

## REACTION OF OH-AL POLYMERS WITH SMECTITES AND VERMICULITES<sup>1</sup>

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**Abstract**—Five montmorillonites, one hectorite, and two vermiculites were treated with OH-Al solutions containing rapid- and slow-reacting polymers of similar concentrations. With all smectites, both rapid- and slow-reacting OH-Al polymers were much more preferentially adsorbed than monomeric species. Relatively slow-reacting OH-Al polymers were more preferentially adsorbed than rapid-reacting ones. The average basicity of the adsorbed Al was 2.46, which was close to that of the OH-Al polymers in the original solution. The OH-Al polymers that enter the interlayer resemble those in original solutions.

With vermiculites, the solution concentration of rapid-reacting OH-Al polymers was much reduced after reaction. The average basicity of the adsorbed Al was 1.99, which was considerably lower than that in the original solution. It is postulated that OH-Al polymers break to monomeric Al ions and then enter the clay. The monomeric Al species that enter the clay interlayers hydrolyze and polymerize *in situ* and become fixed. The H<sup>+</sup> ions released from hydrolysis convert the rapid-reacting OH-Al polymers to monomeric Al in solution. Limited amounts of slow-reacting polymers were adsorbed because of their resistance to acid depolymerization.

**Key Words**—Smectite, Vermiculite, OH-Al, Pillared clay.

### INTRODUCTION

The intercalation of OH-Al polymers in expansible clays has interested scientists of many disciplines (Pinnavaia, 1983; Zelazny and Jardine, 1989; Barnhisel and Bertsch, 1989). The mechanisms of intercalation, however, have not been clear, primarily because of the controversy over the nature of OH-Al polymers. Brosset *et al.* (1954), followed by Hsu and others, first proposed that the OH-Al polymers have a hexagonal-ring structure resembling fragments of Al(OH)<sub>3</sub> crystals (Hsu, 1989). Many recent studies (Akitt *et al.*, 1972; Akitt and Farthing, 1978; Bottero *et al.*, 1980; Bertsch *et al.*, 1986a, 1986b) favored the Al<sub>13</sub> Keggin structure for the OH-Al polymers in solution, originally proposed by Johansson (1963). The presence of the Al<sub>13</sub> species in the interlayer of smectites has also been suggested (Vaughan and Lussier, 1980; Pinnavaia *et al.*, 1984; Plee *et al.*, 1985, 1987; Schutz *et al.*, 1987; Fripiat, 1988). Hsu and his colleagues (Tsai and Hsu, 1984, 1985; Denney and Hsu, 1986; Hsu, 1989) postulated that both of these two proposed polymers were present in OH-Al solutions. Both of them reacted with hydroxyquinoline (Turner, 1976a, 1976b) or ferron (Tsai and Hsu, 1984, 1985) following a pseudo-first-order reaction, but their rate constants differed by some 250 times. They formed distinctly different basic Al sulfates upon the addition of Na<sub>2</sub>SO<sub>4</sub> (Tsai and Hsu, 1984, 1985) and are very different in resistance to acid (Turner, 1976b; Hsu, 1988). The rapid-reacting OH-

Al polymers show a distinct peak in NMR spectra, with its chemical shift 63 ppm downfield from that of Al<sup>3+</sup>, whereas the slow-reacting polymers are not detectable with NMR spectroscopy (Denney and Hsu, 1986). In general, OH-Al solutions freshly prepared by partially neutralizing an Al salt solution with a base are dominated by rapid-reacting polymers that gradually convert to slow-reacting species with time (Turner, 1976a, 1976b; Tsai and Hsu, 1984, 1985; Denney and Hsu, 1986; Hsu, 1988). It has been suggested (Denney and Hsu, 1986; Hsu, 1988, 1989) that only rapid-reacting OH-Al polymers are of Al<sub>13</sub> Keggin structure, but the slow-reacting polymers are of Al(OH)<sub>3</sub>-fragment structure. The objective of the present study is to examine the difference between these two types of polymers in their reactions with smectites and vermiculites.

### MATERIALS AND METHODS

#### *Clay specimens*

Five montmorillonites (SAz-1, SWy-1, W23, W24, W27), one hectorite (SHca-1), and two vermiculites (Libby and Transvaal) were obtained for this study. SAz-1, SWy-1, and SHca-1 were obtained from the Clay Depository, The Clay Minerals Society. W23, W24, and W27 refer to the reference montmorillonite specimens Nos. 23 (Chambers, AR), 24 (Otay, CA), and 27 (Belle Fourche, SD), respectively, supplied by Ward's Natural Science Establishment, Inc. The two vermiculites were also supplied by Ward's Natural Science Establishment, Inc. The <0.2- $\mu$ m fraction was saturated with Mg for this study.

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### Preparation of OH-Al solutions

Three OH-Al solutions (Table 1), all 0.02 M in Al, were used in this study. Solution B516 was prepared by mixing a 3-yr-old solution and a freshly prepared one, both with NaOH/Al molar ratio = 1.8, so that the final solution contained nearly identical concentrations of rapid- and slow-reacting OH-Al polymers. The advantage of this preparation is that we can compare better the rapid- and slow-reacting polymers in their adsorption by clay. Solution B201 was a 5-yr-old, NaOH/Al molar ratio = 1 solution, which was dominated by monomeric and slow-reacting OH-Al polymers. Solution B531 was a freshly prepared OH-Al solution of NaOH/Al molar ratio = 1, which was dominated by monomeric and rapid-reacting polymers. All OH-Al solutions were originally prepared by drop-wise addition of a predetermined amount of 0.1 M NaOH to 400 ml of 0.1 M AlCl<sub>3</sub> at a rate of 1 ml/min under constant stirring and then dilution to 2000 ml. The distribution of different Al species in each solution was determined using the kinetics of Al-ferron color development (see below). To ascertain that all species in solution were not solids, 20 ml of Solution B201 or B531 were shaken with 2 g of Na-saturated AG50 (X8) resin for 1 hr. The Al in each solution was found to have completely entered the resin. Furthermore, no peak corresponding to Al<sub>13</sub> complex was observed in the NMR spectrum of Solution B201 (data not shown).

### Treatment of clay with OH-Al solution for chemical analysis

In the major experiment, appropriate amounts of each clay specimen (<0.2 μm, Mg-saturated) were weighed into 100-ml centrifuge tubes. The amounts of specimen were so determined that the total negative charge for each specimen was approximately 220 μeq. Then 50 ml of OH-Al solution B516 were added, dispersed with an ultrasonic vibrator for 20 min on the first day, and then hand shaken several times a day for 14 days.

### Analysis of OH-Al-clays

The OH-Al-clay specimens were centrifuged to separate the solution from clay. The centrifugates were analyzed for pH, total Al, distribution of various Al species, and Mg. The total Al adsorbed was calculated from the reduction in solution Al concentration. Each specimen was washed once with 50 ml 70% ethanol using centrifugation and then extracted four times with 25 ml 0.5 M NaCl and 15-min shaking each time. The four NaCl extracts were combined and analyzed for total Al, the distribution of various Al species, and Mg.

### Speciation of Al in solution

The Al ions in solution were speciated with a procedure modified from Tsai and Hsu (1984). Eighty

Table 1. Distribution of various Al species in the OH-Al solutions selected for this study.

Solution	OH/Al	Duration of aging, d	pH	Mono <sup>2</sup> (mmol/L)	Rapid <sup>2</sup> (mmol/L)	Slow <sup>2</sup> (mmol/L)
B516 <sup>1</sup>	1.8	—	4.07	3.57	8.03	7.99
B201	1.0	5 yr	3.85	10.93	0.74	7.74
B531	1.0	3 d	4.04	11.30	7.85	nil

<sup>1</sup> Prepared by mixing a 3-yr-old OH-Al solution and a freshly prepared one, both of OH/Al molar ratio = 1.8, to have similar concentrations of rapid- and slow-reacting OH-Al polymers in solution.

<sup>2</sup> Mono, rapid, and slow refer to monomeric ions, and rapid- and slow-reacting OH-Al polymers, respectively.

milliliters of color-developing reagent (ferron-acetate-acetic acid) and an appropriate amount of H<sub>2</sub>O were mixed in a polyethylene container. An appropriate amount of sample or standard Al solution was added. The contents were rapidly mixed, and the absorbance at 366 nm was monitored with time, starting from 40 sec until the color was fully developed. All colored solutions were kept in the dark during the prolonged color-development process. The amount of H<sub>2</sub>O was so determined that the sum of H<sub>2</sub>O and sample aliquot was 120 ml for all samples. The concentrations and rate constants for the slow- and rapid-reacting OH-Al polymers were calculated following two simultaneous pseudo-first-order reaction kinetics. The concentration of monomeric Al was calculated by subtracting the sum of rapid- and slow-reacting polymers from the total Al present. The color-developing reagent was prepared by mixing 500 ml of ferron (2 g/liter), 250 ml of 4 M Na acetate, and 250 ml of 1 M acetic acid (Hsu and Cao, 1991). This reagent can be used immediately after preparation.

### X-ray diffraction analysis

Two 40-mg portions of each specimen were treated with 15 ml of either Solution B201 or B531. Each specimen was dispersed using an ultrasonic vibrator for 20 min on the first day, and then hand-shaking a few times a day for 14 days. The clay was centrifuged to remove the solution, washed once with 10 ml of H<sub>2</sub>O, and then dispersed in 3 ml H<sub>2</sub>O. The clay slurry was transferred onto a glass slide, dried at room temperature, and X-rayed with a Siemens diffractometer, using CuKα radiation.

### General chemical analysis

Aluminum was determined with ferron (Hsu and Cao, 1991). Magnesium was determined with a Perkin-Elmer Model 603 atomic absorption spectrophotometer. Solution pH was determined with a Fisher Accumet 825 pH meter using buffers of pH 6.865 and 4.008 for calibration.

Table 2. Adsorption of Al by smectites and vermiculites from Solution B516, and accompanying replacement of Mg.

Clay	CEC meq/g	Mg replaced, meq/g			Al adsorbed <sup>1</sup>		
		by Al	by Na	SUM	mmol/g	+/Al	OH/Al
SHca-1	0.825	0.840	0.0140	0.854	1.49	0.56	2.44
SWy-1	0.835	0.849	0.0057	0.855	1.46	0.58	2.42
W27	0.894	0.880	0.0070	0.887	1.62	0.54	2.46
W23	1.032	1.024	0.0022	1.026	2.00	0.51	2.49
SAz-1	1.076	1.052	0.0041	1.056	2.07	0.51	2.49
W24	1.123	1.110	0.0044	1.114	2.11	0.53	2.47
Av. smec.		0.959	0.0062	0.965	1.79	0.54	2.46
Libby	1.106	1.029	0.0850	1.114	1.10	0.94	2.06
Trans	1.439	1.334	0.1670	1.501	1.23	1.08	1.92
Av. verm.		1.182	0.1260	1.308	1.17	1.01	1.99

<sup>1</sup> The +/Al is calculated from the ratio of the Mg replaced by Al to the amount of Al adsorbed. The OH/Al of adsorbed Al is calculated by subtracting the +/Al from 3.

## RESULTS AND DISCUSSION

### Adsorption of Al by clay

The adsorption of Al was accompanied by the desorption of Mg from clay (Table 2). With all smectite specimens, the exchangeable Mg was almost completely replaced by Al, with some 1% found in subsequent NaCl extracts. The total Mg observed is close to the cation exchange capacity (CEC) of the specimen determined separately by replacing Mg<sup>2+</sup> with Na<sup>+</sup>. Evidently, all smectites were nearly saturated by Al. The average charge per adsorbed Al was calculated from the ratio of Mg (meq) replaced to Al (mmol) adsorbed. The average basicity of adsorbed Al ranged from 2.42 to 2.49, as calculated by subtracting the average charge per Al from 3. The average basicity of the Al adsorbed was close to that of the OH-Al polymers in the original OH-Al solution, which was 2.46 for rapid-reacting and 2.38 for slow-reacting polymers as determined using sulfate precipitation (Tsai and Hsu, 1984, 1985).

With vermiculites, considerably less Al entered the clay (Table 2). The exchangeable Mg in the clay specimen was not completely replaced by Al, with 8 and

11% of the exchangeable Mg found in subsequent NaCl extracts for Libby and Transvaal vermiculites, respectively. The sum of the Mg replaced by Al and that in the subsequent NaCl extract was close to the CEC determined by directly replacing Mg with Na (Table 2). Therefore, Mg was not trapped by the OH-Al interlayer. The basicity of the adsorbed OH-Al was 2.06 and 1.92 for Libby and Transvaal vermiculites, respectively, with an average of 1.99. Libby vermiculite contains 0.36 mmol K/g because of the presence of hydrobiotite and/or biotite. Therefore, the net CEC of Libby vermiculite was comparable only to SAz-1, W23, and W24.

Table 3 shows that with smectites, a negligible amount of monomeric Al was adsorbed in all the specimens studied. Considerably more slow-reacting OH-Al polymers than rapid-reacting ones were adsorbed by the clay. Evidently slow-reacting OH-Al polymers are more preferentially adsorbed by smectite than the rapid-reacting ones. In general, the higher the original CEC, the more slow-reacting OH-Al polymers were adsorbed. The equilibrium solution pH's were slightly higher than that of the original solution.

Table 3. Distribution of different Al species adsorbed by smectites and vermiculites (Solution B516).

Specimen	Weight (g)	pH	Monomeric Al			Rapid-reacting Al			Slow-reacting Al		
			Solution conc. (mmol/L)	Mole % adsorbed	Quantity adsorbed (mmol/g)	Solution conc. (mmol/L)	Mole % adsorbed	Quantity adsorbed (mmol/g)	Solution conc. (mmol/L)	Mole % adsorbed	Quantity adsorbed (mmol/g)
Control <sup>1</sup>		4.07	3.57			8.03			7.99		
SHca-1	0.259	4.12	3.49	2.2	0.02	4.23	47.3	0.73	4.01	49.8	0.77
SWy-1	0.261	4.11	3.54	0.8	0.01	4.59	42.8	0.66	3.82	52.2	0.80
W27	0.237	4.13	3.43	3.9	0.03	4.05	49.5	0.84	4.12	48.4	0.82
W23	0.210	4.13	3.46	3.1	0.03	4.17	48.0	0.92	3.51	56.1	1.07
SAz-1	0.201	4.10	3.57	0.0	0.00	4.20	47.7	0.95	3.37	57.8	1.15
W24	0.191	4.13	3.61	-1.1	-0.01	4.19	47.9	1.01	3.54	55.7	1.17
Av. smec.			3.52	1.5	0.01	4.24	47.2	0.85	3.73	53.3	0.96
Libby	0.202	4.16	2.53	29.2	0.26	5.43	32.3	0.64	7.24	9.4	0.19
Trans	0.147	4.16	2.45	31.4	0.38	6.16	23.2	0.63	7.09	11.3	0.31
Av. verm.			2.49	30.3	0.32	5.80	27.8	0.64	7.16	10.3	0.25

<sup>1</sup> Control refers to Solution B516.

Table 4. Speciation of NaCl-exchangeable Al from smectites and vermiculites.

Clay	Total Al ads. mmol/g	NaCl-exchangeable Al <sup>2</sup>							
		Total		Mono		Rapid		Slow	
		mmol/g	%	mmol/g	%	mmol/g	%	mmol/g	%
SHca-1	1.49	0.89	59.7	nil	—	0.45	30.2	0.46	30.9
SWy-1	1.46	0.88	60.3	nil	—	0.43	29.5	0.43	29.5
W27	1.62	0.77	47.5	nil	—	0.41	25.3	0.35	21.6
W23	2.00	0.74	37.0	nil	—	0.44	22.0	0.33	16.5
SAz-1	2.07	0.68	32.9	nil	—	0.42	20.3	0.29	14.0
W24	2.11	0.67	31.8	nil	—	0.43	20.4	0.27	12.8
Av. smec.	1.79	0.77	43.1	nil	—	0.43	24.0	0.36	20.1
Libby <sup>1</sup>	1.10	0.15	13.6	0.038	3.5	0.045	4.1	0.067	6.1
Trans <sup>1</sup>	1.23	0.16	13.0	0.053	4.3	0.040	3.3	0.069	5.6
Av. verm.	1.17	0.16	13.7	0.046	3.9	0.043	3.7	0.068	5.8

<sup>1</sup> Libby and Trans refer to Libby and Transvaal vermiculites, respectively.

<sup>2</sup> % total Al adsorbed.

With vermiculites, more rapid-reacting OH-Al polymers were removed from solution compared to monomeric Al and slow-reacting OH-Al polymers. Nevertheless, a relatively small amount of monomeric Al was present in the original OH-Al solution. Percentage-wise, an average of 30% of monomeric Al, 28% of the rapid-reacting, and 10% of the slow-reacting polymers entered the clay. The equilibrium solution pH's were noticeably higher than that of the initial solution.

#### Exchangeability of adsorbed Al

With smectites, the exchangeability of the adsorbed Al decreased with increased CEC of the clay (Table 4). For SHca-1 and SWy-1, 60% of the Al adsorbed was exchangeable, whereas only 33 and 32% of the Al adsorbed by SAz-1 and W24, respectively, were exchangeable. Although fewer rapid-reacting polymers than slow-reacting ones entered the clay (Table 3), more rapid-reacting than slow-reacting polymers were NaCl-exchangeable (Table 4). This comparison is particularly clear with W23, SAz-1, and W24, suggesting that slow-reacting polymers are more tightly held by smectites than rapid-reacting ones.

With vermiculites, the exchangeability of the adsorbed Al was low. Although an average of 0.32 mmol monomeric Al was adsorbed per g clay, only 0.046 mmol monomeric Al per g was found in the NaCl extracts. Also, the total exchangeable Al was only 0.16 mmol/g. These results suggest that the monomeric Al that entered vermiculite converted to polymeric species and became tightly retained (Veith, 1978a, 1978b). Furthermore, slow-reacting OH-Al polymers account for a relatively large portion of the exchangeable Al. This is probably because the slow-reacting polymers are largely adsorbed at the edge.

#### Mechanism of OH-Al polymer adsorption

The results show that smectites and vermiculites behaved differently in their reaction with Al. With smectites, both types of OH-Al polymers were more pref-

erentially adsorbed than monomeric species (Table 3). Similar results were reported earlier (Hsu, 1968; Veith, 1978a, 1978b; Jardine *et al.*, 1985; Schutz *et al.*, 1987). Jardine *et al.* (1985) showed that monomeric Al entered smectite initially, but gave way to OH-Al polymers later. There cannot be three negative charges at any one location in a clay structure. Therefore, monomeric Al<sup>3+</sup> ions are not favorably retained. When the solution pH is low enough to favor the existence of monomeric Al ions, they should be highly exchangeable. The results also show that slow-reacting OH-Al polymers are more preferentially adsorbed (Table 3) and less exchangeable (Table 4) than the rapid-reacting ones. With slow-reacting OH-Al polymers, the charges are distributed at the corners of the hexagonal-ring configuration (Hsu and Bates, 1964). It has been suggested that a part of the negative charges in smectite may be distributed similarly (Hsu, 1968; Brindley and Semple, 1977). When the positive charge distribution of the OH-Al polymers matches the negative charge distribution in smectite, the polymers would be favorably adsorbed. The OH-Al polymers may be enlarged or condensed to match the clay charge distribution, but the same general hexagonal-ring structure should remain. The charge distribution in rapid-reacting OH-Al polymers of Keggin structure (Al<sub>13</sub>) is not known, but it cannot match that in smectites on the basis of steric considerations. Therefore, they are less favorably retained. Other smectites might be different in charge distribution, but probably no smectite has its negative charge distributed completely in Al(OH)<sub>3</sub>-fragment patterns. For those negative clay charges that are not distributed in Al(OH)<sub>3</sub>-fragment patterns, slow- and rapid-reacting OH-Al polymers would have the same chance of being adsorbed. Therefore, considerable amounts of rapid-reacting OH-Al polymers were adsorbed by clay even with excessive amounts of slow-reacting polymers present. The differences among smectite members in adsorption and retention of rapid- and slow-reacting OH-Al polymers

Table 5. Basal spacings (Å) of OH-Al pillared smectites and vermiculites treated with Solution B201 or B531.

Clay	B201	B531
SHca-1	18.51	19.16
SWy-1	19.01	19.38
W27	18.88	19.01
W23	19.47	18.97
SAz-1	19.38	18.93
W24	19.04	18.58
Av. smec.	19.05	19.01
Libby	14.71	14.09
Trans	14.10	14.54
Av. verm.	14.41	14.32

probably are also attributed to their negative charge distribution in clay structure.

Vermiculites cannot be expanded beyond 14-Å spacing. With a Keggin structure, the rapid-reacting OH-Al polymers must be broken down to monomeric Al or some small polymeric species before they can enter the vermiculite interlayer. The pH of the system (Table 3), however, does not permit monomeric Al to exist in the vermiculite interlayer for a long time. The monomeric Al ions that entered the clay then hydrolyze and polymerize *in situ* and become fixed (Veith, 1978a, 1978b; Jardine *et al.*, 1985). The H<sup>+</sup> ions released to solution then react with the rapid-reacting OH-Al polymers in solution and convert them to monomeric species. Limited amounts of slow-reacting OH-Al polymers are adsorbed because of their resistance to acid depolymerization (Hsu, 1988). The negative charges are more densely distributed in vermiculite, and therefore the OH-Al polymers developed are smaller and have an average positive charge 1+ per Al. All adsorbed polymers may be described as of Al(OH)<sub>3</sub>-fragment structure regardless of the original form in solution. The limited amounts of exchangeable OH-Al polymers probably are adsorbed at the edge surface. This investigator observed that OH-Al-treated vermiculite had a high tendency to disperse during washing.

#### XRD basal spacing

The 19-Å basal spacing has been cited as evidence for the intercalation of Al<sub>13</sub> structure in smectites (Pinnavaia *et al.*, 1984; Plee *et al.*, 1985; Schutz *et al.*, 1987; Fripiat, 1988). The results in this report, however, show that both rapid- and slow-reacting OH-Al polymers can be adsorbed by smectites. This experiment was carried out to compare the basal spacing of the smectites pillared with rapid- or slow-reacting polymers. Two series of smectite specimens were treated with either Solution B201, which was dominated by slow-reacting polymers; or Solution B531, which was dominated by rapid-reacting polymers (Table 1). All smectite specimens treated with either solution yielded an approximately 19-Å basal spacing initially (Table 5).

Therefore, an initial 19-Å basal spacing is not specific for the Al<sub>13</sub>-pillared smectites.

With the five montmorillonites treated with Solution B201, the basal spacings slightly reduced to around 18 Å after the slides were stored in the ambient environment for several days, but no further change occurred for up to at least 6 months. Two possibilities should be considered: smectites were intercalated with two layers of Al(OH)<sub>3</sub>-fragment polymers; or one layer of Al(OH)<sub>3</sub>-fragment polymers and two layers of free H<sub>2</sub>O. To differentiate these two possibilities, the clay slides were heated at 105°C for 16 hr and re-X-rayed immediately after heating. No change in basal spacing was observed. It is reasonable to assume that any free H<sub>2</sub>O should have been expelled during the 105°C-16 hr heating. Therefore, the intercalation of smectites with two layers of Al(OH)<sub>3</sub>-fragment polymers is more likely the case.

The smectites treated with Solution B531 seemed to be less stable, with their basal spacings reduced to 15–16 Å later, but the results were poorly reproducible. Research is in progress to search for the factors affecting the stability of Al<sub>13</sub>-clay complex.

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