THE Al PILLARING OF CLAYS. PART II. PILLARING WITH $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$

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Abstract—Hectorite and saponite are exchanged with $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ and the amount of Al^{3+} adsorbed and Na^+ released are followed as a function of the exchange conditions. On saponite the reaction is a pure ion exchange with 2–2.15 mmol Al^{3+}/g adsorbed and release of 0.80 mmol Na^+/g. On hectorite the ion exchange is accompanied by supplementary hydrolysis-polymerization of Al_{13}. When excess Al is offered in the form of Al_{13}, ion exchange is incomplete and is accompanied by precipitation and polymerization of Al_{13} on the surface of both hectorite and saponite. The typical spacing of 1.8 nm is developed after washing, when at least 1.3–1.4 mmol Al^{3+}/g is adsorbed. Above a loading of 2.2–2.5 mmol/g the 1.8 nm spacing is obtained without washing. Only pillared saponite with a loading of at least 1.9 mmol Al^{3+}/g is thermally stable up to 550°C.

Key Words—Aluminium, Hectorite, Keggin ion, Pillaring, Saponite.

INTRODUCTION

Pillaring of clays with Al is thought to be an ion exchange process of the major pillaring agent $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, the so-called Keggin or Al_{13} ion (Plee *et al* 1985; Pinnavaia *et al* 1984). This hypothesis is, however, based on pillaring with solutions that contain a range of Al polymers, and has been challenged by more recent findings. Indeed, (1) pillaring can also be achieved with solutions that do not contain the Keggin ion (Schoonheydt *et al* 1993); and (2) the typical spacing of 1.8–1.9 nm becomes visible only after washing (Schutz *et al* 1987; Schoonheydt and Leeman 1992; Figueras *et al* 1990), indicating important reorganisation of the adsorbed Al species upon washing of the pillared clays.

Recently pillaring was attempted with solutions of Al_{13}, $GaAl_{12}$, $GeAl_{12}$ and Ga_{13}, all of the Keggin ion structure (Seefeld *et al* 1988, 1991a, 1991b; Bradley and Kydd 1991; Gonzalez *et al* 1991, 1992). Seefeld *et al* (1988, 1991a, 1991b) unambiguously showed that these Keggin ions were ion exchanged on smectites. The reaction was not fully reversible due to polymerization on the surface. The degree of polymerization followed the order $GeAl_{12} > GaAl_{12} > Al_{13}$. Pillared products were obtained, the thermal stability of which followed the stability of the Keggin ions: $Ga_{13} < Al_{13} < GaAl_{12}$. In addition, Gonzalez *et al* (1991, 1992) found that not all the adsorbed Ga^{3+} took part in the pillaring. Indeed, the amount adsorbed exceeded that necessary for charge neutralization with the Keggin ions. The average charge per trivalent cation ranged between 0.18 and 0.32, as compared to 0.54 for the Keggin ion. Either the Keggin ions are not the only species adsorbed, or they hydrolyze further on the clay surface, presumably during washing.

To elucidate further the problem of the ion exchange and pillaring in the case of Al^{3+}, we have synthesized Al_{13} solutions and determined the exchange isotherms for saponite and hectorite, taking great care in analyzing the solutions before and after exchange with ^{27}Al NMR and atomic absorption spectrometry (AAS). The effect of washing was studied by X-ray diffraction (XRD) and the thermal stabilities of some of the products were determined.

EXPERIMENTAL

Clays

Saponite and hectorite source clays from the Clay Minerals Society were transferred in their Na^+ forms by repeated dialysis against 1 M NaCl solutions. After washing Cl^- free ($AgNO_3$ test), the clays were fractionated by centrifugation and the fraction <0.5 μm was retained and freeze-dried. The cation exchange capacities (CEC) were determined with the ^{22}Na method as 0.66 and 0.55 mmol Na^+/g respectively (Peigneur *et al* 1975).

Al_{13}

The method of Furrer *et al* (1992) was followed. 250 ml of a 0.25 M $AlCl_3$ solution was heated in a waterbath to 80°C. Then, 600 ml of a 0.25 M NaOH solution were added at a rate of 4 ml/min while stirring at 300 rpm. This solution was labelled as Solution I.

After cooling 625 ml 0.1 M Na_2SO_4 was added and during continuous stirring at 830 rpm a precipitate was formed over a two day period. This precipitate was filtered off and the supernatant was called Solution II. The precipitate, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}] [(SO_4)_{7/2}]$, was washed with distilled water and freeze-dried.

The precipitate was redissolved with $Ba(NO_3)_2$ in

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1200 ml H_2O in an ultrasonic bath for 4½ hours. Excess, or the stoichiometric amounts of $Ba(NO_3)_2$, were used for the precipitation of sulfate anions assuming that the precipitate was pure Al_{13}. It was found however, that the Al_{13} precipitate contained small amounts of Na^+. The $BaSO_4$ precipitate was removed on a Whatman No. 42 filter, followed by centrifugation at 8000 rpm for 15 min. For separation of the finest particles an ultrafilter with pore diameter of 0.1 μm was used. The Al_{13} solution obtained was Solution III.

Solutions I, II and III were investigated with ^{27}Al NMR to identify quantitatively the various NMR-visible Al species in solution before and after exchange. The Al and Na contents of Solution III were determined by AAS.

Exchange

100 mg (dry weight) of clay was put in dialysis membranes together with 10 ml H_2O. These suspensions were shaken for a couple of hours on an end-over-end shaker to allow the clay to swell. Then they were put in 60 ml of pillaring solutions with increasing amounts of Al. Solutions I and III were used as pillaring solutions.

Exchanges were also performed at different Al : clay ratios, either by decreasing the amount of clay at constant initial [Al], or by varying the amount of Al offered to 1 g of clay. For all the exchanges the exchange time was 48 hours. The supernatant solutions were analyzed for Na^+ (only in the case of Solution III) and Al^{3+} by AAS. The pH was determined and the ^{27}Al NMR spectra were recorded.

In some cases the amounts of clay and pillaring solution were increased to obtain enough material for subsequent investigation of the thermal stability, surface area and spacing.

Techniques

^{27}Al NMR spectra were recorded on a Bruker AMX 300 apparatus at 78.208 MHz. The reference was $Al(OH)_4^-$ in D_2O with a single line at 80 ppm. The intensities of the lines were obtained by comparison of the integrated line intensities with that of the 0 ppm line of a $AlCl_3 \cdot 6H_2O$ solution of known concentration. The solid state ^{27}Al MAS NMR spectra of the sulfate salt of the Keggin ion (precipitate from Solution II) were taken on a Bruker MSL 400 instrument at 104.229 MHz. Short radiofrequency pulses of 0.6 ns (pulse angle of ca. 10°), 0.1 s recycle delays and different spinning rates were used.

XRD spectra were recorded on a Siemens Kristalloflex 700 with $CuK\alpha$ radiation and with a position sensitive detector. The standard settings were 40 kV and 20 mA. Surface areas were obtained from the dynamic, massflow controlled adsorption of N_2 at liq N_2 temperature on a Coulter Omnisorp 100 apparatus after in situ evacuation of the samples at 100°C, 200°C
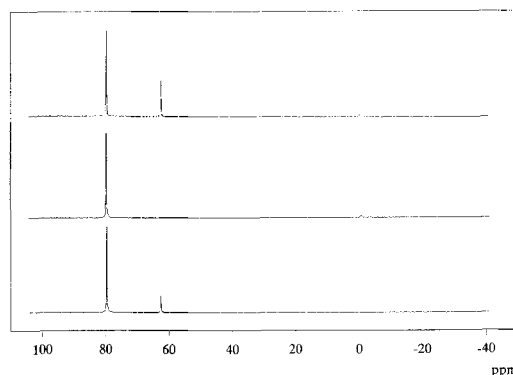

Figure 1. ^{27}Al NMR spectra of Solution I (1), Solution II (2) and of Solution III (3). The line at 80 ppm is due to the $Al(OH)_4^-$ reference.

and 300°C. Surface areas and pore volumes were calculated according to the BET equation, the t-method and the MP-method (Lippens and de Boer 1965; Coulter 1991).

RESULTS

NMR of the Keggin ion

Typical ^{27}Al NMR spectra of Solutions I, II and III are shown in Figure 1. Three lines are visible: the reference line of $Al(OH)_4^-$ at 80 ppm, the 62.5 ppm signal of tetrahedral Al^{3+} in Al_{13}, and a weak broad line around 0 ppm, ascribed to octahedral, monomeric Al^{3+}. The spectra of Solution I contain all three signals. Solution II is characterized by the absence of the 62.5 ppm signal, while Solution III contains the 62.5 ppm signal, but the 0 ppm line is absent. Almost all the Al in the solutions is NMR-visible. Solution I contains 73.5 mmol Al^{3+} as analyzed by AAS; all our NMR measurements give 61–70 mmol Al in the form of the Al_{13} cluster and 1–2 mmol octahedral Al. Solution II contains 0.4–1.5 mmol octahedral Al^{3+}, while Solution III contains 41–52 mmol Al as Al_{13}. This shows that in Solution I, 83–95% of the Al is in the form of the Keggin ion which is quantitatively precipitated with sulfate, leaving some of the octahedral Al in solution. Upon redissolving, the Al_{13} cluster is not destroyed. The yield of Al^{3+} in Solution III is 55–70% of the initial amount of Al in solution. In some cases small amounts of Na^+ were analyzed in Solution III, probably due to coprecipitation.

Figure 2 shows the ^{27}Al MAS NMR spectrum of the sulfate salt of the Keggin ion, measured at two spinning rates. One notices a sharp signal of tetrahedral Al at 60.6 ppm and the broad asymmetric signal of octahedral Al with spinning side bands (indicated by *). The dependence of the form of the latter on the spinning rate is evidence for strong quadrupolar interaction. Only in a high magnetic field (e.g., 9.4 T) and at high spinning rates (15 kHz) is the quadrupolar second-
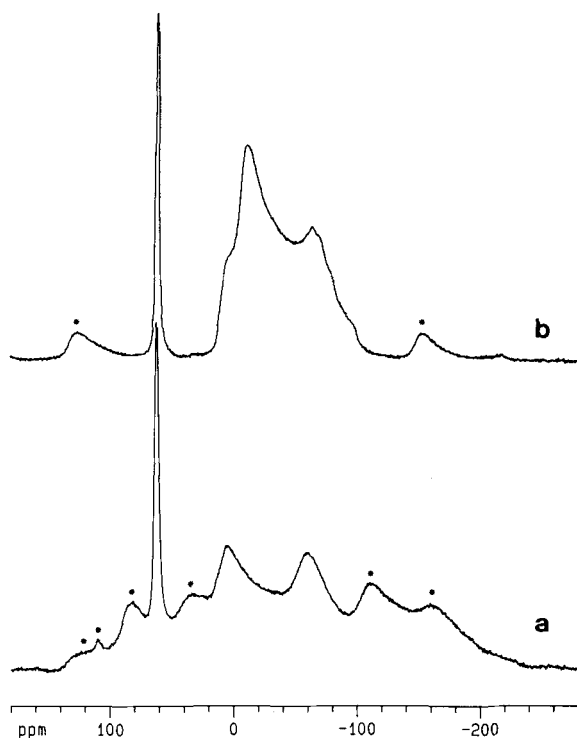
Figure 2. ^{27}Al MAS-NMR spectra of $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]$ $(SO_4)_{7/2}$ taken at different spinning speeds: (a) 5 kHz; (b) 12.5 kHz. Bands indicated by an * are spinning side bands.

Figure 3. Uptake of Al by saponite and by hectorite from Solution I.

order broadening sufficiently reduced to observe the full intensity of the octahedral line (Figure 2b). With due consideration of the intensities of the spinning side bands, the ratio of the intensity of the octahedral Al line to the tetrahedral one is close to 12, as expected from the structure of the Keggin ion.

Pillaring

Both Solutions I and III can be used as pillaring solutions. In the case of Solution I some monomeric, octahedral Al^{3+}, Na^+ and Cl^- are present besides Al_{13}. Solution III is a solution of Al_{13} which might contain some residual Na^+ and excess Ba^{2+} from the redissolution of the sulfate salt of Al_{13}. Figure 3 shows the exchange isotherms as the amount of Al adsorbed per g of dry saponite and hectorite against the concentration of Al in the equilibrium Solution I. A very selective uptake is seen, which tends to a maximum around 2 and 2.15 mmol Al^{3+}/g for saponite and hectorite respectively.

In a second series of experiments the exchange isotherms were repeated and XRD patterns were taken of samples with different Al loadings after washing and freeze-drying. Only the d_{001} line was recorded and the corresponding spacings are reported in Table 1. For saponite the line widths at half maximum are also given. This was not possible for hectorite, because the
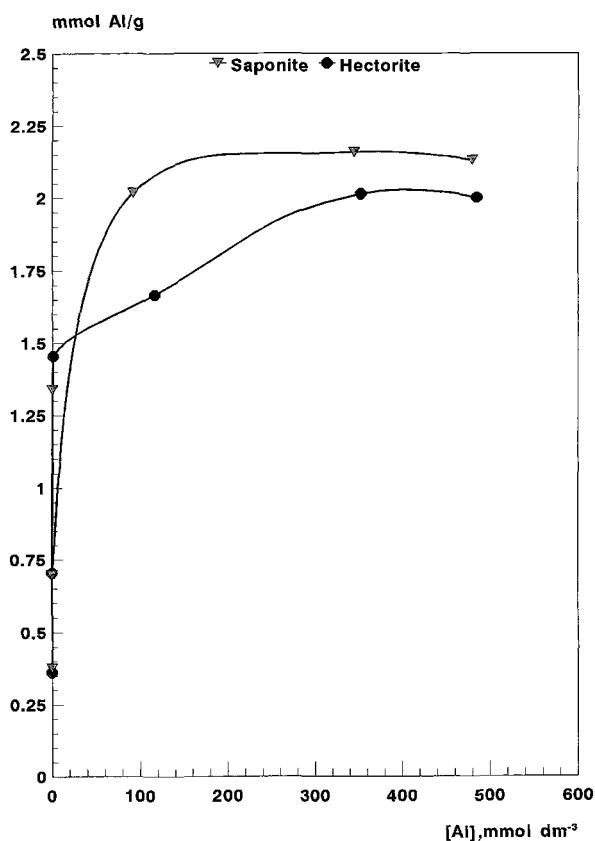
lines were too broad. The data for saponite show that (1) at small loadings the d_{001} line broadens without change of position; (2) the increase of the spacing from 1.25 nm to 1.90 nm occurs for loadings in the range 0.70–1.40 mmol Al^{3+}/g; (3) the d_{001} line sharpens for loadings above 1.40 mmol Al^{3+}/g, but does not change position. For hectorite the data are not so clear, but the jump of the spacing to 1.80 nm occurs in the same range of loadings as for saponite.

In a third set of experiments two pillared saponites were prepared with Solution I, as described for the

Table 1. Al^{3+} loading and d_{001} values.

	Saponite			Hectorite	
Al^{3+} mmol g^{-1}	d_{001}/nm	LWHM[1]		Al^{3+} mmol g^{-1}	d_{001}/nm
0	1.27	18		0	Very broad
0.36	1.24	23		0.36	Very broad
0.70	1.25	23		0.69	Very broad
1.43	1.88	27		1.36	1.76
1.95	1.90	15		1.80	1.79
2.18	1.92	15		2.00	1.80
3.02	1.90	12		2.83	1.76

[1] In arbitrary units.
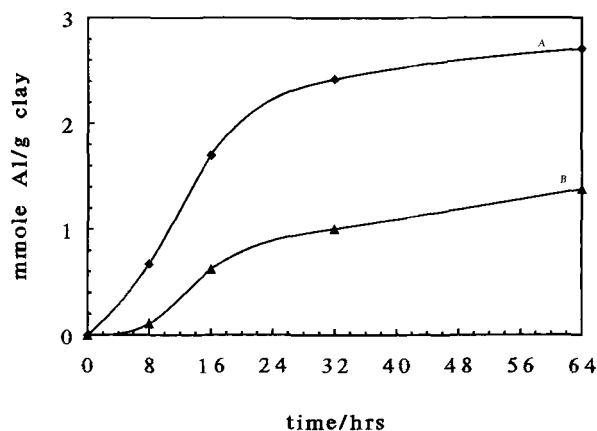
Figure 4.   Time dependence of the uptake of Al_{13}^{7+} by saponite: A, 1500 μmol Al^{3+}; B, 150 μmol Al^{3+}.

exchange isotherms. One sample of about 100 mg saponite was contacted with a solution of 150 μmol Al^{3+}, the second sample of about 100 mg with 1500 μmol Al^{3+}, and the exchange in dialysis membranes was followed as a function of time. The data are shown in Figure 4. In both cases, there is a progressive increase of the loading with time, followed by a levelling off after 32 hours of contact. In the 150 μmol case, Al^{3+} is quantitatively taken up, but for the 1500 μmol case not, in agreement with the data of the isotherm (Figure 3). The XRD spectra after washing and freeze-drying are shown in Figure 5. In the high loading case the d_{001} line is at 2.0–2.1 nm, independent of the exchange time. However, it sharpens upon prolonged contact of the clay with the Al_{13} solution. In the low loading case, the original 1.25 nm line broadens at its low angle side (high spacings) with exchange time. It is only after 64 h of exchange that the typical spacing of a pillared clay appears.

Figures 6 and 7 show the exchange isotherms obtained from Solution III for saponite and hectorite respectively. As for Solution I exchanges, a very selective uptake of Al is seen up to 2–2.2 mmol Al^{3+}/g, followed by a slight leveling off and a steady increase of the amount adsorbed with increasing amounts of Al^{3+} in the equilibrium solution. Initially, the amount of Na^+ released follows the amount of Al^{3+} adsorbed, but it quickly levels off around 0.8 mmole/g for saponite and 0.4 mmole/g for hectorite, and decreases slightly, when more Al^{3+} is adsorbed. The maximum amount of Na^+ released is somewhat higher than the [22]Na-CEC for saponite and somewhat below the [22]Na-CEC for hectorite.

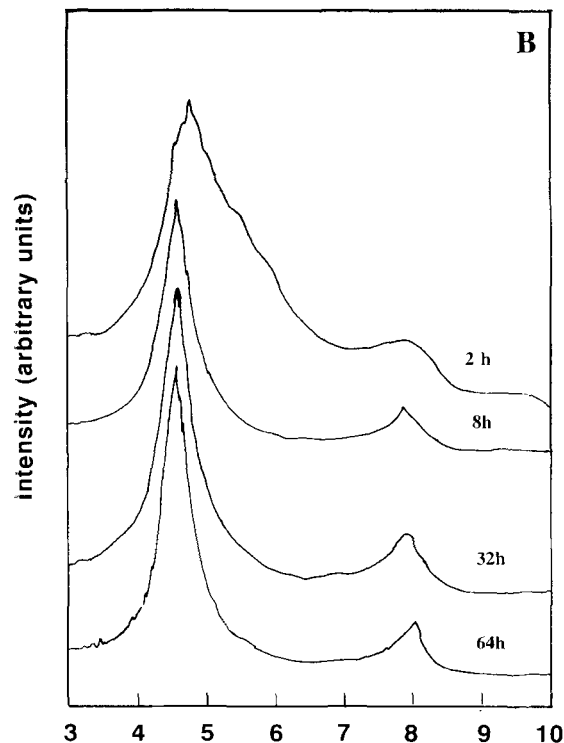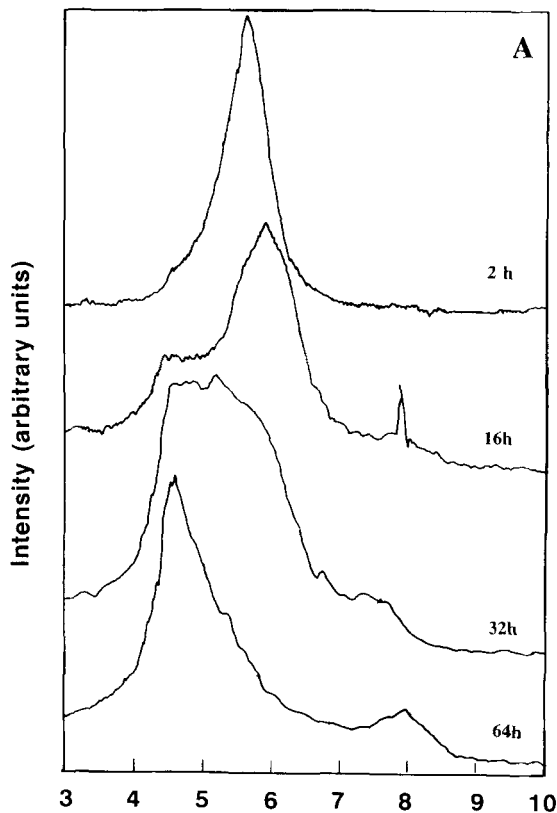$\longrightarrow$

Figure 5.   Evolution of the XRD spectra of saponite with time of exchange: A, 150 μmol Al^{3+}; B, 1500 μmol Al^{3+}.

mmol Al/g   **Na⁺**
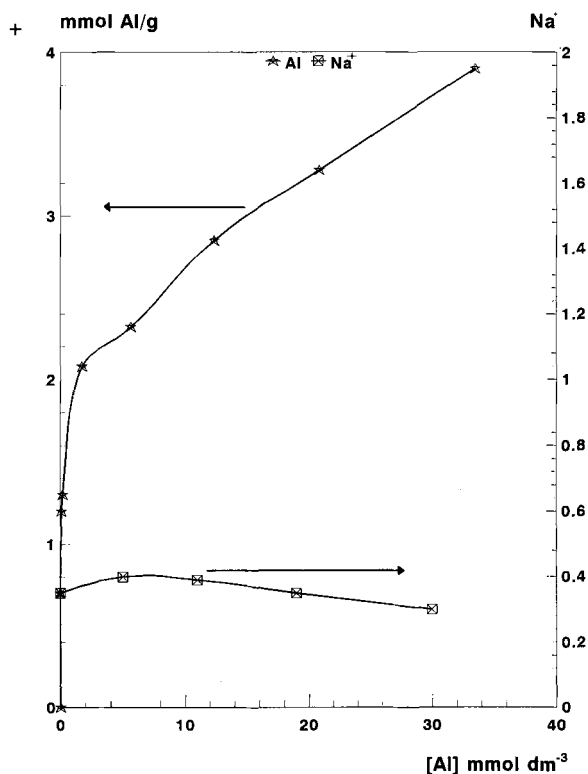

Figure 6. Uptake of Al and release of Na upon contact of saponite with Solution III.
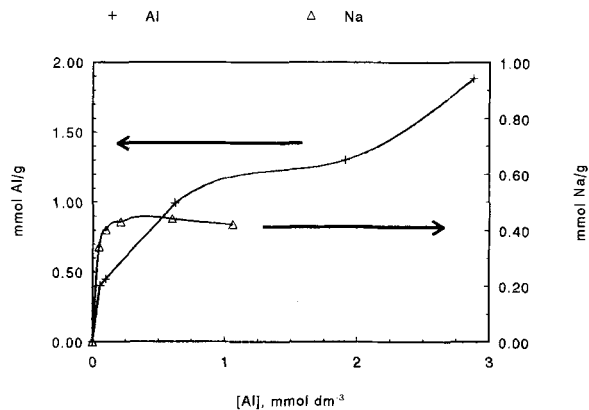

Figure 7. Uptake of Al and release of Na upon contact of hectorite with Solution III.

the following trends: (1) the amount of Al adsorbed increases with increasing amount of Al offered per unit weight of clay, whatever the [Al_{13}] in solution; and (2) at constant amount of clay in suspension, the amount

After exchange, the solutions that contain Al^{3+} are characterized by the 62 ppm signal of Al_{13} only. The ^{27}Al NMR line intensity at 62 ppm, when converted to [Al], corresponds to the amount of Al in solution found by AAS. This shows that Al_{13} is indeed adsorbed, that it is stable in solution during exchange, and that all the Al in solution is NMR active.

The small Al loading regime was investigated in more detail, as shown in Figure 8, where the amount of Al^{3+} adsorbed is plotted against the amount of Na^+ released. The straight line is for a stoichiometric exchange of Al_{13}^{7+} with Na^+. Although there is some scatter of the points, the exchange is close to stoichiometric for saponite and hectorite at the lowest loadings. Some series of experiments gave systematically more release of Na^+ than uptake of Al^{3+} in this low loading regime. This might be due to variability in the composition of the exchange solution, but we did not investigate this aspect further.

One phenomenon that may play a role in pillaring of clays at high Al-loadings is precipitation of Al on the clay particles. If this occurs, the amount of Al_{ads} is expected to be proportional to the exposed surface area or to the amount of clay in the suspension. This was investigated in two series of experiments. In the first, decreasing amounts of clay were offered to solutions (type III) of constant [Al_{13}]. The results of Table 2 show
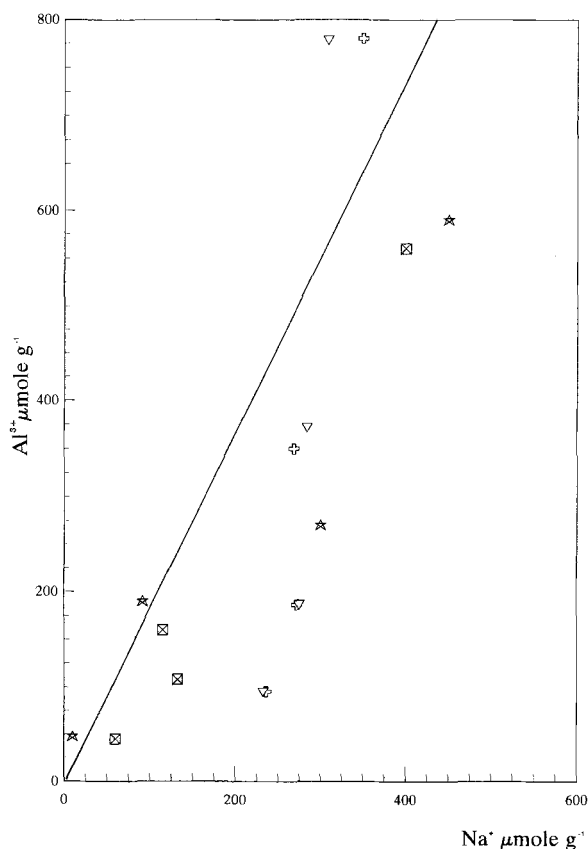

Figure 8. Uptake of Al^{3+} versus the release of Na^+ at small loadings: ☆, saponite; □ ▽ +, hectorite. The points with the symbols ▽ + were corrected for some residual Na^+ in the Al_{13} solutions of type III.

Table 2. Adsorption of Al_{13}: influence of amount of clay.

Clay	Clay mg	Al/g initial mmol	pH eq.	Al/g adsorbed mmol
Hectorite	99	1.08	5.39	0.48
	54	1.98	5.46	0.86
	27	3.95	5.46	1.76
	108	19.75	5.19	1.51
	50	42.66	5.24	1.70
	27	79.00	5.26	2.19
Saponite	108	1.43	5.34	0.41
	49	3.15	5.22	0.81
	28	5.60	5.14	1.33
	117	26.40	4.83	0.57
	56	60.21	4.83	1.96
	26	129.78	4.84	2.96

of adsorbed Al increases with the concentration of Al in solution.

In the second series of experiments, a fixed amount of clay (1 g) was exposed to solutions (type III) containing increasing amounts of Al^{3+}. The results, given in Table 3, confirm the observations in Table 2, that the amount of Al adsorbed increases with the amount of Al offered per g of clay.

Characterization

Three pillared hectorites and saponites with different Al loadings were prepared with solutions of type III for an XRD examination of the washing process and for a study of the thermal stability. The XRD results are summarized in Table 4. If the amount of adsorbed Al is in the range 0.35–0.52 mmole/g or 0.027–0.040 mmole Al_{13}/g, no pillared clay is obtained in that the spacings are 1.50 nm and 1.26 nm for hectorite and saponite, respectively, and do not change upon washing. When 1.37–2.50 mmole Al/g is adsorbed (or 0.1–0.19 mmole Al_{13}/g), a pillared clay with typical 1.78–1.85 nm spacing is obtained only after washing. Finally, when 2.60–4.10 mole Al/g (0.20–0.32 mmole Al_{13}/g) are adsorbed, a pillared clay is produced even without washing. In this last case, washing increases the spacing by 0.15 nm in the case of hectorite, but not in the case of saponite.

Table 3. Al_{13} adsorption: influence of amount of Al^{3+}.

	$[Al^{3+}]$ in mmol/g	$[Al^{3+}]$ sorbed mmol/g
Saponite	2.61	2.01
	5.32	2.22
	10.23	2.91
	16.07	2.85
Hectorite	2.54	1.93
	4.88	2.13
	10.19	2.78
	21.63	3.14

Table 4. d_{001} spacings of pillared hectorite and saponite.

Clay	Al initial mmol/g	Al ad-sorbed mmol/g	d_{001}/nm before washing	d_{001}/nm after 1st washing	d_{001}/nm after 2nd washing	d_{001}/nm after 3rd washing	d_{001}/nm after 4th washing
Hectorite	1	0.52	1.30	1.46	1.54	1.46	1.50
	3.67	2.50	1.46	1.66	1.66	1.78	1.78
	18.73	4.10	1.78	1.85	1.93	1.93	nm
Saponite	1	0.35	1.26	1.33	1.26	1.30	1.26
	3.54	1.37	1.30	1.50	1.54	1.78	1.85
	19.36	2.60	1.93	1.89	1.93	1.93	nm

nm: not measured.

Saponites and hectorites, pillared with solutions of type I, were investigated on their thermal stability, surface areas and pore volumes. When thermal stability is defined as conservation of the typical 1.80 nm spacing after calcination at 550°C, then all the pillared hectorites are thermally unstable. Pillared saponite is thermally stable when the loading exceeds 1.90 mmol Al/g. The data are summarized in Tables 5 and 6. Although the position of the d_{001} line remains at 1.80 nm, its width increases by a factor of two after calcination at 550°C. This is indicative for some structural degradation, which is also seen in the decrease of the surface areas and micropore volumes after evacuation at 400°C.

DISCUSSION

Pillaring chemistry

$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ can be isolated, resolubilized and ion exchanged on smectite clays without loss of its typical Keggin ion structure in solution. In the solid state the ^{27}Al MAS-NMR spectrum has the correct ratio $Al^{VI}/Al^{IV} = 12$, provided the spinning rate is high (15 kHz). In solution the signal of octahedral Al is lost in the background and only the sharp highly symmetric signal of tetrahedral Al is visible. Undoubtedly, the initial adsorption of Al_{13}^{7+} is an ion exchange process and this conclusion is in agreement with the earliest hypotheses about pillaring and with recent findings (Vaughan 1980; Seefeld *et al* 1988, 1991a, 1991b). There are two pieces of evidence: (1) Na^+ release in amounts close the Na-CEC; (2) the ratio $[Al_{ads}]/[Na_{rel}]$ is within experimental accuracy equal to the theoretical ratio of 1.85 for ion exchange.
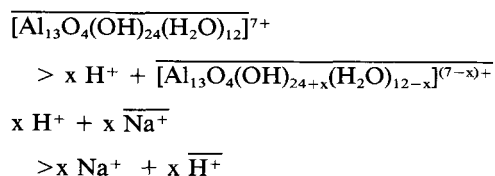
Release of excess Na^+ indicates (i) exchange of mono-

Table 5. d_{001} values of pillared saponites.

Al^{3+} mmol g^{-1}	d_{001}/nm				
	Freeze-dried	100°C	250°C	400°C	550°C
0.39	1.27	1.24	1.17	1.06	0.99
1.12	1.70	1.62	1.51	1.06	1.05
1.94	1.85	1.85	1.79	1.75	1.80
2.54	1.85	1.87	—	1.82	1.79

Table 6.   Surface areas (S) and pore volumes (V) of pillared saponites.

Evacuation temperature (°C)	1.94 mmol Al³⁺/g			2.54 mmol Al³⁺/g		
	100	200	400	100	200	400
S_{BET}, m² g⁻¹	346	343	296	343	348	293
S_{MP}, m² g⁻¹	374	367	314	368	371	313
V_T, ml g⁻¹	0.23	0.24	0.23	0.25	0.25	0.21
$S_{meso+macro}$, m² g⁻¹	76	91	114	88	89	78
V_{micro}, ml g⁻¹	0.14	0.13	0.11	0.14	0.14	0.12

atomic Al^{3+} or clusters with average charge per Al above that of $Al_{13}{}^{7+}$; (ii) hydrolysis of Al^{3+} or its clusters on the surface. For $Al_{13}{}^{7+}$ this hydrolysis can formally be written as:

$$\overline{[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}}$$
$$> x\ H^+ + \overline{[Al_{13}O_4(OH)_{24+x}(H_2O)_{12-x}]^{(7-x)+}}$$
$$x\ H^+ + x\ \overline{Na^+}$$
$$> x\ Na^+ + x\ \overline{H^+}$$

The bar denotes "adsorbed on the clay."

When the release of Na^+ is less than expected, polymerization and/or precipitation of $Al_{13}{}^{7+}$ must be postulated. This may be the case for hectorite at low Al loadings, where the amount of Na^+ released was 0.40–0.45 mmol/g, to be compared with the Na-CEC of 0.55 mmol/g. It is the case both for hectorite and saponite at high Al concentrations, where the amount of Al adsorbed increases, but the amount of Na released decreases slightly (Figures 6 and 7).

Spacings

Three critical observations have been made about the spacings of $Al_{13}{}^{7+}$ pillared clays. (1) After washing and drying the pillared clays can be divided into two groups: those with a loading below 1.3–1.4 mmol Al/g and those with a loading above 1.4 mmol/g. The former have spacings characteristic of non-pillared clays; the latter have the characteristic 1.8–1.9 nm spacing. This is the case both for saponite and hectorite. (2) When pillared hectorite and saponite are examined as a function of the number of washings, three types of samples have been distinguished: (i) those with a loading below 1.3–1.4 mmol Al/g have a spacing in the range 1.2–1.5 nm; (ii) those with loadings in the range 1.3–2.5 mmol Al/g develop the characteristic spacing of 1.8 nm only after washing; (iii) samples with loading above 2.5 mmol Al/g have the 1.8–1.9 nm independently of the number of washings. (3) When the pillaring is examined as a function of time of exchange, two types of behavior have been discerned. When the loading increases from 0.1–1.4 mmol Al/g the d_{001} line broadens towards smaller 2θ values with increasing loading to arrive at 1.9 nm (in the case of saponite) for 1.4 mmol Al/g. When the amount of Al in the exchange solution is 10× higher the 1.9 nm spacing develops immediately

and the d_{001} line sharpens with time of exchange or with loading.

From these data one deduces that a minimum amount of Al is necessary for pillaring. This minimum amount is in the range 1.3–1.4 mmol Al/g or about 0.1 mmol $Al_{13}{}^{7+}$. Secondly, once the 1.8 nm is reached, additional amounts of Al sharpen the d_{001} lines, but do not change the spacing. Thirdly, pillared clays are obtained by washing for intermediate loadings of 1.4–2.5 mmol Al/g, which is indicative for reorganization of the system upon washing.

It is impossible to generate a detailed picture of the pillaring process on the basis of XRD data alone. However, because of the very selective uptake of the Al_{13} cluster, adsorption occurs on a first come first served basis: Al_{13} adsorbs on the first site it encounters, whatever that site may be. A random distribution of the clusters is then unlikely. As the loading increases, many factors intervene such as (i) hydrolysis/polymerization of the adsorbed clusters; (ii) change in the colloidal properties of the clay with loading (aggregation tendency will increase). The non-random distribution of Al_{13} at small loadings leads to an interstratified material, which, upon calcination, must totally collapse, as observed. A minimum amount of Al_{13} pillars on the surface is needed to produce the fully expanded thermally stable material under condition that the Al_{13} pillar is chemically stable and that the clay is highly crystalline. Indeed, pillaring of the more crystalline saponite is much easier than of the less crystalline hectorite. In addition, the two clays behave chemically different in that for saponite at small loadings an almost pure ion exchange reaction takes place. For hectorite, this is not the case. The reason for this difference may be the difference in crystallinity, but also the difference in chemical composition of the clays. Seefeld *et al* (1991a) suggested that on hectorite the Al_{13} cluster interacts with "free, active" (exchangeable?) Mg^{2+}, leading to polymerization of Al_{13} on the surface. Whether this is also the case with our sample of hectorite is not yet investigated.

CONCLUSIONS

$Al_{13}{}^{7+}$ is selectively taken up by saponite and hectorite via an ion exchange reaction. For saponite the amount of Al adsorbed is 2–2.15 mmol/g for a release of 0.8 mmol Na^+. The average charge per Al is then

0.4. For hectorite with a release of 0.4 mol Na^+, the average change per adsorbed Al is only 0.2. This suggests additional polymerization, and certainly at high Al contents, precipitation of Al_{13}. Pillaring requires a minimum amount of 1.3–1.4 mmol Al^{3+} in the form of—mainly—Al_{13}. Thermal stability requires a minimum amount of 1.90 mmol Al^{3+} in the form of Al_{13} and a highly crystalline clay material. The structure of the pillars on the surface and their distribution over the surface require additional investigations.

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