

CROSS-LINKED SMECTITES. II. FLOCCULATION AND MICROFABRIC CHARACTERISTICS OF HYDROXY-ALUMINUM-MONTMORILLONITE

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Abstract—Cross-linking of Li-montmorillonite by hydroxy-aluminum oligomers was performed in a specially constructed mixing apparatus. Observations on flocculation and solution composition were carried out during and after the cross-linking reaction; the dry product was studied by scanning electron microscopy.

Flocculation was most pronounced at Al/montmorillonite ratios between 0.98 and 2.45 mM/g; below and above this range, flocculation was much less intensive. These observations can be explained by heterocoagulation and protecting colloid action. A complete neutralization of the montmorillonite charge was estimated at 1.9 mM adsorbed Al per g clay, and in order to account for the electrical charge of the hydroxy-Al, polymers with an average charge of 0.5 per Al atom must be assumed on the montmorillonite surface. Assuming that the hydroxy-aluminum form in the unreacted solution is $Al_6(OH)^{3+}_{12}$, the adsorbed polymer will be $Al_{24}(OH)^{12+}_{60}$. Alternatively, assuming $Al_6(OH)^{3+}_{15}$ in the unreacted solution, this form will remain unchanged upon adsorption onto the montmorillonite surface.

Differences in the microfabric of dry Al-CLM as a function of Al/montmorillonite ratio can be explained along the lines of the interpretation of the flocculation studies.

Key Words—Aluminum, Flocculation, Heterocoagulation, Ligand, Lithium, Montmorillonite.

INTRODUCTION

In the first part of the present series, the basic requirements for the synthesis of a new type of a cross-linked smectite were described and the general properties of hydroxy-Al cross-linked montmorillonite (Al-CLM) were determined (Lahav et al., 1977). The first stage of the synthesis i.e., the interaction between the relatively large clay unit layers with the very small hydroxy-Al oligomeric species, all of them dispersed in an electrolyte solution, is a special case of heterocoagulation. Heterocoagulation in mixed colloidal systems of two inorganic oxides was recently described (Wiese and Healy, 1975 a,b,c), where the coagulation behavior of several colloids was examined in terms of the electrokinetic potential. It was found that the heterocoagulation depended markedly on the conditions of mixing and equilibration of the reactants, and that the rate of dissolution of Al_2O_3 exerted a profound affect on the isoelectric point of TiO_2 and on its coagulation.

The present system seems to be even more involved than the Al_2O_3 - TiO_2 system studied by Wiese and Healy (1975 a,b,c) because of the heterogeneity of the surface of the clay unit layers, i.e., planar faces vs. edges, and the presence of very small hydroxy-Al oligomeric species which are presumably less stable and more labile than the aluminosilicate particles. Therefore, a quantitative treatment for this system cannot be given at present; however, observations on the flocculation might be helpful in constructing a general picture of the reaction under study.

In the present work we report on the cross-linking process of Al-CLM, and characterize the microfabric of the product in the dry state by scanning electron microscopy.

EXPERIMENTAL

Montmorillonite

Li-bentonite with particle size $<2 \mu m$ was prepared by washing Fisher bentonite B-235 5 times with 1 N LiCl solution, followed by dialysis to remove excess chlorides, and freeze-drying. Stock suspensions were prepared by suspending the dry Li-bentonite in deionized water. The pH of this suspension was 6.4.

Cross-linking agent

Hydroxy-Al solution with OH/Al molar ratio of 1.85 was prepared as described earlier (Lahav et al., 1977), and stored for at least 5 days before use, at 25°C. Most of the experiments were carried out with 20-day-old and 18-month-old solutions having pH of 3.93 and 3.91, respectively.

Al-CLM synthesis

The cross-linking process was carried out in a specially constructed mixing apparatus* described schematically in Figure 1. The apparatus is operated by air pressure generated in a compressor which causes automatic back and forth movement of the piston in cylinder A. The movement direction of this piston is governed by a valve system V_1 which changes the direction of air flow every time that the piston passes a predetermined point on its way from one side to the other side of the cylinder. The piston of cylinder A is connected to three additional pistons, B_1 , B_2 , and C, and thus the four pistons move simultaneously and auto-

* This apparatus was planned and constructed by U. Shani and J. Shani.

matically back and forth. The velocity of this movement is regulated by another cylinder (not shown in Figure 1) in which oil is forced by the piston through an adjustable aperture from one end to the other end of the cylinder. Cylinders B₁ and B₂ are connected to the clay suspension reservoir D, and cylinder C is connected to the hydroxy-Al reservoir, E, the concentration of which was adjusted to the desired level by diluting the stock solution. By means of valves V₂ and V₃ the cylinders are filled by their respective reservoirs every time that the pistons move to the left side, and are emptied from their liquid every time that the pistons move to the right side. The two aqueous suspensions enter the mixing chamber, G, where the cross-linking reaction takes place, and the combined liquid, including the Al-CLM, is collected in H. The Al-CLM thus synthesized was centrifuged and freeze-dried. All reactions were carried out at 25°C.

Scanning electron microscopy

Scanning electron micrographs were carried out on freeze-dried Al-CLM samples using a Cambridge S-180 instrument.

Chemical analyses

pH was determined in solution a short time after the synthesis of the cross-linked montmorillonite by a combined electrode using expanded scale. Differences between measurements before and after centrifugation were negligible. Solution was separated from the Al-CLM by centrifugation. Total aluminum in solution was determined by a Perkin Elmer atomic absorption spectrophotometer model 370, using HGA flameless graphite furnace model 2100. At least three determinations were carried out on each solution.

RESULTS AND DISCUSSION

Samples of Al-CLM with a wide range of Al/montmorillonite ratios[†] were synthesized by varying the concentration of Al-hydroxide solution while using the same montmorillonite concentration of 102 mg/l. For purposes of comparison, AlCl₃ solution was also reacted with the Li-montmorillonite using the same reaction conditions.

Flocculation

Observations on the flocculation characteristics of the treated montmorillonite were made shortly after the cross-linking reaction. Fast flocculation of the montmorillonite was observed in all samples treated with AlCl₃ solution; however, several flocculation modes were observed upon reacting montmorillonite with Al-

hydroxide solution (Table 1). At Al/montmorillonite ratio of 0.49, 0.98, and 4.90 mM/g, an increased turbidity was observed compared with pure montmorillonite suspension but the suspension remained rather stable. Considerable heterogeneity, i.e., tiny spots with somewhat higher turbidity, was observed at Al/montmorillonite ratios of 2.45 and 2.94 mM/g, but strong flocculation and clear supernatant were observed at the intermediate ratios of 1.47 and 1.96 mM/g (Table 1). No differences could be detected between 20-day-old and 18-month-old solutions.

The results of the flocculation study can be explained in the following general way (see also van Olphen, 1963): Positively charged hydroxy-Al oligomers are attracted to negatively charged montmorillonite lamellae, thus forming aggregates consisting of several clay unit layers. When the concentration of hydroxy-Al oligomers is very low compared with that of montmorillonite unit layers, the cross-linking is effective for the formation of small aggregates only. The turbidity of the suspension increases but the tiny aggregates, which consist of cross-linked unit layers and still possess an effective electrical double layer with negative charge, repel each other, do not associate to form bigger aggregates, and settle slowly. When the hydroxy-Al concentration is very high in comparison to that of montmorillonite, the clay unit layers are covered with many oligomers to the extent that their net electrical charge becomes slightly positive, and the tendency to form aggregates is again small due to the electrical repulsion. Such an excess adsorption of hydroxy-Al oligomers may be the result of a low energy barrier (due to small electrical repulsion and a high van der Waals interaction), and fast chemical changes of the Al-hydroxide oligomers, as explained below. The suspension is again rather stable and this can be considered as a protective colloid action. Suspension heterogeneity in the Al/montmorillonite ratios of 2.45 and 2.94 mM/g may be the result of heterogeneous distribution of the Al-hydroxide oligomers in the montmorillonite suspension.

In this general interpretation of the observations the only parameters of the montmorillonite which have been taken into account are the size and net negative charge of the clay unit layers. Obviously the planar area and the edges of each unit layer react differently with hydroxy-Al oligomers, because these two sites have different surface properties (van Olphen, 1963). However, until more information on the differentiation between these sites is available, the possible role of the edges will be neglected.

It is noted that gelation may be considered as another explanation for the stability of the clay suspensions at the high hydroxy-Al concentrations. According to this alternative explanation, the cross-linked montmorillonite unit layers form a very delicate network while in an energy minimum, resulting in a gel-like structure. However, for a montmorillonite concentration of 100

[†] (Total added Al)/(Total montmorillonite) in the reaction cell. The final Al/montmorillonite ratio of the Al-CLM was somewhat less than this, since not all the added aluminum was attached to the clay. (See below.)

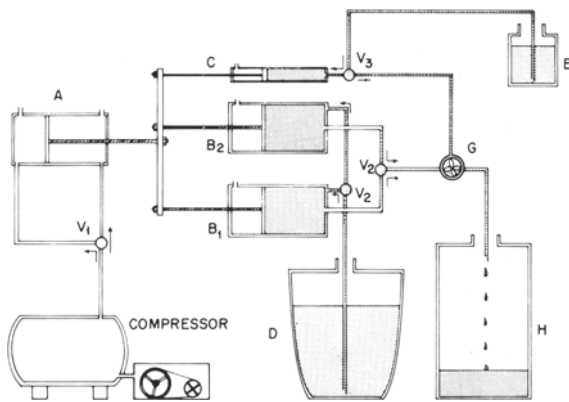


Fig. 1. Schematic diagram of the mixing apparatus.

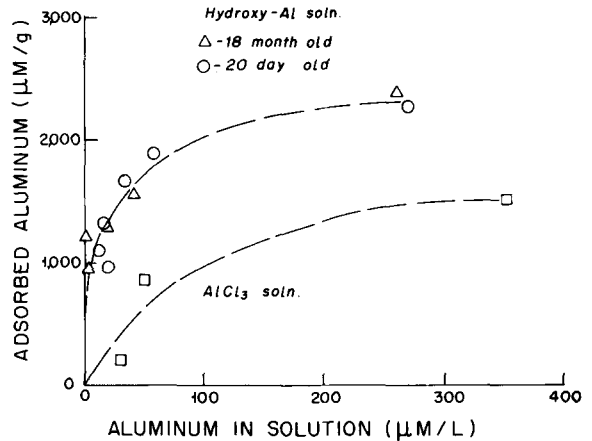


Fig. 2. Adsorption isotherm of Al applied as either hydroxy-Al or AlCl₃ on Li-bentonite.

mg/l the average distance between the unit layers would be >50,000 Å (van Olphen, 1963), which is considerably greater than the average unit layer size. Therefore, in order to be formed, the structural framework must either be based on second energy minima (M'Ewen and Pratt, 1957) or occupy only part of the total liquid volume, leaving the other part free of montmorillonite par-

ticles. No separation of a gel-like structure was observed during the first stages of the reaction and it is thus assumed that the stability of the montmorillonite suspensions at the low and high hydroxy-Al concentration is mainly the result of electrical interaction of either negatively charged or positively charged particles, as explained above.

Table 1. Observation on flocculation and turbidity of Al-CLM and of aluminum treated montmorillonite. Four types of flocculation are differentiated: (A) Very large floccules. Clear supernatant; (B) Medium size floccules. Clear supernatant; (C) No observed flocculation. Increased turbidity; (D) Very small and rather stable floccules. The intensity of flocculation or turbidity is designated by +, ++, and +++.

Al/montmorillonite (mM/g)	form	Flocculation type	Intensity	
			flocculation	turbidity of nonflocculated suspension
0.49	Al-hydroxide	C	-	+++
0.98	"	A	++	
		C		+
1.22	"	A	+++	
1.47	"	A	+++	
1.96	"	A	+++	
2.45	"	A	++	
		D		++
2.94	"	A	+	
		D		+++
4.90	"	A	+	
		D		+++
0.49	AlCl ₃	B	+++	
4.9	"	B	+++	

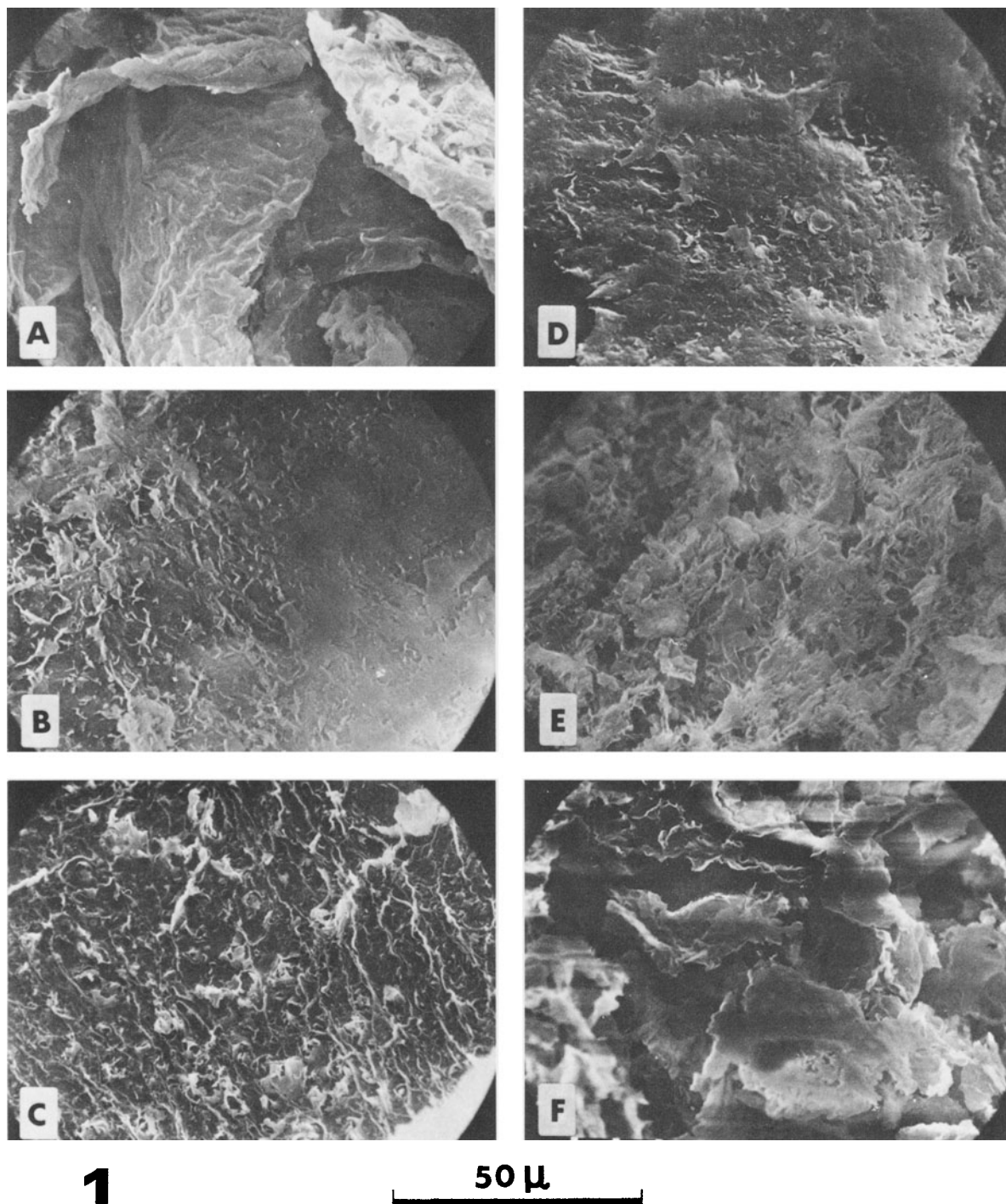


Fig. 3. Part 1.

Fig. 3. Scanning electron micrographs of Al-treated montmorillonite at three magnifications (1, 2, and 3). Al/montmorillonite ratios (mM/g) are: a = 0 (L_1 -Bentonite); b = 1.22; c = 1.47; d = 1.96; e = 2.45; f = 4.90 ($AlCl_3$ -treated bentonite).

Solution composition

Separation of solution from solid phase was difficult when the suspension was stable (Table 1). An incomplete separation was noted by wide fluctuations in tri-

plicate Al determinations of individual solutions, and such samples were rejected. The pH, however, was not significantly affected by the presence of small amounts of suspended particles. The data of pH and Al concen-

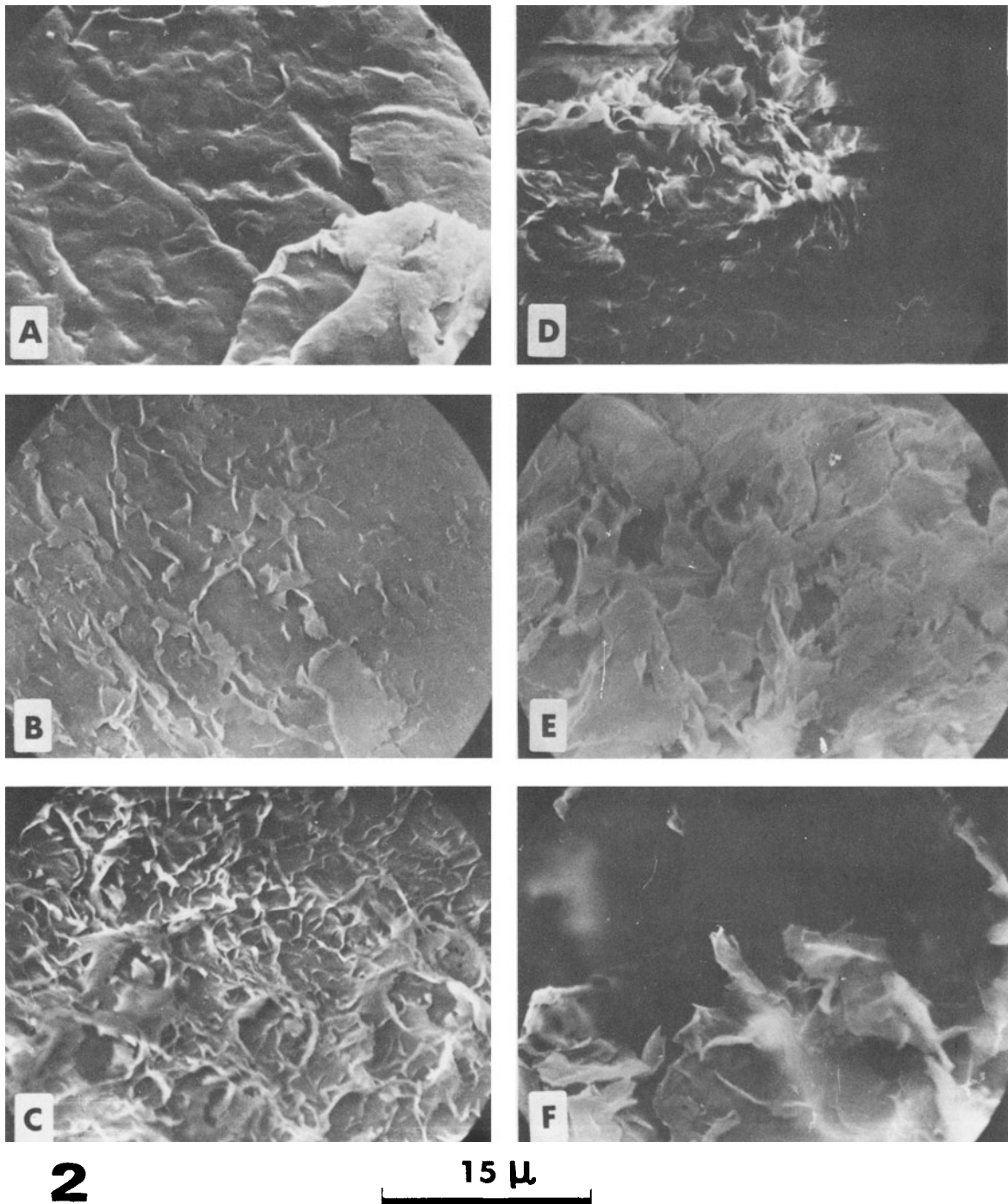


Fig. 3. Part 2.

tration are summarized in Table 2. It is noted that the two cross-linking agents, i.e., the 20-day-old and the 18-month-old hydroxy-Al solutions, gave very similar results.

Adsorbed Al was calculated by subtracting the final concentration from the initial concentration. The re-

sults are given in the form of an adsorption isotherm (Figure 2). Lithium was determined in the filtrate of the treatments possessing Al/montmorillonite ratio greater than 0.49 mM/g and was found to have an average value of 0.88 me per g montmorillonite. Assuming that all this Li was in an exchangeable form before being re-

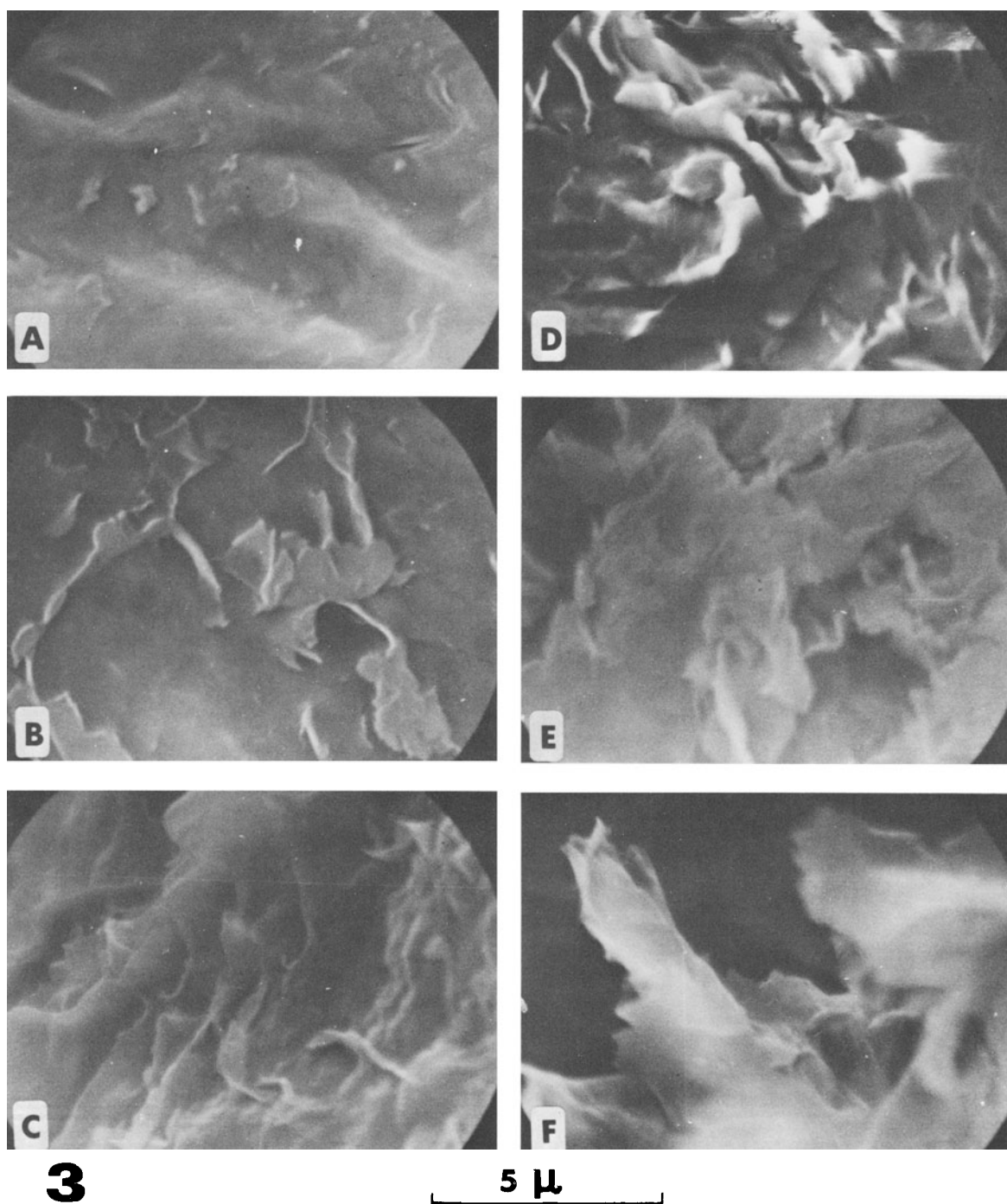


Fig. 3. Part. 3.

placed by hydroxy-Al, this value should be compared to the cation exchange capacity of the montmorillonite under study which is 0.9 me/g (Lahav, unpublished). Thus it is seen that the great majority of the exchangeable Li^+ was replaced by hydroxy-Al in all the Al/montmorillonite ratios above 0.49 mM/g.

The maximum amount of total Al adsorbed on the montmorillonite surface is much greater than the CEC, if all the aluminum would be in the Al^{3+} form. In order to explain the adsorption, various forms of hydroxy-Al, including polymers, should be assumed, both in the case of AlCl_3 solution and hydroxy-Al solution.

Table 2. pH and total Al in solution before and after cross-linking reaction.

Total Al montmorillonite (mM/g)	Solution pH				Total Al (μ /l)				
	20 day old solution		1 yr old solution		20 day old solution		1 yr. old solution		
	before reaction	after reaction	before reaction	after reaction	before reaction	after reaction	before reaction	after reaction	
<u>hydroxy-Al</u>	<u>D.F.*</u>								
0.49	10.0	4.31	5.91	4.40	5.89	50	-	50	-
0.98	5.0	4.20	5.10	4.27	5.12	100	19	100	4.4
1.22	4.0	4.19	4.90	4.25	4.95	125	12	125	0.74
1.47	3.5	4.10	4.88	4.18	4.89	150	16	150	18
1.96	2.5	4.08	4.77	4.11	4.86	200	33	200	41
2.45	2.0	4.04	4.73	4.06	4.81	250	57	250	-
2.94	1.7	4.01	4.73	4.02	4.79	300	-	300	-
4.90	1.0	3.93	4.66	3.91	4.72	500	270	500	260
<u>AlCl₃</u>		<u>AlCl₃ solution</u>							
0.49	10.0	3.79	4.86						
4.9	1.0	3.10	4.52						

* - D.F. - Dilution Factor - Dilution of stock solution prior to cross-linking reaction.

The adsorption of Al added in the form of AlCl_3 was much lower than that of Al added in the hydroxide form (Figure 2). Obviously the positively charged hydroxy-Al oligomers are adsorbed more strongly than the monomers or low molecular weight species of the AlCl_3 solution due to both magnitude of electrical charge and van der Waals interactions. However, the dynamics of the reaction under study complicates the interpretation of the seemingly straight forward cross-linking process. The interpretation must take into account both the size and size distribution of the oligomeric species of Al-hydroxide, as well as the kinetics of the oligomerization and hydrolysis reactions.

The stock solution of hydroxy-Al used in the present study ($\text{OH}/\text{Al} = 1.85$; see Experimental) was apparently in a state of equilibrium. The dominant form of hydroxy-Al in this solution is presumably the hexamer $\text{Al}_6(\text{OH})^{6+}_{12}$ (Hsu and Bates, 1964; Stol et al., 1976), but other forms may also be found. Except for the treatment with the highest Al/montmorillonite ratio, this solution was diluted before the cross-linking reaction, which resulted also in a pH change (Table 2).

The presence of montmorillonite in the present system calls for a great care in the interpretation of the

experimental results. The relaxation studies of Stol et al. (1976) cannot be used directly for the system under study, not only because of simultaneous changes in Al concentration and pH, but also because of the presence of montmorillonite surface area; the adsorption characteristics and buffering capacity of this surface area greatly complicate the interpretation.

Diluting hydroxy-Al solution by mixing with dilute solution of the same pH brings about the release of hydroxyl ions to the solution as well as the formation of lower polymers from higher polymers (Stol et al., 1976). In the present experimental system, hydroxy-Al solutions with pHs between 3.9 and 4.3 were mixed with much larger volumes of montmorillonite suspension in which the concentration of soluble Al was practically zero, and the pH was 6.4. Under these conditions not only the release of hydroxyl ions and decomposition of polymer would not take place, but condensation and formation of higher polymers might be feasible. The presence of montmorillonite might even enhance such a process (Ragland and Coleman, 1960), and since the polymerization reaction is relatively fast (Stol et al., 1976) it may even take place during the cross-linking reaction.

Analysis of the adsorption isotherm (Figure 2) shows that detectable concentrations of Al in the equilibrium solution are obtained only after adsorption of approximately 1 mM Al per g clay. Based on the observations of flocculation, which indicate a protective colloid action, it is estimated that a complete neutralization of the CEC takes place between Al/montmorillonite ratios of 2.45 and 2.94 mM/g. Above this range there is an excess adsorption of hydroxy-Al according to the protective colloid assumption. Using the adsorption isotherm in Figure 2, the adsorbed Al at this point is estimated as 1.9 mM/g and the charge per Al atom on the average will be roughly 0.5. Using this estimate, assuming only one oligomeric species, and following the structural model suggested by Hsu and Bates (1964), it can be calculated that the oligomeric form which neutralized the negative charge of the montmorillonite surface is $\text{Al}_{24}(\text{OH})^{12+}_{60}$. Thus, if indeed the oligomeric species on the montmorillonite surface is $\text{Al}_{24}(\text{OH})^{12+}_{60}$, then it is formed during the cross-linking process as a result of the sudden increase in pH and, presumably, because of additional and unknown effects of the clay surface area. According to Brosset et al. (1954), the ringlike complex $\text{Al}_6(\text{OH})^{3+}_{15}$ is the most probable form of hydroxy-aluminum in the acid range. Adopting this model implies that the pH jump associated with the cross-linking reaction has no effect on the degree of polymerization of the adsorbed hydroxy-aluminum polymers. It is possible that in the range of Al/montmorillonite ratios employed in the present study, several oligomeric species would be present on the montmorillonite surface area. In the case of AlCl_3 solution, the pH jump during the mixing with clay suspension (Table 2) increases the proportion of AlOH^{2+} in the solution (See Hem and Roberson, 1967) but this would not be enough to explain the adsorption of aluminum in excess of CEC. Presumably some oligomerization of Al under these conditions might take place.

The exact distribution of the adsorbed hydroxy-Al oligomers on the montmorillonite surface is of the greatest importance because it determines both the distance between the clay unit layers and the pore size of the molecular sieve thus formed. It is shown in Part I of the present series that two Al-hydroxide oligomers can be stacked in a parallel position and thus form a stable and porous structure. The detailed configuration of these cross-linked montmorillonite systems will be discussed in another part of the present series.

Scanning electron microscopy

This study was carried out on Li-montmorillonite, Al-treated montmorillonite and four Al-CLMs of different Al/montmorillonite ratios. All these samples were dehydrated by freeze-drying and therefore a comparative scanning electron microscopy study is possible. The resulting photomicrographs were assembled in three separate sets, each consisting of the same group

of the above mentioned six preparations, and having the same magnification (Figure 3).

A careful examination of these photomicrographs leads to the following conclusions: 1) The microfabric of Li-montmorillonite is more compact than those of all the other preparations even though the macrofabric appears as loosely wrapped leaves; 2) both the micro- and macrofabric of Al-treated montmorillonite are more loose and porous than those of all the other products.

In analyzing the observations on flocculation and scanning electron microscopy, three morphological levels can be differentiated i.e., floccules (suspension), macrofabric (dry state) and microfabric (dry state). The floccules, which are formed almost instantaneously, have a fluffy and delicate structure and are easily destroyed by stirring. They are made of many aggregates, where the microfabric as well as orientation of unit layers are determined by the flocculating agent. In the absence of a flocculating agent, i.e., in Li-montmorillonite, the unit layers are forced to associate in a close contact only upon dehydration and then assume a parallel orientation. The resulting microstructure is dense but because of contraction, packets of dense layers are separated to form "leaves" (see Figure 3). On the other hand, the presence of ionic aluminum (Al-treated montmorillonite) brings about strong flocculation where edge-to-face is the predominant form of association of unit layers (van Olphen, 1963). The resulting structure is porous and fluffy both in suspension and after dehydration.

The fabric characteristics of Al-CLM greatly depend on the relative amounts of hydroxy-aluminum oligomers and montmorillonite unit layers. When the relative amount of the oligomers is small compared with that of montmorillonite, i.e., 0.49 mM/g, no appreciable flocculation takes place and the montmorillonite unit layers, with the adsorbed oligomers, are forced into a close contact only after dehydration. Parallel (face-to-face) orientation is probably the dominant mode of association even though edge-to-face association exists too. The resulting structure is more porous than Li-montmorillonite. At intermediate Al/montmorillonite ratios, i.e., 1.22 and 1.96 mM/g, there are enough cross-linking units to bring about flocculation and to induce a face-to-face association between montmorillonite unit layers. The resulting aggregates are presumably rather dense, but many such aggregates are associated to form big and loose floccules. Upon dehydration, a relatively compact structure is formed due to a large proportion of parallel association between montmorillonite unit layers. At high Al/montmorillonite ratio, i.e., 2.54 mM/g, only partial flocculation takes place. Close association between montmorillonite unit layers is induced by dehydration and a relatively loose structure is the result of increasing proportion of nonparallel orientation.

In conclusion, the structural characteristics of Al-

CLM in suspension can be explained by the chemistry of hydroxy-Al complexes on the one hand and colloid chemistry of interacting particles on the other hand, and they are reflected in the microfabric of the dry Al-CLM.

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REFERENCES

- Brosset, C., Biedermann, G. and L. G. Sillen. (1954) Studies on the hydrolysis of metal ions. XI. The aluminum ion, Al^{3+} : *Acta Chem. Scand.* **8**, 1917–1926.
- Hem, J. D. and Roberson, C. E. (1967) Form and stability of aluminum hydroxide complexes in dilute solution: *U.S. Geol. Surv. Water-Supply Pap.* **1827-A**, 55 pp.
- Hsu, Pa Ho and Bates, T. F. (1964) Formation of X-ray amorphous and crystalline aluminium hydroxides: *Mineral. Mag.* **33**, 749–768.
- Lahav, N., Shani, U. and Shabtai, J. (1978) Cross-linked smectites. I. Synthesis and properties of hydroxy aluminum montmorillonite: *Clays & Clay Minerals* **26**, 107–115.
- M'Ewen, M. B. and Pratt, M. I. (1957) The gelation of montmorillonite. I. The formation of a structural framework in sols of Wyoming bentonite: *Trans. Faraday Soc.* **53**, 535–547.
- Ragland, J. L. and Coleman, A. T. (1960) The hydrolysis of aluminum salts in clay and soil systems: *Soil Sci. Soc. Am. Proc.* **24**, 457–460.
- Smith, R. W. and Hem, J. D. (1972) Effect of aging on aluminum hydroxide complexes in dilute aqueous solutions: *U.S. Geol. Surv. Water-Supply Pap.* **1827-D**, 51 pp.
- Stol, R. J., van Helden, A. K. and de Bruyn P. L. (1976) Hydrolysis—precipitation studies of Aluminum (III) solutions 2. A kinetic study and model: *J. Colloid Interface Sci.* **57**, 115–131.
- van Olphen, H. (1963) *Clay Colloid Chemistry*: Interscience Pub., New York, 301 pp.
- Wiese, G. R. and Healy, T. W. (1975a) Coagulation and electrokinetic behaviour of TiO_2 and Al_2O_3 colloidal dispersions: *J. Colloid Interface Sci.* **51**, 417–442.
- Wiese, G. R. and Healy, T. W. (1975b) Solubility effects in Al_2O_3 and TiO_2 colloidal dispersions: *J. Colloid Interface Sci.* **52**, 452–457.
- Wiese, G. R. and Healy, T. W. (1975c) Heterocoagulation in mixed TiO_2 - Al_2O_3 dispersions: *J. Colloid Interface Sci.* **52**, 458–467.

Резюме— Образование поперечных связей монтмориллонита, содержащего Li, с олигомером гидроксида алюминия было достигнуто с помощью специально сконструированного смешивающего аппарата. Наблюдение за флокулированием и составом раствора проводилось в течение и после реакции образования поперечных связей, сухой продукт был изучен под развертывающим электронным микроскопом.

Флокулирование было наиболее резко выражено при отношении Al/монтмориллонит в пределах 0,98 и 2,45 мм/г. Ниже и выше этого диапазона флокулирование было значительно менее интенсивным. Это наблюдение может быть объяснено гетерокоагуляцией и защитным действием коллоида. Полная нейтрализация заряда монтмориллонита была определена при 1,9 мм адсорбированного Al на 1 г глины. Чтобы подсчитать электрический заряд гидроксида алюминия, следует принять на поверхности монтмориллонита средний заряд в 0,5 на атом Al. Предполагая, что гидроксида алюминия в невступившем в реакцию растворе находится в форме $Al_6(OH)_{12}^{3+}$, адсорбированный полимер будет $Al_{24}(OH)_{60}^{3+}$, и, наоборот, предполагая, что в растворе до реакции находился $Al_6(OH)_{15}^{3+}$, эта форма останется без изменения при адсорбции на поверхности монтмориллонита.

Различия в микроструктуре сухого Al-ПСМ, представленные в виде функции отношения Al/монтмориллонит могут быть объяснены при интерпретации результатов изучения флокулирования.

Kurzreferat— Querverknüpfung von Li-Montmorillonit mit Hydroxyl-Aluminiumoligomeren wurde in einem spezial-hergestellten Mischungsapparat durchgeführt. Beobachtungen über Ausflocken und Zusammenstellung der Lösung wurden während und nach der Querverknüpfungsreaktion gemacht; das trockene Produkt wurde durch SEM untersucht. Ausflocken war am meisten bemerkbar bei Al/Montmorillonit Verhältnissen zwischen 0,98 und 2,45 mm/g; über und unter diesem Bereich war Ausflocken viel weniger intensiv. Diese Beobachtungen können durch Heterokoagulation und Schutzkolloidaktion erklärt werden. Eine vollständige Neutralisation der Montmorillonitladung wurde auf 1,9 mm adsorbiertes Al per g Ton geschätzt und um die elektrische Ladung des Hydroxyl-Aluminiums zu erklären, muß angenommen werden, daß sich Polymere mit einer durchschnittlichen Ladung von 0,5 per Al Atom an der Montmorillonitoberfläche befinden. Wenn man annimmt, daß die Hydroxyl-Aluminiumform in der nichtreagierten Lösung $Al_6(OH)_{12}^{3+}$ ist, wird der adsorbierte Polymer $Al_{24}(OH)_{60}^{3+}$ sein. Andererseits, wenn angenommen wird, daß sich $Al_6(OH)_{15}^{3+}$ in der nichtreagierten Lösung befindet, dann wird diese Form unverändert bleiben während der Adsorption auf der Montmorillonitoberfläche. Unterschiede in der Mikrostruktur von trockenem Al/CLM, abhängig vom Al/Montmorillonit Verhältnis, kann durch dieselben Grundsätze wie in den Ausflockuntersuchungen erklärt werden.