

REACTIONS OF POLYNUCLEAR HYDROXYALUMINUM CATIONS WITH MONTMORILLONITE AND THE FORMATION OF A 28-Å PILLARED COMPLEX¹

S. SHAH SINGH AND H. KODAMA

Land Resource Research Centre, Research Branch, Agriculture Canada
Ottawa, Ontario K1A 0C6, Canada

Abstract—Polynuclear hydroxy-Al cations were prepared by partially neutralizing dilute solutions of aluminum chloride. These cations were introduced in the interlayer space of montmorillonite by cation exchange, which formed heat-stable pillars between the silicate layers. Polynuclear hydroxy-Al was preferentially adsorbed on montmorillonite compared with monomer-Al; the maximum amount adsorbed was ~400 meq/100 g of montmorillonite. Of this amount 320 meq was non-exchangeable. The 001 X-ray powder diffraction reflection of the polynuclear hydroxy-Al-montmorillonite complex was at 27 Å, with four additional higher-order basal reflections, giving an average $d(001)$ value of 28.4 Å. This complex was thermally stable to 700°C. An analysis of the basal reflections by the Fourier transform method indicated that the 28-Å complex had a relatively regular interstratified structure of 9.6- and 18.9-Å component layers with a mixing ratio of 0.46:0.54. This ratio implies that the hydroxy-Al pillars occupied every second layer. Considering the relatively small amount of Al adsorbed and the thermally stable nature of the structure, the hydroxy-Al pillars must have been sparsely but homogeneously distributed in the interlayer space.

Key Words—Fourier transform, Hydroxy-Al, Montmorillonite, Pillared interlayer complex, Thermal stability.

INTRODUCTION

Aluminum is an integral structural component of phyllosilicate minerals. Al ions solubilized from phyllosilicates and other Al compounds hydrolyze readily and form many simple and complex hydroxy-Al species in solution. The reactions of hydroxy-Al ions with 2:1 clay minerals have been of interest for many years in connection with the formation of secondary chlorites in soils and the intercalation of smectite clays as catalysts. Numerous researchers have prepared hydroxy-Al interlayer complexes with montmorillonite and have studied their properties (Slaughter and Milne, 1960; Shen and Rich, 1962; Barnhisel and Rich, 1966; Brydon and Kodama, 1966; Sawhney, 1968; Singh and Brydon, 1967; Singh and Kodama, 1972; Lahav *et al.*, 1978; Brindley and Kao, 1980; Pinnavaia, 1982, 1983; Pinnavaia *et al.*, 1979; Plee *et al.*, 1987).

Many of these studies have reported the results of suspending montmorillonite in Al solutions and the subsequent hydrolysis by the addition of an alkali in predetermined amounts or by progressive titrations. No information, however, has been reported on what type of hydroxy-Al-montmorillonite complex was produced, if stable polynuclear hydroxy-Al cations were formed in solution prior to the reaction and adsorbed by montmorillonite. Lack of such information is due mainly to the difficulty in preparing stable, polymeric Al solutions.

In the present work, stable, polynuclear hydroxy-Al cations were prepared by slow titration of Al solutions with diluted NaOH. This report describes the reactions of these polynuclear hydroxy-Al cations with montmorillonite and the large-spacing materials produced by these reactions.

MATERIALS AND METHODS

Material

The clay used in this investigation was montmorillonite from Clay Spur, Wyoming, which was supplied by the Baroid Division, National Lead Corporation. The <2- μm size fraction of this clay was obtained by sedimentation and was saturated with Na by repeated washings with 1 M NaCl. Excess Cl was removed by washing with water. To prevent excessive dispersion of the Na-saturated montmorillonite, the amount of water added for each washing was based on a dilution factor that depended on the amount of solution left after centrifugation. The concentration of Na and Cl was reduced to <10⁻⁴ mole/liter. The cation-exchange capacity of the montmorillonite was determined to be 85 meq/100 g.

Preparation of hydroxy-Al-montmorillonite complex

A stock solution of 0.1 M AlCl₃·6H₂O was prepared in CO₂-free redistilled water. From this stock solution fresh 0.01 M Al solutions were prepared for this research. The concentration of Al in the dilute solution

¹ Land Resource Research Centre Contribution 87-89.

Table 1. Distribution of monomer Al and polynuclear hydroxy-Al cations in partially neutralized solutions of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$.¹

Aging time (days)	Monomer Al ²		Mono + poly-	Poly-
	(10^{-4} mole/liter)	(%)	nuclear Al (10^{-4} mole/liter)	nuclear Al ³ (%)
1	29.8	34.8	85.6	65.2
5	29.3	34.2	85.6	65.8
10	29.5	34.5	85.5	65.5
90	29.3	34.4	85.2	65.6

¹ OH/Al = 1.82.

² 10-s reaction time with 8-hydroxy quinolinolate.

³ 0.5-hr reaction time with 8-hydroxy quinolinolate.

(0.01 M) was determined by the 8-quinolinolate extraction method (Okura *et al.*, 1962). One hundred milliliters of 0.01 M $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ solution was titrated with 0.1 M NaOH under a nitrogen atmosphere using a Metrohm titroprocessor. Increments of 0.05 ml of 0.1 M NaOH solution were added with vigorous stirring at time interval of 5 min. Each incremental addition of OH was only sufficient to neutralize 0.167% of the total Al present in the bulk solution. The final OH/Al molar ratio of the titrated solution was 1.82; the titration time was about 30 hr. Table 1 shows the concentration of monomer and polynuclear Al species in solution; no change in their distribution on aging was noted.

Three hundred milligrams of the Na-saturated montmorillonite was weighed into a 50-ml centrifuge tube, and 25 ml of the solution containing monomer Al and polynuclear hydroxy-Al cations was added. The suspension was stirred and allowed to react for 1 hr, after which it was centrifuged and another 25 ml of solution added. The clay sample was equilibrated with polynuclear hydroxy-Al cations four times by this batch technique. The above experiment was further extended to 10 equilibrations using a duplicate sample and a total volume of 250 ml.

Analytical techniques

The supernatant solutions obtained after equilibration of the montmorillonite were titrated on an automatic Metrohm titroprocessor. The pHs were determined with an Orion ion analyzer: Na by atomic absorption spectrophotometry, and Al by an 8-quinolinolate extraction method (Okura *et al.*, 1962). Different species of Al were determined by a modified 8-quinolinolate method (Turner, 1969, 1976; Turner and Sulaiman, 1971).

For X-ray powder diffraction analysis the resulting complex was separated from the supernatant by centrifugation and an appropriate quantity of water added to the sediment immediately thereafter so that it could be resuspended by sonification. One milliliter of the suspension containing about 30 mg of solid was pipeted

Table 2. Average chemical composition of polynuclear hydroxy-Al cation from colorimetric and potentiometric determinations of different aluminum species.

	Colorimetrically measured Al	Potentiometrically measured Al
Total Al (mmole/liter)	8.55	4.00
Monomer Al(10-s reaction) (mmole/liter)	2.95	—
Monomer (1st inflection point) (mmole/liter)	—	2.96
Polynuclear Al (0.5 hr Al minus 10-s Al) (mmole/liter)	5.60	—
Positive charge neutralized between 2nd and 1st inflection point (mmole/liter)	—	3.12
Average composition of polynuclear hydroxy-Al cation	$\text{Al}_{5.60}(\text{OH})_{3.12} = \text{Al}(\text{OH})_{2.44}^{0.36+}$	

onto a 25 × 30 mm glass slide and dried for 3 days under ambient conditions. X-ray powder diffraction (XRD) patterns were obtained on the oriented specimens before and after various diagnostic treatments under specific conditions, including ambient and extremely dry conditions, by a fully automated SCINTAG Pad V X-ray diffractometer equipped with a graphite crystal monochromator using $\text{CoK}\alpha$ radiation ($\lambda = 1.7902 \text{ \AA}$). The extremely dry conditions were achieved by putting a small dish containing P_2O_5 in the sample chamber. An air-dry oriented specimen was kept over P_2O_5 in a desiccator overnight, then transferred immediately to the sample holder on the goniometer, and equilibrated there for 15 min before being irradiated by X-rays.

RESULTS AND DISCUSSION

Composition of partially neutralized aluminum chloride solutions

The time-rate reactions of 8-quinolinol with partially neutralized Al solutions showed that Al ions were present in monomeric and polymeric forms. On aging, the proportional distribution of these species did not change (Table 1); thus, the partially neutralized Al solutions were stable. At an OH/Al molar ratio of 1.82 the concentrations of monomeric and polymeric Al were 29.5×10^{-4} and 56.0×10^{-4} mole/liter, respectively. The average percentage of monomer and polynuclear hydroxy-Al cations was 34.5 and 65.5% respectively (Table 1). The titration determination of Al in the partially neutralized solution on an automatic Metrohm titroprocessor was similar to the spectrophotometric measurements of monomer Al. The first inflection volume of 0.89 ml of 0.1 M NaOH for 10 ml of partially neutralized solution was equivalent of 29.6×10^{-4} mole/liter. The second inflection point was at 1.20 ml of 0.1 M NaOH. From the 8-quinolinol

Table 3. Amounts of monomer Al, polynuclear hydroxy-Al, and Na adsorbed (+) and desorbed (-) by montmorillonite on four successive equilibrations.

Solution	Al			Charge characteristics	
	Monomer (meq/100 g)	Polynuclear (meq/100 g)	Na (meq/100 g)	Charge on polynuclear cation	OH/Al ratio of polynuclear cation
1st equilibration	+46.67	+111.55	-73.90	+0.73	2.23
2nd equilibration	-14.05	+111.35	-7.32	+0.57	2.43
3rd equilibration	-13.02	+109.35	-6.29	+0.53	2.47
4th equilibration	-10.72	+61.82	n.d.	+0.52	2.48
Total cations adsorbed and desorbed after four equilibrations	+8.90	+394.07	-87.51		
Weighted average polynuclear composition	-	-	-	0.60	2.40

n.d. = not detected.

extraction measurements of Al by colorimetric and potentiometric titrations of partially neutralized solution, the average composition of the polynuclear hydroxy-Al cations was $\text{Al}(\text{OH})_{2.44}^{0.56+}$ (Table 2). This average composition does not permit an exact definition of the composition and configuration of the polynuclear hydroxy-Al cations; however, the average ($\text{Al}(\text{OH})_{2.44}^{0.56+}$) composition of the polynuclear hydroxy-Al cation found in this investigation is similar to those which have been suggested in the literature for Al aqueous solutions; e.g., $\text{Al}_6(\text{OH})_{13}^{3+}$ (Brossett *et al.*, 1954), $\text{Al}_{13}(\text{OH})_{12}^{7+}$ (Sillen, 1959), $\text{Al}_8(\text{OH})_{20}^{4+}$ (Matijevic *et al.*, 1961), $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ (Johansson, 1960), and $\text{Al}_{13}(\text{OH})_{32}^{7+}$ (Aveston, 1965).

Adsorption of polynuclear hydroxy-Al cations

The data in Table 3 show that in the first equilibration of montmorillonite with partially neutralized Al solutions, monomer and polynuclear Al cations were adsorbed and Na ions were desorbed. During subsequent equilibrations, polynuclear hydroxy-Al cations were preferably adsorbed over the monomer Al ions, and after four equilibrations of the montmorillonite, the net accumulated status of the various ions was: monomer Al adsorbed, 8.9 meq; polynuclear hydroxy-Al adsorbed, 394 meq; and Na desorbed, 87.5 meq per 100 g of clay.

Another sample was equilibrated ten times; however, chemical data and potentiometric titrations of supernatants showed little if any change in the adsorption and desorption of Al species and Na and the activity of hydrogen beyond the fourth equilibration (Figure 1). About 400 meq/100 g of polynuclear hydroxy-Al cation was the maximum amount adsorbed. The pH decreased from 4.18 first to 3.83 and then to 3.67, and then increased to 3.79, 4.03, and 4.10, respectively, for first five equilibrations. The amount of polynuclear hydroxy-Al cations adsorbed was 111.55, 111.35, 109.35, and 61.82 meq/100 g and the amount of the monomer aluminum adsorbed (+) and desorbed (-) was +46.67, -14.05, -13.02, and -10.72 meq/100

g of montmorillonite after the first, second, third, and fourth equilibrations, respectively. Thus, after the first equilibration the polynuclear hydroxy-Al cations adsorbed at the expense of desorption of monomer Al ions, and polynuclear hydroxy-Al was preferably adsorbed over monomer Al. The titration curve of the fifth supernatant solution was identical to that of the initial starting solution.

The exchangeability of the adsorbed Al species was evaluated for the sample equilibrated four times by extraction with 1 M KCl solution. All of the monomer Al ions (8.9 meq/100 g clay) were readily exchangeable, and only 80 meq/100 g clay of the polynuclear hydroxy-Al cations was extracted in 1 M KCl solution.

OH/Al molar ratio of polynuclear hydroxy-Al cations adsorbed by montmorillonite

After the first equilibration the calculated average charge of the complex was +0.73/mole Al in the complex, and the OH/Al molar ratio of the complex was 2.23. On successive equilibrations the OH/Al molar ratio was 2.43, 2.47, and 2.48 for the second, third, and fourth equilibrations, respectively. These ratios indicated that after the second equilibration, the OH/Al molar ratio of the adsorbed polymeric Al was essentially constant and similar to the OH/Al molar ratio of the polynuclear hydroxy-Al cations in the solution. The weighted average positive charge of the polynuclear hydroxy-Al cation was calculated from total desorption and adsorption of Na and Al after four equilibrations. Inasmuch as the amount of Na desorbed was 87.5 meq and the amount of monomeric Al adsorbed was 8.9 meq, the difference (78.6 meq) was neutralized by polymeric Al ($394.07 \text{ mmole}/3 = 131.36 \text{ mmole}$). Therefore, the weighted average charge of the polymeric Al cation was 0.6/mole Al. Of significance is the fact that the total amount of exchangeable Na measured was 87.5 meq/100 g after four equilibrations, compared with 85.0 meq/100 g of exchangeable Na of the initial Na-saturated montmorillonite, suggesting an inherent error of at least 3%.

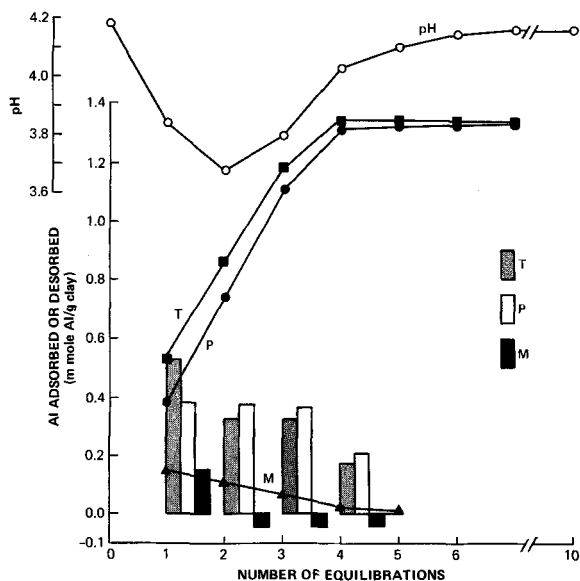


Figure 1. Amounts of Al adsorbed and desorbed and pH changes on successive equilibrations of montmorillonite with partially neutralized solutions of Al containing monomeric and polymeric Al. M = monomer Al; P = polynuclear Al; T = total Al.

X-ray powder diffraction data

The XRD pattern taken at 0% RH and room temperature of an oriented specimen of the sample after four equilibrations with polymeric Al solution showed five major peaks at 27, 14.6, 9.6, 4.7, and 3.16 Å (Figure 2). Heating the samples to as high as 700°C caused no significant change in the pattern except for the relative intensity ratio, indicating that the structure of the complex was thermally stable in that temperature range (Figure 2). Assuming that the peak at 27 Å is an 001 reflection, the other reflections can be interpreted as higher orders. The series of the basal reflections of the untreated sample gave an average $d(001)$ value of 28.41 Å, with the coefficient of variation, CV of 2.99, indicating the presence of substantial structure irregularity, inasmuch as a good regular structure requires a CV of ≤ 0.75 (Bailey *et al.*, 1982). The series of basal reflections

Table 4. Observed peak heights on Fourier transform and calculated peak heights for polynuclear hydroxy-Al-montmorillonite complex prepared after four equilibrations.¹

Spacing (Å)	Observed intensity (I/I_0)	Calculated intensity (I/I_0)
9.6	0.46	0.46
18.9	0.54	0.54
28.5	0.82	0.82
38.1	0.40	0.40
47.4	0.59	0.53
57.0	0.73	0.62

¹ RH = 0%; room temperature.

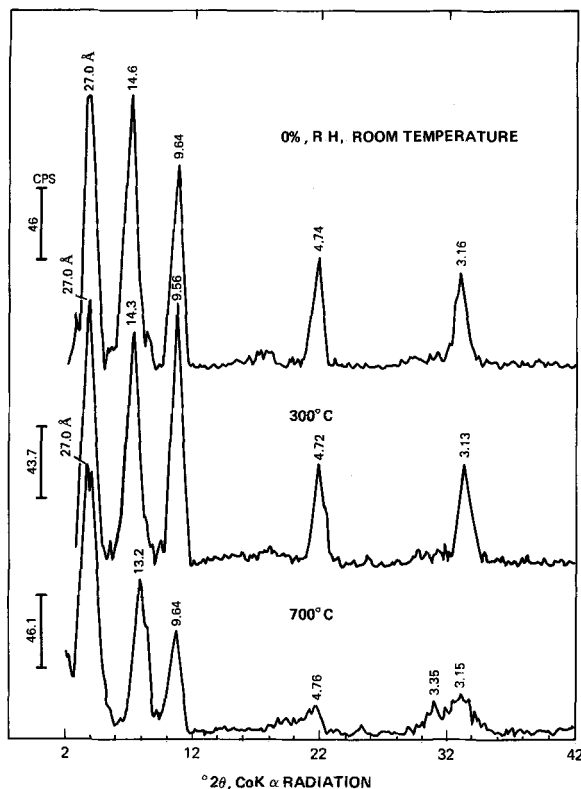


Figure 2. X-ray powder diffraction patterns of polynuclear hydroxy-Al-montmorillonite complex (after four equilibrations) at room temperature, 300°C, and 700°C.

tions of the sample heated at 700°C gave an average $d(001)$ value of 27.68 Å (CV = 3.65), indicating that heating induced more structural irregularity.

If an air-dry, unheated specimen after four equilibrations was saturated with glycerol, the 28-Å phase was transformed into an 18-Å phase having an XRD pattern similar to that of glycerolated montmorillonite (Figure 3). The difference from the material described above was that the average value of $d(001)$ was 18.8 Å, which is slightly larger than the 17.8-Å value recorded for the glycerolated montmorillonite. On heating the glycerolated complex at 550°C, a 15-Å phase appeared instead of expected 9.6-Å dehydrated montmorillonite, indicating that glycerolation did not significantly alter hydroxy-Al sheets between the silicate layers. These data suggest that the 28-Å phase may have been an interstratified structure.

Some structural considerations

Direct Fourier-transform analysis was made (MacEwan, 1956, 1961; MacEwan and Wilson, 1980) to determine the component layers of the polynuclear hydroxy-Al-montmorillonite complex. The thickness (t) of the sample on glass slide was about 10–20 μm. The observed peak intensities (I_{obs}) were corrected for

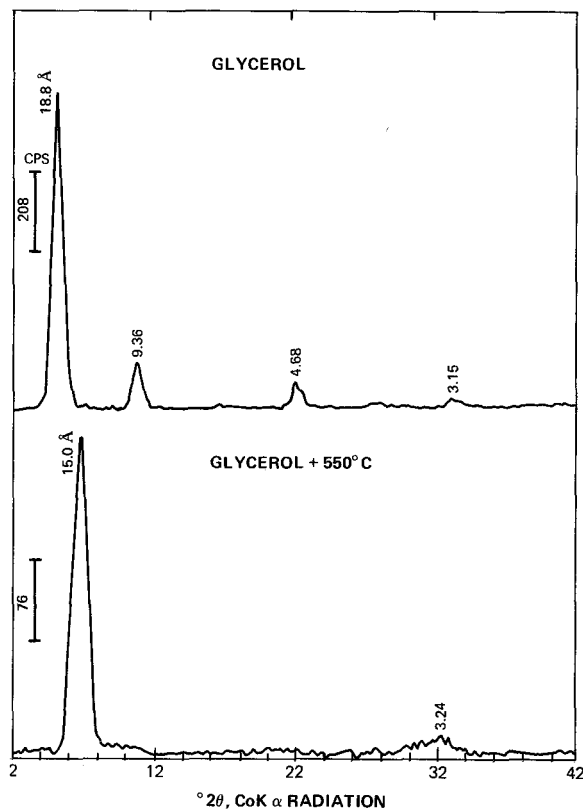


Figure 3. X-ray powder diffraction patterns of polynuclear hydroxy-Al-montmorillonite complex (after four equilibrations) on glycerolation and after heat treatment.

the thickness according to the relation

$$I_{\text{cor}} = I_{\text{obs}} / (1 - e^{-2\mu t / \sin\theta}),$$

where μ is the linear absorption coefficient of the complex for X-rays and θ the diffraction angle where reflection peaks appear (Alexander, 1969). The corrected intensities were used for the Fourier transform. The results (Figure 4) showed two fundamental component layers having spacings of 9.6 and 18.9 Å. The presence of 9.6-Å component layers implies that hydroxide sheets were missing from interlayer spaces of some montmorillonite layers. The 18.9-Å spacing of the second component layer indicates that the thickness of the interlayer sheet in the component layer should have been about 9.3 Å, which is twice as thick as that of an ordinary hydroxide sheet. The assignments for peaks on the Fourier transforms are given in Table 4. Due to the coincidence that the spacing of component layer A is about half that of component layer B, the probabilities of layer sequences, such as AAA, BB, AAAB, and BBB, may have partially contributed to heights of the peaks having spacings >28.5 Å. Because no appropriate way was found to assess such contributions and assuming that these contributions were small, the observed peak heights on Fourier transform were com-

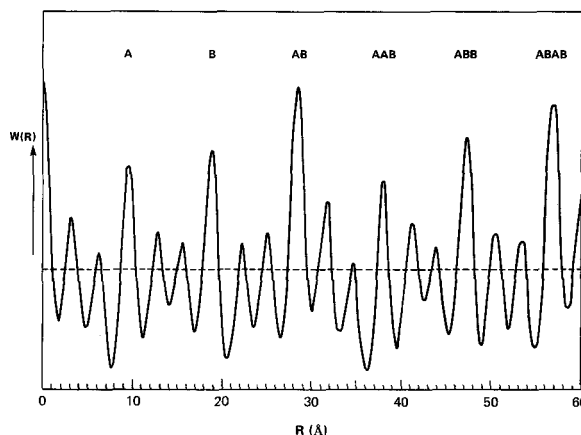
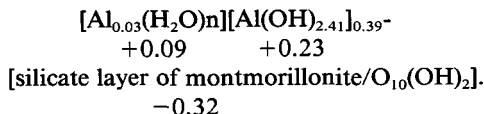


Figure 4. Fourier transform of basal reflections of the polynuclear hydroxy-Al-montmorillonite complex.

pared with the calculated peak heights. The peak heights agreed well (Table 4), except for the peak at 57 Å, suggesting that the assumption was valid. The following probability coefficients were then deduced from the observed peak heights; $P_A = 0.46$, $P_B = 0.54$, $P_{AA} = 0.18$, $P_{AB} = 0.82$, $P_{BA} = 0.70$ and $P_{BB} = 0.30$, where P_{AA} indicates the probability that a layer A succeeds another layer A, and P_{AB} indicates the probability that a layer B succeeds a layer A and so forth. The mixing ratio of the A (9.6 Å) B (18.9 Å) component layers for the complex was 0.46:0.54, nearly 1:1, as obtained directly from probability coefficients for the two fundamental components (Figure 4; Table 4). Although the mixing ratio was nearly 1:1, the ABAB... layer sequence was not completely regular, as indicated by $P_{AB} = 0.82 (<1)$. This degree of irregularity was further supported by the XRD data described above, which showed a noticeable irregularity of the basal reflections.

Structurally, the complex consisted of alternating two montmorillonite silicate layers; one having a hydroxy-Al interlayer sheet and another without it. The chemical data indicate that of the 394 meq polymeric Al adsorbed on 100 g montmorillonite, 80 meq was exchangeable and the remainder, 314 meq, was non-exchangeable. The amount of non-exchangeable Al was far less than the 1600 meq which is required to form a chloritic structure having Al hydroxide sheet between montmorillonite layers (Brydon and Kodama, 1966). Thus, the interlayer space of the complex is only partially occupied by hydroxy-Al materials, leaving more than 75% of the interlayer space vacant. The structure, however, must have had considerable stability, as indicated by the heat-treatment data. Thus, small Al hydroxide blocks must have been sparsely but homogeneously distributed in the interlayer space of the complex and acted like pillars to support its porous structural frame. From chemical data, an average structural formula for the complex is:



Its porosity was about 27%, and its estimated micro-pore size was 9–10 Å.

The results described here and from experiments in which different OH/Al ratios also produced long-spacing complexes suggest that polynuclear hydroxyaluminum cations may contribute to the formation of regular interstratified structures.

ACKNOWLEDGMENTS

We are grateful to C. R. Dekimpe, N. M. Miles, G. J. Ross, and R. C. Turner for valuable discussion, to A. J. Dekker for chemical analyses, and to G. Scott for X-ray powder diffraction analyses.

REFERENCES

- Alexander, L. E. (1969) *X-ray Diffraction Methods in Polymer Science*: Wiley, New York, 582 pp.
- Aveston, J. (1965) Hydrolysis of the aluminum ion: Ultracentrifugation and acidity measurements: *J. Chem. Soc.*, 4438–4443.
- Bailey, S. W., Brindley, G. W., Kodama, H., and Martin, R. T. (1982) Report of The Clay Minerals Society Nomenclature Committee for 1980–1981: *Clays & Clay Minerals* **30**, 76–78.
- Barnhisel, R. I. and Rich, C. I. (1966) Preferential hydroxy-aluminum interlayering in montmorillonite and vermiculite: *Soil Sci. Soc. Amer. Proc.* **20**, 35–39.
- Brindley, G. W. and Kao, C. C. (1980) Formation, compositions, and properties of hydroxyl-Al- and hydroxy-Mg-montmorillonite: *Clays & Clay Minerals* **28**, 435–442.
- Brosssett, C., Biedermann, G., and Sillen, L. G. (1954) Studies on the hydrolysis of metal ions: XI. The aluminum ion, Al^{3+} : *Acta Chem. Scand.* **8**, 1917–1926.
- Brydon, J. E. and Kodama, H. (1966) The nature of aluminum hydroxide-montmorillonite complexes: *Amer. Mineral.* **51**, 875–889.
- Johansson, G. (1960) On the crystal structures of some basic aluminum salts: *Acta Chem. Scand.* **14**, 771–773.
- Lahav, N., Shani, U., and Shabtai, J. (1978) Cross-linked smectites. 1. Synthesis and properties of hydroxy-aluminum montmorillonite: *Clays & Clay Minerals* **26**, 107–115.
- MacEwan, D. M. C. (1956) Fourier transform methods for studying scattering from lamellar systems. A direct method for analyzing interstratified mixtures: *Kolloidzeitschrift* **149**, 96–108.
- MacEwan, D. M. C. (1961) Montmorillonite minerals: in *The X-ray Identification and Crystal Structures of Clay Minerals*, G. Brown, ed., Mineralogical Society, London, p. 143.
- MacEwan, D. M. C. and Wilson, M. J. (1980) Interlayer and intercalation complexes of clay minerals: in *Crystal Structures of Clay Minerals and their X-ray Identification*, G. W. Brindley and G. Brown, eds., Mineralogical Society, London, p. 197.
- Matijević, E., Mathai, K. G., Ottewill, R. H., and Kerker, M. (1961) Detection of metal ion hydrolysis by coagulation. III. Aluminum: *J. Phys. Chem.* **65**, 826–830.
- Okura, T., Goto, K., and Yotuyanagi, T. (1962) Forms of aluminum determined by an 8-quinolinolate extraction method: *Anal. Chem.* **34**, 581–582.
- Pinnavaia, T. J. (1982) Intercalation of molecular catalysts in layered silicates: *ACS Symp. Ser.* **192**, 241–253.
- Pinnavaia, T. J. (1983) Intercalated clay catalysts: *Science* **220**, 365–371.
- Pinnavaia, T. J., Raythatha, R., Guo-Shuh Lee, R., Halloran, L. J., and Hoffman, J. F. (1979) Intercalation of catalytically active metal complexes in mica-type silicates. Rhodium hydrogenation catalysts: *J. Amer. Chem. Soc.* **101**, 6891–6897.
- Plee, D., Gatineau, L., and Fripiat, J. J. (1987) Pillaring processes of smectites with and without tetrahedral substitution: *Clays & Clay Minerals* **35**, 81–88.
- Sawhney, B. L. (1968) Aluminum interlayers in layer silicates. Effect of OH/Al ratio of Al solution, time of reaction, and type of structure: *Clays & Clay Minerals* **16**, 157–163.
- Shen, M. J. and Rich, C. I. (1962) Aluminum fixation in montmorillonite: *Soil Sci. Soc. Amer. Proc.* **26**, 33–36.
- Sillen, L. G. (1959) Quantitative studies of hydrolytic equilibria. *Quart. Rev.* **13**, 146–168.
- Singh, S. S. and Brydon, J. E. (1967) Precipitation of aluminum by calcium hydroxide in the presence of Wyoming bentonite and sulfate ions. *Soil Sci.* **103**, 162–167.
- Singh, S. S. and Kodama, H. (1972) Hydroxy aluminum sulfate-montmorillonite complex: *Can. J. Soil Sci.* **52**, 209–218.
- Slaughter, M. and Milne, I. H. (1960) Formation of chlorite-like structures from montmorillonite: in *Clays & Clay Minerals, Proc. 7th Natl. Conf., Washington, D.C., 1958*, Ada Swineford, ed., Pergamon Press, New York, 114–124.
- Turner, R. C. (1969) Three forms of aluminum in aqueous systems determined by 8-quinolinolate extraction methods: *Can. J. Chem.* **47**, 2521–2527.
- Turner, R. C. (1976) Effect of aging on properties of polynuclear hydroxy aluminum cations: *Can. J. Chem.* **54**, 1528–1534.
- Turner, R. C. and Sulaiman, W. (1971) Kinetics of reactions of 8-quinolinol and acetate with hydroxyaluminum species in aqueous solutions: *Can. J. Chem.* **49**, 1683–1687.

(Received 10 November 1987; accepted 14 March 1988; Ms. 1733)