

DECOMPOSITION OF KAOLIN BY GRINDING

by

CLYDE WILLIAM PARKERT

B. S., State Teachers College,
Platteville, Wisconsin, 1948

A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1949

TABLE OF CONTENTS

INTRODUCTION	1
GENERAL PROCEDURE.	6
AVERAGE PARTICLE SIZE.	9
SOLUBILITIES	12
pH	16
BASE-EXCHANGE.	19
THERMAL CURVES	24
X-RAY.	31
WET GRINDING	35
SUMMARY.	39
CONCLUSIONS.	41
ACKNOWLEDGMENT	43
BIBLIOGRAPHY	44

Docu-
ment
LD
2668
T4
1949
P31
C.2

INTRODUCTION

Kaolinite, muscovite and montmorillonite are three clay minerals of importance in the study of soils. The reactions and characteristics of these closely related minerals are not only important in the field of soils but also in industry. Among the industrial uses of clay minerals are filtering and clarifying media, as ceramic materials, as portland cement raw materials, as a source of alumina (19), etc.

Kaolinite is classified in the kaolin group of minerals (7). This group contains kaolinite, dickite and nacrite. The difference between these minerals lies in the relative positions of the atoms in successive layers. The usage of the term kaolinite in some of the literature has been interchangeable with the word kaolin. The kaolinite chemical formula might be given as $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_3$.

Muscovite is a mica, with the characteristic thin flaky crystals, of chemical formula $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$. Montmorillonite, $\text{Al}_4\text{Si}_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$, occurs in bentonite. The montmorillonite used in these studies was California bentonite obtained from the Filtrol Corporation and contains a large percentage of montmorillonite.

The arrangement of the atoms in these three minerals kaolin, muscovite and montmorillonite have been fairly well established and are illustrated in Figs. 1-6.

The structure of these minerals, as seen by the lateral diagrams, Fig. 1-3, are similar. Kaolin, $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_3$, and montmorillonite $\text{Al}_4\text{Si}_8\text{O}_{20} \cdot n\text{H}_2\text{O}$, differ in that one hydrogen

atom bonded to an oxygen atom in kaolin is replaced by a silicate group in the montmorillonite. The muscovite, $KAl_2(AlSi_3O_{10})(OH)_2$, differs from the montmorillonite in that Al is substituted for a Si at periodic intervals, the valence is satisfied by the addition of a K atom.

The effects of grinding various clay minerals have been studied by numerous investigators (14, 18, 20, 25, 27). The characteristics of the grinding products have been studied with reference to base-exchange, solubility, thermal curves, x-rays and other phenomena. In this investigation kaolin, muscovite and montmorillonite were ground for various periods of time. The majority of the grinding has been dry grinding with preliminary studies on some wet grinding.

The clay minerals were ground to study various chemical and physical phenomena as particle size decreased. In the grinding of any material it is expected that finer particles will be produced. For instance a molecular type crystal, if ground long enough should reach the unit cell dimensions of the crystalline structure. If enough energy could be put into the unit crystal by grinding, the bonds will break, leaving the molecule. This phenomenon would not occur in crystals where the bonding is strong, with the introduction of extremely large amounts of energy. The phenomenon of breaking the weak bonds could be a possibility in the larger, more weakly bound crystals which have structures within structure. The clay minerals fall under such a classification, for instance kaolinite, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, as seen in the illustration, Figs. 1-6. With this possibility in mind and with the evidence

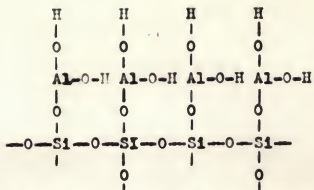


Fig. 1. Lateral view of Kaolin.

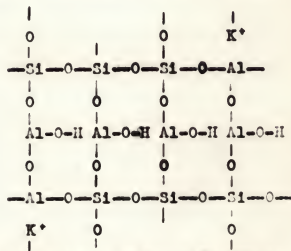


Fig. 2. Lateral view of Muscovite.

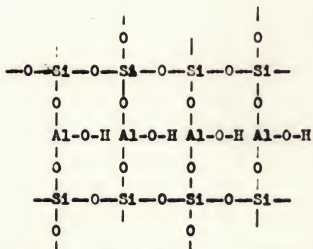


Fig. 3. Lateral view of Montmorillonite.

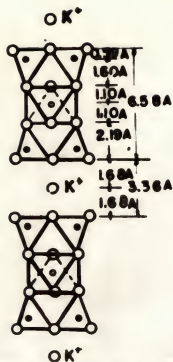


Fig. 4. Muscovite

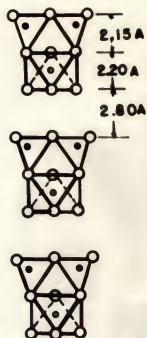


Fig. 5. Kaolin

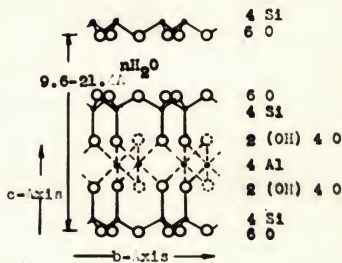
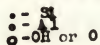


Fig. 6. Montmorillonite



of other investigators (13, 17, 19, 24, 26) this grinding operation was carried out. The main study was with kaolin, the muscovite and montmorillonite were used principally for purpose of comparison.

The statement by Grim (7), "it is generally true that a chemical analysis alone, without x-ray, optical and other mineralogical data tells very little about the properties of a clay material and, in fact, the analysis may be completely misleading.", was taken into consideration in this investigation. Therefore, studies have been made on the ground materials by using average particle size, solubility, pH, base-exchange, thermal curves and some x-rays to interpret the results of grinding the minerals over a period of 25 weeks.

Particle size has been investigated by Perkins (23) using sedimentation, by Grim (6) and by Shaw (25) using the electron-microscope. Jackson and Truog (14) have studied the influence of fine sub-divisions on the solubility and base-exchange capacity. Base-exchange has been studied by many investigators including Hendricks (11), Kelley (15), Perkins (24), and Johnson and Lawrence (15). The studies of thermal curves include Grim (8, 9), Mellor (21), Comerford, Fischer and Bradley (5), and Spiel, Berkelhamer, Pask and Davies (25). X-ray studies have been made by Gruner (10), Brindley and Robinson (3), and Clark, Grim and Bradley (4). The preceding investigators being but a few of the many helpful studies which were reviewed before and during the time of this investigation.

GENERAL PROCEDURE

The three soil minerals 100 mesh kaolin from Langly, South Carolina; muscovite separated into paper thin layers, with impurities removed by hand picking, pre-ground to pass a 1 mm screen; and 100 mesh California bentonite (Filtrol) were ground in a porcelain ball mill with porcelain balls using 250 g samples of each mineral. The ball mill was of the quart size using approximately 1.7 lbs. of 3/4 in. balls and rotated on friction rollers at 96 r.p.m. Each jar was sampled at 18 hours, 4 days, 2, 4, 10 and 25 weeks grinding time taking 30 g samples after passing the pulverized material through a 100 mesh screen. The materials being ground were periodically broken loose from the jar due to a tendency for the ground material to pack in the ball jar.

Contamination of the sample during grinding the dry minerals was negligible (14). The clay minerals, being relatively soft, form a thin protective coating of the mineral on the surface of the porcelain balls; thus, the friction is between the clay particles and the porcelain jar of 7.0 hardness, minimizing the contamination by porcelain. The freedom from contamination is supported by the work of Jackson and Truog (14).

Average particle size; solubilities in water, acid and base solutions; pH; base-exchange; thermal curves; and x-ray data were obtained for the ground samples, including the original sample.

Table 1. Particle size in microns (sub-sieve sizer).

Sample	0	18 hrs.	4 days	2 wks.	4 wks.	10 wks.	25 wks.	Porosity
Kaolin	1.51	1.38	1.20	1.06	0.95	0.60	0.60	0.65
Muscovite	7.70	8.15	4.80	1.51	1.10	0.55	0.67	0.65
Montmorillonite	18.65	19.30	4.15	2.46	1.75	0.90	1.20	0.50

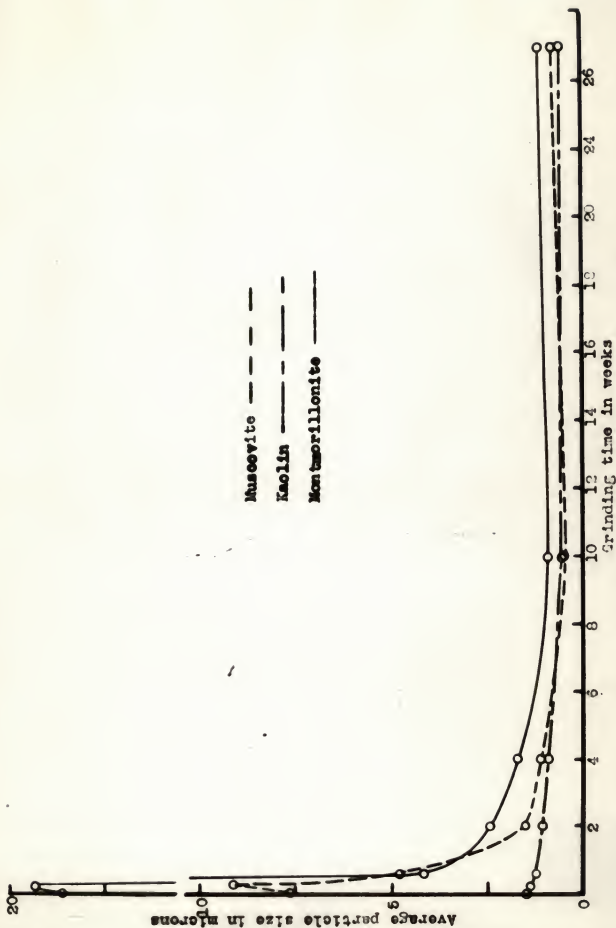


FIG. 7. Average particle size of dry Grinds,

Preliminary investigations were made with wet-grinding of kaolin by controlling the pH of the slurry. Preliminary data were also obtained on grinding kaolin and silice gel in $\text{SiO}_2\text{Al}_2\text{O}_3$ ratios of montmorillonite in an excess of water and controlling the pH. The data obtained from wet grinding were thermal curves and solubilities.

AVERAGE PARTICLE SIZE

The average particle size of the ground samples were determined by the use of the Fisher Sub Sieve Sizer. Using specific gravities of the minerals as given by Lange (17), the specific gravities used were:

Kaolin = 2.6

Muscovite = 2.9

Montmorillonite = 2.0

The particle size data as reported in Table 1 and Fig. 7 show that with increasing grinding time, the size of the kaolin particles decreased from 1.51μ at the start to 0.60μ at 10 weeks, but increased to 0.80μ at 25 weeks. The muscovite particles increased slightly in size from 7.70μ to 8.10μ at 18 hours grinding, but they decreased in size to 0.55μ at 10 weeks, then followed by a slight increase in size to 0.67μ at 25 weeks. Montmorillonite increased in particle size from 18.65μ to 19.30μ for 18 hours grinding, decreasing sharply to 4.15μ at 4 days, and 0.90μ at 10 weeks with an increase to 1.20μ at 25 weeks.

Table 2. Solubilities mg/100 ml soln.

		Time of grinding, as indicated							
		Sam-	18	4	2	4	10	25	
Media:	ple	0	hrs.	days	wks.	wks.	wks.	wks.	
Water Solubili- ties	SiO ₂	1	0.5	6.5	0.5	0.9	1.5	1.2	1.05
		2	0.6	0.75	0.6	1.1	0.55	1.05	0.9
		3	4.1	4.15	2.9	4.0	4.6	2.8	1.85
	K ₂ O ₃	1	0.5	0.5	0.35	0.25	0.35	1.15	0.75
		2	0.75	0.45	0.6	0.6	1.0	1.5	1.75
		3	2.8	1.25	2.75	0.55	0.45	1.35	0.90
Acid Solubi- ties	SiO ₂	1	0.6	1.05	2.55	9.75	15.3	15.5	19.85
		2	4.4	6.3	15.4	34.75	58.0	133.15	187.6
		3	27.4	27.9	27.5	25.6	23.95	16.5	11.6
	K ₂ O ₃	1	3.25	3.3	6.3	23.2	51.0	219.45	352.35
		2	9.1	10.75	22.95	64.6	93.85	197.4	339.85
		3	21.85	32.35	40.9	43.5	67.05	129.75	173.35
Base Solubi- ties	SiO ₂	1	6.15	6.65	9.7	35.1	67.7	221.45	214.75
		2	7.8	9.45	20.15	61.3	88.15	198.35	233.4
		3	13.4	15.15	26.25	53.75	94.5	253.8	369.85
	K ₂ O ₃	1	5.2	5.55	8.6	28.1	60.25	196.3	202.4
		2	5.5	2.9	13.4	49.45	68.65	161.15	189.05
		3	5.0	4.2	8.0	7.2	20.75	66.0	94.35

1 - Kaolin; 2 - Muscovite; 3 - Montmorillonite

Table 3. Ratio of $\text{SiO}_2/\text{H}_2\text{O}_3$ of soluble material.

Material :	Media :	0 :	18 hrs. :	4 days :	2 wks. :	4 wks. :	10 wks. :	25 wks. :
Kaolin	H ₂ O	1.00	1.00	1.23	3.60	2.30	1.09	1.40
	Acid	0.185	0.318	0.405	0.420	0.300	0.071	0.056
	Base	1.19	1.20	1.13	1.25	1.12	1.13	1.06
Luscovite	H ₂ O	0.900	1.67	1.00	1.53	0.550	0.700	0.514
	Acid	0.483	0.588	0.671	0.528	0.354	0.875	0.552
	Base	1.42	3.26	1.50	1.24	1.28	1.23	1.24
Montmorillonite	H ₂ O	1.46	3.32	1.05	7.27	10.2	3.07	2.06
	Acid	1.25	0.855	0.672	0.588	0.357	0.127	0.067
	Base	2.68	3.61	3.53	7.47	4.56	3.84	3.62

The original samples of kaolin and montmorillonite had been passed through a 100 mesh screen which has openings of 149 μ . The kaolin passed through the screen must have consisted of smaller particles than the montmorillonite or the montmorillonite would have consisted of aggregates. Further evidence of the aggregation of montmorillonite is noted from the montmorillonite particles passed through a 100 mesh screen are greater in size than the muscovite particles passed through a 1 mm screen.

The decrease in average particle size of kaolin on grinding was to be expected, but one notes that after 10 weeks grinding the sample showed a minimum average particle size. At 25 weeks the average particle size had increased from the minimum point. This increase in particle size from 10 to 25 weeks was also noted in the other two minerals. There are at least two possibilities: either the formation of aggregates or the formation of a compound of larger structure occurs.

The slight rise in average particle size of the muscovite and montmorillonite for the first period of sampling were probably caused by aggregate formation due to charges on the ground particles.

SOLUBILITIES

Determination of solubilities was made by placing 2.5 g of the various ground samples of kaolin, muscovite and montmorillonite in 250 ml of solution in a pyrex bottle and agitating with a mechanism rotating at 6 r.p.m. The agitation of each sample was for 18 hours in a constant temperature room kept at 25°C.

The water solubility was determined by using 250 ml of distilled water; the acid solubility by using 250 ml of 1.3 N hydrochloric acid; and the base solubility by using 250 ml of 1.3 N sodium hydroxide.

The solutions were filtered by suction after forming a mat of the sample on the filter paper and refiltering through the mat until clear solutions were obtained. Aliquot portions of the clear solutions were then acidified with hydrochloric acid and the SiO_2 present determined gravimetrically by AOAC methods (1). The filtrates were then treated with ammonium hydroxide to precipitate the $\text{Al}(\text{OH})_3$ which was filtered and ignited as Al_2O_3 . The Al_2O_3 precipitate was Al_2O_3 of a high degree of purity.

The water solubility of the SiO_2 of the ground samples of kaolin as reported in Tables 2 and 3 increased with the time of grinding up to four weeks and then decreased slightly at 10 and 25 weeks. The solubility of the Al_2O_3 decreased at two weeks grinding, reached a maximum at 10 weeks and then decreased.

The SiO_2 and Al_2O_3 solubilities of the ground muscovite in water were somewhat erratic. The SiO_2 solubilities increased for 18 hours grinding, decreased at four days, increased at two weeks, decreased at 14 weeks, increased at 10 weeks and decreased at 25 weeks; while the Al_2O_3 solubilities decreased at 18 hours, increased at four days, remained constant at two weeks, increased at 4, 10 and 25 weeks.

The water solubility of the SiO_2 of the ground montmorillonite samples decreased until four days grinding and increased to a maximum at four weeks, gradually decreased for 10 and 25 weeks; while the solubility of Al_2O_3 decreased for 18 hours,

increased at four days, decreased at four weeks, then increased at 10 weeks, finally decreased at 25 weeks.

The overall results for the water solubilities of the three minerals show small differences from each of the other minerals.

The solubility of SiO_2 in 1.3N HCl increased with time of grinding. The Al_2O_3 solubility increased at a faster rate. In the 1.3 N basic (NaOH) solution the solubilities of the SiO_2 and Al_2O_3 increased at approximately the same rate but the solubility of the SiO_2 being just slightly greater.

The solubility of the SiO_2 and Al_2O_3 in acid in the ground muscovite samples increased. The Al_2O_3 being slightly more soluble than the SiO_2 throughout the grinding range. The solubilities of SiO_2 and Al_2O_3 in basic solution increased with the SiO_2 being slightly more soluble than the Al_2O_3 .

The montmorillonite samples in acid solution showed a decrease in the solubility of SiO_2 and an increase in Al_2O_3 solubility. In the basic solution the SiO_2 solubility is greater than the Al_2O_3 solubility.

The respective solubilities of the minerals in acidic and basic media agree with data reported in the literature (19, 26). The Al_2O_3 or $\text{Al}(\text{OH})_3$, if formed in the grinding process, would be the most soluble in the acid medium while SiO_2 or $\text{Si}(\text{OH})_4$, if formed, would be somewhat less soluble. The reverse situation in the basic medium would exist.

It is of interest to note the $\text{SiO}_2/\text{R}_2\text{O}_3$ ratio of the dissolved material is not necessarily the same as the ratio of the original minerals. It can be seen from the $\text{SiO}_2/\text{R}_2\text{O}_3$ ratios of the soluble materials that there are possibilities of physical

Table 4. pH of dry ground samples.

		pH		
Material	Grinding	1 gram/10ml H ₂ O	1 gram/50ml H ₂ O	1 gram/100ml H ₂ O
Kaolin	0 hrs	4.89	5.99	5.80
	18 hrs	5.08	5.73	5.86
	4 days	5.31	5.79	5.84
	2 wks	5.68	6.03	6.94
	4 wks	5.77	6.10	6.01
	10 wks	5.90	6.05	6.02
"	25 wks	5.65	6.12	5.45
Muscovite	0	7.72	6.90	6.46
	18 hrs	7.85	7.20	6.60
	4 days	8.39	7.78	6.97
	2 wks	8.95	8.51	8.15
	4 wks	9.05	9.05	8.40
	10 wks	9.10	9.17	8.55
"	25 wks	9.05	8.95	8.38
Bentonite	0	7.92	8.05	7.05
	18 hrs	8.30	8.08	7.00
	4 days	7.95	8.75	8.21
	2 wks	8.91	8.78	8.72
	4 wks	8.34	8.91	8.60
	10 wks	8.71	8.75	8.57
"	25 wks	9.18	9.35	9.05

or chemical reactions taking place during grinding. It is doubtful if the explanation lies totally in the formation of aggregates. It has been shown in Tables 2 and 3 that there is a formation of several forms of alumina silicates as the grinding progresses, with the possible formation of $\text{Al}(\text{OH})_3$ or Al_2O_3 and $\text{Si}(\text{OH})_4$ or SiO_2 . Mellor (21) has shown that by the heating of the respective minerals there is at one stage a formation of amorphous material. The grinding process (if it could be satisfactorily measured) would probably show energies present due to friction and crystal fracture in the amount necessary to effect the various changes observed.

pH

One gram samples of the ground minerals were suspended in 10 ml of distilled water, the pH determined and the suspension diluted to 50 ml and finally to 100 ml for additional pH determinations. The data are reported in Table 4. The pH of each sample was determined in duplicate with a Beckman pH meter using the glass electrode.

Dilutions of the various samples indicate a slight change in pH with dilution, which could be explained by the solubility of the materials present, or by the formation of larger particles in water solution, i.e., exposing less surface area. Another possibility is the presence of amphoteric materials such as $\text{Si}(\text{OH})_4$ and $\text{Al}(\text{OH})_3$.

It is seen that the general tendency for the respective minerals is an increasing pH for increasing grinding. This may be attributed to the exposure of the larger surface area,

Table 5. Base-exchange capacity mg. eq./100.

Sample	:	:	18	:	4	:	2	:	4	:	10	:	25
	:	0	hrs.	:	days	:	wks.	:	wks.	:	wks.	:	wks.
Kaolin	10.0	13.6	21.4	38.6	72.5	44.3	84.4						
Muscovite	30.7	11.4	23.6	69.3	98.0	92.2	97.2						
Montmorillonite	109.0	106.5	103.5	111.5	128.0	162.0	180.0						

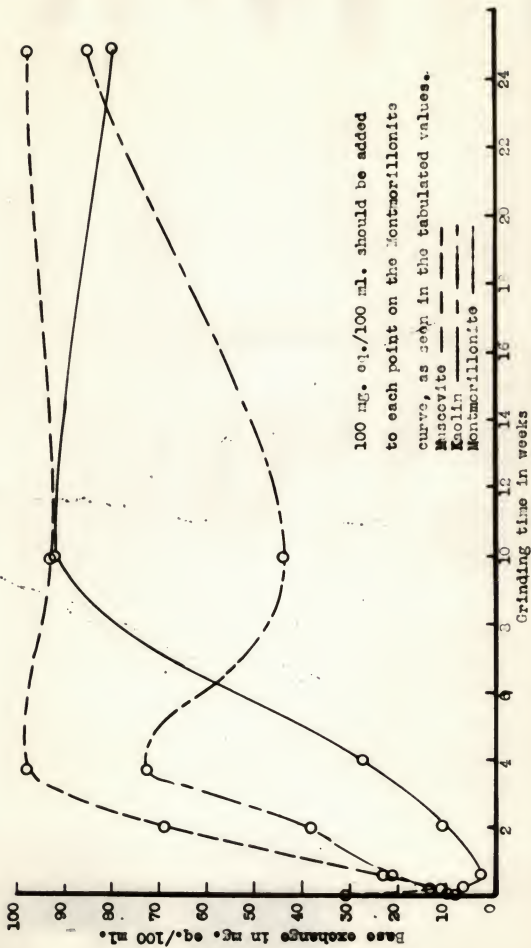


FIG. 8. Base exchange of dry grinds

i.e., the exposure of a greater number of hydroxyl groups, resulting from the cleavage of the original particles. However, the sample ground for 25 weeks had an average particle size greater than the 10 week ground samples, which would indicate a lower pH. In interpretation of the pH data, reference should be made to the table of SiO_2/H_2O_3 ratios. Since these solubility ratios are somewhat erratic it is difficult to attribute the increasing pH, entirely to solubilities. The pH is probably effected by a variety of factors including effective surface areas, solubilities and presence of substances of an amphoteric nature.

BASE-EXCHANGE

A one gram sample was stirred with 50 ml of neutral, normal ammonium chloride and filtered, then washed with fifteen 20 ml portions of neutral normal ammonium chloride. The residue was then washed free of the chloride ion with 75-85 percent ethyl alcohol. The completeness of the wash was tested with silver nitrate. The ammonia present was then determined by the Kjeldahl method using magnesium oxide and paraffin (1). The carbon dioxide was boiled from the acid distillate before titrating with standard base. Calculations are then made for mg. eq./100 gm. The samples were run in duplicate and several in triplicate.

The base-exchange capacity for kaolin as reported in Table 5 and Fig. 8 increased with grinding for four weeks, showed a decrease at 10 weeks followed by an increase at 25 weeks. The decrease in base-exchange capacity at 10 weeks

grinding could mean the formation of either aggregates or a new material of larger crystals of less base-exchange capacity. Then on further grinding the base-exchange capacity again increased which might be due to formation of new surface areas of exchange. According to Jackson and Truog (14) the base-exchange capacity of SiO_2 increases with grinding.

Muscovite decreased in base-exchange capacity at 18 hours, but then steadily increased, with a slight decrease at 10 weeks followed by an increase at 25 weeks. The first decrease in base-exchange capacity was probably due to the formation of aggregates as the base-exchange capacity increases at four weeks grinding. The minimum and maximum points and the deflections in the curves could be determined more accurately if samples were taken at shorter intervals; thus, the minima and maxima given throughout are only approximate, the accuracy being limited by the sampling intervals.

The montmorillonite decreased in base-exchange capacity for four days, reached a maximum of 192 mg. eq./100 gm. at 10 weeks, followed by a slight decrease at 25 weeks. The first decrease was attributed to aggregate formation. The montmorillonite has approximately twice the base-exchange capacity of either the kaolin or muscovite, but the portions grinding 25 weeks show a decrease for montmorillonite and increases for both kaolin and muscovite.

Various publications (14, 18, 25) have given base-exchange capacities of ground minerals. The grinding was carried out over a shorter period of time giving data over the respective time range of grinding. Time is often the limiting factor in



Fig. 9. Thermal curves of dry ground kaolin.

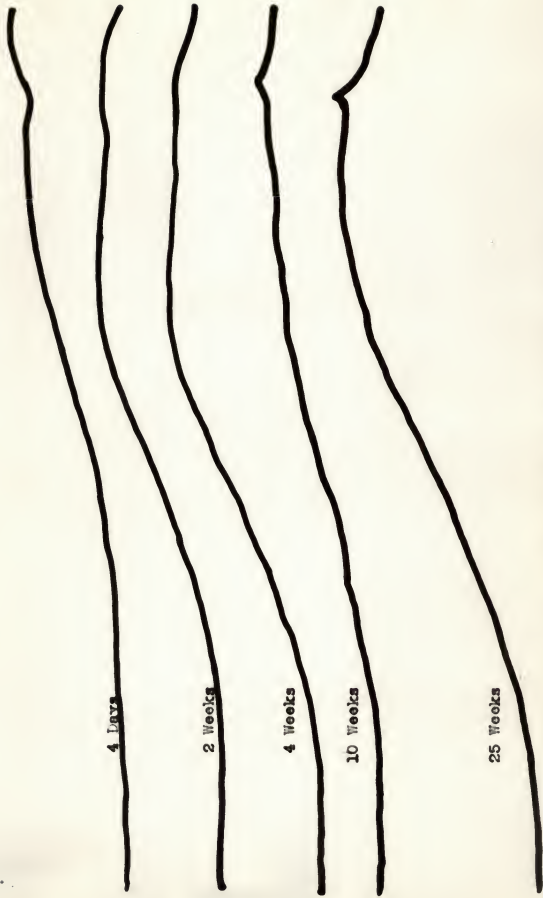


FIG.10. Thermal curves of dry ground Muscovite



FIG. 11. Thermal curves of dry ground Montrillonite

such operations.

Jackson and Truog (14) indicate that free SiO_2 in the form of quartz increases its base-exchange capacity as do the silica gels after grinding. Base-exchange has been attributed by Kelley (16) to effective surface area. On grinding, the effective surface area of kaolin and muscovite should be increased due to the fracture of the crystals and exposure of more exchangeable bonds. Montmorillonite has an expanding lattice (7, 12) and the effective area is not only the outer surface, as in kaolin and muscovite but also due to the internal surfaces of the expanding lattice.

The average particle size must be considered in determining the results of base-exchange. The results of the base-exchange and average particle size are in fair agreement, since base-exchange is related to the effective area of the material.

THERMAL CURVES

The thermal curves were obtained from an apparatus designed by the suggestion of Grim and Jefferies (Personal Communications). This consists of a nickel sample block containing four holes, two for an unknown sample and two for a reference sample; a resistance furnace controlled by a variac connected to a rotating drum of constant speed. The drum was enclosed in a light proof black box. Platinum-platinum rhodium double junction thermocouples were placed with one junction in the sample (reference or unknown) and the other junction in calcined alumina. The drum was covered with positive photographic paper and the galvanometer deflections indication exothermic and endothermic

reactions were recorded.

Thermal curves of the ground and unground minerals kaolin, muscovite and montmorillonite were obtained. Comparison of the ground kaolin sample curves (Fig. 9) with the curve for the unground sample shows that up to 10 weeks grinding the endothermic dip of kaolin due to the loss of water (6) steadily decreases; the exothermic peak due to the transitions of α -alumina to γ -alumina (6) remains unchanged. An increasing shallow dip (endothermic) was noticed between 0-500°C. on grinding. Also in the original sample there was a slight endothermic dip, just before the exothermic transition peak, which gradually disappears. Grim (4) attributes the shallow endothermic dip between 0-500°C. and the lack of the slight dip before the exothermic transition peak to the lower degree of crystallinity in the kaolin crystal lattice.

The montmorillonite samples, ground up to 10 weeks show a gradual decrease in the depth of the endothermic dip with a resulting shallow dip increasing between 0-500°C. The peak at 980°C. remains practically constant up to 10 weeks.

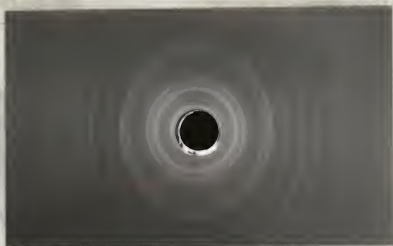
The thermal curves of muscovite develop a shallow dip between 0-500°C. up to the 10 week grind and also an exothermic alumina transition peak started at 980°C. on the 10 week thermal curve. This peak was not in evidence on the thermal curves of grinding times less than 10 weeks.

The three minerals ground for 25 weeks had similar thermal curves, the same shallow endothermic dip was in evidence between 0-500°C. and the exothermic transition peak was recorded for each mineral. It is of interest to note the height of the kaolin

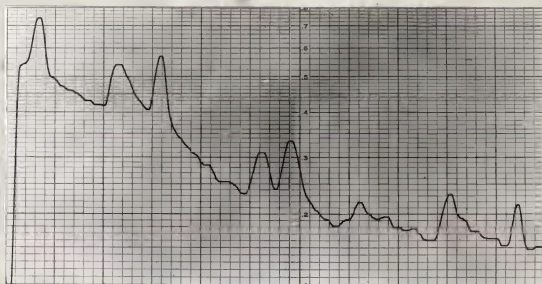
transition peak in reference to the unground kaolin sample and the other two minerals ground for 25 weeks. The energy released by kaolin ground 25 weeks was much greater at the α,γ -alumina transition point than for the other kaolin samples and the muscovite and montmorillonite ground 25 weeks.

The possible explanation of the high exothermic energy is that energy has been accumulated by the existing particles from the energy released by friction in the grinding operation and in the fracture of the crystals. Since a portion of the extra energy is released at 980° as evidenced in the height of the alumina transition peak, the indication is that extra energy is accumulated in the alumina present.

The thermal curves indicate the loss of tightly bound hydroxyl groups by grinding, which is best shown by kaolin. The shallow endothermic dip is evidence of lightly bound hydroxyl groups. This is supported by Grim's investigations (9) on the loss of water from the sample between $0-700^\circ$ C., the loss of the water being of a gradual nature throughout the temperature range. The moisture lost at 110° did not influence the percentages of H_2O in any way in the kaolin formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ as determined gravimetrically (1) on the dried samples; thus, it is assumed that a slight amount of moisture was picked up by the ground particles from the atmosphere in the grinding operation. As stated before, Grim (9) has attributed this shallow endothermic dip as an indication of lower crystalline form. The presence of $Si(OH)_4$ and $Al(OH)_3$ are possibilities in the ground samples, since the silica compound loses water in the proximity of 100° C. and $Al(OH)_3$



Diffraction pattern

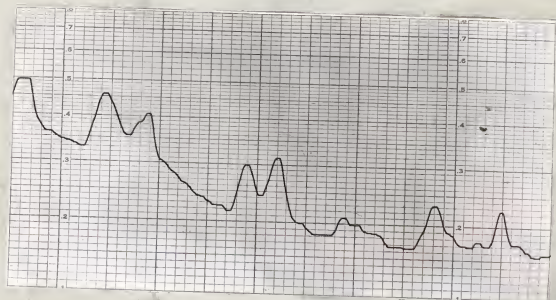


Densitometer trace

Fig. 12a. X-ray studies of unground kaolin.



Diffraction pattern

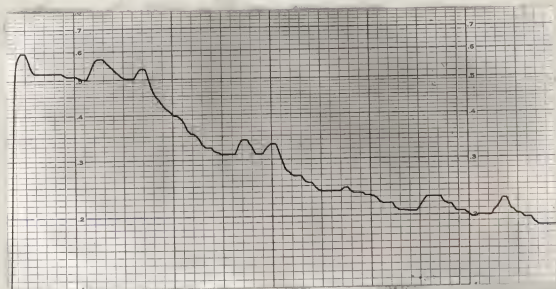


Densitometer trace

Fig. 12b. X-ray studies of 4 week ground kaolin.



Diffraction pattern

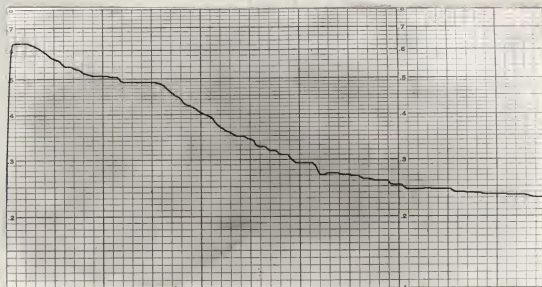


Densitometer trace

Fig. 120. X-ray studies of 10 week ground Eaolin.



Diffraction pattern



Densitometer trace

Fig. 12d. X-ray studies of 25 week ground kaolin.

loses its water from 300 to 400° C. (12).

Several investigators including Eitel, Müller and Radczewski (6) and Grim (8) have shown thermal curves of various particle sizes. The endothermic dip due to the loss of water becomes shallower with decreasing particle size according to Grim (8) and Spiel, Berkelhamer, Fask and Davies (26). This evidence of decreasing endothermic dip is supported by the grinding range up to 10 weeks, but at 25 weeks the endothermic dip disappears. The only material present in this ball jar was kaolin and the porcelain balls. Herrera and Ferrandis (12) have shown that 5 to 10 percent kaolin is detectable in the mixtures of soil minerals by the use of thermal curves; therefore, kaolin the only mineral present should be detected by the thermal curve if present in the products of grinding.

The thermal curves for the three minerals ground 25 weeks are approximately the same. These minerals all contain SiO_2 , Al_2O_3 and H_2O in various ratios. With this in mind the 25 week grinding thermal curves give evidence as to the existence of the SiO_2 or $\text{Si}(\text{OH})_4$, Al_2O_3 or $\text{Al}(\text{OH})_3$ and H_2O present in an unbound or loosely bound state unless the ground materials form an amorphous alumina silicate. The indication is that the grinding of these minerals results in the formation of similar compounds.

X-RAY

Several powder diffraction patterns were taken with a 57.3 mm rotating, a 143.3 mm and a 171.9 mm x-ray camera using a copper target tube with a nickel filter (Cu K_α radiation) at

30 kv. and 20 ma. The samples for the 57 mm and 172 mm cameras were rolled with Duco cement to form a long thin cylindrical rod. The sample for the 143 mm camera was pecked in a wedge sample holder. Pin hole collimators were used with the rod samples, and a slit system was used with the wedge sample to give shorter exposure time. The best exposure and development times were determined for the respective cameras and samples using Eastman "No Screen" x-ray film.

Preliminary investigation of kaolin with the 57 mm rotating powder camera with Cu K_α radiation for structure studies showed diffuse scattering and an increasing broadness of lines as the grinding time increased. This was also true of the muscovite and montmorillonite samples on increased grinding time.

The kaolin diffraction patterns were microphotomered with an automatic Leeds and Northrup tracing mechanism and densitometer. The traces show an increase in diffuse scattering with increased grinding time. Any lines present are approximately the same intensity as the background on increased grinding, especially for the sample ground for 25 weeks. It is also noticed that the 4th and 5th peaks of the microphotometer trace of the original unground kaolin and the kaolin ground 10 weeks show a reversal in the peak intensities of the respective lines. Number 4 is lower than peak number 5 on the unground sample and vice versa on the 10 week ground sample. The reversal is not evident in the 4 week grind.

Several lines of different intensities exist under these two different intensity peaks as shown by Brindley and Robinson (3) in their determination of the structure of kaolinite.

Table 6. One week pH controlled. Silica gel and kaolin.
Wet grind.

pH at start	SiO ₂ mg/100ml	Al ₂ O ₃ mg/100ml
11	749.0	3.8
9	29.3	2.1
7	11.2	2.6
5	16.0	5.7
3	16.4	5.7
Blk	22.2	10.0

Table 7. One week wet grind pH uncontrolled.

pH at start	1 : day	2 : days	3 : days	4 : days	5 : days	6 : days	7 : days
11.00	10.60	9.90	9.40	8.92	8.57	8.35	8.10
9.05	7.20	7.15	7.02	7.00	7.00	6.90	6.90
7.00	6.53	6.80	6.85	6.88	6.90	6.90	6.90
5.00	5.55	6.10	6.35	6.48	6.60	6.80	6.65
2.95	4.30	4.60	4.95	5.22	5.37	5.45	5.55
4.45		5.60	5.95	6.20	6.28	6.40	6.45

Table 8. One week pH uncontrolled after initial adjustment.

pH	SiO ₂ mg/100ml	Al ₂ O ₃ mg/100ml
11	2.2	1.1
9	4.2	1.0
7	4.25	1.0
5	4.8	0.75
3	4.5	1.3
Blk	4.1	1.0

Table 9. One week pH controlled by adding NaOH or HCl every 12 hrs to adjust the pH to the desired values.

pH :	SiO ₂ mg/100ml :	Al ₂ O ₃ mg/100ml :
11	2.9	3.6
9	2.0	1.0
7	2.8	0.8
5	4.6	1.2
3	34.2	19.5
Blk	12.1	0.5

Table 10. Three week pH controlled.

pH :	SiO ₂ mg/100ml :	Al ₂ O ₃ mg/100ml :
11	3.3	3.6
9	1.8	1.2
7	3.3	1.1
5	4.3	1.5
3	26.2	424.7
Blk	19.0	3.0

Table 11. Six week pH controlled.

pH	SiO ₂ mg/100ml	Al ₂ O ₃ mg/100ml
11	2.7	2.4
9	1.7	0.4
7	3.3	0.7
5	4.0	0.9
3	15.6	570.6
Blk	38.6	6.0

Therefore, larger cameras of 143 mm and 172 mm were used to see if the lines could be resolved sufficiently for study. It was found that the larger cameras were not of sufficient resolving power to separate the individual lines under the two peaks. Further investigations are to be carried on when a spectrometer table, geiger counter and scaling circuit are available.

The change in the peak intensities, at this time, could be attributed to a random reorientation of the planes associated with these peaks; i.e., some planes making up the kaolin lattice might be shifted slightly from their exact periodicity. The increasing diffuseness of the x-ray patterns as a function of grinding time has two possibilities (1) the increasing of randomness in the structure or (2) the formation of amorphous materials. Biscoe and Warren (2) have studied randomness in carbon black, which loses its randomness on heating too high temperatures and becomes more crystalline giving sharp, intense lines in the diffraction instead of broad, less sharp lines. The difficulty in studying kaolin in this manner is the high temperature required to decrease the randomness in the structure, but the investigation is to be carried on at lower temperatures over a period of time to see if the crystal structure will return to its original form.

WET GRINDING

A one week grinding run was made on kaolin in water solutions of pH 11, 9, 7, 5 and 3; the pH was checked on each solution every 24 hours without further pH adjustment.

Then runs of 1, 3 and 6 weeks grinding were made on kaolin

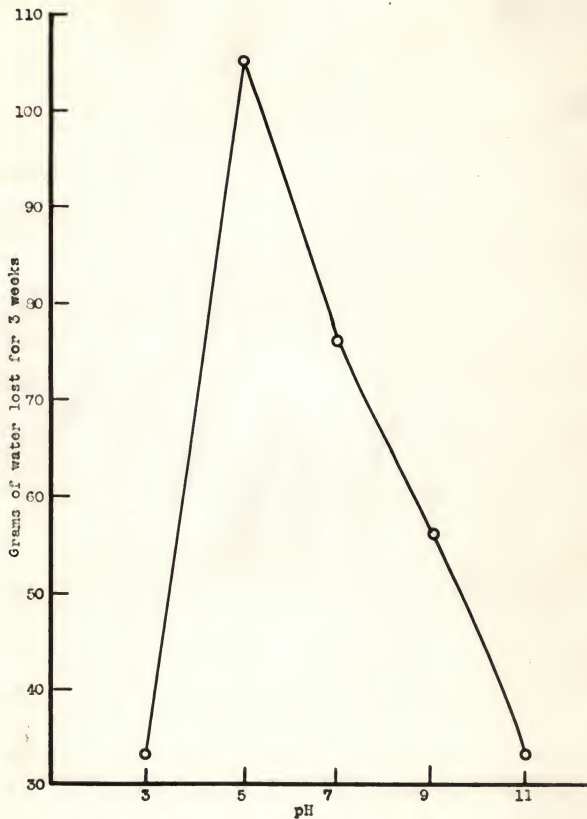


Fig.13. Loss of water in wet grinding.

using water solutions of pH 11, 9, 7, 5 and 3 and adjusting the pH to these values periodically.

A third type of wet grind was made, this consisted of adjusting the pH of a solution of kaolin and silica gel with the $\text{SiO}_2/\text{H}_2\text{O}_3$ ratio equal to the ratio of montmorillonite. The pH was adjusted to 11, 9, 7, 5 and 3 for the respective solutions every 12 hours.

A blank jar containing balls and water was run with each set of grinds to determine the contamination by the porcelain jar and balls.

The solutions were filtered after each period of grinding and the respective solutions analyzed for SiO_2 and Al_2O_3 . The contamination was excessive as can be seen from the blanks, (Tables 6-11) which remained at $\text{pH } 7.0 \pm 0.2$ throughout each period of grinding. Thus, a true picture has not been given by the blanks as there should be as many blanks as there are solutions of different pH.

An approximate correction for contamination by the jar and balls can be applied if the assumption is made that the loss of weight of the jar and balls is SiO_2 . The calculations were made with this assumption. An interesting phenomenon was noted in regards to the loss of water in these weight checks for contamination data. It was found that water had to be added periodically in definite amounts that varied for each jar of different pH. The seepage or loss of water was around the rubber gaskets on the jars; there was no detectable loss of the kaolin. The graph in Fig. 13 illustrates this loss of water.

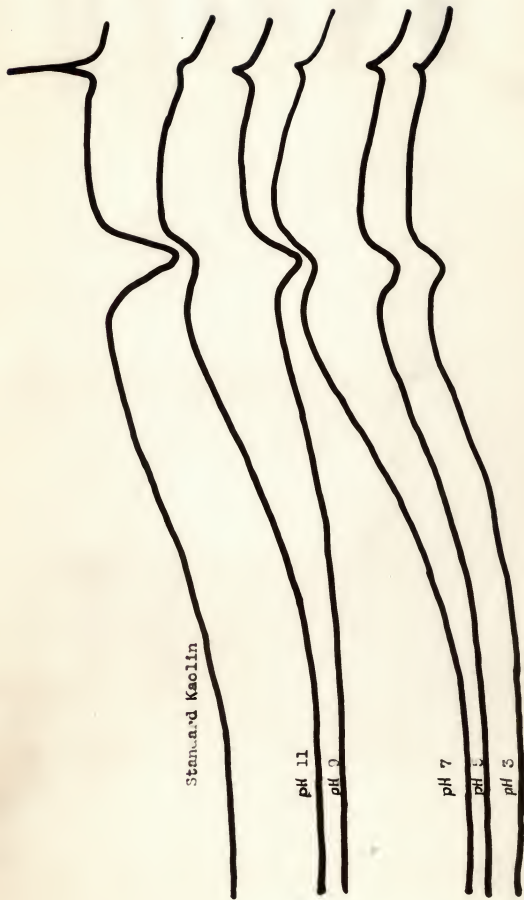


FIG. 14. Titration curves of 6 week ground kaolin with controlled pH

The one week uncontrolled grind was interesting in that from Table 7 the pH of each sample was decreasing or increasing to pH 7.0, which can be explained by the behavior of the blank. The blank containing primarily SiO_2 also approached pH 7.0; thus, the change in pH can be attributed to contamination from the jar and balls, as can be the solubilities.

Tables 9, 10 and 11 of the controlled pH grinds for 1, 3 and 6 weeks respectively indicate that acid extraction of Al_2O_3 is possible, which is reported (19). From the other data in these tables it is seen that interpretation is difficult because of contamination. The preceding also holds true for the one week grind of kaolin and silica gel in $\text{SiO}_2/\text{R}_2\text{O}_3$ ratio of montmorillonite in that the interpretation of solubilities due to contamination is difficult.

The thermal curve data on the various samples of the controlled pH with and without silica gel show no significant changes over the periods of grinding.

SUMMARY

The average particle size decreased with the grinding time of the respective samples for the first 10 weeks. At 25 weeks an increase in size was shown.

The solubility of each ground sample varied with the time of grinding and with the solubility media (water, 1.3 N acid and 1.3 N base). The SiO_2 present in the ground samples was more soluble than the Al_2O_3 in a 1.3 N basic (NaOH) solution while the reverse was true in the 1.3 N acidic (HCl) solution. The $\text{SiO}_2/\text{R}_2\text{O}_3$ ratios of the soluble material was not that of

the original minerals at each period of sampling of the ground minerals.

The pH, generally, increased with time of grinding. The dilution of each sample did not follow a specific increase or decrease of pH.

The base-exchange capacity increased up to a maximum, then was followed by a decrease. Kaolin and muscovite on further grinding showed an increase in base-exchange capacity. The 25 week base-exchange capacity of montmorillonite was decreasing while the 25 week ground kaolin and muscovite was increasing. Montmorillonite had approximately twice the base-exchange capacity of either kaolin or muscovite.

The thermal curves gave indications of the disappearance of strongly bound hydroxyl groups with the development of weakly bound hydroxyl groups on the grinding of the three minerals. On grinding the α -, γ -alumina transition was noted to develop in the muscovite and remained in the kaolin and montmorillonite with greater exothermic energy released in the 25 week ground kaolin at 980° C.

The x-ray patterns indicated (1) a possible development of randomness of structure or (2) the formation of amorphous materials. This was indicated by the reversal of two peak intensities and by development of diffuse scattering in the diffraction patterns of ground kaolin. The increased diffuse background of the diffraction patterns of the other minerals, muscovite and montmorillonite, on grinding were also noted.

The various wet-grinding procedures gave very little information over the periods of grinding. It was shown that

extraction of Al_2O_3 from clay minerals, as also seen in Table 2 on acid solubilities, is probable by the process of grinding in an acid solution.

CONCLUSIONS

The combined evidences of average particle sizes, solubilities, pH's, base-exchange capacities, thermal curves and x-ray diffraction patterns indicate that grinding permits the formation of amorphous materials differing greatly from the original material in chemical reactions and crystal structure. The more random structure induced by grinding being of lower crystal structure has less bonding energies (strained bonding energies).

The chemical compounds of these three minerals are various combinations of Al_2O_3 , SiO_2 and H_2O . Muscovite in addition has K present. The chemical formulas are $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$ for kaolin, $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ for muscovite and $\text{Al}_4\text{Si}_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ for montmorillonite. The linear representations are shown in Fig. 1-3. From the chemical formulas and the linear representations it is seen that grinding the minerals might result in the formation of Al_2O_3 , SiO_2 , and H_2O with the possibility of the aluminum and silicon compounds existing as $\text{Al}(\text{OH})_3$ and $\text{Si}(\text{OH})_4$. The existence of these hydroxides requires more hydroxyl groups than exists in the respective minerals; thus, a source of hydroxyl groups is needed if the grinding products are to exist as such.

The materials present in the grinding operations were kaolin, muscovite and montmorillonite respectively and their

decomposition products. The only foreign materials present would either come from the jar and balls or the atmosphere, each having been ruled out except for the moisture from the atmosphere. It has been shown from the experimental data that the original mineral if it exists in the final 25 week grind, exists only as part of the total material present. The other materials present being the decomposition products resulting from the grinding operations. These decompositions as the result of grinding are attributed to the amorphous forms of $Al_2O_3 \cdot nH_2O$ and $SiO_2 \cdot nH_2O$. The $n \cdot H_2O$ is used because of the absence of sufficient hydroxyl groups to form $Al(OH)_3$ and $Si(OH)_4$.

It is evident that the clay minerals of the soil may be decomposed probably into $Al(OH)_3$, $Si(OH)_4$ or similar compounds and that these compounds may recombine either into the same mineral or a different mineral of the clay group.

ACKNOWLEDGMENT

The author wishes to gratefully acknowledge the interest and counsel of Dr. A. T. Perkins of the Chemistry Department with thanks for making this investigation possible. Appreciation for help and counsel is extended to Dr. A. D. Dragsdorf of the Physics Department and Dr. A. C. Andrews of the chemistry Department.

BIBLIOGRAPHY

- (1) Association Official Agricultural Chemists
Methods of analysis. Washington, D. C., 1945.
- (2) Elascoe, J. and B. E. Warren.
An x-ray study of carbon black. Journ. Appl. Phys.
13: 364-371, 1942.
- (3) Brindley, G. W. and K. Robinson.
Structures of kaolinite. Nature 156: 661-662, 1945.
- (4) Clark, G. L., R. E. Grim, and W. F. Bradley.
Notes on the identification of minerals in clays by
x-ray diffraction. F. Kristollogr. 98: 322-324, 1937.
- (5) Comeforo, J. E., R. B. Fischer, and W. F. Bradley.
Mullitization of kaolinite. J. Am. Ceram. Soc.
31: 254-259, 1948.
- (6) Bitel, W., H. O. Müller, and Radczewski.
Investigation of clay minerals with an electron
microscope. Ber. deut. keram. Ges. 20: 165-180, 1939.
- (7) Grim, R. E.
Modern concepts of clay materials. Journ. of Geol.
50: 225-275, 1942.
- (8) Grim, R. E.
Differential thermal analysis of clay minerals and
other hydrous materials. Am. Mineral. 27: 746-771,
801-818, 1942.
- (9) Grim, R. E.
Differential thermal curves of prepared mixtures of
clay minerals. Am. Mineral. 32: 443-501, 1947.
- (10) Gruner, J. W.
The crystal structure of kaolinite. Ftschr. Krist.
86: 75-88, 1932.
- (11) Hendricks, S. E.
Base-exchange in crystallin silicates. Ind. Eng. Chem.
37: 625-630, 1945.
- (12) Herrera, J. M. A. and V. A. Ferrandis,
The additivity of the thermal dehydration characteristics
of clay mineral mixtures. Anales. inst. espan. edafol.,
ecol. y fisiol. vegetal (Madrid) 6: 603-631, 1948.
- (13) Hoffman, U., K. Endell, and D. Wilm.
Crystal structure and swelling of montmorillonite.
Festschr. Krist. 86: 257-71, 1939.

- (14) Jackson, W. L. and E. Truog.
Influence of grinding soil minerals to near molecular size on their solubility and base-exchange properties. Soil Sci. Soc. Am. proc. 4: 136-143, 1939.
- (15) Johnson, A. L. and W. C. Lawrence.
Fundamental study of clay: IV. Surface area and its effect on exchange capacity of kaolinite. Journ. Amer. Ceram. Soc. 25: 344-346, 1942.
- (16) Kelley, W. P.
Cation Exchange in Soils, Reinhold, N. Y., 1948.
- (17) Lange, N. A.
Handbook of Chemistry, Handbook Publ. Sandusky, Ohio.
- (18) Laws, D. W. and J. B. Page.
Change produced in kaolinite by dry grinding. Soil Science. 62: 319-336, 1946.
- (19) March, C. C.
Alumina from clays: I Wash. State Col. Electronic Res. Lab. Bul. 2-3, 1943.
- (20) Marshall, C. E.
The colloidal properties of clays as related to their crystal structure. Journ. Phys. Chem. 41: 935-942, 1937.
- (21) Mellor, J. W.
The chemical constitution of the clay minerals. VI review of late theories. Trans. Ceram. Soc. 37: 118-125, 1938.
- (22) Pauling, L.
Nature of the Chemical Bond, Ithaca, N. Y.: Cornell Univ. Press, 1945.
- (23) Perkins, A. T.
Structure of kaolin and related minerals. Trans. Kans. Acad. Sci. 50, No. 2, 1947.
- (24) Perkins, A. T.
Kaolins and treated kaolins and their reactions. Soil Science 65: 185-191, 1948.
- (25) Shaw, B. T.
The nature of colloidal clay as revealed by the electron microscope. Journ. Phys. Chem. 46: 1032-1043, 1942.
- (26) Spiel, S., L. R. Berkelhammer, J. H. Pask, and E. Davies.
Differential thermal analysis, its applications to clays and other aluminous minerals. U. S. Dept. of Interior, Bur. of Mines. Tech. Bul. 664, 81 p., 1945.

(27) Stout, F. R.

Alterations in the crystal structure of clay minerals
as a result of phosphate fixation. Soil Sci. Soc. Am.
Proc. 4: 177-182, 1939.

