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DESORPTION OF AMMONIUM FROM
MONTMORILLONITE CLAY

BY

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DESORPTION OF AMMONIUM FROM MONTMORILLONITE CLAY

This thesis is approved as a creditable, independent investigation by a candidate for the degree, Master of Science, and acceptable as meeting the thesis requirements for this degree; but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

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INTRODUCTION

Clay minerals are secondary alumino-silicates, synthesized from colloidal silica and alumina. These oxides are products of weathering, separating from the crystalline structure of primary and secondary minerals.

The silica and alumina molecules are oriented in two-dimensional sheets of linked tetrahedrons and octahedrons, thus forming the basic framework of most clay minerals.

The classification of the clay minerals is based upon the structure of their crystals. The kaolinites consist of lattices formed by an alumina sheet and a silica sheet joined through common oxygen ions. The montmorillonitic and illitic clays have lattices composed of a sheet of alumina octahedrons between two layers of silica tetrahedrons. The lattices of montmorillonites will expand upon hydration, while the illitic minerals fail to expand because potassium ions perform a bridging action between lattices. The structure of the chlorites is characterized by the alternate stacking of 1 : 1 and 2 : 1 lattices. The chain-type clay minerale, of which attapulgite is a member, have a fibrous structure formed by double chains of linked silica tetrahedrons.

The clay minerals are extremely important constituents of the inorganic solid phase of the soil primarily because of their ability to adsorb cations. There are essentially two sources which develop the negative charges associated with most silicate clay particles. The exposed hydroxyl radicals along the broken edges of most minerals and the external surface of the alumina sheet of the kaolinitic clays supply a negative charge, since the hydrogen ion dissociates slightly and is readily exchangeable. Isomorphous substitution of a higher-valent cation by a lower-valent cation within the crystal lattice results in an unsatisfied negative valence. The total negative charge is satisfied with adsorbed cations. These cations are exchangeable with chemically equivalent cations in the solution which surrounds the particle.

The adsorbed cations are distributed around the clay particles in a diffuse layer, the nature of which for a given particle is determined by its surface charge density, the kind of adsorbed ion, the temperature and the concentration of electrolytes in the outer solution. The exchangeable ions are surrounded by water molecules and may thus be considered as forming an ionic swarm around the clay mineral particle. The concentration of the adsorbed ions is the greatest in the immediate vicinity of the surface and decreases at first rapidly and then asymptotically to the outer solution of uniform composition.

The montmorillonitic clay minerals have a relatively high capacity to adsorb cations resulting from many ionic substitutions within the crystal lattice and also because the lattices may expand upon hydration, thus opening the interplanar surfaces for cation adsorption. Upon dehydration of a clay system the individual lattices are drawn together, thus diminishing the area of oscillation of the adsorbed cations between the lattices.

Some clay minerals are capable of adsorbing certain cations so tenaciously, that these ions cannot be readily extracted with a neutral solution of a salt. Potassium and ammonium are nutrient cations that may suffer a decrease in their availability to plants by this phenomenon, which is commonly referred to as cation fixation.

This research was undertaken to study the behavior of ammonium ions adsorbed by montmorillonite as affected by heating at various temperatures and to test the hypothesis that ammonium ions are adsorbed with varying levels of energy, depending on the site of adsorption. It is postulated that the fixation of cations is dependent upon the site of adsorption alone, and that fixed cations can be identified by the significantly greater demand for the energy required for desorption of such ions.

REVIEW OF LITERATURE

The retention of certain cations by soils and clay minerals in such a manner that they are not readily exchangeable with other cations has been widely recognized and studied for many years. Such cations have been referred to as being difficultly exchangeable or "fixed". Kardos and Bear (13) have reviewed the subject of cation fixation quite thoroughly.

Ion fixation was first discovered relative to potassium and this ion has received the greatest attention until recently. Since the late 1940's, however, considerable work has been devoted to the behavior of ammonium ions with reference to fixation, particularly since ammonium is a very common constituent of nitrogen-carrying commercial fertilizers.

In 1917, McBeth (14) reported that no more than 81 per cent of the quantity of ammonium salt added to a California soil could be recovered after prolonged extraction with 10 per cent hydrochloric acid. Chaminade and Drouneau (9) noticed incomplete recovery of ammonia in soils and the liberation of this apparently fixed ammonium after grinding the soil in a ball mill. They attributed this phenomenon to the movement of ammonium into the interior of the crystalline soil particles.

Research done during the past fifteen years by Allison, Barshad, Bower, Hanway, Stanford and others has pointed out that fixation of ammonium varies widely for different clay minerals and for different soils. Illite, vermiculite and montmorillonite are the clay minerals capable of fixing ammonium. Soils containing these minerals are reported to fix from .5 to 8 milliequivalents of ammonium per 100 grams (1).

Subsoils can usually fix more ammonium than surface soils. Allison et al. (5) suggested that the low values for fixation in the surface layer were due to the fact that the fixation capacity of the surface soil had been satisfied by potassium, by organic matter and by naturally occurring fixed ammonium. Hanway et al. (12) found that potassium may prevent the entrance of ammonium into the clay lattice and vice versa. Organic compounds, as proteins and soil humus, are known to form complexes with clay minerals and therefore may limit the fixation capacity of these minerals. About five per cent of the total nitrogen in the surface soil and up to 60 per cent of the total nitrogen in the subsoil has been reported to be naturally occurring fixed ammonium (18).

The mineral illite, a 2 : 1 lattice type mineral, fixes about one milliequivalent of ammonium per 100 grams in the unweathered state (3). After weathering and removal of part of the potassium from the interplanar positions the ammonium fixation capacity of illite increases considerably, particularly upon drying or heating.

Vermiculite fixes potassium and ammonium under moist conditions (4). When immersed in water, vermiculite saturated with potassium and ammonium shows no hydration in its X-ray diffraction pattern (6).

Montmorillonitic clays are reported to fix about the equivalent of 10 per cent of their cation exchange capacity, when heated to 100° C. (3). Stanford and Pierre (17) have demonstrated that the sum of fixation of potassium and ammonium for a particular soil is constant and therefore the mechanism of fixation for both ions must be identical.

Truog and Jones (19) suggested that potassium becomes fixed between the sheets of montmorillonite upon drying and prevents re-swelling of the clay mineral. They theorized that fixation should cause a corresponding reduction in exchange capacity, which they found to occur. They pointed out that it was not clear why the complex could not be entirely loaded with fixed potassium and thus completely destroy the exchange capacity. This would not be expected to be possible, since considerable cation exchange occurs on the broken edges and exterior faces of the crystals, which cations should not become fixed upon drying. These investigators tested calcium, magnesium and sodium for fixation and found them to be but little affected. Their final conclusions were that the potassium ions were larger and probably more easily trapped, but that the mechanism remained to be determined.

Page and Baver (15) tested the hypothesis that potassium fixation caused by drying should be related to the size of the potassium ion and the contraction of the expansible lattice of montmorillonitic clay minerals. Their theory linked the diameter of the dehydrated potassium ion, 2.66 Angstrom units, (A), with the size of the empty cavity in the center of the oxygen hexagonals at the exposed surface of the silica tetrahedral layers, which is 2.80 A. As dehydration of the potassium system progressed, it appeared probable that the contracting sheets might force the ion into the hexagonal cavity on the interplanar surface. Their reasons for claiming this mechanism to cause potassium ions to be held very tenaciously are the closer proximity of the ion to the origin of the negative charge within the crystal lattice, the prevention of re-expansion of the sheets by their close contact, and the diminished area of oscillation of the potassium ion trapped within the oxygen layer.

Wear and White (20) noted that there existed a direct relationship between the total quantity of potassium in the crystal structure of montmorillonite after fixation and the amount of tetrahedral substitution of a trivalent cation for quadrivalent silicon. They proposed a mechanism of fixation within a mineral of expanding lattice according to which after rehydration some of the layers remain contracted while the remainder re-expand. The relatively great resistance of contracted potassium-saturated 2 : 1 type lattices against re-expansion and potassium replacement results from a combination of two factors: the agreement between the diameter of the potassium ion and that of the cavity in the oxygen hexagonal space and the lack of hydration of potassium ions and the interlayer surfaces when potassium-saturated. Thermal decomposition studies of ammonium clays by Scott et al. (16) indicate that "the interplaner exchangeable ammonium ions in montmorillonite are not more resistant to thermal decomposition than the ions adsorbed at the exterior positions of the mineral lattice." They stated that thermal decomposition of ammonium-clays cannot be used as a method to determine the ammonium-fixing capacity of the clay minerals, because they were able to distinguish no sharp point of differentiation between the desorption of exchangeable and of fixed ammonium ions. They concluded, however, that ammonium ions held on sites where it is fixed required a higher decomposition temperature than ammonium ions held on sites where they were not fixed. These researchers found that bentonite clay "fixed" considerable ammonium when heated at 300° to 350° C.

EXPERIMENTAL PROCEDURE

The clay minerals used in this study were obtained from Ward's Natural Science Establishment, Rochester, New York. The kaolinite standard was labeled: Kaolinite No. 2, Birch Pit, Macon, Georgia. The montmorillonite standard was labeled: Montmorillonite No. 19, Polkville Mine (Bentonite), Polkville, Mississippi.

The minerals were ground in an agate mortar and passed through a 300 mesh screen to insure homogeniety of samples. The exchange capacities of the clays were saturated with NH_4^+ by soaking the finely ground minerals overnight in 1 N NH_4Cl, having a pH adjusted to 7.0, followed by three additional washes with 1 N NH_4Cl.

The NH_4^+-saturated clays were washed with 95 per cent alcohol to leach out all soluble NH_4^+, until the leachate showed a negative test with Nessler reagent. The clays were air-dried and stored in covered petri dishes.

To measure the quantity of adsorbed ammonium decomposed by heat, air-dry samples weighing .5000 grams were placed in porcelain boats, designed for use in an organic carbon combustion train (Figure 1). An additional variable rheostat was wired in series with the existing rheostat, controlling the heat produced by the 12 inch-long, 760 watt unit, to obtain accurate divisions of temperature within the muffle. The porcelain boat with sample was placed inside the pyrex tube in the center of the heating unit and a thermometer was inserted.

Before subjecting the sample to heat, helium gas was allowed to flow through the tube for five minutes to drive off other gases that may

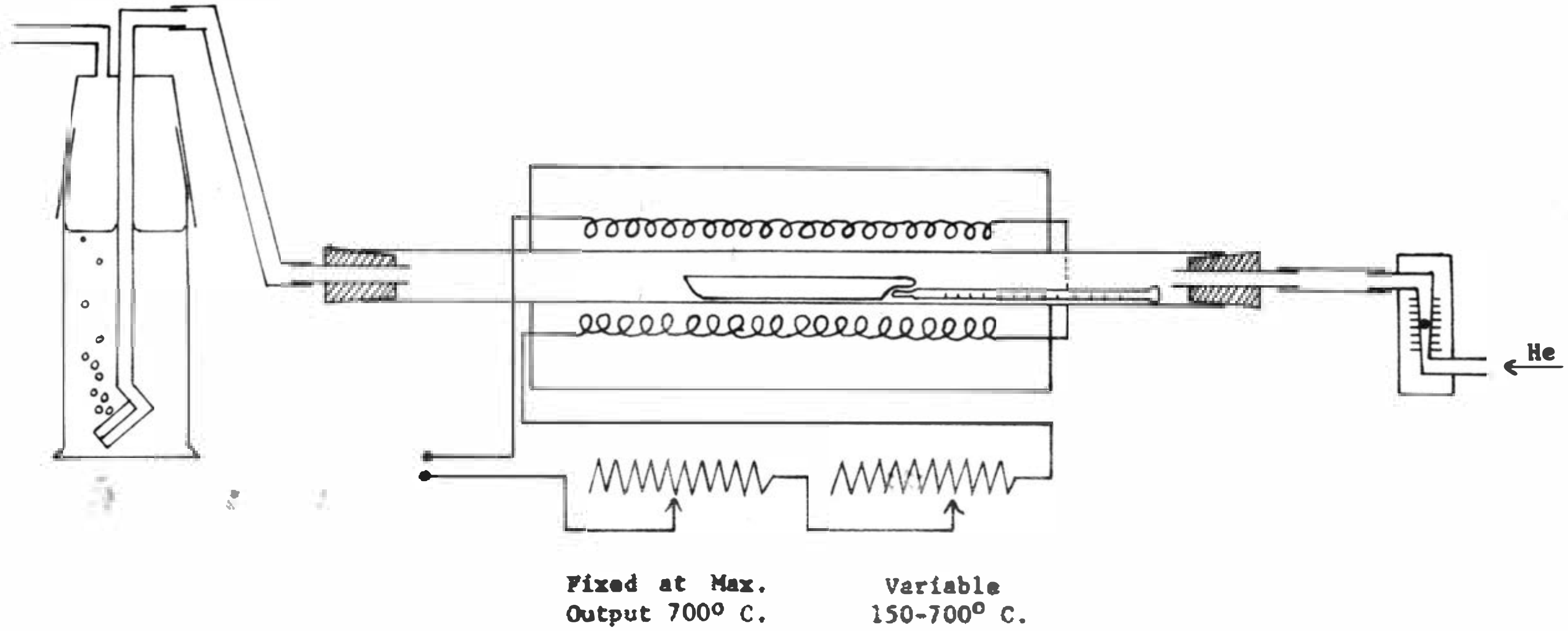

Figure I. Diagrammatic Cross-section of Experimental Equipment reduce or oxidize NH_3. The gas mixture was then bubbled through 75 ml of .01 N H_2SO_4 at the rate of about 10 liters per hour as the clay was subjected to certain temperatures ranging from 150° C. to 675° C. The time of heating at any one temperature was set at five hours. Each determination of decomposed NH_4^+ at each of the temperatures tested was done with a new sample.

The quantity of ammonia, driven off from the clay minerals and trapped in .01 N H_2SO_4, was measured colorimetrically. The color was developed with Nessler reagent, which was prepared as described by Yuen and Pollard (21). The transmittance of light was measured with an Evelyn colorimeter, using a 420 mu filter. A standard curve was made, employing a NH_4Cl stock solution containing 1 me NH_4^+ per liter. Aliquots of this standard were placed in 100 ml volumetric flasks, 2 ml of a 10 per cent potassium-sodium tartrate solution were added and 4 ml of Nessler reagent were used to develop the color. The flasks were brought to volume with .01 N H_2SO_4 and contained from .03 to .3 me NH_4^+ per liter.

The residues of the montmorillonite and kaolinite clay samples heated at each one of the temperatures, were transferred into centrifuge tubes and leached with three 25 ml aliquots of 1 N KCl (pH=7.0) and .01 N H_2SO_4, respectively by shaking for 15 minutes on a reciprocal shaker, centrifuging and decanting of the supernatant liquid. The leachates were stored in 100 ml flasks, which were made up to volume with 1 N KCl. Ammonium present in the leachates was measured as described above.

The residues of a second set of montmorillonite samples heated at each one of the temperatures, were transferred into distillation flasks designed for use with a Parnas-Wagner steam distillation unit. Ten ml of 10 N NaOH were added to the sample. The time of distillation was 5 minutes and the ammonium was distilled into 50 ml of .01 N H_2SO_4. The distillate was transferred to 100 ml volumetric flasks and made to volume with .01 N H_2SO_4. The NH_4^+ in the distillate was measured colorimetrically as described above.

RESULTS AND DISCUSSION

Ammonium-kaolinite and ammonium-montmorillonite were used in this study to determine the effects of supplying energy in the form of heat to these systems. Scott et al. (16) approached this problem by heating ammonium-saturated clays in a muffle furnace and analyzing the mineral residues for ammonium-nitrogen which was left after the decomposition process. They assumed that the NH_4 ions released at any given temperature decomposed into NH_3 molecules and H ions, the latter remaining near the colloidal surface to satisfy the exchange capacity. An electrical imbalance would be imposed on the system if this were not the case.

The kaolinite clay, incapable of fixing NH_4 ions because of its crystalline structure (3), was used to test the assumption that adsorbed NH_4^+ can be removed entirely from an ammonium-clay system by heating and that these escaping ions decompose into free NH_3 and H ions. To exclude the possibility of reduction or oxidation of NH_3 molecules by heat in the presence of H_2 or O_2, the experimentation was carried on in a H_2- and O_2-void system through replacement of these and other foreign gases by helium.

The mineral residues, after heating at the various temperatures, were leached with .01 <u>N</u> H_2SO_4 to remove the remaining NH_4 ions, which were measured quantitatively with the colorimetric technique, employing Nessler reagent to develop the color. The Nessler reagent is a chromogen specific for the NH_4 ion. The results of the ammonium-kaolinite decomposition and the subsequent treatment of the residues are presented in Table I.

TABLE I. NH_4^+ RELEASED FROM KAOLINITE AT VARIOUS TEMPERATURES BY DIFFERENT PROCEDURES

Temperature, ° C.	NH_4^+, me/100 g. Kaolinite		
	by Heat	by .01 N H_2SO_4	Total
22	--	9.70	9.70
200	3.66	6.20	9.86
300	5.79	3.84	9.63
400	8.00	1.92	9.92
500	8.80	.75	9.55
600	9.62	.00	9.62

The quantitative determination of expelled NH_3, absorbed in .01 N H_2SO_4 was also done colorimetrically. When the temperature of heating was 600° C., the release of adsorbed NH_4^+ from kaolinite was complete, corresponding with the quantity of ammonium recovered by leaching with .01 N H_2SO_4 of an unheated sample. This experiment showed that complete decomposition of adsorbed NH_4^+ by heat is possible and that all decomposed ammonium-nitrogen may be recovered as NH_3.

To eliminate the time of heating at any one temperature as a variable in the quantitative analyses of decomposed NH_4^+ from an ammonium-clay, NH_4^+-kaolinite and NH_4^+-montmorillonite samples were subjected to heating at 200° and 300° C. for periods of 5 hours and 10 hours. The results of their thermal decomposition are reported in Tables II and III, respectively.

The results show that heating for 5 hours or for 10 hours did not

TABLE II. NH_4^+ RELEASED FROM KAOLINITE BY HEAT AS INFLUENCED BY TEMPERATURE AND DURATION OF HEATING

Temperature, ° C.	NH_4^+, me/100 g. Kaolinite	
	5 Hours Heating	10 Hours Heating
200	3.66	3.76
300	5.79	5.79

TABLE III. NH_4^+ RELEASED FROM MONTMORILLONITE BY HEAT AS INFLUENCED BY TEMPERATURE AND DURATION OF HEATING

Temperature, ° C.	NH_4^+, me/100 g. Montmorillonite	
	5 Hours Heating	10 Hours Heating
200	8.3	8.5
300	47.4	48.0

significantly alter the amount of ammonium decomposed at either of the two temperatures for both clay minerals. Accordingly, all subsequent thermal decomposition studies were carried on by applying the desired heat for a five hour period.

Samples of NH_4-montmorillonite were subjected to thermal decomposition at different temperatures. One set of clay mineral residues, decomposed at the various temperatures for a five hour period, was leached with 1 <u>N</u> KCl according to standard procedures to extract the K^+-exchangeable NH_4^+ remaining after heating. A similar set of residues was subjected to NaOH distillation to recover all NH_4^+ remaining after heat treatment. The quantities of NH_4^+ decomposed by heat and displaced by KCl leaching and alkaline distillation are presented in Table IV.

TABLE IV. NH_4^+ DECOMPOSED FROM MONTMORILLONITE BY HEATING AT VARIOUS TEMPERATURES AND SUBSEQUENTLY DISPLACED BY POTASSIUM OR SODIUM

Temperature, ° C.	NH_4^+ in me/100 g. Montmorillonite		
	by Heat	by 1 N KCl	by NaOH Distillation
22	--	110.0	107.0
150	2.9	98.0	99.0
200	8.3	95.0	97.0
250	20.4	79.0	85.0
300	47.4	37.6	54.5
350	62.0	7.9	43.0
400	81.0	1.4	20.5
450	97.5	.0	10.6
520	104.0	.0	4.0
580	108.0	.0	1.0
675	110.0	.0	.0

From the data it is evident that the amount of KCl-extractable ammonium diminishes sharply between the temperature range of 250° and 350° C. To demonstrate the effect of heating on the apparent "fixation" of NH_4^+ in montmorillonite, the amounts of NH_4^+ released by KCl extraction were determined. These were then graphically superimposed in Figure 2 on the amounts of NH_4^+ decomposed by heat for all temperatures tested. The maximum amount of NH_4^+ retained by montmorillonite after the KCl treatment occurred when a sample had been heated at 350° C., and represented 41 me NH_4^+ per 100 g. montmorillonite or 37.3 per cent of the total exchange capacity. This portion of the total NH_4^+ was recovered however, when the heat-treated residues were distilled with NaOH, as illustrated in Figure 3, where the amounts of NH_4^+ removed by alkaline distillation are graphically superimposed on the amounts of NH_4^+ released by heating for all temperatures tested.

According to differential thermal curves of montmorillonite clays, endothermic maxima occur at temperatures ranging from 150° to 200° C. and from 500° to 800° C. (10). At the low range of temperatures the peaks in the curve are attributed to the energy required to remove the interlayer water between the silica sheets. The shallower inflections at the higher range are caused by the loss of OH lattice water. The temperatures at which either of these water losses occur are somewhat dependent on the type of cation adsorbed on the mineral.

The NH_4^+ desorption at 150° to 200° C. is very small, as indicated by the data presented in Table IV. Apparently the adsorbed NH_4 ions are also gradually losing their water of hydration, thus reducing their effective radius. The diffuse layer of NH_4 ions surrounding the mineral lattice thus decreases in thickness, moving the NH_4 ions closer to the source of the negative valency. These ions will be held with a greater attractive force and therefore will not be decomposed or replaced as readily as would be expected under normal desorption conditions.

To implement this theory, the NH_4^+ release curve at the various temperatures is presented in Figure 4, where $\frac{1}{T}$ is plotted along the

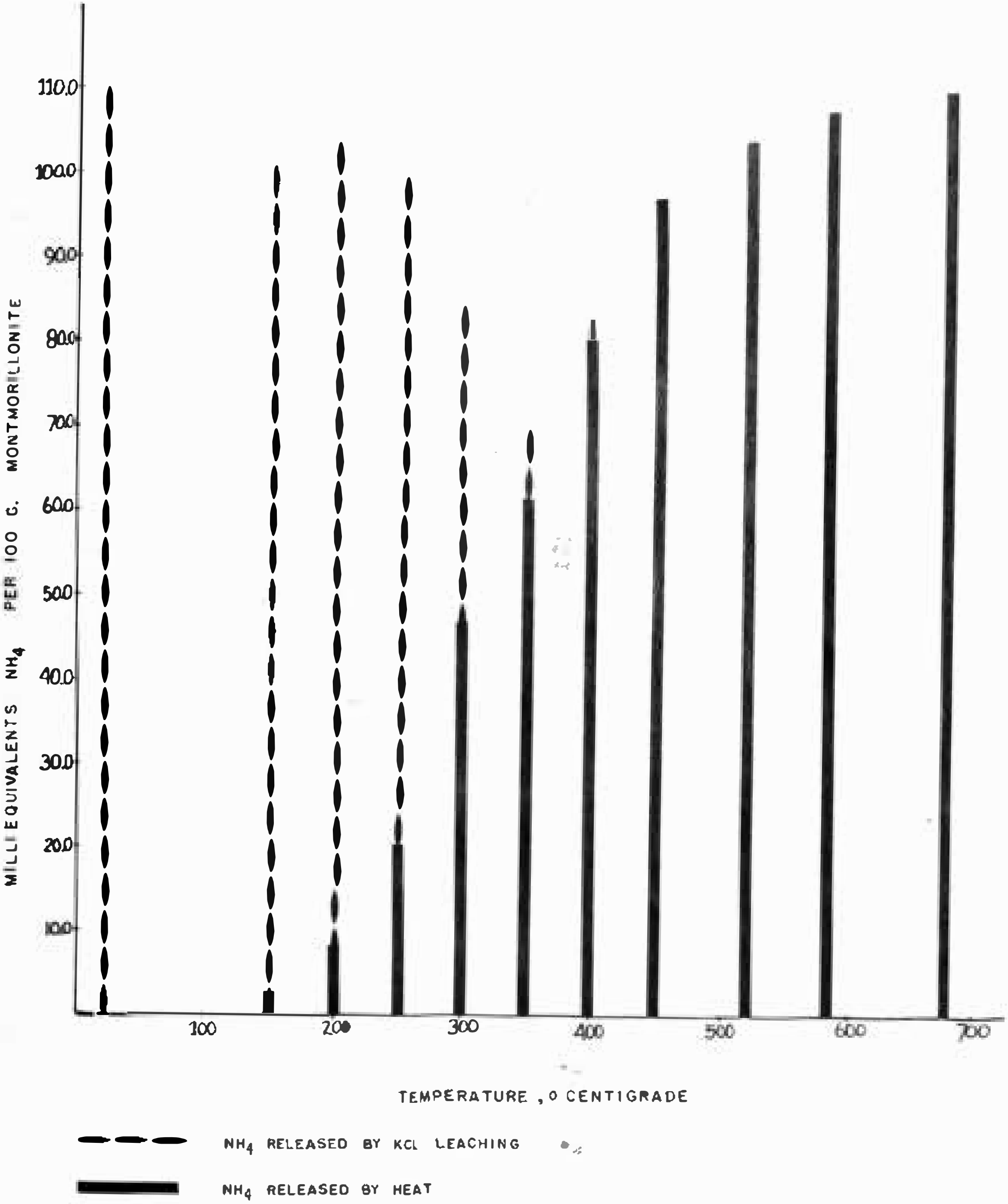

Figure 2. Ammonium Released from Montmorillonite by Heating at Different Temperatures and by Subsequent KCl Leaching

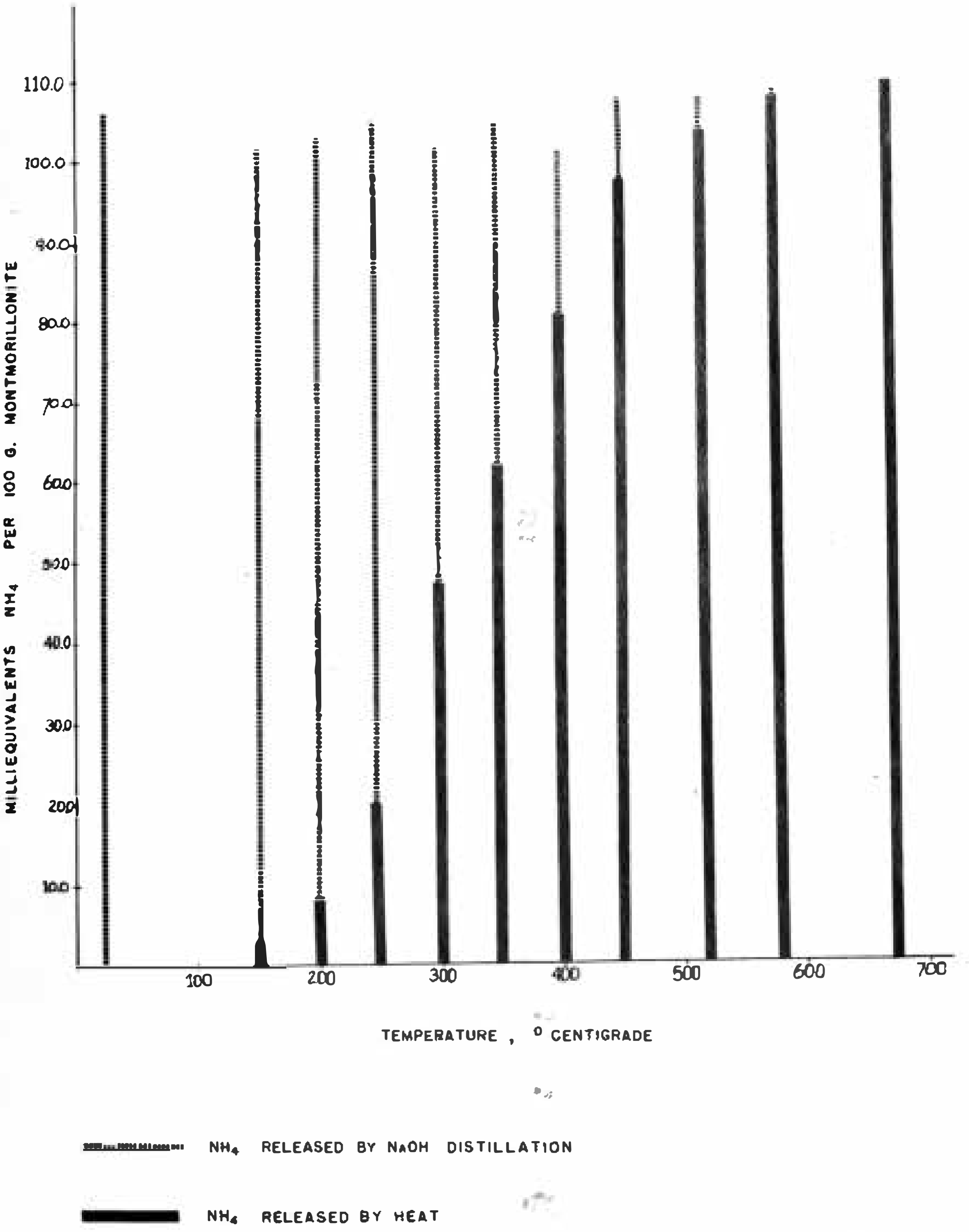

Figure 3. Ammonium Released from Montmorillonite by Heating at Different Temperatures and by Subsequent NaOH Distillation

x-axis and the logarithm of the milliequivalents NH_4^+ per 100 g. montmorillonite released at the various temperatures is plotted on the y-axis. According to the Gouy theory of the distribution of adsorbed ions in a diffuse layer around a clay micelle, the change in concentration of these ions follows Boltzmann's distribution law,

$$n = n_o^{-\frac{k\,e}{T}} \qquad (1)$$

where n means the number of NH_4 ions per unit volume at an arbitrary point in the diffuse layers, n_o is the total number of ions in the diffuse layer, e equals the potential of the ions at this point, T stands for the absolute temperature and k is a constant, incorporating the valence of the ion, the charge of the proton and the Boltzmann constant.

Rearranging equation (1) will give:

$$\log \frac{n}{n_o} = -\frac{k'e}{T}$$

When plotting the quantity of NH_4 ions decomposed by heat per 100 g. montmorillonite on a logarithmic scale against $\frac{1}{T}$, the relationship should show the energy levels at which the NH_4 ions are held at the different temperatures. In an ideal case where the distribution of ions in the diffuse layer follows Boltzmann's law, this relationship will be a linear function where the slope of the line is indicative of the rate of NH_4^+ desorption with reference to temperature. The dotted line i in Figure 4 represents the ideal desorption curve. It is assumed that under ideal circumstances the NH_4^+-montmorillonite system is at equilibrium at room temperature (22° C.). Therefore, line i intercepts the x-axis at T = 295° C.

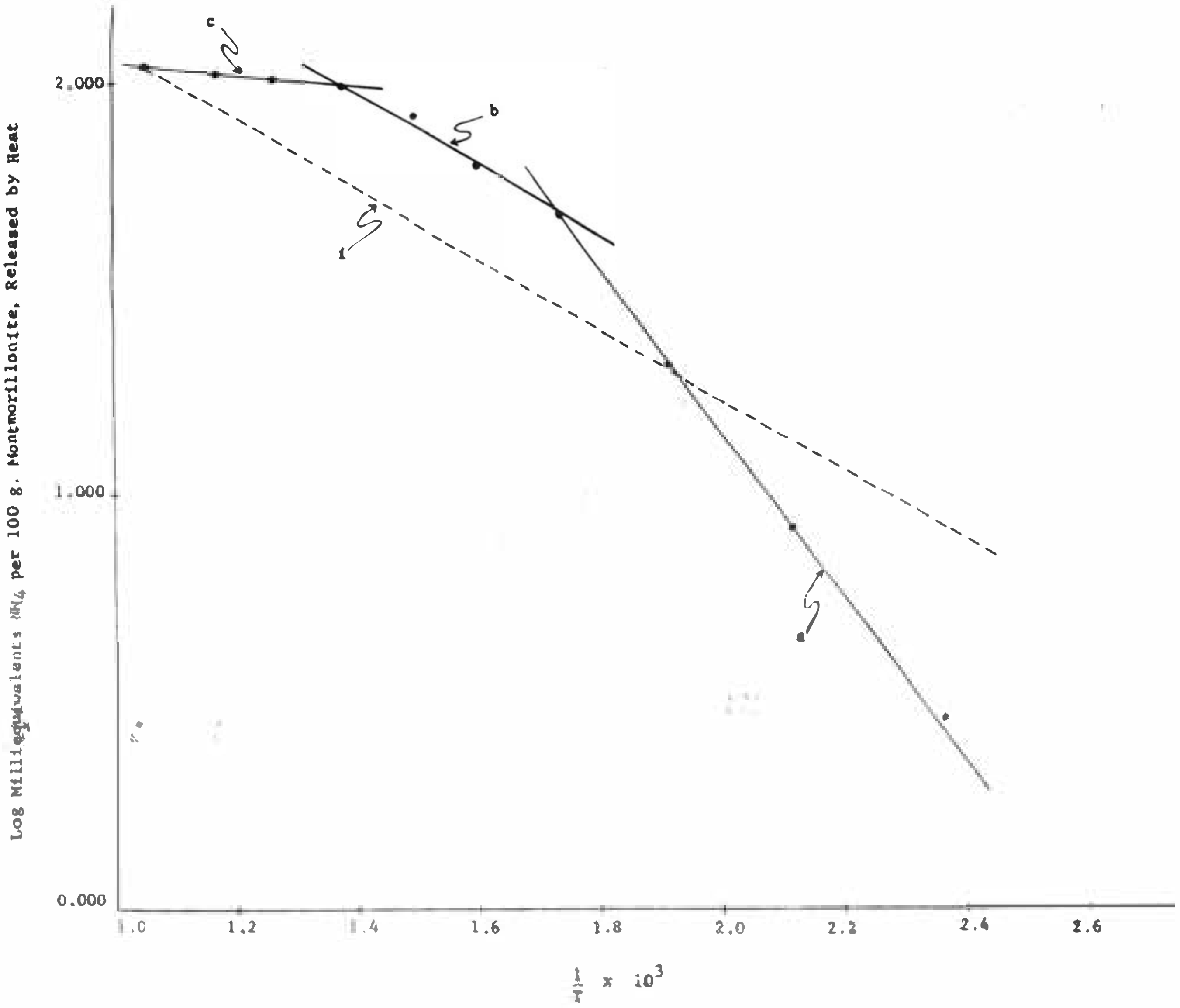

Figure 4. Theoretical and Thermal Experimental Ammonium Desorption Curve for Montmorillonite

The actual quantity of ions released at 150° to 200° C. is considerably smaller than suggested by the ideal release curve, which is probably due to the additional attractive force supplied to these ions upon desiccation and subsequent reduced thickness of the ionic layer around the particles. At these lower temperatures the rate of decomposition of NH_4 ions is much greater than the rate of ideal desorption, because the concentration of ions held at these lower energy levels is comparatively large. Therefore, when the temperature of heating exceeds 250° C. and line g, representing the first section of the NH_4^+-montmorillonite desorption curve, intercepts line i the amount of NH_4 ions decomposed is larger than predicted for the ideal case. This first section of the release curve represents about 20 me NH_4^+ per 100 g. montmorillonite.

At 300° C. the slope of the NH_4^+ decomposition curve changes and becomes parallel to the ideal curve. This suggests that the rate of NH_4^+ release between 300° and 450° C. is similar to the rate expected under ideal conditions. It may be assumed that the desorption of NH_4^+ from an ammonium-montmorillonite through this temperature range is identical to the theoretical release for the energy supplied to the system and that no restriction in release of NH_4 ions is offered, either of electrostatic or mechanical nature. Figure 2 indicated that 41 me NH_4^+ per 100 g. montmorillonite were not exchangeable with a 1 N solution of KCl after heating the sample at 350° C. The observations of this research suggest that just a small portion of the non-exchangeable NH_4 ions is actually fixed, since the desorption curve shows that the NH_4^+ ions are released at a normal rate when the clay sample is heated at 350° C. and no additional increments of energy are required to remove most of the non-exchangeable

NH_4^+. The portion of the NH_4^+ desorption curve where the rate of NH_4^+ release is normal is marked b in Figure 4 and represents about 77 me NH_4^+ per 100 g. montmorillonite.

The last segment of the NH_4^+ desorption curve, section c, starts at 450° C. and shows a decreased rate of NH_4^+ release. None of the NH_4^+ held beyond this temperature is exchangeable with KCl, as reported in Table IV. More energy is necessary to remove a given quantity of NH_4^+ from the ammonium-montmorillonite at this temperature range than is indicated for the ideal release curve. Evidently, some form of inhibition is offered to the escape of the remaining NH_4 ions. These ions require more energy to overcome these restrictions and therefore the pattern of part c of the desorption curve does not follow that of the ideal curve. It is interesting to note that the quantity of NH_4 ions per 100 g. montmorillonite represented by section c corresponds to about 11 per cent of the total exchange capacity. This concurs with the observations of Allison et al. (3) that montmorillonite clay is capable of fixing approximately 10 per cent of its exchange capacity. Therefore, it seems that the method of thermal decomposition of an ammonium-clay may be employed as a means to determine the NH_4^+ fixing capacity of the clay mineral, when the results are presented as in Figure 4.

A theory for the mechanism of fixation must explain the need for such additional amounts of energy required for desorption of the fixed cations. Mere entrapment of NH_4 ions between the dehydrated lattices of montmorillonite makes a large portion of the total exchange capacity non-accessible to K ions as demonstrated in Figure 2. However, these non-exchangeable NH_4 ions are not all restricted in their escape from the clay mineral lattice since no extra amounts of energy are required for desorption of most of these ions as shown by section b of the heat release curve in Figure 4. This would indicate that these ions are not "fixed".

The above considerations are evidence that there exists a need for re-definition of "fixed ammonium". It is proposed that the term : "fixed ammonium" shall apply only to those NH_4 ions that require more energy for desorption than is indicated by the ideal release curve and that the quantity of NH_4 ions adsorbed by a mineral lattice and non-accessible to K ions be separated into non-exchangeable ions and fixed ions, the former group consisting of NH_4 ions that do not require extra energy for desorption.

It is postulated that the truly fixed NH_4 ions are located in the hexagonal cavities in the oxygen sheets of the silica tetrahedrons, as suggested by Page and Baver (15), and that the principal reason for the high energy requirements of these ions is the closer proximity to the source of negative charge. The purely mechanical restriction to the desorption of fixed ions by the clamping together of two lattices does not appear logical, since the majority of NH_4 ions released between 350° and 450° C. were not held with higher than theoretical energy bonds and yet were non-exchangeable to K ions, indicating that these ions were located between dehydrated lattices.

SUMMARY

Ammonium-montmorillonite was subjected to different temperatures of heating in a carbon combustion chain. Evolving NH_3 was driven off by helium gas and bubbled through .01 N H_2SO_4. The clay mineral residues after heating were leached with 1 N KCl and distilled with NaOH to determine residual NH_4^+. All quantitative NH_4^+ analyses were done colorimetrically.

After heating at 350° C., 37.3 per cent of the ammonium adsorbed by the clay was not recovered by heating and KCl leaching. This quantity of NH_4^+ is not considered to consist entirely of fixed ammonium, since the semi-logarithmic NH_4^+ desorption curve shows that the release of NH_4^+ with respect to temperature takes place at a faster than theoretical rate up to 300° C., continues at the predicted rate through the range of 300° to 450° C. and goes on at a slower than theoretical rate beyond 450° C. until all NH_4^+ is desorbed at 675° C. It is postulated that the NH_4^+ decomposed at the higher than predicted energy levels are truly fixed ions and that these fixed NH_4 ions are located in the hexagonal openings in the oxygen sheets of silica tetrahedrons. The reason for the higher energy requirements for the decomposition of these ions is thought to be the closer proximity of the ion to the source of the negative charge. A re-definition of fixed and non-exchangeable ammonium is offered.

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