HETEROGENEITY OF MONTMORILLONITE SURFACE AND ITS EFFECT ON THE NATURE OF HYDROXY-ALUMINUM INTERLAYERS

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Abstract—A specimen montmorillonite (Arizona bentonite) was treated with hydroxy-aluminum solutions of various basicity. The cation exchange sites of this clay were found not to be homogeneous in their strength of retaining hydroxy-aluminum polymers; this strength varied from very weak, with which the Al polymers were only loosely held, to very strong, with which stable interlayer Al-clay complexes were formed. When a large amount of clay was treated with a small amount of solution, the polymers were held only in positions of strong affinity; the polymers were difficult to extract with neutral salt solutions and did not change to crystalline $Al(OH)_3$ during prolonged aging. When a small amount of clay was treated with a large amount of solution, the exchange sites were completely occupied by polymers; a portion of these polymers was easily extractable with neutral salt solutions and, during aging, changed to $Al(OH)_3$. This contrast is significant in any attempt to compare results obtained under different experimental conditions and to correlate laboratory experimentation with the occurrence of gibbsite and interlayer Al-clay complexes in nature.

INTRODUCTION

THAT certain forms of Al can be fixed in the interlayer space of expandable clay minerals has long been known. A number of workers have endeavored to characterize the nature of the interlayer Al in order to assess its significance to the genesis of gibbsite and other clay minerals in nature (Barnhisel and Rich, 1963 and 1965; Coleman and Thomas, 1964; Frink and Peech, 1963; Hsu and Bates, 1964b; Jackson, 1960 and 1963; Kaddah and Coleman, 1967; Ragland and Coleman, 1960; Rich, 1960; Shen and Rich, 1962; Singh and Brydon, 1967; Thomas, 1960; Turner, 1965; Turner and Brydon, 1965 and 1967; Weismiller *et al.* 1967). A majority of the workers now believe that Al is present as positively charged hydroxy-aluminum polymers in the interlayer space in the initial stage but have some uncertainty as to its fate during prolonged aging. Some workers suggested that such Al-clay complexes are stable and are the intermediate products of chloritization. Many others believe that hydroxy-aluminum polymer interlayers are not stable and will be transformed into

gibbsite after prolonged aging. The effects of mineral surface, the OH/Al ratio of the original Al solution, time of aging, and the amount of Al "precipitated" per unit weight of clay on the gibbsite formation process, have been discussed in several papers.

That the surface of many clay minerals is not homogeneous in its strength of holding cations has been demonstrated by Marshall and his associates in numerous reports, and was recently summarized in a monograph (Marshall, 1964). The present report illustrates the significance of this concept in the study of interlayer Al in clay. With the montmorillonite used in this study, Al was not found to be of uniform strength over the entire interlayer surface. This was indicated by the diverse exchange ability of these polymers and their tendency to form gibbsite.

MATERIALS

Montmorillonite

The clay used came from Chambers, Arizona (obtained from Ward's Natural Science Establishment, Inc., Reference Clay Minerals, No. 23). The coarse clay fraction (0.2–$2\,\mu$ equivalent spherical diameter), fractionated according to Jackson's (1956) procedure, was saturated with Na^+ and used in this study. The cation-exchange capacity of this clay is 110.1 meq/100 g.

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Hydroxy-aluminum solutions

The solutions were prepared by adding, drop-wise, the appropriate amount of 0·1 N NaOH to 200 ml of 0·2 M AlCl$_3$ solution at approx. 100 ml/hr, and then diluting the solutions to 2 l. with water to give a final concentration of 0·02 M Al. The amount of NaOH was so adjusted as to give desired molar ratios of from 0·6 to 2·7. The nature of these solutions was discussed in a previous report (Hsu and Bates, 1964a).

METHODS

Preparation of specimen

Portions (0·4 g) of Na-saturated montmorillonite were mixed with varying amounts of hydroxy-aluminum solutions having molar ratios of NaOH/Al between 0·6 and 2·7. Immediately after preparation samples were shaken for 6 hr and then frequently during every day. The NaOH/Al molar ratio and amount of Al solution will be shown for the individual experiments.

Pretreatment of sample for chemical analysis

The sample was centrifuged after it had been aged for a predetermined length of time. The solution was analyzed for its pH and Al content. Part of the aluminum would, of course, be present at the edge site, but for the purpose of this study all the Al sorbed by the clay was assumed to be in the interlayer space. The clay was washed once with 100 ml of 50 per cent alcohol and then successively extracted eight times, each time using 40 ml N NaCl solution and 30 min shaking. Each extract was collected separately and analyzed for its Al content, referred to as exchangeable Al. After eight extractions the residual Al was referred to as nonexchangeable Al and was calculated by subtracting the exchangeable Al from the total amount of Al sorbed by the clay. The interlayer Al is so classified for the convenience of discussion, but the distinction here between exchangeable Al and non-exchangeable Al is an arbitrary one. The clay was then washed twice with 100 ml of 90 per cent alcohol and extracted four times with 25 ml N MgCl$_2$ solution with 30 min shaking. The four MgCl$_2$ extracts were combined and the Na$^+$ content of the combination was determined and referred to as the cation-exchange capacity of the clay after Al solution treatment.

General chemical analysis

The pH was measured with a Beckman Model G or a Heath recording pH meter. Aluminum was determined with aluminon (Hsu, 1963). Sodium was determined with a Beckman DU Flamephotometer.

Basicity of exchangeable aluminum

The first NaCl extract was titrated with 0·1 N NaOH to pH 8 and the basicity of exchangeable Al calculated as follows:

$$\text{Basicity of exch. Al} = 3 - \frac{\text{NaOH consumed (meq)}}{\text{Exch. Al (mM)}}.$$

Basicity of non-exch. Al

The basicity of non-exchangeable Al was calculated as follows:

Basicity of non-exch. Al =

$$3 - \frac{\text{Exch. charge inact. (meq)}}{\text{Non-exch. Al (mM)}}.$$

The inactivated exchange charge was estimated by subtracting the cation-exchange capacity after treatment from that of the original clay. The amount of non-exchangeable Al was estimated by subtracting the exchangeable Al from the total amount of Al sorbed by the clay.

Differential thermal analysis

After the chemical analysis the residual clay was washed once with 100 ml of water and then washed with alcohol onto a filter paper and dried. The differential thermal analysis was made with a portable unit made by Eberback.

RESULTS

Exchangeability of interlayer aluminum

The results (Table 1) were obtained by treating 0·4 g of clay with 100 ml of hydroxy-aluminum solutions of basicities 0·6, 1·8, and 2·25, and then successively extracting with N NaCl solution eight times (40 ml each). Total Al in the eight extracts varied from 11 per cent of the total Al sorbed by the clay to 55 per cent, depending on the OH/Al ratio of the original solution and the time of aging. Of the total Al extracted, over 50 per cent was found in the first extract. The Al contents in successive extracts decreased progressively with the increased order of extraction. The Al concentrations in the last five extracts were very small, even though a large amount of Al was present in the interlayer space. For example, for the sample treated with the Al solution of basicity of 0·6 and aged for 2 weeks, 21·7 per cent of the interlayer Al was present in the first extraction, 9·0 per cent in the next two extractions, and only 6·1 per cent in the remaining five extractions despite the fact that 63 per cent of the total interlayer Al still remained in the clay. In contrast, when this clay was rapidly washed with a large excess of 1 N AlCl$_3$ solution, the interlayer Al was found to be entirely

Table 1. Data illustrating diverse exchangeability of interlayer aluminum in montmorillonite, successfully extracted eight times with N NaCl solution

Basicity of original Al solution*	0·6				1·8				2·25			
Time of aging, weeks	2	6	10	34	2	6	10	34	2	6	10	34
Al in solution (ppm)	394·8	390·5	391·5	390·7	297·0	249·0	213·7	170·7	286·4	249·5	219·5	90·2
pH	3·90	3·92	3·87	3·82	4·14	4·16	4·10	3·93	4·35	4·35	4·12	4·05
Al entered clay (mg/g)	36·30	37·38	37·13	37·33	60·75	72·75	81·58	92·33	63·40	72·63	80·13	112·45
Exchangeable Al, (%) Al entered clay:												
1st ex.	21·71	17·50	15·30	15·87	30·48	20·36	14·07	6·92	30·61	23·26	18·74	5·46
2nd	5·92	4·47	4·07	4·00	9·87	6·43	4·53	2·26	10·19	8·09	6·38	2·11
3rd	3·03	2·28	1·97	1·83	4·85	3·05	1·93	1·20	5·13	3·71	2·97	1·16
4th	2·13	1·40	1·23	1·35	3·02	1·83	1·04	0·90	3·22	2·27	1·77	0·79
5th	1·45	0·98	0·81	0·85	1·97	1·10	0·66	0·56	2·23	1·44	1·17	0·62
6th	0·96	0·88	0·69	0·65	1·61	0·86	0·52	0·49	1·65	1·20	0·81	0·42
7th	0·96	0·77	0·60	0·67	1·16	0·77	0·42	0·40	1·35	1·05	0·82	0·34
8th	0·62	0·55	0·45	0·47	0·95	0·55	0·31	0·35	1·05	0·76	0·61	0·31
Total	36·78	28·92	25·12	25·69	53·91	34·91	23·51	13·10	55·43	41·79	33·26	11·19
Non-exchangeable Al, (mg/g clay)	22·95	26·70	27·90	27·78	28·00	47·35	62·40	80·28	28·25	42·27	53·15	99·85
C.E.C. (meq/100 g)	75·0	70·0	66·7	66·8	70·4	52·4	38·6	68·3	71·3	60·3	47·7	56·3
Basicity of interlayer Al:												
Exchangeable	1·16	0·74	0·65	0·49	2·43	2·41	2·40	0·99	2·46	2·41	2·41	1·37
Non-exchangeable	2·58	2·60	2·58	2·58	2·61	2·68	2·72	2·86	2·64	2·65	2·67	2·86
Detection of crystalline Al(OH)$_3$	—	—	—	—	—	—	—	+	—	—	—	+

*Basicity is defined as the NaOH/Al molar ratio; each sample contains 100 ml of Al solution and 0·4 g of montmorillonite; initial Al concentration = 540 ppm.
— = No Al(OH)$_3$ detected; + = Al(OH)$_3$ detected.

present as Al^{3+} and could be completely removed with a neutral salt solution in three extractions.

In all samples, amount of non-exchangeable Al increased with time of aging. For the two samples prepared with solutions of basicities 1·8 or 2·25, obvious decreases in pH and in solution Al concentration were observed. The cation-exchange capacity of these two samples first decreased, but later, in association with the occurrence of crystalline $Al(OH)_3$, they increased. Evidently, part of the interlayer Al converted to $Al(OH)_3$ during aging. Nevertheless, for the sample prepared with a solution of basicity 0·6, the solution pH and the Al concentration decreased only slightly, probably within the experimental uncertainty. No $Al(OH)_3$ was observed even after prolonged aging.

The results (Table 2) demonstrate the effect of amount of solution added on exchangeability of the interlayer Al. In this experiment, 0·4-g portions of clay were treated with a hydroxy-aluminum solution of basicity 2·25, but varying amounts of solution were added. These samples were allowed to stand for 2 weeks and then were extracted with N NaCl eight times (40 ml each). In these samples prepared with 2, 5, and 10 ml of Al solution, prior to the addition of clay the solution was diluted with water to 20 ml. In addition, K-saturated instead of Na-saturated clay was employed. It was found that when 2 ml of Al solution was used, all the aluminum entered the clay and less than 5 per cent of it was exchangeable with NaCl. The proportion of exchangeable Al over the total interlayer Al gradually increased with the amount of solution used until at 50 ml of solution a peak was reached. Nevertheless, the absolute amount of non-exchangeable Al continued to increase with increase in the solution/clay ratio. In all instances the cation-exchange capacity of clay decreased in association

with the increase in the non-exchangeable Al. The clay was far from being completely inactivated even when 400 ml of Al solution was used.

Two other samples were prepared by treating 0·4-g portions of clay with 200 ml of hydroxy-aluminum solutions of basicities 2·55 and 2·7, respectively. These two samples became very compact, and clay particles stuck together shortly after preparation. All the Al sorbed by the clay was not easily extracted, and the cation-exchange capacity decreased to less than 10 meq per 100 g. After 3 months of aging, however, the cation-exchange capacity increased to over 50 meq per 100 g, and, upon differential thermal analysis, gibbsite was detected. These two samples have not been studied in detail, but the preliminary information presented here is considered to be of significance in the interpretation of the nature of interlayer Al.

Basicity of interlayer aluminum

The basicity of the non-exchangeable interlayer aluminum falls within the narrow range of 2·5–2·7 (Tables 1–3) provided no crystalline $Al(OH)_3$ was observed. For the solution of NaOH/Al molar ratio 0·6, the basicity of non-exchangeable Al remained unchanged during aging up to at least 8 months. For other samples, however, the basicity gradually increased during aging, suggesting a gradual growth in size of the polymers. The average basicity of non-exchangeable Al rose to beyond this range when crystalline $Al(OH)_3$ was observed.

The basicity of the rapidly exchangeable* Al varies from 0 to 2·5, depending on amount and

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*Only the first NaCl extract was titrated with NaOH to estimate the basicity of the Al present, the Al concentrations in later extracts being too low for titration.

Table 2. Effect of solution volume on the exchangeability of interlayer aluminum*

Volume of Al solution added (ml)	Al remaining in solution (ppm)	Exchangeability of interlayer Al†			Exch. charge reduction (meq/100 g)	Basicity of interlayer Al	
		Total (mg)	Exchangeable (%)	Non-exchangeable (mg)		Exchangeable	Non-exchangeable
2‡	nil	1·08	4·65	1·03	—	—	—
5‡	nil	2·70	20·4	2·15	—	—	—
10‡	nil	5·40	26·7	4·06	—	—	—
20	nil	10·80	43·4	6·12	26·9	1·70	2·52
50	65·5	23·73	60·6	9·35	32·4	2·45	2·62
100	286·4	25·36	55·4	11·30	38·8	2·46	2·64
200	408·0	26·40	54·3	12·35	41·9	2·49	2·63
400	473·7	26·51	54·0	12·21	40·7	2·55	2·64

*Basicity of Al solution = 2·25. Initial Al concentration = 540 ppm. Weight of clay = 0·4 g. All samples analyzed 2 weeks after preparation.
†All the aluminum sorbed by clay was assumed to be in the interlayer space. It is not essential to distinguish the edge site from the interlayer space for the purpose of this report.
‡Diluted to 20 ml before the addition of montmorillonite.

Table 3. Basicities of exchangeable and non-exchangeable Al in samples other than those listed in Tables 1 and 2

| Al solution added | | Basicity of interlayer Al | |
Basicity	Volume (ml)	Exchangeable	Non-exchangeable
0	100	0	N.D.
0·6	20	0·12	N.D.
0·6	50	0·25	2·51
0·6	100	1·16	2·58
0·6	200	1·96	2·70
0·6	500	2·10	2·68
0·6	1000	2·33	N.D.
1·2	100	2·26	2·60
1·2	200	2·33	2·71
1·5	100	2·23	2·68
1·5	1000	2·47	N.D.
1·8	2 × 50*	2·25	2·62
2·4	200	2·30	2·70
2·4	2 × 50*	2·39	2·63

*Treated with Al solution twice, 50 ml each time.

basicity of the original solutions added and time of aging. The exchangeable Al was found to be present almost entirely as Al^{3+} when the clay was rapidly treated with N $AlCl_3$ solution. The effect of the amount of solution added on the basicity of exchangeable Al is shown in Table 3. When several samples were prepared from the same Al solution of basicity 0·6 but with different volumes of solution, the basicity of the exchangeable Al increased from 0·12 to 2·33 as the solution volume increased from 20 ml to 1 l. Evidently the clay prefers to take up hydroxy-aluminum species, either exchangeable or non-exchangeable. When a small amount of solution was employed, the amount of hydroxy-aluminum polymers is not sufficiently large to exclude all the Al^{3+} and this results in a lower average basicity. With a large amount of solution, Al^{3+} was for the most part excluded from the interlayer Al and the average basicity is thus high.

It is also shown (Table 1) that the basicity of the exchangeable Al decreased with the increased time of aging, in association with the increasing amount of Al fixed and the decrease in the cation-exchange capacity. The original exchangeable Al was mainly a mixture of Al^{3+} and polymers. When a portion of the polymers gradually became non-exchangeable, the basicity of the exchangeable Al gradually decreased approaching Al^{3+}.

Formation of crystalline $Al(OH)_3$ from hydroxy-aluminum interlayers

Differential thermal analysis provides a sensitive method for the detection of crystalline $Al(OH)_3$, as characterized by an endothermic peak near 300°C. The tendency for the interlayer Al to form $Al(OH)_3$ is related (Table 4) to both the basicity and the volume of the original Al solution added, these two factors being interrelated. For example, when 20 ml portions of solutions having NaOH/Al molar ratios of 2·25 or below were added, no crystalline $Al(OH)_3$ was detected even after aging was prolonged to 3 yr. Nevertheless, when 100 ml of the same solutions were added, crystalline $Al(OH)_3$ was detected at a basicity 1·8 after 6 months and at a basicity 2·4 after 3 months.

When identical solutions were allowed to age in the absence of montmorillonite, they became turbid after 6 months to 1 yr, and eventually $Al(OH)_3$ precipitated (Hsu, 1966). Therefore, in the presence of montmorillonite, the formation of $Al(OH)_3$ from the hydroxy-aluminum interlayers is prevented, or at least much delayed, when a small amount of solution is added, whereas it is accelerated when a large amount of solution is added.

DISCUSSION

Diverse exchangeability of interlayer aluminum

The results indicated that the interlayer Al in montmorillonite did not have a uniform extractability, some of it being difficultly extracted with N NaCl solution. Three possible mechanisms may be proposed to interpret this phenomenon:

1. Part of the aluminum is precipitated as insoluble $Al(OH)_3$ and thus difficultly exchanged with NaCl. Crystalline $Al(OH)_3$ has been found in some samples (Tables 1 and 4);

2. Different Al species are present in the original solution. Some species, such as polymers of basicity 2·5 and 2·7, may be held tightly by clay, whereas others, such as Al^{3+}, are rapidly exchangeable;

3. The exchange sites of this montmorillonite are not homogeneous in their strength in holding interlayer Al.

The first two mechanisms are obvious from the results presented, but they are not adequate to interpret all the results. This report, therefore, emphasizes the significance of the third mechanism.

The results indicated that non-exchangeable Al was also present in many samples in which crystalline $Al(OH)_3$ was not present. The sample prepared with the solution of basicity 0·6 is the most convincing example. From the results available, the most favorable conditions for the formation of $Al(OH)_3$ are: high OH/Al ratio of original Al solutions; large amount of Al solution for a certain weight of clay; and a long time of aging. That the non-exchangeable Al is not present as crystalline $Al(OH)_3$ in samples prepared with the solution of basicity 0·6 is obvious.

Table 4. Occurrence of crystalline $Al(OH)_3$ in hydroxy-aluminum-montmorillonite systems

Basicity of Al solution	Volume of Al solution added (ml)	Detection of $Al(OH)_3$ during aging*						
		2	6	10	8	1	2	3
		(weeks)			(months)		(years)	
0·6	20	—	—	—	—	—	—	—
	100	—	—	—	—	—	N.D.	N.D.
	200	—	—	—	—	—	N.D.	N.D.
1·2	20	—	—	—	—	—	—	—
	100	—	—	—	—	—	N.D.	N.D.
	200	—	—	—	—	—	N.D.	N.D.
1·8	20	—	—	—	—	—	—	—
	100	—	—	—	†	†	N.D.	N.D.
	200	—	—	—	N.D.	†	N.D.	N.D.
2·25	20	—	—	—	—	—	—	—
	100	—	—	—	†	†	N.D.	N.D.
	200	—	—	—	N.D.	†	N.D.	N.D.
2·4	20	—	—	—	†	†	†	†
	100	—	—	†	†	†	N.D.	N.D.
	200	—	—	†	†	†	N.D.	N.D.
2·55	20	—	—	—	†	†	†	†
	100	—	—	—	†	†	N.D.	N.D.
	200	—	—	—	†	†	†	N.D.
2·7	20	—	—	—	†	†	†	†
	100	—	—	†	†	†	N.D.	N.D.
	200	—	—	†	†	†	N.D.	N.D.

*— = No $Al(OH)_3$ detected; † = $Al(OH)_3$ detected; N.D. = not determined.

If the composition of the original Al solution were the sole reason for the difference in exchangeability, the following two phenomena should be observed: (a) when several samples are prepared from an identical solution but different volumes are added, the ratio of exchangeable to total interlayer Al should be constant, provided the amount of Al is not so large that all the Al enters the clay, and (b) the exchange charge inactivated should be proportionate to the amount of solution added. The results (Table 2) do not support either of these two possibilities. When the solution volume increased from 2 to 20 ml, the ratio of exchangeable Al to total interlayer Al increased from 4·6 to 43·4 per cent. Also, when the solution volume increased from 20 to 400 ml, the inactivated exchange charge increased from 26·9 to only 41·9 meq/100 g of clay.

To complement these two mechanisms, the hypothesis that the exchange sites of montmorillonite are not homogeneous in their strength in holding interlayer Al is proposed. It has been shown by Marshall and his associates (1964) that in many clay minerals the surface is not homogeneous in nature, and that at different positions the same kind of cation may be held with quite different strength. It is reasonable to suggest that the exchangeability of interlayer Al at different positions may also be different. For convenience, the clay mineral surface may be schematically categorized as strong, moderate, or weak, on the basis of the strength of the clay to hold hydroxy-aluminum polymers. The Al polymers held by these positions are, respectively, non-exchangeable, slowly exchangeable, and rapidly exchangeable by a neutral salt solution. When a small amount of Al is present, all of it goes to the strong position and is thus nearly completely non-exchangeable. With an increasing amount of Al, more and more Al goes to moderate and weak positions and thus becomes slowly or rapidly exchangeable.

Mechanism of fixation

It has been shown that the basicity of the non-exchangeable Al varied within the narrow range of 2·5 and 2·7, regardless of the OH/Al of the original solution and the solution/clay ratio in the sample preparation, provided that crystalline $Al(OH)_3$ was not present. Turner (1965) also reported the species

of basicity 2·6–2·7 for four clay minerals including an Arizona bentonite. This suggests that the species of basicity in this range are favorably retained by the clay. According to the model of polymerization proposed by Hsu and Bates (1964a), the polymerized hydroxy-aluminum species should be written respectively as $[Al_{24}(OH)_{60}]^{12+} \cdot 24H_2O$ and $[Al_{54}(OH)_{144}]^{18+} \cdot 36H_2O$. Other species of intermediate basicities are also plausible. The structures of these polymers resemble fragments of gibbsite, but the Al ions at the edge sites are only partially neutralized by OH^-, which accounts for the source of positive charge. In montmorillonite, the arrangement of aluminum and oxygen atoms in the octahedral sheet is identical to that of gibbsite, and thus also identical to that of hydroxy-aluminum polymers. One negative charge is created when one Mg ion is substituted for one Al ion. Probably the polymer can be most tightly held when the negative charge distribution in the clay exactly matches the positive charge distribution of the Al polymer, but it can only be loosely held when the charge distribution of the polymers and the clay do not match each other closely. The gradual increase in nonexchangeable Al during aging probably is due to the changes in the size and basicity of Al polymers.

On the basis of this interpretation, the basicity of the interlayer Al is related to the characteristic of clay but is not necessarily the same as those present in the original solution. Small Al polymers in the original solution may be enlarged to the units of basicity 2·5–2·7 in the presence of clay. On the other hand, in their study of Al-vermiculite system, Hsu and Bates (1964b, Table 3) demonstrated that when vermiculite was treated with solutions of basicity 2·1 or lower, the basicity of the interlayer Al was only 2·0. When the same vermiculite was treated with Al solution of basicity 2·25 or above, the basicity of initial interlayer Al was high, but later, during aging, it gradually decreased, indicating the gradual breakdown of polymer, although Hsu and Bates did not emphasize this point in their original report. The hydroxy-aluminum species of basicity 2 has been observed with Dowex-50 resin (Hsu and Rich, 1960) and with Wyoming montmorillonite (Shen and Rich, 1962). In contrast, Ragland and Coleman (1960) favor the composition of $Al(OH)_3$. The significance of the clay minerals surface on the nature of interlayer Al has been emphasized by Thomas (1960).

Formation of crystalline $AL(OH)_3$

It has been shown in a previous report (Hsu, 1966) that when the positively charged hydroxy-aluminum polymers were countered by Cl^- ions, they were only meta-stable and tended to hydrolyze further and to polymerize into larger units, eventu-ally forming $Al(OH)_3$, unless an extremely high Cl^- concentration was present. Further studies indicated that certain anions, such as sulfate and phosphate, had a strong affinity for Al and could effectively prohibit the process of $Al(OH)_3$ formation by preventing the polymers from further hydrolysis. The retention of hydroxy-aluminum polymers by montmorillonite may be considered to be the formation of basic salts. Polymers held at various positions may be considered to be different basic salts. Thus, when a small amount of Al solution is added, all of the Al goes to the positions that have a strong affinity for Al. The resultant Al interlayer is stable, comparable to basic Al sulfate or phosphate, and no $Al(OH)_3$ formed even after prolonged aging. When a large amount of Al solution is added, part of the Al goes to those moderate or weak positions. The products are only meta-stable, compared to basic aluminum chloride or perchlorate, and eventually are converted to $Al(OH)_3$. Others (Turner, 1965; Singh and Brydon, 1967; Turner and Brydon, 1965 and 1967) found that a large amount of Al "precipitated" per unit weight of clay was an essential factor for the formation of gibbsite.

On the other hand, the exchange sites in clay may function as a templet which helps the conversion of small polymers to larger units and thus accelerates the formation of $Al(OH)_3$ (Barnhisel and Rich, 1963; Jackson, 1963). In this case, the role of clay mineral is similar to the function of catalyst.

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Résumé — Un échantillon de montmorillonite (bentonite d'Arizona) a été traité avec des solutions d'hydroxyde d'aluminium à bases différentes. Les emplacements d'échange de cations ne se montrent pas homogenes dans leur force de rétention de polymères d'hydroxide d'aluminium. Cette force peut être minimale, en quel cas les polymères d'Al ne sont que légèrement tenus, ou, à l'autre extrême, très importante, avec formation de complexes d'argile-Al en couches intermédiaires stables. Lorsqu'on traite une quantité importante d'argile avec une petite quantité de solution, les polymères ne sont tenus que dans des positions de forte affinité. Les polymères sont difficiles à extraire avec des solutions de sels neutres et ne se transforment pas en Al(OH)_3 cristallin avec le temps. Lorsqu'on traite une petite quantité d'argile avec une importante quantité de solution, les emplacements d'échange sont totalement occupés par des polymères. Une partie d'entre eux est facile à extraire avec des solutions de sels neutres et se transforme avec le temps en Al(OH)_3. Ce contraste prend toute sa signification lorsqu'on essaie de comparer les résultats obtenus fans des conditions d'expérimentation différentes et de mettre les expériences de laboratoire en corrélation avec l'existence dans la nature de complexes de gypsite et d'argile-Al en couches intermédiaires.

Kurzreferat — Eine Proble von Montmorillonit (Arizona Bentonit) wurde mit Aluminumhydroxydlösungen verschiedener Basizität behandelt. Es wurde festgestellt, dass sich die Kationenaustauschstellen dieses Tones in ihrem Festhaltevermögen für Aluminiumhydroxyd Polymere nicht homogen verhalten. Dieses Festhaltevermögen variierte von sehr schwach, wenn die Al-Polymere nur locker gehalten werden, bis zu sehr stark, wenn stabile Zwischenschichten von Al-Tonkomplexen gebildet werden. Bei Behandlung einer grossen Menge von Ton mit einer kleinen Menge Lösung wurden die Polymere nur an Stellen starker Affinität festgehalten; in diesen Fällen war es schwierig, die Polymere mit neutralen Salzlösungen zu extrahieren, und es ergab sich bei ausgedehnter Alterung keine Umwandlung in kristallines Al(OH)_3. Wurde hingegen eine kleine Menge von Ton mit grossen Mengen Lösung behandelt, so wurden die Austauschstellen vollständig durch Polymer besetzt; ein Teil dieser Polymere konnte ohne weiteres durch neutrale Salzlösungen extrahiert werden und veränderte sich während der Alterung in Al(OH)_3. Dieser Gegensatz ist wichtig, wenn es darum geht, unter verschiedenen Versuchsbedingungen erhaltene Ergebnisse miteinander zu vergleichen, oder bei der Feststellung von Zusammenhängen zwischen Laboratoriumsversuchen und natürlich vorkommendem Gibbsit und zwischengeschichtetem Al-Ton.

Резюме—Образец монтмориллонита (Аризонского бентонита) обрабатывали гидрокси-алюминиевыми растворами различной основности. Было обнаружено, что катионообменные места этой глины не однородны по силе удержания гидрокси-алюминиевых полимеров. Сила эта была разной, начиная с очень слабой, которая лишь слегка удерживала полимеры Al до очень сильной, когда образовывались устойчивые глинистые комплексы с алюминиевыми прослойками. Там, где крупное количество глины обрабатывалось малым количеством раствора, полимеры удерживались только в местах сильного сродства. Трудно было извлечь полимеры неймралвныии соляныии раствораии и они не превращались в Al(OH)$_3$ в течение продолжительного старения. Когда небольшое количество глины обрабатывалось крупным количеством раствора, места обмена были совершенно заняты полимерами; часть этих полимеров легко подвергалась извлечению нейтральными соляными растворами и в ходе старения превращалас ьв Al(OH)$_3$. Контраст этот является важным при любой попытке сравнения результатов, достигнутых в разных условиях экспериментирования и для сопоставления проведения экспериментов в лаборатории с залеганием гиббсита и глины с алюминиевыми прослойками.