

## HYDROXY-AL PILLARING OF CONCENTRATED CLAY SUSPENSIONS

**Key Words**—Al pillared clays, Pillaring of clay slurries.

Since the early work of Vaughan *et al.* (1979) on alumina pillared montmorillonites and their potential uses as sorbents and catalysts, almost all suitable natural and synthetic smectites have been pillared with metal elements which form oxy-hydroxy type species.

Pillaring is generally carried out in dilute systems wherein a dilute clay suspension is brought in contact with a dilute pillaring solution. This requires handling large volumes of suspension during the preparation as well as the washing steps. Although the use of large dilute volumes is generally uneconomical from a practical viewpoint, almost no data on the pillaring of concentrated clay suspensions can be found in the literature. Recently, Vaughan (1988) stressed the importance of three prerequisites for the making of real catalysts: using the clay with minimal or no refining and no pre-exchange, and pillaring in concentrated clay suspensions. This author also mentioned the successful pillaring of a 40% clay slurry, but with no further details. In a recent note, Schoonheydt and Leeman (1992) reported the preparation of hydroxy-Al pillared saponite, using 6 to 10 wt. % clay suspensions.

This note briefly describes laboratory trials to prepare hydroxy-Al pillared montmorillonite with heat resistant 18 Å spacings from a 40 wt. % clay slurry.

## EXPERIMENTAL

*Material and methods*

Pillaring experiments were carried out with Westone-L montmorillonite (from ECC, U.K.). The clay was used as received without previous fractionation. Its cation exchange capacity determined on the  $\text{NH}_4^+$  exchanged form is 73 meq/100 g, and the BET ( $\text{N}_2$ ) surface area is 69  $\text{m}^2/\text{gr}$ .

A partially hydrolysed solution was prepared by slow addition of 0.5 M sodium hydroxide to 0.2 M aluminium nitrate to achieve an OH/Al molar ratio (R) of 1.6. Distilled water was supplied to obtain a final concentration in  $\text{Al}^{3+}$  of 0.1 M. Vigorous stirring was maintained throughout the hydrolysis. The pillaring solution was aged for 24 h at room temperature.

Dialysis bags containing weighed amounts (10 g of clay on dry basis) of a 40 wt. % clay slurry were dipped in glass vessels containing the partially hydrolyzed aluminium solution. The volumes of the pillaring so-

lution were adjusted in order to supply 25, 50, 75, and 100 meq  $\text{Al}^{3+}$  per g of clay. Each system was aged under mild stirring for 24 or 48 hr at room temperature. Samples of the clay slurry were taken for X-ray analysis. Washing was performed by dipping the dialysis bags containing the clay slurry in distilled water, and renewing the water until the conductivity was reduced to its initial value (20  $\mu\text{s}$ ). Only two washes were necessary. Samples of the clay slurry were taken for X-ray analysis before and after washing.

*Characterization*

The X-ray diagrams were recorded with a Philips diffractometer, fitted with a Ni-filtered  $\text{CuK}\alpha$  radiation source. The scanning speed was  $2^\circ 2\theta/\text{min}$ .

The specific surface areas and pore volumes were obtained from the  $\text{N}_2$  adsorption isotherms, using a Micromeritics ASAP 2000 instrument.

## RESULTS

The X-ray diagrams of the clays pillared with different amounts of partially hydrolysed aluminium solutions, aged for 24 and 48 hr and washed, are shown in Figure 1. The same figure also shows the corresponding diagrams after calcination at 400°C for 4 hr.

As can be seen, stable pillars (18 Å spacings) are formed with 50 and 75 meq  $\text{Al}^{3+}/\text{g}$  of clay. With 100-meq  $\text{Al}^{3+}$ , although a 17.0–17.7 Å spacing is observed for the room temperature dried sample (Figure 1, right-hand diagrams a and b), partial collapse of the clay is noticed after heating at 400°C ( $d_{001} = 14$  Å) (a' and b'), indicative of inadequate pillaring. The reason for this collapse is not clear. A similar observation has been reported in the earlier literature (Slaughter and Milne, 1960; Sawhney, 1968) and was attributed to the removal upon calcination of a layer of hydration water molecules, the resulting interlayered clay being a pseudo-chlorite like mineral. The slightly but significantly lower d values (17.0–17.7 Å) of the room temperature dried samples are consistent with such an interpretation, assuming that the thickness of a monolayer of water molecules is  $\sim 3$  Å. However, additional information on the amount of Al intercalated in the interlayer region and on the possible formation of a separate gel-like phase outside the clay particles is necessary.

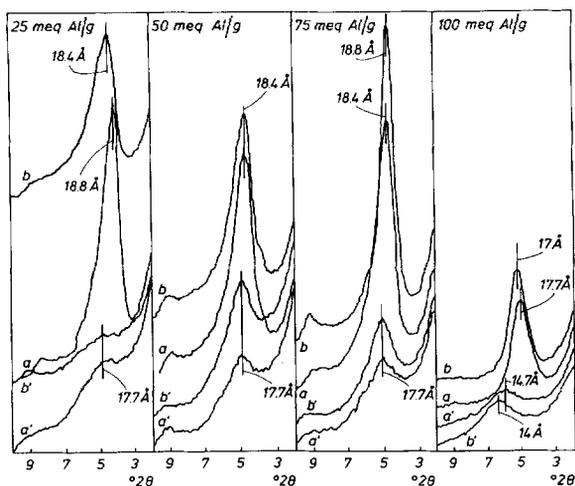


Figure 1. X-ray diagrams of clays pillared with 25, 50, 75, and 100 meq  $\text{Al}^{3+}/\text{g}$  of clay aged for 24 hr (a) and 48 hr (b), recorded after drying at room temperature and calcination at  $400^\circ\text{C}$  for 4 hr (a', b').

No turbidity whatsoever was noticed in the pillaring solution.

With 25 meq  $\text{Al}^{3+}/\text{g}$ , an 18 Å spacing is also observed for the room temperature dried sample. Heating the sample at  $400^\circ\text{C}$  does not collapse the clay particles but lowers the stacking order of the clay sheets, as may be inferred from the peak broadening and loss of intensity. Suitable pillaring was achieved when supplying 50 and 75 meq  $\text{Al}^{3+}/\text{g}$  of clay. Indeed, as shown in Figure 1, these two samples exhibit stable spacings at 17.7 Å (diagrams a' and b'), typical of hydroxy-Al pillared montmorillonite obtained in dilute conditions. Increasing residence time of the clay in the pillaring solution from 24 to 48 hr improves the development of the pillars, as inferred from the narrower peak width and greater intensity for the samples obtained after 48 hr, calcined at  $400^\circ\text{C}$ . For the samples prepared with 25 and 100 meq  $\text{Al}^{3+}/\text{g}$ , this effect is not observed.

The X-ray diagrams recorded on the samples pillared with 50 meq  $\text{Al}^{3+}/\text{g}$  for 24 hr at different steps during the washing are shown in Figure 2. The upper and lower part of this figure refer to room temperature dried samples and to the calcined ones, respectively.

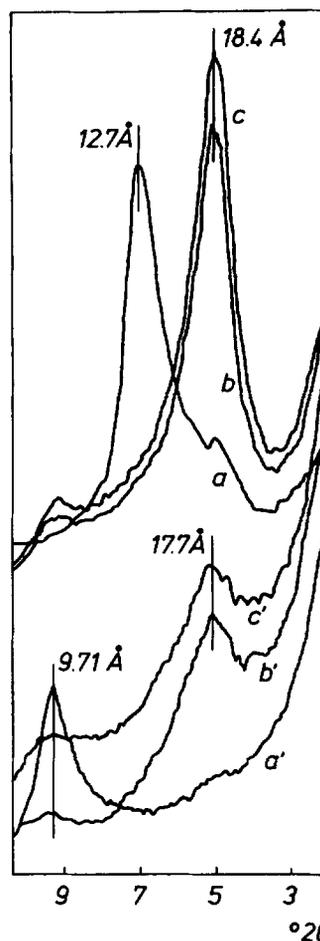


Figure 2. X-ray diagrams of the samples prepared with 50 meq  $\text{Al}^{3+}/\text{g}$ , without washing (a: drying at room temperature; a': calcined at  $400^\circ\text{C}$ ), and after 1 (b; b') and 2 washings (c; c').

The unwashed clay (diagram a) exhibits a 12.6 Å spacing after drying at room temperature, which falls to 9.7 Å (a') after heat treatment at  $400^\circ\text{C}$ . Those which have been washed once (b, b') or twice (c, c') show heat-resistant 18 Å spacings which characterize Al-pillared clays. A similar phenomenon was observed when the pillaring was carried out in dilute clay suspensions ( $\sim 1$  wt. %) (Schutz *et al.*, 1987; Vieira-Coelho and Poncelet, 1991).

The BET surface areas and micropore volumes (from t-plot) of the three pillared clays are given in Table 1. The samples were outgassed at  $200^\circ\text{C}$  for 4 hr.

As expected from the X-ray data, the poorly pillared montmorillonite prepared with 100 meq  $\text{Al}^{3+}/\text{g}$  has the lowest values. The best of the three samples (50 meq  $\text{Al}^{3+}/\text{g}$ ) develops the highest area and pore volumes (total and micro). The values obtained for a sample of the same montmorillonite pillared in diluted suspension (1%) are given for comparison.

Table 1. Surface area (BET) and pore volume.

Amount of $\text{Al}^{3+}$ (meq/g)	BET surface area ( $\text{m}^2/\text{g}$ )	Total pore volume ( $\text{cc}/\text{g}$ )	Micropore volume ( $\text{cc}/\text{g}$ )
50	277	0.238	0.079
75	229	0.202	0.064
100	142	0.160	0.023
15 <sup>1</sup>	229	0.198	0.068

<sup>1</sup> Sample pillared in diluted clay suspension (1 wt. %) (Vieira-Coelho and Poncelet, 1991).

## CONCLUSION

It is thus possible to obtain hydroxy-Al pillared clays with textural characteristics—heat resistant basal spacings, surface area, and pore volume—which do not differ from similar materials prepared in dilute systems.

In the present experimental approach, the use of dialysis membranes offers the advantage of easy recovery of the concentrated pillared material, handling small volumes, and reducing the washing operations.

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(Received 23 March 1992; accepted 8 June 1992; Ms. 2201)