

## THE NATURE OF ALUMINUM HYDROXIDE-MONTMORILLONITE COMPLEXES<sup>1</sup>

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### ABSTRACT

Aluminum hydroxide-Wyoming bentonite complexes were compared with dioctahedral chlorite and with various synthetic pure aluminum hydroxides by *x*-ray diffraction, DTA TGA and IR absorption.

Aluminum hydroxide enters entirely into the interlayer of montmorillonite, and assumes a gibbsite-like monolayer structure in amounts up to 8 me Al/gm clay. Beyond this amount, but below the amount (16 me Al/gm clay) required for a perfect gibbsite layer, some hydroxide is present external to the montmorillonite interlayer.

On heating, there was an interaction of the interlayer hydroxide with the montmorillonite so that montmorillonite OH<sup>-</sup> was liberated at below the characteristic temperature. DTA and DTGA peaks below 300° C. and an IR band at 1680 cm<sup>-1</sup> were associated with the external hydroxide. DTA peaks at 400° and 495° C. and IR bands at 3700 and 3480 cm<sup>-1</sup> were associated with the interlayer hydroxide.

### INTRODUCTION

A number of recent publications have been concerned with the identification of aluminum hydroxide-clay mineral complexes (Frink, 1965; Kawasaki and Aomine, 1965) and the preparation and properties of synthetic materials (Slaughter and Milne, 1960; Barnhisel and Rich, 1963; Turner and Brydon, 1965). There is some doubt as to the nature of the interlayer material either in "partial" or "complete" interlayer compositions, and in the synthetic samples it is not known if all of the precipitated hydroxide is in the interlayer position.

In view of the natural occurrence of relatively complete hydroxide interlayers in the Alberni dioctahedral chlorite (Brydon *et al.*, 1961) and of the effect of the interlayer hydroxide on the lime potential (Turner *et al.* 1963) in the synthetic samples, it was decided to examine in detail the nature of complexes of varying composition. The results are described herein.

### MATERIALS AND METHODS

Wyoming bentonite, supplied by the Baroid Division, National Lead Corporation was fractionated at <2 micron by gravity separation without treatment. Aliquots equivalent to 3 gm oven-dry clay were flocculated with N AlCl<sub>3</sub>, centrifuged, and equilibrated twice with 150 ml N AlCl<sub>3</sub>. The clay was then washed with 0.01N HCl, 0.001N HCl and H<sub>2</sub>O until chloride-free. One sample (zero Al(OH)<sub>3</sub>) was freeze-dried.

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Various quantities of 0.3N  $\text{AlCl}_3$  (equivalent to 8.50, 11.0 and 15.0 me/gm clay) were added to other samples and while being stirred vigorously were titrated slowly with saturated  $\text{Ca}(\text{OH})_2$  at room temperature to give a final pH of 5.0 (OH/Al ratio = 2.7). The samples were equilibrated with gentle shaking for 4 days then centrifuged and washed 6-8 times with  $\text{H}_2\text{O}$  until chloride-free. The samples were then freeze-dried.

Aluminum hydroxides precipitated at a similar acid pH but in the absence of clay were prepared in different ways (Turner and Brydon, 1965; Gastuche and Herbillon, 1962) in order to compare with the hy-

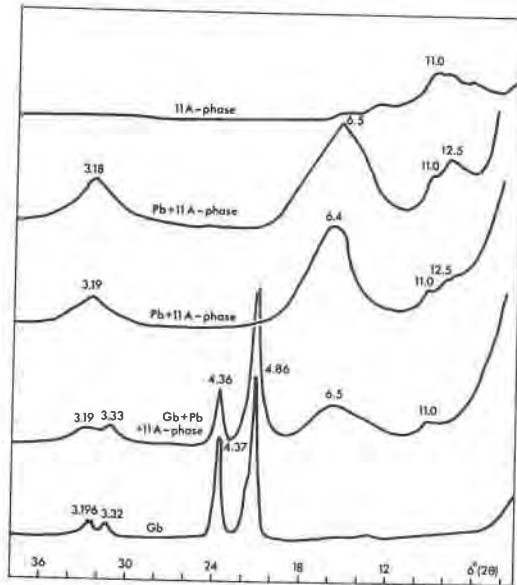


FIG. 1. X-ray diffraction patterns of the various pure hydroxides.

droxide-clay complexes. For convenience, the samples are identified below according to the phases shown in Fig. 1.

1. (11 Å phase)  $\text{AlCl}_3$  solution was titrated with  $\text{NaOH}$  while stirring at room temperature to a pH of 4.95. The suspension was boiled 2 hours and the large flocs were separated from a cloudy supernatant by centrifugation. The precipitate was freeze-dried without washing.
2. (Pseudoboehmite + 11 Å phase)  $\text{NH}_4\text{OH}$  was added to  $\text{AlCl}_3$  solution to give a slight excess. The suspension was boiled for 7 hours and centrifuged. The precipitate was washed once with  $\text{H}_2\text{O}$  to which  $\text{NH}_4\text{OH}$  was added. The precipitate was separated from the cloudy supernatant by centrifugation and freeze-dried.
3. (Pseudoboehmite + 11 Å phase)  $\text{AlCl}_3$  was titrated at room temperature with  $\text{NaOH}$  to a pH of 4.6. The suspension was dialyzed against distilled water at room temperature for 1 month. The resulting sol was freeze-dried.

4. (Gibbsite+pseudoboehmite+11 Å phase) AlCl<sub>3</sub> was titrated to pH 4.95 with NaOH at room temperature. The suspension was boiled for 7 hours. The resulting sol was dialyzed as above and freeze-dried.
5. (Gibbsite) AlCl<sub>3</sub> was titrated to 4.6 with NH<sub>4</sub>OH at room temperature. The suspension was dialyzed for 1 month as above. The suspension first became a sol and toward the end had a small amount of sediment. The entire dialyzed suspension was freeze-dried.

The samples were analyzed x-ray spectrographically by the Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-fusion method using synthetic standards (Kodama *et al.* 1966). Soluble aluminum was determined by the Hashimoto and Jackson (1960) and modified Tamm procedures (McKeague and Day, 1966).

Oriented specimens were prepared by drying aliquots of a suspension containing 30 mgm of sample on  $\frac{1}{2}$  microscope slides. Diffraction patterns were obtained, using Fe-filtered Co radiation on a Philips Diffractometer with proportional counter and pulse height analysis, on specimens air-dry, solvated with glycerol and after successive heat treatments at 350, 450, 550 and 700° C. Peak positions and intensities were obtained by scanning the air-dry and glycerol-solvated samples at  $\frac{1}{4}$ ° 2 $\theta$ /minute. Relative intensities were obtained by measuring the areas under the peaks with a planimeter and normalizing to (004) equal to 1000.

Diffraction patterns of randomly oriented specimens were obtained with powder specimens in 114.7 mm cameras.

DTA patterns were obtained on specimens diluted 50-50 with alumina with equipment run at 10.5° C. per minute (Brydon *et al.*, 1961). TGA patterns were obtained using an analytical balance and a Fisher Balance Assembly mounted over a cylindrical furnace heated at 5° C. per minute, with the specimen contained in a Pt dish suspended from the left arm of the balance. The balance was calibrated with an equal weight of calcined bentonite. Differential TGA curves were plotted manually.

Infrared adsorption curves were obtained with a Beckman IR7 grating Spectrophotometer on Nujol mull specimens.

## RESULTS AND DISCUSSION

*Chemical Analysis.* As the Al<sub>2</sub>O<sub>3</sub> content of the clay samples increased, the SiO<sub>2</sub> content decreased regularly as a consequence of the dilution (Table 1). The low Cl<sup>-</sup> values suggest that the precipitated hydroxide had a negligible degree of proxying by Cl<sup>-</sup>. The slight variations in the CaO and Cl contents were caused by different washing efficiencies. The added aluminum, when calculated as per cent of the oven-dry weight of the total sample, agreed with the value calculated from the total analysis to be the Al external to the bentonite lattice. Furthermore, this non-lattice Al<sub>2</sub>O<sub>3</sub> was quantitatively removed by the Hashimoto and Jackson (1960) extraction with NaOH. The oxalic acid extraction of Tamm

TABLE 1. TOTAL CHEMICAL ANALYSIS AS PER CENT OF TOTAL IGNITED WEIGHT

me Al precipitated/gm clay	Zero	8.5	11.0	15.0
SiO <sub>2</sub>	66.60	58.10	55.52	53.00
TiO <sub>2</sub>	0.12	0.11	0.10	0.10
Al <sub>2</sub> O <sub>3</sub>	26.02	35.24	37.52	40.97
Fe <sub>2</sub> O <sub>3</sub>	4.30	3.87	3.53	3.62
MnO <sub>2</sub>	.01	.00	.01	.01
MgO	2.00	1.87	1.58	1.76
CaO	.03	.28	.06	.15
K <sub>2</sub> O	.04	.04	.03	.03
Cl <sup>-</sup>	.28	.15	.05	.10
<sup>1</sup> H <sub>2</sub> O <sup>+</sup>	7.65	11.19	12.12	13.42

Al <sub>2</sub> O <sub>3</sub> as per cent of oven-dry weight of the total sample				
<sup>2</sup> Al <sub>2</sub> O <sub>3</sub> added	1.2	12.1	15.0	18.4
<sup>3</sup> Non-lattice Al <sub>2</sub> O <sub>3</sub>	1.2	11.9	14.4	18.0
<sup>4</sup> NaOH-extract.	1.9	10.7	14.7	17.9
<sup>5</sup> HOx-extract.	1.8	3.7	6.2	10.7

<sup>1</sup> H<sub>2</sub>O<sup>+</sup> is loss in weight 1000–110° C. as per cent of 110° C. weight.

<sup>2</sup> Al<sub>2</sub>O<sub>3</sub> is the added Al plus exchangeable Al calculated on basis of 110° C. weight of total sample assuming an added weight equivalent to Al(OH)<sub>3</sub>.

<sup>3</sup> Al<sub>2</sub>O<sub>3</sub> is calculated from above analyses by deducting Al<sub>2</sub>O<sub>3</sub> from the bentonite lattice and calculated on same weight basis as <sup>2</sup>.

<sup>4</sup> Hashimoto and Jackson (1960).

<sup>5</sup> Tamm (McKeague and Day, 1966).

(McKeague and Day, 1966) on the other hand removed a proportion of the added aluminum which varied with the total amount present.

*X-ray Diffraction.* The basal spacings of the four clay samples after various treatments are shown in Table 2. The Al-bentonite expanded nor-

TABLE 2. BASAL SPACINGS OF ORIENTED SPECIMENS OF THE BENTONITE-HYDROXIDE COMPLEXES

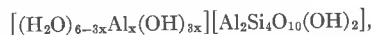
	0 me Al/gm	8.5 me Al/gm	11 me Al/gm	15 me Al/gm
air-dry	12.5 (3) <sup>1</sup>	14.5 (5)	14.6 (5)	14.6 (5)
glycerol	17.8 (10)	14.5 (5)	14.5 (5)	14.4 (5)
300°	13.1 (2)	14.2 (4)	14.3 (5)	14.2 (5)
450°	12.6 (2)	13.8 (2)	13.8 (1)	13.9 (1)
550°	12.1 (2)	12.8 (1)	13.1 (1)	13.1 (1)
700°	9.9 (3)	12.3 (1)	12.7 (1)	12.8 (1)

<sup>1</sup> The number in parentheses denotes the number of orders present.

mally with glycerol but did not collapse irreversibly until a temperature of 700° C. was reached. The hydroxide-clay complexes gave a 14.5 Å spacing but unlike most synthetic materials (Slaughter and Milne, 1960; Barnhisel and Rich, 1963; Turner and Brydon, 1965) did not expand with glycerol. They gave steadily decreasing basal spacings with increasing heat treatment until at 700° C., the basal spacing was 12.8 Å for the 15 me/gm sample. The latter behavior was similar to that reported for similar synthetic materials (Turner and Brydon, 1965) but the collapse is greater than that reported for naturally occurring dioctahedral chlorites (Brydon *et al.*, 1961). There is no doubt that at least part of the added hydroxide is present as an interlayer in the montmorillonite lattice.

Accurate peak positions of the first five orders of the basal spacings of the air-dry samples were obtained by scanning at  $\frac{1}{4}^\circ 2\theta/\text{minute}$ . The orders of the three hydroxide-clay complexes were rational within experimental error, leading to the conclusion that the hydroxide was uniformly distributed among the montmorillonite interlayers.

Powder patterns of the four clay samples were all similar except for the basal reflections. Microdensitometer traces of the films showed the *hk* lines to be in the same position and to have the same shape. Apparently, the added hydroxide had no effect on the *a* or *b* dimension and did not change the randomness of the *a* and *b* orientation. On the basis of the x-ray results, the hydroxide-clay complex was considered to have properties intermediate between those of aluminian dioctahedral chlorite and vermiculite. However, the observed structure factors (*F*<sub>obs</sub>) calculated from the intensities of the basal reflections were closer to those calculated for dioctahedral chlorite (Brindley and Gillery, 1956) than those of dioctahedral vermiculite (Cotton, 1965). Calculations using various models for the configuration of the interlayer matter showed that the gibbsite-like structure gave the best agreement. Because the population of aluminum ions in the gibbsitic layer of the complex might be related to the amount of added hydroxide, the *F*-values of chloritic structures with various amounts of Al ions were calculated. Calculation was made on the chlorite structure having its layer thickness of 14.56 Å and its ideal chemical formula,



where  $1.0 \leq x \leq 2.0$  using the atomic scattering factors for Si<sup>4+</sup> and Al<sup>3+</sup> from the International Tables (1962) and for O<sup>2-</sup> from Tokonami (1965). Although in the mica-like layer the ionic substitutions of Al by Mg and/or, of Si by Al should be taken into account, the substitutions were ignored because the atomic scattering factors for Mg<sup>2+</sup>, Al<sup>3+</sup> and Si<sup>4+</sup> are all much the same in the range  $\sin \theta/\lambda = 0 \sim 0.18$ , in which the five

orders of the basal reflections were observed. The comparison of the calculated values with the observed values (Table 3) indicated that the 15 and 11 me/Al gm clay complexes were almost identical and were similar to the chloritic structure with  $x=1.5$  and that the 8 me/Al gm clay complex is similar to the structure with  $x=1.0$ .

Thus, it could be concluded that the interlayering of aluminum hydroxide was performed up to about  $x=1.5$  which corresponded to the composition of 11 me/Al gm clay complex, and that the excess of aluminum hydroxide in the 15 me/Al gm clay complex was absorbed probably on the external surface of the structure.

X-ray diffraction patterns of the five pure aluminum hydroxides are shown in Fig. 1. The first, which contains an abundance of NaCl, has a broad diffraction effect from 10–15 Å peaking at about 11 Å. This

TABLE 3. COMPARISON OF THE OBSERVED F-VALUES FOR THE THREE COMPLEXES WITH CALCULATED F-VALUES FOR SOME MODEL STRUCTURES<sup>1</sup>

Order	8.5 me Al/gm	11 me Al/gm	15 me Al/gm	Dioc <sup>2</sup> Chlorite	Dioc <sup>3</sup> Vermicu- lite	[(H <sub>2</sub> O) <sub>6-3x</sub> Al <sub>x</sub> (OH) <sub>2x</sub> ][Al <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> ]			
						x=2.0	x=1.8	x=1.5	x=1.0
001	35	34	33	+22	+110	+23	+26	+30	+38
002	18	24	22	+21	+6	+23	+22	+20	+16
003	55	55	55	-55	-55	-55	-55	-55	-55
004	43	41	45	+62	+54	+38	+38	+37	+35
005	58	51	52	+55	+89	+57	+62	+68	+80

<sup>1</sup> All data are normalized to 55 (003).

<sup>2</sup> After Brindley and Gillery's data (1956).

<sup>3</sup> After Cotton's data (1965).

material which occurs in three of the other preparations is designated "11 Å phase" to distinguish it from the crystalline or the truly amorphous hydroxides. The next three samples each contain pseudoboehmite (Gastuche and Herbillon, 1962). The fourth sample also contains gibbsite and the last one was pure gibbsite. These materials are representative of the kind of material which can be produced by precipitating AlCl<sub>3</sub> in the cold at a pH similar to that used in the preparation of the hydroxide-clay complexes. In no case was one of these diffraction patterns found in the hydroxide-clay complex samples, although the "11 Å phase" may have been masked by the montmorillonite.

*Differential Thermal Analysis.* The Al-bentonite showed the normal montmorillonite curve having an endothermic doublet at low temperature, the main endotherm at 675° C. and the endothermic-exothermic feature above 900° C. (Fig. 2). Added hydroxides reduced the size of the low temperature endotherm as might be expected from the displace-

ment of interlayer water by hydroxide. The area of 675° C. endotherm was reduced more than was calculated from a dilution of the mass of bentonite by added hydroxide. Measured areas were 445, 269, 195, 141 mm<sup>2</sup> vs calculated values of 445, 364, 347, 322, respectively for the samples with increasing added hydroxide. The high temperature endotherm at 917° C. was reduced in size and occurred approximately 50° C. lower in temperature in the presence of hydroxides. The exotherm at 940° C. occurred about 20° C. lower and the area under the peak in-

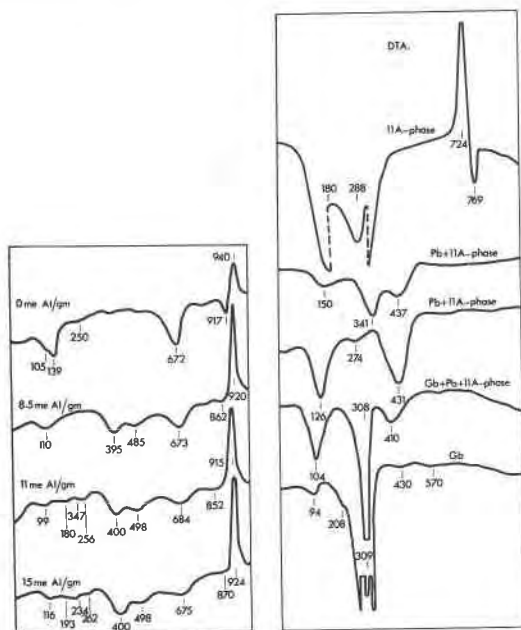


FIG. 2. Differential thermal analysis curves of a) the hydroxide-clay complexes and b) the various pure hydroxides.

creased markedly when hydroxides were present. The areas/unit of total Al<sub>2</sub>O<sub>3</sub> were 11.3, 9.5 and 11.8 mm<sup>2</sup>/per cent total Al<sub>2</sub>O<sub>3</sub> in the 8.5, 11 and 15 me/gm samples as compared to a value of 4.3 for the pure bentonite. Added Al<sub>2</sub>O<sub>3</sub> apparently increased the spinel formation which increased the size of the exothermic peak. These shifts in peak temperatures were also shown in Fig. 3 of the paper of Barnhisel and Rich (1963) and occur at much lower levels (2 me Al/gm) of added aluminum than those used in the present work. The peak area relationships are unclear but it appears from their Figure that when the added Al<sub>2</sub>O<sub>3</sub> is present as gibbsite the high temperature endothermic-exothermic feature is similar to pure bentonite.

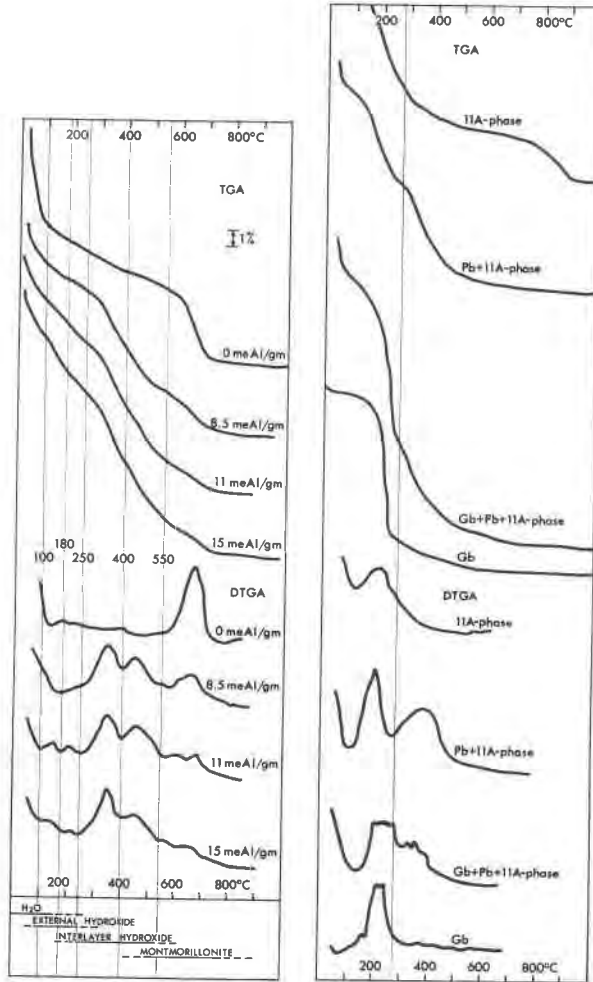


Fig. 3. Thermogravimetric analysis curves and differential thermogravimetric curves of a) the hydroxide-clay complexes and b) the various pure hydroxides.

There were five endothermic peaks in the hydroxide-bentonite complexes which were not common with the pure bentonite. The two major peaks occurred at 395–400° and at 485–498° C. which corresponded to peaks at 360° and 470° C. (Barnhisel and Rich, 1963) and 360° C. (Kawasaki and Aomine, 1965) which have been attributed to interlayer hydroxide in similar materials. No other peaks were present in the 8.5 me/gm sample but the 11 and 15 me/gm samples showed small peaks at 180, 234–245, and 265° C. None of these peaks could be matched with



pure aluminum hydroxide materials in the present investigation. On the other hand, Kawasaki and Aomine (1965) found an endotherm at 250–275° C. in hydroxide-clay complexes and at 280° C. in a pure hydroxy-Al material precipitate at pH 5.0, which they attributed to material formed outside of the interlayer spaces of the montmorillonite. Thus, the two major peaks were associated with the decomposition of interlayer hydroxide whereas the three minor peaks could not be attributed with confidence.

The curves for the five synthetic pure aluminum hydroxides are similar to those published by MacKenzie (1957) except that the peak temperatures are lower. For gibbsite this seemed to be due to a fine particle size, for a naturally occurring well-crystallized gibbsite (not shown) showed an endothermic peak at 320° C. The curve for pseudo-boehmite is in good agreement with the curve for "poorly crystallized boehmite" given by MacKenzie (1957).

*Thermogravimetric Analysis.* From the TGA curve for Al bentonite, adsorbed water (<100° C.) and lattice OH<sup>-</sup> (600–700° C.) can be distinguished. However, there was a rather continuous loss in weight from 100–600° C., amounting to about 4 per cent H<sub>2</sub>O, which is considered to be the overlapping of a slow loss of adsorbed water and a slow loss of lattice OH<sup>-</sup> (Neumann, 1963). Fripiat *et al.* (1960) have recently presented direct evidence that the two occur simultaneously. Because the TGA curves for the hydroxide-clay complexes were more complicated than the pure bentonite, the DTGA curves were plotted (Fig. 3). The prominent features were delineated by comparison with the corresponding DTA curves and the incremental weight losses were obtained from the TGA curve (Table 4).

The loss above 550° C. from Al-bentonite was slightly higher than that calculated from the ideal unit cell composition (Table 4), while in the hydroxide-clay complexes, the >550° C. loss from the bentonite portion is 25–30 per cent less than that calculated when the dilution with aluminum hydroxide is taken into account. As Barnhisel and Rich (1963) have shown, the interlayer aluminum hydroxide lowered the initial temperature of bentonite OH<sup>-</sup> loss. From Fig. 3, it can be seen that there are two indistinct maxima between 550° C. and 700° C. for the hydroxide-treated samples. Since approximately  $\frac{1}{3}$  of the lattice OH<sup>-</sup> had been lost below 550° C. (Table 4), the added aluminum hydroxide apparently has caused the bentonite to lose its OH<sup>-</sup> in three stages, one below 550° C. and two above 550° C.

The over-all loss in weight between 100 and 550° C. given in column 11, Table 4, was higher than that calculated from the added aluminum

(col. 9) assuming an ideal  $\text{Al}(\text{OH})_3$  composition. When the minus  $550^\circ\text{C}$ . weight loss from the bentonite  $\text{OH}^-$  was included (col. 10) a much better agreement was reached, although the measured values of loss between 100 and  $550^\circ\text{C}$ . were still high. The loss between 180 and  $550^\circ\text{C}$ . was lower than the calculated value, which shows the difficulty in distinguishing free water from  $\text{OH}^-$  in these materials. Nevertheless, the high measured loss in weight and the fair agreement with the calculated value leaves little doubt that the composition of the added aluminum is closer to the trihydroxide than to the monohydroxide.

If it is arbitrarily assumed that the loss from 250– $550^\circ\text{C}$ . (col. 12)

TABLE 4. LOSS IN WEIGHT DATA FROM THERMOGRAVIMETRIC ANALYSIS PER CENT OF OVEN-DRY ( $100^\circ\text{C}$ .) WEIGHT

1	2	3	4	5	6	7	8	9	10	11	12	13
$\text{Al}_2\text{O}_3$ me/gm benton- ite	100– 180 C.	180– 250 C.	250– 400 C.	400– 550 C.	>550 C.	$\text{OH}^-$ from benton- ite <sup>1</sup>	$\text{OH}^-$ from benton- ite –550 C.	$\text{OH}^-$ from added $\text{Al}_2\text{O}_3$ <sup>2</sup>	$\text{OH}^-$ from $\text{Al}_2\text{O}_3$ + benton- ite defi- ciency	Loss 100– 550 C.	Loss 250– 550 C.	Inter- layer hydrox- ide <sup>3</sup>
0	0.9	0.8	1.4	1.0	5.2	4.9	+0.3	0.6	—	4.1	2.4	—
8.5	1.0	0.7	3.7	2.8	3.0	4.0	–1.0	6.4	7.4	8.2	6.5	0.86
11	1.5	1.3	4.0	3.2	2.3	3.8	–1.5	7.7	9.3	10.0	7.2	0.74
15	2.0	1.4	4.6	3.5	2.5	3.6	–1.1	9.7	10.8	11.5	8.1	0.72

<sup>1</sup> Calculated from ideal bentonite composition and assuming added aluminum as trihydroxide for the dilution factor.

<sup>2</sup> Calculated as trihydroxide.

<sup>3</sup> Calculated from the ratio of the loss from 250– $550^\circ\text{C}$ . minus the calculated bentonite deficiency (column 8) to the  $\text{OH}^-$  from the added aluminum (column 9).

represents interlayer hydroxide, plus the calculated bentonite deficiency (col. 8), it is readily apparent that the amount of interlayer material increases with increasing aluminum hydroxide. If it is also assumed that the added aluminum was present as the trihydroxide, the ratio of the corrected 250– $550^\circ\text{C}$ . loss in weight to the calculated hydroxide  $\text{OH}^-$  (col. 9) would give the proportion of added hydroxide which exists in the interlayer region. The values (col. 13) show that a greater proportion of the 8.5 me  $\text{Al}/\text{gm}$  hydroxide is in the interlayer position than is the case for the 11 and 15 me  $\text{Al}/\text{gm}$  samples. Obviously, the error involved in such a calculation cannot be measured but the trend appears to be reliable.

*Infrared Adsorption.* The hydroxide complexes showed characteristic absorptions in two separate regions— $3000\text{--}4000\text{ cm}^{-1}$  and  $800\text{--}1200$

cm<sup>-1</sup>—in which adsorption bands have been assigned to OH<sup>-</sup> stretching and bending of aluminum hydroxide, respectively (Frederickson, 1954).

In the 3000–4000 cm<sup>-1</sup> region, the hydroxide complexes showed a peak at 3700 cm<sup>-1</sup> which was not shown by the Al-bentonite and the various hydroxides (Fig. 4) but which was shown by the Albemni clay.

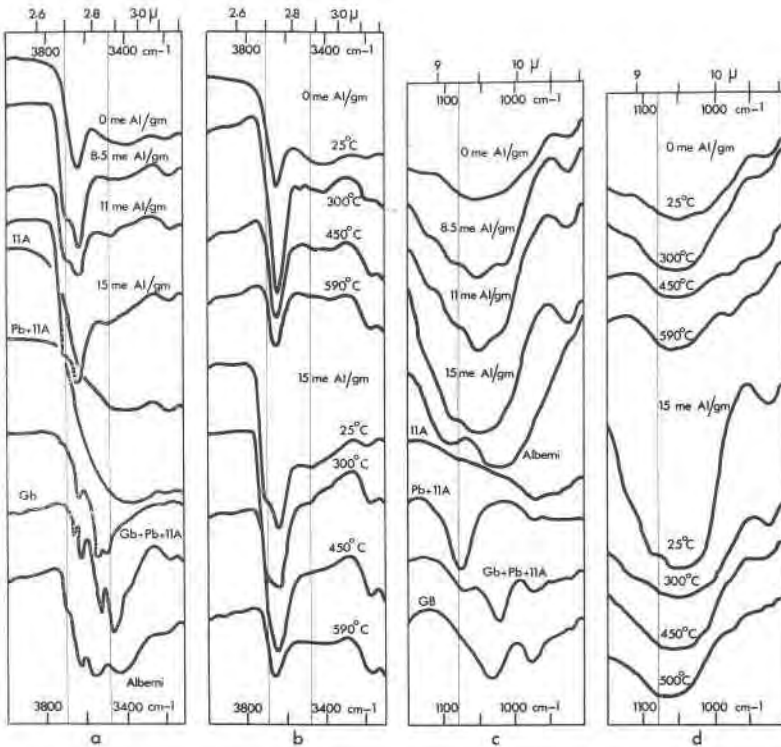


FIG. 4. Infrared absorption curves of the hydroxide-clay complexes, of a dioctahedral chlorite (Albemni) and of the various preparations of pure hydroxides. a) 3100–4000 cm<sup>-1</sup> at 25° C., b) 3100–4000 cm<sup>-1</sup> after heating to the temperatures indicated, c) 900–1150 cm<sup>-1</sup> at 25° C., d) 900–1150 cm<sup>-1</sup> after heating to the temperatures indicated.

The 3630–3640 cm<sup>-1</sup> and 3190–3200 cm<sup>-1</sup> peaks were common to all of the materials. The peak at 3480 in the 11 and 15 me samples was not common with either bentonite, the various hydroxides or the Albemni clay. In an attempt to match these peaks with the DTA and DTGA features, the samples were heated in the DTA furnace to 300, 450 and 590° C. After cooling in a desiccator the samples were mullied quickly in Nujol and rerun. Under these conditions the 3700 cm<sup>-1</sup> and 3480 cm<sup>-1</sup> peaks disappeared at 450 and 590° C., respectively.

In the 800–1200  $\text{cm}^{-1}$  region, the hydroxide complexes showed peaks at 1080 and 1120  $\text{cm}^{-1}$  which were not shown by the Al bentonite. Pseudoboehmite and the Albern clay each had prominent absorptions at 1080–1090  $\text{cm}^{-1}$  but none of the materials showed a peak at 1120  $\text{cm}^{-1}$ . On heating the hydroxide complexes as outlined above, the 1080  $\text{cm}^{-1}$  and 1120  $\text{cm}^{-1}$  peaks disappeared at 300 and 450° C., respectively.

The infrared absorptions at 3700  $\text{cm}^{-1}$  and 1080  $\text{cm}^{-1}$  are both common with the Albern dioctahedral chlorite and the 1080  $\text{cm}^{-1}$  peak was found in pseudoboehmite. The 3700  $\text{cm}^{-1}$  adsorption corresponds to an O-H—O distance of 3.4–3.5 Å (Nakamoto *et al.*, 1955) which is evidence of a low degree of H-bonding. Differences between 8.5, 11 and 15 me Al/100 gm samples were not apparent.

The curves for the pure hydroxides correspond to those of Gastuche and Herbillon (1962) in the 3000–4000  $\text{cm}^{-1}$  region and for gibbsite only in the 800–1200  $\text{cm}^{-1}$  region. On the other hand, they found an intense adsorption band at 1004  $\text{cm}^{-1}$  in their “pregibbsitic” material which was not shown by any of the present products with or without clay.

*Nature of the Aluminum Hydroxide Precipitated in the Presence of Bentonite.* As has been amply documented (Slaughter and Milne, 1960), aluminum hydroxide added to montmorillonite pre-empts the interlayer positions of the montmorillonite lattice. A gibbsite-like structure of  $\text{OH}^-$ ,  $\text{H}_2\text{O}$  and  $\text{Al}^{3+}$  seemed to be the model best fitting the observed x-ray data. This was true whether the amount of added hydroxide was either  $\frac{1}{2}$ ,  $\frac{3}{4}$ , or 1 times the amount theoretically required to construct a complete gibbsite monolayer (16 me Al/gm montmorillonite). Each of these compositions gave a regular interstratification indicating that the hydroxide entered all layers. The structure factor calculations indicated that the  $\text{OH}^-$  and  $\text{H}_2\text{O}$  occupy equivalent positions in the gibbsite-like structure. This suggests that  $\text{H}_2\text{O}$  molecules are arranged octahedrally around vacant sites and the  $\text{OH}^-$  radicals are arranged octahedrally around  $\text{Al}^{3+}$  ions. The distribution pattern of the vacant sites cannot be predicted from this work.

Heat treatments of the various samples allow some interpretations as to the nature of the material. The (001) d-spacings decrease from 14.5–12.8 Å upon heating at 700° C. as compared to a 0.3 and 0.7 Å decrease with orthochlorites and dioctahedral chlorites, respectively (Brydon, *et al.*, 1960). There is some disorder for there is only a diffuse nonintegral (003) reflection on heating and the (001) reflection did not increase in intensity on heating. On the basis of DTA, TGA and IR absorption, and as shown by others (Barnhisel and Rich, 1963; Kawasaki and Aomine, 1965) the hydroxide  $\text{OH}^-$  is released in stages. The TGA data

showed the difficulty in resolving these stages because of the overlapping of the loss of H<sub>2</sub>O, the loss of OH<sup>-</sup> from the hydroxides and the loss of montmorillonite lattice OH<sup>-</sup>. The DTA and TGA patterns of the complexes do not match those of the pure hydroxides prepared in different ways, a result which is expected from the interaction of the interlayer hydroxide and the montmorillonite lattice (Barnhisel and Rich, 1963, and our Fig. 2). The 1080 cm<sup>-1</sup> infrared absorption band was found in the hydroxide-clay complexes, the Albern clay and strongly in the pseudoboehmite sample. It disappeared on heating at 300° C. and, therefore, was related to the two weak DTA endotherms at 235 and 265° C. and the two low temperature DTGA peaks in the 11 and 15 me Al/gm clay samples. These features are interpreted as being due to aluminum hydroxide external to the interlayer position of montmorillonite (Kawasaki and Aomine, 1965). A comparison with the DTA and DTGA patterns of the pure aluminum hydroxides indicates a similarity to the "11 Å material" rather than pseudoboehmite. The 3700 and 3480 cm<sup>-1</sup> infrared absorption bands are associated with the DTA peaks at 400 and 495° C., respectively, and the DTGA peaks at 350 and 450° C., respectively. These are features of the interlayer hydroxide (Barnhisel and Rich, 1963; Kawasaki and Aomine, 1965). The existence of two IR bands at room temperature related to two high temperature peaks would indicate two kinds of OH<sup>-</sup> rather than a progressive decomposition from the trihydroxyl to the monohydroxyl to the anhydrous condition as with gibbsite (Mackenzie, 1957).

The structure factor calculations generally agree with the above evidence. The over-all data indicate that when 8.5 me Al hydroxide is added per gm of bentonite, the hydroxide was entirely in the interlayer space, whereas with 15 me Al/gm clay, approximately  $\frac{3}{4}$  of the added hydroxide was present in the interlayer space. The evidence for the 11 me Al/gm sample is mixed and the state of the added hydroxide cannot be delineated with confidence.

In previous work (Turner and Brydon, 1965) it was found that 8.8 me Al hydroxide/gm clay was retained in the interlayer space for a period of 6 months while the ion product Al(OH)<sub>3</sub> remained constant. On the other hand, in the 11 and 16 me Al/gm clay, the hydroxide gradually disappeared from the interlayer space as gibbsite formed and as the ion product Al(OH)<sub>3</sub> decreased to 10<sup>-33.8</sup>. It seems reasonable to suggest that the difference in behavior is caused by aluminum hydroxide precipitated externally to the interlayer space in the 12 and 16 me Al/gm clay samples. Even though both amorphous aluminum hydroxide and interlayer hydroxide should be metastable to gibbsite (Turner and Brydon, 1965) the interlayer hydroxide alone was incapable of recrystal-

lizing to gibbsite (in a period of 6 months laboratory conditions). When external aluminum hydroxide was present, it slowly recrystallized to gibbsite (Turner and Brydon, 1965; Gastuche and Herbillon, 1962) and, once seeded, the metastable interlayer hydroxide recrystallized.

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