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

M. M. MORTLAND and K. V. RAMAN†

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Abstract—Equilibrium studies on clay films exposed to NH_3 and H_2O 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_3 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_4^+ 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_4^+ 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_4^+ 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_4^+ ion where the product of the reaction of NH_3 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_4^+ formation from NH_3 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 $< 2\mu$ 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:

$[Al^{3+}_{1.53}\,Fe^{3+}_{0.16}\,Mg^{2+}_{0.33}]\,[Al^{3+}_{0.05}\,Si^{4+}_{3.95}]\,O_{10}[OH]_2$ -- bentonite

$[Al^{3+}_{0.13}\,Fe^{3+}_{1.85}\,Mg^{2+}_{0.02}]\,[Al^{3+}_{0.40}\,Si^{4+}_{3.60}]\,O_{10}[OH]_2$ -- nontronite.

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†Professor, and Research Associate in Soil Science, Michigan State Univ., East Lansing, Michigan.

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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/cm²) could be readily stripped from the aluminum. The films were equilibrated over NH_4OH solutions of varying concentrations and NH_4OH-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_2SO_4 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^{-1} (ν_4) band of NH_4^+ determined. The amount of NH_4^+ on the film could then be determined by reference to a standard curve prepared from NH_4^+-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_3 and NH_4^+ found by nitrogen analysis from the total amount of adsorbate found gravimetrically. The amount of NH_3 on the films was found by subtracting the NH_4^+ 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:

$$M(H_2O)_x^{+n} + NH_3 \rightleftarrows M(H_2O)_{x-1}OH^{+n-1} + NH_4^+ \quad (1)$$

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_4^+ 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_4^+ 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_3 in some systems. A third characteristic of these data is the significant effect of mineralogy on the NH_4^+ 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_4^+ (me/100 g) formed in bentonite and nontronite, over NH_3–H_2O (0·7% NH_4OH) solutions and the calculated equilibrium constants (K_e)

Cation on clay	Bentonite				Nontronite			
	Low H_2O*		High H_2O†		Low H_2O*		High H_2O†	
	NH_4^+	K_e	NH_4^+	K_e	NH_4^+	K_e	NH_4^+	K_e
Li	23	$2·5 \times 10^{-3}$	17	$1·02 \times 10^{-3}$	68	$17·4 \times 10^{-2}$	34	$3·96 \times 10^{-3}$
Na	16	$11·8 \times 10^{-3}$	10	$4·30 \times 10^{-3}$	49	$10·8 \times 10^{-2}$	16	$1·04 \times 10^{-3}$
K	10	$5·9 \times 10^{-3}$	11	$6·80 \times 10^{-4}$	18	$4·4 \times 10^{-2}$	16	$5·91 \times 10^{-3}$
Ca	80	$12·0 \times 10^{-2}$	16	$4·40 \times 10^{-3}$	62	$2·8 \times 10^{-2}$	14	$1·27 \times 10^{-3}$
Mg	101	$7·5 \times 10^{-2}$	74	$2·09 \times 10^{-2}$	75	$6·2 \times 10^{-2}$	64	$3·04 \times 10^{-2}$
Al	101	$2·9 \times 10^{-2}$	100	$2·20 \times 10^{-2}$	74	$10·3 \times 10^{-2}$	72	$3·07 \times 10^{-2}$

*H_2O $P/P_0 = 0·20$.
†H_2O $P/P_0 = 0·98$.

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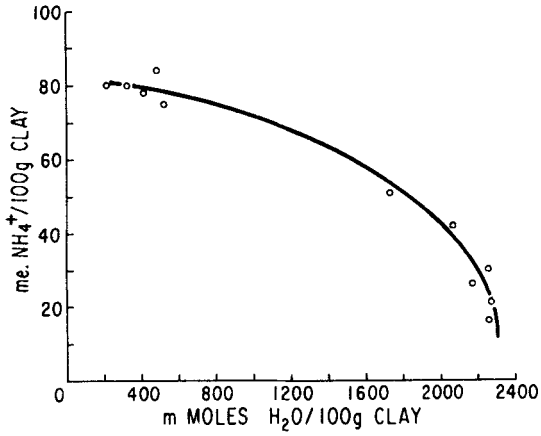


Fig. 1. Relationship of NH_4^+ produced to H_2O content of Ca-bentonite over $NH_3 \cdot H_2O$ solutions under conditions of equilibrium.

the amount of NH_4^+ 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_e, from the expression:

$$K_e = \frac{[OH][NH_4^+]}{[H_2O][NH_3]} \qquad (2)$$

Since the proportion of (OH) formed is stoichiometrically equal to the amount of (NH_4^+) formed, the expression can be rewritten as:

$$K_e = \frac{[NH_4^+]^2}{[H_2O][NH_3]} \qquad (3)$$

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_3, NH_4^+, and H_2O on some of the Ca-bentonite films and the equilibrium constants (K_e) calculated from the concentration values. The equilibrium constants show a progressive increase from $4{\cdot}4 \times 10^{-3}$ in the wet, to 120×10^{-3} in the dry systems. Table 1 also gives the K_e 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_2O systems may result from H_2O 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 pK 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 pK 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:

$$M(H_2O)_x^{n+} \overset{K_1}{\rightleftharpoons} \underset{x-1}{M(H_2O)(OH)^{(n-1)^+}} + H^+ \qquad (4)$$

and

$$M(H_2O)_x(H_2O)_y^{n+} \overset{K_2}{\rightleftharpoons} M(H_2O)_{x-1}(OH)(H_2O)_y^{(n-1)^+} + H^+ \qquad (5)$$

Table 2. Proportion of H_2O, NH_3 and NH_4^+ on Ca-bentonite films at equilibrium after exposure to varying vapor pressures of water and ammonia

Per cent H_2O on clay*	mmole H_2O /100 g clay	mmole NH_3 /100 g clay	mmole NH_4^+ /100 g clay	Equilibrium constant K_e
40·7	$2{\cdot}26 \times 10^3$	26	16	$4{\cdot}4 \times 10^{-3}$
39·0	$2{\cdot}17 \times 10^3$	33	26	$9{\cdot}4 \times 10^{-3}$
31·1	$1{\cdot}73 \times 10^3$	108	51	$13{\cdot}9 \times 10^{-3}$
5·9	$3{\cdot}27 \times 10^2$	163	80	120×10^{-3}

*Oven dry basis (105°C).

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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 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 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 NH_3 would be increased as the result of increased 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 techmust be mentioned and that is that the work reported here was approximately under equilibrium conditions with respect to vapor pressures of NH_3 and H_2O while Russell's (1965) method was to pass a stream of NH_3 gas over the clay film for a $\frac{1}{2}$ hr. This latter technique would result in a system lower in H_2O 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 NH_3 replacing H_2O as solvating molecules around the exchangeable metal cations.

The K^+/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 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 K^+ saturation would prevent any NH_4^+ formation due to the fixation reaction at vermiculite-like sites, these levels of 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 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" K^+ or NH_4^+. It is therefore suggested that under equilibrium conditions in the presence of NH_3 and H_2O, water molecules which have the same crystallographic radii as NH_4^+ may occupy the ditrigonal cavities at the clay surfaces, preventing the "fixation" of NH_4^+. It is proposed that the difference in the 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 $Li > Na > K$ is in accord with their effects on proton donation by H_2O to NH_3 in both bentonite and nontronite. This effect is especially evident in the drier systems.

The ability of different ions to coordinate with H_2O is dependent upon the electrostatic field around the central cation and upon the total dipole moment of the coordinated H_2O. However the total dipole moment of the H_2O 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 H_2O:

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

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

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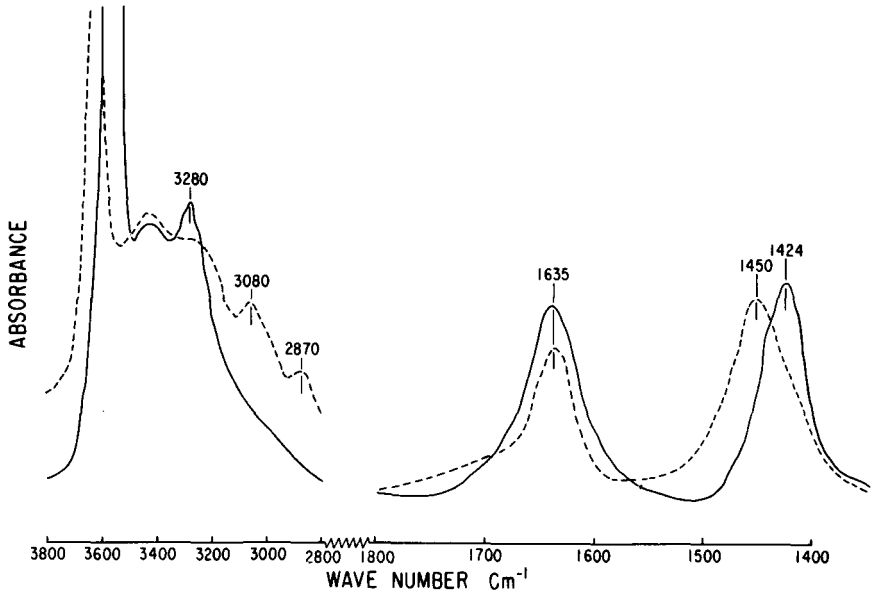


Fig. 2. Infrared spectra of Ca-bentonite (dashed line) and Ca-nontronite (solid line) equilibrated over $NH_3 \cdot H_2O$ solution (24% NH_4OH).

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

Environment of NH_4^+ *ion in bentonite and nontronite*

There is some indication from this work that the NH_4^+ ions reside largely in different environments in the bentonite as compared with the nontronite. This is shown in Fig. 2 where infrared spectra of Ca-bentonite (dashed line) and Ca-nontronite (solid line) are shown after adsorption of NH_3. The deformation band (ν_4) of the NH_4^+ ion formed occurs at 1424 cm^{-1} in the nontronite and at 1450 cm^{-1} in the bentonite. Concomitantly, some NH stretching vibrations of NH_4^+ occur at 2870 and 3080 cm^{-1} in the bentonite and a single band at 3280 cm^{-1} in the nontronite. The amount of water on these samples is roughly the same as indicated by the deformation band at 1635 cm^{-1}, although there is some contribution from the ν_4 vibration of adsorbed NH_3 here. These spectra indicate that the NH_4^+ ion in the nontronite is relatively unperturbed, while in the case of the bentonite it is strongly perturbed by hydrogen bonding with H_2O. These results suggest that the NH_4^+ in the nontronite 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 H_2O. On the other hand, in the bentonite where the charge site is more distantly located in the octahedral layer, the 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 NH_4^+ formed with the nontronite data reported in the preceding manuscript. The amounts of NH_4^+ formed by Li^+—and Na^+—saponite under identical conditions to those of nontronite at the low H_2O environment (Table 1) were only 10–15 me/100 g and thus considerably lower than nontronite. This suggests that the proposal made that charge site location of itself is responsible for differences noted between bentonite and nontronite 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 NH_3 et H_2O 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 NH_3 était Al > Mg > Ca = Li > Na = K pour la bentonite du Wyoming et Al > Mg > Li > Ca = Na = K pour la nontronite. Cependant à une humidité relative de 20%, l'ordre était le suivant: Al > Mg > Ca > Li > Na > K pour la bentonite et Al = Mg > Li > Ca > Na > 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 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 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 dûes à l'emplacement de la charge et de ses effets sur l'hydratation des ions. Le 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'absorbtion infrarouges.

Kurzreferat—Gleichgewichtsstudien an dünnen Tonschichten, die NH_3 oder H_2O 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 NH_3 angedeutete, Reihenfolge der Azidität auf der Tonoberfläche Al > Mg > Ca = Li > Na = K für Wyoming Bentonit und Al > Mg > Li > Ca = Na = K für Nontronit. Bei einer relativen Feuchtigkeit von 20% hingegen war die Reihenfolge Al = Mg > Ca > Li > Na > K für den Bentonit und Al = Mg > Li > Ca > Na > K für Nontronit. Die weitgehendste Veränderung in den Protonabgabeneigenschaften infolge von Hydratationswirkungen trat bei den Calciumtonen auf. Beim Ca-Bentonit betrug die NH_4^+ Bildung 16 me/100 g bei 98% gegenüber 80 me/100 g bei 20% relativer Feuchtigkeit. Beim Ca-Nontronit war die 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 Infratot Absorptionsspektren ersichtlich trat das durch den Protonisierungsprozess entstandene NH_4^+ im Bentonit und im Nontronit in voneinander verschiedenen Umgebungen auf.

Резюме—Исследование равновесия, предпринятое на глинистых пленках подвергнутых парам NH_3 и H_2O, 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 NH_3, был следующим: Al > Mg > Ca = Li > Na = K для виомингского бентонита и Al > Mg > Li > Ca = Na = K для нонтронита. Однако при относительной влажности 20%, порядок был Al = Mg > Ca > Li > Na > K для бентонита и Al = Mg > Li > Ca > Na > K для нонтронита. Наибольшее изменение в протодонорной способности пол воздействием гидратации произошло в кальциевых глинах. Для Ca-бентонита формирование NH составило 16 *мэ*/100 г при 98% и 80 *мэ*/100 г при 20% относительной влажности. В Ca-нонтроните, формирование NH составило 14 и 64 *мэ*/100 г для влажной и сухой системы соответственно. Разница между бентонитом и нонтронитом касательно протодонарной способности является вероятно сіедствием местоположения заряда и эффектом этого на ионную гидратацию. NH образованный процессом протонотации вероятно имеется в разных окружающих породах в бентоните и нонтроните, как это указывается в спектрах инфракрасного поглощения.

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