

## FIXATION OF HYDROXY-ALUMINUM BY MONTMORILLONITE

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### ABSTRACT

An aluminum hydroxide-montmorillonite complex prepared at an OH/Al ratio of 3.0 (16 meq Al/g clay) and immediately cleaned of any free hydroxy-aluminum behaves like aluminum-chlorite and shows no change after six months ageing. Hydroxy-aluminum completely precipitates within the interlayer space of montmorillonite. Electrophoresis studies show that the hydroxy-aluminum precipitated in montmorillonite is present as uncharged aluminum hydroxide.

X-ray diffraction analysis, thermal (DTA and TGA) studies, infrared absorption analysis, polarographic reduction behaviour, and cation exchange capacity measurements confirm the complete (and stable) transformation of montmorillonite to chlorite structure.

When the hydroxy-aluminum montmorillonite complex is allowed to age in the presence of free aluminum hydroxide (external to the montmorillonite layers), a "seeding" effect takes place and the "fixed" hydroxy-aluminum comes out from the interlayer space.

### INTRODUCTION

Much work has been done on the preparation and characterization of aluminum hydroxide-clay complexes, with the objective of explaining the occurrence of varieties of chlorites in sediments, slates, soils, and other pedogenic processes (Slaughter and Milne, 1960). The precipitation of hydrous aluminum oxides in the interlayer spaces of 2:1 type layer silicates (Shen and Rich, 1962; Hsu and Bates, 1964a; de Villiers and Jackson, 1967). Nothing precise can be said as to the nature and position of the precipitated hydrous oxide. Slaughter and Milne (1960) and Barnishel and Rich (1965) stress the adsorption of a layer of the precipitated hydroxide over the entire surface of the clay mineral, possibly through hydrogen bonding, rather than the direct formation of a gibbsite-like layer in the interlayer space. Shen and Rich (1962) have shown that the cation exchange capacity (CEC) of montmorillonite is reduced by positively charged hydroxy-aluminum groups occupying exchange sites. Hsu and Bates (1964a) have shown that, with solutions of NaOH/Al in molar ratios 0.3 to 2.1, the groups held by vermiculite are of nearly constant composition having the formula  $[Al_6(OH)_{12}]^{6+}$  for a single ring, or  $[Al_{10}(OH)_{22}]^{8+}$  for a double ring, and are present as a single layer in the interlayer space. With a NaOH/Al molar ratio equal to three, no hy-

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droxy-aluminum is found in the interlayer space but crystalline  $\text{Al}(\text{OH})_3$  forms outside the clay lattice.

The effect of factors like  $\text{NaOH}/\text{Al}$  molar ratio (Barnishel and Rich, 1963), pH and mineral surfaces (Barnishel and Rich, 1965), and presence of foreign anions (Singh and Brydon, 1967) also have been studied. The major contributing factor seems to be the length of time of reaction between the clay mineral and the metal hydroxide (Turner and Brydon, 1967).

To date the work has involved clay complexes aged with the precipitated metal hydroxide in the presence of mother liquor. This could possibly result in the removal of interlayer hydroxide due to the "seeding effects" by the free hydroxide (Turner and Brydon, 1967). The object of the present study was to investigate the clay mineral-metal hydroxide complexes, the influence of free metal hydroxide, and the nature of the precipitated hydroxy-aluminum.

#### MATERIALS AND METHODS

*Montmorillonite.*—The 2-0.2  $\mu\text{m}$  fraction of montmorillonite (supplied by British Drug House) was obtained from a water-dispersed system. No other preliminary treatment (or cation saturation) was given; in similar studies Slaughter and Milne (1960), and Barnishel and Rich (1965), have stressed the absence of any effects of homo-ionic saturation. The clay contained no organic matter. A 6 g portion of the clay was suspended in 100 ml of distilled water for each treatment.

*Precipitation of hydroxy-aluminum.*—Anhydrous aluminum chloride (analytical grade) was added to the clay suspension to give a 2 N solution. The suspension was neutralized by a controlled dropwise addition of 200 ml of normal  $\text{NH}_4\text{OH}$  at a rate of one ml per five min, while stirring continuously at a high speed with a magnetic stirrer (approximately 2,000 rpm). This precipitated about 200 meq of aluminum hydroxide per 6 g montmorillonite at an  $\text{OH}/\text{Al}$  molar ratio of 3.0 in about 17 hours. The precipitation was conducted in triplicate. Similar precipitations were also performed in solutions of aluminum chloride without adding the clay.

*Hydroxy-aluminum clay complex (System No. I).*—The precipitate was filtered, washed with a 1:1 alcohol-water mixture until free from chloride ions and dried at 105°C. The only cations that could be detected in the filtrate were  $\text{NH}_4^+$  ions.

*Acid-washed hydroxy-aluminum clay complex (System No. II).*—For the second treatment, after precipitation the complex was mixed with 0.05 N  $\text{HCl}$  (preliminary experiments were first conducted to estimate its capacity for dissolving only the free aluminum hydroxide external to montmorillonite), stirred for ten minutes, and filtered. The precipitate was leached with  $\text{HCl}$  until no more  $\text{Al}^{3+}$  ions appeared in the filtrate. After washing the residue with the alcohol-water mixture it was dried at 105°C.

*Storage.*—The complexes were stored in desiccators over anhydrous calcium chloride between analysis.

*pH-measurement.*—The pH was measured with a Cambridge bench-type pH-meter using a glass calomel electrode assembly.

*Cation exchange capacity.*—CEC was determined by a number of different methods, viz. analytical (ammonium acetate leaching), flame-photometric, polarographic, and potentiometric and conductimetric titrations both in aqueous and alcoholic media (Malik and Gupta, 1968). Results of only the analytical method are given here.

*Exchangeable aluminum.*—Exchangeable aluminum was determined by displacing  $Al^{3+}$  from a 2 g sample of hydroxy-aluminum clay complex with four washes, each consisting of 25 ml of normal NaCl. No "fixed" aluminum could be removed after NaCl treatment even with 0.5 N NaCl. Aluminum was estimated, wherever required, by EDTA titrations as well as by polarographic reduction (Kolthoff and Lingane, 1952).

*X-ray diffraction.*—Patterns were obtained on powder specimen (minus 300 British Standard Sieve) with a Philips 1051 PW Diffractometer using a copper target with nickel filter, at 26 KeV and 10 mA. Different combinations of the beam, Soller and detector slits at a scan speed of  $0.2^\circ 2\theta/\text{min}$  were used to provide greater precision in determining the  $2\theta$  values.

*Infrared analysis.*—Infrared spectra were obtained with a Perkin-Elmer Spectrophotometer No. 021 with "Nujol" mull specimens.

*Charge determination.*—Migration of hydroxy-aluminum clay complex colloidal particles under the influence of an applied e m f was observed in a Burton-type electrophoresis apparatus.

## RESULTS AND DISCUSSION

*Montmorillonite.*—Exchangeable cation analysis by flame photometric-method showed the presence of  $Na^+$  and  $Ca^{++}$  ions only in the montmorillonite. X-ray diffraction data of the montmorillonite used are comparable to that reported in Card No. 3-0019 (X-ray Powder Data File, 1962). On treatment with glycerol, the 001 spacing expands to 17.7 Å whereas on heating ( $600^\circ\text{C}$ , 2 hours) it collapses to 9.3 Å.

*Aluminum-chloride + Ammonia System.*—Immediately after precipitation the pH of the mixture was 8.6. No aluminum ions could be detected in the filtrate. The dry precipitate contained 34.5 percent aluminum equivalent to the composition  $Al(OH)_3$ . The freshly prepared product was largely amorphous according to X-ray diffraction analysis. Peaks for bayerite (4.71 and 4.37 Å) were observed after six hours. No change in the patterns was observed after 12 hours. Formation of bayerite is justified considering: (1) the period of ageing; shorter period of ageing leads to the formation of bayerite and not gibbsite (McKenzie, 1957), (2)  $NH_4OH$  used as the precipitant rather than NaOH (Hsu and Bates, 1964b) or  $Ca(OH)_2$  (Turner and Brydon, 1967), and (3) alkaline pH

(compare Hsu and Bates, 1964b; Barnishel and Rich, 1965). No chloride ions could be detected adsorbed on the precipitate. The product was soluble (100%) in normal HCl up to 4 hours after precipitation, but became resistant (85%) to acid attack after 12 hours. After heating (600°C, 2 hours) bayerite changed to  $\gamma$ -alumina.

*Hydroxy-aluminum Clay Complex (Acid Unwashed, System No. I).*—The pH of the montmorillonite suspension was 5.1; after  $\text{Al}(\text{OH})_3$  precipitation it rose to 7.8. Ammonium ions were the only cations in the filtrate after precipitation, indicating that aluminum was completely precipitated and the original exchangeable cations of montmorillonite were either not displaced at all or accommodated elsewhere in the new product formed. The lack of adsorption of chloride ions by the precipitated complex indicates that the complex had no affinity for chloride ions.

Following precipitation the washed and dried product was found amorphous to X-ray diffraction analysis. This does not agree with the conclusion of Slaughter and Milne (1960) that new structures develop only upon association of the unit layers through dehydration. After 10 hours, peaks at 14.71 and 7.30 Å developed, resembling the aluminum-chlorite of Slaughter and Milne (1960). Peaks at 4.71 and 4.37 Å appeared only after 16 hours by which time the aluminum-chlorite pattern was completely developed; peaks at 4.81, 4.37, and 3.20 Å should not be confused with gibbsite at this stage since other peaks at 4.31, 3.31 and 2.38 Å never developed. The peak at 4.81 Å is due to aluminum-chlorite and peaks at 4.37 and 3.20 Å are of bayerite.

Formation of bayerite in this case is logical, because the pH is more alkaline than observed by Brydon and Kodama (1966) for the formation of gibbsite or pseudo-boehmite. After 2 days the pattern for bayerite was also completed. At this stage the peaks at 3.20, 2.90, 2.21, and 1.72 Å do not indicate the presence of montmorillonite because on acid leaching (0.05 N HCl) these peaks (except 2.90 Å) disappear.

Intensities of all these peaks increased for as long as one month (Fig. 1) indicating crystal growth and reactions in the "solid" state. Thereafter, only intensities of the bayerite peaks increased with a corresponding decrease for the peaks of aluminum-chlorite. This possibly is due to the "seeding" effects of free bayerite (Turner and Brydon, 1967). Slaughter and Milne (1960) have also observed a decrease in the completeness of the brucite-type layer of artificial structures (magnesium-chlorite) when the product is aged in the final solution. Between 3 and 6 months the pattern did not change appreciably. The peaks characteristic of montmorillonite were never present. During one month of ageing, no expansion of the 14.71 Å peak was observed on glycerol treatment.

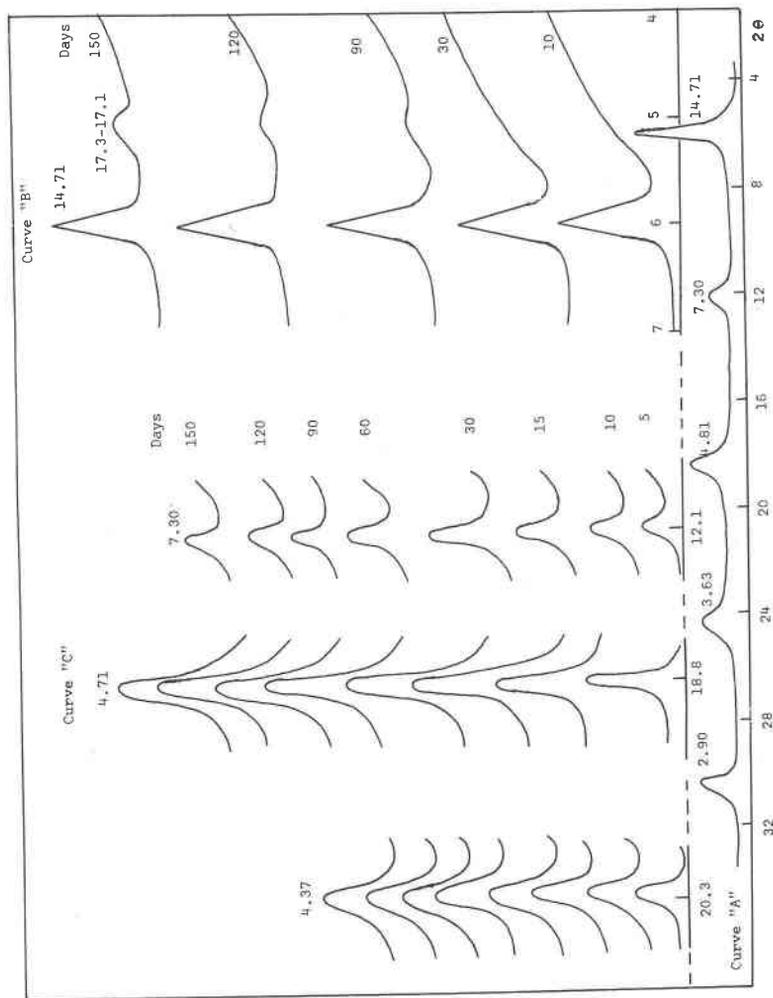


FIG. 1. (A) X-ray diffraction pattern (smoothed) of acid washed hydroxy-aluminum clay complex (System II). (B) X-ray diffraction traces (smoothed) of glycerol treated hydroxy-aluminum clay complex (System I) at different time intervals. (C) X-ray diffraction traces (smoothed) of hydroxy-aluminum clay complex (System I) at different time intervals.

Samples aged longer showed, on glycerol treatment, a small broad peak between 17.1–17.3 Å.

*Hydroxy-aluminum Clay Complex (Acid Washed, System No. II).* The aluminum hydroxide precipitated external to montmorillonite unit layers was removed immediately after precipitation by dilute acid leaching. The quantity of aluminum hydroxide thus leached out with acid treatment was 101 meq for 6 g montmorillonite. The quantity of the hydroxide complexed with montmorillonite amounts to 16.5 meq per g clay. Exchangeable aluminum displaced by NaCl treatment was 0.4 meq per g clay, leaving approximately 16 meq  $\text{Al}(\text{OH})_3$  per g montmorillonite in a "fixed" form in its lattice. This is the quantity (calculated) required for the transformation of montmorillonite to chlorite structure (Slaughter and Milne, 1960).

CEC values of montmorillonite and hydroxy-aluminum clay complex were 91.0 and 32.0 meq per 100 g clay, respectively. The value for the hydroxy-aluminum clay complex did not change noticeably even after 6 months ageing or after another leaching with 0.5 N HCl.

The X-ray pattern of System II resembles that of aluminum-chlorite of Slaughter and Milne (1960). It does not show any change with time (Fig. 1, curve A) up to 6 months (unlike Barnishel and Rich, 1963) and suggests the stability of the complex obtained. It confirms the view that only in the presence of free aluminum-hydroxide (external to montmorillonite unit layers) will these aluminum hydroxide clay complexes "expel" the "fixed" hydroxide layer. No peak for montmorillonite or any hydroxide was observed at any time.

After heating the sample (System II) to 550°C for 2 hours the X-ray pattern showed an increase in the intensity of the 001 reflection (14.71 Å), and a decrease in other reflections without any change in basal spacings. The pattern is unlike that of (1) Slaughter and Milne (1960) where only the 001 spacing is left, (2) Brydon and Kodama (1966) where no increase in intensity is observed, and the spacing collapses to 13.1 Å from 14.6 Å at 550°C, and to 12.8 Å at 700°C, and (3) Barnishel and Rich (1963) where the spacing collapses to 13.3 Å from 16.6 Å at 550°C. Only on heating to 650°C does the 001 reflection decrease to 14.19 Å. Such a collapse on heating is comparable to that reported for naturally occurring dioctahedral chlorites (Brydon, *et al.*, 1961). At this temperature (650°C) the other order reflections are still present reflecting the high stability of the chlorite formed. Resistance to collapse on heating even after 6 months ageing confirms that no interlayer material had left the lattice at any time.

On none of the samples did the 001 spacing expand on glycerol treat-

ment resembling the complex of Slaughter and Milne (1960) and Brydon and Kodama (1966); and differs from those of Barnishel and Rich (1963), Shen and Rich (1962), and Turner and Brydon (1965). X-ray patterns of these samples (System II) after another acid leaching (0.5 N HCl) remained the same but after drastic treatment (2 N HCl, in a boiling water bath for 2 hours) the residue showed an amorphous character with no peaks for montmorillonite.

The X-ray data prove that under these conditions the synthesized chlorite structure is stable even when 16 meq  $\text{Al}(\text{OH})_3$  per g montmorillonite is precipitated. The experiments of Brydon and Kodama (1966), and Turner and Brydon (1965) showed that no more than 8 meq of  $\text{Al}(\text{OH})_3$  per g clay enters the interlayer space. This is due to the ageing of the suspensions in presence of free  $\text{Al}(\text{OH})_3$  leading to a "seeding" effect (Turner and Brydon, 1967). Also, the properties of the montmorillonite used influence the extent to which the interlayer hydroxide can be removed. This was observed earlier when comparing an Arizona bentonite with a Wyoming bentonite (Turner and Brydon, 1967).

*Thermal Analysis.*—Differential thermal analysis and thermogravimetric analysis of these hydroxy-aluminum clay complexes lends support to this interpretation of chemical and X-ray data (Gupta and Malik, 1968).

*Polarographic Analysis.*—The polarographic reduction behaviour of these hydroxy-metal montmorillonite complex systems both in the presence and absence of surface active agents also confirms the transformation of montmorillonite to these new structures (Malik and Gupta, 1968).

*Infrared Analysis.*—The montmorillonite spectrum (Fig. 2) shows well pronounced absorption bands at 3703, 3450, 1655, and 1042  $\text{cm}^{-1}$  (with some minor shoulders at 982 and 945  $\text{cm}^{-1}$ ). The absorption bands (for the major OH bands) at 3703 and 3450  $\text{cm}^{-1}$  resemble those of Bishui and Prasad (1960) for Otay California montmorillonite. The lattice OH band at 3703  $\text{cm}^{-1}$  has been observed also for montmorillonite by Fripiat (1964). The Al-OH band, between 900–950  $\text{cm}^{-1}$ , though not completely missing, is very broad.

Extra absorption bands appear in the hydroxy-aluminum clay complex (acid washed, System II) spectrogram at about 2750, 2445 and 908  $\text{cm}^{-1}$  (with a shoulder band at 1315  $\text{cm}^{-1}$ ) pointing towards the development of new atomic groupings and possibly the transformation of the original montmorillonite structure. Bands for gibbsite-bayerite which were seen in the acid unwashed (System I) complex were absent in this case. Ageing did not change the spectra in any way.

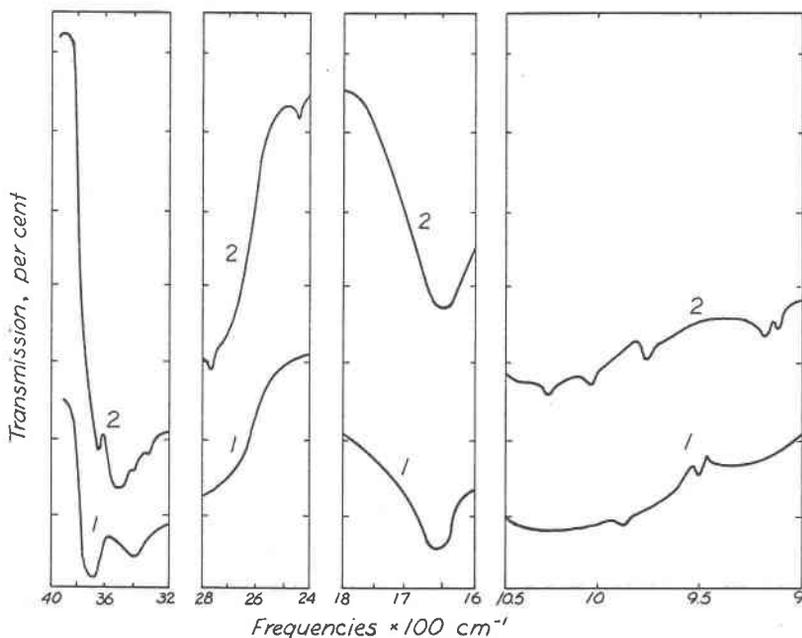


FIG. 2. Infrared absorption spectra: (1) montmorillonite; (2) hydroxy-aluminum clay complex (acid washed).

The spectra obtained for System II complex after heating ( $200^{\circ}\text{C}$ , 2 hours Weismiller *et al.*, 1967) or after another acid leaching (0.5 N HCl) did not change appreciably but some band intensities increased confirming the absence of any metal hydroxide external to montmorillonite layers. Increased hydration on  $\text{Al}(\text{OH})_3$  precipitation with montmorillonite is in conformity with the dehydration and infrared data of Brydon and Kodama (1966). Somewhat different infrared spectra from that of Brydon and Kodama (1966) or Weismiller *et al.* (1967) or Ahlrichs (1968) in the spectral range of  $3300\text{--}3500\text{ cm}^{-1}$  are primarily due to the different specimens of montmorillonite used and the methods of preparation.

*Electrophoresis Study.*—Migration of clay, hydroxy-aluminum clay complex particles (in a colloidal sol) towards the positive electrode indicates that both montmorillonite and the hydroxy-aluminum clay complexes are negatively charged. This points to the formation of uncharged hydroxy-aluminum interlayer rather than assumption of the adsorption of anionic clay on the positively charged  $\text{Al}(\text{OH})_x$  groups (Hsu and Bates, 1964a), or the “fixation” of positively charged hydroxy-aluminum groups on the exchange sites of the clay (Shen and Rich, 1962) or the adsorption

of the precipitated hydroxide over the entire surface of the clay through hydrogen bonding (Slaughter and Milne, 1960).

A consideration of all X-ray patterns, thermal analyses, polarographic analyses, infrared spectra, CEC data and electrophoretic studies stresses the complete conversion of montmorillonite to aluminum-chlorite by the precipitation of unchanged  $\text{Al}(\text{OH})_3$  within the interlayer space of montmorillonite.

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