THERMAL STUDIES OF AMMONIUM FIXATION AND RELEASE IN CERTAIN CLAY MINERALS[1]

A. D. Scott, J. J. Hanway, and G. Stanford.[2]

Abstract

The thermal decomposition of NH_4 ions adsorbed on kaolinite, illite, bentonite and vermiculite occurred over a wide range in temperature. The temperature of decomposition appeared to be influenced by the nature of the exchange site and by the entrapment of NH_4 ions in the lattice. The H ions that remained when NH_4 ions were decomposed interfered with this method of determining the amount of NH_4 held on the different exchange sites or fixed in the lattice of the clay materials.

Wyoming bentonite fixed 15 m.e. of NH_4 per 100 grams when the NH_4 saturated clay material was heated at 300° to 350° C. The loss of NH_3 from these fixed NH_4 ions produced an exothermic peak at 550°C. in the differential thermal analysis curve for NH_4 bentonite.

The thermal decomposition of NH_4 saturated bentonite and a kaolinite clay has been investigated by Bottini (6, 7) and Cornet (9). They have shown that NH_3 is volatilized from these clays as the NH_4 ions are decomposed at high temperatures. Furthermore, from the relative rate of NH_3 loss at different temperatures, Cornet concluded that the site of the NH_4 ions on the clay determined the temperature at which they were decomposed. Working with NH_4 saturated bentonite, Cornet suggested that temperatures up to 125° C. decomposed NH_4 ions on the broken bond surfaces, while the rapid loss of NH_3 at 275° and 400 ° C. was due to NH_4 on exterior planar and interplanar surfaces, respectively.

In a study of vermiculite and its relation to biotite, Barshad (2) determined the weight loss due to NH_3 and water when NH_4 vermiculite was heated. Up to 255° C. the weight loss was due to water alone. Apparently the NH_4 ions on the vermiculite were not decomposed at this temperature. Between 255° and 500° C. a small amount of NH_3 was lost, whereas temperatures of 550° to 600° C. decomposed all of the NH_4 on the exchange.

It would appear from these investigations that NH_4 saturated clay minerals differ in the manner in which they lose NH_3 at elevated temperatures. Some of these differences are probably associated with the type of exchange sites holding the NH_4 ions on the clay. It is, however, also possible that differences arise because NH_4 ions are fixed in some clay minerals and not in others. The difference in thermal decomposition of NH_4 vermiculite and NH_4 bentonite, for instance, may be due to the fact that NH_4 ions are fixed in vermiculite but generally not in bentonite. If fixed

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[1] Journal Paper No. J-2867 of the Iowa Agricultural Experiment Station, Ames, Iowa. Project No. 1234, Department of Agronomy.

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NH_4 ions are decomposed at a characteristic temperature that is different from the exchangeable NH_4 ions, it is possible that thermal decomposition measurements could be used to determine fixed NH_4 in clays as well as to identify the presence of NH_4 fixing clay minerals. The objective of this study, therefore, was to determine whether a relationship existed between the thermal decomposition of adsorbed NH_4 and its fixation in clay minerals.

Differential thermal analyses are commonly used as one means of characterizing clay minerals. While each clay mineral group has in general a characteristic differential thermal curve, the individual curves obtained vary with the cation adsorbed on the clay. The differential thermal curves of NH_4 saturated clay minerals are of particular interest since the loss of NH_3 as well as water will influence the shape of the curve. It is evident from the differential thermal curves of vermiculite and bentonite obtained by Barshad (2, 3) that the effect of the adsorbed NH_4 varies with the clay mineral involved. Since these differences are probably related to the manner in which the clay minerals hold the NH_4 ions, differential thermal analyses were made in the present study to gain further information about the relationship between the thermal properties of adsorbed NH_4 and its fixation in the clay minerals. Differential thermal curves of the clays saturated with other ions were also obtained to further identify the clay minerals used in this study.

MATERIALS AND METHODS

Samples of the two vermiculites investigated by Allison, *et al.* (1) were obtained from Dr. F. E. Allison for this study. One vermiculite was from Libby, Montana; the other, from Greenville, South Carolina. According to Allison, *et al.*, both materials are actually vermiculite-biotite mixtures. Wyoming (Volclay) bentonite from the American Colloid Company and Goose Lake Grundite from the Illinois Clay Products Company were used as sources of montmorillonite and illite, respectively. Kaolinite of unknown origin was also used in this investigation.

The vermiculite flakes were about 0.25 inch in diameter. In some cases, therefore, the vermiculite was ground in a Christy-Norris Laboratory hammermill using a screen with round holes 1/16-inch in diameter. The other clay materials were used without previous fractionation except as noted in the individual experiments.

Fifty to 100 grams of the clay minerals was placed on a Buchner funnel and leached with 1000 ml. of 1 *N* NH_4Cl to saturate them with NH_4. They were washed with 70 per cent methanol until the leachate gave a negative test with Nessler reagent and then air dried. The dry NH_4 saturated clays were placed in a muffle furnace on a raised platform near the thermocouple to be heated at different temperatures and for varying lengths of time. The temperature fluctuated within plus or minus 20° C. of the desired temperature.

To determine the amount of exchangeable and fixed NH_4 on the clays, both before and after the heat treatment, the systems were made alkaline with NaOH or KOH and the NH_3 distilled into a measured amount of 0.05 *N* HCl. The excess acid was titrated with a standard NaOH solution. Blank controls were included in each set of distillations. The NH_4 on the clay mineral displaced by K will be regarded as exchangeable, while that displaced by Na but not by K will be regarded as fixed in this investigation. In some cases the total NH_4 in vermiculite was determined by first digesting the sample in concentrated H_2SO_4.

Differential thermal analyses were made with automatic recording equipment. The sample holders and covers were made of 18-8 chrome-nickel steel. Pt—Pt (10% Rh) thermocouples were used to measure the differential temperature. The furnace temperature was measured with a chromel-alumel thermocouple in the center of the sample block. Powdered alumina was used as the inert material. The temperature was increased at the rate of 10° C. per minute.

Time of Heating

A study was first made to determine how long the NH_4 clay minerals should be heated at any one temperature. There is no evidence in the literature to indicate the stability of the adsorbed NH_4 to prolonged heating. It was, therefore, entirely possible that all of the NH_4 could be decomposed even at a relatively low temperature if the NH_4 clay mineral were heated long enough.

To determine the effect of time of heating, one gram samples of NH_4 saturated vermiculite, bentonite and illite were heated at a few specified temperatures for different periods of time. The NH_4 remaining on the clay mineral after the heating period was determined by distillation in 200 ml. of 1 *N* NaOH for 1 hour. In some cases, duplicate samples were distilled in 200 ml. of 1 *N* KOH for 1 hour.

Bentonite. The NH_4 saturated bentonite contained 74 m.e. NH_4 per 100 grams prior to heating. All of this NH_4 was displaced by distillation in either NaOH or KOH. That is, there was no fixed NH_4 in the initial NH_4 bentonite.

The heated bentonite was distilled only in NaOH. In each case the NaOH displaced all of the NH_4 on the bentonite. The results shown in Fig. 1 therefore indicate the total amount of NH_4 remaining on the bentonite after it was heated at different temperatures for different periods of time. It is apparent from these results that there was a rapid initial loss of NH_3 at any one temperature followed by a slow but consistent loss as the heating period was extended.

Since NH_4 on the bentonite continues to be decomposed as the heating time is increased, it may be concluded that the fractions of NH_4 held on the different exchange sites cannot be sharply distinguished by this method. This does not preclude the possibility that the decomposition temperature of the NH_4 ions varies with the exchange site occupied. In fact, the temperature dependence of the rapid initial loss of NH_3 would suggest that the NH_4 ions on the bentonite do vary in their decomposition temperature. The difficulty in distinguishing between the different NH_4 exchange sites is probably due to the H ions that remain on the exchange sites when the NH_3 is driven off. These H ions may interchange with exchangeable NH_4 ions on other sites. By this process, NH_4 ions that would normally not be decomposed at the temperature employed may be transferred to sites where they can be decomposed. Thus, the process involved

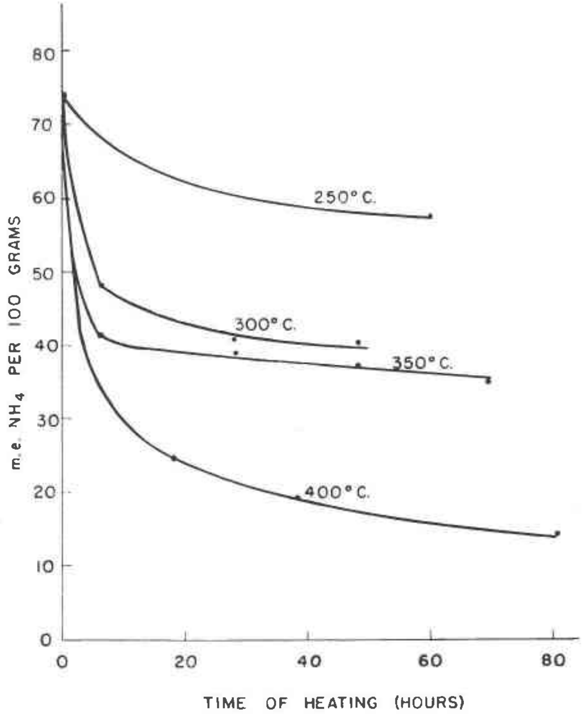

FIG. 1. NH_4 released from Wyoming bentonite by a one hour distillation in 200 ml. of 1 N NaOH after the NH_4 saturated bentonite has been heated at different temperatures for varying lengths of time.

in these prolonged heating experiments is probably not merely a volatilization of NH_3 from the NH_4 ions on certain exchange sites at a specific temperature but one of H—NH_4 exchange as well.

Evidence that H ions are left on the bentonite when NH_4 bentonite is heated was obtained by Cook (8), who prepared a H saturated bentonite by heating NH_4 bentonite at 450° C. for 48 hours. In the present study, the pH of the NH_4 bentonite was determined before and after heating at 400° C. for 24 hours. The pH determinations were made with a glass electrode and a 1:5 bentonite to water ratio. The pH of the unheated sample was 7.3 and of the heated sample was 4.0.

Vermiculite. Unground Montana vermiculite which had been exfoliated with H_2O_2 prior to NH_4 saturation was used in this experiment. The NH_4 saturated vermiculite contained 83 m.e. of NH_4 per 100 grams. Distillation for 1 hour in 200 ml. of 1 *N* NaOH released 69 m.e. of NH_4 per 100 grams, whereas a similar distillation with KOH released only 3 m.e. of NH_4 per 100 grams. Data reported elsewhere[3] show that a longer distillation with NaOH would release all of the NH_4 but the KOH would release no more if the time of distillation were increased. Thus, according to the procedure of Barshad (4), the vermiculite contained 80 m.e. of fixed NH_4 per 100 grams.

When the NH_4 vermiculite was heated at temperatures up to 400° C. and for as long as 80 hours, there was little or no loss of NH_3 as shown in Fig. 2. Apparently, temperatures greater than 400° C. are needed to decompose the NH_4 on vermiculite. These results, therefore, cannot be used to evaluate the effect of time of heating. That is, it is not known if there would be a gradual loss of NH_3 with time once the decomposition temperature of at least part of the adsorbed NH_4 is exceeded.

The results of this study do, however, show that the relative ease of NH_4 displacement by Na is influenced by the temperature at which the samples were previously heated. With temperatures up to 250°C. a one hour NaOH distillation continued to replace about 69 out of the 83 m.e. of NH_4 on the vermiculite. When the samples were heated at 300° or 350° C., however, more of the NH_4 on the vermiculite was displaced by NaOH. Although the vermiculite used in this experiment was exfoliated with H_2O_2 before it was NH_4 saturated, it exfoliated even more when it was heated at 300° C. or higher. The increase of NH_4 displacement by NaOH is, apparently, the result of this exfoliation. Since NH_4 was not lost at these temperatures (see the constancy of the total NH_4 values in Fig. 6 also) the exfoliation observed must have been due to the volatilization

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[3] Hanway, J. J., Scott, A. D., and Stanford, G., Replaceability of ammonium fixed in clay minerals as influenced by ammonium and potassium in the extracting solution. Submitted for publication.

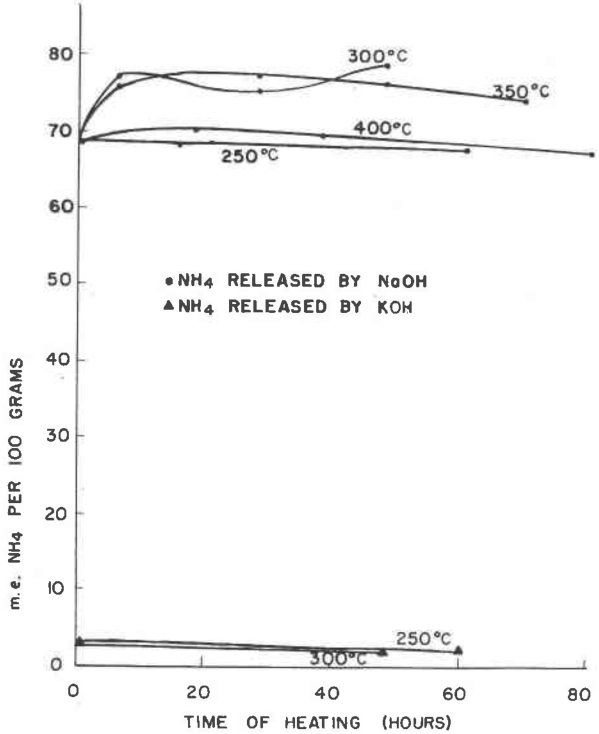

FIG. 2. NH_4 released from Montana vermiculite by a one hour distillation in 200 ml. of 1 *N* NaOH or KOH after the NH_4 saturated vermiculite has been heated at different temperatures for varying lengths of time.

and loss of water alone. It should be noted that the amount of NH_4 replaced by KOH distillation was not influenced by this exfoliation. That is, the NH_4 would still be considered as being fixed.

Samples heated at 400° C. did not release as much NH_4 to NaOH in one hour as those heated at 300° C. even though exfoliation occurred in both cases. As the heating temperature was increased from 350° C. to 400° C., it is possible that K was released from the biotite present in the sample. Kolterman and Truog (10) have shown that heating NH_4 biotite to 500° C. does release K. Such a release of K in the present study would account for the decrease in NH_4 displacement since Hanway, *et al.*[3] have shown that very small amounts of K interfere with the release of fixed NH_4 by NaOH. The fact that the samples heated at 400° C. released the same amount of NH_4 as those heated at 250° C. is probably coincidental.

Results from a similar experiment with unground South Carolina vermiculite are given in Fig. 3. This vermiculite sample was not exfoliated with H_2O_2. The results are quite similar to these obtained with the Montana vermiculite. In this case there is a more pronounced decrease in the NH_4 displaced by Na as the time of heating at 400° C. was increased. This decrease is probably not due to a loss of NH_3 since the total NH_4 data given in Fig. 7 shows that there is no loss of NH_3 after heating for 24 hours at 400° C. The decrease is more likely due to a gradual release of K from the biotite which renders the fixed NH_4 less and less easily replaced by Na.

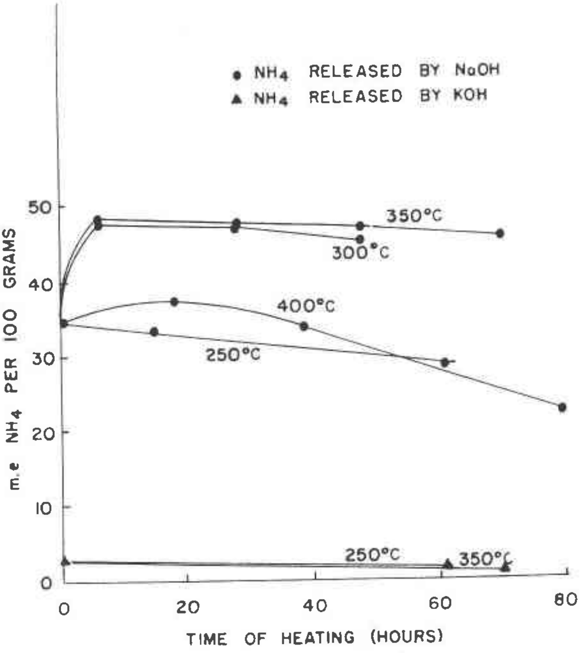

FIG. 3. NH_4 released from South Carolina vermiculite by a one hour distillation in 200 ml. of 1 *N* NaOH or KOH after the NH_4 saturated vermiculite has been heated at different temperatures for varying lengths of time.

Illite. Prior to heating, the NH_4 saturated illite used in this study contained 26 m.e. of adsorbed NH_4 per 100 grams which could be displaced by distillation in NaOH. Distillation in KOH displaced all but 1 m.e. of this adsorbed NH_4. The heated illite was distilled only in NaOH.

The effect of heating the NH_4 illite at different temperatures for varying lenths of time is shown in Fig. 4. These results are similar to those obtained with bentonite in that NH_3 was lost rapidly at first and then gradually as the heating time was extended. However, essentially all of the NH_4 on the illite was decomposed by heating at 300° C., while a considerable portion of the NH_4 remained on the bentonite even after prolonged heating at 400° C. This difference must be associated with the interlayer NH_4 ions that are present in the bentonite but not in the illite. It will be shown later that some of these interlayer NH_4 ions in bentonite are fixed when the clay mineral is heated to about 350° C. and that these fixed NH_4 ions in bentonite resist decomposition at temperatures below 400° C. There was little or no NH_4 fixation in the illite. It is, therefore, apparent from the illite results that prolonged heating at 300° C. will decompose most of the adsorbed NH_4 as long as it is exchangeable.

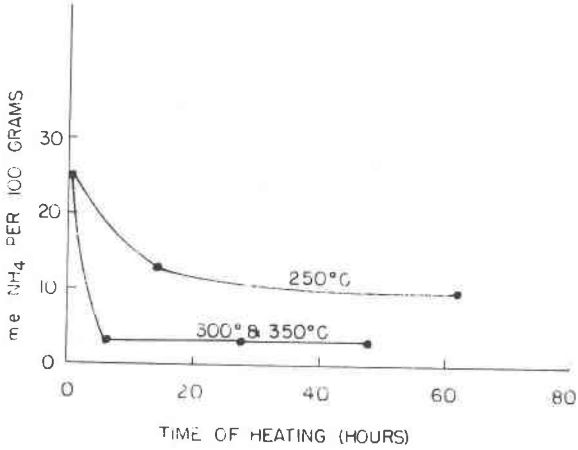

FIG. 4. NH_4 released from illite by a one hour distillation in 200 ml. of 1 *N* NaOH after the NH_4 saturated illite had been heated at different temperatures for varying lengths of time.

TEMPERATURE OF HEATING

To determine the relationship between the decomposition of NH_4 on various clay minerals and the temperature of heating, one or two gram samples of NH_4 saturated minerals were heated for 24 hours. This time of heating was selected because it was beyond the period in which the initial rapid loss of NH_3 occurred and should provide for reasonably reproducible results. The total NH_4 remaining on the clay minerals was determined by boiling a sample for 1 hour in concentrated H_2SO_4, making the digest alkaline with NaOH and distilling. NH_4 released by NaOH and KOH was determined by distilling a sample in 200 ml. of 1 *N* solutions of the hydroxides for one hour.

Bentonite. The amount of NH_4 released from the bentonite by NaOH distillation was the same in all cases as that released by the H_2SO_4 digestion; therefore, in Fig. 5 a curve for the release to NaOH is not given. The curve showing the total NH_4 retained by the bentonite at various temperatures is similar to those obtained by other workers (5, 6, 7). Little NH_3 was lost at temperatures up to 200° C. The loss of NH_3 increased rapidly as the temperature increased from 200° to 300° C. and again from 350° to 450° C. with a decreased rate of NH_3 loss as the temperature increased from 300° to 350° C. Very little NH_4 remained on the bentonite after heating at 500° C. for 24 hours.

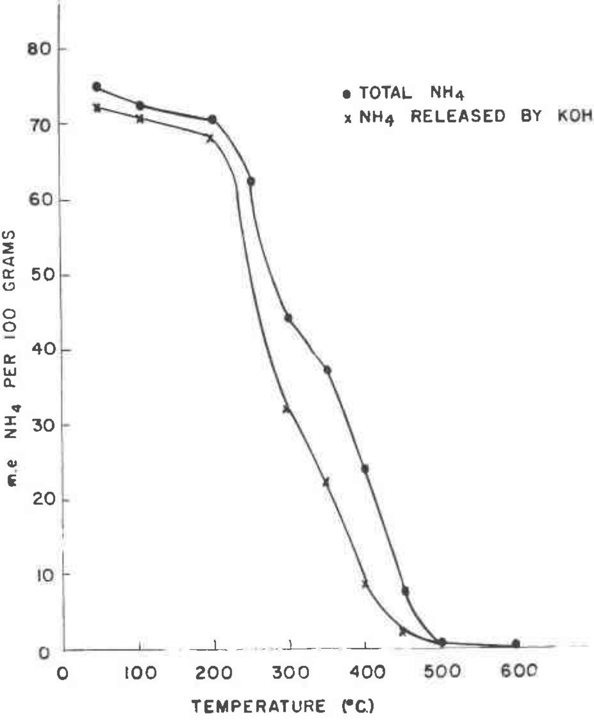

FIG. 5. Fixation and release of ammonium by Volclay bentonite as influenced by heating for 24 hours at different temperatures.

Barshad (3) has proposed that adsorbed NH_4 not replaced by distillation in KOH may be considered to be fixed. After heating at temperatures up to 200° C., KOH released all but 2 m.e. of the NH_4 on the bentonite. However, after heating at temperatures above this, and especially at temperatures from 300° to 400° C., a considerable portion of the NH_4 on the mineral was fixed; i.e., it was not replaced by KOH. As much as 15 m.e. of NH_4 per 100 grams was fixed at these higher temperatures.

Since the bentonite sample used in this study was not fractionated, the question arose as to whether the NH_4 fixation which occurred represented fixation by a normally expanding lattice mineral like montmorillonite or was due to the presence of a degraded micaceous mineral such as illite in the bentonite. In this case, since the essentially non-expanding micaceous materials would tend to exist in larger particle sizes, the $<.2$ micron fraction of the bentonite should be relatively free of these materials. A suspension of the Volclay bentonite, which is normally Na saturated, was therefore run through a Sharples super centrifuge to separate out some of the $<.2$ micron fraction. This fraction was NH_4 saturated by passing the suspension through an NH_4 saturated Amberlite IR-100 resin exchange column.

The NH_4 released by NaOH and KOH distillation from this NH_4 saturated $<.2$ micron fraction following different heating treatments is shown in Table 1. There was no fixed NH_4 in the unheated samples or in the sample dried at 110° C. However, just as in the original unfractionated bentonite sample, there was 15 m.e. of NH_4 per 100 grams fixed in the $<.2$ micron clay material after it was heated at 350° C. for 24 hours.

TABLE 1. EFFECT OF HEATING NH_4 SATURATED $<.2$ MICRON VOLCLAY BENTONITE ON NH_4 RELEASED BY DISTILLATION IN NaOH AND KOH SOLUTIONS

Heating temperature	Time of heating, hrs.	m.e. NH_4 released per 100 grams of bentonite by:		m.e. NH_4 fixed per 100 grams of bentonite (NaOH—KOH)
		NaOH	KOH	
Unheated	0	126	126	0
110° C.	24	118	118	0
350° C.	24	38.8	23.6	15.2

The distillation was continued for 4 hours to assure complete release of all the NH_4 that would be released, but very little was released after the first hour. It was observed that the NH_4 clay, after drying and heating at 350° C. consisted of large flakes. These flakes broke up and the clay was completely dispersed in the NaOH solution whereas the large flakes persisted in the KOH solution. These results suggest that NH_4 is fixed in montmorillonite at this higher temperature because the contracted lattice resists re-expansion by KOH.

Vermiculite. The vermiculites lost no NH_3 at temperatures up to 400° C. as shown in Figs. 6 and 7. At temperatures above 500° C. the Montana vermiculite lost large amounts of NH_3 but still retained 9 m.e. of NH_4 per 100 grams after heating at 600° C. for 24 hours. The South Carolina vermiculite started to lose NH_3 at a slightly lower temperature, and after heating at 550° C. it contained essentially no NH_4.

After heating at temperatures up to 250° C., NaOH distillation failed to replace 2 to 3 m.e. of the total NH_4 per 100 grams during a one-hour distillation. However, heating at 300° C. resulted in essentially complete release of the NH_4 by NaOH. As discussed earlier, the exfoliation of vermiculite at 300° C. definitely resulted in the NH_4 being more easily replaced by NaOH. After heating at temperatures greater than 400° C., a one hour distillation in NaOH failed to release considerable quantities of the NH_4 present. This reduction in the amount released by Na was probably due to a release of K at these high temperatures from the biotite present in the sample. This conclusion was substantiated by the observation that prolonged distillation, which has been shown to be effective when small amounts of K were present (10), resulted in complete release of the NH_4. Furthermore, removal of the potassium by precipitation resulted in a complete replacement of the NH_4 by Na in one hour.

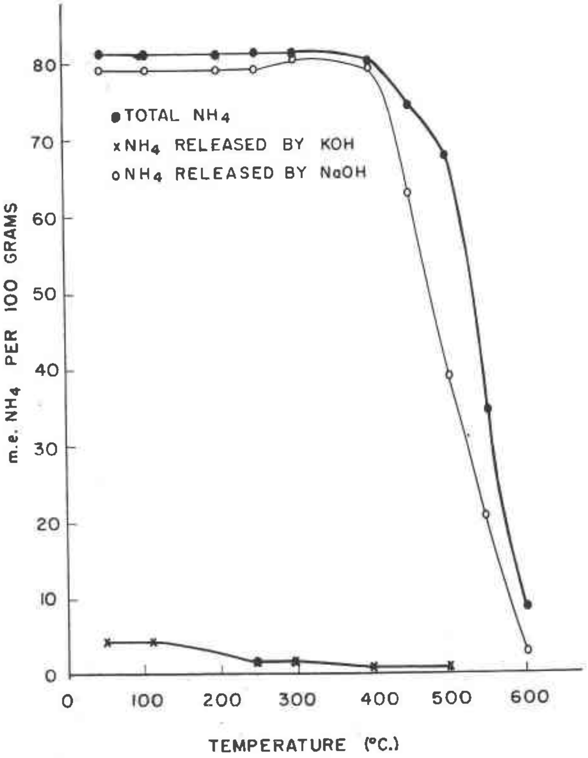

FIG. 6. Fixation and release of ammonium by Montana vermiculite as influenced by heating for 24 hours at different temperatures.

The KOH distillation removed very little NH_4 from the vermiculite, but it continued to release some NH_4 even when the samples were heated at 500° C. There was no increase in the release of NH_4 by KOH even though on heating at temperatures of 300° or above the vermiculite exfoliated, with an expansion of two to three times its orginal volume. This expansion of the lattice obviously did not make the NH_4 ions more easily replaced by K.

Illite. The NH_4 saturated illite used in this study released 20 m.e. of NH_4 when it was distilled in NaOH. When it was digested in concentrated H_2SO_4 for 1 hour and then distilled in NaOH it released a total of 24 m.e. of NH_4. The difference in NH_4 released is probably due to the presence of organic matter since the original untreated illite contained nitrogen equivalent to 4.7 m.e. of NH_4 per 100 grams as determined by Kjeldahl analysis. The NH_4 displaced by distillation in NaOH alone is probably a good measure of the NH_4 adsorbed on the illite. In any case, both the total NH_4 and NaOH released NH_4 values given in Fig. 8 show the same general change in the NH_4 retained at different temperatures. Up to 200° C., there was a slow but gradual loss of NH_3, a more rapid loss between 200° and 350° C., and by 400° C. essentially all of the NH_4 was decomposed.

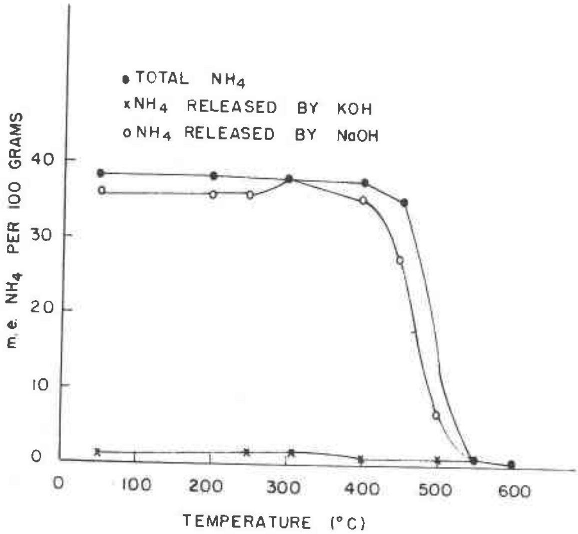

FIG. 7. Fixation and release of ammonium by South Carolina vermiculite as influenced by heating for 24 hours at different temperatures.

The amount of NH_4 released by KOH was consistently 1 to 2 m.e. per 100 grams less than that released by NaOH. Thus, there was little NH_4

fixed in this illite, and the amount fixed was not influenced by heating at higher temperatures. The relative absence of NH_4 fixation is probably due to the fact that the illite received no pretreatment, such as electrodialysis, that would remove fixed K. Thus, all positions capable of fixation were already occupied by K ions.

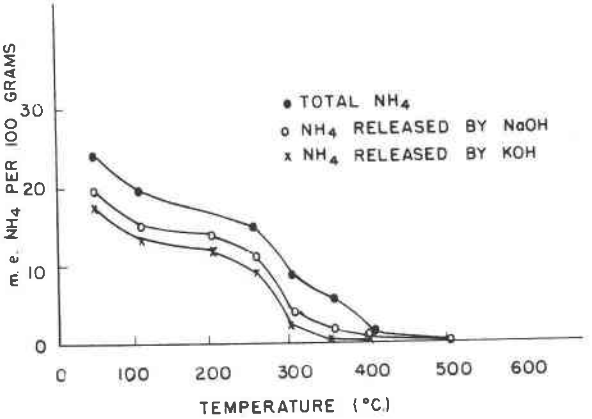

Fig. 8. Fixation and release of ammonium by illite as influenced by heating for 24 hours at different temperatures.

Kaolinite. The NH_4 saturated kaolinite contained 7.5 m.e. of NH_4 per 100 grams. NaOH distillation, KOH distillation and H_2SO_4 digestion prior to alkaline distillation all released the same amount of NH_4 from kaolinite. Therefore, only the total NH_4 values have been used in Fig. 9 to show the effect of heating NH_4 kaolinite. From these results, it appears that the NH_4 on kaolinite is gradually decomposed as the temperature is increased from 50° to 400° C.

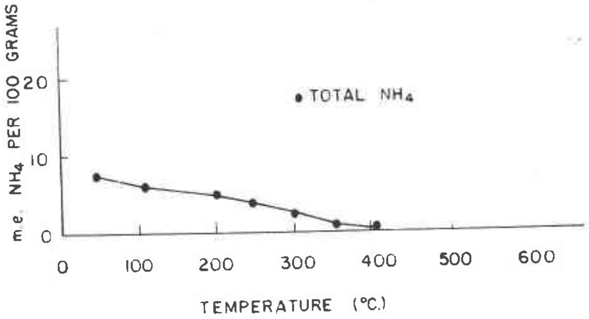

Fig. 9. Release of ammonium by kaolinite as influenced by heating for 24 hours at different temperatures.

Comparison of different minerals. The percentage of the total NH_4 lost by each of the minerals at different temperatures is given in Fig. 10. In general each of the minerals loses NH_3 over a wide range of temperatures. One of the biggest differences between minerals is that illite, kaolinite and bentonite begin to lose NH_3 at 100° C., while vermiculite loses little or no NH_3 until 400° C. Illite and kaolinite lose all of their NH_3 by 400° C.; thus their curves do not overlap the vermiculite curve. The NH_4 bentonite thermal decomposition curve, however, overlaps both the illite and vermiculite curves. These differences appear to be primarily determined by the presence of fixed NH_4.

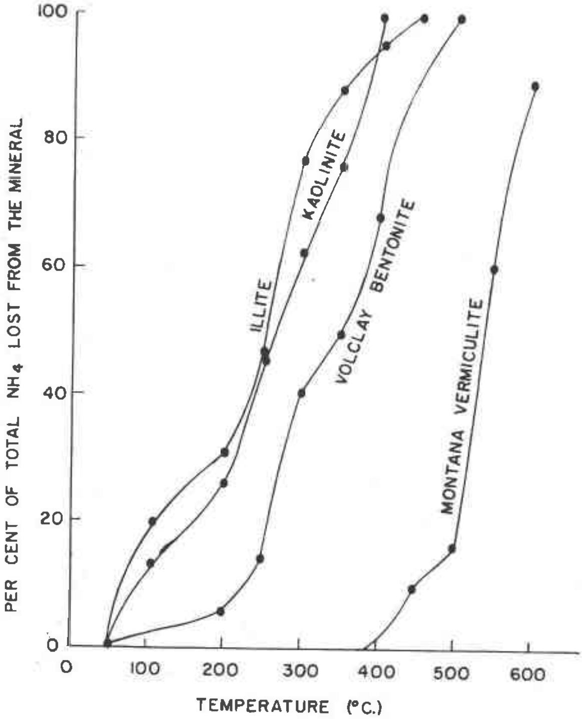

FIG. 10. Percentage of the total NH_4 lost from different minerals on heating for 24 hours at different temperatures.

Illite and kaolinite with NH_4 primarily on external surfaces and in an exchangeable location readily lose NH_3 by thermal decomposition. The illite curve conforms with the suggestion of Cornet (9) that NH_4 on broken bond surfaces is decomposed by 125° C., while the maximum evolution of NH_3 from exterior planar surfaces occurs at 275° C. The NH_4 on kaolinite, which is presumably all on broken bond surfaces, however, was not entirely decomposed by 125° C. Instead, there was a gradual loss of NH_3 up to 400° C. with only a slight indication of a decrease in slope of the curve between 100° and 200° C. It should also be noted that this kaolinite curve is very different from the curve Bottini (7) obtained with a kaolinite clay.

The inflections in the bentonite curve showing a more rapid loss of NH_3 at temperatures of about 275° C. and 400° C. are similar to those observed by Cornet (9). The inflection at 275° C. is probably associated with the loss of NH_3 from planar surfaces as Cornet has suggested, since illite also shows an inflection at this temperature. The results of this investigation, however, indicate that the fixation of NH_4 on bentonite caused the decrease in the slope of the total NH_4 curve between 300° and 350° C., which gave rise to another distinct inflection at 400° C. The exchangeable NH_4 ions, on the other hand, continued to decrease at a fairly constant rate over the temperature range of 300° to 400° C. It may be concluded that the interplanar exchangeable NH_4 ions on bentonite are not more resistant to thermal decomposition than the exterior planar ions. It is expected that in the absence of NH_4 fixation the curve for the decrease in total NH_4 on bentonite would be similar to that of illite. In fact, a plot of the decrease in exchangeable NH_4 only does show very little indication of separate inflections at 275° and 400° C.

It is apparent from Fig. 5 that the fixed NH_4 ions resisted thermal decomposition until the temperature exceeded 400° C. The NH_3 loss at higher temperatures was, however, partly due to exchangeable NH_4 ions. Since the exchangeable NH_4 ions were not entirely decomposed before the fixed NH_4 ions started to decompose, the fixed and exchangeable NH_4 on bentonite cannot be distinguished by this method. It is entirely possible that the observed exchangeable NH_4 at these higher temperatures become exchangeable because of a H displacement of the fixed NH_4 during the cooling period. This point is being investigated at the present time.

The NH_4 in vermiculite resists decomposition until 400° C. The high temperature of decomposition is probably due to the fact that essentially all of the NH_4 on vermiculite is fixed. A comparison of the vermiculite and bentonite curves shows that most of the fixed NH_4 in vermiculite required a higher temperature for decomposition than fixed NH_4 in bentonite. This observation is in line with the ease with which NH_4 is fixed in the two minerals. While vermiculite will fix NH_4 under moist conditions, NH_4 bentonite must be dehydrated at 300° to 350° C. before the lattice is sufficiently contracted to fix the NH_4.

In general it may be concluded from these results that NH_4 held on sites where it is fixed required a higher decomposition temperature than NH_4 ions on sites where they were not fixed. There was, however, no case where heating at one temperature resulted in the loss of NH_3 from the exchangeable NH_4 leaving just the fixed NH_4 on the clay. The temperature of decomposition, therefore, cannot be used to distinguish sharply between fixed and exchangeable NH_4.

DIFFERENTIAL THERMAL ANALYSIS

The differential thermal curves obtained for the various clay minerals are given in Figs. 11, 12, 13 and 14. The curves obtained with the natural material; that is, the first curve in each figure, are quite typical for the mineral concerned. It is apparent from Fig. 11 that adsorbed NH_4 had no effect on the kaolinite curve.

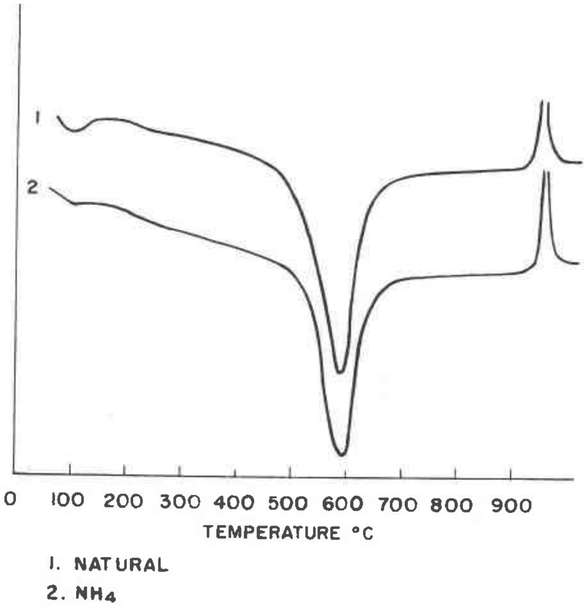

FIG. 11. Influence of adsorbed cation on the differential thermal curve for kaolinite.

The large ill-defined exothermic peak with a maximum at 400° C. in the illite curve, Fig. 12, is not usually observed. This peak is probably due to the presence of organic matter as indicated by the nitrogen content of the untreated illite. This exothermic peak detracts from the usefulness of the differential thermal curve in the thermal study of NH_4 on the clay. Curve 3 in Fig. 11 indicates that the NH_4 does influence the curve, either by its own decomposition, or by its effect on the impurity giving rise to the peak.

The curves for the natural (Na saturated) and K saturated bentonite in Fig. 13 are characteristic of those generally obtained for montmorillonite clay. The two endothermic troughs were not affected by any of the

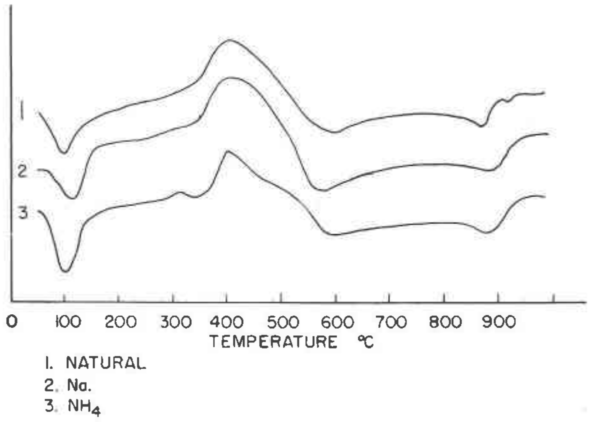

FIG. 12. Influence of adsorbed cation on the differential thermal curve for illite.

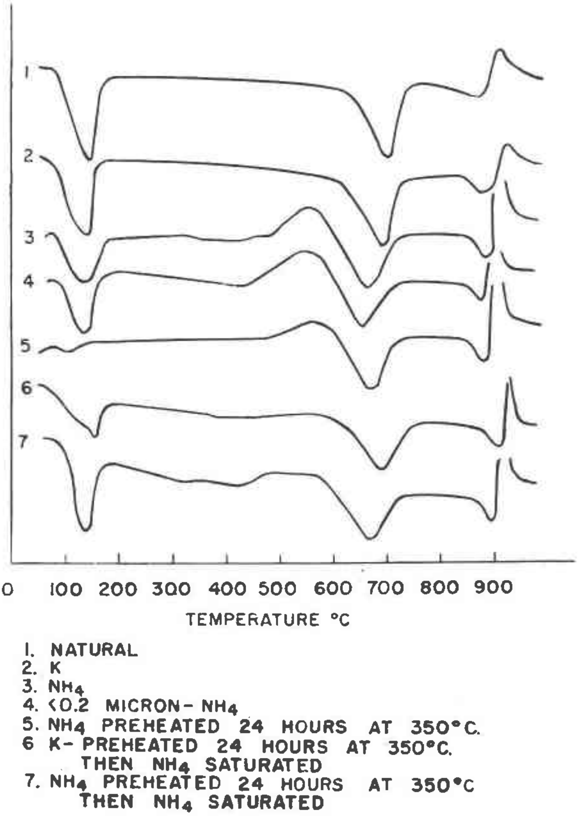

FIG. 13. Influence of adsorbed cation on the differential thermal curve for Wyoming (Volclay) bentonite.

other treatments except that shown by curve 5. In this case, the differential thermal analysis was made soon after the bentonite had been heated at 350° C. and the clay mineral apparently had not had time to become rehydrated. Since the bentonite was not protected from the atmosphere during the intervening period, it apparently does not exhibit the rapid rehydration Barshad (2) observed with vermiculite.

Saturating the bentonite with NH_4 resulted in the production of an exothermic peak at about 550° C. This was observed with both the unfractioned and the $<.2$ micron material. Curves obtained for an NH_4 saturated Mississippi bentonite were similar except that the exothermic peak occurred at 425° C. These results differ from those of Barshad (3) in that only one exothermic peak was found, whereas the NH_4 bentonites he studied showed two peaks, one at 360° C. and another at 470° C.

It is evident from curves 5, 6 and 7 that the NH_4 fixed in bentonite at 300° to 350° C. is responsible for the 550° C. exothermic peak in the differential thermal curve. The peak was still evident in curve 5 for NH_4 bentonite that had been previously heated at 350° C. for 24 hours even though the sample retained only 31 of the original 80 m.e. of NH_4 per 100 grams after the preheating. On the other hand, when a K saturated bentonite was heated at 350° C. for 24 hours and then leached with NH_4Cl to saturate the clay with NH_4, the differential thermal curve exhibited no exothermic peak. Preheating the K bentonite at 350° C. apparently fixed K ions in those sites capable of fixing NH_4 ions. As a result the 66 m.e. of NH_4 per 100 grams adsorbed by this sample of clay prior to the differential thermal analysis were exchangeable ions that were decomposed without influencing the differential thermal curve. Curve 7 was obtained with bentonite that had been previously heated at 350° C. for 24 hours to fix NH_4 ions and then saturated with NH_4. In this case the sample was found to contain 66 m.e. of exchangeable NH_4 per 100 grams.

The exothermic peak in the bentonite differential thermal curves occurred in all cases where fixed NH_4 was present. If the NH_4 ions were blocked from the fixing sites by prior fixation of K, the curve exhibited no exothermic effects from NH_4 ions on the bentonite. Apparently any exothermic effect due to the loss of NH_3 from the exchangeable NH_4 ions is counteracted by a concurrent loss of water. On the other hand, the fixed NH_4 ions are decomposed and NH_3 lost without a concurrent loss of water, since an exothermic peak occurs. This indicates that the exchangeable NH_4 ions in bentonite are closely associated with water molecules while the fixed NH_4 ions are not.

The differential thermal curves obtained for Montana vermiculite, Fig. 14, correspond with those obtained by Barshad (2). In the curve for the natural vermiculite there are low temperature endothermic troughs characteristic of Ca or Mg on the exchange complex. When the Ca and Mg were replaced by NH_4 ions, these low temperature troughs were eliminated. In this regard, vermiculite is different from bentonite which exhibits a low temperature endothermic trough even with NH_4 on the exchange complex. Apparently there is much more water associated with the exchangeable NH_4 ions in bentonite which gives rise to this endothermic effect as it is lost.

According to Barshad (2), each NH_4 ion in vermiculite is associated with one molecule of water. Furthermore, he has shown that the NH_3 lost from vermiculite by heating is accompanied by an equivalent loss of water. Any exothermic effects from the loss of NH_3 are apparently counteracted by the endothermic effect of the concurrent water loss since the NH_4 vermiculite differential thermal curve has the appearance of an anhydrous material.

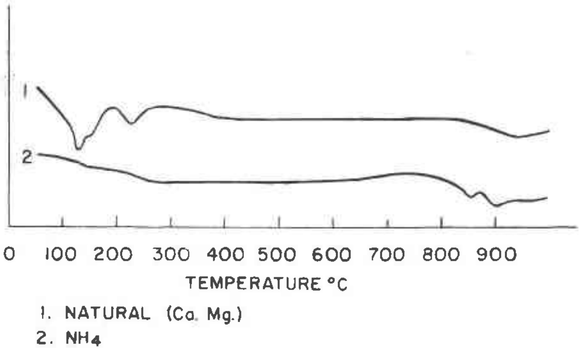

FIG. 14. Influence of adsorbed cation on the differential thermal curve for Montana vermiculite.

CONCLUSIONS

The NH_4 ions on the kaolinite and illite used in this study were largely exchangeable. These exchangeable NH_4 ions started to decompose at temperatures below 100° C. and were completely decomposed by heating for 24 hours at 400° C. On the other hand, fixed NH_4 ions on vermiculite were stable until nearly 400° C. and required 24 hours of heating at 600° C. to decompose them entirely. The thermal decomposition curve for the NH_4 ions on bentonite was unique because some of the NH_4 ions which were initially exchangeable were fixed when the clay was heated at 300° to 350° C. Like kaolinite and illite the exchangeable NH_4 ions on bentonite started to decompose below 100° C., and like vermiculite the fixed NH_4 did not decompose until the temperature exceeded 400° C.

From these results it may be concluded that fixed NH_4 ions are not as readily decomposed as the exchangeable ions.

The thermal decomposition curve for the NH_4 adsorbed on illite supports Cornet's (9) suggestion that the exchange site of the NH_4 ions influences the temperature at which they are decomposed. In the case of NH_4 bentonite, however, the two distinct inflections in the curve between 200° and 500° C. does not occur because of the decomposition of NH_4 ions on different exchange sites. Instead, the two inflections occur because there is a decrease in the amount of NH_3 lost as NH_4 ions are fixed in the bentonite when this clay material is heated at 300° to 350° C.

While the fixed NH_4 ions appears to resist thermal decomposition more than the exchangeable NH_4 ions, no sharp distinction could be made between the two forms by the method used. In bentonite, some exchangeable NH_4 remained on the clay up to 500° C. where the fixed NH_4 was also decomposed. Likewise, a sharp distinction between the fractions of exchangeable NH_4 ions held on different sites could not be made because there was a slow but consistent loss of NH_3 when NH_4 saturated illite or bentonite was heated at one temperature for an extended period of time. The difficulty in both cases was that H ions remained when the NH_4 ions were decomposed. By exchange these H ions caused NH_4 ions that were normally not decomposed at the temperature employed to be transferred to sites where they were decomposed.

An exothermic peak occurred at 550° C. in the differential thermal analysis curve for NH_4 bentonite. This peak was due to the loss of NH_3 from the NH_4 ions fixed in bentonite at 300° to 350° C. The fixed NH_4 ions in vermiculite on the other hand produced no exothermic effects. It is apparent that the fixed NH_4 ions in bentonite do not have water associated with them like they do in vermiculite.

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Manuscript received Dec. 23, 1955.