

THE Al PILLARING OF CLAYS. PART I. PILLARING WITH DILUTE AND CONCENTRATED Al SOLUTIONS

ROBERT A. SCHOONHEYDT,¹ J. VAN DEN EYNDE,¹ H. TUBBAX,¹ H. LEEMAN,¹
M. STUYCKENS,¹ I. LENOTTE,¹ AND W. E. E. STONE²

¹ Centrum voor Oppervlaktechemie en Katalyse, Materials Research Center
K. U. Leuven, K. Mercierlaan, 92, 3001 Heverlee, Belgium

² Section Physico-Chimie Minérale (MRAC), UCL, Place Croix du Sud, 2 Boite 18
1348 Louvain-La-Neuve, Belgium

Abstract—Saponite, hectorite, and laponite have been pillared with cationic Al clusters, and special attention has been given to the solution chemistry of Al. Pillared saponite is obtained after exchange with refluxed Al solutions; while for hectorite, Al solutions treated with ammonium acetate give a pillared product with 1.8–1.9 nm spacing and thermal stability up to 873 K. In both types of solutions, the Keggin ion Al cluster is a minority species or totally absent. The typical 1.8–1.9 nm spacing is only obtained after washing. The quality of the pillared material can be judged from its thermal stability, its surface area, and the width of the d001 line before and after pillaring. The width should not exceed 0.3 nm before calcination and 0.5 nm after calcination. The latter criterion reflects the importance of the crystallinity of the parent clay for successful pillaring. Pillaring in concentrated conditions occurs by a combination of ion exchange and precipitation of Al and gives materials that exhibit poor thermal stability.

Key Words—Aluminium, Hectorite, Laponite, Pillaring, Saponite.

INTRODUCTION

Pillaring of smectites with robust, polynuclear inorganic cations remains a lively research area. The materials obtained have potentialities not only as catalysts and selective sorbents, but also in membranes, in electrochemical and optical devices, and as hosts for enzyme mimics and dyes (Mitchell, 1990). Large-scale and reproducible production of these materials requires a knowledge of all the factors influencing the pillaring process. This knowledge is not yet fully available.

Pinnavaia *et al.* (1984) and Plee *et al.* (1985) showed that the pillaring agent is $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, the so-called Keggin ion. This implies that pillaring is an ion exchange process, the maximum amount of adsorbed Al being about twice the CEC (the average charge per Al being 0.54). Usually, larger quantities of Al are adsorbed, and this is attributed to partial hydrolysis of the Keggin ion upon exchange (Figueras, 1988). It could also be that other Al species are exchanged. This is evidenced by the observations that pillaring is possible with hydrothermally treated Al solutions (Sterte and Otterstedt, 1987) and with concentrated solutions (Schoonheydt and Leeman, 1992), in which the Keggin ion is almost totally absent. Moreover, the 1.8–1.9 nm spacing is only generated by washing the pillared product (Schutz *et al.*, 1987; Figueras *et al.*, 1990b; Schoonheydt and Leeman, 1992). This shows that 1) the Keggin ion is not the only pillaring species and 2) important chemical changes are going on in the interlamellar space during washing.

The structure of the gallery Al ions, the distribution of the Al species in the interlamellar space, the particle

size of the clay, the clay aggregation in the suspension, and the layer charge are factors that possibly influence this interlamellar chemistry (Pinnavaia *et al.*, 1985; Plee *et al.*, 1987; Urabe *et al.*, 1988; Figueras *et al.*, 1990b). Figueras *et al.* (1990a) and Figueras (1988) have stressed the importance of the distribution of the Al species in the interlamellar space. A homogeneous distribution is advantageous for a successful pillaring, which can be achieved by competitive ion exchange and high temperature exchange.

One of the major problems is that the various species of Al in the pillaring solutions are not fully known. NMR spectroscopy usually detects three lines: monomeric, octahedral Al^{3+} at 0 ppm, dimeric to pentameric (oligomeric) Al^{3+} at around 5 ppm, and tetrahedral Al^{3+} at 62.5 ppm (Akitt *et al.*, 1972; Akitt and Elders, 1988). The latter is ascribed to the Keggin ion. A major part of the Al is, however, NMR-silent (Sterte, 1988).

We have set up a program along two lines. On one hand, we have explored the conditions for preparing thermally stable pillared clays. On the other hand, clays were pillared with solutions containing only the Keggin ion (Schönherr *et al.*, 1981; Furrer *et al.*, 1992). In the latter case, exchange isotherms can be established that give insight into the pillaring process. This will be discussed in part II. All the solutions were investigated by ²⁷Al NMR spectroscopy.

EXPERIMENTAL METHODS

Preparation of the Al solutions

Dilute solutions. The solutions were prepared by adding by drops and at room temperature a 0.4 M (or 0.2 M)

NaOH solution to a 0.4 M (or 0.2 M) $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ solution at a rate of 1 ml/min with vigorous stirring. The R values $[(\text{OH})/(\text{Al}) \text{ molar ratios}]$ were 1.25, 1.5, 2, and 2.25. The initial Al^{3+} concentrations were chosen so as to obtain a final Al^{3+} concentration of 0.1 M in all cases. The effect of Ce^{3+} was studied by adding a 0.2 M $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ to the $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ solutions before neutralization with NaOH. The R values, now defined as $(\text{OH})/[(\text{Al}) + (\text{Ce})]$, were the same as for the Al^{3+} solutions, and the final concentration in $[(\text{Al}^{3+}) + (\text{Ce}^{3+})]$ was 0.1 M. The ratio $(\text{Ce})/(\text{Al})$ was 1/12. In another series of experiments, 1 M $\text{NH}_4\text{OOCCH}_3$ solutions were added to the partially neutralized Al solutions with $[\text{Ac}^-]/[\text{Al}^{3+}]$ molar ratios ranging between 1 and 10 ($\text{Ac}^- = \text{acetate}$).

In a second series of experiments, the solutions were refluxed for 24 hr prior to use. In the case of Ac^- , the reflux was done before the Ac^- addition.

Concentrated solutions. These were prepared by adding 1 M or 2 M NaOH solutions to 1 M or 2 M $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ solutions with vigorous stirring so as to obtain R values of 1 and 2. Colloidal particles were invariably formed in such conditions, but the solutions became clear after refluxing for a few minutes or upon heating at 60°C . The effects of aging at room temperature and the addition of $\text{NH}_4\text{OOCCH}_3$, and of LaCl_3 at a given R value have also been studied.

Materials

Saponite and hectorite (Clay Minerals Society) and laponite B (Laporte Inorganics) were converted in their Na^+ form by repeated dialysis against 1 M NaCl solutions. After washing until free of Cl^- (AgNO_3 test), the clay was fractionated by centrifugation and the $< 2 \mu\text{m}$ fraction was retained. The clays in suspension were precipitated by addition of NaCl, washed until free of Cl^- , and freeze-dried. The cation exchange capacities (CEC) were taken from van Olphen and Fripiat (1979) as 0.439 and 0.733 meq/g for hectorite and laponite, respectively. The CEC of saponite was determined with the ^{22}Na method as 1 meq/g.

Pillaring

One wt% clay suspensions were prepared and agitated for 24 hr. Dilute Al^{3+} solutions were prepared as described above. The amount of Al^{3+} in the solutions was 15 mmol/g clay. The solutions were added to the clay suspensions at a rate of 8 ml/min. After addition, the suspensions were stirred for 24 hr, washed until free of Cl^- , and freeze-dried.

In separate experiments, the conditions for pillaring saponite and hectorite were investigated (reflux time of the solutions prior to pillaring or no reflux, amount of Al and of clay in the suspensions, addition of NH_4Ac).

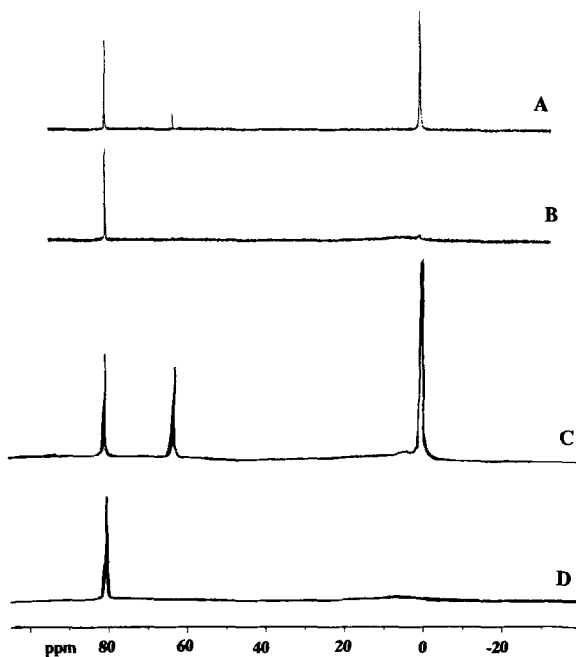


Figure 1. ^{27}Al -NMR spectra of Al-solutions: A) $[\text{Al}^{3+}] = 0.1 \text{ M}$; $R = 1$; $[\text{Ac}^-]/[\text{Al}^{3+}] = 0$; B) $[\text{Al}^{3+}] = 0.09 \text{ M}$; $R = 1$; $[\text{Ac}^-]/[\text{Al}^{3+}] = 1$; C) $[\text{Al}^{3+}] = 0.5 \text{ M}$; $R = 2$; $[\text{Ac}^-]/[\text{Al}^{3+}] = 0$; and D) $[\text{Al}^{3+}] = 0.5 \text{ M}$; $R = 2$; $[\text{Ac}^-]/[\text{Al}^{3+}] = 5$.

Techniques

^{27}Al NMR spectra of the solutions were collected on a Bruker WM 250 at 65.14 MHz and on a Bruker AMX 300 apparatus at 78.208 MHz. The standard was $\text{Al}(\text{OH})_4^-$ in D_2O .

XRD patterns of powdered, pillared clays were recorded on a Siemens Kristalloflex 700 apparatus at 40 kV and 20 mA with the $\text{CuK}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$). Spectra were recorded of the freeze-dried samples and of the samples calcined in air up to 550°C .

The surface areas of the pillared clays were measured by the one point BET method at $p/p_0 = 0.3$ with a Beta Surface Analyzer model 4200 after removal of physisorbed water at 120°C .

The cation exchange capacity (CEC) before and after calcination was determined with the ^{23}Na method (Maes *et al.*, 1975), and elemental analysis of a few samples was performed by the Bodemkundige Dienst van België after dissolution in HF (Na^+ , Al^{3+} , Mg^{2+}).

RESULTS

^{27}Al NMR of the pillaring solutions

Four signals are observed in the spectra of partially neutralized Al solutions (Figure 1); the signal at 0 ppm is ascribed to octahedral Al^{3+} , the 5 ppm signal to oligomeric Al^{3+} , the signal at 63 ppm to tetrahedral Al^{3+} in the Keggin ion structure, and the 80 ppm signal to the external reference $\text{Al}(\text{OH})_4^-$. The evolution of the intensities of the first three signals with R for room

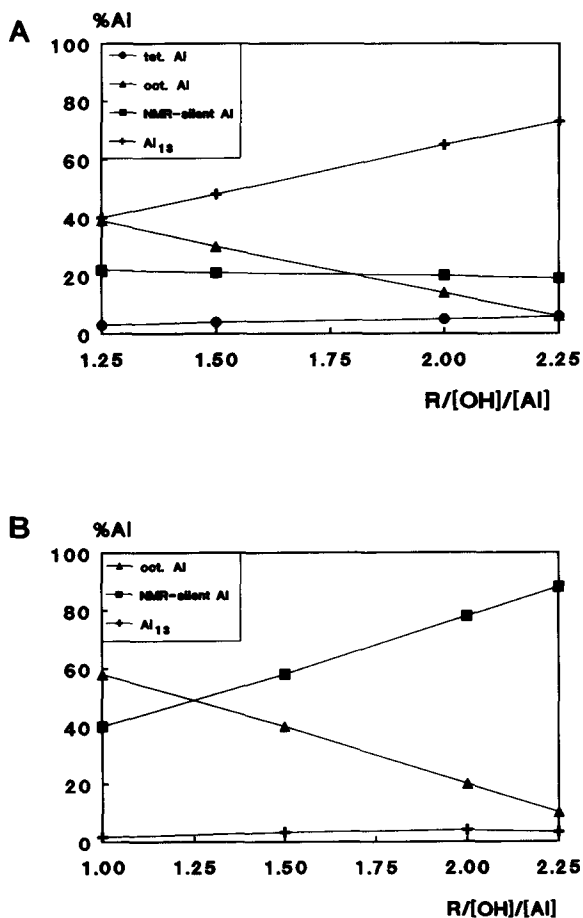


Figure 2. Relative amounts of Al species in solution as a function R for $[Al^{3+}] = 0.1$ M: A) room temperature; B) reflux. ●, tetrahedral Al; ▲, octahedral Al; ■, NMR-silent Al; +, Al_{13} = tetrahedral Al $\times 13$.

temperature and refluxed solutions is shown in Figure 2. In this figure, the intensities of octahedral Al are the sum of those of the 0 ppm and 5 ppm lines. The amount of Al in the Keggin ion is equal to the amount of tetrahedral Al, multiplied by 13. Figure 2 shows that, for the room temperature solutions, the amount of Al in the form of the Keggin ion increases linearly from 38% to 75% when R increases from 1.25 to 2.25. The amount of octahedral Al decreases from 38% to 6% and the amount of NMR-silent Al remains constant at about 20%. After reflux, the concentration of Al in the form of the Keggin ion is very low whatever the value of R ($< 3.5\%$). Most of the Al is NMR-silent (from 40% for $R = 1.25$ to 89% for $R = 2.25$) and the octahedral Al decreases from 60% for $R = 1.25$ to 10% for $R = 2.25$.

Ce^{3+} in the ratio $[Al]/[Ce] = 12$ has no measurable effect on the ^{27}Al signals of the room temperature solutions. The addition of ammonium acetate (NH_4Ac),

Table 1. Relative amounts of Al^{3+} species in solutions of $R = 1$ in the presence of NH_4OOCCH_3 .

[acetate] [Al^{3+}]	[Al], total mmol/dm ³	[Al], 0 ppm		[Al], 63 ppm		[Al], NMR-silent	
		mmol/ dm ³	mol%	mmol/ dm ³	mol%	mmol/ dm ³	mol%
0	100	38	38	43	43	19	19
1	91	6	7	—	—	85	93
5	66	10	15	—	—	56	85
10	50	—	—	—	—	50	100

however, leads, for $[Ac^-]/[Al^{3+}] = 1$, to the complete disappearance of the 0 and 63 ppm signals, leaving a weak broad line at around 5 ppm, which becomes unmeasurably small for $[Ac^-]/[Al^{3+}] = 10$ (Figure 1). The quantitative data, given in Table 1, show that Al-NMR-silent solutions are obtained.

The effect of aging was studied for 0.5 M and 1 M Al^{3+} solutions with $R = 2$ and 1, respectively. At 0.5 M Al^{3+} and $R = 2$, the solution is relatively stable over a 7-day period in that the amount of NMR-silent Al is constant at about 50% of the total Al content. However, there is a tendency of the concentration of octahedral Al to increase with time at the expense of the Keggin ion concentration (Table 2). The 1 M solution with $R = 1$ does not contain tetrahedral Al^{3+} . It is stable over a 6-day period at room temperature and contains 45 mol% octahedral Al^{3+} (0 ppm), 15 mol% oligomeric Al^{3+} (5 ppm), and 40 mol% NMR-silent Al^{3+} .

NH_4Ac has the same effect as in dilute solutions. The NMR-signals at 0 ppm and 63 ppm have completely disappeared at $[Ac^-]/[Al^{3+}] = 5$. The broad signal around 5 ppm increases in intensity to reach a maximum for $[Ac^-]/[Al^{3+}]$ in the range 1–5, and decreases for higher acetate concentrations, thus giving a solution that is Al-NMR-silent. The quantitative data are given in Table 3. In the presence of La^{3+} , most of the Al^{3+} is also NMR-silent. Only traces of octahedral, oligomeric and tetrahedral Al^{3+} are detected (Table 4).

Pillaring under dilute conditions

Only pillaring with refluxed solutions gives pillared clays with typical spacings of 1.8–1.9 nm (Figure 3). The d001 line is sharp for saponite, broad for laponite, and has an intermediate width in the case of hectorite. Also, the parent clays have a d001 line width that increases from saponite over hectorite to laponite (Figure 4). The line width is defined as the width in nm of the d001 line at half height. After calcination, the d001 lines of pillared saponite and laponite shift to lower values by 0.1–0.2 nm. For saponite, a concomitant increase of the line width from 0.3 nm to 0.5 nm (Table 5) was observed. The line widths of laponite, whether pillared or not, are too large to be discussed in terms of line-width variations. The pillared hectorite is not

Table 2. Relative amounts of Al³⁺ species in a 0.5 M solution with [OH]/[Al] = 2 as a function of aging.

Aging time in days	[Al], 0 ppm		[Al], 5 ppm		[Al], 62.5 ppm		[Al], NMR-silent	
	mol/dm ³	mol%	mol/dm ³	mol%	mol/dm ³	mol%	mol/dm ³	mol%
0	0.075	15	0.024	5	0.156	31	0.245	49
1	0.079	16	0.024	5	0.143	29	0.254	51
2	0.078	16	0.024	5	0.138	28	0.261	52
6	0.097	19	0.014	3	0.125	25	0.263	53
7	0.098	20	0.020	4	0.134	27	0.248	50

thermally stable and collapses to a spacing of 1.34 nm upon calcination at 550°C.

The surface area (Table 6) of saponite increases from 38 m²/g to 250–300 m²/g upon pillaring, decreasing to 190–247 m²/g after calcination at 550°C for 1 hr. The ranges are derived from observations made on several samples. Calcination at 550°C for 16 hr produces essentially a collapsed pillared saponite. Also, if the pillared saponite is left in air for long time periods, it slowly loses surface area equal to about 20–50 m²/g after 50 days. A similar observation has been reported by Chevalier *et al.* (1992).

There is no significant gain in surface area upon pillaring of laponite, while the surface area of pillared hectorite increases slightly (70 m²/g at most), but collapses almost completely after calcination at 550°C (Table 6).

The addition of Ce³⁺ to the pillaring solutions up to Ce/Al = 1 has no significant effect on the spacings and the thermal behaviour of the pillared clays. Chemical analysis shows that the amount of Ce³⁺ adsorbed by the clay is negligible. Thus, under our experimental conditions, Ce³⁺ is neither hydrolyzed nor incorporated in the Al-species taken up by the clay, and these Al-species are more selectively adsorbed than the Ce ions, which is in line with previous findings (Figueras, 1988).

Finally, before calcination, the pillared clays have a negligible CEC. After calcination, the CEC is in the range 0.24–0.31 meq/g, independently of the chemical composition of the pillaring solution.

Study of the pillaring conditions of saponite

The effect on pillaring in order of increasing concentrations of Al³⁺ and clay was studied in more detail

with saponite. If the pillaring solution is refluxed for 96 h instead of 1 hr, the same spacings but slightly larger line widths are observed. If the solution is aged for 4 days at room temperature, pillared products are obtained that are thermally unstable. Also, refluxing the pillaring solution in the presence of saponite gives the expected 1.8–1.9 nm spacing.

In Table 7, d001 spacings, line widths, and surface areas are reported of pillared saponites prepared with dilute, refluxed solutions of Al. This shows that, for successful pillaring, the minimum amount of Al³⁺ in the pillaring solution is 8–10 × CEC. This is not only obvious from the spacing, but also from the width of the d001 line. Well-pillared saponites should have a line width of about 0.30 nm after freeze-drying, increasing upon calcination to 0.50 nm. If the line widths exceed these values, an unstable material is produced.

There are several ways of increasing the concentration of Al³⁺ and clay in the pillaring process. The clay concentration can be increased by addition of clay powder to the pillaring solution 1) before reflux; 2) after reflux; 3) after reflux but in successive portions; or 4) by exchange of clay pastes (4–23 wt. % clay) with the pillaring solution followed by dialysis in the pillaring solution. All these methods give the required spacing after washing and freeze-drying of the pillared clays, provided the Al³⁺ concentration is at least 10 × CEC. This is illustrated in Figure 5. In Figure 5A, the d001 lines are shown for 2 g of saponite sample pillared with decreasing amounts of a 0.2 M Al pillaring solution so as to obtain the indicated weight percentages of clay in the suspensions. A strong line-broadening and decrease of the average position of the d001 line is observed with increasing wt. % of clay in suspension. This is because the [Al³⁺] decreases from 15 × CEC to 2.4

Table 3. Concentration of Al species in solution in the presence of ammonium acetate at R = 1.

[NH ₄ ⁺] [Al ³⁺]	[Al] total M	pH	[Al], 0 ppm		[Al], 5 ppm		[Al], 62.5 ppm		[Al], NMR-silent	
			mol/dm ³	mol%	mol/dm ³	mol%	mol/dm ³	mol%	mol/dm ³	mol%
0	0.5	3.2	0.270	54	0.045	9	0.022	4	0.163	33
0.5	0.25	3.6	0.091	35	0.044	18	0.010	4	0.105	42
1	0.25	3.9	0.036	14	0.060	24	0.005	2	0.149	60
5	0.25	5.4	—	—	0.073	29	—	—	0.177	71
10	0.25	5.8	—	—	0.013	5	—	—	0.237	95

Table 4. Effect of La³⁺ on concentration of Al species at R = [OH]/[Al + La] = 2.

[Al] [La]	[Al] total M	0 ppm		5 ppm		63.0 ppm		Undetected Al	
		mol/dm ³	mol%	mol/dm ³	mol%	mol/dm ³	mol%	mol/dm ³	mol%
10	0.313	0.030	10	0.003	1	0.017	5	0.263	84
5	0.294	0.008	2	—	—	0.014	5	0.272	93
2	0.250	—	—	—	—	—	—	0.250	100

× CEC, and an increasing fraction of saponite becomes un-pillared. After dialysis of the same pastes in pillaring solutions with [Al³⁺] = 15 × CEC, the expected d001 spacing is obtained (Figure 5B).

The amount of clay can also be increased together with [Al³⁺]; the required spacing is obtained as long as [Al³⁺] is at least 8 × CEC. This is shown in Figure 6 for A) a 13 wt. % suspension in 0.4 M Al, and B) a 23.5 wt. % suspension in 0.8 M Al. The preparation in concentrated media has been reported in a separate note (Schoonheydt and Leeman, 1992) and will not be further discussed. We only note that all these materials exhibit lower thermal stability than those prepared in dilute conditions. This is also illustrated in Figure 6 by the broadening of the d001 lines after calcination.

Study of the pillaring of hectorite

Table 8 lists the pillaring conditions of hectorite, which all lead to d001 spacings in the range 1.67–1.8 nm. These spacings are only generated after washing. The amount of Al adsorbed increases with the Al³⁺ concentration and with the amount of clay in the suspension. This is indicative of precipitation of Al in

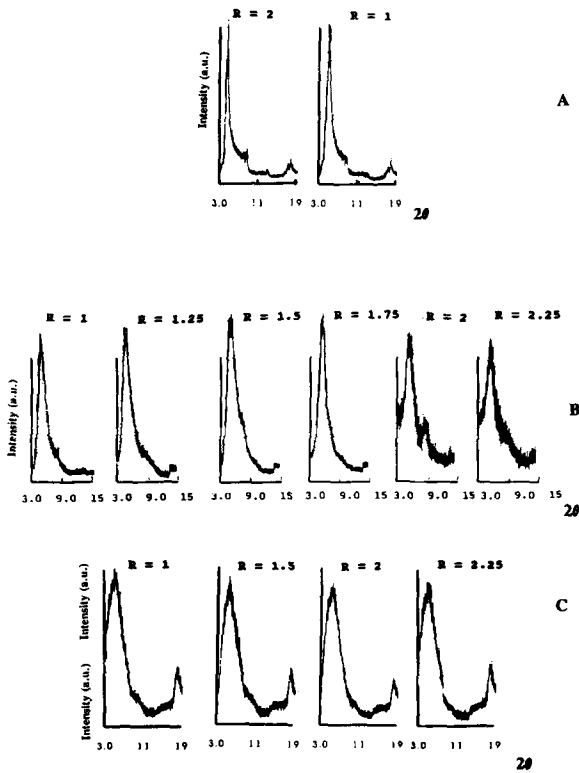


Figure 3. XRD patterns (CuKα) of clays pillared with refluxed solutions of different R-values: A) saponite; B) hectorite; and C) laponite.

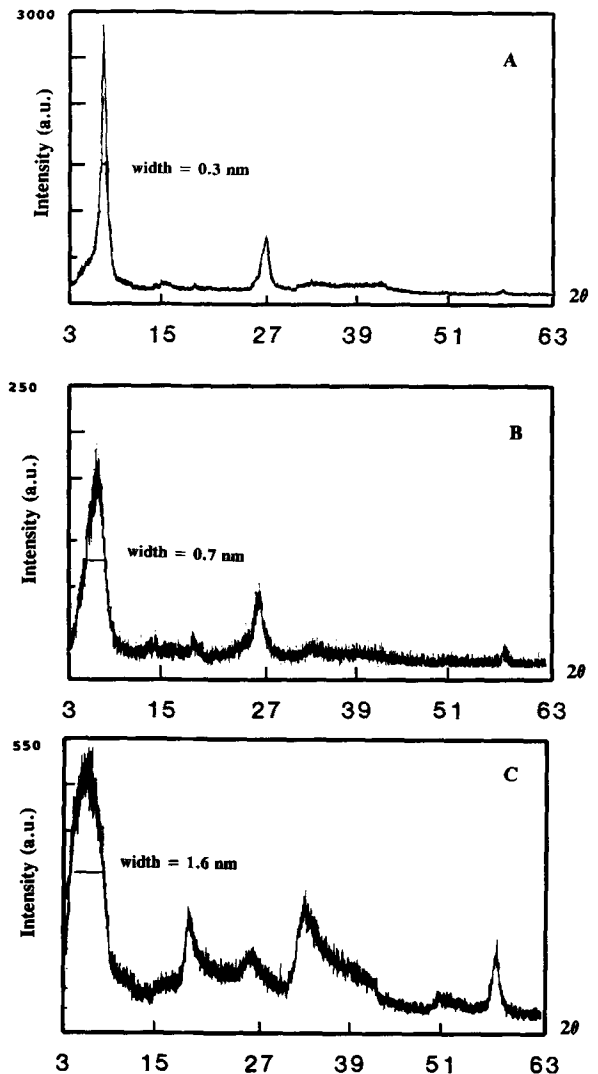


Figure 4. XRD patterns (CuKα) of A) saponite, B) hectorite, and C) laponite.

Table 5. d_{001} spacings (nm) and d_{001} line widths of pillared clays.

Calcination Temp/°C	Saponite				Hectorite		Laponite	
	R = 1		R = 2		R = 1	R = 2	R = 1	R = 2
	d_{001}	Width/nm	d_{001}	Width/nm				
Freeze-dried	1.87	0.29	1.89	0.27	1.83	1.60	1.71	1.64
250°	1.82	0.49	1.82	0.33	1.49	1.51	1.60	1.70
550°	1.82	0.50	1.75	0.28	1.34	1.34	1.74	1.66

conjunction with ion exchange. The only sample found to be thermally stable is the one from experiment N°4. Here, a 0.2 M Al solution was neutralized with a 0.4 M NaOH solution at a rate of 0.35 ml/min up to $R = 2$ and a pH of 4.01. The 1M NH_4Ac added up to $[\text{Ac}^-]/[\text{Al}] = 10$ raises the pH to 6. The pillaring is done with a presuspended clay (4g). The overall volume is 800 ml, and the concentration of Al^{3+} is 0.05 M. Pillaring is performed at 80°C, and the suspension is stirred for an additional 1 hr at room temperature. The freeze-dried material has a BET surface area of 210 m^2/g . After calcination at 600°C, the surface area is 222 m^2/g with a corresponding d_{001} spacing of 1.92 nm.

DISCUSSION

²⁷Al NMR of pillaring solutions

It is possible to prepare a whole range of partially neutralized Al solutions with varying amounts of NMR-visible octahedral, tetrahedral, and oligomeric Al^{3+} . The concentration of the Keggin ion is maximized in solutions prepared by the slow addition of NaOH to Al^{3+} solutions up to $R = 2.25$, the final $[\text{Al}^{3+}]$ being 0.1 M. Increase of $[\text{Al}^{3+}]$, reflux, and addition of NH_4Ac or La^{3+} drastically decrease not just the Keggin ion concentration, but also the overall amount of NMR-visible Al. The solutions are relatively stable with time, with only minor changes in relative concentrations of NMR-visible Al over 7 days.

Reflux destroys the Keggin ion almost completely. It leads to a small increase of octahedral Al (0 ppm), but a drastic increase of the concentration of NMR-silent Al. Presumably, NMR-silent oligomeric complexes are formed, composed of $[\text{Al}(\text{OH})_{2.5}]^{0.5+}$ units (Akitt and Elders, 1988), the average positive charge per Al being very close to that of Al in the Keggin ion (+0.54). The structure of these polymeric species cannot be elucidated on the basis of NMR results alone. A two-dimensional polymer of pseudo-octahedral Al has our preference in view of the absence of the 1.8–1.9 nm spacing before washing (Hem and Robertson, 1967). It is only with concentrated solutions that 1.8 nm can be obtained before washing (Schoonheydt and Leeman, 1992). In that case, one could envisage, as in Bottero *et al.* (1987, 1982), that the Al polymer is a cluster of Keggin ions.

In the presence of NH_4Ac both the 0 ppm and the 63 ppm signals disappear, while the 5 ppm signal goes

through a maximum with increasing $[\text{Ac}^-]$. This behavior shows that the Keggin ion and the monomeric octahedral Al^{3+} are transformed into oligomeric species, which become almost totally NMR-silent at $[\text{Ac}^-]/[\text{Al}^{3+}] = 10$. Ac^- is known to attack $\text{Al}[\text{H}_2\text{O}]_6^{3+}$ to form $[\text{H}_2\text{O}]_4\text{Al}[\lambda\text{-OH}]_2\text{Al}[\text{H}_2\text{O}]_4^{4+}$ below $[\text{Ac}^-]/[\text{Al}^{3+}] = 1.5$ and $\text{Al}_2[\text{OH}]_2[\text{Ac}]_4$ above $[\text{Ac}^-]/[\text{Al}^{3+}] = 1.5$ (Akitt and Milic, 1984; Thompson *et al.*, 1987). Our data show that Ac^- attacks all NMR-visible Al species. Two reactions can be envisaged: 1) abstraction of a proton from coordinated water to form a coordinated OH^- and acetic acid; 2) substitution of H_2O and/or OH^- ligands by Ac^- . We assume that the former is predominant below the pK_a of HAC and the latter above the pK_a where Ac^- is dominant. In any case, NMR-silent, oligomeric acetate complexes are formed with highly distorted octahedral coordination spheres, both from the Keggin ion and from the monomeric octahedral Al^{3+} . La^{3+} and Ce^{3+} are not hydrolyzed under the pH conditions of the present Al solutions (Charlot, 1957), and incorporation into Al clusters is not evident, certainly not under dilute conditions. This is what has been observed for Ce^{3+} . In the more concentrated conditions of the La^{3+} experiments, all NMR signals are affected, showing that La^{3+} is incorporated in all types of Al clusters, irrespective of their shape and size.

Pillaring

In general, successful pillaring requires 1) partially polymerized Al solutions with an effective charge of about +0.5 per Al; 2) suspensions, relatively dilute in Al and in clay to promote ion exchange and to avoid precipitation; 3) washing; 4) a heat-resistant spacing of 1.80 nm; and 5) surface areas of about 180–300 m^2/g .

To achieve 4) and 5), the range of conditions of ion exchange as expressed by 1) to 3) is narrower for hectorite than for saponite. The main reasons seem to be

Table 6. Surface areas (m^2/g) of pillared clays.

Calcination Temp/°C	Saponite		Hectorite		Laponite	
	R = 1	R = 2	R = 1	R = 2	R = 1	R = 2
Parent clays	37		110		290	
100°	301	300	159	183	307	275
550°	247	214	127	133	274	264

Table 7. Influence of Al^{3+} concentration on spacing and surface area of pillared saponite.

[Al^{3+}] Multiple of CEC First series	d001 nm		Surface area m^2/g	
	2	1.66		18
4	1.84		173	
8	1.88		295	
15	1.86		300	

Second series	Freeze-dried		After calcination at			
	d_{001}/nm	Width/nm	250°C		550°C	
			d_{001}	Width/nm	d_{001}	Width/nm
10	1.87	0.36	1.77	0.52	1.85	0.95
15	1.87	0.29	1.82	0.49	1.82	0.50
20	1.93	0.29	1.80	0.47	1.82	0.35
30	1.91	0.30	1.77	0.45	1.82	0.53

1) the difference in crystallinity between saponite and hectorite as evidenced by the sharper width of the d001 lines of the parent and pillared saponite materials (Figures 3 and 4), and 2) the origin and amount of the layer charge. Hectorite has a smaller charge and swells better in water. This means that the individual platelets diffuse independently of each other, making it more dif-

icult to organize them around the pillaring species in a regular fashion. Addition of NH_4Ac , La^{3+} or Ce^{3+} increases the ionic strength of the medium and reduces the thickness of the double layers around the clay particles, thus promoting pillaring. At the same time the competitive ion exchange phenomenon, as suggested by Figueras *et al.* (1990b) may be operative. Our data

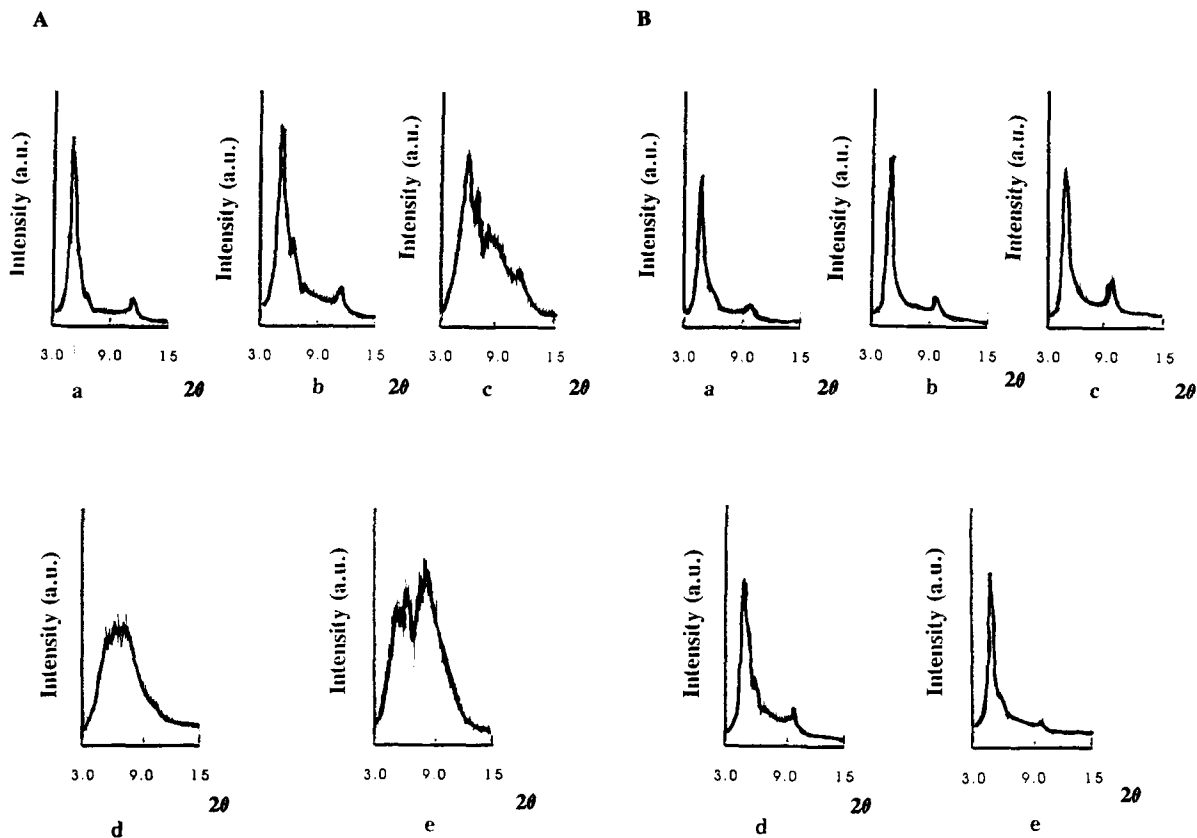


Figure 5. Relative intensities of d001 lines of pillared saponites at increasing clay concentration, but constant Al^{3+} concentration and $R = 2$. Weight % clay: a = 4; b = 9; c = 13; d = 17; e = 20. The spectra in B are obtained after additional dialysis in Al^{3+} solutions with $[Al^{3+}] = 15 \times CEC$.

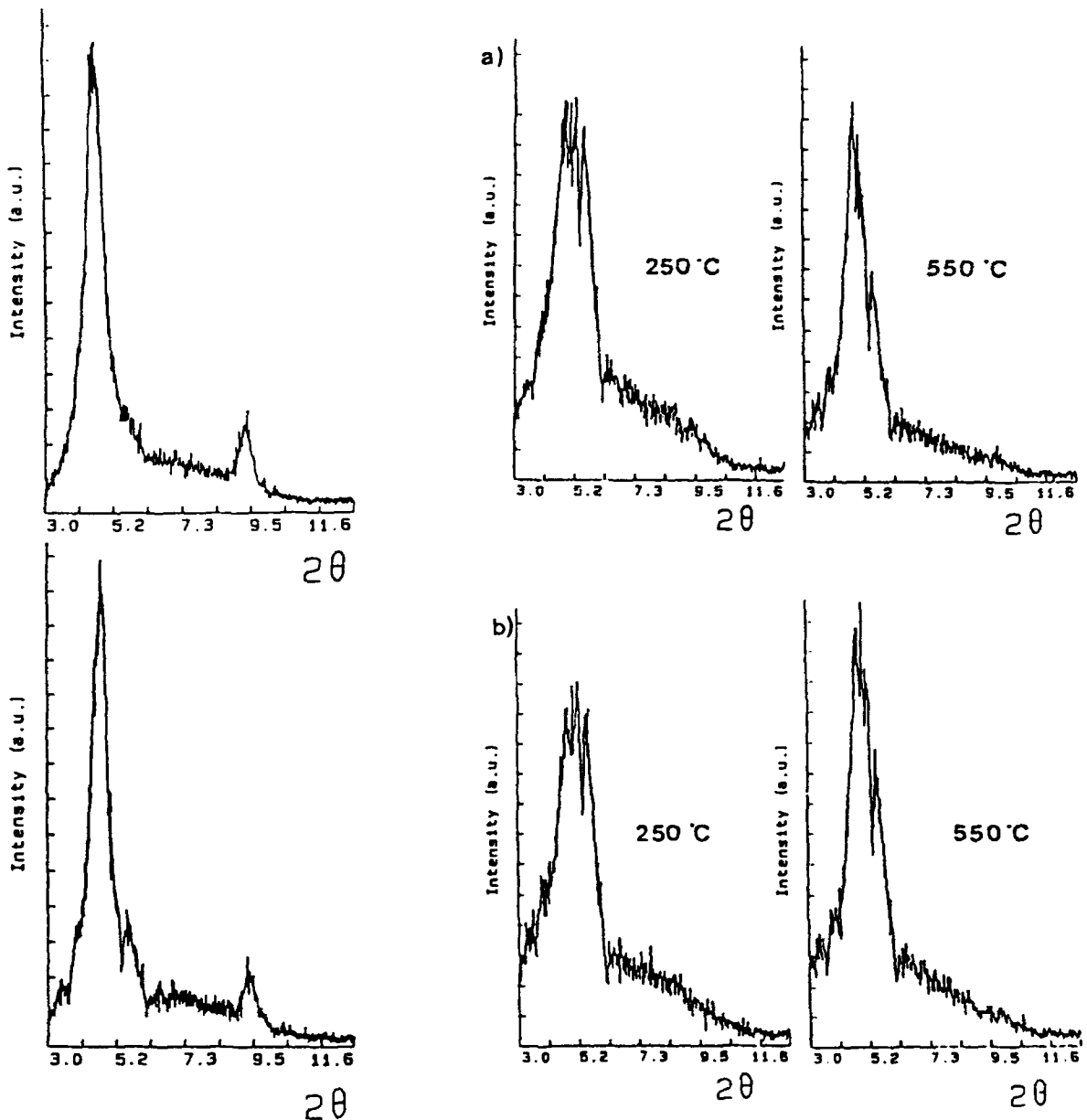


Figure 6. XRD patterns of pillared saponite: a) 13 wt% clay in 0.4 M Al^{3+} at $R = 2$; and b) 23.5 wt% clay in 0.8 M Al^{3+} at $R = 2$.

with Ce^{3+} do not confirm this hypothesis, but more systematic work is necessary for a definite answer.

According to criteria 1) through 5), the pillared laponite obtained cannot be considered a true pillared material. The d_{001} line width of the parent and pillared material is too large to make any conclusion about the spacing. Since the surface area before and after pillaring is the same, this criterion cannot be used. It is a reasonable hypothesis to assume—in view of the large N_2 -BET surface area—that the pillars are deposited both on the interlamellar surface and on the external surface of laponite. In that case, the distinction between both

types of surfaces becomes obscure. The observation by Occelli *et al.* (1987) that a pillared laponite has mainly macroporosity, is an indirect confirmation of our conclusions. True pillaring of laponite requires selective deposition of the pillaring agent on the interlamellar surface, and the conditions to achieve this still must be explored.

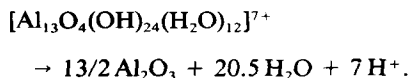
Washing the pillared clays decreases the ionic strength and increases the pH slightly. This induces a swelling of the clay, allowing polymerization of Al into a three-dimensional structure of 1 nm thickness with creation of the typical 1.8–1.9 nm spacing. An alternative hy-

Table 8. Composition of pillaring solutions and d_{001} spacings of pillared hectorite.

N:	[Al ³⁺] M	[OH ⁻] M	[OH ⁻] [Al ³⁺]	[Ac ⁻] [Al ³⁺]	Reflux time in min	pH	g clay/ 100 ml	d_{001} nm	mmol Al/g
2	0.50	1	2	0	30	3.49	1	1.73	2.7
3	0.10	0.2	2	0	0	4.01	1.3	1.70	4.9
4	0.05	0.1	2	10	0	6.00	0.4	1.77	2.1
6	0.50	1	2	0	120	3.47	4.0	1.80	3.9
7	0.50	1	2	10	30	4.50	4.0	1.70	5.6
8	0.50	—	2	—	45	4.68	—	1.67	—
10	0.67	1.33	2	0	120	3.43	4.0	1.67	—

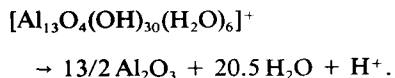
pothesis is that the Al-pillars migrate into the interlamellar space upon washing. This is however not very likely, as pillaring in concentrated Al solutions gives 1.8 nm without washing, showing that Al species are indeed exchanged in the interlamellar space and rearrange on the spot during the washing (Schoonheydt and Leeman, 1992).

Finally, it is remarkable that the spacing and the surface area are largely maintained in a good pillared material after calcination in view of the severe dehydration-dehydroxylation reactions, which were visualized for the Keggin ion by Vaughan and Lussier (1980) as:



If all the protons migrate into the clay structure, an acidic pillared clay should be recovered with a CEC exactly equal to that of the parent material. This is not the case. Indeed, values of 0.25–0.31 meq/g are found. This means 1) that few protons are liberated, which could indicate that the pillaring agent is not only the Keggin ion and/or the pillar may retain some residual positive charge; 2) that not all the protons are exchangeable; and 3) that dehydroxylation occurring upon calcination is only partial.

An alternative view is that the pillaring species is not the Keggin ion, because successful pillaring has been achieved with Al solution free of Al_{13}^{7+} . This can be visualized for a Keggin ion structure with a positive charge of one as:



The ratio of $\text{Al}^{3+}:\text{H}^+$ is now 13. The real situation is not probably that simple, in that more than one type of Al species is present and these species must not all have the Keggin ion structure.

CONCLUSIONS

The conditions for the preparation of pillared clays have been explored and criteria for assessing the quality of the pillared products have been proposed.

Any partially hydrolyzed Al solution with an average charge per Al of +0.5 is a suitable starting solution for ion exchange of the cationic pillar on the interlamellar surface. The quality of the pillared product after washing can be appreciated from the position and the width of the d_{001} line before and after calcination.

The pillaring conditions are clay-dependent. This can be traced back to the quality of the parent material as evidenced by the width of its d_{001} XRD peak.

The nature of the Al species that are exchanged on the surface is unknown. The ultimate test is the exchange of $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ itself which will be reported in part II.

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