

SELECTIVITY AND ADSORPTION CAPACITY OF SMECTITE AND VERMICULITE FOR ALUMINUM OF VARYING BASICITY*

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Abstract—Smectite (from South Dakota, Wyoming, and Mississippi) and vermiculite (Transvaal) were treated with solutions of $\text{Al}(\text{OH})_B^{(3-B)+}$, with B varying from 0 to 2.5. The average basicity ($\text{OH}/\text{Al} = B$) of the Al adsorbed differed very much from the basicity of the Al added. The average basicity of the Al adsorbed by smectite was always above the average basicity of the Al added. In contrast to smectite, vermiculite adsorbed smaller hydroxy-Al complexes. One reason for the different selective behavior was the difference in expansion between smectite (about 18 Å) and vermiculite (about 14 Å). Because of the adsorption of the relatively more basic OH-Al by smectite, smectite adsorbed considerably more Al than vermiculite. The total amount of aluminum in the interlayer generally could not be calculated by the difference between Al added and that remaining in solution after the reaction because of possible protonation of the clay mineral and adsorption of structural Al and other cations, which is more pronounced for vermiculite. The results in the present study demonstrated that neither the quantitative nor the qualitative composition of an $\text{Al}(\text{OH})_B$ -treated exchanger can be deduced from B of the Al salts added. These points are frequently overlooked when cation exchangers are pretreated with Al of variable basicity and are used for further investigations, such as studies of CEC, surface area, interlayer spacing, anion reactions, the formation of gibbsite, etc. Before these kinds of investigations are conducted employing the pretreated OH-Al-exchangers, their composition should be known precisely.

Key Words—Adsorption, Aluminum, Expansion, Smectite, Vermiculite.

INTRODUCTION

Numerous investigations have been concerned with the properties of hydroxy-Al-exchangers under laboratory conditions (e.g., Rich, 1968; Coulter, 1969). These exchangers usually have been prepared by pretreatment with Al salts of varying basicity ($B = \text{OH}/\text{Al}$), e.g., $\text{Al}(\text{OH})_B\text{Cl}_{3-B}$. The resulting OH-Al-containing exchangers then are used for further investigations; e.g., for studies of CEC, interlayer spacing, surface area, the formation of gibbsite, and the sorption of anions such as phosphate. The results of these investigations often have been interpreted in relation to composition of the pretreating solution of $\text{Al}(\text{OH})_B\text{Cl}_{3-B}$ with the assumption that the basicity of the Al added is also that of the Al adsorbed by the exchangers. The quantity and the basicity of Al adsorbed frequently has not been measured, although these parameters have an undeniable impact on the physical, chemical, and mineralogical properties of the exchanger. The main objectives of the research reported in this paper were to elucidate this problem by investigating: (1) the amount and the average basicity of the Al adsorbed by 2:1 clay minerals when treated with Al of varying basicity; (2) the stability of OH-Al-exchangers.

MATERIALS AND METHODS

Four 2:1 clay minerals were used in this study: vermiculite (Transvaal) from South Africa (S.A.), and smectites from Wyoming (Wyo.), South Dakota (S.D.),

and Mississippi (Miss.). The smectites were obtained through Ward's Natural Science Establishment, Rochester, New York. The vermiculite was ground in a blender. All the clay samples were washed and suspended in H_2O to separate the fraction less than $2 \mu\text{m}$ by gravity separation. The vermiculite was treated several times with 5 N NaCl (Rich, 1960) and shaken for 5 days each time until a strong 14 Å spacing was detected. The CEC (Na) of the vermiculite was 1.3 meq/g. All of the exchangers were saturated with Na or Ca by three pretreatments with N NaCl or N CaCl_2 . The excess salts were removed with H_2O .

Hydroxy-aluminum chloride, $\text{Al}(\text{OH})_B\text{Cl}_{3-B}$, was prepared by slow addition of an appropriate quantity of 0.05 M NaOH to 0.1 M AlCl_3 under constant stirring. The average basicity values selected ranged from $B = 0$ to $B = 2.5$. If precipitation occurred during the titration of AlCl_3 with NaOH, the mixtures were stirred at 80°C until a true solution was obtained.

All samples were shaken at $21 \pm 0.5^\circ\text{C}$ during the sorption experiments. Na, Ca, and Al were measured by atomic absorption spectrophotometry (AAS). The amounts of Al sorbed were determined by the difference between $\text{Al}(\text{OH})_B\text{Cl}_{3-B}$ added and Al in solution after a certain period of time. In the same solution whose Al had been determined by AAS (Al_{AAS}), the number of equivalents of this Al (Al_{titr}) was gained from the two last inflection points of titrimetric potentiograms (potentiograph, Metrohm). Thus it was possible to calculate the average basicity of the remaining Al after the reactions:

$$\text{OH}/\text{Al} = 3 - \frac{\text{meq Al}_{\text{titr}}}{\text{mmoles Al}_{\text{AAS}}} \equiv b$$

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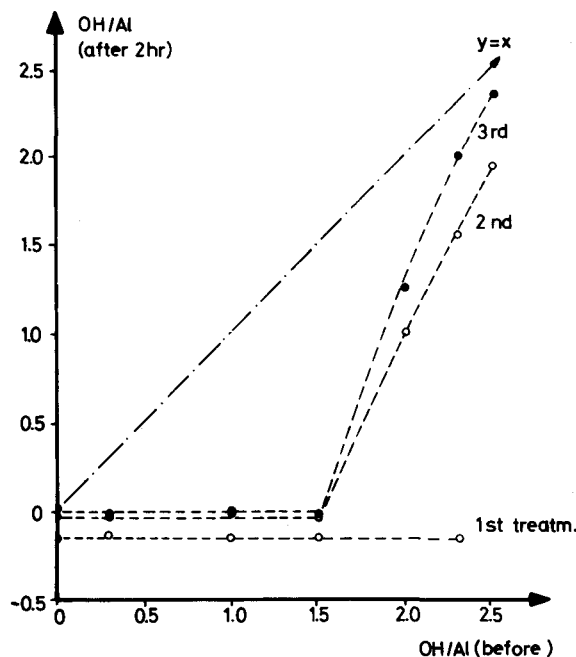


Fig. 1. Average OH/Al ratios of Al in solution before and after the first, second and third 2-hr treatment of Na-montmorillonite (Wyo.) with equivalent $\text{Al}(\text{OH})_B\text{Cl}_{3-B}$.

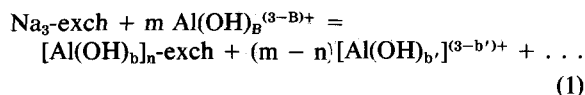
From a knowledge of the difference between $\text{Al}(\text{OH})_B\text{Cl}_{3-B}$ added and $\text{Al}(\text{OH})_b\text{Cl}_{3-b}$ after the reaction, the amount of Al adsorbed (if not stated otherwise) and its average basicity were determined.

X-ray powder diffraction patterns of the clay minerals were obtained at 25°C.

RESULTS AND DISCUSSION

Selectivity of smectite and vermiculite for Al of varying OH/Al

Average OH/Al of Al in solution when $\text{Al}(\text{OH})_B\text{Cl}_{3-B}$ is reacted with the exchanger. For this experiment, Na-saturated smectite and a Na-vermiculite were treated three times with equivalent amounts of $\text{Al}(\text{OH})_B\text{Cl}_{3-B}$. The main reactions between the exchanger and the aluminum added are summarized in Equation (1):



where $b = 3 - 3/n$ and $b' = (mB - 3n + 3)/(m - n)$. The results in Figure 1, which are typical for all three smectites investigated, show that smectite adsorbs preferentially the relatively more basic Al, leaving the relatively less basic Al in solution ($B > b'$, Equation 1). The difference between B of the $\text{Al}(\text{OH})_B^{(3-B)+}$ added and b' of the remaining Al in solution becomes smaller with more treatments, especially with B above 1.5 (Fig-

Table 1. Data before and after a 4-day reaction between 1 meq Ca-montmorillonite (S.D.) and 0.88 mmoles $\text{Al}(\text{OH})_B\text{Cl}_{3-B}$ in 100 ml.

before	Solution phase		pH		Al ads. %
	OH/Al after	before	before	after	
0	0	3.72	3.61		41
0.4	0	4.19	3.80		50
0.8	0	4.24	3.85		61
1.4	0	4.31	3.92		67
2.0	0	4.46	4.25		98
2.4	0	4.75	4.74		99

$\frac{1}{2}$ Al adsorbed in % of the $\text{Al}(\text{OH})_B\text{Cl}_{3-B}$ added.

ure 1). After the first treatment, the b' values of the remaining Al in solution were negative (minus 0.15, Figure 1) for all B values of the $\text{Al}(\text{OH})_B^{(3-B)+}$ added. This result implies that the remaining solution had an H/Al molar ratio of 0.15. The adsorption of the relatively more basic Al thus was followed by an expected drop in pH (Table 1). This decrease in pH also has been reported in the literature (Rich, 1960; Shen and Rich, 1962; Barnhisel and Rich, 1963; Hsu, 1968; Sawhney, 1968; Veith and Sposito, 1977).

In contrast to smectite, Na-vermiculite reacted (except for $B \leq 0.2$) with the relatively less basic Al during the first 2-hr treatment with $\text{Al}(\text{OH})_B^{(3-B)+}$, leaving the relatively more basic Al in solution (Figure 2). Essentially no reactions were measured during the second and third 2-hr treatment. The basicity of b of the OH-Al adsorbed by vermiculite not only depends on B of the $\text{Al}(\text{OH})_B^{(3-B)+}$ added (Figure 2) but also on time, as shown in Table 2 compared to Figure 2. When vermiculite was treated with $\text{Al}(\text{OH})_B^{(3-B)+}$ for 4 days, the OH/Al ratio of the Al adsorbed was larger for B below 1.2 ($b > B$ for $B < 1.2$, Equation 1). After the 2-hr treatment, b was greater than B only for B below 0.2. These selective reactions are consistent with the pH values measured before and after reaction (Table 2), which means that there was a pH decrease by adsorption of the relatively more basic Al ($b > b'$) and a pH increase by adsorption of the relatively less basic Al ($b < b'$).

Average OH/Al of Al adsorbed. Figure 3 illustrates the OH/Al molar ratio of the Al adsorbed by Na-montmorillonite after the first, second, and third 2-hr treatment with equivalent $\text{Al}(\text{OH})_B^{(3-B)+}$. As expected from Figure 1, smectite adsorbs the relatively more basic Al ($B < b$ in Equation 1). The average basicity, b , of the OH-Al in the interlayer region increases with the number of treatments and approaches its upper limit when $b \approx 2.7$. Similar b values of 2.6–2.7 also are given in Table 3 for the three smectites after they were treated either three or six times with $\text{Al}(\text{OH})_B^{(3-B)+}$. Comparable b values have been reported for "nonexchangeable" OH-Al on smectite (Hsu, 1968; Kozak and Huang, 1971; Brown and Newman, 1973).

Table 2. Data before and after a 4-day treatment of 0.96 meq Ca-vermiculite (S.A.) with 0.88 mmoles $\text{Al}(\text{OH})_b\text{Cl}_{3-b}$ in 100 ml.

Solution phase		pH		Al ads. $\frac{1}{2}$ %
before	after	before	after	
0	n.d.	3.72	3.65	49
0.4	0	4.19	3.77	59
0.8	0.4	4.24	3.85	67
1.2*	1.2*	--	--	--
1.4	1.7	4.31	4.36	78
2.0	2.4	4.46	5.05	61
2.4	2.6	4.75	5.64	58

$\frac{1}{2}$ Al adsorbed in % of the $\text{Al}(\text{OH})_b\text{Cl}_{3-b}$ added.

* Interpolated values.

It must be pointed out that the OH/Al molar ratios given are statistical mean values and do not designate the exact composition of the OH-Al compound(s) in solid or solution phases. At b of about 2.8, the total amount of Al "adsorbed" by smectite is 500 mmoles/100 meq CEC. Under this condition, the formation of gibbsite must be expected, as shown previously by Barnhisel and Rich (1963). In the presence of gibbsite (OH/Al = 3.0), the average OH/Al ratio b of Al adsorbed must, therefore, be below the measured value of 2.8. Indeed, the basicity of OH-Al extracted from montmorillonite is 2.4–2.5 (Hsu, 1968). A similar value of about 2.4 of extracted OH-Al is approached in the case of $\text{Al}(\text{OH})_b$ -montmorillonite (S.D.) (Veith, 1977). These results are in agreement with the OH-Al adsorbed by sulfonic resin whose OH/Al ratio approached a ratio at equilibrium of 2.5 in a pH range measured of 4.5 to 5.4 (Veith and Sposito, 1977).

These maximal OH/Al ratios of Al adsorbed by smectite and sulfonic resin cannot be observed with vermiculite. When vermiculite was treated four times with equivalent $\text{Al}(\text{OH})_b^{(3-b)+}$, the OH/Al ratio of the OH-Al adsorbed reached its "maximum" at about 1.53 with $B = 1.5$ (Table 3). As already shown, the b values of the OH-Al adsorbed are very time-dependent. In a long-time experiment, the final OH/Al ratio measured for the OH-Al adsorbed by Montana vermiculite was 2.0–2.2 (Hsu and Bates, 1964). As will be seen in the following section, the OH/Al ratio, at equilibrium, of the OH-Al adsorbed cannot be derived from the difference between Al added and measured after the reaction because of the structural instability of Al-vermiculite.

Internal factors affecting the OH/Al ratio and the amount of Al adsorbed

Hydrolysis of adsorbed Al caused by protonation of structural sites. It has been suggested on kinetic grounds (Jackson, 1960, 1963) that aluminosilicates react as relatively weak acids. Thus, in the presence of

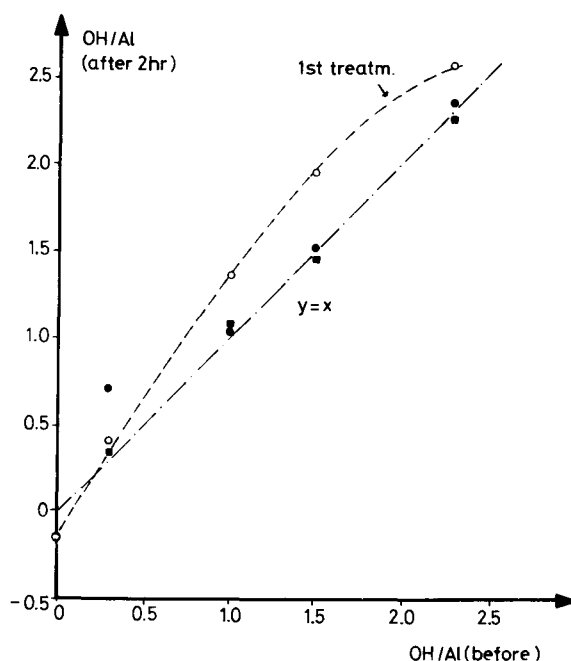
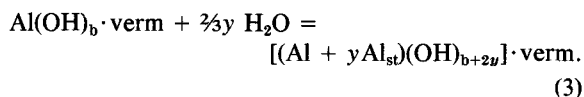
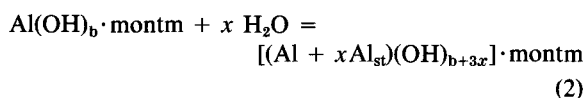


Fig. 2. Average OH/Al ratios of Al in solution before and after the first, second and third 2-hr treatment of Na-vermiculite (S.A.) with equivalent $\text{Al}(\text{OH})_b\text{Cl}_{3-b}$. (O = 1st, ● = 2nd, and ■ = 3rd treatment).

a relatively stronger acid (such as Al^{3+}) in the interlayer space, the clay mineral reacts as a proton acceptor. The protonation of structural sites is followed by a release of equivalent amounts of structural cations, e.g., Al, which can react with permanent negative charges on the mineral to maintain electroneutrality. These reactions, the hydrolysis of the adsorbed $\text{Al}(\text{OH})_b^{(3-b)+}$, the protonation of structural sites, and the liberation and adsorption of the structural Al (Al_{st}), can be summarized as follows for dioctahedral montmorillonite and trioctahedral vermiculite:



It is obvious that the degree of protonation and, consequently, the amount of Al_{st} liberated, depends very much on the OH/Al ratio ($= b$) of the Al adsorbed. The basicity at equilibrium of montmorillonite (OH/Al = $(b + 3x)/(\text{Al} + x\text{Al}_{st})$) and vermiculite (OH/Al = $(b + 2y)/(\text{Al} + y\text{Al}_{st})$) depends on the respective acidic stability of the $\text{Al}(\text{OH})_b$ -saturated exchangers. It is known that vermiculite is less stable than montmorillonite under acid conditions (e.g., Veith and Schwertmann, 1972). Consequently, the variable x in Equation (2) must be expected to be smaller than y in Equation (3).

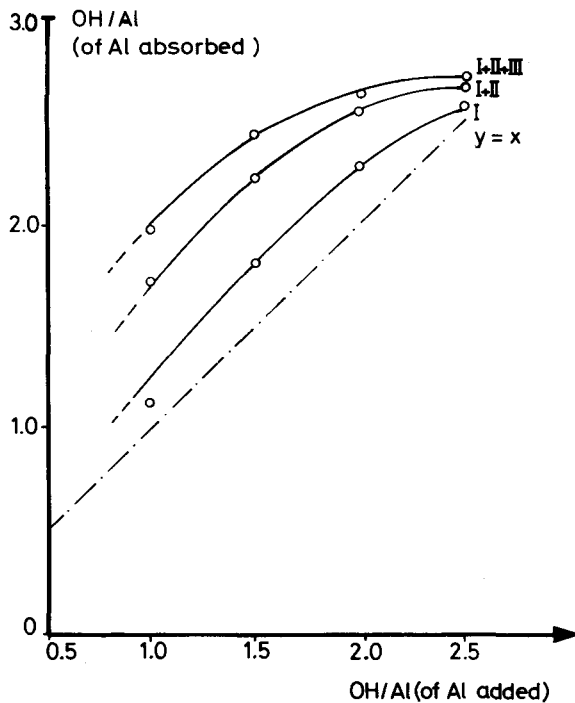


Fig. 3. Average OH-Al ratios of Al adsorbed and added when Na-montmorillonite reacted I to III times with equivalent $\text{Al}(\text{OH})_b\text{Cl}_{3-b}$ for 2 hr each time.

This relative stability of smectite and vermiculite is illustrated by the data in Table 4. All of the smectites pretreated with AlCl_3 and followed by KCl saturation collapsed to 12.2–12.8 Å. Vermiculite, with the same pretreatments, did not collapse. This shows that

$\text{Al}(\text{OH})_b$ -montmorillonite, with $b \approx 0$, is relatively stable compared to $\text{Al}(\text{OH})_b$ -vermiculite, which transforms to $(\text{Al} + y\text{Al}_{\text{st}})(\text{OH}_{b+2y})$ -vermiculite (Equation 3). This result agrees with exchange measurements of AlCl_3 -treated montmorillonite and vermiculite (Veith, 1977) and with a stability study of the same clay minerals treated with CO_2 (Veith and Schwertmann, 1972). In addition, it has been shown (Thomas, 1960; Shen and Rich, 1962; Brown and Newman, 1973; Veith, 1977) that, under comparable conditions, basic Al is not exchangeable. Consequently, the $\text{Al}(\text{OH})_b$ -montmorillonite with $b \approx 0$ (Equation 2) remained stable, whereas $\text{Al}(\text{OH})_b$ -vermiculite ($b \approx 0$, Equation 3) transformed to a OH-Al-vermiculite with a y (Equation 3) much greater than x (Equation 2). Similar X-ray data for Al^{3+} -montmorillonite and “ Al^{3+} -vermiculite” have been published (Rich, 1960; Shen and Rich, 1962; Turner and Brydon, 1965; Brydon and Kodama, 1966; Sawhney, 1968; and Veith, 1977). From these results it can be concluded that the OH/Al ratio of the Al in the interlayer of vermiculite cannot be assumed to be identical with b (Equation 3), especially for small b values.

When Hsu and Bates (1964) studied the OH/Al ratio of the Al fixed by Montana vermiculite, they measured only the b values, which were in the range of 2.0–2.1 at pH 4.35 and below. At pH 4.65 and 5.92, b values of 2.27 and 2.65, respectively, were calculated. On the basis of the b values measured (Hsu and Bates, 1964) it was concluded that between a pH of about 3.6 to 4.2, the OH/Al ratio of Al held by the vermiculite is 2.0 or 2.2. In the pH range 4.8 to 6.2, higher basicities of the OH-Al adsorbed were expected. These data are analogous with b (Equation 3) and do not consider the possible liberation of structural cations such as Al that in-

Table 3. Amounts of Al adsorbed and their average OH/Al ratio when 1 meq of Na-clays were treated 3, 4, or 6 times with equivalent $\text{Al}(\text{OH})_b\text{Cl}_{3-b}$ and shaken for 2 hr each time.

Before each treatment		3*		6*		4*	
OH/Al	$\text{Al}^2_{\text{added}}$	Na-mont. (Wyo.)		Na-mont. (Miss.)		Na-verm. (S.A.)	
		OH/Al ¹	$\text{Al}^2_{\text{ads.}}$	OH/Al ¹	$\text{Al}^2_{\text{ads.}}$	OH/Al ¹	$\text{Al}^2_{\text{ads.}}$
0	33	0.22	36	0.30	37	0.78	45
0.3	37	1.00	50	1.25	57	1.15	54
1.0	50	1.97	97	2.32	147	1.18	55
1.5	67	2.15	117	2.52	207	1.53	68
2.3	143	2.56	228	2.69	327	0.92	48

* Number of treatments.

¹ If all Ca or Na had been exchanged.

² mmoles per 100 meq CEC.

Table 4. d spacing at 25°C of Na-clays treated 3 times with equimolar $\text{Al}(\text{OH})_B\text{Cl}_{3-B}$ and shaken for 2 hr each time followed by a 0.1 M KCl treatment.

OH/Al added	d values (Å) of			
	Montm. (S.D.)	Montm. (Wyo.)	Montm. (Miss.)	Verm. (S.A.)
0	12.8	12.2	12.2	14.1
1.0	15.4	14.2	14.8	14.2
1.5	17.8	18.2	18.0	14.2
2.3	19.5	18.2	18.1	14.2

crease the total amount of Al in the interlayer ($\text{Al} + y\text{Al}_{\text{st}}$) and its basicity, $\text{OH}/\text{Al} = (b + 2y)/(1 + y)$. The parameter y increases with decreasing pH. In a study of the stability of CO_2 -treated Ca-montmorillonite (South Dakota) and Ca-vermiculite (South Africa), structural Al were found in the interlayers at pH below ≈ 5.0 for montmorillonite and pH below ≈ 5.6 for vermiculite (Veith and Schwertmann, 1972). Thus, the OH/Al ratios of 2.0 or 2.2 of Al adsorbed by vermiculite (Hsu and Bates, 1964) are too small and could reach the value of about 2.5 found for OH-Al adsorbed by smectite in the present study and by a sulfonic resin (Veith and Sposito, 1977).

Expansibility of clay minerals. The expansibility of vermiculite was limited to 14.2 Å, whereas smectite expanded to 18.1–19.5 Å when treated three times with equivalent $\text{Al}(\text{OH})_B\text{Cl}_{3-B}$ (Table 4). The same behavior of vermiculite and/or montmorillonite has been reported elsewhere (Rich, 1960; Shen and Rich, 1962; Jackson, 1963; Barnhisel and Rich, 1963; Kawasaki and Aomine, 1964; Turner and Brydon, 1965; Carstea, 1968; Sawhney, 1968; Barnhisel, 1969; Veith, 1977). It is known that the degree of polymerization, p , of the hydrated OH-Al complexes $[\text{Al}_p(\text{OH})_{np}]^{(3p-np)+}$ increases with the basicity, and with it, the particle size (Jahr and Brechlin, 1952; Brosset et al., 1954; Kudelka, 1960). The difference in d(001) spacing between smectite and vermiculite (Table 4) explains partially the specific behavior of smectite and vermiculite toward the selective adsorption of OH-Al in Figures 1 and 2, respectively. This selective behavior towards $[\text{Al}_p(\text{OH})_{pn}]^{(3p-pn)+}$ can also be seen by the quantities of OH-Al adsorbed which, of course, are highly dependent on the degree of its basicity n : $\text{Al}_{\text{ads}} = 100/3 - n$ (in mmoles/100 meq exchanger). The quantitative results are given in Table 3, which shows that the amount of OH-Al adsorbed by smectite grows with n of the Al added. With vermiculite, it decreases when the OH/Al ratio of Al added was about 1.5 and above because of the adsorption of the relatively less basic OH-Al. Data on the surface area of $\text{Al}(\text{OH})_B$ -treated montmorillonite (Barnhisel, 1969) can also be used to interpret the measurements on smectite given in Table 3. Barnhisel (1969) also measured the surface area of $\text{Al}(\text{OH})_B$ -treated vermiculite. The surface area decreased with $B = 1.5$ – 2.25 , above which it increased again. This result was unexpected and cannot be explained at present. Barn-

hisel's data can now be explained by the decreased adsorption of OH-Al at a certain basicity of the Al added. An "adsorption maximum" can also be seen in a study (Hsu and Bates, 1964) in which 1 g of Na-vermiculite (Montana) was reacted with 0.95 mmoles of $\text{Al}(\text{OH})_B\text{Cl}_{3-B}$ for 2 weeks to 10 months. After 2 weeks, the maximum of Al in the solid phase appeared at $B = 2.1$, but shifted to 2.25 after 6 weeks (this is also shown by the CEC minima). These maxima of Al in the solid phase were not mentioned by the authors since the maxima disappeared after 10 weeks. The steric effect of vermiculite is well demonstrated by Kozak and Huang (1971) who treated 1 g samples of biotites with different degrees of K-depletion with 1 mmole $\text{Al}(\text{OH})_B\text{Cl}_{3-B}$. One gram of biotite adsorbed 0.19 and 0.20 mmole Al when B was equal to 2 and 2.5, respectively; an 82% K-depleted biotite adsorbed 1.0 and 0.56 mmole of Al at $B = 2$ and 2.5, respectively. In the first case, the spacing was already too small for Al-polymers formed at $B = 2$; in the second case, far more Al was adsorbed at $B = 2$ compared to the large Al polymer formed at $B = 2.5$.

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Резюме— Сукновальная глина /из Южной Дакоты, Вайоминга и Миссисипи/ и вермикулит /Трасвааль/ были обработаны раствором $\text{Al}(\text{OH})_3^{(3-B)+}$, с B, изменяющимся от 0 до 2,5. Средняя валентность (OH/Al=B) адсорбированного Al значительно отличается от валентности добавленного Al. Средняя валентность Al, адсорбированного сукновальной глиной, была всегда выше средней валентности добавленного Al. В противоположность сукновальной глине вермикулит адсорбировал меньше соединений гидрокси Al. Одной из причин их различного селективного поведения было различие в растяжимости сукновальной глины /около 18 Å/ и вермикулита /около 14 Å/. В связи с адсорбцией сукновальной глиной относительно более основной OH-Al, сукновальная глина адсорбировала значительно больше Al, чем вермикулит. Обычно нельзя подсчитать полное количество алюминия в прослое по различию в количестве добавленного Al и оставшегося в растворе после реакции, в связи с возможной реакцией иона H^+ с глинистым минералом и адсорбцией структурного Al и других катионов, что более ясно выражено для вермикулита. Результаты настоящего исследования показывают, что из B добавленных солей Al нельзя выводить заключение ни о количественном, ни о качественном составе обменного раствора, обработанного $\text{Al}(\text{OH})_3$. Эти положения часто остаются незамеченными, когда катионные обменные растворы предварительно обрабатываются Al различной валентности и используются для дальнейших исследований, таких как изучение катионной обменной способности, поверхностной площади, промежутка между слоями, анионных реакций, формирования гиббсита и т.д. До проведения таких исследований, использующих предварительно обработанные OH-Al обменные растворы, необходимо точно знать их состав.