FORMATION, COMPOSITIONS, AND PROPERTIES OF HYDROXY-Al- AND HYDROXY-Mg-MONTMORILLONITE

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Abstract—Hydroxy-Al- and hydroxy-Mg-montmorillonite were prepared by treating dispersed Na-montmorillonite with aluminum and magnesium nitrate solutions and titrating with NaOH solutions so that the OH/Al ratio varied from zero to 3.0 and the OH/Mg ratio from zero to 2.0. External precipitation of Al and Mg hydroxides was observed when the OH/M ratios (M = metal) approached 3 and 2, respectively. From chemical analyses of the initial Na-montmorillonite and the hydroxy-metal montmorillonites, structural formulae were derived by assuming that the silicate layer compositions remained unchanged. Prior to the addition of NaOH, the average interlayer material approximated in composition to $[Al(OH)_2]^+$ and $[Mg(OH)]^+$. With additions of NaOH the interlayer compositions moved progressively towards $Al(OH)_3$ and $Mg(OH)_2$. When the hydroxy interlayers approached completion, external precipitation was observed. X-ray powder diffraction data showed that the hydroxy-Mg products have less tendency to swell in ethylene glycol and water, and greater thermal stability than the hydroxy-Al products. Initially, when the average interlayer compositions were near $Al(OH)_2$ and $Mg(OH)$, swelling followed more nearly the normal behavior.

Key Words—Hydrolysis, Hydroxy interlayer, Montmorillonite, Swelling, Thermal stability.

INTRODUCTION

The formation and properties of hydroxy-metal montmorillonites, particularly hydroxy-Al- and hydroxy-Mg-montmorillonites, have been studied very extensively, particularly in relation to the formation and alteration of clay minerals in soils and sediments. Rich (1968) gave a detailed review of naturally occurring and laboratory-prepared smectites and vermiculites containing hydroxy interlayers. Extensive references to the literature are given by Hsu (1968), Gupta and Malik (1969a, 1969b, 1969c), Carstea *et al.* (1970a, 1970b), Brydon and Turner (1972), and Lahav *et al.* (1978). Earlier work was reviewed by Marshall (1964, especially Ch. 8).

Various procedures have been used previously to prepare hydroxy-metal montmorillonites: (1) solutions containing hydroxy-metal cations formed by addition of a base, usually NaOH, to a metal salt solution to give a desired OH/M ratio can be added to a dispersed, usually Na-montmorillonite; (2) the base and the salt solution may be added simultaneously in a drop-wise manner to a vigorously agitated, dispersed montmorillonite; (3) the salt solution can be added first to the dispersed montmorillonite, and the system subsequently titrated with base. Ion hydrolysis and the formation of complex ions is intrinsically a difficult subject, particularly in the presence of finely dispersed clays. Rich (1968, p. 23) remarked: "The hydrolysis and polymerization (of ions) near clay surfaces is an even more complex problem. A certain amount of hydrolysis in place must occur in the interlayer space. Basic monomers and small polymers may diffuse into the interlayer space, but hydrolysis must also proceed."

The present experiments have used method (3) and have followed closely the work of Yamanaka and Brindley (1978) on the formation and properties of hydroxy-Ni-montmorillonite. They differ from most previous studies in emphasizing the chemical compositions of the hydroxy products prepared. The nature of the method is such that *average* compositions of the interlayer materials are obtained and inhomogeneities such as Hsu (1968) has discussed will not be apparent. However, this approach which has received little attention in the past provides useful supplementary information on the progressive development of the interlayer hydroxy material. X-ray powder diffraction (XRD) data indicate related changes in the swelling behavior of the products.

EXPERIMENTAL

A <2-μm fraction of Wyoming montmorillonite, previously saturated with Na, was treated twice with 1 M NaCl solution, washed with distilled water by repeated centrifugation and then by dialysis until free of Cl^- (AgNO$_3$ test), and finally dried in air at $\sim$55°C. The clay contained no impurities detectable by XRD.

Altogether, seven samples of hydroxy-Al- and seven of hydroxy-Mg-montmorillonite were prepared. For each series, seven 300-mg samples of clay were taken and to each was added either 20 ml of 0.1 M aluminum or 30 ml of 0.1 M magnesium nitrate solution. These amounts of solution correspond to 2000 meq Al and 2000 meq Mg per 100 g clay which is far in excess of the exchange capacity of the clay, about 85 meq/100 g clay. Complete hydroxide interlayers with 3 Mg^{2+} or 2 Al^{3+} ions per formula unit require about 1550 meq/100 g clay;

Table 1. Chemical analyses and derived formulae of Na-montmorillonite and of hydroxy-Al-montmorillonites (0, . . . , 6, see text).

	Na-mont-morillonite	0	1	2	3	4	5	6
SiO_2	58.4	52.4	50.6	48.7	46.2	44.3	41.4	37.5
Al_2O_3	20.30	22.32	25.87	29.68	31.59	33.23	34.45	38.54
Fe_2O_3	3.88	3.62	3.36	3.20	2.94	2.88	2.82	2.52
MgO	2.60	2.25	2.13	2.09	1.94	1.90	1.79	1.68
CaO	0.62	0	0.12	0.12	0.13	0.13	0.45	0.46
Na_2O	2.34	0	0	0	0	0	0	0.83
K_2O	0.17	0.07	0.15	0.06	0.13	0.07	0.07	0.12
$H_2O > 110°C$	6.17	8.87	10.85	10.98	12.75	12.35	13.70	15.50
$H_2O < 110°C$	4.74	8.49	5.96	4.93	3.46	3.74	3.49	3.14
Total	99.22	98.04	99.04	99.76	99.14	98.60	98.17	100.29
Layer composition								
Si	3.93	3.93	3.93	3.93	3.93	3.93	3.93	3.93
Al	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
Al	1.54	1.55	1.55	1.56	1.56	1.56	1.55	1.54
Fe	0.20	0.20	0.20	0.19	0.19	0.19	0.20	0.20
Mg	0.26	0.25	0.25	0.25	0.25	0.25	0.25	0.26
Anions				$O_{10}(OH)_2$				
Interlayer composition								
Na	0.30	0	0	0	0	0	0	0.17
K	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.02
Ca	0.04	0.00	0.01	0.01	0.01	0.01	0.04	0.05
Al	0.0	0.35	0.75	1.19	1.54	1.84	2.23	3.15
OH	0.08	0.76	1.94	3.30	4.32	5.26	6.48	8.84
H_2O	0.35	0.84	0.84	0.31	0.46	0.03	0.10	—
								O = 0.28
OH/Al	—	2.17	2.59	2.77	2.80	2.86	2.90	2.98
$(OH + H_2O)/Al$	—	4.57	3.71	3.03	3.10	2.88	2.95	—

the solutions added were therefore in excess of this amount.

The samples in each series are labelled 0, 1, 2, . . . , 6. After adding 20 ml or 30 ml of the appropriate nitrate solution to all samples and after 1 day of equilibration with the samples kept in continuous movement, 10 ml of 0.1 M NaOH solution was added slowly and with vigorous stirring to samples 1, . . . , 6. After 2 days, a further 10 ml of NaOH was added to samples 2, ..., 6. This process was continued until, on the sixth day, a final 10 ml of NaOH was added to sample 6. After 1 week, seven samples of each series were available, and the nth sample, n = 0, 1, 2, . . . , 6, had received 10n ml of NaOH. Following these treatments, the clay samples were repeatedly washed with distilled water, pH ~4.8–5.2, dried at about 55°C in air, and stored in stoppered tubes. The addition of 10 ml 0.1 M NaOH solution to 20 or 30 ml of the appropriate 0.1 M nitrate solution corresponds to a ratio OH/Al = 1/2, OH/Mg = 1/3. Therefore, the maximum addition of 60 ml NaOH solution gives OH/Al = 3 and OH/Mg = 2, i.e., enough to convert all Al to a gibbsite-like arrangement and all Mg to a brucite-like arrangement.

The products were analyzed chemically by atomic absorption analysis (Perkin-Elmer 403 instrument and $LiBO_2$ fusion method of Medlin *et al.* (1964)). Samples

were equilibrated under room conditions prior to weighing; in Tables 1 and 2, $H_2O < 110°$ refers to the weight loss from room conditions to 110°C, and $H_2O > 110°$ to the weight loss from 110° to 1000°C. All samples were examined as thin, oriented clay layers on glass slides by XRD using a Philips Norelco diffractometer (Ni-filtered CuKα radiation and 1°2θ/min recording rate). Samples were equilibrated in ethylene glycol vapor (4 days, 50°C), in various relative humidities at room temperature, and at various elevated temperatures to 500°C.

RESULTS

The chemical analyses and derived formulae are set out in Tables 1 and 2; the XRD data are summarized in Tables 3 and 4. The possible precipitation of $Al(OH)_3$ and $Mg(OH)_2$ is highly important in any discussion of the data in Tables 1 and 2. In the Al-system, bayerite was clearly formed when 60 ml of NaOH was added and possibly was formed when 50 ml was added. In the Mg-system, brucite was precipitated when 60 ml of NaOH was added, but was doubtfully present when 50 ml was added. No corrections have been applied for these hydroxides in evaluating the formulae; thus, some of the Al, Mg, and OH shown as interlayer material for samples in columns 5 and 6 of Tables 1 and 2 must be attributed to externally precipitated hydroxides.

Table 2.   Chemical analyses and derived formulae of Na-montmorillonite and of hydroxy-Mg-montmorillonites (0, . . . , 6, see text).

	Na-mont-morillonite	0	1	2	3	4	5	6
SiO_2	58.3	53.1	50.0	47.6	44.6	42.5	41.1	39.1
Al_2O_3	20.21	18.43	17.31	16.43	15.55	14.71	14.26	13.63
Fe_2O_3	3.68	3.42	3.28	3.02	2.78	2.66	2.42	2.41
MgO	2.79	5.25	8.82	13.16	15.98	20.19	22.86	25.26
CaO	0.50	—	—	—	—	—	—	—
Na_2O	2.77	0.26	0.17	0.15	0.11	0.11	0.06	0.36
K_2O	tr	tr	tr	tr	tr	tr	tr	tr
$H_2O > 110°C$	6.16	7.85	8.58	10.04	11.79	13.00	14.26	14.65
$H_2O < 110°C$	4.68	11.31	10.33	8.14	7.20	6.00	4.41	4.09
Total	99.09	99.62	98.49	98.54	98.01	99.17	99.37	99.50
Layer composition								
Si	3.93	3.93	3.93	3.93	3.93	3.93	3.93	3.93
Al	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
Al	1.53	1.54	1.53	1.53	1.54	1.53	1.54	1.54
Fe	0.19	0.19	0.19	0.19	0.18	0.19	0.17	0.18
Mg	0.28	0.27	0.28	0.28	0.28	0.28	0.29	0.28
Anions				$O_{10}(OH)_2$				
Interlayer composition								
Ca	0.04	—	—	—	—	—	—	—
Na	0.36	0.04	0.03	0.02	0.02	0.02	0.01	0.07
Mg	—	0.31	0.75	1.34	1.82	2.50	2.97	3.50
OH	0.10	0.32	1.18	2.36	3.32	4.68	5.60	6.72
H_2O	0.34	0.78	0.66	0.58	0.80	0.67	0.75	0.55
OH/Mg	—	1.03	1.57	1.76	1.82	1.87	1.89	1.92
$(OH + H_2O)/Mg$	—	3.55	2.45	2.19	2.26	2.14	2.14	2.08

tr = trace.

DISCUSSION
Derivation of crystal-chemical formulae

Structural formulae of montmorillonites are usually derived by one of two methods: (1) when the exchange positions are occupied by ions, such as Na^+ and Ca^{2+}, which cannot enter the 2:1 layer structure, the total number of Si, Al, Mg, Fe, and other non-exchangeable ions is normalized to 6.0 to fill the tetrahedral and octahedral layer sites, (2) the total cation valence for layer and interlayer cations is normalized to +22 to correspond with the anions $O_{10}(OH)_2$. When both methods give essentially identical results, the montmorillonite can be assumed to be close to the ideal arrangement. Grim and Güven (1978, 149–151) discussed the uncertainties involved in these procedures and concluded that method (1) has important advantages. The present analyses are based on method (1) but, as is discussed below, additional problems arise with hydroxy-metal montmorillonites.

Using method (1), for Na-montmorillonite in Table 1, O and H_2O^+ were found to be 11.04 and 1.39, which is interpreted as $O_{11}(H_2O)$ or $O_{10}(OH)_2$ in the layer structure and $O_{0.04}(H_2O)_{0.39}$ or $(OH)_{0.08}(H_2O)_{0.35}$ in the interlayer. The difference between $O_{11.04}$ and the ideal value O_{11} is trivial and well within the accuracy of the experimental data. Evidently for this montmorillonite, both

methods of deriving the formula give essentially the same result. The interlayer water retained at 110°C, $0.35 H_2O$, may be a significant result since it is numerically close to the number of interlayer cations, $Na_{0.30}Ca_{0.04}$; it suggests that one H_2O molecule is associated with each interlayer cation at this temperature, 110°C.

Neither of the usual methods can be used for hydroxy-metal montmorillonites and one can proceed only on the supposition that the layer structure remains unchanged. In Tables 1 and 2, the Si ions in the layer structure were assumed to remain unchanged at 3.93. The tetrahedral and octahedral sites were filled with 6.00 cations, and the remaining cations were placed in interlayer positions. Anions and water molecules in excess of $O_{11}(H_2O)$, i.e., $O_{10}(OH)_2$, also were placed in interlayer positions.

One important example can be considered. In column 0 of Table 1, which corresponds to zero addition of NaOH, the O, H_2O contents are found to be $O_{11.38}(H_2O)_{2.22}$, values that correspond to $O_{11}(H_2O)$ or $O_{10}(OH)_2$ in the layer structure, and $O_{0.38}(H_2O)_{1.22}$ or $(OH)_{0.76}(H_2O)_{0.84}$ in the interlayer. The number of Al ions in the interlayer is 0.35 and the ratio OH/Al, 2.17, is close to $[Al(OH)_2]^+$ for the interlayer cations. The ratio $(OH + H_2O)/Al$, 4.57, is less than an anticipated
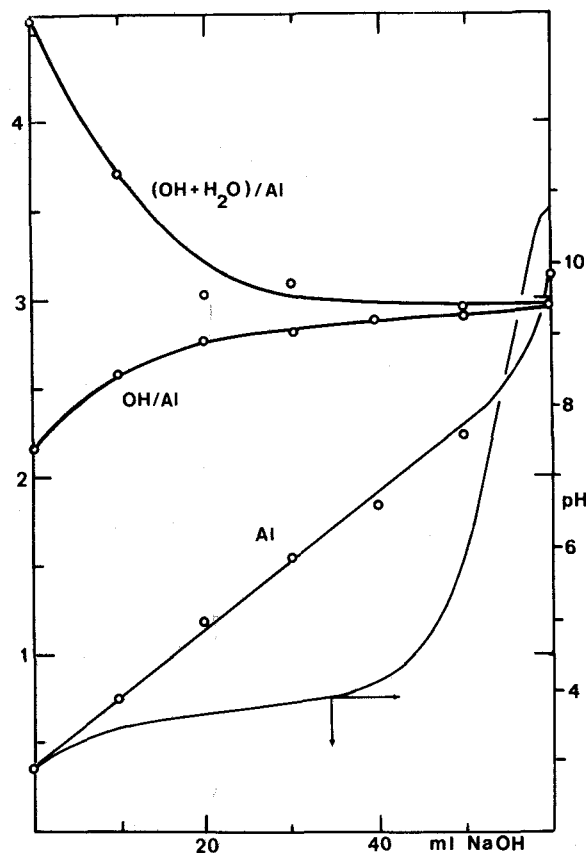
Figure 1. Al ions per formula unit and ratios OH/Al and $(OH + H_2O)/Al$ in interlayer compositions, with increase of NaOH in the system. pH of the system with increase of NaOH.

Figure 2. Mg ions per formula unit and ratios OH/Mg and $(OH + H_2O)/Mg$ in interlayer compositions, with increase of NaOH in the system. pH of the system with increase of NaOH.

six-fold coordination but some coordinated water could easily have been lost at 110°C.

The results for the hydroxy-Al and hydroxy-Mg systems are shown in Tables 1 and 2, respectively. Also shown are the ratios OH/Al and $(OH + H_2O)/Al$ and similar ratios with Mg. The changes in these ratios and in the amounts of interlayer Al and Mg are shown in Figures 1 and 2 in relation to the amount of added NaOH; also shown are the pH variations in the two systems.

The nature of the interlayer hydroxy materials

Probably about 45 ml of NaOH is the maximum amount of NaOH that can be added to the Al-system without hydroxide being precipitated; the hydroxide is bayerite rather than gibbsite. When this amount of NaOH was added, the pH was near 5 and began to rise rapidly. Figure 1 shows that with this amount of NaOH, about 2 Al per formula unit with OH/Al ≃ 2.8 was present in the interlayer.

Probably about 45–50 ml of NaOH is the maximum amount which can be added to the Mg-system without brucite being formed. When this amount of NaOH was
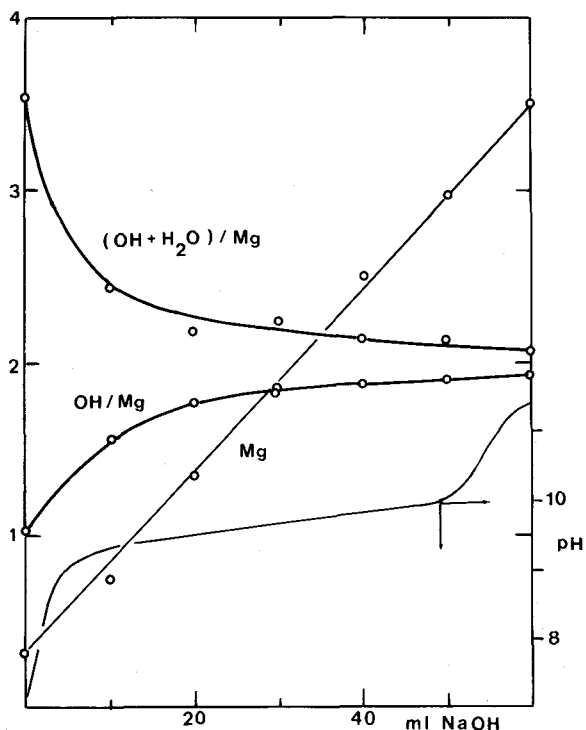
added, the pH was near 10 and began to rise rapidly. Figure 2 shows that with this amount of NaOH, almost exactly 3 Mg per formula unit with OH/Mg ≃ 1.9 was present in the interlayer. The results, therefore, indicate very clearly the development of gibbsite-like and brucite-like layers in the montmorillonite.

As has been mentioned above, prior to addition of NaOH, the OH/Al ratio was 2.17, which corresponds closely to the formula $[Al(OH)_2]^+$. In the magnesium system, the corresponding value was OH/Mg = 1.03, corresponding to a formula of $[Mg(OH)]^+$. These formulae depend on small amounts of Al, Mg, and OH remaining after tetrahedral and octahedral sites have been filled with 6.00 cations and after $O_{10}(OH)_2$ anions have been placed in the silicate layers. The results must be interpreted cautiously as must the ratios $(OH + H_2O)/M$ which fall below the ideal value of 6.0 for monomeric ions. It would not be reasonable to estimate an average degree of polymerization, with M ions linked by 2(OH). While the need for caution in interpreting the results is evident, the tendency to form singly charged ions cannot be ignored. Mering and Glaeser (1954), in their study of (Na,Ca)-montmorillonites, emphasized the importance of local neutralization of layer charges in accordance with Pauling's rules. This local neutralization raises no problems for monovalent ions but is less easy for di- and polyvalent cations and will depend

Table 3.   Interlayer compositions and basal spacings of hydroxy-Al-montmorillonites after various treatments.

Sample	Partial interlayer composition[1]			Basal spacings (Å)[2]							
	Na	Al	OH	Ethylene glycol	100% RH	55% RH	55°C	100°C	170°C	300°C	500°C
0		0.35	0.76	17.20	ML	12.6	12.2	ML	ML	10.0	9.75
1	—	0.75	1.94	17.45	ML	ML	ML	ML	ML	ML	10.2
2	—	1.19	3.30	21.8	19.90	20.0	14.5	14.4	ML	ML	ML
3	—	1.54	4.32	21.7	19.80	19.90	14.5	14.5	14.4	ML	ML
4	—	1.84	5.26	21.8	19.75	19.95	14.60	14.50	14.45	14.25	13.25
5	—	2.23[3]	6.48	21.8	19.85	19.95	14.55	14.55	14.55	14.4	13.6
6	0.17	3.15[4]	8.84	17.25	ML	15.9	ML	ML	ML	ML	10.0

[1] See also Table 1.
[2] Where basal spacings are given to two decimal figures, four or more basal reflections were measured and the accuracy is of the order ±0.1 Å or better; where one decimal figure is given, three or four basal reflections were measured and the accuracy is ±0.1 Å or poorer. ML = mixed-layer material giving non-integral reflections.
[3] Al(OH)$_3$ impurity may be present.
[4] Al(OH)$_3$ impurity seen in XRD patterns.

on the statistical distribution of the layer charges. Local neutralization may be difficult with Al^{3+} ions. One can visualize an interlayer Al^{3+} with an excess of positive charge after neutralizing the local conditions arising from the layer replacements. This excess positive charge will attract hydroxyl ions. The monovalent ions [Al(OH)$_2$]$^+$ and [Mg(OH)]$^+$ will satisfy local conditions in the same manner as Na$^+$ ions.

X-ray powder diffraction data

Tables 3 and 4 show that the hydroxy-Mg-montmorillonites exhibited much less tendency to swell in ethylene glycol and in water and were thermally more stable than hydroxy-Al-montmorillonites. The last observation correlates with the greater thermal stability of Mg(OH)$_2$ compared with Al(OH)$_3$.

Hydroxy-Mg-montmorillonites, Table 4, have well-defined basal spacings in the range 14.6–14.9 Å for most of the conditions shown in the table. These spacings are greater than those of normal chlorites which lie in the

range 14.2–14.4 Å. Nevertheless, they have generally been accepted as indicating chlorite-like products. It is now well established that the basal spacings of chlorites increase as the layer charges decrease, and the following relations have been given: d(001) = 14.55 − 0.29x (Brindley, 1961, p. 269) and d(001) = 14.648 − 0.378x (Bailey, 1975, p. 245), where x is the number of Al-for-Si substitutions. When x = 0.07, as in the hydroxy-Mg-montmorillonites, d = 14.53 or 14.62 from these relations. Evidently the larger observed spacings can be attributed mainly to the smaller electrostatic attractions between the layers and interlayers. Hydroxy-Al montmorillonites, Table 3, showed a similar spacing of about 14.5 Å at 55°C and higher temperature, but with a greater tendency to decompose, as shown by the many entries of ML = mixed-layer formation in the table.

With small additions of NaOH to both the Al- and the Mg-system, the products expanded to about 17.1–17.3 Å with ethylene glycol, which is normal behavior for many montmorillonites. Evidently the interlayers were

Table 4.   Interlayer compositions and basal spacings of hydroxy-Mg-montmorillonites after various treatments.

Sample	Partial interlayer composition[1]			Basal spacings (Å)[2]							
	Na	Mg	OH	Ethylene glycol	100% RH	55% RH	55°C	100°C	300°C	400°C	500°C
0	0.04	0.31	0.32	17.15	ML	15.55	14.7	14.7	9.55	9.45	9.55
1	0.03	0.75	1.18	17.10	ML	15.35	14.95	14.9	9.65	9.65	9.65
2	0.02	1.34	2.36	ML	15.0	14.95	14.85	14.85	ML	ML	ML
3	0.02	1.82	3.32	ML	14.9	14.9	14.85	14.85	ML	ML	ML
4	0.02	2.50	4.68	14.85	14.85	14.85	14.80	14.60	14.5	ML	decomp.
5	0.01	2.97	5.60	14.80	14.80	14.80	14.80	14.75	14.5	ML	decomp.
6	0.07	3.50[3]	6.72[3]	14.80	14.80	14.80	14.85	14.70	14.5	ML	decomp.

[1] See also Table 2.
[2] See footnote, Table 3. ML = mixed layer. decomp. = decomposed.
[3] Mg(OH)$_2$ impurity seen in X-ray powder diffraction patterns.

not occupied by large complexes which might prevent the entry of ethylene glycol. With larger additions of NaOH, the Mg-hydroxy system did not expand with ethylene glycol and, therefore, resembled a chlorite, while the Al-hydroxy system showed abnormal swelling to 21.8 Å. This last value can be interpreted as 14.5–14.6 Å for the "normal" chlorite-like spacing plus 7.2 Å expansion for two single sheets of ethylene glycol molecules. (Ethylene glycol expands most dry montmorillonites with spacings near 9.8 Å to spacings near 17 Å by two sheets of ethylene glycol molecules.) Water vapor at 100 and 55% RH also expanded the hydroxy-Al system to about 19.8–19.9 Å, which corresponds to about two sheets of water molecules additional to the hydroxy-Al complexes. The last line of Table 3 for sample 6 shows that with 60 ml NaOH added to the Al-system about half of the exchange positions were occupied by 0.17 Na^+; the montmorillonite then behaved more nearly in the manner of a monovalent ion montmorillonite.

Comparison with other data for Mg- and R^{2+}-hydroxy montmorillonites

In the early work of Caillère and Hénin (1949), a partial chemical analysis of a Mg-hydroxy-montmorillonite gave SiO_2 49.8%, Al_2O_3 29%, CaO 2.3%, MgO 18.9% (total 100%) with a much higher proportion of Al_2O_3 than the analyses of Table 2. On the basis of the SiO_2/MgO ratio, their product appears similar to that shown in Table 2, composition 3, prepared with 30 ml of NaOH and therefore only about half-way towards a maximum filling of the interlayers; the reported XRD data also are consistent with an intermediate product. Slaughter and Milne (1960) gave no chemical analyses but used X-ray basal diffraction intensities to check the development of brucite-like interlayers. The diffraction intensities are related to interlayer compositions but do not differentiate between OH and H_2O, and when only five orders of diffraction are used, the method is indicative rather than precise. Slaughter and Milne (1960) and subsequently Gupta and Malik (1969a) considered that the basal spacings might be larger than those of normal chlorites because of "the necessity of accommodating the original exchange cations." The present chemical data show, however, that the initial Na^+ ions were fully exchanged by Mg or hydroxy-Mg ions. The increased spacings are most likely related to the weaker electrostatic attractions discussed above.

The data in Table 4 show that the hydroxy-Mg products were less stable to heat-treatment than normal chlorites in that decomposition occurred below 400°C in all cases. This lower stability can be attributed to smaller particle sizes and weaker electrostatic bonding. Fine-grained natural chlorites have been shown to decompose at lower temperatures, in agreement with the results of Slaughter and Milne (1960). However, Gupta

and Malik (1969b) obtained results which were closer to the thermal behavior of normal chlorites.

Slaughter and Milne (1960) remarked that products with fully developed hydroxy interlayers showed no expansion with water or ethylene glycol, but with incomplete layers they expanded to 18.8 Å and 17 Å, respectively. The present data, Table 4, show 17.1-Å spacings with ethylene glycol when zero NaOH and 10 ml NaOH were added to the system. In 100% RH, expansion gave rise to mixed-layering; a fully developed 18.8-Å spacing was not observed.

Carstea *et al.* (1970b) remarked that $[Mg(OH)]^+$ is "an intermediate step towards hydroxide formation," which is confirmed by the present results. Yamanaka and Brindley (1978), discussing the mechanism of formation of hydroxy-Ni interlayers, suggested an internal mechanism related to dissociation of interlayer H_2O molecules, as follows:

$$[Ni\ nH_2O]^{2+} \rightarrow [Ni(OH)(n-1)H_2O]^+ + H^+,$$

with subsequent exchange of $2H^+$ by additional Ni^{2+} ions. A similar mechanism is conceivable with other divalent ions provided the electrostatic field of the cations increases significantly the tendency for dissociation of interlayer water molecules.

Among the various studies of hydroxy-Ni montmorillonites, only Yamanaka and Brindley (1978) gave chemical analyses and structural formulae of the products. Their results, when plotted in the manner of Figure 2, show similar variations of Ni ions per formula unit and of the ratios OH/Ni and $(OH + H_2O)$/Ni. Without the addition of NaOH, the OH/Ni ratio was 0.40, so that the interlayer cations may have been about equally Ni^{2+} and $[Ni(OH)]^+$, but when as little as 3 ml NaOH was added to the system, the ratio increased to 1.0, corresponding to $[Ni(OH)]^+$ ions.

Comparison with other data for hydroxy-Al- and hydroxy-R^{3+}-montmorillonites

Many studies have been made of hydroxy-Al-montmorillonites and a few with other hydroxy-R^{3+}-montmorillonites. Caillère and Hénin (1949) and Slaughter and Milne (1960) included Fe^{3+} and Cr^{3+} ions, Carstea (1968) and Carstea *et al.* (1970a, 1970b) considered Fe^{3+} ions, and Brindley and Yamanaka (1979) studied Cr^{3+} ions. In this last study it was found that without addition of NaOH to the system, the interlayer composition corresponded very closely to cations of the form $[Cr(OH)(H_2O)_5]^{2+}$, and with a very small addition of NaOH, to cations of the form $[Cr(OH)_2(H_2O)_4]^+$.

In the hydroxy-Al system, it seems that in the early stages of reaction where the OH/Al ratio <2, monomeric ions, such as $[Al(OH)]^+$ and $[Al(OH)_2]^{2+}$, are likely to be present; with higher ratios of OH/Al various polymerized forms are developed, such as $[Al_4(OH)_8]^{4+}$ with OH/Al = 2, $[Al_7(OH)_{16}]^{5+}$ with OH/Al = 2.29,

and $[Al_{13}(OH)_{32}]^{7+}$ with OH/Al = 2.46. Still more complex forms, such as $[Al_{24}(OH)_{60}]^{12+}$ and $[Al_{54}(OH)_{144}]^{18+}$, all having various numbers of associated water molecules, may be formed. These hydroxy polymers represent progressive developments towards $Al(OH)_3$ (Frink and Peech, 1963; Hsu and Bates, 1964; Aveston, 1965; Fripiat et al., 1965; Hsu, 1968; Van Cauwelaert and Bosmans, 1969). Hsu (1968) considered that the polymerized hydroxy-Al material will be "most tightly held when the negative charge distribution in the clay exactly matches the positive charge distribution of the Al-polymer," which corresponds broadly with the concepts of Mering and Glaeser (1954) on local charge balancing.

Few studies have hitherto been concerned directly with the compositions and crystal-chemical formulae of hydroxy-Al montmorillonites, but some (Slaughter and Milne, 1960; Brydon and Kodama, 1966; Rich, 1968) have used X-ray basal diffraction intensities to trace the evolution of the interlayer material towards a gibbsite-like form. Brydon and Kodama (1966) gave chemical analyses of products after various additions of $AlCl_3$ solution and titration with $Ca(OH)_2$ to a final pH of 5.0 showing similarities to those presented here in Table 1. However, without an analysis of the montmorillonite prior to treatment, the compositions of the products cannot be converted to structural formulae. H. Kodama (Soil Research Institute, Canada Department of Agriculture, Ottawa, Ontario, personal communication) furnished a chemical analysis of montmorillonite which probably corresponded to the material used by Brydon and Kodama in 1966. With the aid of this analysis, the results for their hydroxy-Al products appear broadly consistent with those of the present experiments; differences in detail can probably be attributed to the different experimental conditions.

The swelling behavior of hydroxy-Al-montmorillonites has been considered by other investigators. Sawhney (1968) recorded spacings of 19.0 Å and 19.6 Å in solutions of OH/Al = 2.0 and 2.4, particularly after the samples were aged for several weeks, when "sharp, integral orders of the basal spacing" were obtained. Slaughter and Milne (1960, p. 120) noted the formation of a 20-Å basal spacing "at a very wet stage" and a 21.7-Å spacing with ethylene glycol; both results correspond well with the data in Table 3. They noted also that smaller spacings could be obtained, which have not been recorded here. The possible development of superlattice effects when dehydration occurs was noted by Barnhisel and Rich (1966), but in the present work, only the formation of mixed-layer sequences which are probably mixtures of 14-Å and 10-Å layers can be affirmed. Gupta and Malik (1969c, p. 1630) recorded that their hydroxy-Al-montmorillonite, when heated to 550°C, gave an increased intensity of the 001 reflection which corresponds to the behavior of chlorites.

The present results can be compared with those obtained in a study of hydroxy-Al-beidellite (Brindley and Sempels, 1977) in which the tetrahedral cation substitutions amounted to about $Al_{0.26}$ as compared with $Al_{0.07}$ in the present work. This clay, after treatment with solutions having OH/Al = 2.0 and 2.4, gave larger spacings at 110°C (17.0–17.9 Å) and significantly larger spacings at 500°C (in the range 15.6–17.2 Å) than the values for hydroxy-Al-montmorillonites. In other words, beidellite gave more stable interlayers than montmorillonite, probably because of the higher tetrahedral charge and stronger electrostatic attractions.

CONCLUSIONS

The present studies show the progressive development of hydroxy-Al and hydroxy-Mg interlayers towards gibbsite-like and brucite-like compositions when the OH/Al and OH/Mg ratios in the interlayers increased towards the values of 3 and 2, respectively. Without addition of NaOH to the systems, the interlayer cations approximated to $[Al(OH)_2]^+$ and $[Mg(OH)]^+$. Swelling in ethylene glycol and in water vapor and the stability or instability to heating depended on the OH/Al and OH/Mg ratios in the interlayers. The present results confirm most of the published data on these systems, but show more clearly the progressive changes of composition and properties with the amount of NaOH added.

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Резюме—Гидрокси-Al и гидрокси-Mg-монтмориллониты были подготовлены путём воздействия растворов алюминиевых и магниевых нитратов на дисперсный Na-монтмориллонит с последующим титрованием растворами NaOH, так что соотношение OH/Al изменялось от нуля до 3,0, а соотношение OH/Mg от нуля до 2,0. Внешнее осаждение гидроокисей Al и Mg наблюдалось, когда соотношение OH/M (M = металл) достигало 2 и 3 соответственно. На основе химического анализа, исходя из предположения, что силикатный состав слоёв не изменялся, были получены структурные формулы исходных Na-монтмориллонитов и гидрокси-металл монтмориллонитов. Перед добавкой NaOH межслойный материал напоминал по состоянию [Al(OH)₂]⁺ и [Mg(OH)]⁺. После добавки NaOH межслойный состав постепенно сдвинулся в сторону Al(OH)₃ и Mg(OH)₂. Внешние осаждения выступали, когда гидрокси-слои достигали завершения. Данные по рентгеновской порошковой дифракции показали, что гидрокси-Mg продукты имеют меньшую тенденцию к набуханию в этиленовом гликоле и воде, и большую термическую стабильность, чем гидрокси-Al продукты. В случае, когда средние межслойные составы были близки к Al(OH)₂ и Mg(OH), набухание проходило по более нормальному пути. [Е.С.]

Resümee—Hydroxy-Al- und Hydroxy-Mg-Montmorillonite wurden hergestellt, indem man dispergierten Na-Montmorillonit mit Aluminium- und Magnesiumnitratlösungen behandelte und mit NaOH-Lösungen titrierte, so daß das OH/Al-Verhältnis von 0 bis 3,0, und das OH/Mg-Verhältnis von 0 bis 2,0 variierte. Al- und Mg-Hydroxyde fielen aus, wenn das OH/M-Verhältnis (M = Metall) 3 bzw. 2 erreichte. Aus chemischen Analysen des ursprünglichen Na-Montmorillonites und der Hydroxy-Metall-Montmorillonite wurden unter der Annahme Strukturformeln abgeleitet, daß die Zusammensetzung der Silikatlagen unverändert bleibt. Vor der Zugabe von NaOH hatte die durchschnittliche Zwischenschichtsubstanz etwa die Zusammensetzung [Al(OH)₂]⁺ bzw. [Mg(OH)]⁺. Durch die Zugabe von NaOH verschob sich die Zusammensetzung der Zwischenschict immer mehr in Richtung Al(OH)₃ bzw. Mg(OH)₂. Wenn die Hydroxy-Zwischenlagen vollständig waren, war eine Ausfällung zu beobachten. Röntgendiffraktometerdaten zeigten, daß die Hydroxy-Mg-Produkte eine geringe Tendenz zum Quellen in Ethylenglycol und Wasser, sowie eine größere thermische Stabilität haben als die Hydroxy-Al-Produkte. Anfänglich, wenn die durchschnittliche Zusammensetzung der Zwischenschicht etwa Al(OH)₂ bzw. Mg(OH) ist, zeigt sich nahezu das übliche Quellverhalten. [U.W.]

Résumé—Les montmorillonites hydroxy-Al et hydroxy-Mg ont été préparées en traitant de la montmorillonite-Na dispersée avec des solutions de nitrate d'aluminium et de magnesium et en titrant avec des solutions de NaOH, de telle façon que la proportion OH/Al variait de zéro à 3,0 et la proportion OH/Mg de zéro à 2,0. Une précipitation externe d'hydroxides d'Al et de Mg a été observée lorsque les proportions OH/M (M = metal) approchaient 3 et 2, respectivement. A partir d'analyses chimiques des montmorillonites-Na initiales et des motmorillonites hydroxy-metal, des formules structurales ont été dérivées en assumant que les compositions de la couche silicate demeuraient inchangées. Avant l'addition de NaOH, la composition moyenne du matériel intercouche était approximativement $[Al(OH)_2]^+$ et $[Mg(OH)]^+$. Avec l'addition de NaOH, les compositions intercouche se sont déplacées progressivement vers $Al(OH)_3$ et $Mg(OH)_2$. Lorsque les intercouches hydroxy étaient presque complètes, la precipitation externe a été observée. Les données de diffraction poudrée aux rayons-X ont montré que les produits hydroxy-Mg avaient moins tendance á gonfler dans le glycol éthylène et dans l'eau, et avaient une plus grande stabilité thermale que les produits hydroxy-Al. Initialement, lorsque les compositions moyennes d'intercouches étaient près d'$Al(OH)_2$, et $Mg(OH)$, la conduite du gonflement était plus près de la normale. [D.J.]