AMMONIUM ION FIXATION IN SOILS

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INTRODUCTION

The use of ammoniacal forms of nitrogenous fertilizers has been found satisfactory and successful. However, this cationic form of nitrogen is endowed with various chemical and physical characteristics that should be understood if the full role of the material is to be appreciated.

It is possible to apply this form of nitrogen in either the gaseous form as ammonia, or directly as the cation of a salt. In either event, the reaction between the ammonia and water and subsequent ionization or the ionization of the added salt forms the ammonium cation which is free in solution and may enter the processes of cation exchange and associated functions.

The purpose of this study was to describe some of the manifestations of the reactions of the ammonium ion in soils. It was intended to give special emphasis to the observation of actions referred to as fixation.

Fixation as used in this instance is the process wherein the cations become so tightly held by the soil particles as to render them unavailable by means normally employed in the determination of exchangeable cations. If fixation of ammonium ions by soils were to occur, it might cause the loss of significant quantities of the nitrogen applied in ammoniacal fertilizers. A knowledge of the factors influencing such fixation and the subsequent release of fixed ammonium ions might be of considerable practical importance.

Fixation has been observed and recognized with the potassium ion, therefore, the methods followed in this study paralleled the methods that have been employed with potassium in so far as was possible.

REVIEW OF LITERATURE

Views of the various investigators on the subjects of potassium and ammonium ion fixation have not differed as to the validity of the theory that fixation does occur, but rather as to the conditions bringing it about. Workers in the field generally recognized a condition of equilibrium present between the soluble, exchangeable, and fixed forms of the potassium ion. The presence of the soluble form of potassium in the equilibrium system inferred that fixation should therefore take place in the moist state.

Work carried out by Attoe and Truog (1), published in 1945, showed little or no fixation of the potassium ion after treatment with from 100 pounds to 3200 pounds of potassium as KCl per acre and a subsequent 18 month moist storage. In a paper published in 1946 Attoe (2) indicated accomplishing fixation in 8 of 10 soils with 2 months moist storage. It was found in this experiment that liming aided fixation in the moist state using potassium fertilized Spencer silt loam. This was the same soil that showed no moist fixation in the earlier experiment.

Bray and DeTurk (4) found conversion of the water soluble and salt replaceable potassium to foxed forms in fixation-release equilibrium studies on Illinois soils. Release of fixed forms to more soluble forms was obtained when the concentration of the soluble and replaceable fractions had been reduced prior to equilibration. DeTurk, Wood and Bray (5) reemphasized the equilibrium aspect of the fixation process and estimated that a 6 month period was necessary for the equilibration to be completed under the conditions that they were studying. They also found that the reaction may be made to go in either direction; i.e. toward further fixation of the potassium ion or toward release of the fixed ion, by altering the concentration of the solutions with which they were treating the soils.

Hoover (7), studying the fixation of potassium by a kaolinitic and a montmorillonitic soil, found that both soils fixed approximately as much in one month as over a longer period. However, it is believed that the estimation made by Hoover was incorrect since the soils that he was using were air dried before determinations were carried out on them. Drying has been found to increase fixation over that occurring in the moist state.

Martin, Overstreet, and Hoagland (17) found considerable fixation of potassium to take place in the moist state. These workers suggested that increases in the fixed potassium due to drying may have been due to the increased concentration of the salts employed.

While investigators have found increased fixation of potassium and ammonium due to drying the soil or the colloidal fraction the explanations offered for the increased fixation due to drying are not entirely consistent.

Page and Baver (18) explained the increase by the space arrangement of the hydrated and unhydrated crystal lattices of the colloids. When the colloids of various expanding lattice type minerals are hydrated the platy structure of the material allows for swelling and expansion in one direction so that the individual colloids are distorted and the distance between plates greatly increased allowing comparatively free entry of the ion. After the ion has entered between the plates and the drying process has taken place the ions are trapped between the plates. The entrapment is the result of the plates returning to dehydrated spacings and the relative size of the ions. Potassium and ammonium have radii of such magnitude as to allow them to become "seated" in the center of six hexagonally arranged oxygen atoms found on adjacent surfaces of the plates. These investigators have found fixation occurring with several other ions. The relative magnitude of the fixation being generally in the same order as the relative ionic radii and their approximation of the radius of the oxygen-atom bordered opening.

Page and Baver described the expansion theory further by preventing contraction of the expanding lattices with large organic ions. The fixations of the ions studied were reduced by this method. The above workers showed greatly increased fixation due to drying. Moist fixation was nevertheless accomplished.

In earlier work Joffe and Kolodny (8) found that complexes of iron, aluminum, calcium and magnesium phosphates were capable of fixing potassium, with the fixation increasing with increased acidoid: basoid ratio. The phosphates were believed instrumental in fixing potassium. Other anions in the colloidal complex were considered as possible sources of fixation action. In this early paper they indicated that the wetting and drying of soils with

with phosphorus present would also act to fix potassium. The problem of potassium release was thought to be intimately tied up with the mobilization of phosphates.

In a study of the distribution and fixation of potassium in the profile of podzolic soils, Joffe and Kolodny (9) found that fixation power for potassium within each profile was correlated with the phosphorus content of the horizons. When the soils were compared for fixation capacity with reference to phosphorus content there was no correlation. Some soils with low phosphorus content fixed more potassium than soils with higher phosphorus contents.

Montmorillonite and like materials were found capable of fixing large quantities of potassium even though the phosphorus content was very low. Soils analyzed and found to be high in divalent bases were also found to have high fixation capacities confirming the earlier observations of the positive role of calcium and magnesium in the fixation process.

In studying the effect of alternate wetting and drying on the base-exchange complex Joffe and Kolodny (10) and Joffe and Levine (14) found that preheating montmorillonite to a temperature above 200° C. decreased the fixation capacity of the clay. Fixation was at a maximum when the wetting and drying of the montmorillonite was carried out at 200° C. The exchange capacity, fixation capacity, and lattice expansion disappeared simultaneously at 500° C. The relation between the exchange capacity and the fixation capacity of soils was investigated. Bentonite samples indicated equivalence of potassium fixed to the decrease in exchange capacity. Soils were not found to have this equivalent relationship.

Joffe and Levine (11) carried out experiments to show the associative fixation of other cations with potassium with particular emphasis on ammonium. Fixation by alternately wetting and drying the chlorides of potassium and ammonium and H-bentonite and H-Montalto colloids indicated potassium and ammonium fixed in similar amounts in the H-Montalto up through one symmetry concentrations added to the colloid. With H-bentonite, lesser amounts of the ammonium were fixed than potassium. Kaolinite showed no potassium fixation. Fixation was found to increase with increase in the amount of cation applied seeming to suggest the exchange complex as the channel for fixation. Equivalent exchange quantities fixed equal amounts of potassium in H-Montalto and H-bentonite.

When ammonium and potassium were fixed together and in competition with each other the results showed that at the higher concentrations of the cations ammonium fixation exceeded potassium fixation. The ions were taken up in different ratios when their concentrations were varied. Prior potassium fixation effected subsequent ammonium fixation inversely. Prior ammonium fixation was found to effect the fixation of potassium in the same manner. Many similarities were observed between the fixation of potassium and the fixation of ammonium.

Joffe and Levine (12, 14) found that potassium must enter into the exchange complex to be fixed. Removal of free iron and aluminum oxides having no appreciable effect on the exchange capacity of a given colloid had no effect upon the fixation of potassium. Alcohol, acting to dehydrate the ions dissolved therein, proved to be a better solvent of potassium in bringing about greater fixation than water. Anions of highly dissociated acids were found to exhibit little differing influence on fixation. However, weakly dissociated acid anions, when used with potassium in fixation experiments, were found to increase fixation over anions of the highly dissociated acids.

Organic matter, in competing with the overall potassium ion content of the system, reduced the fixation of potassium although the organic matter itself had no fixation capacity. Soluble iron was found to reduce the exchange capacity and in turn to reduce the potassium fixation. Large organic molecules were found to block the exchange complex thus reducing the fixation capacity. Conditions of higher pH favored fixation by increasing the effectiveness of the potassium ion as a replacing ion by reducing the hydrogen ion saturation. Sodium seemed to be a more favorable ion for potassium to replace than did calcium.

In studying the release of fixed potassium Joffe and Levine (13), failed to release any fixed potassium by alternate freezing and thawing. Prolonged treatment on the steam bath with 0.05 N HCl released no potassium. There appeared to be no release with acid less than 0.1 N. Almost all fixed potassium was released by 0.5 N and 1.0 N acid, however, no fixed potassium was released by treatment with alkali of like strength when used with Collington colloid. The stronger acid seemed to break down the crystal of the colloid. Wyoming bentonite released fixed potassium due to action of both the acid treatments and the similar basic treatments.

Refixation experiments showed that the fixed potassium was apparently tightly held and that when no release had been accomplished little further fixation could take place. Refixation could be accomplished if some release had occurred.

Levine and Joffe (15) presented results giving evidence of fixation through the exchange complex. Montalto H- colloid was used. With increasing potassium concentrations, increasing quantities of potassium were fixed. The rate of fixation declined as the potassium concentrations were increased. The rate of change of increase of potassium fixation with application reached a maximum at approximately the quantity of potassium fixed at the point when the potassium added was equal to the exchange capacity of the colloid sample. The amount of potassium that entered the exchange complex increased to a critical point in the curve, then the rate of entry with application declined. The maximum in rate of change of entry occurred approximately at the equivalence point. Fixation was found to be a linear function of the potassium entering the exchange complex. Decreases in exchange capacity and potassium fixed were not related linearly.

Using Wyoming bentonite the curve of increase in fixation with increased application was similar to that found with H-Montalto. With greatest applications of potassium the fixation was still far below the exchange capacity. The potassium fixed was less than the quantity able to enter the exchange complex. The break in the application-fixation curve occurred near the point of application equal to exchange capacity. This point was described as critical and significant independent of the material employed as the fixing agent.

Levine and Joffe (16) determined, as had Page and Baver, that minerals acting to fix potassium had layer lattice structures. Pyrophyllite with low exchange capacity and no fixation capacity reground in a ball mill showed increased exchange capacity and fixed potassium, indicating the association of the exchange complex and the process of fixation. H-bentonite with high exchange capacity showed no increases when reground.

Levine and Joffe stated that the cation fixed becomes part of the fixing-agent mineral. Diminished space lattice dimensions were reflected in specific gravity determinations.

Ayers, Takahashi, and Kanehiro (3) converted nonexchangeable potassium to exchangeable forms by cropping continuously to Napier grass. The same reaction was accomplished in the laboratory by electrodialysis. The levels of potassium in the plants decreased during the first two and one-half years of cropping. After that period there was little change. As high as 3400 pounds to 4200 pounds of K_2O were removed per acre. The quantity of potassium removed from the soil by electrodialysis in a period of one month was found equal to one and one-half times the exchangeable potassium initially present.

Martin, Overstreet, and Hoagland (17) indicated that certain cations, when present in the exchange complex of some soils, could pass from loosely held to very strongly held forms. Potassium fixation seemed to involve first, adsorption in exchange positions for other ions, then fixation, resulting in a reduction in total exchangeable cations of the soil. These investigators concluded that potassium, rubidium and hydrogen could be fixed whereas lithium, sodium, calcium, magnesium, barium, and ammonium could not be fixed. Fixation was believed to be chemical in nature since it possessed chemical characteristics in regards to concentration effects and equilibration rate. Potassium fixation was considered dependent upon the existence of attraction spots due to clay lattice positions or the nature of soil minerals. Martin, Overstreet, and Hoagland stated that fixation was not dependent upon the expanding lattice clay mineral. Organic matter was not considered the agent of fixation. Prolonged grinding affected partial release of non-exchangeable rubidium to the exchangeable form.

Fine, Bailey, and Truog (6) in determining the influence of freezing and thawing on the availability of fixed potassium, found releases of five pounds to 155 pounds per acre. Three of the 12 soils sampled showed fixation of 35 pounds to 170 pounds per acre. Prior fixation of potassium gave a slightly greater release than the soils without prior fixation. Excesses of $CaCl_2$ and NaCl present during freezing and thawing inhibitted liberation. Ammonium acetate and ammonium chloride had opposite effects.

Wood and DeTurk (22) described fixation of potassium as a slowly shifting equilibrium system of water soluble, replaceable, and fixed potassium. The fixed fraction was further subdivided into acid soluble and acid insoluble. Equilibrium was reached after 16 weeks to one year. Associated acid anions were thought to have exerted a pronounced effect on the water soluble to replaceable ratio and on the acid-soluble to acid-insoluble ratio. Moist fixation was not considered in agreement with the Page-Baver theory of entrapment. Wood and DeTurk defined fixation as a formation of phosphate complexes, difficultly or slowly soluble potassium, or replacement of iron in the colloid by potassium.

Stanford and Pierre (20) found fixation equilibrium to be obtained quite rapidly with moist contact between soil and salt, particularly in soils of relatively high fixing capacities. The rate was influenced by the soil to water ratio, 1:1 being more rapid than other ratios for the first ten minutes. After 24 hours the ratio made little difference. Fixed potassium and ammonium were not removed by 0.2N and 1N acetic acid extraction. Prior extraction of two calcareous soils with N ammonium acetate or 0.2N acetic acid prevented potassium fixation in moist contact. Fixation of either potassium or ammonium gave an equivalent reduction in the fixation of the other.

Volk (21) observed that 10 alternate wettings and dryings usually served to cause maximum fixation. Soils kept continuously moist exhibited very little fixation. In four soils investigated the ultra clay fraction, smaller than 0.0003 mm, contained the lowest percentage of total potassium but was by far the most active in potassium fixation. One-hundred soils treated with 1000 pounds of potash per acre showed fixation capacities from nothing to the entire amount added. A lateritic soil containing 90 percent colloid did not fix potash, whereas Miami silt loam, 24 percent colloid, fixed 495 pounds per acre of the 1000 pounds added. Mineralogical, chemical, and x-ray analyses of Hagerstown silt loam, some of which had received 5000 pounds of KCl per acre over a period of 50 years, led to the conclusion that a portion of the added potassium had reacted with colloidal silicates and become fixed in the form of muscovite.

Raney and Hoover (19) obtained greater fixation of potassium when the soil was air-dried after moist storage than when the soil was leached while moist. In kaolinitic soil, potassium fixation was insignificant. Soils containing small quantities of artificially fixed potassium released greater quantities of potassium into exchangeable form when saturated with calcium than when saturated with hydrogen. Calcium and hydrogen saturation had little difference in effect when medium quantities of fixed potassium were present. The order of release due to calcium and hydrogen was reversed, as compared to the order of release when the quantities of fixed potassium were low, when the quantities of potassium fixed were high.

METHODS OF AMMONIUM ION FIXATION AND RELEASE

The soil materials used in the experiment were selected as representatives of three regions of the state where ammoniacal forms of nitrogen fertilizers had been or might profitably be employed in crop production. In the fixation and release studies the soil materials used were Geary silt loam from the uplands of The Agronomy farm, Kansas State College; Parsons silt loam from the Thayer Experiment field in southeastern Kansas; and a soil from Gray county Kansas representing second bottom soils along the Arkansas River in the western half of the State.

The colloidal materials were selected to represent extremes in clay types that might normally be expected in soils. In the fixation and the release studies Volclay bentonite, obtained through the courtesy of the American Colloid Company, and kaolin, from Drybranch, Georgia, were employed to respresnt montmorillonitic and kaolinitic clay types respectively.

A fourth soil, the Sharpsburg silt loam found on the lower slopes on the Agronomy farm, Kansas State College, was used in release studies only.

Table 1 shows the exchange capacities and relative percentages of clay of the soil and colloidal materials used in the fixation and release studies.

The exchange capacities of the materials shown in Table 1, with the exception of the Volclay bentonite, were determined by saturating two gram samples of 20 mesh material with potassium as N potassium acetate, pH 7, using four additions of the solution. Each addition was followed by stirring until suspension was obtained. The suspensions were centrifuged and the supernatant liquid decanted and discarded. One wash of 0.5 percent KCl was

Table 1. Exchange capacities as determined by use of the flame photometer and relative percentages of clay as determined by the Bouyoucos hydrometer method of the soil and colloidal materials used in ammonium ion fixation and release experiment.

Soil or colloidal material.	Exchange capacities M.E. per 100 g. as determined by the flame photometer method.	Relative percentages of clay as determined by the Bouyoucos hydrometer method.
Geary silt loam	23.00	29.04
Parsons silt loam	8.80	12.52
Gray county soil	19.52	14.70
Volclay bentonite	66.45	100.00
Kaolin	8.56	87.88

made and the samples subsequently rinsed with 95 percent ethyl alcohol until there was no test for chlorides using $AgNO_3$ solution.

The exchangeable potassium was replaced with N ammonium acetate, pH 7, with five washings as described above. The supernatant liquid of the centrifugings were saved. The solutions were made up to 250 ml with N ammonium acetate pH 7, and sufficient $LiNO_3$, dissolved in N ammonium acetate, to make the resulting solutions 100 ppm lithium.

The concentrations of potassium in the solutions were determined using the Perkin-Elmer Flame Photometer, Model 52 A.

This method of exchange capacity determination is now practiced in the soils laboratories, Kansas State College.

The exchange capacity of Volclay bentonite was determined in a similar manner using 2 N NaCl, pH 1.3, as the saturating solution. The sodium in the exchange capacity after rinsing was replaced by N ammonium acetate, pH 7, and the concentration of the sodium ion in the resulting solution was determined, employing the internal standard method with the flame photometer as described above.

The relative percentages of clay were determined in the soils by the normal Bouyoucos hydrometer method except that the organic matter was destroyed in 50 g samples of the soils with repeated H_2O_2 treatments. The soils were then suspended with sodium oxalite and sodium silicate as dispersing agents and the percentages of clay determined at the end of two hours with a Taylor Instrument Company Bouyoucos soil colloid hydrometer.

The relative percentages of clay in the colloidal materials were determined by suspending 10 grams of the colloidal material, using sodium oxalate and sodium silicate as dispersing agents, in water. A reading was taken with the Bouyoucos hydrometer at the time the dispersion and suspension was complete. Another reading was taken at the end of two hours. The clay content indicated by the second reading was expressed as the percentage of the clay content represented by the first hydrometer reading. This figure was taken as the percentage of clay in the colloidal material.

Moist fixation of the ammonium ion was attempted with the Geary silt loam and the Gray county soil. Ammonium as NH_4Cl was added in eight levels of symmetry concentration to 25 gram samples of 20 mesh material. The pH's of the samples were adjusted to approximately 3.0 with 1 N HCl. The suspended samples were shaken end over end for 12 hours. At the end of the shaking period the suspensions were transferred to Whatman 42 filter papers in Buchner funnels and leached with 400 ml of water. The leachates were saved to determine the water soluble ammonium. Following the water leaching, 250 ml volumes of approximately 2 N NaCl, pH 1.3, were filtered through the samples while on the filter paper. The leachates from this operation were saved to determine the exchangeable ammonium.

All ammonium determinations were carried out by making the leachates alkaline with 45 percent NaOH and distilling the ammonium over into standard acid. The excess acid was titrated with standard NaOH using the mixed indicator, brom cresol green and methyl red, to determine the end point.

Fixation by alternate wetting and drying was attempted with Geary silt loam and the Parsons silt loam by treating 10 gram samples of 20 mesh soils with four levels of symmetry concentration of ammonium as NH_4Cl. The soils were adjusted to approximately pH 5 and put in water suspension and evaporated to dryness (75° to 90° C.) twice. The samples were then suspended in water and centrifuged. The supernatant liquids were decanted and saved until 200 ml volumes had been obtained and water soluble ammonium was determined. The samples were then suspended in 2 N NaCl, pH 1.3, and again centrifuged. Again the supernatant liquids were decanted and saved to make the volumes up to 200 ml and exchangeable ammonium was determined from these solutions.

Two gram samples of Volclay bentonite were treated with six levels of symmetry concentration of ammonium as NH_4Cl. The pH's were adjusted to approximately 5 and the samples were alternately moistened and dried (75° to 90° C.) five times. NaCl extractable ammonium was removed and determined. The fixation of the ammonium added was determined by difference between ammonium added and ammonium recovered.

After fixation of ammonium by Volclay bentonite, the fixed samples were subjected to release action. Two of the duplicates were alternately moistened and dried five times; two duplicates were frozen and thawed five times (frozen at -5° C. in the freezing compartment of a Frigidaire refrigerator); and one set of duplicates was boiled (100° C.) and cooled to room temperature five times. Following the release, extractable ammonium was removed and determined.

Fixation of potassium by Volclay bentonite was attempted in a similar manner as fixation of ammonium. The extractable potassium was determined using the Perkin-Elmer Flame Photometer as described previously. Fixation of the potassium added was determined by differences.

In the studies of fixation and release levels of 0, and 0.20 M.E. of ammonium were added to two gram 20 mesh samples of the soil and colloidal materials. The pH's of the samples were adjusted to approximately 5. The samples were treated as described for the fixation of ammonium by Volclay bentonite above. Following the fixation treatment the samples were extracted with 2 N NaCl solution. Fixation was determined by difference.

Two of the four individual samples of each material treated with 0.20 M.E. ammonium were treated with 0.20 M.E. potassium as KCl before release was attempted by moistening and drying. Release was carried out by moistening and drying five times. Released ammonium was determined directly by distillation of extracted ammonium.

For release studies alone two soils were sampled in the field and release determinations carried out by moistening and drying five times with and without potassium added. The soils sampled were the Geary silt loam and the Sharpsburg silt loam. The Geary soil was taken from wheat fertilization plots where treatments had been 50 pounds of nitrogen as anhydrous ammonia and 60 pounds of P_2O_5; 60 pounds of nitrogen as NH_4NO_3 and 50 pounds P_2O_5; and a no treatment check plot. The fertilizer treatments had all been applied at wheat seeding time the fall before the sampling in the late spring.

The treatments sampled on the Sharpsburg soil came from bromegrass fertilization plots where treatments had been 300 pounds of nitrogen as anhydrous ammonia; 200 pounds of nitrogen as NH_4NO_3; and a no treatment check plot. The field treatments on the brome had been applied on frozen ground in the late fall before the sampling in the late spring.

The field samples taken were composites of 20 samples each, taken at random over the individual plots. The samples were air dried and rolled to pass a 20 mesh seive and thoroughly mixed by tabling.

Determinations carried out on the field samples were exchangeable ammonium, release by moistening and drying five times, and release by moistening and drying with 0.1 M.E. potassium added as KCl per gram of soil.

The exchangeable ammonium was determined by extracting 10 gram samples with 2 N NaCl, pH 1.3. The samples were put in suspension with the NaCl solution and allowed to stand at room temperature over night. The samples were then shaken in a reciprocating shaker for five minutes, centrifuged for five minutes at 2000 r.p.m., and the supernatant liquids decanted and saved for ammonium determinations. The samples were shaken and centrifuged four times with additions of NaCl solution to make the final volumes of the extractants to 200 ml.

The samples for release were extracted in the same manner after the release process.

RESULTS

The results of attempted moist fixation of the ammonium ion when added to 25 gram 20 mesh samples in 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 4.0 symmetry concentrations to the Geary silt loam and the Gray county soil are shown in Tables 2 and 3. Very slight to no fixation was found with either of the soils used. However, the results of the study offered interesting data concerning the distribution of the ammonium added to the soils between the water soluble fraction and the exchangeable fraction.

Tables 2 and 3 and Figs. 1 and 2 indicate an increase in the exchangeable fraction with increases in the ammonium added to the samples. This increase was not a constant rate increase but rather an increase at a decreasing rate as shown in Figs, 1 and 2. Tables 2 and 3 illustrate the increasing percentage of ammonium found in the water soluble fraction and the decreasing percentage found in the exchangeable fraction with increasing additions of ammonium to the soils. The similarity of the curves showing the exchangeable fraction and the tabular data seem to indicate the role played by the exchange complex. The Geary silt loam was found to have an exchange capacity of 23 M.E. per 100 grams while the Gray county soil was found to have an exchange capacity of 19.52 M.E. The quantities of ammonium in the exchange complex after similar additions of ammonium to the soil were of similar relative magnitudes.

After additions of 0, 0.10, 0.20, 0.30 M.E. of ammonium to 10 gram 20 mesh samples, Geary silt loam and Parsons silt loam were alternately wetted and dried to bring about fixation. Exchangeable ammonium increased with increased addition of ammonium as in the case of the moist fixation studies. This is illustrated by Tables 4 and 5 and Figs. 3 and 4. Since the Geary silt loam was used in both studies it is interesting to compare the results in the two instances. With additions of approximately 0.50 symmetry concentration of ammonium the exchangeable ammonium was not widely different in the two studies, 4.24 M.E. and 4.45 M.E. per 100 grams for moist and alternating treatment respectively.

The alternate wetting and drying did, however, show slightly more ammonium in the exchange complex than moist fixation showed. At approximately two symmetry additions the alternate wetting and drying with 15 M.E. exchangeable ammonium per 100 grams had apparently doubled the quantity of ammonium entering the exchange complex by moist treatment, with 6.32 M.E. exchangeable ammonium per 100 grams.

In the alternate wetting and drying fixation study the effect of exchange capacity was not as pronounced as in the moist method. The Parsons silt loam was found to have an exchange capacity of 8.80 M.E. as compared to the Geary silt loam with 23 M.E. per 100 grams. The exchangeable ammonium found in the experiment did not indicate the spread between the two materials in this respect.

Tables 4 and 5 indicate that fixation had been accomplished in the alternate wetting and drying treatment method. Fixation values were not found for all levels of symmetry additions. The trend of the values obtained, nevertheless, seemed to indicate that at least threshold fixation was accomplished with the two alternate wettings and dryings.

Figures 1, 2, 3, and 4 illustrate that the ammonium entering the exchange complex had approached an equilibrium state even at relatively low symmetry additions. The increases of exchangeable ammonium did not correspond to the magnitude of the increases in the ammonium added. A saturation point was not reached in either case. It would have been necessary to add high concentrations of ammonium in order to have completed the exchange of ammonium for the other ions normally found in the exchange complex of the colloids.

Table 6 and Fig. 5 indicate that five alternate moistenings and dryings at the temperatures of the experiment brought about fixation of the ammonium ion in the Volclay bentonite colloidal material. Under these conditions fixation approached the magnitude of the ammonium entering the exchange complex of the soils in the experiments already described. Fixation followed the same general trend as did the ammonium concentration found in the exchange capacity of the soils. Fixed ammonium increased as the additions of ammonium to the samples increased but not at a regular rate. The shape of the curve in Fig. 5 showing fixation, assumes a similar flattened or leveled out form as found with the exchangeable ammonium curves at rather low levels of ammonium addition.

Attempted potassium fixation data as presented in Table 7 showed a condition comparative to the ammonium fixation data. Fixation was accomplished but at higher levels of addition than the ammonium fixation. The increasing fixation with increasing additions series seemed to be in evidence. This portion of the experiment was conducted to act as a check for the fixation methods being employed.

Artificially fixed ammonium was found to be released from Volclay bentonite by all methods applied as illustrated in Table 8. The freezing amd thawing, the boiling and cooling, and the moistening and drying methods indicated that heating of the colloidal material gave higher yields on release than methods that did not employ elevated temperatures.

Five treatments of moistening and drying gave fixation of added ammonium with Geary silt loam, Parsons silt loam, Gray county soil, Volclay bentonite, and kaolin. Results were not consistent under all conditions, and they were not in keeping with expected results from the knowledge of the exchange capacities of the materials used. Releases by moistening and drying following extraction of excess ammonium after fixation were accomplished in all instances. The presence of 0.1 M.E. potassium per gram added to the sample before release action gave lower percentages of release of the ammonium fixed in four of the five samples tested than treatment for release without potassium being present. Percentages of fixed ammonium released were not found in any association with the percentages of the added ammonium that had been artificially fixed. Table 9 presents the data of this portion of the experiment.

The magnitude of possible fixation under field conditions as illustrated by release of fixed ammonium was indicated in the release studies made on field fertilized soils (Table 10). Check plots were found to give comparatively high yields of released ammonium. In five of the six samples in these studies the presence of potassium added prior to release reduced the yields of ammonium released by moistening and drying five times without potassium present.

Table 2. Ammonium found in the water soluble and exchangeable fractions of Gray silt loam 12 hours after its addition to the suspension.

Symmetry concentrations of ammonium added	M.E. ammonium added per 100 grams	M.E. water soluble ammonium per 100 grams	M.E. exchangeable ammonium per 100 grams	Percent water soluble ammonium	Percent exchangeable ammonium
0	0	-0.28	0.16		
0.50	11.52	3.44	4.24	29.86	36.80
1.00	23.00	17.48	6.12	76.00	26.61
1.52	34.96	28.04	7.16	80.21	20.48
2.00	46.00	40.00	6.32	86.96	13.74
2.50	57.52	51.36	7.08	89.29	12.31
3.00	69.00	62.96	7.16	91.25	10.38
4.00	92.00	85.20	7.80	92.61	8.48

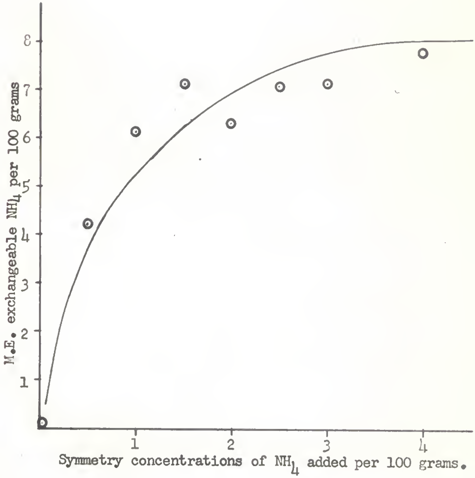

Figure 1. The relationship between symmetry concentrations of NH_4 added to Geary silt loam and exchangeable NH_4 after 12 hours in suspension.

Table 3. Ammonium found in the water soluble and exchangeable fractions of a Gray county soil 12 hours after its addition to the suspension.

Symmetry concentrations of ammonium added	M.E. ammonium added per 100 grams	M.E. water soluble ammonium per 100 grams	M.E. exchangeable ammonium per 100 grams	Percent soluble ammonium	Percent exchangeable ammonium
0	0	0.20	0.24		
0.52	10.12	8.12	2.32	80.24	22.92
1.04	20.24	17.24	3.40	85.18	16.80
1.60	31.28	27.48	4.28	87.85	13.68
2.10	41.00	37.00	4.96	90.24	12.10
2.64	51.52	46.88	5.20	90.99	10.09
3.42	66.84	60.96	5.52	91.20	8.26
4.19	81.88	76.32	6.60	93.21	8.06

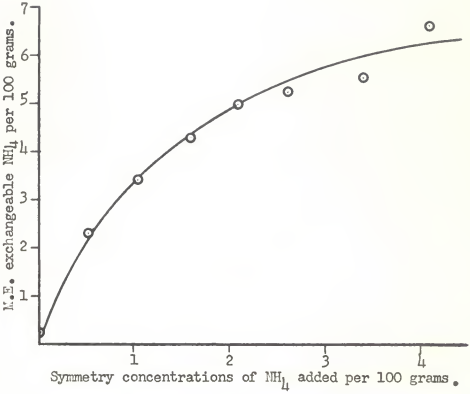

Figure 2. The relationship between symmetry concentrations of NH_4 added to a Gray county soil and exchangeable NH_4 after 12 hours in suspension.

Table 4. Added ammonium found in the water soluble and exchangeable fractions of Geary silt loam after wetting and drying (75° to 90° C.) the soil twice.

Symmetry concentrations of ammonium added	M. E. ammonium added per 100 grams	M.E. water soluble ammonium / 100 grams	M.E. exchangeable ammonium per 100 grams	Percent water soluble ammonium	Percent exchangeable ammonium	M.E. ammonium fixed per 100 grams	Percent ammonium fixed
0	0	0	-0.01				
0.04	1.10	0.37	0.81	37.00	81.00	-0.18	
0.09	2.00	0.57	1.33	28.50	66.50	0.10	5.00
0.13	3.00	0.97	1.80	32.33	60.00	0.23	7.67
0.43	10.00	4.73	4.45	47.30	44.50	0.82	8.20
2.17	50.00	38.69	15.00	77.38	30.00	-3.69	

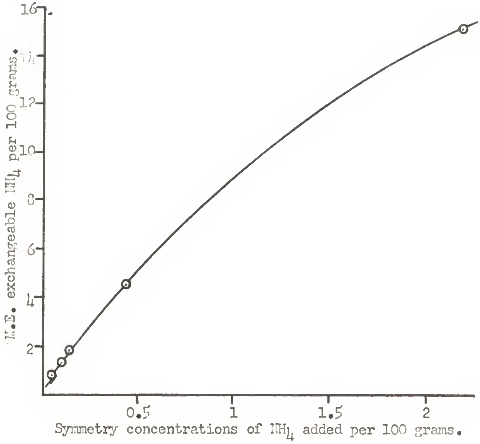

Figure 3. The relationship between symmetry concentrations of NH$_4$ added to Geary silt loam and exchangeable NH$_4$ after wetting and drying (75° to 90° C.) twice.

Table 5. Added ammonium found in the water soluble and exchange fractions of Parsons silt loam after wetting and drying (75° to 90° C.) the soil twice.

Symmetry concentrations of ammonium added	M.E. ammonium added per 100 grams	M.E. water soluble ammonium per 100 grams	M.E. exchangeable ammonium per 100 grams	Percent water soluble ammonium	Percent exchangeable ammonium	M.E. ammonium fixed per 100 grams	Percent ammonium fixed
0	0		0.02				
0.11	1.00	0.32	0.71	32.00	71.00	-0.03	
0.23	2.00	0.98	1.00	49.00	50.00	0.02	1.00
0.34	3.00	1.43	1.58	47.67	52.67	-0.01	
1.14	10.00	6.65	2.83	66.50	28.30	0.52	5.20
5.68	50.00	44.48	9.70	88.96	19.40	-4.18	

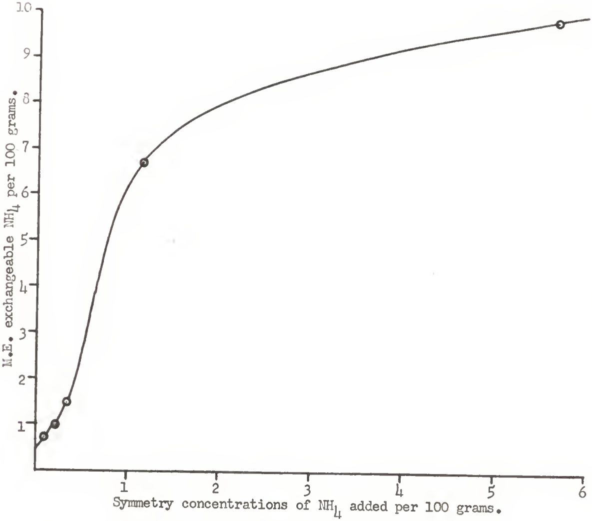

Figure 4. The relationship between symmetry concentrations of NH_4 added to Parsons silt loam and exchangeable NH_4 after wetting and drying (75° to 90° C.) twice.

Table 6. Ammonium ion fixation by Volclay bentonite induced by alternate moistening and drying at 75° to 90° C. five times.

Symmetry concentrations of ammonium added	M.E. ammonium added per 100 grams	M. E. ammonium fixed per 100 grams	Percent ammonium fixed
0	0	0.53*	
0	0	-0.26	
0.03	2.00	1.65	82.50
0.06	4.00	2.47	61.75
0.12	8.00	3.89	48.63
0.15	10.00	4.27	42.70
0.75	50.00	8.56	17.12

*Exchangeable ammonium determined before moistening and drying.

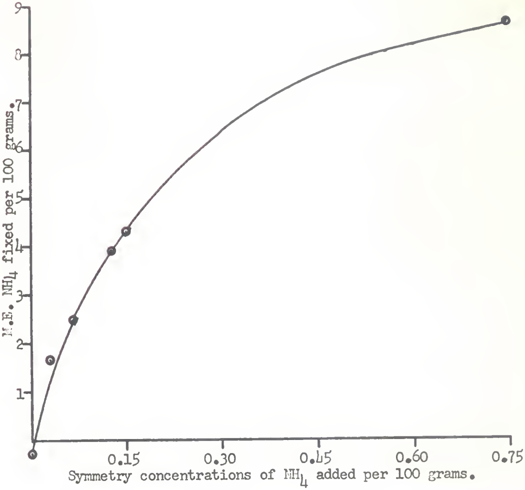

Figure 5. The relationship between symmetry concentrations of NH_4 added to Volclay Bentonite and NH_4 fixed by wetting and drying (75° to 90° C.) five times.

Table 7. Potassium ion fixation by Volclay bentonite induced by moistening and drying at 75° to 90° C. five times.

Symmetry concentrations of potassium added	M. E. potassium added per 100 grams	M. E. added potassium fixed per 100 grams	Percent of added potassium fixed
0	0	-0.68	
0.03	2.00	-0.55	
0.06	4.00	-0.13	
0.12	8.00	1.53	19.13
0.15	10.00	2.45	32.45

Table 8. Release of fixed ammonium from Volclay bentonite induced by the treatments shown:

Symmetry concen-trations of ammonium added	M.E. ammonium added per 100 grams	Ammonium fixed		Ammonium released	
		M.E. per 100 grams	Percent of that added	M.E. per 100 grams	Percent of that fixed
Release by freezing (-5° C.) and thawing five times					
0.06	4.00	2.47	61.75	0.53	21.46
0.12	8.00	3.89	48.63	0.50	12.85
Release by wetting and drying (75° to 90° C.) five times					
0.03	2.00	1.65	82.50	0.84	50.91
0.15	10.00	4.27	42.70	0.99	23.18
Release by boiling (100° C.) and cooling five times					
0.75	50.00	8.56	17.12	1.12	13.08

Table 9. Ammonium fixation induced by moistening and drying (75° to 90° C.) five times and ammonium release by moistening and drying (75° to 90° C.) with and without additions of 10 M.E. of potassium per 100 grams prior to release using three Kansas soils, Volclay bentonite, and kaolin clay.

Soil or colloidal material used.	Symmetry concentrations of ammonium added	Ammonium fixed		Ammonium released	
		M.E. per 100 grams	Percent of that added	M. E. per 100 grams	Percent of that fixed
Geary silt loam	0			2.02	
"	0.43	0.95	9.50	0.77	81.05
"	0.43*	0.60*	6.00*	0.38*	63.33*
Parsons silt loam	0			1.48	
"	1.14	4.42	44.20	0.05	1.13
"	1.14	4.03	40.30	0.84*	2.08*
Gray county soil	0-			0.47	
"	0.51	2.98	29.80	1.26	42.28
"	0.51	5.38	53.80	0.46*	8.55
Volclay bentonite	0			0.26	
"	0.15	4.27	42.70	0.99	23.18
"	0.15	2.86	28.60	0.13*	4.55*
Kaolin clay	0			0.98	
"	1.17	3.24	32.40	0.57	17.59
"	1.17	4.84	48.50	-0.15*	*

*10.00 M.E. potassium as KCl added per 100 grams to the fixed samples before release was attempted.

Table 10. Exchangeable and released ammonium from field fertilized Sharpsburg silt loam and Geary silt loam. Release of fixed ammonium induced by moistening and drying (75° to 90° C.) with and without 10.00 M.E. of potassium added per 100 grams before release.

Soil	Field fertilization (Sampled June 1949)	Pounds of ammonium per acre*		
		Exchangeable	Released	Released with K present
Sharpsburg silt loam	300# as anhydrous NH_3 on brome grass in December, 1948	50.4	316.8	194.4
" "	200# N as NH_4NO_3 on brome grass in December, 1948	28.8	234.0	208.8
" "	No treatment	75.6	288.0	205.2
Geary silt loam	60# N as anhydrous NH_3 50# P_2O_5 on wheat at seeding time, 1948	32.4	201.6	288.0
" "	60# N as NH_4NO_3 50# P_2O_5 on wheat at seeding time, 1948	64.8	248.4	219.6
" "	No treatment	18.0	230.4	212.4

*Acre considered to be 2,000,000 pounds.

DISCUSSION

Although the moist fixation experiment gave negligible results it is believed that moist fixation might have been evidenced if either the method of ammonium determination had been more refined or the time allowed for equilibration to take place had been longer. The former seemed to be the more important in light of the findings of other investigators on potassium fixation (2, 18, 21, 24).

In attempting to show fixation the ammonium recovered from the soil or other material after treatment was subtracted from the amount of ammonium added to the material. This involved a complication of determination. The strengths of the standard acid and base used in the ammonium distillations in the moist fixation portion of the experiment were adjusted for determinations of the water soluble ammonium. As indicated in the results the values for the water soluble were much larger than those for the exchangeable and of course many times greater than the values for the differences between added concentrations and concentrations of ammonium recovered. It is probable that the accuracy was not fine enough to discern the minute results, positive or negative, of these differences.

Martin, Overstreet and Hoagland (17) attributed the effect of drying on the process of potassium fixation to increasing concentrations of the reacting materials. Page and Baver (18) believed that the effect of drying was primarily physical causing shrinkage of the crystal lattice of the colloid in one direction and providing entrapment of the potassium and other ions studied depending upon the size of the ion. The results of the alternate wetting and drying process to promote fixation seemed to indicate that the former theory may be more valid. Here again the refinement of the technique was probably not sufficient for complete determination of the actually existing conditions. However, the principle effects of the wetting and drying were the increases in amounts of exchangeable ammonium. Some fixation was evidenced. Longer periods of treatment or more repetition of the process would probably have shown greater fixation as well as the effect described.

Moistening and drying five times was severe enough treatment to produce fixation of the ammonium ion by all soil and colloidal materials employed. Different results were obtained when fixation was carried out on the same material at different times; i.e. on different days. The differences were not consistent. Fixation of the ammonium by kaolin clay was not expected since kaolin does not have an expanding crystal lattice but was nonetheless encountered.

Results obtained indicated that the presence of sodium and potassium with the soil and colloidal materials during release inhibited the release of ammonium. This condition was further suggested in the release experiment with the field fertilized samples. The action of the potassium and sodium in these instances were not clear unless the ions altered the equilibrium reactions between the fractions of the ammonium.

Table 9 indicates greater releases of ammonium from all materials, except Volclay bentonite, by alternate moistening and drying and subsequent extraction with sodium than when release was carried out with sodium present from extraction after fixation and with sodium and potassium present from the extraction and additions described. Release with sodium present generally gave higher results than when sodium and potassium were present from extractions and additions. These observations inferred association between ions present in the exchange capacity at the time of release and the magnitude of the release.

Volclay bentonite may have been excepted in this apparent association because of the natural saturation of the colloids with sodium. Further sodium added would then be less effective in the activity described.

All methods of release employed with Volclay bentonite yielded released ammonium. These results seemed to bear out the proposed equilibrium conditions of several investigators. The increased release due to heating was thought to be due to greater chemical activity of the reacting substances at elevated temperatures.

Volclay bentonite was not found to be particularly more effective as an agent of fixation than other materials although the exchange capacity and percentages of clay were higher. This discrepancy may have been attributable to erroneous experimental procedure and determinative methods.

Release of fixed ammonium from field fertilized soils indicated the magnitude to which fixation may occur. In several samples release was found to be greater than the quantities added to the soils in the field treatments. The check plots gave greater releases than some of the treated plots. This may have been due to the much smaller vegetative yields of the crops growing on the check plots. Fertilization with ammonium caused heavier initial growth. As the season progressed the heavier growth reduced the water soluble and exchangeable fraction thus promoting release and subsequent use of released ammonium. Lighter growth on check plots subsisted on water soluble and exchangeable ammonium without causing large releases and removal by the plants.

The overall results of the problem seemed to indicate several general conditions. Fixation was produced in the laboratory and was found to be existent in the field. Entry of the ammonium ion into the exchange capacity and into conditions referred to as fixed seemed to be a function of the degree of relative saturation of the soil and colloidal materials with the ions studied.

Although the laboratory methods for inducing fixation were severe as compared to field conditions encountered, it was inferred that fixation in the field takes place and may be found in some magnitude.

However, release was also inferred from the laboratory experiments. Therefore, a condition of gain and loss balance of available ammonium was considered probable from a long range point of view. Severe drought within a single season might act as a fixing or a releasing condition depending upon the ammonium concentration in the various fractions. Later, plant growth, reducing available fraction concentrations, might act to accomplish release or spring or fall freezing and thawing bring about similar conditions.

Use of ammonium fertilizers in heavy application would apparently alter conditions to bring about ammonium fixation. Greater plant growth due to such applications might then act to use up available ammonium and thus shift the reaction to promote release.

It is believed that further studies could be carried out with a greater array of soils. Fixation capacities and release behaviors could well be studied under field and laboratory controlled conditions in an attempt to evaluate the magnitude and resulting effects of ammonium fixation and release.

For a technical approach radioactive studies are suggested to attempt to determine the seats or positions of fixation.

SUMMARY

Moist fixation of the ammonium ion was attempted using Geary silt loam and a Gray county, Kansas bottom land soil. The results showed no fixation but gave data for distribution of the added ammonium in water soluble and exchangeable fractions. Exchangeable ammonium was found to increase at a decreasing rate with additions.

Alternate wetting and drying as a means of inducing fixation was tried with Geary silt loam and Parsons silt loam. Incipient fixation was indicated and a definite shift in equilibrium reactions between water soluble and exchangeable increasing the exchangeable was observed, being double that found with moist treatment in one case.

More severe action with moistening and drying produced fixation by all soil and colloidal materials studied.

Fixation data for Volclay bentonite gave a curve with fixations at various addition levels resembling the curves described by the exchangeable ammonium series with various addition levels.

Release was found with wetting and drying, boiling and cooling, and freezing and thawing using Volclay bentonite with artificially fixed ammonium present.

Release of fixed ammonium, either artificially fixed or fixed under field conditions, was accomplished with all soil and colloidal materials by moistening and drying. The presence of sodium and potassium seemed to reduce the quantity of ammonium released.

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