

PILLARING PROCESSES OF SMECTITES WITH AND WITHOUT TETRAHEDRAL SUBSTITUTION

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Abstract—Pillaring of montmorillonite and beidellite with aluminum polyhydroxypolymer takes place first by the saturation of the cation-exchange capacity by monomeric and/or dimeric aluminum hydroxide species and then the intercalation of the so-called Al_{13} -polyhydroxypolymer. The clay slurry must have a solid concentration greater than 0.01% (w/w) to produce a basal spacing of about 18 Å. Sizeable clay tactoids must therefore exist in the slurry in order to produce a turbostratic structure ordered along the *c* axis. The main difference between pillared montmorillonite and pillared beidellite seems to be a more ordered distribution of pillars within the interlamellar space of the clays that are rich in tetrahedral substitutions. Recent ^{27}Al and ^{29}Si high-resolution nuclear magnetic resonance data suggest that this higher degree of ordering results from the reaction of the aluminic pillars and the clay sheet near the sites of the tetrahedral substitutions.

Key Words—Beidellite, Hydroxy-aluminum complex, Nuclear magnetic resonance, Pillared interlayered complex, Smectite, Tetrahedral substitution.

INTRODUCTION

The first objective in pillaring clays is to achieve as large a basal spacing as possible. Large basal spacing contributes to the development of large surface areas and porous volumes which are the main requirements of acceptable catalysts or catalyst carriers. In particular, intercalation compounds obtained from montmorillonite and aluminum polyhydroxypolymers have been studied by many workers because of their thermal stability (~500°C) and their rather large specific surface areas.

Brindley and Sempels (1977) intercalated beidellite with these same types of polymers. Basal spacings of about 18 Å and specific areas of 250–300 m²/g were reported by Pinnavaia (1983) and Vaughan and Lussier (1980) for various smectites. These authors suggested that the intercalated species giving rise to this stable basal spacing is the so-called Al_{13} -polyhydroxypolymer, which has been characterized by small-angle X-ray scattering (Raush and Bale, 1964) and by ^{27}Al nuclear magnetic resonance (NMR) (Bottero *et al.*, 1980) data. This polymer (structural formula = $Al_{13}O_4(OH)_{24} \cdot (H_2O)_{12}^{7+}$) is composed of 12 Al octahedra and one Al tetrahedron. It exists in aluminic solution having $1 < OH/Al < 2.5$, and its concentration increases with increasing OH/Al (*vide infra*). It contains the four layers of superimposed oxygen atoms (or water or hydroxyls) needed for expanding the clay basal spacings to 18 Å; its “lateral” expansion, however, is limited. The surface area occupied by one polymeric unit, hereafter called the pillar, is about 110 Å².

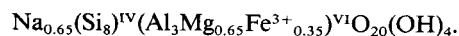
The aim of the present work was to study as quantitatively as possible the intercalation of Al_{13} with respect to various parameters (Al concentration, OH/Al

ratio, removal of excess anions, clay concentration) using a clay having either octahedral substitutions (Wyoming bentonite = montmorillonite) or tetrahedral substitutions (synthetic beidellite). The influence of the origin of the structural charge on the pillaring process was also investigated. These two types of calcined pillared clays have, in fact, different structures according to the location of the cationic substitutions, as shown recently by high-resolution solid state ^{27}Al and ^{29}Si nuclear magnetic resonance (Plee *et al.*, 1985). In both, however, the pillaring species is indeed the Al_{13} polyhydroxypolymer before calcination.

EXPERIMENTAL

Starting clays

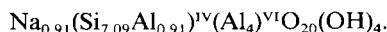
The <2- μ m fraction of a Na-bentonite (Wyoming), free of quartz, kaolinite, and carbonate, was obtained by sedimentation after washing it five times with a 1 M NaCl solution and removing the excess electrolyte. The cation-exchange capacity (CEC) measured by the ammonium acetate technique was 92 meq/100 g on an air-dried basis. A chemical analysis yielded the following formula:



Na-beidellite was synthesized as follows: First a gel of Na, Al, and Si oxides in adequate proportions was prepared following the procedure proposed by Luth and Ingamells (1965). After calcination at 300°C, the ground material was introduced in gold tubes filled with a 0.01 N NaOH solution (Frank-Kamenetsky *et al.*, 1973) at a NaOH/gel ratio of 4×10^{-4} mole/g. The loading ratio, i.e., the volume fraction of the gold tube occupied by the gel + the NaOH solution was 0.72.

The total volume of the gold tube was 28 cm³. The reaction was carried out at 340°C for 10 days under a pressure of 600 bars.

Under these conditions beidellite was the only crystalline material obtained. The number of tetrahedral substitutions in beidellite was estimated by the technique of Chourabi and Fripiat (1981), using the fact that in beidellite, NH₄⁺, with C_{3v} symmetry, displays a strong infrared band at about 3030 cm⁻¹. The CEC was found to be 100 meq/100 g on air-dried basis. A chemical analysis yielded the following formula:



The (Al^{IV}/Al total) ratio obtained from ²⁷Al high-resolution solid state NMR was of the order of 22%. The measured CEC was smaller than that expected from the chemical analysis. Such discrepancy is not unusual and has been attributed by many workers to the collapse of some portion of the interlayer space.

Aluminum polyhydroxypolymer solution

Aluminum polyhydroxypolymer solutions were prepared by adding 0.2–0.4 M NaOH solution dropwise to a stirred 0.4 M Al(NO₃)₃·9H₂O solution in such a way as to obtain OH/Al ratios between 1 and 2. The final Al concentration of all solutions was about 0.133 mole/liter. The turbid solution was then aged at 50°C for 1 hr, at which time it turned completely clear.

From the intensity of the ²⁷Al signal observed at +61 ppm with respect to an Al(H₂O)₆³⁺ reference, the relative content of Al₁₃ increased almost linearly from about 20% at OH/Al = 1 to 80% at OH/Al = 2. This variation was only slightly sensitive to the total Al concentration between 0.05 and 0.5 mole/liter, in agreement with Bottero *et al.* (1980). From titration curves and NMR results, Bottero *et al.* (1980) suggested that the other aluminic species present in solution were either monomeric Al(OH)_x(H₂O) or dimeric Al₂(OH)_x(H₂O).

Pillaring process and characterization of the pillared clays

In all experiments, except when otherwise specified, a clay slurry containing 20 g of solid/liter was used. The Al hydroxide solution was rapidly added to a specified volume of the clay slurry so as to adjust the Al content to the desired value. One hundred twenty-five milliliters of the flocculated suspension was introduced into a cellulose hose immersed for one day in distilled water using 1 liter of water per gram of clay. The distilled water was changed every day for 4 days unless otherwise specified. This procedure was described by Jacobs *et al.* (1981).

After dialysis, the pillared clay was freeze-dried. Before freeze-drying, oriented clay films were prepared by spreading a few drops of the suspensions on a glass

slide. The film was either dried at room temperature or calcined at 300°C. After freeze-drying, the pillared clay was used as such for CEC measurements or calcined at 300°C for surface area or porosity measurements using N₂ at -196°C.

To obtain additional information on the porosity, 25 ml of a solution of pyrene in n-hexane was brought into contact with 0.175 g of pillared and calcined clays that had been carefully outgassed. The initial concentration ranged between 0.01 and 30 × 10⁻³ mole/liter in order to scan the complete adsorption isotherm. The adsorption was carried out at 25°C under vigorous stirring for 3 hr. The final equilibrium concentration of pyrene was measured by UV spectrometry in the 300-nm region; the adsorbed amount was determined by difference with the starting concentration.

Chemical analyses were performed by atomic absorption on samples calcined at 900°.

RESULTS AND DISCUSSION

In view of the numerous factors that can affect the pillaring process, it was necessary to study the influence of the OH/Al molar ratio, the Al/clay ratio, the duration of the dialysis process, and the concentration of the clay slurries in order to optimize the preparation procedure of the pillared montmorillonite (PM) and of the pillared beidellite (PB). The calcined equivalents of these materials are abbreviated here as CPM and CPB.

Figure 1 shows two typical X-ray powder diffraction (XRD) diagrams of the CPM and CPB obtained with the optimized procedure discussed below. Because of preferential orientation, these materials give XRD patterns typical of turbostratic solids in which ordering along the *c* axis only was visible. Obviously, 001 spacings were not rational because of some interstratification of expanded and nonexpanded domains. The intensity of the 001 reflection was therefore considered to be only a relative or approximate measure of the number of permanently expanded domains.

Influence of OH/Al ratio and Al/clay ratio

The variation of the basal spacing with the Al/clay ratio (between 2 and 20 meq/g clay was studied for three OH/Al ratios. In Figure 2, the intensity of the diffracted X-ray beam in the region of the 001 reflections is shown for pillared montmorillonite. Clearly a distinct 17.5-Å reflection was obtained at lower Al/clay ratios and higher OH/Al ratios. These conditions favored the uptake of the Al₁₃ polymer from solutions in which this species was increasingly abundant. The expansion of the basal spacing is therefore attributable to the intercalation of this polymer. Figure 3 shows the behavior of beidellite with respect to the variation of the same parameters.

Whereas at lower Al/clay ratios montmorillonites

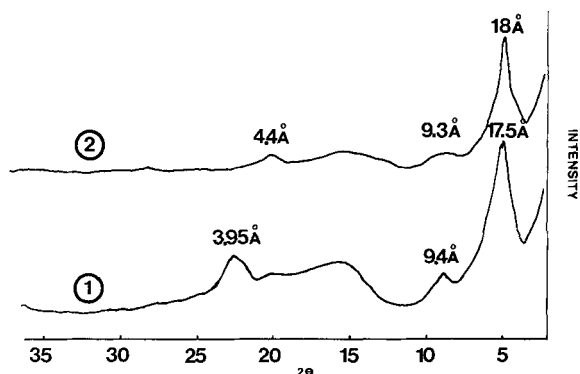


Figure 1. X-ray powder diffraction patterns of (1) calcined (500°C) film of pillared montmorillonite (OH/Al = 1.2; Al/clay = 30 meq/g) and (2) calcined (300°C) film of pillared beidellite (OH/Al = 1.2, Al/clay = 30 meq/g). CuK α radiation.

collapsed ($d(001) \approx 10 \text{ \AA}$) despite calcination, the (001) in beidellite changed to $\sim 12.3 \text{ \AA}$. For this clay the reflection shifted progressively to 17.5 \AA , but it reached that value for a higher Al/clay ratio than that observed for montmorillonite.

That a higher absolute concentration of the Al₁₃ polymers is needed for expanding beidellite compared with montmorillonite is consistent with the higher structural charge of the former versus the latter. For beidellite, however, the interstratification involved a 12.3-\AA phase in which, for steric reasons, Al₁₃ could not have been the intercalated species.

Therefore, to guarantee large spacings irrespective of the nature of the clay, the Al/clay ratio had to be equal to or greater than 20 meq/g. Thus, a systematic study of the influence of the OH/Al ratio on the 001 spacings was undertaken using an Al/clay ratio of 30 meq/g. As shown in Table 1, there was no significant difference for OH/Al ratios between 1.2 and 2, most probably because at high Al/clay ratios, the absolute concentration of Al₁₃ was always large enough throughout the overall intercalation process.

A decrease of about 1 \AA in $d(001)$ was observed between the calcined and untreated pillared clays. In

Table 1. $d(001)$ values (\AA) of calcined and uncalcined pillared montmorillonites and beidellites having different OH/Al ratios.¹

	OH/Al					
	1	1.2	1.4	1.6	1.8	2
PM	18	18.8	18.6	18.8	18.6	18.4
CPM	17.2	17.5	17.3	17.4	17.4	17
PB	18.4	18.5	18.5	18.1	18.6	18.2
CPB	17	17.6	17.5	17.6	17.5	17.6

¹ PM = pillared montmorillonite; CPM = calcined pillared montmorillonite; PB = pillared beidellite; CPB = calcined pillared beidellite.

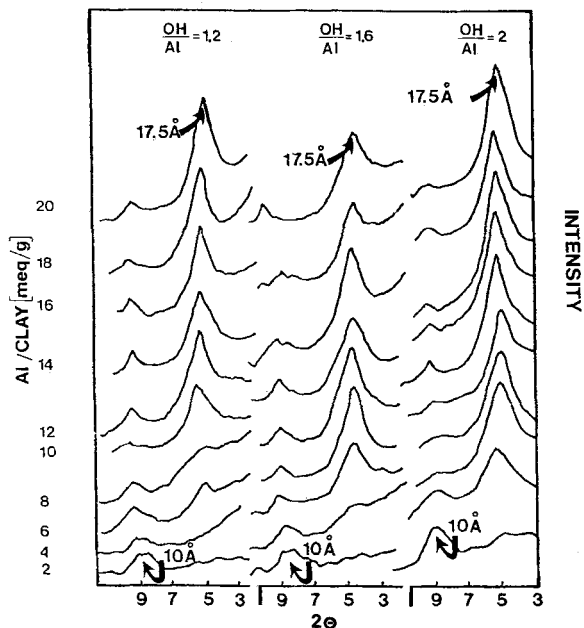


Figure 2. 001 reflections of calcined (500°C) films of pillared montmorillonite as a function of the initial Al/clay ratio for OH/Al ratios of 1.2, 1.6, and 2. CuK α radiation.

this respect, montmorillonite and beidellite behaved similarly.

Basal spacing as a function of the duration of dialysis

The development of the pillared structure was studied as a function of the number of times the fresh

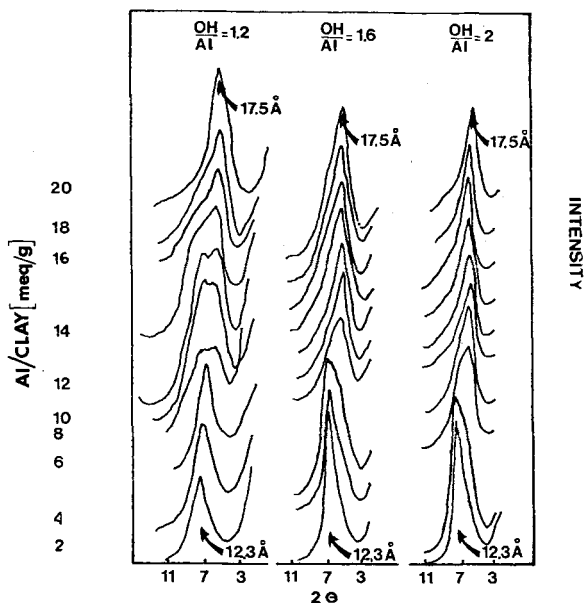


Figure 3. 001 reflections of calcined (300°C) films of pillared beidellite as a function of the initial Al/clay ratio for OH/Al ratios of 1.2, 1.6, and 2. CuK α radiation.

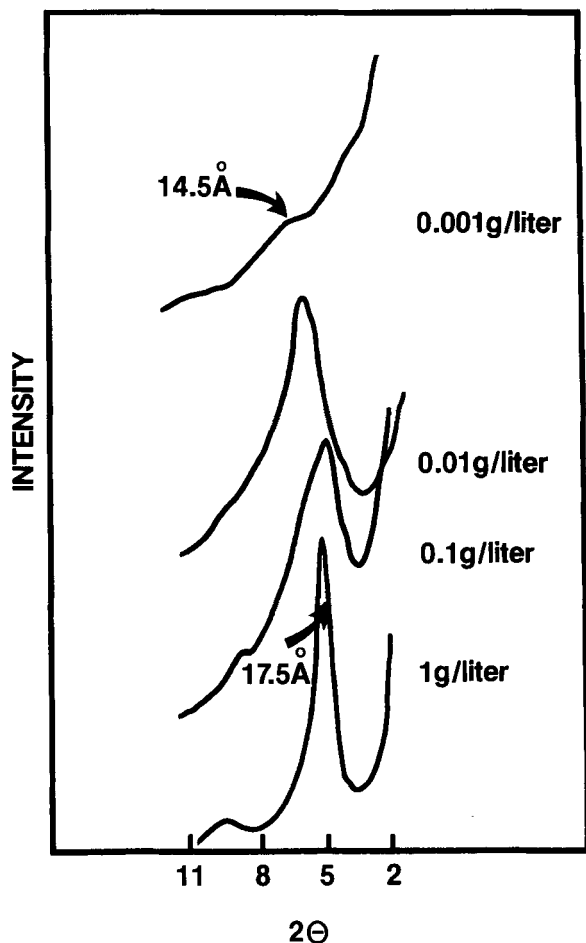


Figure 4. Basal spacings of calcined (500°C) films of pillared montmorillonite (OH/Al = 1.2; Al/clay = 30 meq/g) as a function of clay concentration before pillaring. CuK α radiation.

distilled water in contact with the dialysis bag was replaced. Each replacement corresponded to a 1-day dialysis period. Before dialysis and after stirring the 2% clay slurry (weight of clay/weight of water + aluminum polyhydroxypolymer solution), the 001 spacing of the calcined montmorillonite was about 14.5 Å, and the initial OH/Al and Al/clay ratios were 1.2 and 30 meq/g, respectively. After two replacements (i.e., the second "dialysis") the 17.5-Å peak had developed, but the shoulder at about 10 Å was still present. After four replacements, the high-spacing reflection became sharper. The large spacing was achieved only after the initial aluminum hydroxide solution had been aged for 1 hr at 50°C.

By using a "fresh" aluminum hydroxide solution at OH/Al = 1.2, even after the fourth dialysis, the maximum swelling was 14.5 Å. The necessity of aging the starting aluminum hydroxide solution seemed to favor the formation of Al₁₃ at the expense of monomeric and

Table 2. BET surface area¹ (S) and total pore volume (V_t) of calcined pillared montmorillonite (CPM) and calcined pillared beidellite (CPB) after degassing.²

OH/Al	CPM		CPB		CPM	CPB
	S (m ² /g)	V _t (cm ³ /g)	S (m ² /g)	V _t (cm ³ /g)	V _m ³ (cm ³ /g)	V _m ³ (cm ³ /g)
1	260	0.29	225	0.3	0.13	0.12
1.2	253	0.25	313	0.31	0.12	0.15
1.4	247	0.28	315	0.38	0.10	0.15
1.6	256	0.29	308	0.36	0.12	0.18
1.8	229	0.28	319	0.36	0.1	0.17
2.0	260	0.3	318	0.38	0.13	0.18

¹ N₂, -196°C.

² After degassing at 220°C for 3 hr under vacuum.

³ V_m = micropore volume.

dimeric aluminum species, as suggested by qualitative NMR results. Dialysis or some other process that removes the anions surrounding the Al₁₃ polymer appears to be needed to obtain 001 spacing > 14.5 Å. The spacings at about 14.5 Å were probably due to the formation of aluminum chlorite.

Basal spacing as a function of the clay slurry concentration

Experiments to study the variation of basal spacing as a function of clay slurry concentration were carried out using the optimized factors: Al/clay ratio = 30 meq/g, four "dialysis," and OH/Al \approx 1.2. Four slurries containing 1, 0.1, 0.01, and 0.001 g clay/liter were used. A 001 reflection at 17.5 Å (after calcination) was observed for concentrations as small as 0.1 g clay/liter. At lower concentrations the spacing shifted to lower values and eventually disappeared for a clay slurry containing 0.001 solid/liter (Figure 4). Fripiat *et al.* (1982) showed that in a 0.1% (w/w) hectorite suspension, most of the clay particles are aggregated in tactoids, the presence of which seems to be a prerequisite for the formation of turbostratic pillared species. A completely disordered flocculation of individual clay particles probably exists for clay concentrations < 0.01%.

Increasing the temperature of the addition of aluminum hydroxide to the slurry to 75°C decreased the 001 spacing of the calcined final product to about 16 Å. Simultaneously, the 001 XRD reflection became broader. The negative effect of increasing the temperature (observable also at 50°C) could have resulted from the disorganization of the tactoid structure or from a partial depolymerization of Al₁₃, inasmuch as its formation is exothermic (Bottero *et al.*, 1982a).

Surface area (BET) and porosity of pillared clays

The samples used to study the surface area and porosity of the pillared clays were those for which the influence of the OH/Al ratio on the 001 spacing is

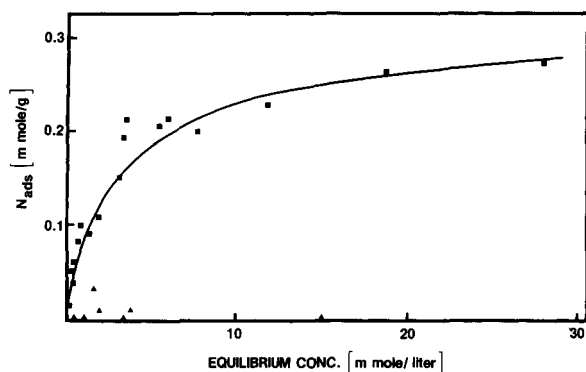


Figure 5. Pyrene adsorption by calcined pillared montmorillonite (▲) (OH/Al = 1.2; Al/clay = 30 meq/g) and calcined pillared beidellite (■) (OH/Al = 1.2; Al/clay = 30 meq/g).

reported in Table 1. The N_2 (-196°C) BET surface area and the total porous volume (volume of N_2 adsorbed at $P/P_0 \approx 0.95$) are presented in Table 2. The results of these measurements are practically constant for OH/Al ratios between 1.2 and 2, in agreement with the constancy of the 001 spacings.

The surface area and the total pore volume were always larger for the CPBs than for the CPMs. For the Wyoming bentonite used for this work, the BET external surface is $S = 53 \text{ m}^2/\text{g}$ and $V_t = 0.11 \text{ cm}^3/\text{g}$, whereas for the synthetic beidellite these values are $107 \text{ m}^2/\text{g}$ and $V_t = 0.18 \text{ cm}^3/\text{g}$. These values were obtained for the freeze-dried samples outgassed also at 220°C . Thus, the higher surface areas and pore volumes observed for the CPBs might be due to its smaller particle size.

An interlamellar microporosity measurement would be more interesting; however, the difficulty of making such measurement is well known. The microporous volume V_m may be approximated by application of the Dubinin equation (Fripiat *et al.*, 1971, and references therein)

$$\log V = \log V_m - K(\log P_0/P)^2,$$

where V is the adsorbed volume of the N_2 (assumed to form a liquid phase) at the equilibrium pressure P , and K is a proportionality constant. The results obtained by applying this equation to the adsorption isotherms are reported in Table 2.

The microporous volume calculated on the basis of a $7.5\text{-}\text{\AA}$ interlamellar thickness should be about $0.19 \text{ cm}^3/\text{g}$. This value is similar to that obtained for the CPB, but larger than that reported for the CPM. This difference may be due to: (1) interstratification between collapsed and open lamellae and (2) different types of ordering of the pillars within the interlamellar space of a montmorillonite and a beidellite. The ordering may be different because of the more localized character of the layer charge in a smectite having tetrahedral

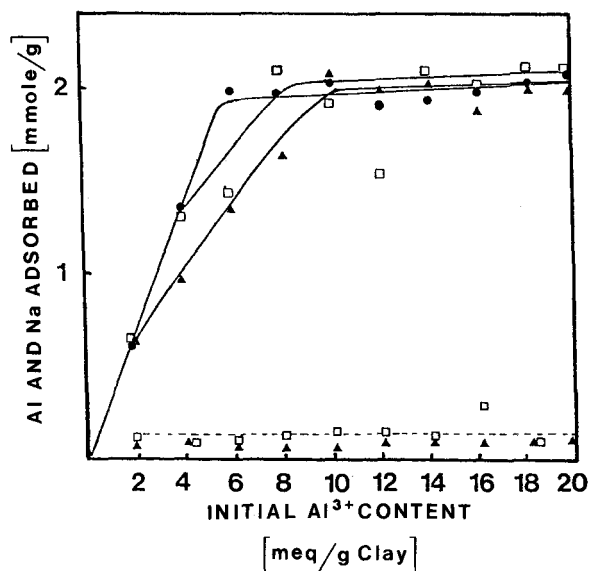


Figure 6. Adsorbed Al (solid line) and Na (dashed line) contents of pillared montmorillonite as a function of Al/clay ratio for three OH/Al ratios (▲ = 1.2; □ = 1.6; ● = 2).

substitutions. A random distribution of pillars may prevent the access of a fraction of that space to the adsorbate.

Pyrene adsorption by calcined pillared clays

The in-plane van de Waals dimensions of the pyrene molecule are $11.6 \times 8.8 \times 3.5 \text{ \AA}$. These dimensions are such that a fairly regular distribution of the pillars should be critical for adsorbing this molecule. Indeed, as shown in Figure 5, pyrene was adsorbed from solution in *n*-hexane by CPB, but not by CPM. The higher adsorption point of the Freundlich isotherm in Figure 5 corresponds to $0.275 \times 10^{-3} \text{ mole/g}$ and to an available surface area of about $170 \text{ m}^2/\text{g}$, assuming that the molecules lie flat.

Thus, adsorption occurs to a considerable extent within the interlamellar space of CPB, but not at all in CPM. This difference suggests that the ordering of the pillars in CPB allows an appreciable fraction of the internal surface to be available to pyrene molecules. This interpretation is in qualitative agreement with those obtained from microporous volume measurements. Moreover, subtracting the external surface area from the total surface area of CPB yields an internal surface area of $\sim 200 \text{ m}^2/\text{g}$, in reasonable agreement with that observed for pyrene lying flat at maximum loading.

Pillaring mechanism

To this point, nothing has been said about the role of the adsorption processes in pillaring, except that indirect evidence suggests that the pillaring species is

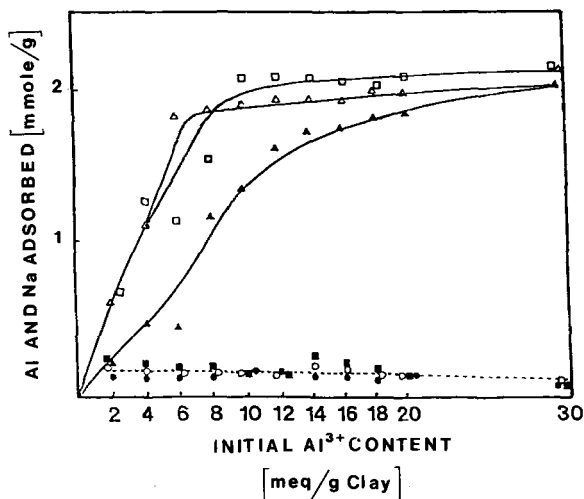


Figure 7. Al and Na contents of pillared beidellite as a function of Al/clay ratio for three OH/Al ratios. \blacktriangle Al and \blacksquare Na uptakes for OH/Al = 1.2; \triangle Al and \circ Na uptakes for OH/Al = 1.6, \square Al and \bullet Na uptakes for OH/Al = 2.

the Al_{13} polyhydroxypolymer and that the nature of the pillaring species has been confirmed by high-resolution solid state ^{27}Al NMR (Plee *et al.*, 1985). To obtain information on the pillaring mechanism the amount of adsorbed Al and the amount of residual sodium were measured in the "final" sample obtained after four dialyses and in the initial clay. These measurements are plotted as a function of the initial Al content of the pillaring solution expressed in meq Al/g clay. In these calculations, Al was arbitrarily taken to be a trivalent positive cation. This assumption is not realistic because of the presence of aluminum polymers having lower charges. The amount of adsorbed Al could not be expressed as a function of the Al_{13} concentration because it changed continuously during dialysis. The experimental results are shown in Figures 7 and 8 for montmorillonite and beidellite, respectively, and for three OH/Al ratios—namely OH = 1.2, 1.6, and 2. The initial percentages of Al in the Al_{13} polymers are of the order of 25, 50, and 75, respectively.

For both clays, the maximum amount of Al adsorbed was about 2×10^{-3} mole/g, whereas the residual amount of Na was about 10^{-4} mole/g. The higher the OH/Al ratio, the lower was the Al/clay ratio needed for the maximum Al uptake. These results are in good agreement with the XRD data shown in Figures 2 and 3; the largest 001 spacing was obtained when the Al uptake was at its maximum.

The CEC of the pillared clays having the compositions shown in Figures 6 and 7 decreased progressively with increasing Al/clay ratio. The decrease of the CEC must be due to non-exchangeable Al, namely that in the pillars, whereas Al monomer or dimer may be con-

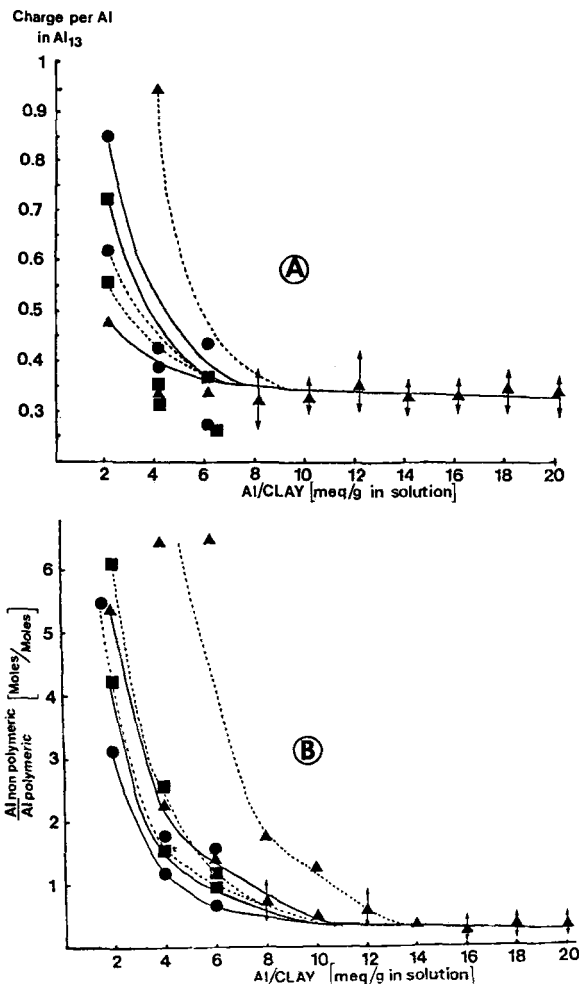


Figure 8. (A) Evolution of the apparent charge per Al in the pillars as a function of the Al/clay ratio for three OH/Al ratios (\blacktriangle = 1.2; \blacksquare = 1.6; \bullet = 2). Solid line refers to PM; dashed line refers to PB. (B) Evolution of the [Al non-polymeric (exchangeable)]/[Al polymeric (non-exchangeable)] ratio as a function of the Al/clay ratio for three OH/Al ratios (\blacktriangle = 1.2; \blacksquare = 1.6; \bullet = 2). Solid line refers to PM; dashed line refers to PB. Arrows show the spread of the experimental data.

sidered exchangeable. Therefore, knowing the residual Na content and the difference between the initial and final CEC, the apparent charge per adsorbed Al atom and the ratio of the nonpolymeric (monomer + dimer) to polymeric Al can be computed. The variation of this apparent charge with respect to the initial Al/clay ratio is shown in Figure 8 for both clays. At maximum Al uptake, the average charge per Al_{13} is 0.32, which corresponds to a Al_{13}^{4+} species, and the fraction of non-polymeric Al to polymeric Al is <0.3 .

These observations are in good agreement with earlier data of Barnhisel (1977). Actually, Figure 8 shows that at lower Al/clay ratios, monomeric Al cations were the main adsorbed species, whereas the Al_{13} polymer

was progressively preferred as the Al/clay ratio increased, namely with increasing content of Al₁₃ polymer. The behaviors of montmorillonite and beidellite differ only by the fact that a higher concentration was needed in beidellite to reach the threshold spacing of 17.5 Å.

CONCLUSIONS

From the experimental results obtained in this work it is evident that an expansion of smectites to a thermally stable 001 spacing of 18 Å requires a rather well defined aluminum polymer, such as the so-called Al₁₃ species. The gyration radius of this polymer, however, with its anionic and hydration cloud is about 10 Å (Bottero *et al.*, 1982a, 1982b). Its total positive charge (between 4+ and 7+, depending on the number of OH or H₂O in the Al octahedra) is partially screened by firmly attached anions (Axelos *et al.*, 1985). Inasmuch as the selectivity in a cationic exchange reaction is strongly dependent on the net cationic charge, the monomeric aluminum (and perhaps dimeric) species in equilibrium with Al₁₃ in the initial aluminum hydroxide solution are probably preferentially adsorbed because of a lower steric hindrance to diffusion within the interlamellar space. Some oligomerization of the adsorbed monomeric species may also occur between the lamellae. As dialysis proceeds, the anions coordinated to the Al₁₃ species in solution are removed, as shown by Gastuche and Herbillon (1962) and Axelos *et al.* (1985).

The net charge increases, whereas the gyration radius decreases. These two factors enhance the selectivity of the clay structure towards Al₁₃. Thus, the Al monomer or oligomer is progressively removed from the interlamellar space to the benefit of Al₁₃ until the maximum uptake of this species occurs. This step requires a relatively high concentration of Al₁₃, which is favored by high OH/Al and/or high Al/clay ratios.

On the basis of chemical analyses of six samples, the final compositions (after calcination at 900°C) are as follows: pillared montmorillonite (CPM): Na_{0.064}1.65(Al_p)(Si₈)^{IV}(Al₃Mg_{0.65}Fe_{0.35})^{VII}O_{24.18}; pillared beidellite (CPB): Na_{0.06}1.5(Al_p)(Si_{7.09}Al_{0.91})^{IV}(Al₄)^{VII}O_{23.84}; where Al_p stands for one Al atom in the pillar.

The surface density of the pillars is slightly lower in CPB than in CPM. Because of localization of the charge in the tetrahedral layer, beidellite requires a higher threshold concentration of Al₁₃ to achieve the maximum swelling, but the basal spacings are practically the same for both types of pillared clays. The main difference observed in the present work lies in the ordering of the pillars within the interlamellar space. In CPB, the microporous volume and the pyrene adsorption are compatible with a distribution of the pillars on a hexagonal network, the centers of which being

21.6 Å from each other. Windows of about 10 × 10 × 7.5 Å allow pyrene molecules to invade the interlamellar space. The disordered distribution of the pillars in CPM prevents this adsorption.

High-resolution solid state ²⁷Al and ²⁹Si NMR of pillared beidellite and magnesium smectites (Plee *et al.*, 1985), however, has shown very different local structural arrangements between pillared clays with or without tetrahedral substitutions. Calcining pillared beidellite results in the formation of specific linkages between Al₁₃ and the clay's tetrahedral layer. Calcining pillared smectites without tetrahedral substitution does not modify the clay's tetrahedral layer nor does it transform the aluminic pillar into a pseudospinel.

Calcining PB appears to result in seeding the growth of a three-dimensional network grafted on the two-dimensional network of the clay; the resulting high-area solid could be considered a two-dimensional zeolite. This transformation is most probably initiated by the Al tetrahedral substitutions in beidellite. Thus, calcining pillared smectites leads to two distinct types of solids differing by the presence or absence of Si due to Al substitution in the tetrahedral layer.

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