

# SURFACE ACIDITY OF SMECTITES IN RELATION TO HYDRATION, EXCHANGEABLE CATION, AND STRUCTURE\*

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**Abstract**—Equilibrium studies on clay films exposed to NH<sub>3</sub> and H<sub>2</sub>O vapors demonstrate the effect of exchangeable cations on surface acidity and its relationship to hydration. At a relative humidity of 98 per cent the order of acidity on the clay surface as indicated by protonation of NH<sub>3</sub> was Al > Mg > Ca = Li > Na = K for Wyoming bentonite and Al > Mg > Li > Ca = Na = K for nontronite. At a relative humidity of 20 per cent, however, the order was Al = Mg > Ca > Li > Na > K for the bentonite and Al = Mg > Li > Ca > Na > K for nontronite. The largest change in proton donation properties due to hydration effects was in the calcium clays. For Ca-bentonite the NH<sub>4</sub><sup>+</sup> formation was 16 me/100 g at 98 per cent and 80 me/100 g at 20 per cent relative humidity. In Ca-nontronite, the NH<sub>4</sub><sup>+</sup> formation was 14 and 64 me/100 g for the wet and dry systems respectively. The differences in proton donation between the bentonite and nontronite clays are believed to be due to charge site location and its effects on ion hydration. The NH<sub>4</sub><sup>+</sup> formed by the protonation process seemed to exist in different environments in the bentonite and nontronite as indicated in the i.r. absorption spectra.

## INTRODUCTION

THE unusual acidity or proton-donating properties of clay films and suspensions have been observed by a number of workers (see ref. list). The major proton donating process has been suggested to result from water molecules strongly polarized by exchangeable metal cations on the clay surface. It has been observed that the proton donation (or acidity) of this water is greater than would be expected upon consideration of the pK values of the same hydrated metal cations in water. The structure of the clay may have an indirect effect on this process if a special affinity for the protonated base exists as in the case of vermiculite for NH<sub>4</sub><sup>+</sup> ion where the product of the reaction of NH<sub>3</sub> with the mineral is being removed by fixation. In addition, the clay structure may affect the exchangeable cation and in turn its effect on surrounding water molecules in connection with the site of electric charge on the clay. Data obtained by Russell (1965) on NH<sub>4</sub><sup>+</sup> formation from NH<sub>3</sub> on montmorillonite (Wyoming bentonite) and saponite suggests some effect of site of charge.

Farmer and Mortland (1966) found that when pyridine is adsorbed on a highly hydrated Mg-montmorillonite, it is coordinated to the Mg ion largely by bridging through directly coordinated water molecules. As this system is dehydrated,

pyridinium ions are observed, suggesting an increase in acidity of the clay surface. Probably the polarizing effect of the exchangeable cation increases as the number of coordinated water molecules around it decreases by dehydration with the result that the remaining water molecules are better able to give up a proton to a base. The following work was designed to investigate in a quantitative manner the effect of hydration level, nature of the exchangeable cation, and the site of layer charge on the surface acidity of smectites. Special attention was given to observing proton donation under conditions of equilibrium and measurement of reactant and product concentration on the clay surface.

## METHODS

Homoionic samples of the < 2μ fraction of Wyoming bentonite (A.P.I. H-25), and nontronite (A.P.I. H-33a) were prepared by washing the clay with appropriate salt solutions (1 N) and removing the excess salts by repeated washings with water and methanol in a centrifuge. The half unit cell formulae for these two clays as determined from total chemical analysis are:



bentonite

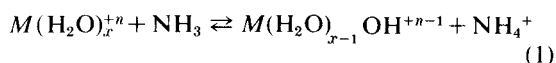


nontronite.

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Thin clay films were prepared by evaporating water suspensions of the clay in aluminum dishes. The resulting films (2.5 mg/cm<sup>2</sup>) could be readily stripped from the aluminum. The films were equilibrated over NH<sub>4</sub>OH solutions of varying concentrations and NH<sub>4</sub>OH-salt solutions of various kinds designed to give varying partial pressures of water and ammonia. After at least 24 hr of equilibration, one portion of the film was removed from the container, weighed, then placed in concentrated H<sub>2</sub>SO<sub>4</sub> and micro-kjeldahl analysis made. Another portion of the same film was placed in a Beckman IR-7 spectrophotometer and the absorbance of the 1430 cm<sup>-1</sup> ( $\nu_4$ ) band of NH<sub>4</sub><sup>+</sup> determined. The amount of NH<sub>4</sub><sup>+</sup> on the film could then be determined by reference to a standard curve prepared from NH<sub>4</sub><sup>+</sup>-montmorillonite or nontronite. Film thickness variation was compensated for by using i.r. absorption bands arising from the clay matrix itself as internal standards as suggested by Russell (1965). Amounts of water on the clay could be determined by subtracting the total amount of NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> found by nitrogen analysis from the total amount of adsorbate found gravimetrically. The amount of NH<sub>3</sub> on the films was found by subtracting the NH<sub>4</sub><sup>+</sup> ion content found spectroscopically from the total nitrogen content. Using these techniques it was possible to measure the amounts of reactants and products of the following reaction at equilibrium:



where *M* represents an exchangeable metal ion, *n* the valence of the ion, and *x* the amount of water.

#### DISCUSSION OF RESULTS

Table 1 reports the amounts of NH<sub>4</sub><sup>+</sup> ion produced at equilibrium in homoionic clay films at two

different relative humidities as well as the calculated equilibrium constants. The first most obvious characteristic of these data is the great effect of exchangeable cation on the formation of NH<sub>4</sub><sup>+</sup> ion. Therefore, in accounting for the protonation reaction observed, any explanation of the mechanism must include the exchangeable metal cation. A second observation is the significant effect of hydration on the protonation of NH<sub>3</sub> in some systems. A third characteristic of these data is the significant effect of mineralogy on the NH<sub>4</sub><sup>+</sup> ion formation. Thus the charge site location (octahedral vs. tetrahedral) is also a factor that must be considered in accounting for these results.

#### *Effect of hydration and exchangeable cations on proton-donor properties*

The effect of exchangeable cation on the protonation process may be related to the hydrolysis properties of these cations in water. Each hydrated cation can act as an acid or proton donor and each hydrated cation has a hydrolysis constant or pK which describes its acidic properties and which reflect the properties of the cation vis-a-vis its associated water molecules. The acid properties of hydrated metal cations vary greatly and are summarized by Hunt (1963). Mortland (1968) has shown the relationship between electronegativity of the exchangeable cations and the protonation of some bases on montmorillonite. It is thus not surprising to find that the exchangeable cation is a major factor in protonation of bases on the clay surface. What is surprising is the large variation in the proton donor properties of the clay surface and the great change in proton donation for some kinds of exchangeable cations in moist as compared with relatively dry systems. A general observation might be that the clay surface becomes more acidic as it is dehydrated. This is exemplified in Fig. 1 where

Table 1. Amounts of NH<sub>4</sub><sup>+</sup> (me/100 g) formed in bentonite and nontronite, over NH<sub>3</sub>-H<sub>2</sub>O (0.7% NH<sub>4</sub>OH) solutions and the calculated equilibrium constants (*K<sub>e</sub>*)

Cation on clay	Bentonite				Nontronite			
	Low H <sub>2</sub> O*		High H <sub>2</sub> O†		Low H <sub>2</sub> O*		High H <sub>2</sub> O†	
	NH <sub>4</sub> <sup>+</sup>	<i>K<sub>e</sub></i>	NH <sub>4</sub> <sup>+</sup>	<i>K<sub>e</sub></i>	NH <sub>4</sub> <sup>+</sup>	<i>K<sub>e</sub></i>	NH <sub>4</sub> <sup>+</sup>	<i>K<sub>e</sub></i>
Li	23	2.5 × 10 <sup>-3</sup>	17	1.02 × 10 <sup>-3</sup>	68	17.4 × 10 <sup>-2</sup>	34	3.96 × 10 <sup>-3</sup>
Na	16	11.8 × 10 <sup>-3</sup>	10	4.30 × 10 <sup>-3</sup>	49	10.8 × 10 <sup>-2</sup>	16	1.04 × 10 <sup>-3</sup>
K	10	5.9 × 10 <sup>-3</sup>	11	6.80 × 10 <sup>-4</sup>	18	4.4 × 10 <sup>-2</sup>	16	5.91 × 10 <sup>-3</sup>
Ca	80	12.0 × 10 <sup>-2</sup>	16	4.40 × 10 <sup>-3</sup>	62	2.8 × 10 <sup>-2</sup>	14	1.27 × 10 <sup>-3</sup>
Mg	101	7.5 × 10 <sup>-2</sup>	74	2.09 × 10 <sup>-2</sup>	75	6.2 × 10 <sup>-2</sup>	64	3.04 × 10 <sup>-2</sup>
Al	101	2.9 × 10 <sup>-2</sup>	100	2.20 × 10 <sup>-2</sup>	74	10.3 × 10 <sup>-2</sup>	72	3.07 × 10 <sup>-2</sup>

\*H<sub>2</sub>O *P*/*P*<sub>0</sub> = 0.20.

†H<sub>2</sub>O *P*/*P*<sub>0</sub> = 0.98.

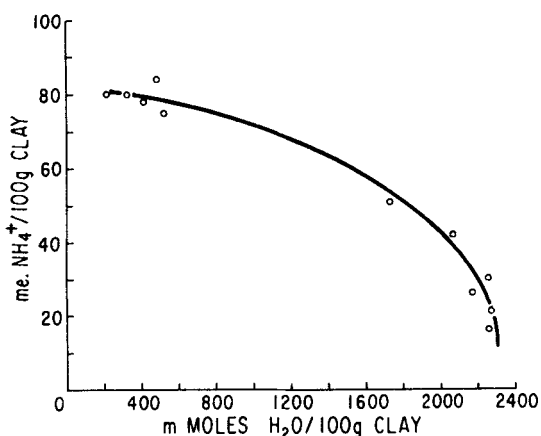


Fig. 1. Relationship of NH<sub>4</sub><sup>+</sup> produced to H<sub>2</sub>O content of Ca-bentonite over NH<sub>3</sub>-H<sub>2</sub>O solutions under conditions of equilibrium.

the amount of NH<sub>4</sub><sup>+</sup> formed on Ca-bentonite is plotted versus the amount of water on the clay surface at equilibrium.

From the reactants and products expressed in Eq. (1), it is possible to calculate the equilibrium constants, *K<sub>e</sub>*, from the expression:

$$K_e = \frac{[\text{OH}][\text{NH}_4^+]}{[\text{H}_2\text{O}][\text{NH}_3]} \quad (2)$$

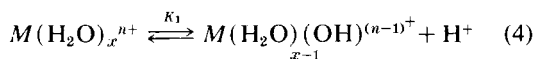
Since the proportion of (OH) formed is stoichiometrically equal to the amount of (NH<sub>4</sub><sup>+</sup>) formed, the expression can be rewritten as:

$$K_e = \frac{[\text{NH}_4^+]^2}{[\text{H}_2\text{O}][\text{NH}_3]} \quad (3)$$

While activities are the more rigorous values used in the calculation of equilibrium constants, concentrations are used here since activities were not measurable.

Table 2 indicates the proportions of NH<sub>3</sub>, NH<sub>4</sub><sup>+</sup>, and H<sub>2</sub>O on some of the Ca-bentonite films and the

equilibrium constants (*K<sub>e</sub>*) calculated from the concentration values. The equilibrium constants show a progressive increase from 4.4 × 10<sup>-3</sup> in the wet, to 120 × 10<sup>-3</sup> in the dry systems. Table 1 also gives the *K<sub>e</sub>* values for the dry and wet ends of the system for both bentonite and nontronite with different exchangeable cations. As in the case of Ca, the equilibrium constants in all the other systems are larger in the low water systems, though the magnitude of variation from the high water system depends on the nature of the interlayer cation and the type of clay mineral. Undoubtedly some of the differences in equilibrium constants between the high and low H<sub>2</sub>O systems may result from H<sub>2</sub>O present in the clay (particularly the high level) which is not in fact involved in the reaction as expressed in equation (1). Nevertheless, the results in Fig. 1, Table 1, and Table 2 conclusively show that the proton donor properties of the clays change with water content. These findings are interpreted to mean that the water remaining on the clay surface becomes more acidic as dehydration proceeds. Put another way, it might be said that the p*K* of the hydrated exchangeable cations decreases with dehydration. When a great deal of water is present, polarization forces of the exchangeable cations may be said to be distributed among a large number of water molecules and the p*K* of such a system might approach that of these ions in an aqueous solution. However, as water content is decreased, polarization forces become more concentrated on the fewer remaining water molecules causing an increase in hydrolysis and so in their proton donating abilities. In fact, it may be reasonable to express the ionization of the aquo complexes as follows:



and

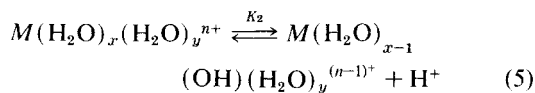


Table 2. Proportion of H<sub>2</sub>O, NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> on Ca-bentonite films at equilibrium after exposure to varying vapor pressures of water and ammonia

Per cent H <sub>2</sub> O on clay*	mmole H <sub>2</sub> O /100 g clay	mmole NH <sub>3</sub> /100 g clay	mmole NH <sub>4</sub> <sup>+</sup> /100 g clay	Equilibrium constant <i>K<sub>e</sub></i>
40.7	2.26 × 10 <sup>3</sup>	26	16	4.4 × 10 <sup>-3</sup>
39.0	2.17 × 10 <sup>3</sup>	33	26	9.4 × 10 <sup>-3</sup>
31.1	1.73 × 10 <sup>3</sup>	108	51	13.9 × 10 <sup>-3</sup>
5.9	3.27 × 10 <sup>2</sup>	163	80	120 × 10 <sup>-3</sup>

\*Oven dry basis (105°C).

Where  $M$  is an exchangeable metal cation on the clay,  $x$  the amount of inner sphere coordinated water,  $y$  the amount of outer sphere coordinated water, and  $K_1$  and  $K_2$  the ionization constants for the two systems. Equation (4) would represent the drier system where only directly coordinated water remained while Eq. (5) represents the moist system where there is outer as well as inner sphere coordinated water. From the preceding discussion one would conclude that  $K_1$  is greater than  $K_2$  and thus the drier system would be the more efficient proton donor. As dehydration proceeds, the amount of  $\text{NH}_3$  on the clay surface increases as noted in Table 2 and thus it might be argued that increase in this reactant drives the reaction to the right (Eq. 1) with the resulting increase in  $\text{NH}_4^+$  ion formation. This does not seem to be a reasonable explanation since in many cases the amount of change is much greater than that expected from mass action effects. Also it is difficult to understand why the basicity of  $\text{NH}_3$  would be increased as the result of increased  $\text{NH}_3$  adsorption.

#### *Mineralogical effects on proton donation*

The reasons for the mineralogical effect on the proton donation process are not obvious. The site of charge was the main variable in the two smectites used, being located in the octahedral layer of the Wyoming bentonite and in the tetrahedral layer of the Garfield, Washington, nontronite. Presumably then the site of charge may have some influence. Shainberg and Kemper (1966) have pointed out some effects of charge site on the exchangeable cations and their hydration properties. This influence may be indirect through the interaction between the site and the exchangeable cation with resulting differences in the polarization effects on associated water molecules. The most obvious differences between the two kinds of smectites indicated in Table 1 is that at the dry end (20 per cent relative humidity) the Ca-bentonite is more acidic than the Ca-nontronite while the Li and Na-bentonite is less acidic than the corresponding nontronite systems. These results for the Ca system agree with results of Russell (1965) where he compared bentonite and saponite but differ with his results for the alkali metals. One difference in technique must be mentioned and that is that the work reported here was approximately under equilibrium conditions with respect to vapor pressures of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  while Russell's (1965) method was to pass a stream of  $\text{NH}_3$  gas over the clay film for a  $\frac{1}{2}$  hr. This latter technique would result in a system lower in  $\text{H}_2\text{O}$  content than the driest used in this study. In fact, the technique of Russell would probably result in almost complete dehydration of the clay surface due to mass action effects of  $\text{NH}_3$  replacing

$\text{H}_2\text{O}$  as solvating molecules around the exchangeable metal cations.

The  $\text{K}^+/\text{NH}_4^+$  fixation capacities estimated according to the method of Alexiades and Jackson (1965) were 6 and 17 me/100 g for the bentonite and nontronite respectively. The cation exchange capacities (Ca/Mg) were 92 and 85 me/100 g for the bentonite and nontronite respectively. The uniformity of  $\text{NH}_4^+$  formation at the high and low water vapor pressures in both K-bentonite and K-nontronite are reported in Table 1. Since the  $\text{K}^+$  saturation would prevent any  $\text{NH}_4^+$  formation due to the fixation reaction at vermiculite-like sites, these levels of  $\text{NH}_4^+$  formation may be attributed to weakly acidic hydroxyl groups probably at the mineral edges. The fact that Na-clays at high water levels have the same amount of  $\text{NH}_4^+$  formation as the K-clays would indicate that the fixation sites as measured by the method of Alexiades and Jackson (1965) are not operating. It is well known that dehydration as in the Alexiades and Jackson method is an important treatment in getting most smectites to "fix"  $\text{K}^+$  or  $\text{NH}_4^+$ . It is therefore suggested that under equilibrium conditions in the presence of  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , water molecules which have the same crystallographic radii as  $\text{NH}_4^+$  may occupy the ditrigonal cavities at the clay surfaces, preventing the "fixation" of  $\text{NH}_4^+$ . It is proposed that the difference in the  $\text{NH}_4^+$  formation in the alkali metal and alkaline earth systems are due to difference in polarization effects on water as modified by the different mineral structures. Within the alkali metal group used in this work, the order of decreasing solvation energy  $\text{Li} > \text{Na} > \text{K}$  is in accord with their effects on proton donation by  $\text{H}_2\text{O}$  to  $\text{NH}_3$  in both bentonite and nontronite. This effect is especially evident in the drier systems.

The ability of different ions to coordinate with  $\text{H}_2\text{O}$  is dependent upon the electrostatic field around the central cation and upon the total dipole moment of the coordinated  $\text{H}_2\text{O}$ . However the total dipole moment of the  $\text{H}_2\text{O}$  depends upon its permanent dipole moment  $P$ , and the induced moment  $P'$ . In turn the induced moment  $P'$  is determined by the strength of the inducing electrostatic field,  $E$ , and upon the electronic polarizability,  $a$ , of the  $\text{H}_2\text{O}$ :

$$\text{Total Moment} = P + P' = P + aE \quad (6)$$

The electrostatic field,  $E$ , around the central cation may be affected to some degree by the force field exerted by the clay structure itself on the cation, and it is well known that the type of anion affects the energy of formation of some coordination compounds. Thus the location of the charge in the clay structure may differentially influence the polarization of the water, resulting in differences in

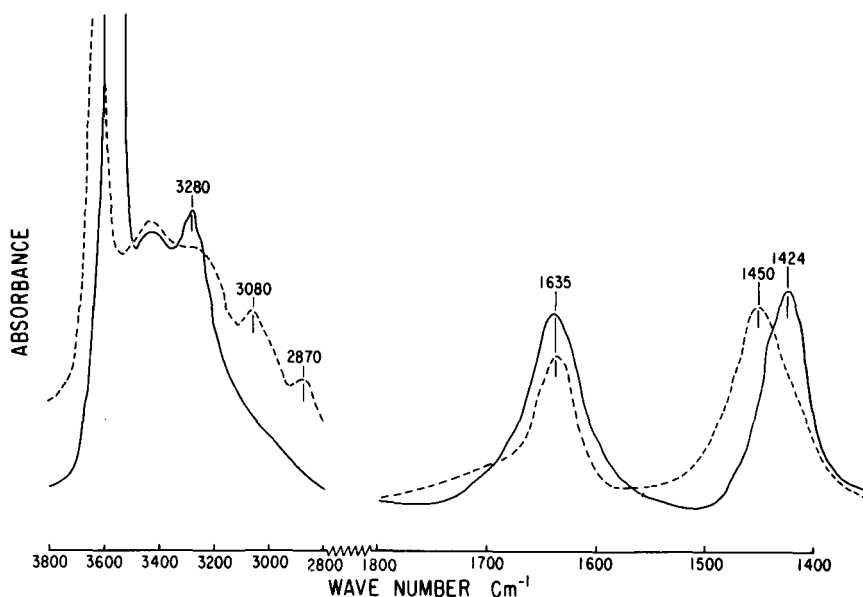


Fig. 2. Infrared spectra of Ca-bentonite (dashed line) and Ca-nontonite (solid line) equilibrated over  $\text{NH}_3 \cdot \text{H}_2\text{O}$  solution (24%  $\text{NH}_4\text{OH}$ ).

proton donating properties and accounting for the mineralogical effects noted in this work.

#### *Environment of $\text{NH}_4^+$ ion in bentonite and nontonite*

There is some indication from this work that the  $\text{NH}_4^+$  ions reside largely in different environments in the bentonite as compared with the nontonite. This is shown in Fig. 2 where infrared spectra of Ca-bentonite (dashed line) and Ca-nontonite (solid line) are shown after adsorption of  $\text{NH}_3$ . The deformation band ( $\nu_4$ ) of the  $\text{NH}_4^+$  ion formed occurs at  $1424 \text{ cm}^{-1}$  in the nontonite and at  $1450 \text{ cm}^{-1}$  in the bentonite. Concomitantly, some NH stretching vibrations of  $\text{NH}_4^+$  occur at  $2870$  and  $3080 \text{ cm}^{-1}$  in the bentonite and a single band at  $3280 \text{ cm}^{-1}$  in the nontonite. The amount of water on these samples is roughly the same as indicated by the deformation band at  $1635 \text{ cm}^{-1}$ , although there is some contribution from the  $\nu_4$  vibration of adsorbed  $\text{NH}_3$  here. These spectra indicate that the  $\text{NH}_4^+$  ion in the nontonite is relatively unperturbed, while in the case of the bentonite it is strongly perturbed by hydrogen bonding with  $\text{H}_2\text{O}$ . These results suggest that the  $\text{NH}_4^+$  in the nontonite may occupy the cavities created by the hexagonal network of oxygen atoms on the surface of the clay structure, in close proximity to the tetrahedral charge site in which case they might not have an opportunity to hydrogen bond with  $\text{H}_2\text{O}$ . On the other hand, in the

bentonite where the charge site is more distantly located in the octahedral layer, the  $\text{NH}_4^+$  ions may be located mainly on the surface of the clay structure where they can interact with adjoining water molecules in hydrogen bonding.

*Addendum.* Since the submission and approval of this manuscript, Dr. V. C. Farmer of Macaulay Institute for Soil Research in Aberdeen provided us with a small quantity of saponite. With this tetrahedrally charged mineral, it was possible to compare quantities of  $\text{NH}_4^+$  formed with the nontonite data reported in the preceding manuscript. The amounts of  $\text{NH}_4^+$  formed by  $\text{Li}^+$ - and  $\text{Na}^+$ -saponite under identical conditions to those of nontonite at the low  $\text{H}_2\text{O}$  environment (Table 1) were only 10–15 me/100 g and thus considerably lower than nontonite. This suggests that the proposal made that charge site location of itself is responsible for differences noted between bentonite and nontonite may not be valid. Another possibility may be that the differences in the ditrigonal arrangement of the oxygen atoms at the mineral surfaces differentially affect the reactions discussed here.

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**Résumé**—Des études d'équilibre de pellicules d'argile exposées à des vapeurs de  $\text{NH}_3$  et  $\text{H}_2\text{O}$  démontrent l'effet de cations échangeables sur l'acidité de surface et son rapport avec l'hydratation. A une humidité relative de 98%, l'ordre d'acidité sur la surface d'argile tel qu'il était donné par la protonisation de  $\text{NH}_3$  était  $\text{Al} > \text{Mg} > \text{Ca} = \text{Li} > \text{Na} = \text{K}$  pour la bentonite du Wyoming et  $\text{Al} > \text{Mg} > \text{Li} > \text{Ca} = \text{Na} = \text{K}$  pour la nontronite. Cependant à une humidité relative de 20%, l'ordre était le suivant:  $\text{Al} > \text{Mg} > \text{Ca} > \text{Li} > \text{Na} > \text{K}$  pour la bentonite et  $\text{Al} = \text{Mg} > \text{Li} > \text{Ca} > \text{Na} > \text{K}$  pour la nontronite. C'est pour les argiles à calcium que l'on a noté les plus grands changements dans les propriétés d'abandon de protons par suite d'hydratation. Pour la Ca-bentonite, la formation  $\text{NH}_4^+$  était de 16 me/100g à 98% et de 80 me/100 g à 20% d'humidité relative. Pour la Ca-nontronite, la formation  $\text{NH}_4^+$  était de 14 et de 64 me/100 g pour les systèmes sec et humide respectivement. Les différences d'abandon de protons entre les argiles de bentonite et de nontronite semblent être dues à l'emplacement de la charge et de ses effets sur l'hydratation des ions. Le  $\text{NH}_4^+$  formé par le processus de protonisation semblait exister dans des milieux différents dans la bentonite et la nontronite comme indiqué dans les spectres d'absorption infrarouges.

**Kurzreferat**—Gleichgewichtsstudien an dünnen Tonschichten, die  $\text{NH}_3$  oder  $\text{H}_2\text{O}$  Dämpfen ausgesetzt waren, zeigen den Einfluss von austauschbaren Kationen auf die Oberflächenazidität und deren Beziehung zur Hydratation. Bei einer relativen Feuchtigkeit von 98% war die, durch die Protonisierung des  $\text{NH}_3$  angedeutete, Reihenfolge der Azidität auf der Tonoberfläche  $\text{Al} > \text{Mg} > \text{Ca} = \text{Li} > \text{Na} = \text{K}$  für Wyoming Bentonit und  $\text{Al} > \text{Mg} > \text{Li} > \text{Ca} = \text{Na} = \text{K}$  für Nontronit. Bei einer relativen Feuchtigkeit von 20% hingegen war die Reihenfolge  $\text{Al} = \text{Mg} > \text{Ca} > \text{Li} > \text{Na} > \text{K}$  für den Bentonit und  $\text{Al} = \text{Mg} > \text{Li} > \text{Ca} > \text{Na} > \text{K}$  für Nontronit. Die weitgehendste Veränderung in den Protonabgabeneigenschaften infolge von Hydratationswirkungen trat bei den Calciumtonen auf. Beim Ca-Bentonit betrug die  $\text{NH}_4^+$  Bildung 16 me/100 g bei 98% gegenüber 80 me/100 g bei 20% relativer Feuchtigkeit. Beim Ca-Nontronit war die  $\text{NH}_4^+$  Bildung 14 und 64 me/100 g für das feuchte bzw. trockene System. Die Unterschiede in der Protonenabgabe bei Bentonit und Nontronit Tonen scheint mit dem Sitz der Ladung und dessen Einfluss auf die Ionenhydratation zusammenzuhängen. Wie aus den Infrarot Absorptionsspektren ersichtlich trat das durch den Protonisierungsprozess entstandene  $\text{NH}_4^+$  im Bentonit und im Nontronit in voneinander verschiedenen Umgebungen auf.

**Резюме**—Исследование равновесия, предпринятое на глинистых пленках подвергнутых парам  $\text{NH}_3$  и  $\text{H}_2\text{O}$ , демонстрирует воздействие обмениваемых катионов на поверхностную кислотность и на отношение ее к гидратации. При относительной влажности 98% порядок кислотности на поверхности глины, как это указывается протонотацией  $\text{NH}_3$ , был следующим:  $\text{Al} > \text{Mg} > \text{Ca} = \text{Li} > \text{Na} = \text{K}$  для виомингского бентонита и  $\text{Al} > \text{Mg} > \text{Li} > \text{Ca} = \text{Na} = \text{K}$  для нонтронита. Однако при относительной влажности 20%, порядок был  $\text{Al} = \text{Mg} > \text{Ca} > \text{Li} > \text{Na} > \text{K}$  для бентонита и  $\text{Al} = \text{Mg} > \text{Li} > \text{Ca} > \text{Na} > \text{K}$  для нонтронита. Наибольшее изменение в протодонорной способности под воздействием гидратации произошло в кальциевых глинах. Для Ca-бентонита формирование  $\text{NH}_4^+$  составило 16 мэ/100 г при 98% и 80 мэ/100 г при 20% относительной влажности. В Ca-нонтроните, формирование  $\text{NH}_4^+$  составило 14 и 64 мэ/100 г для влажной и сухой системы соответственно. Разница между бентонитом и нонтронитом касательно протодонорной способности является вероятно следствием местоположения заряда и эффектом этого на ионную гидратацию.  $\text{NH}_4^+$  образованный процессом протонотации вероятно имеется в разных окружающих породах в бентоните и нонтроните, как это указывается в спектрах инфракрасного поглощения.