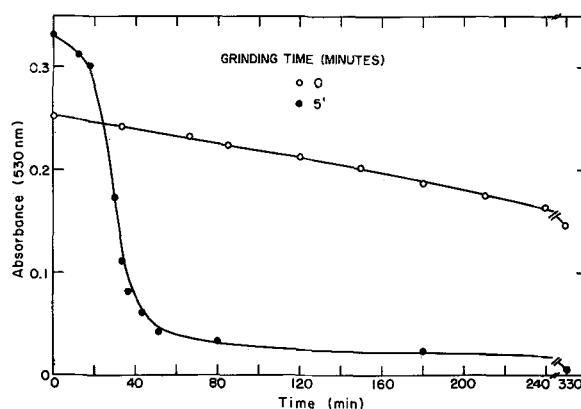
lamination. Another obvious effect of grinding of importance with all homoionic clays in the determination of the rate of adsorption, especially at short times, is the breakdown of the larger and looser aggregates present in the clay after freeze-drying (see, in Figure 2, the adsorption rates up to 5 hr of mixing).

Observations on the ground clay aqueous suspensions

The mild grinding employed affected significantly the behavior of bentonite particles in aqueous suspension, even after equilibration. The light absorbance of the suspensions, the rates of precipitation and the shape of the precipitation curves varied with the time of grinding (Table 3 and Figure 3). Even after 1 min of grinding a significant change in behavior was observed. The effect of grinding was not uniform. It may increase or decrease the light absorbance, as well as the precipitation rate (Table 3). The rate of precipitation furthermore may change suddenly during the precipitation process. The light absorbance while stirring for different periods up to 9 days, in some ground clay suspensions also increased with time. This behavior may be explained (assuming that Rayleigh's law holds) by the increased tendency to form secondary aggregates in the suspension upon grinding. This was particularly conspicuous with Na-montmorillonite, where the rate of precipitation was strongly increased by grinding. As shown below there is a marked decrease in the dimensions of the individual plates of the clays upon grinding and hence the marked increase in the rate of precipitation must be due to secondary aggregation. Such a grinding-induced tendency to aggregate was actually observed with the TEM (Figure 4). In the case of the Na-clay ground for 5 min, a sudden increase in the precipitation rate was observed after about 20 min of precipitation, indicating sudden coagulation (Figure 3). The strong effect on the behavior of this well-dispersed bentonite in suspension should arise from the effect of grinding on the individual

Table 1. Adsorption of parathion from n-hexane on some homoionic bentonites as affected by grinding. (After 1 hr of mixing; 1% clay suspension; 100 ppm initial parathion concentration.)

Grinding time (min)	Exchangeable cation	Kd (cc/g)				
		Na	Ca	Al	Zn	Cu
0		16.3	127.3	69.5	21.9	13.6
1		78.6	234.5	222.6	51.5	63.9
4		170.3	431.9	300.0	177.8	300.0
10		257.1	488.2	334.8	257.0	809.0
25		354.5	525.0	455.6	270.3	1233.3

plates rather than from a delamination effect. Zn-bentonite suspensions also exhibited a dependence of the precipitation rate on grinding.

While the "absorbance" readings at 530 nm arise from scattering of the light from the suspended clay particles, there appears a small peak of specific absorption at 245 nm. This peak, which was also observed in montmorillonite suspensions by Banin and Lahav (1968), increased upon grinding in the case of Ca-bentonite. Lahav and Banin (1968) suggested an inverse relation between the intensity of the 245 nm peak and the number of plates per tactoid.

When Zn-montmorillonite was added to a water solution of parathion, the adsorption after 24 hr of shaking was somewhat greater if the clay was initially ground for 25 min (Kd = 283 and 227 cc/g for ground and unground clay, respectively). When the clay was resuspended for 24 hr before adding parathion, a smaller effect of grinding on adsorption was observed. The effect of grinding on adsorption of parathion in an aqueous suspension seems to be a rate effect. Presuspension of the clay results in maximum dispersion at the time of contact with the parathion and thus decreases the effect of grinding on the rate of adsorption. It seems that the structure of the clay after freeze-drying contains sites in which adsorption is hindered (such as capillary channels). These sites open up by grinding as well as by presuspension (and the resulting dispersion) in water. Saltzman (1977) observed a sharp minimum in parathion adsorption from water after 1 hr of mixing on bentonite preequilibrated at 98% relative humidity, as compared with both drier and presuspended clays. This agrees with the importance of capillary channels which at 98% RH are filled with water which hinders adsorption, and which disappear in suspension due to the clay's dispersion. Since many interactions of interest in soils as well as in industry (e.g., formulation chemistry) are not equilibrium interactions, such parameters as the structure of the clay aggregates before it achieves equilibrium in suspension and the rates of sorption processes from both aqueous and nonaqueous solvents, as well as their equilibrium state, are of interest.

As mentioned above, grinding such as employed here, or more severe grinding, is practiced in the preparation of bentonite samples in scientific investigations and in industry. If mild grinding is important in the clay's eventual behavior, other stresses—such as those brought about by the ice expansion during freezing and freeze-drying or by some cultural techniques—may affect the nature and rates of processes involving clays in both soil and the laboratory. Bowman (1975) and others demonstrated the effect of freeze-drying on the clay's subsequent behavior. Bowman demonstrated that freeze-dried clay (Ca- and Na-montmorillonites and illites) resuspended in water adsorbed more fensulfathion than a suspended clay not previously freeze-dried. He suggested that freeze-drying might have dis-

Table 2. Adsorption of parathion from n-hexane on some homoionic kaolinites as affected by grinding. (After 1 hr of mixing; 2% clay suspension; 50 ppm initial parathion concentration.)

Grinding time (min)	Kd (cc/g)		
	Na	Ca	Al
0	39.3	33.3	19.4
1	33.3	33.3	19.4
4	36.2	36.2	23.5
10	39.3	39.3	33.3
25	75	63.6	69.0

The leftmost column header reads "Exchangeable cation" above "Grinding time (min)".

rupted the stacking of the bentonite sheets, resulting in smaller "stacks" and a finer particle size as well as possible fraying of the edges of the "stacks."

Observations on deposits obtained upon drying ground clay suspensions

Important information regarding the properties of the clay in suspension as well as the effect of grinding on the behavior of the clay upon drying may be obtained from studying the deposits obtained after drying the clay suspensions. The most illuminating data concerning the effect of grinding were obtained from the TEM observations (Figure 4). With the Ca-clay, both the area of the plates and the tactoid thickness (i.e., number of plates per tactoid) were reduced drastically by grinding. The tendency to form a secondary structure is very marked in the case of Ca-bentonite ground for 25 min and can be observed after 5 min. After 1 min of grinding the tactoids' edges became frayed, and delamination was already observable. Grinding for 5 min caused the predominant appearance of tactoids with smaller plates' area (Figure 4).

Table 3. Turbidity data for Na- and Ca-bentonite suspensions as affected by grinding. (500 ppm suspensions; reading at 530 nm.)

Exchangeable cation	Grinding time (min)	Precipitation rate (min)[*]
Ca	0	135 (0.80)
	1	81 (0.80)
	5	114 (0.86)
	25	174 (0.89)
Na	0	400 (0.25)
	1	450 (0.20)
	5	31 (0.33)
	25	36 (0.44)

[*] Time taken to reduce turbidity to half its initial value.

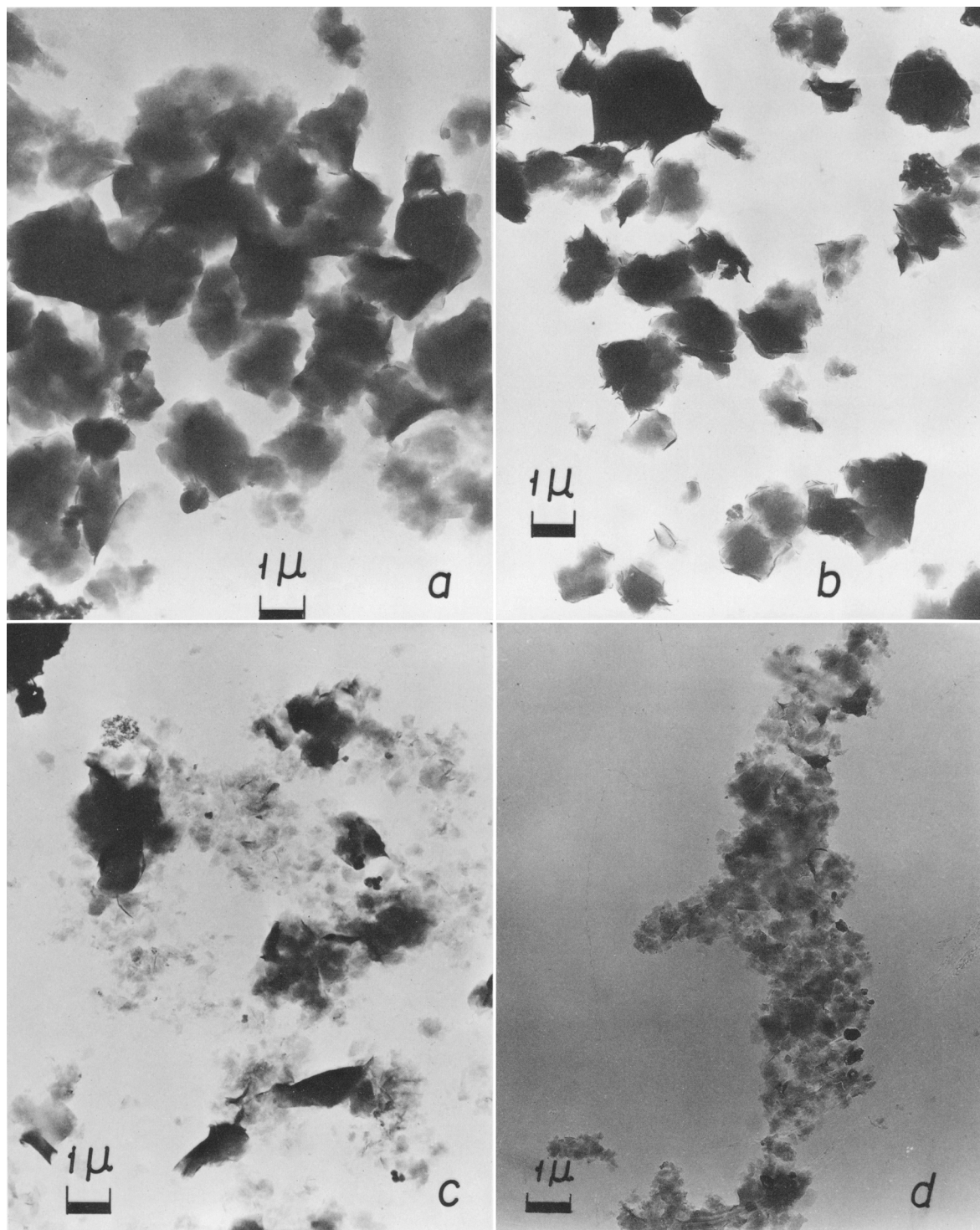Figures in parentheses are the initial absorbance.

Fig. 4. a–d: Transmission electron micrographs of Ca-bentonite after equilibration in aqueous suspensions, as affected by grinding. Ca-bentonite ground for 0, 1, 5, 25 min, respectively; magnification ×5000.
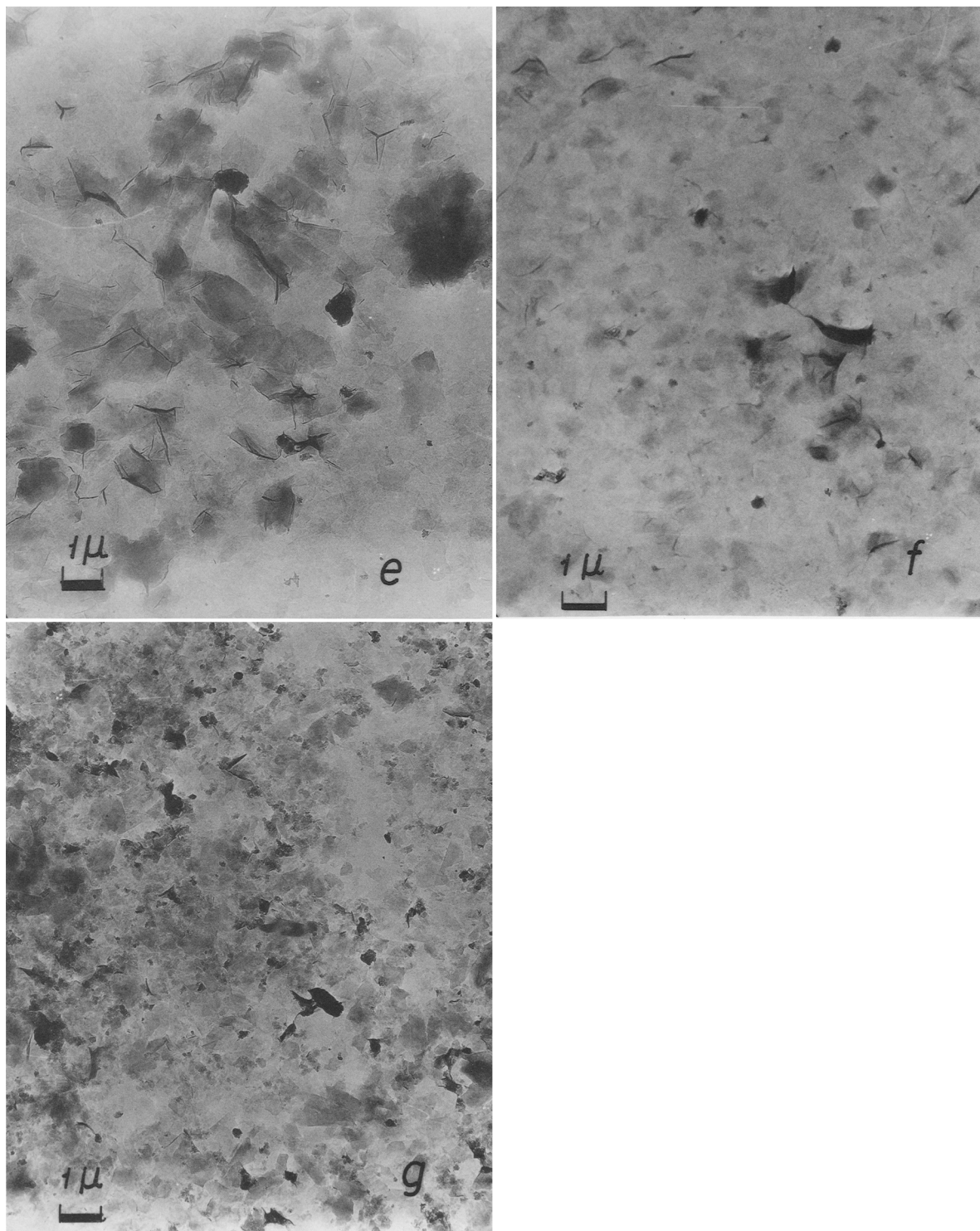
Fig. 4.   e–g: Transmission electron micrographs of Na-bentonite after equilibration in aqueous suspensions as affected by grinding. Na-bentonite ground for 0, 1 and 25 min, respectively; magnification ×5000.
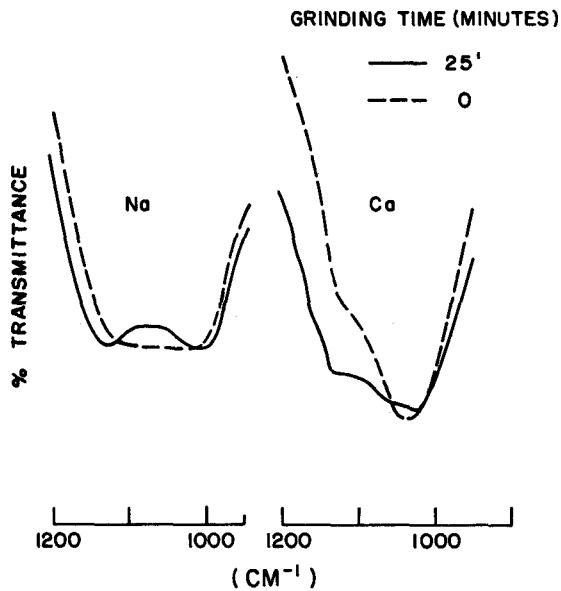
Fig. 5. IR spectra of Na- and Ca-bentonites unground or ground for 25 min, after equilibration in aqueous suspension. (Polyethylene supported films made from 0.16% clay suspension, run against polyethylene blanks.)

With Na-bentonite, breakage of the plates was evident after 1 min of grinding, but delamination of course was not observable. The presence of effects common to both Ca- and Na-bentonites in aqueous suspensions enabled the exclusion of delamination as the cause of such phenomena (e.g., the formation of secondary aggregates in aqueous suspensions upon grinding). The formation of secondary aggregates is therefore probably due to the exposure of active broken edges upon the breakage of the plates. The well-known tendency of Na-bentonite to cluster upon drying, already exhibited in the unground clay, makes the grinding-induced formation of secondary aggregates in suspension (which is evident from the turbidity observations) difficult to observe with the TEM.

From the TEM observations it is evident that the plates' area is very sensitive to mechanical stresses and that this sensitivity varies with the exchangeable cation. Even before any grinding (but after freeze-drying), Na- and Ca-bentonites had different plate areas. One implication of this observation is the danger of assuming a similar plate area for different bentonites (Shainberg and Otoh, 1968), when attempting to determine the tactoid thickness of various homoionic montmorillonites from viscosity or transmittance data. Lahav and Banin (1968) and Banin and Lahav (1968) recognized the importance of the variation in the major dimension of the plates in determining the number of plates per tactoid from optical data. They stated (Lahav and Banin, 1968) that even air-drying of suspended clay to 11% moisture content and resuspending it, apparently al-

tered to some extent the plates' area. This was claimed for Ca-, Ba- and, to the largest extent, for Na-montmorillonites, However, the possible existence of secondary aggregation further complicates the situation and makes absorbance data even harder to interpret. The SEM observations indicated that upon drying Ca-montmorillonite suspensions, more uniform clay surfaces were formed from ground than from nonground clay. Before grinding, a rough surface with undulations (approximate dimension of 10 μ) was observed. After 25 min of grinding the surface was considerably smoother, seemingly composed of undulations of approximately 1 μ in size. Even after 1 min of grinding, smoothening of the surface was observed, but it retained the general appearance of the surface of the unground clay. The effect of grinding on the surface formed by drying the Na-clay suspension was much less pronounced than the effect on the surface of the Ca-clay. The uniformity of the surface of the dried Ca-clay brought about by grinding is analogous to the destruction of soil structure caused by the use of heavy farm machinery in agriculture.

The IR spectra of clay films also exhibited interesting modifications upon grinding (Figure 5). In both Na- and Ca-bentonite there was some increase in the small peaks in the 825–900 cm^{-1} region upon grinding, but otherwise grinding affected very little the spectrum of Na-bentonite. The complex band about 1000–1150 cm^{-1} broadened appreciably on the high-frequency side upon grinding of Ca-bentonite, making the spectrum of the Ca-clay more similar to that of the Na-clay. Specifically, there was a marked increase in the shoulder at about 1125 cm^{-1} with the Ca-clay.

The region below 950 cm^{-1} contains the peaks associated with the Al–OH deformation mode. The higher frequency region up to around 1125 cm^{-1} contains the Si–0 stretching modes (Yariv and Shoval, 1975). Si–0 in a framework absorbs more at lower frequencies than Si–0 in a single layer (Black et al., 1965). The strong absorption appearing after grinding at about 1125 cm^{-1} suggests, therefore, thinner tactoids caused by delamination. Delamination was given as the reason for the appearance of a sharp peak at above 1110 cm^{-1} in the case of halloysite and kaolinite (Yariv and Shoval, 1975, 1976). The increase in the peaks below 900 cm^{-1} apparently were associated with the exposure of Al–OH at broken edges. The IR spectrum of Zn-bentonite displayed a behavior similar to that of Ca-clay.

Some understanding of the effect of mechanical stress on the behavior of clays upon wetting and drying, can be achieved from the ability of the clays to form self-supporting films after various grinding times. Grinding of Na- and Zn-bentonite improved the capacity of the clay suspension to dry into self-supporting films. The capacity to form self-supporting films increased with grinding, apparently due to the better ability of the smaller particles to become oriented during

the film-formation process. With Ca-montmorillonite, grinding for up to 5 min produced better films. Further grinding, up to 25 min, greatly decreased the stability of the produced films. Possibly, this was due to the formation of secondary aggregates and colloidal matter, which may hinder the formation of a well-oriented film.

The present work demonstrates the importance of the history of the bentonite before suspension, on tactoid thickness. Thus, attempting to assign the tactoids' thickness in a given suspension to the exchangeable cation (e.g., Shainberg and Otoh, 1968; Banin and Lahav, 1968) seems hazardous. The effect of past history of bentonites on their tactoid thickness in suspension was already pointed out by Lahav and Banin (1968).

SUMMARY AND CONCLUSIONS

It is evident that mild grinding strongly affects the behavior of bentonites. In many respects, mechanical stress will affect bentonites more than it will kaolinites. The effect of grinding on parathion adsorption from the apolar solvent on bentonites, and the much smaller effect on the adsorption on kaolinites, for example, demonstrated the great sensitivity of bentonites to even mild grinding.

The nature of the effect of grinding is complex. There is the obvious breakage of the relatively weakly bound large aggregates. In addition, delamination, formation of colloidal matter, and a marked reduction in the average size of the plates, were observed. The reduction in the size of the tactoids in the equilibrated aqueous suspension is caused most likely by the delamination process. A tendency to form secondary aggregates in the suspension may arise from the exposure of active broken edges when the plates are broken. The various homoionic bentonites responded similarly to grinding, with the obvious exception that clays which underwent practically complete dispersion in aqueous suspensions (e.g., Na-bentonite) were not affected—with regard to their tactoid thickness in suspension—by delamination. The effects of grinding and other mechanical stresses on the properties of bentonite clays

have implications in many areas, such as agrotechnology, formulation chemistry, soil engineering and various aspects of clay research.

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Резюме- Процедура растирания,которой часто подвергаются глины,оказывала заметное влияние на структуру и поведение гомоионных бентонитов. Основными изменениями,которые наблюдались в порошках глин,было разрушение слабосвязанных больших агрегатов,уменьшение толщины тактоидов в результате расслаивания, уменьшение площади пластин и образование коллоидального вещества. Тенденция глин к образованию вторичных агрегатов в водных суспензиях возможно вызвана появлением после растирания обломанных активных граней.

Умеренное механическое сжатие увеличивает скорость адсорбции и количество адсорбированного глиной паратиона из неполярного растворителя.

Эффект растирания на адсорбцию паратиона в водных суспензиях глин заключается,повидимому,в изменении скорости адсорбции.

Kurzreferat- Die Struktur und das Verhalten von homoionischen Bentoniten war ausgesprochen beinflußt durch eine Vermahlmethode, die oft bei Tonerden angewendet wird. Die hauptsächlichen Veränderungen, die in den Tonpulvern sichtbar war, waren das Brechen von schwächlich gebundenen, großen Aggregaten, die Reduktion in der taktoiden Schicht durch Schichtenspaltung, die Re-duktion in der Plattenfläche und die Formation von kolloidem Material. Die Neigung von Tonerden, sekondäre Aggregate in wässrigen Suspensionen zu formen, geht wahrscheinlich darauf zurück, daß die aktiven, gebrochenen Ecken nach dem Vermahlen entblößt sind. Wenn ein wenig mechanischer Druck angewen-det wird, nimmt sowohl die Geschwindigkeit , wie auch die Menge von Parathion, die von Tonerden aus nicht-polaren Lösungsmitteln adsorbiert wird, zu. Der Effekt, den das Vermahlen auf die Parathionadsorption in wässrigen Suspensionen ausübt, scheint ein Geschwindigkeitseffekt zu sein.

Résumé-La structure et le comportement de bentonites homoioniques sont profondément affectés par un procédé de broyage souvent appliqué aux ar-giles.Les changements principaux observés dans les poudres argileuses sont la brisure de larges aggrégats faiblement liés,la réduction d'épaisseur dans les tactoïdes par délamination,la réduction dans la région des pla-ques,et la formation de matière colloidale.La tendance des argiles à for-mer des aggrégats secondaires dans les suspensions aqueuses est probable-ment due à l'exposition de bords actifs brisés après le broyage.La légère charge mécanique qui est appliquée fait croître à la fois la vitesse et les quantités de parathion adsorbées par les argiles d'un solvant apolaire. L'effet de broyage sur l'adsorption de parathion dans les suspensions aqueu-ses d'argiles semble être un effet de vitesse.