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AMMONIUM FIXATION OF  
SELECTED SOILS  
IN LEBANON

By  
HABIBUR REHMAN

A THESIS

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AMMONIUM FIXATION

REHMAN

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## AN ABSTRACT OF THE THESIS OF

Habibur Rehman for M.S. in Soils.

Title: Ammonium fixation of selected soils in Lebanon.

Studies on ammonium fixation of two calcareous soils and one non-calcareous soil of Lebanon were conducted in the Division of Soils and Irrigation of the American University of Beirut. The quantities of ammonium fixed in the black, gray, and brown soils were 46, 16, and 41 percent of the ammonium applied, respectively. The presence of the calcium carbonates in the soils resulted in less recovery of the fixed ammonium. An increase of 20 to 142 percent was obtained in the two calcareous soils when the carbonates were destroyed before estimating the fixed ammonium.

Total ammonium fixing capacity of the black soil ranged from 1.95 to 2.47 me per 100 g. The quantities of ammonium fixed in the gray, and the brown soils ranged from 0.53 to 0.78 and 1.51 to 2.10 me per 100 g of soil, respectively. The fixation of ammonium was determined under the wet, air dry, and oven dry conditions.

All the soils fixed considerable amounts of ammonium under wet conditions. Air drying or heating of the calcareous soils after saturating with  $\text{N NH}_4\text{Cl}$  caused reduction in the ammonium fixation but the non-calcareous brown soil gave an increase in the ammonium fixation. The above reduction was probably due to the volatilization of the ammonium as ammonia from the calcareous soils. The increase of the ammonium fixation in the non-calcareous soil was due to the removal of water from the interplanar spaces and collapse of the lattice.

The fixation of ammonium by all the soils investigated was fairly rapid. The rate of fixation ranged from 85 to 99 percent after 12 hours of ammoniation when based on the total ammonium fixed after 144 hours of ammoniation.

Destroying the carbonates of the calcareous soils in the presence of  $\text{N KCl}$ , before ammoniation, resulted in a reduction of the ammonium fixing capacity of the soils;

but when the carbonates were destroyed in the presence of  $\underline{\text{N}} \text{CaCl}_2$ , the ammonium fixing capacity was increased. The low fixation of ammonium with the potassium treatment indicated that the sites of fixation were already occupied by potassium, while the high fixation of ammonium with the calcium treatment indicated expansion of the mineral lattice.

Removal of the exchangeable ammonium, after saturating the soils with  $\underline{\text{N}} \text{NH}_4\text{Cl}$ , with different cations and with cations plus glycerol resulted in different amounts of the fixed ammonium left in the soils. The highest amounts of fixed ammonium were obtained when the exchangeable ammonium was removed with  $\underline{\text{N}} \text{KCl}$  followed by  $\underline{\text{N}} \text{CaCl}_2$  and  $\underline{\text{N}} \text{NaCl}$  in that order.

Calcium plus glycerol removed more of the adsorbed ammonium than with calcium alone because of the greater increase in expansion of the lattice by glycerol. Sodium plus glycerol gave almost the same values as with sodium alone because of the great lattice expansion in both cases.

Substantial amounts of fixed ammonium were found in the silt plus sand fractions of the original soils. The total ammonium fixing capacity of the clay and the silt plus sand fractions varied under different conditions. On the percentage basis the silt plus sand fractions of the black, gray, and brown soils fixed about 31, 43, and 45 percent of the total ammonium fixed by the whole soils.

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## I. INTRODUCTION

Ammonium fixation is defined as adsorption of ammonium ions ( $\text{NH}_4^+$ ) by soils or minerals in such a form that these ions are neither water soluble nor readily exchangeable. McBeth (34) reported in 1917 that ammonium added in the salt form to certain soils of California could not be quantitatively recovered as soluble or exchangeable ammonium.

Recent work has shown (2, 3, 28, 53) that many soils have the ability to fix considerable amounts of  $\text{NH}_4^+$ . Several clay minerals have been found (6, 40) to fix  $\text{NH}_4^+$ , but present evidence indicates that the clay minerals chiefly responsible for ammonium fixation in soils are vermiculite, illite and montmorillonite (2, 3, 6, 53).

Soils differ markedly in their ability to hold  $\text{NH}_4^+$  in a fixed or difficultly exchangeable form. They also differ in the readiness with which they release this fixed ammonium when leached with various salts. Salts of elements such as potassium and rubidium that tend to contract the crystal lattice of clay minerals remove less ammonium than do salts of elements such as calcium and sodium that expand the lattice (3, 4, 5, 9, 10).

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It has been established that ammonium fixation occurs on the clay minerals of the soil (2, 10, 14) but there is little information with respect to ammonium fixation in the silt and sand fractions. Hinman (28) and Rich and Lutz (43) reported that substantial amounts were held in the silt fraction.

The increased use of ammonium fertilizers, such as anhydrous ammonia and ammonium salts, would seem to increase the possibility for reaction of  $\text{NH}_4^+$  with the clay minerals normally found in soil.

No data are available to indicate the extent of ammonium fixation by the Lebanese soils. These studies were conducted, during the year 1965-66, in the Division of Soils and Irrigation of the American University of Beirut, with the following objectives:

1. To determine the amount of original fixed ammonium in 3 soils of Lebanon.
2. To evaluate the total ammonium fixing capacity of these soils.
3. To investigate some factors which may influence the fixation of added ammonium.
4. To determine the ammonium fixing capacity of calcareous soils after and before destroying the carbonates.
5. To evaluate the role of the clay and the silt plus sand fractions in ammonium fixation.

## II. REVIEW OF LITERATURE

Fixation of ammonium by soils was first reported by McBeth (34) in 1917 after he found that a considerable portion of added ammonium could not be removed by leaching with HCl. The ammonium which was not recovered was termed as "fixed" by McBeth. The definition of fixed ammonium as approved by the Soil Science Society of America (49) is "adsorption of  $\text{NH}_4^+$  by soils or minerals in such a form that they are neither water soluble nor readily exchangeable". Since 1917, many methods have been proposed by various workers for the determination of fixed ammonium and the factors affecting ammonium fixation in soils.

### Methods of Determining Ammonium Fixation

The methods frequently employed have been the extraction of added ammonium by certain acids like HCl and salts like  $\underline{\text{N}}$  KCl,  $\underline{\text{N}}$  NaCl or  $\underline{\text{N}}$   $\text{CaCl}_2$ . The original method of McBeth (34, pp. 142-143) consisted in saturating the soils with known quantity of an ammonium salt, such as ammonium sulfate, ammonium chloride or ammonium nitrate, and in extracting the ammonium added by 10 percent HCl. It was reported that 10 percent HCl could not remove more



than 81 percent of the added ammonium.

Barshad (10) proposed the alkaline distillation technique for the determination of fixed ammonium. In his method, the soil sample was distilled with NaOH and a duplicate sample was distilled with KOH. The fixed ammonium was estimated from the difference between the amounts of ammonium released by the two distillations. The method was based on Barshad's finding that fixed ammonium was released from vermiculite by distillation with NaOH but was not released by distillation with KOH.

Dhariwal and Stevenson (19) attempted to use Barshad's method for estimating naturally occurring fixed ammonium in soils but were unable to obtain satisfactory results. One difficulty was traced to the inability of NaOH to remove fixed ammonium completely from illite clay mineral. A second difficulty was that the amount of ammonium liberated from the soil organic matter by alkaline distillation varied with the rate and length of distillation.

Bremner (16, p. 147) criticized Barshad's method in that its value for the determination of fixed ammonium in soils seemed limited, since it had been found that distillation of some soils with NaOH did not release all of the fixed ammonium present. This was because the release of fixed ammonium by distillation with NaOH was blocked effectively by small amounts of potassium (5, 24, 25).

A further objection to the above method was that it involved the dubious assumption that the amount of ammonium released from organic nitrogen compounds on distillation of soil with KOH was the same as that released on distillation with NaOH.

Rodrigues (46) was the first to estimate clay fixed ammonium directly by digesting the clay mineral fraction with 40 percent HF and 50 percent  $H_2SO_4$ . This method, too, was open to criticism (16, p. 147) on the grounds that the technique used to release fixed ammonium and to estimate the amount released seemed likely to convert some of the organically bound soil nitrogen to ammonium nitrogen. A further difficulty in evaluating this method was that it had not so far been demonstrated that the treatment with hydrofluoric and sulfuric acids effected quantitative release of fixed ammonium from clay minerals.

Dhariwal and Stevenson (19) reported that probably the best approach to the problem of determining fixed ammonium in soils would be by HF extraction. Interference resulting from the deamination of nitrogenous organic materials possibly could be eliminated by treating the soils with hot KOH before removing the fixed ammonium.

The suggested method consisted in treating the soil with N KOH and autoclaving the sample for a certain period of time. The residue was centrifuged and treated with HF solution. The fixed ammonium was then determined by

distilling the sample.

The concentration of hydrofluoric acid required to remove fixed ammonium from bentonite, illite and vermiculite was determined by treating the clays with acid solutions of various strengths. An acid mixture consisting of  $\underline{N}$  HF:  $\underline{N}$  HCl removed only about 96 percent of the fixed ammonium from vermiculite. But a complete removal was obtained when an acid mixture of 5.0  $\underline{N}$  HF, 0.75  $\underline{N}$  HCl, and 0.6  $\underline{N}$  H<sub>2</sub>SO<sub>4</sub> was used.

The advantage of this method was that it was suitable for the determination of both naturally occurring fixed ammonium and ammonium fixing capacity of the soils. Also, the analysis was rapid and required only a small quantity of soil.

Bremner (16, pp. 148-149) and Bremner and Harada (18) developed a reliable method for determining directly the fixed ammonium by clays in the surface soils without destroying the organic matter. The method was based on extracting the soluble and exchangeable ammonium by  $\underline{N}$  KCl using a soil-salt ratio of 1:10. Total ammonium content was determined by digesting the soil or silicate clay minerals with  $\underline{N}$  HF:  $\underline{N}$  HCl. The residue was separated from the acid mixture by filtration and the acid mixture filtrate was distilled with MgO. This treatment of  $\underline{N}$  HF:  $\underline{N}$  HCl did not cause the release of nitrogen as ammonium from soil organic matter. The difference of the total

ammonium and exchangeable ammonium gave the amount of ammonium fixed.

Walsh and Murdock (57) found that  $\underline{N}$  HF:  $\underline{N}$  HCl was as effective in removing the fixed ammonium as 5.0  $\underline{N}$  HF, 0.75  $\underline{N}$  HCl, and 0.6  $\underline{N}$  H<sub>2</sub>SO<sub>4</sub> used by Dhariwal and Stevenson (19) provided that high solution:clay ratio was used.

Mogilevkina (37, p. 191) proposed the heat treatment method for the determination of fixed ammonium. This method involved the calcinating of the soils in a muffle furnace at 400°C ( $\pm$  20°C) to destroy the organic matter and remove exchangeable ammonium. The fixed ammonium in the calcinated soil was then determined by the usual Kjeldahl method.

Nelson and Bremner (41) reported that Mogilevkina's method of determining fixed ammonium, when used with soils and ammonium saturated clays, gave much lower values than HF methods and was unsatisfactory. The heat treatment used in this method for removal of organic-N and exchangeable ammonium-N led to loss of fixed ammonium and the Kjeldahl procedure used to determine the nitrogen in the residue from this treatment failed to remove this nitrogen quantitatively.

#### Methods of Determining Total Ammonium Fixing Capacity of Soil

In general the methods employed for the

determination of native fixed ammonium in soils can also be used for the determination of total ammonium fixing capacity of soils or soil minerals.

Allison et al. (2) suggested the addition of a known quantity of ammonium salt, dissolved in sufficient water to wet the soil thoroughly. The soils were then kept in a closed system for the desired time. Free and exchangeable ammonium were leached out with N KCl. The leachate was then distilled, and the liberated ammonium was titrated. The difference between the quantity added and that removed by leaching represented the quantity fixed.

In another study these workers (3) proposed the saturation of the soil with ammonium salt and the removal of the free ammonium by leaching with alcohol or water. The exchangeable ammonium was removed by leaching with N KCl. A similar non-ammonium treated soil was leached with N KCl. The difference between the total nitrogen determined by the Kjeldahl method on the extracted ammonium treated and on the extracted non-ammonium treated soil represented the quantity of ammonium fixed. This method, however, when used on soils that were high in nitrogen gave somewhat less accurate results than when fixation was determined by the method proposed by Allison et al. (3). It was further reported by these authors (3) that the closed system procedure was, however, entirely

impracticable when used to prepare several hundred grams of soil for availability studies. Obviously no method of determining fixation by difference can be used with a calcareous soil unless in a closed system, since such soils evolve ammonia readily on drying.

Dhariwal and Stevenson (19) suggested the HF-method for determining the total ammonium fixing capacity of soils. The procedure used was essentially the same as described for determining the native fixed ammonium (19). The difference between total fixed ammonium, determined after saturating the soils with an ammonium source, and naturally occurring fixed ammonium was the amount of ammonium fixed by the treatment. However, it was found that the amount of ammonium fixed depended upon the nature of treatment (4, 24).

Leggett and Moodie (31) proposed the aeration-recovery method for determining ammonium fixation by soils under moist conditions. In this method, a solution of  $K_2CO_3$  was added to the ammoniated soil and the system was then aerated as a means of distilling off ammonium without concurrent release of soil organic nitrogen. Alkaline aeration in the presence of K was used to remove soluble and exchangeable  $NH_4^+$  from  $NH_4^+$ -treated soils. The liberated  $NH_3$  was collected in standard acid and determined by titrating with standard NaOH. The ammonium fixed by the soil was obtained from the difference between the

ammonium added and that recovered.

The method was comparatively simple and could be used to advantage when large numbers of determinations were made in routine manner. The method was versatile in that it could be adopted to the use of small samples of soil or mineral and to the use of a small quantity of  $\text{NH}_4^+$ . One serious disadvantage of the aeration-recovery method was that  $\text{NH}_4^+$  fixation after air- or oven-drying could not be determined.

#### Ammonium Fixing Clay Minerals

Clay minerals of the soil have been studied extensively (23, 42, 44). As a result the theories for both the crystal structure and the chemical behavior of the clay-ammonium fixation reaction have been supported by many workers. Giesecking (23), Reitemier (42), and Rich and Thomas (44) have written reviews which cover the extensive literature in this field.

The fixation of ammonium in soils and rocks is achieved by the three layer silicate minerals, 2:1 silica to alumina. These minerals are chiefly found in the clay fraction of the soil. For this reason the distribution of fixed ammonium in the soil profile mostly corresponds to the distribution of clay in it (46, 52). Silicate clay minerals of the 1:1 layer lattice type have not shown any appreciable capacity to fix ammonium. Of the 2:1 clay

minerals, vermiculite and illite have the capacity to fix considerable amounts of ammonium under moist conditions at room temperature. Montmorillonite type clay minerals fix ammonium to a considerable extent especially when subjected to air-drying or heating.

Structure of the 2:1 type clay minerals: The structure of the 2:1 type of clay minerals has been postulated as follows. A layer of aluminum hydroxide (gibbsite) in the form of aluminum octahedron has been sandwiched between two layers of silicon tetrahedrons. The apices of the silica tetrahedrons are pointed inward and toward the aluminum octahedrons. The apical oxygen of the silica tetrahedron is shared with one of the oxygens of the aluminum octahedron. The silica tetrahedron has a hexagonal arrangement so that voids surrounded by six oxygen atoms occur in the outer oxygen (base and top of the tetrahedron) layer. The radius of the voids has been estimated to be  $1.25^{\circ}\text{A}$  which is only slightly smaller in radius than the radius of a dehydrated ammonium ion,  $1.43^{\circ}\text{A}$ . Up to 15 percent isomorphous substitution of aluminum for silicon has been found in the silica tetrahedron and some isomorphous substitution of divalent ions has been found for aluminum in the aluminum octahedral layer. These substitutions result in a net negative charge in the clay crystal which must be balanced by a cation exterior to the crystal lattice. Vermiculite and



illite have been found to have a larger amount of isomorphous substitution of aluminum for silicon than found in montmorillonite. Isomorphous substitution of divalent ions for aluminum in the aluminum octahedral layer has been found to account for most of the negative charge found in montmorillonite.

Mechanism of ammonium fixation: The fixation of  $\text{NH}_4^+$  by the clay minerals of the mica type is not the only example of the fixation of cations. These minerals can fix  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$  in the same manner. Most of the investigators are of the opinion that the mechanism of fixation of these cations is the same (10, 51). This is confirmed by the fact that when  $\text{NH}_4^+$  and  $\text{K}^+$  are adsorbed from mixed solutions of their salt, these cations compete with each other. It has also been confirmed by Barshad (10) that if a mineral or soil is treated with potassium salt or hydroxide before saturation with  $\text{NH}_4^+$ , the magnitude of  $\text{NH}_4^+$ -fixation is reduced or altogether absent.

The phenomenon of fixation consists in that the cations penetrate between the interplanar spaces of the crystal lattice of the mineral when it is expanded and fit into the hexagonal voids in the lattice of oxygen atoms of tetrahedral layer. By interacting with both negatively charged oxygen layers, the cations attract them and as a result the crystal lattice of the mineral contracts (11). This leads to the joining of the hexagonal voids of two

opposite silicon oxide layers and the cations become trapped in the closed spaces formed by oxygen atoms that can be approximately considered as a sphere having a radius from 1.30 to 1.65<sup>0</sup>A (9, 11, 55).

#### Some Factors Influencing Ammonium Fixation by Soil

The clay minerals mainly responsible for the fixation of ammonium in soils are vemiculite, illite and montmorillonite. Allison and Roller (6) reported that halloysite and Attapulgite showed some tendency to trap  $\text{NH}_4^+$  and held it against extraction with N KCl. Nash and Marshall (40) reported feldspars to fix ammonium.

Stevenson et al. (53), while working with an Elliott silt loam, where illite was the predominant clay mineral, found that the soil contained larger amounts of fixed ammonium than a Cisne silt loam, where montmorillonite was the predominant clay mineral. Stevenson and Dhariwal (52), while working with some soils of the North Central region of the United States, reported that the amount of fixed ammonium in soils was found to depend upon the type and amount of clay minerals present. With respect to the clay mineral type, the order was illite > montmorillonite > Kaolinite.

The depth from which the soil sample is taken is frequently an important factor in the determination of the

ammonium fixing power of the soil. Allison et al. (3) and Hanway and Scott (24) reported that fixation was generally less in surface soils than in the sub-soils. It has been suggested (3) that the low fixation in surface soils is probably due to the presence of ammonium and potassium already fixed in the clay minerals and to the interfering effect of organic matter. Mela Mela (36) reported that sub-soil fixed more ammonium than the top soil.

Van Schreven (56) found that the inherent fixed ammonium tended to decrease by 2.1 to 3.0 percent in 20 to 60 cm layer in the case of fallow plots but in case of plots bearing a cereal crop the decrease was 7.1, 4.5, and 3.5 percent in the 0 to 20, 20 to 40, and 40 to 60 cm layers, respectively. Hinman (28) while working with four soil profiles of Saskatchewan, reported that increasing amounts of fixed-NH<sub>4</sub><sup>+</sup> were observed with increasing depth. Total amounts found in the 4-feet profile varied from 1300 to 2300 ppm and ranged from 7 percent of the total nitrogen in the surface soil to as much as 58 percent in the soil at 4-feet depth. Adams and Stevenson (1) found that a considerable portion of nitrogen in the C horizon existed as ammonium and was retained by primary silicate minerals, especially micas.

Moore (38), while working with Alberta soils, reported that concentration of fixed ammonium decreased

with depth in the brown and black soils but increased for the gray wooded soils. In all cases, however, the relative proportion (fixed  $\text{NH}_4^+$ -N expressed as percentage of total-N) increased markedly with depth, varying from 22 to 49 percent in the C horizon. Moore and Ayeke (39) reported that HF-extractable ammonium, presumably mostly in fixed form, increased with depth in four Nigerian soil profiles. Amounts varied from 2 to 6 percent in the surface layers to 45 to 63 percent at a depth of 5 to 7 feet.

Effect of different cations on ammonium fixation: The fixation value obtained for clay fixed ammonium depends upon the type of cation employed for replacement of the "readily exchangeable ammonium".

Bower (14) reported that when  $\text{NH}_4 \text{Cl}$  was applied at the rate of 10 me per 100 g of soil, the amounts of ammonium fixed by various samples against extraction by 0.5N KCl ranged from 0.0 to 6.2 me per 100 g.

Barshad (10) reported that in vermiculite, and to some extent in soils, all of the adsorbed  $\text{NH}_4^+$  was found to be replaceable with  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{++}$ ,  $\text{Ca}^{++}$  or  $\text{Ba}^{++}$ ; but only a fraction was replaceable with  $\text{K}^+$ ,  $\text{Rb}^+$  or  $\text{Cs}^+$ . The cause for these differences appear to lie in the nature of the crystal lattice of the exchange material associated with each of the different cations. It was reported that vermiculite saturated with  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{++}$ ,  $\text{Ca}^{++}$  or  $\text{Ba}^{++}$

had a crystal lattice with an expanded interlayered space equivalent to one or two layers of water molecules; but vermiculite saturated with  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  or  $\text{Cs}^+$  had no such interlayer space in its crystal lattice even when immersed in water (9). Accordingly, Barshad (9) defined the "ammonium fixation" of a soil or a mineral as the adsorbed ammonium not replaceable by  $\text{K}^+$ .

Allison et al. (4) reported that  $\text{CaCl}_2$  removed more ammonium from an ammonium saturated soil than did  $\text{KCl}$ . Soils high in vermiculite were most retentive of the ammonium when leached with N  $\text{CaCl}_2$ , whereas montmorillonitic Yolo soil was the least retentive. Illitic soils showed an intermediate behavior. It was further reported that the end point of extraction, as shown by Nessler test, was sharp where  $\text{KCl}$  was used but often much less sharp with  $\text{CaCl}_2$ .

Allison et al. (3) showed that vermiculite adsorbed a large quantity of ammonium ions that were not released by leaching with N  $\text{KCl}$ . These ammonium ions were slowly extracted with either N  $\text{NaCl}$  or N  $\text{CaCl}_2$  and were readily removed by boiling with 0.2 N  $\text{NaOH}$ , but not with 0.2 N  $\text{KOH}$ .

Allison and Roller (5) found that when ammonium saturated soils were leached with various reagents, the N  $\text{NaCl}$  removed the largest portion of the  $\text{NH}_4^+$ , whereas, N  $\text{KCl}$  removed the least. The values obtained by leaching

with  $\underline{N}$   $\text{CaCl}_2$ ,  $\underline{N}$   $\text{MgCl}_2$  and  $0.05 \underline{N}$   $\text{HCl}$  were intermediate. In another study Allison and Roller (6) found that when  $\text{NH}_4$  Cl-treated bentonites were extracted with  $\underline{N}$   $\text{CaCl}_2$ ,  $\underline{N}$   $\text{NaCl}$  or  $0.05 \underline{N}$   $\text{HCl}$ , much less fixed ammonium remained than where  $\underline{N}$   $\text{KCl}$  was the extractant.

Stojanovic and Broadbent (54), while working with four New York soils and one Colorado soil, reported that sodium acetate-acetic acid (pH 4.8) and potassium chloride-hydrofluoric acid (pH 1.0), when employed as extractant agents, removed comparable amounts of ammonium-nitrogen from untreated soils.

Frenay (21) reported that fixed- $\text{NH}_4^+$  could be completely recovered from clay minerals by leaching small amounts of the clay with large volumes of salt solutions containing the cations  $\text{Na}^+$ ,  $\text{Ca}^{++}$ , or  $\text{Mg}^{++}$  but not  $\text{K}^+$ ,  $\text{Rb}^+$  or  $\text{Cs}^+$ .

Effect of potassium: Stanford and Pierre (51) reported that potassium and ammonium were fixed in the same manner and that the capacity to fix these cations was constant.

Hanway et al. (25) found that fixed ammonium in vermiculite and bentonite was completely released by distillation in  $\text{NaOH}$  solution. Small amounts of  $\text{K}$  in the solutions, however, blocked this release of  $\text{NH}_4^+$ . If the amount of  $\text{K}$  was in excess of two  $\text{K}$  ions per 100  $\text{Na}$  ions, no fixed ammonium was released from vermiculite.

Leggett and Moodie (32) studied the release of fixed

ammonium from soils by Na. It was observed that when no K was added to  $\text{NH}_4^+$ -saturated air-dried soil, 86 to 98 percent of the fixed ammonium was released during alkaline distillation or aeration. But when small amounts of K were added to the alkalizing agents, the release was markedly decreased.

Effect of aluminum, hydrogen and iron: McBeth (34, p. 149) reported that Al and Fe salts added to soils prior to ammoniation reduced the magnitude of ammonium fixation. Stanford (50) observed that Al, H and Fe ions, which he classed as difficultly exchangeable ions, reduced the potassium fixation by illite and bentonite clay minerals.

Barshad (12, p. 63) reported that the presence of difficultly exchangeable  $\text{H}^+$  caused a decrease in  $\text{NH}_4^+$ -fixation, but replacement of this  $\text{H}^+$ , at a high pH, restored the fixation capacity of minerals. Edward, according to McIntosh (35, p. 16), reported that extraction of Fe and Al oxides and interlayer Al tended to increase the exchange capacity and the ammonium fixing capacity of bentonite. It has been suggested that the reduction in fixation caused by Al, H and Fe may be due to one of the following: Firstly, blockage of the collapse of adjacent crystal units; secondly, inability of ammonium ions to effect complete exchange with Al, H or Fe ions or thirdly, formation of insoluble precipitates with phosphate anions present in the system as described below.

Effect of anions: Soluble phosphate has been shown to react with soluble iron and aluminum to form insoluble complexes. If the cation associated with phosphate is  $\text{NH}_4^+$ , then an ammonium-aluminum-phosphate,  $(\text{NH}_4)_2 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ , or ammonium-iron-phosphate,  $(\text{NH}_4)_2 \cdot \text{Fe}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ , precipitate may be formed, (26, p. 263; 27).

Stojanovic and Broadbent (54) reported that consistently lower recoveries of nitrogen were obtained from  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  than from  $(\text{NH}_4)_2\text{HPO}_4$  and  $\text{NH}_4\text{NO}_3$  in acid soils.

Leggett found that changing the anion accompanying the ammonium had little effect on ammonium fixation by vermiculite. The vermiculite was found to fix 4.1, 4.0, 4.7, 3.8, 4.0, and 4.2 me  $\text{NH}_4^+$  per 100 g of soil when ammoniated with ammonium salts of chloride, sulfate, phosphate (dibasic), citrate, tartrate and acetate, respectively, (35, p. 17).

Concentration of fixable cation: McBeth (34, p. 146) reported that the addition of the same quantity of an ammonium salt in concentrated and diluted solutions showed the greatest fixation when added in concentrated solutions. Nommik, reviewed by McIntosh (35, p. 18), reported that the amount of added ammonium fixed by the mineral fraction of soil was 0.83, 3.18, 4.48, and 6.00 me  $\text{NH}_4^+$  per 100 g. when ammonium was added at concentration of 1.0, 10.0, 40.0, and 50.0 me  $\text{NH}_4^+$  nitrogen per 100 g of soil,



respectively.

pH of the extracting solutions: Scott et al. (47)

extracted the  $\text{NH}_4\text{Cl}$  saturated ground vermiculite with various neutral and acid solutions. Neutral solutions of N NaCl did not effectively remove the ammonium, however, there was a linear increase in  $\text{NH}_4^+$  removal when the pH of the N NaCl solution was decreased by the addition of acid. Using N KCl as extractant, the amount of  $\text{NH}_4^+$  removed increased when the pH of the solution decreased. Ghildyal and Singh (22) reported that leaching with N NaCl at pH 1 gave the maximum recovery (82 percent) of added ammonium nitrogen.

Effect of temperature: McBeth (34, p. 148) reported that heating a soil to a high temperature caused marked changes in the chemical and physical nature of the soil. Sohn and Peech (48) reported that heating an ammoniated soil reduced the ammonia retention capacity but increased the ammonia fixing capacity. Allison et al. (7) found that soils rich in illite and vermiculite fixed ammonium under moist condition, where soils rich in montmorillonite fixed little or no ammonium under these conditions. In another study Allison et al. (3) reported that, in soils containing illite as predominant clay mineral, the quantity of ammonium fixed was increased about 6 percent by air-drying and 18 percent by heating at  $100^\circ\text{C}$ .

Effect of ammoniation time: Leggett, reviewed by McIntosh

(35, p. 18), found that ammonium fixation by soil clay minerals and vermiculite was rapid. The fixation of ammonium was 92 and 98 percent complete after an ammoniation period of 1 and 24 hours, respectively, when based on total ammonium fixed after 7 days. Nommik, according to McIntosh (35, p. 18), reported that ammonium fixation by soil clay minerals was 77 and 90 percent complete after 1 and 24 hours of ammoniation, respectively, when total fixation was based on an ammoniation period of six days.

McIntosh (35, p. 113) found that ammonium fixation by vermiculite was 92 percent complete within 12 hours when based on the total ammonium fixed after 24 hours of ammoniation. When the soil was ammoniated for 96 hours, fixation by the soil clay was 68 and 88 percent after one minute and 24 hours, respectively.

#### Importance of Fixed Ammonium

The soluble and exchangeable forms of ammonium have been shown to be readily available or nearly so to a biological system. Bower (15) reported that only 13 to 28 percent of the difficultly exchangeable ammonium was nitrified, whereas the values for readily exchangeable ammonium were 78 to 87 percent for the same period. Allison et al. (2) showed that usually less than 10 percent of the fixed ammonium was converted into nitrates by nitrifying bacteria during a period of 6 to 16 weeks.

Millet grown in the green house assimilated 7 percent of the nonexchangeable ammonium that had been fixed by air drying (3).

The reduced availability of clay fixed ammonium to biological systems is further supported by data indicating that many soils contain several hundred pounds of clay fixed ammonium per acre (3, 7, 28, 57) under conditions where an active biological population has reduced the level of exchangeable and soluble ammonium to nearly zero pounds per acre.

In summary, it can be concluded from the work of various investigators that large quantities of  $\text{NH}_4^+$  may become fixed in soils where the predominant clay minerals are vermiculite, illite and montmorillonite. Various factors may influence the fixation of  $\text{NH}_4^+$  in soils. The values of fixed  $\text{NH}_4^+$  obtained, in the laboratory, depend upon the type of cation employed to remove exchangeable  $\text{NH}_4^+$  from the exchange complex. Fixation of  $\text{NH}_4^+$  may be of considerable importance, since the availability of fixed  $\text{NH}_4^+$  is considerably lower than an equivalent amount of either soluble or exchangeable  $\text{NH}_4^+$ .

### III. MATERIALS AND METHODS

#### Soils

The soil samples for the present study were obtained from the Lebanese Agricultural Research Institute, Tell Amara, where a fertilizer pot experiment to evaluate the fertility status of 10 different soils, representing 10 soil series of South Lebanon, was conducted. They collected the soil samples during May, 1964. A bulk sample, about 200 Kg, was taken to a depth of 30 cm from 6 to 8 points in the field. Each field was a few dunums in size. The soil samples were air dried, the clods crushed and then passed through a 5 mm screen to remove larger stones and gravels. Each sample was thoroughly mixed and divided into four quarters. A sample of 2 Kg soil per pot was taken from these quarters.

The experimental design used by them for the crop response study was a central composite, rotatable, incomplete factorial. The variables were the nutrients, N, P, K, S, and Mg and were applied to the soils in the form of solutions. Wheat was grown for about six months.

At the end of the experiment, conducted at Tell Amara, 2 samples from each of 3 soils were selected

for the ammonium fixation study reported here. One of the two samples of each soil received a high level of ammonium and one a low level with all nutrients kept constant. The various amounts of fertilizers added to these soils are given in Table 1.

The 3 soils used were the brown, Bazouriye series, and the black, Innsar series, both from Babliye and the gray soil, Zaoutar series, from Nabatiye Zaoutar (8, pp. 26-33).

The soils from the pots were ground, passed through a 28 mesh sieve and stored in glass jars for use. Table 2 lists the chemical and physical characterization made on these soils for the ammonium fixation investigations.

#### Analytical Methods

pH: The pH values of the soils were determined on 1:2.5 soil-water suspension using a pH meter with a glass electrode.

Cation exchange capacity: The cation exchange capacity was determined by extracting with sodium acetate (pH 7.4) as suggested by the U.S. Salinity Laboratory (45, p. 101). The sodium concentrations was then determined photometrically by the use of Beckman spectrophotometer, model DU with flame photometer attachment.

Total nitrogen: Total nitrogen on soils was determined by the Kjeldahl procedure recommended by Bremner (17, p. 13).

Table 1. Amounts of various fertilizers added, mg per 2 Kg of soil, before planting wheat.

Pot 1, low in $\text{NH}_4^+$			Pot 2, high in $\text{NH}_4^+$		
Source of nutrients	Nutrient	Amount added	Source of nutrients	Nutrient	Amount added
$\text{K}_2\text{SO}_4$	K	100.0	$\text{KNO}_3$	K	100.0
	S	41.0			
$\text{Mg}(\text{H}_2\text{PO}_4)_2$	Mg	39.2		$\text{NO}_3^-$	158.9
	P	100.0	$\text{Mg}(\text{H}_2\text{PO}_4)_2$	Mg	39.2
$\text{MgSO}_4$	Mg	44.7		P	100.0
	S	59.0	$\text{MgSO}_4$	Mg	60.5
$\text{MgNO}_3$	Mg	16.1		S	80.2
	$\text{NO}_3^-$	81.8	$(\text{NH}_4)_2\text{SO}_4$	$\text{NH}_4^+$	22.2
$\text{NH}_4\text{NO}_3$	$\text{NO}_3^-$	14.4	$\text{NH}_4\text{NO}_3$	$\text{NO}_3^-$	767.8
	$\text{NH}_4^+$	4.2		$\text{NH}_4^+$	222.9
Total $\text{NO}_3^-$	-	96.2	Total $\text{NO}_3^-$	-	926.7
Total $\text{NH}_4^+$	-	4.2	Total $\text{NH}_4^+$	-	245.1

Table 2. Characterization of the soils used in ammonium fixation investigations.

Properties	Soils					
	Black		Gray		Brown	
pH	8.2		8.4		7.2	
C.E.C. me per 100 g	68.27		25.72		39.66	
Total Nitrogen %	0.21 <sup>x</sup>	0.22 <sup>xx</sup>	0.10 <sup>x</sup>	0.11 <sup>xx</sup>	0.10 <sup>x</sup>	0.11 <sup>xx</sup>
Organic Matter %	2.36 <sup>x</sup>	3.28 <sup>xx</sup>	1.38 <sup>x</sup>	1.40 <sup>xx</sup>	1.25 <sup>x</sup>	1.58 <sup>x</sup>
CaCO <sub>3</sub> %	3.72		71.00		0.00	
Clay	50.8		42.8		46.8	
Silt	34.2		41.0		40.0	
Sand	15.0		16.2		13.2	
Textural Class	Clay		Silty clay		Clay	

x and xx represent the data of soils receiving 2 and 122 ppm NH<sub>4</sub><sup>+</sup>, respectively.

Organic matter: Organic matter was determined by the method of Walkley-Black as described by Jackson (30, pp. 219-221).

Calcium carbonate: The alkaline earth carbonates were determined by the manometer method proposed by Woodward (58).

Mechanical analysis: The percentage of sand, silt and clay was determined by the Bouyoucos method (13), using sodium hexametaphosphate as the dispersing agent.

Textural classes were determined from the conventional textural triangle.

Determination of original total ammonium and exchangeable ammonium: The method of Bremner (16, pp. 148-149) was used for the determination of original and exchangeable ammonium. In the case of calcareous soils, the original ammonium was also determined after destroying the carbonates by the method of Dhariwal and Stevenson (19).

Estimation of fixed ammonium: Fixed ammonium was estimated by subtracting the ammonium extracted by  $\underline{N}$  KCl - exchangeable  $\text{NH}_4^+$  - from the original total ammonium released by the treatments with hydrofluoric acid.

Determination of total ammonium fixing capacity of the soils: Two g of the soils (oven dry basis) were weighed into a centrifuge tube and 20 ml of  $\underline{N}$   $\text{NH}_4\text{Cl}$  were added. The soils were shaken for five minutes and the supernatant liquid discarded after centrifugation. This procedure was



repeated for three times.  $\text{NH}_4\text{Cl}$  was added for the fourth time, the tubes were stoppered and stored for the desired period of time. Ammonium fixing capacity was determined after 12, 24, and 144 hours of ammoniation by the procedure described below.

Free  $\text{NH}_4^+$  was removed by washing with 80 percent ethyl alcohol until a negative Nessler test was obtained. Usually the soils required 4 to 5 washings, using 25 ml each time. Total ammonium content was determined on wet, air dry, and oven dry basis by the  $\underline{\text{N}}$  HF:  $\underline{\text{N}}$  HCl method as described by Bremner (16, pp. 148-149). In the case of calcareous soils, the carbonates were destroyed by the method of Dhariwal and Stevenson (19) before treating the soils with  $\underline{\text{N}}$  HF:  $\underline{\text{N}}$  HCl.

An electric fan was used to air dry the soils after the free  $\text{NH}_4^+$  was removed with alcohol. For oven dry treatments the soils were kept in an oven at a temperature of  $50^\circ\text{C}$  for 24 hours. A flow sheet for the determination of total ammonium, after saturating the soil with  $\underline{\text{N}}$   $\text{NH}_4\text{Cl}$ , is given in Figure 1.

Determination of total exchangeable and total fixed ammonium after saturating the soils with  $\underline{\text{N}}$   $\text{NH}_4\text{Cl}$ : The term total exchangeable ammonium and total fixed ammonium will refer to the exchangeable and fixed ammonium following the ammoniation of the soils compared to the exchangeable ammonium and the fixed ammonium as originally

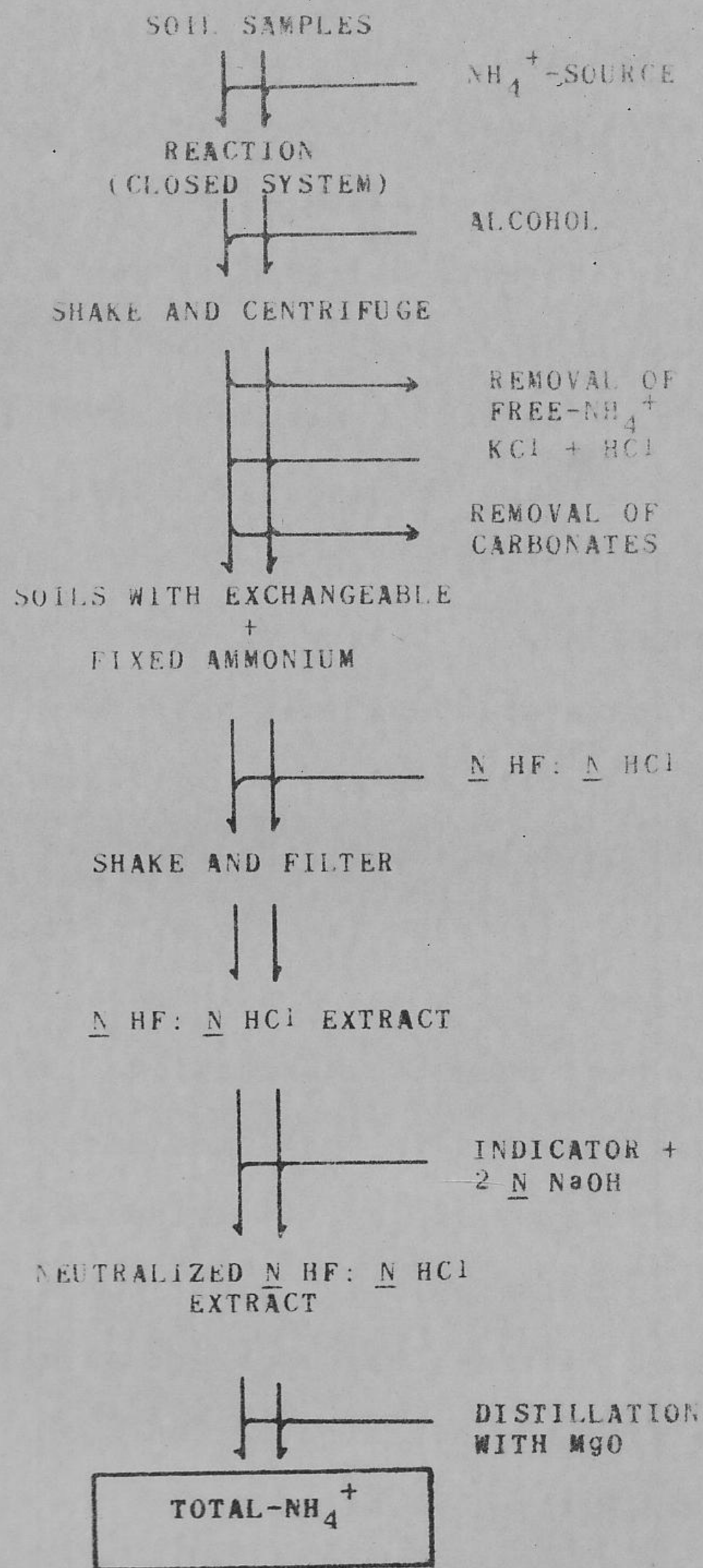


Figure 1. Flow sheet for determining total (exchangeable + fixed) ammonium in soils after saturating with  $\text{N NH}_4\text{Cl}$ .

found in the soil before ammoniation. The total exchangeable and total fixed ammonium on these soils were determined separately as described below. The purpose of these determinations was to evaluate the estimated total fixed ammonium values as compared with the values obtained by direct determination of the total fixed ammonium. The estimated total fixed ammonium values were obtained by subtracting the total exchangeable ammonium from the total ammonium determined by the  $\underline{\text{N}}$  HF:  $\underline{\text{N}}$  HCl method.

Soil samples were saturated with  $\underline{\text{N}}$   $\text{NH}_4\text{Cl}$ , following the procedure given under section "determination of total ammonium fixing capacity of the soils".

The free  $\text{NH}_4^+$  was washed out with 80 percent alcohol. Following the alcohol washings, exchangeable ammonium was extracted with  $\underline{\text{N}}$  KCl until a negative Nessler test was obtained. Potassium ions were used to replace "readily exchangeable ammonium" without the concurrent release of fixed ammonium (44, p. 26). Chloride was selected as the anion since chloride salts are water soluble and chloride has not been reported to form complexes with the aluminum silicate and with the iron and aluminum hydrous oxides in soils (44, p. 27). The KCl extract was collected and diluted with distilled water to a volume of 200 ml. Exchangeable  $\text{NH}_4^+$ , using an aliquot of this extract, was determined by distillation with MgO.

After removing the "readily exchangeable ammonium"

from the soils (carbonates were destroyed in case of calcareous soils), the fixed ammonium was determined by the method of Bremner (16, pp. 148-149). A flow sheet showing the different steps followed in the above determinations is given in Figure 2.

Effect of different extractants on the amount of fixed ammonium in the soils: Total ammonium fixing capacity of the soils was also determined on wet, air dry, and oven dry bases using the following extractants to replace the "readily exchangeable ammonium" from the soils:

1.  $\underline{N}$   $\text{CaCl}_2$
2.  $\underline{N}$   $\text{NaCl}$
3.  $\underline{N}$   $\text{CaCl}_2$  + 10 percent glycerol
4.  $\underline{N}$   $\text{CaCl}_2$  + 20 percent glycerol
5.  $\underline{N}$   $\text{NaCl}$  + 10 percent glycerol
6.  $\underline{N}$   $\text{NaCl}$  + 20 percent glycerol

The procedure followed in the determination of the "readily exchangeable ammonium" with the above extractants was the same as the method using  $\underline{N}$   $\text{KCl}$  as the extractant mentioned in section on "determination of total  $\text{NH}_4^+$  fixing capacity of the soils". The difference between the total ammonium (as determined previously) and the ammonium removed by these extractants gave the values of the total fixed ammonium.

Ammonium fixation of the calcareous soils when the carbonates were destroyed before ammoniation: Total

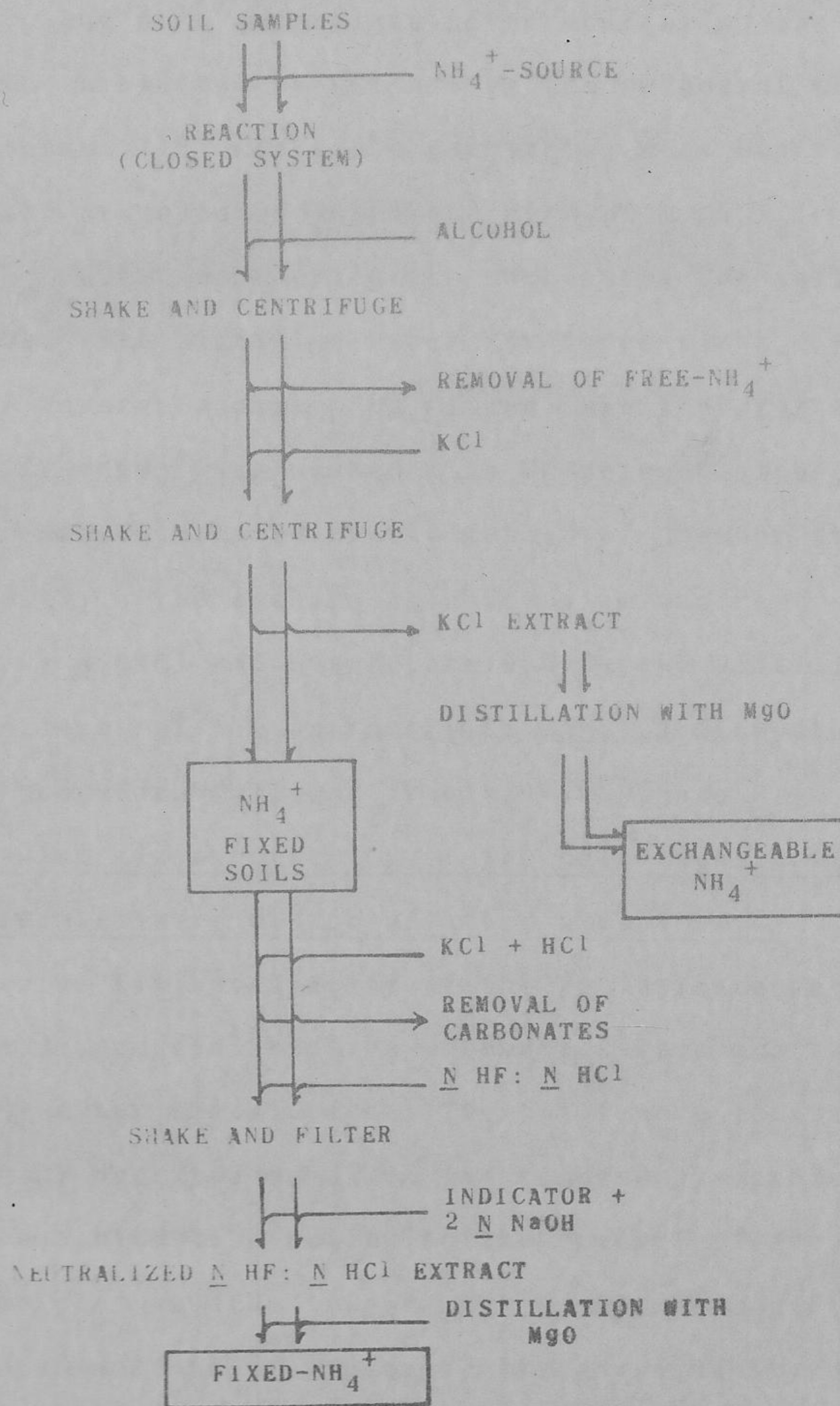


Figure 2. Flow sheet for determining exchangeable and fixed ammonium in the soils after saturating with  $\text{N NH}_4\text{Cl}$ .

ammonium fixation of the two calcareous soils, black and gray, was also determined after destroying the alkaline earth carbonates by HCl and by the method of Dhariwal and Stevenson (19) where the carbonates were destroyed by HCl in the presence of  $\underline{N}$  KCl and also of  $\underline{N}$  CaCl<sub>2</sub>.

After destroying the carbonates the soils were washed with distilled water for three times. The soils were saturated with  $\underline{N}$  NH<sub>4</sub>Cl and then kept for 144 hours. The free NH<sub>4</sub><sup>+</sup> was washed with 80 percent alcohol. Total NH<sub>4</sub><sup>+</sup> was determined by the method of Bremner (16, pp. 148-149). The exchangeable ammonium was removed by  $\underline{N}$  KCl and by  $\underline{N}$  NaCl and was determined by the distillation of an aliquot of the extract with MgO. A flow sheet showing the procedure followed is given in Figure 3.

Ammonium fixing capacity of the calcareous soils when the carbonates were destroyed after ammoniation: The ammonium fixing capacity of the two calcareous soils was also determined when the carbonates were destroyed with  $\underline{N}$  HCl after ammoniation. The soils were saturated with  $\underline{N}$  NH<sub>4</sub>Cl and free ammonium was removed by washing with 80 percent alcohol. Following the removal of free ammonium, carbonates were destroyed with  $\underline{N}$  HCl. Ammoniated soil samples were then exposed to air dry or heat treatments. Total ammonium, KCl exchangeable ammonium, and NaCl exchangeable ammonium were then determined by the method of Bremner (16, pp. 148-149).

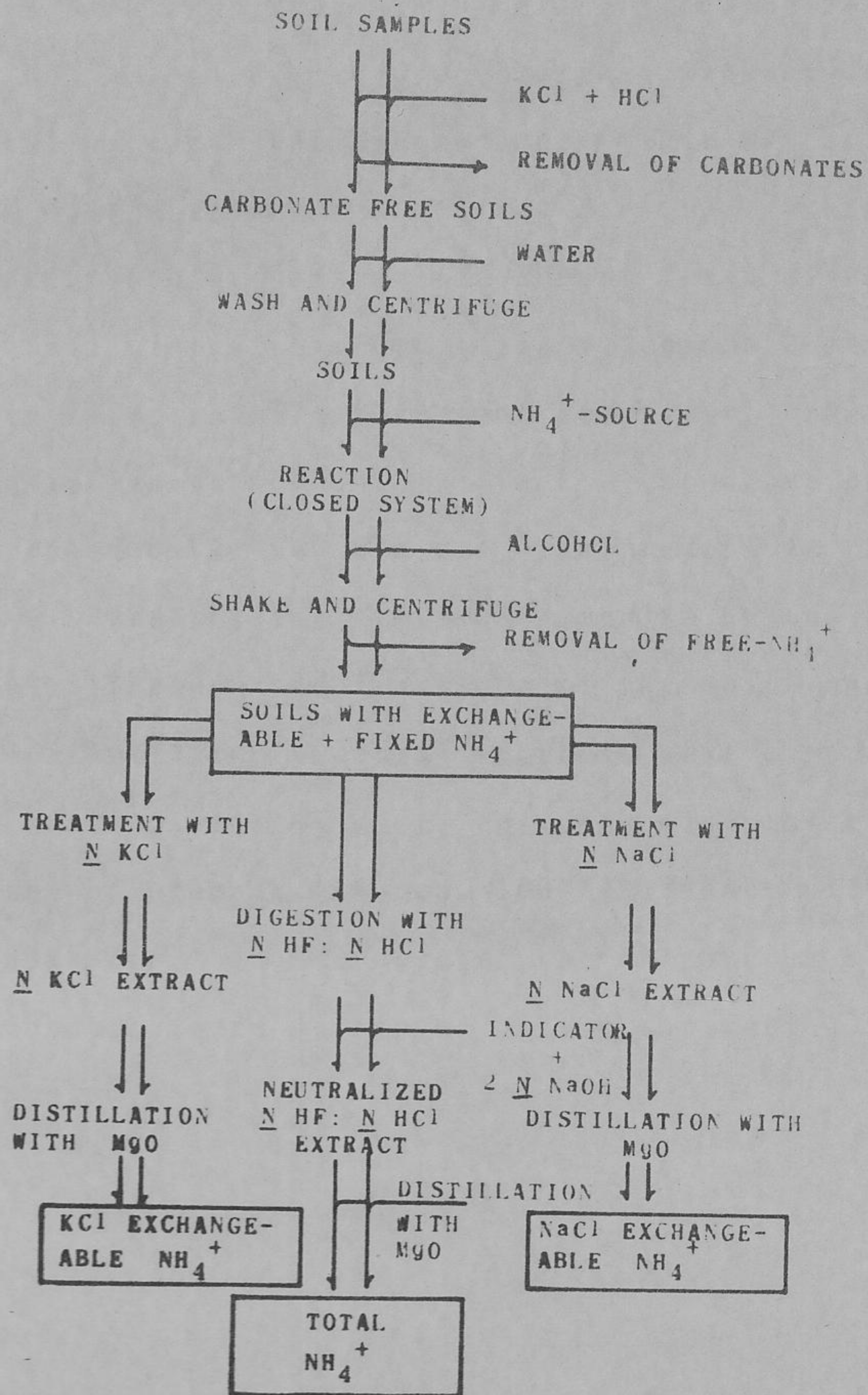


Figure 3. Flow sheet for determining total ammonium, N KCl exchangeable ammonium, and N NaCl exchangeable ammonium after destroying the carbonates.

Ammonium fixation by the clay and by the silt plus sand fractions of the soils: The clay was separated from the silt plus sand fractions by dispersing the soils in dilute  $\text{Na}_2\text{CO}_3$  solution (1 g per 9 liters) without destroying the alkaline earth carbonates and organic matter.

The soils were stirred for five minutes and centrifuged at a speed of 750 rpm for 5 minutes using a Sorvall centrifuge. This separated the 2 micron or less clay from the silt plus sand fractions. The supernatant liquid was poured into a flask. The above operation was repeated until no more clay was present in the suspension.

The originally fixed ammonium by the clay and by the silt plus sand fractions of the soils and the total ammonium fixing capacity of these soil separates after saturating with  $\underline{\text{N}}$   $\text{NH}_4\text{Cl}$ , was determined by the method given by Bremner (16, pp. 148-149) under different conditions. In the case of the calcareous soils, the carbonates were destroyed before estimating the fixed ammonium.



#### IV. RESULTS AND DISCUSSION

##### Original Fixed Ammonium in the Soils

The results (Table 3) indicate that all the soils investigated contained fixed ammonium. The black soil which received 2 ppm of  $\text{NH}_4^+$  contained 0.61 me of  $\text{NH}_4^+$  per 100 g of soil (110 ppm) before destroying the carbonates. The quantities of ammonium fixed, in the same soil, were 0.92 me per 100 g (166 ppm) when the  $\text{NH}_4^+$  was applied at the rate of 122 ppm. The corresponding values for the gray soils were 0.12 and 0.23 me of  $\text{NH}_4^+$  per 100 g of soil (22 and 41 ppm), respectively. When the  $\text{NH}_4^+$  was applied at the rate of 2 ppm to the non-calcareous brown soil, the fixed ammonium was 0.77 me per 100 g (139 ppm); the amount of fixed ammonium was 1.05 me per 100 g (189 ppm) when the  $\text{NH}_4^+$  was applied at the rate of 122 ppm. However, the quantities of fixed ammonium, in the calcareous soils, when estimated without destroying the carbonates, were less than when compared to the values obtained after destroying the carbonates. In the case of the black soil which received a low level of  $\text{NH}_4^+$ , the quantities of fixed ammonium increased by 30 percent when estimated after destroying the carbonates. The corresponding increase for the same soil, receiving high level

Table 3. Original fixed ammonium in the different soils without destroying and after destroying the carbonates.

Soil	Level of $\text{NH}_4^+$ applied	me of $\text{NH}_4^+$ per 100 g					
		Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>
		Without destroying the carbonates			After destroying the carbonates		
Black	Low <sup>x</sup>	1.78	1.17	0.61	1.96	1.17	0.79
	High <sup>x</sup>	2.31	1.39	0.92	2.49	1.39	1.10
Gray	Low <sup>x</sup>	0.84	0.72	0.12	1.01	0.72	0.29
	High <sup>x</sup>	1.01	0.78	0.23	1.18	0.78	0.40
Brown	Low <sup>x</sup>	1.53	0.76	0.77	-	-	-
	High <sup>x</sup>	1.87	0.82	1.05	-	-	-

<sup>x</sup> The low level refers to 2 ppm and the high level refers to 122 ppm of  $\text{NH}_4^+$

<sup>xx</sup> Exch. = the exchangeable  $\text{NH}_4^+$  was extracted with N KCl.

<sup>++</sup> The fixed ammonium was calculated by subtracting the exchangeable- $\text{NH}_4^+$  from the total- $\text{NH}_4^+$ .

of  $\text{NH}_4^+$ , was 20 percent. The percentage increase in the gray soil, receiving low and high levels of  $\text{NH}_4^+$ , was 142 and 74 percent, respectively.

These results indicate the necessity of destroying the carbonates before making a quantitative estimate of the fixed ammonium. This agrees with Dhariwal and Stevenson (19) who suggested that in the case of calcareous soils, the carbonates should be destroyed before estimating the fixed ammonium in soils. The reason is that sufficient amounts of HF would be inactivated as insoluble  $\text{CaF}_2$  in the presence of  $\text{CaCO}_3$  which lowers the efficiency of extracting the fixed ammonium.

The results also showed that the quantities of fixed ammonium were more than the amounts applied to the soils. This indicated that the soils already contained considerable amounts of fixed ammonium.

The quantities of ammonium fixed in the black, gray, and brown soils were 46, 16, and 41 percent of the ammonium applied, respectively. These increases in the amounts of fixed ammonium were obtained after a period of about 6 months from the time of the fertilizer application. With high rates of  $\text{NH}_4^+\text{-N}$  application, a considerable amount was tied up in a fixed form which was not used by the crop grown. Further work is needed to determine the rate of release to succeeding crop under field conditions. Also, further study is needed with regard to the amount

of fixation with different rates of  $\text{NH}_4^+$  application.

#### Total Ammonium Fixing Capacity of the Soils

Total  $\text{NH}_4^+$  (exchangeable plus fixed) was determined by digesting the soils with N HF: N HCl and then the extract was distilled with MgO. The exchangeable ammonium was removed by N KCl, after washing the free ammonium with alcohol, and determined by distillation of the extract with MgO. The fixed ammonium was calculated by subtracting the exchangeable ammonium from the total ammonium. Tables 4, 5, and 6 represent the data of total, exchangeable, and fixed ammonium determined by the method given above.

Using an alternative method, the total fixed ammonium was determined experimentally. After washing the free ammonium with alcohol, the exchangeable ammonium was removed with N KCl. The fixed ammonium was then determined by digesting the soils with N HF: N HCl and the extract was then distilled with MgO. The results (Table 7) show that the calculated fixed ammonium agreed with the quantities of fixed ammonium determined directly by digesting the soils with N HF: N HCl (Table 6), after removing the exchangeable ammonium with N KCl. Therefore, in subsequent studies the fixed ammonium content of the soils was calculated by subtracting the exchangeable ammonium, removed by various cations, from the total

Table 4. Total ammonium, exchangeable ammonium extracted with N KCl and total fixed ammonium in the soils, under different conditions, based on ammoniation period of 12 hours.

Soils	me of $\text{NH}_4^+$ per 100 g								
	Wet basis			Air dry basis			Oven dry basis		
	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>
Black I <sup>x</sup>	52.96	50.56	2.40	52.96	50.94	2.02	52.84	50.92	1.92
II <sup>x</sup>	53.54	51.10	2.44	52.98	50.96	2.02	51.98	50.02	1.96
Average	53.25	50.83	2.42	52.97	50.95	2.02	52.41	50.47	1.94
Gray I <sup>x</sup>	22.56	21.85	0.71	22.54	22.01	0.53	21.40	20.90	0.50
II <sup>x</sup>	22.76	22.07	0.69	22.24	21.65	0.59	21.96	21.50	0.46
Average	22.66	21.96	0.70	22.39	21.83	0.56	21.68	21.20	0.48
Brown I <sup>x</sup>	37.76	36.29	1.47	38.02	36.50	1.52	38.92	36.85	2.07
II <sup>x</sup>	37.74	36.31	1.43	38.42	36.98	1.44	39.00	36.91	2.09
Average	38.25	36.80	1.45	38.72	36.74	1.48	38.96	36.88	2.08

<sup>x</sup> Soils I and II refer to low level (2 ppm) and high level of  $\text{NH}_4^+$  (122 ppm), respectively, applied to the soils before planting.

<sup>xx</sup> Exch. = Exchangeable.

<sup>++</sup> The fixed- $\text{NH}_4^+$  was calculated by subtracting the exchangeable- $\text{NH}_4^+$  from the total- $\text{NH}_4^+$

Table 5. Total ammonium, exchangeable ammonium extracted with  $\text{N KCl}$  and total fixed ammonium in the soils, under different conditions, based on ammoniation period of 24 hours.

Soils	me of $\text{NH}_4^+$ per 100 g											
	Wet basis					Air dry basis					Oven dry basis	
	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>
Black I <sup>x</sup>	53.64	51.23	2.41	52.96	50.94	2.02	52.90	50.96	1.94			
II <sup>x</sup>	54.00	51.55	2.45	53.08	51.02	2.06	52.84	50.88	1.96			
Average	53.82	51.29	2.43	53.02	50.98	2.04	52.87	50.92	1.95			
Gray I <sup>x</sup>	22.63	21.95	0.68	22.50	21.90	0.60	21.40	20.92	0.48			
II <sup>x</sup>	22.71	21.99	0.72	21.76	21.24	0.52	21.88	21.38	0.50			
Average	22.67	21.97	0.70	22.13	21.57	0.56	21.64	21.15	0.49			
Brown I <sup>x</sup>	38.88	37.40	1.48	38.68	37.20	1.48	38.78	36.74	3.04			
II <sup>x</sup>	39.20	37.74	1.46	38.96	37.44	1.52	38.86	36.72	2.14			
Average	39.04	37.57	1.47	38.82	37.32	1.50	38.82	36.73	2.09			

<sup>x</sup> Soils I and II refer to low level (2 ppm) and high level of  $\text{NH}_4^+$  (122 ppm), respectively, applied to the soils before planting.  
<sup>xx</sup> Exch. = Exchangeable.  
<sup>++</sup> The fixed- $\text{NH}_4^+$  was calculated by subtracting the exchangeable- $\text{NH}_4^+$  from the total- $\text{NH}_4^+$ .

Table 6. Total ammonium, exchangeable ammonium extracted with N KCl and total fixed ammonium in the soils, under different conditions, based on ammoniation period of 144 hours.

Soil	me of $\text{NH}_4^+$ per 100 g								
	Wet basis		Air dry basis		Oven dry basis				
	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>
Black I <sup>x</sup>	54.64	52.16	2.48	53.24	51.18	2.06	52.87	50.93	1.94
II <sup>x</sup>	54.28	51.82	2.46	53.58	51.46	2.12	52.53	50.51	2.02
Average	54.46	51.99	2.47	53.41	51.32	2.09	52.70	50.72	1.98
Gray I <sup>x</sup>	23.74	22.94	0.80	22.40	21.77	0.63	21.45	20.94	0.51
II <sup>x</sup>	23.79	23.03	0.76	22.36	21.81	0.55	22.40	21.84	0.56
Average	23.76	22.98	0.78	22.38	21.79	0.59	21.92	21.39	0.53
Brown I <sup>x</sup>	39.97	38.42	1.55	39.97	38.24	1.73	39.31	37.21	2.10
II <sup>x</sup>	39.65	38.18	1.47	39.31	37.54	1.77	39.43	37.33	2.10
Average	39.81	38.30	1.51	39.64	37.89	1.75	39.37	37.27	2.10

<sup>x</sup> Soils I and II refer to low level (2 ppm) and high level of  $\text{NH}_4^+$  (122 ppm), respectively, applied to the soils before planting.

<sup>xx</sup> Exch. = Exchangeable.

<sup>++</sup> The fixed- $\text{NH}_4^+$  was calculated by subtracting the exchangeable- $\text{NH}_4^+$  from the total- $\text{NH}_4^+$ .

Table 7. Total fixed ammonium in the soils, determined and calculated, under different conditions, based on ammoniation period of 144 hours.

Soils	meq of $\text{NH}_4^+$ per 100 g					
	Wet basis		Air dry basis		Oven dry basis	
	Determined <sup>x</sup>	Calculated <sup>xx</sup>	Determined <sup>x</sup>	Calculated <sup>xx</sup>	Determined <sup>x</sup>	Calculated <sup>xx</sup>
Black I <sup>xxx</sup>	2.48	2.48	2.06	2.06	1.87	1.94
II <sup>xxx</sup>	2.47	2.46	2.12	2.12	2.03	2.02
Average	2.48	2.47	2.09	2.09	1.95	1.98
Gray I <sup>xxx</sup>	0.75	0.80	0.63	0.63	0.52	0.51
II <sup>xxx</sup>	0.80	0.76	0.55	0.55	0.56	0.56
Average	0.78	0.78	0.59	0.59	0.54	0.53
Brown I <sup>xxx</sup>	1.54	1.55	1.73	1.73	2.10	2.10
II <sup>xxx</sup>	1.50	1.47	1.78	1.77	2.08	2.10
Average	1.52	1.51	1.76	1.75	2.09	2.10

x Determined by digesting the soils with  $\text{NHF}$ :  $\text{NHCl}$  after removing the exchangeable  $\text{NH}_4^+$  with  $\text{N KCl}$ .

xx The calculated fixed  $\text{NH}_4^+$  was taken from Table 6.

xxx Soils I and II refer to low level (2 ppm) and high level (122 ppm), of  $\text{NH}_4^+$  respectively, applied to the soil before planting.



ammonium (exchangeable plus fixed) determined by  $\underline{N}$  HF:  
 $\underline{N}$  HCl.

It has been known for many years that ammonium can be retained by soil minerals. The three main types of soil minerals capable of fixing ammonium are vermiculite, illite, and montmorillonite. Since these minerals vary in different soils, therefore, the quantities of ammonium fixed will also vary in different soils, depending upon the type and amount of the minerals present.

The data in Tables 4, 5, and 6 give the quantities of total- $\text{NH}_4^+$ , exchangeable- $\text{NH}_4^+$ , and fixed- $\text{NH}_4^+$  in the different soils, under different conditions, after 12, 24, and 144 hours of ammoniation, respectively. In general the black soil showed the highest ammonium fixing capacity and the gray soil gave the lowest ammonium fixing capacity. The quantities of  $\text{NH}_4^+$  fixed by the brown soil were intermediate. This trend of  $\text{NH}_4^+$  fixation, in the different soils could be attributed to the kind and amount of clay minerals content of these soils.

The  $\text{NH}_4^+$  fixing capacity of these soils could also be related to the cation exchange capacity of these soils. Usually the mechanism of  $\text{NH}_4^+$  fixation is explained by the cation exchange reaction. The phenomenon of fixation is explained by the fact that  $\text{NH}_4^+$  replaces the interlayer cations such as  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ , and  $\text{Na}^+$  and becomes entrapped when the mineral lattice collapses. Therefore, the soil

having high cation exchange capacity, in general, will also have high  $\text{NH}_4^+$  fixing capacity. Thus the black soil having the highest cation exchange capacity also had the highest  $\text{NH}_4^+$  fixing capacity. The cation exchange capacity of the gray soil was the lowest of the three soils and this also gave the lowest values of the  $\text{NH}_4^+$  fixation. The cation exchange capacity and the  $\text{NH}_4^+$  fixing capacity of the brown soil were intermediate.

Figure 4 shows the effect of ammoniation time on the fixation of  $\text{NH}_4^+$  by the black soil under different conditions. The reaction of  $\text{NH}_4^+$ , with the soil, under all the conditions, was rapid. The fixation of  $\text{NH}_4^+$ , on wet, air dry, and oven dry bases, was found to be 97.9, 96.6, and 97.9 percent complete, respectively, after 12 hours of ammoniation when based on the total  $\text{NH}_4^+$  fixed after 144 hours of ammoniation. The percentage fixation in the same soil after 24 hours of ammoniation was found to be 98.4, 97.6, and 98.5 percent complete, under wet, air dry, and oven dry conditions, respectively, when based on the total  $\text{NH}_4^+$  fixed, after 144 hours of ammoniation. These results are in fair agreement with those reported by McIntosh (35, p. 113) who found that the fixation of  $\text{NH}_4^+$  by vermiculite was 92 percent complete within 12 hours of ammoniation when based on the total  $\text{NH}_4^+$  fixed after 24 hours of ammoniation. Similar results were reported by Nommik, and Leggett (35, p. 18).

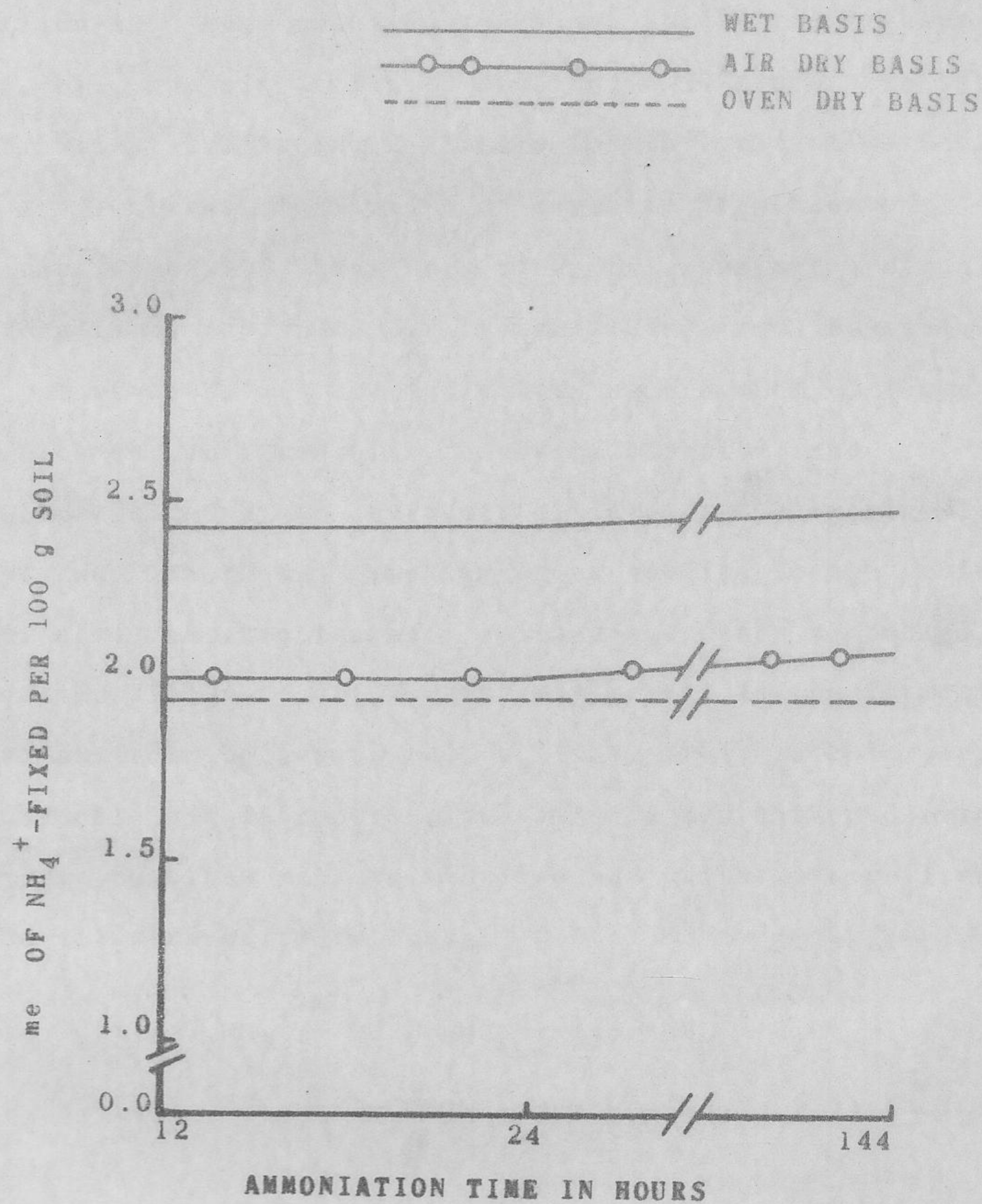
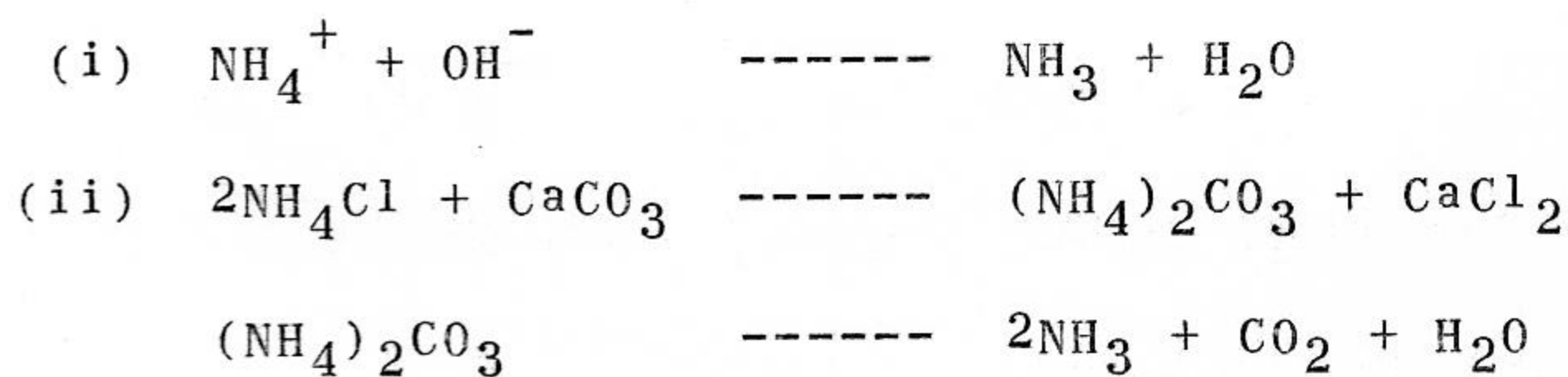


Figure 4. Effect of ammoniation time on the fixation of ammonium by the black soil under different conditions.

The results also show that the maximum levels of fixed- $\text{NH}_4^+$  were obtained under wet conditions (Tables 4, 5, 6). But air drying or heating to  $50^\circ\text{C}$  decreased the fixation, indicating a sizeable loss by volatilization.

Losses of nitrogen as ammonia, from sources containing- $\text{NH}_4^+$ , have been shown to occur under certain conditions (20, p. 193). These losses from the surface applied materials are influenced by a number of factors of which the soil reaction, exchange capacity, and temperature may be instrumental in either promoting losses or reducing them. Ammonium salts applied to the surface of alkaline or calcareous soils can undergo a double decomposition reaction which may result in the formation of ammonium carbonate (20, p. 193). This salt is very unstable and decomposes into ammonia and carbon dioxide. These reaction with an alkaline and calcareous soil may be illustrated as follows:



In general, higher losses are sustained under higher temperatures. Since the black and the gray soils under investigation were calcareous, having an alkaline reaction (Table 2), it is expected that the losses of ammonium as ammonia occurred through the reactions described above on

air drying or heating to 50°C.

Figure 5 shows the effect of ammoniation time on the fixation of  $\text{NH}_4^+$  by the gray soil under wet, air dry, and oven dry conditions. The percentage fixation, under different conditions, ranged from 90 to 95 percent after 12 and 24 hours of ammoniation when based on the total- $\text{NH}_4^+$  fixed after 144 hours. The results of this soil are also in close agreement with the findings of McIntosh (35, p. 113).

The results (Tables 4, 5, 6) of the gray soil also show that the amounts of  $\text{NH}_4^+$  fixed under wet conditions were considerably higher than the values obtained after air drying or heat treatment. The results indicated that the losses of ammonium as ammonia occurred by volatilization through the reactions already explained in the case of the black soil.

A comparison of the black and the gray soils in Table 6 shows that, on the percentage bases, the black soil lost about 15 and 20 percent of the  $\text{NH}_4^+$  after air drying and heating, respectively, when based on the  $\text{NH}_4^+$  fixed under wet conditions. The corresponding losses in the gray soil were 23 and 32 percent. The greater loss of the ammonium in the case of the gray soil could be related to its lower cation exchange capacity (Table 2).

Figure 6 shows the effect of ammoniation time on the fixation of  $\text{NH}_4^+$  by the non-calcareous brown soil

air drying or heating to 50°C.

Figure 5 shows the effect of ammoniation time on the fixation of  $\text{NH}_4^+$  by the gray soil under wet, air dry, and oven dry conditions. The percentage fixation, under different conditions, ranged from 90 to 95 percent after 12 and 24 hours of ammoniation when based on the total- $\text{NH}_4^+$  fixed after 144 hours. The results of this soil are also in close agreement with the findings of McIntosh (35, p. 113).

The results (Tables 4, 5, 6) of the gray soil also show that the amounts of  $\text{NH}_4^+$  fixed under wet conditions were considerably higher than the values obtained after air drying or heat treatment. The results indicated that the losses of ammonium as ammonia occurred by volatilization through the reactions already explained in the case of the black soil.

A comparison of the black and the gray soils in Table 6 shows that, on the percentage bases, the black soil lost about 15 and 20 percent of the  $\text{NH}_4^+$  after air drying and heating, respectively, when based on the  $\text{NH}_4^+$  fixed under wet conditions. The corresponding losses in the gray soil were 23 and 32 percent. The greater loss of the ammonium in the case of the gray soil could be related to its lower cation exchange capacity (Table 2).

Figure 6 shows the effect of ammoniation time on the fixation of  $\text{NH}_4^+$  by the non-calcareous brown soil

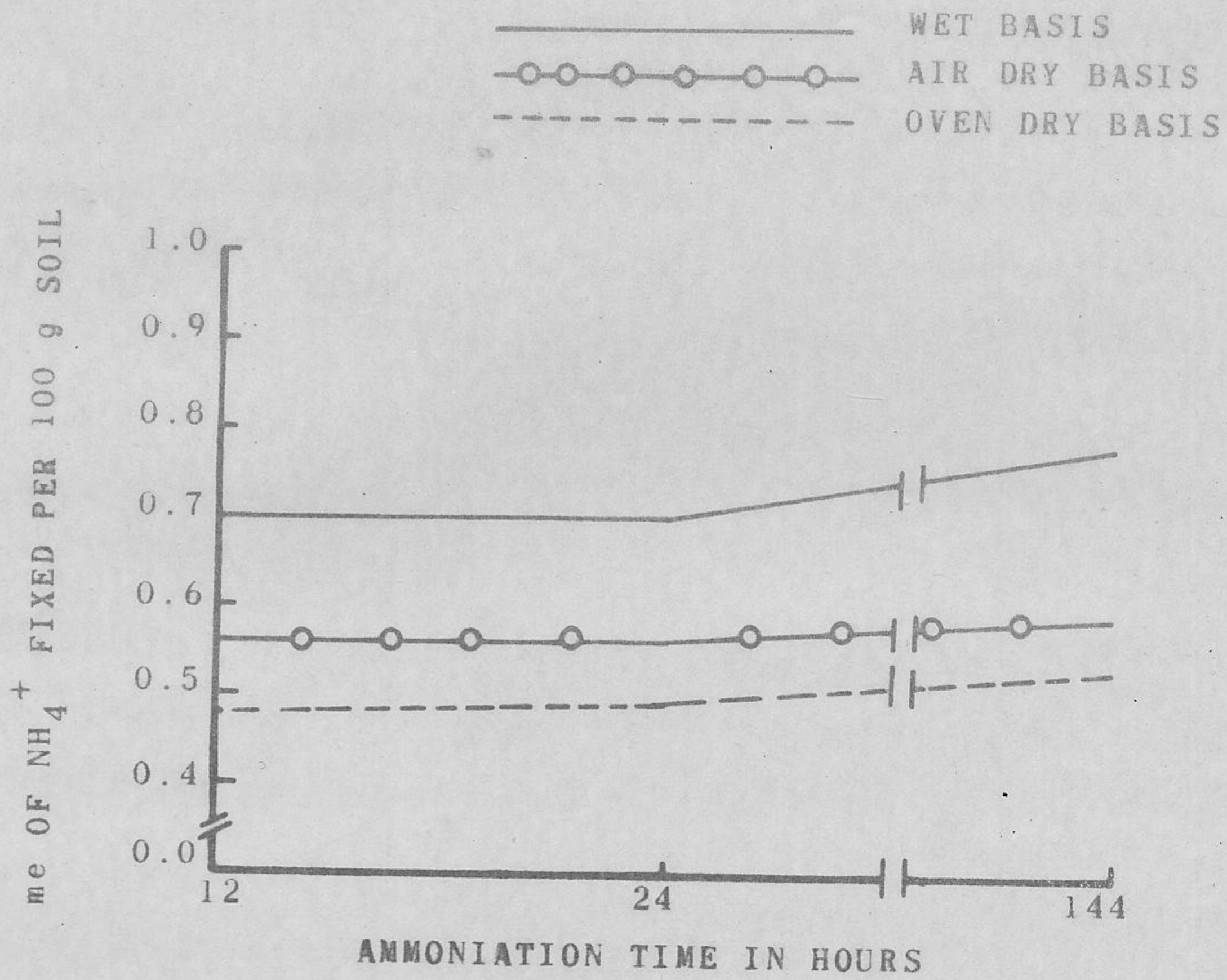


Figure 5. Effect of ammoniation time on the fixation of ammonium by the gray soil under different conditions.

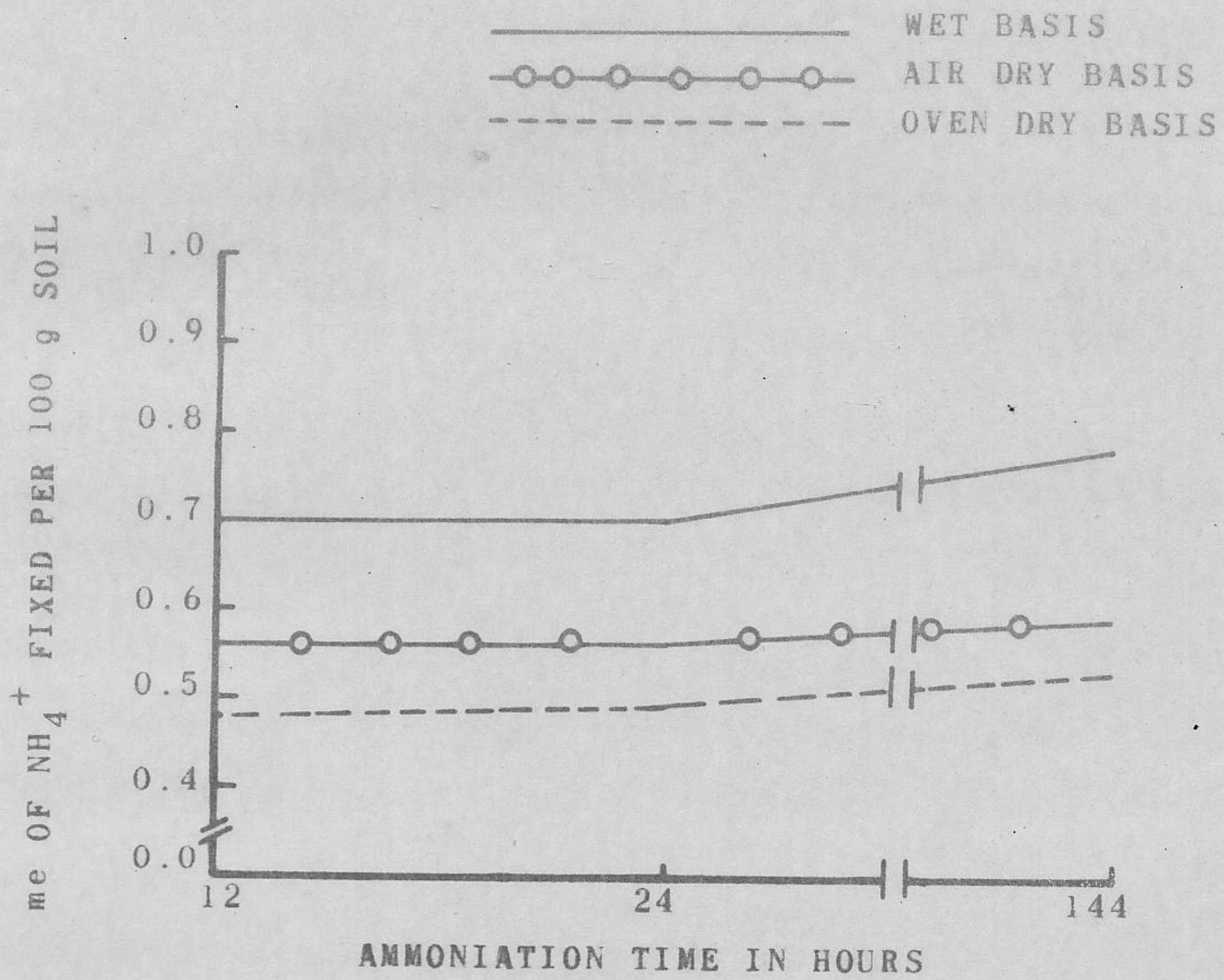


Figure 5. Effect of ammoniation time on the fixation of ammonium by the gray soil under different conditions.



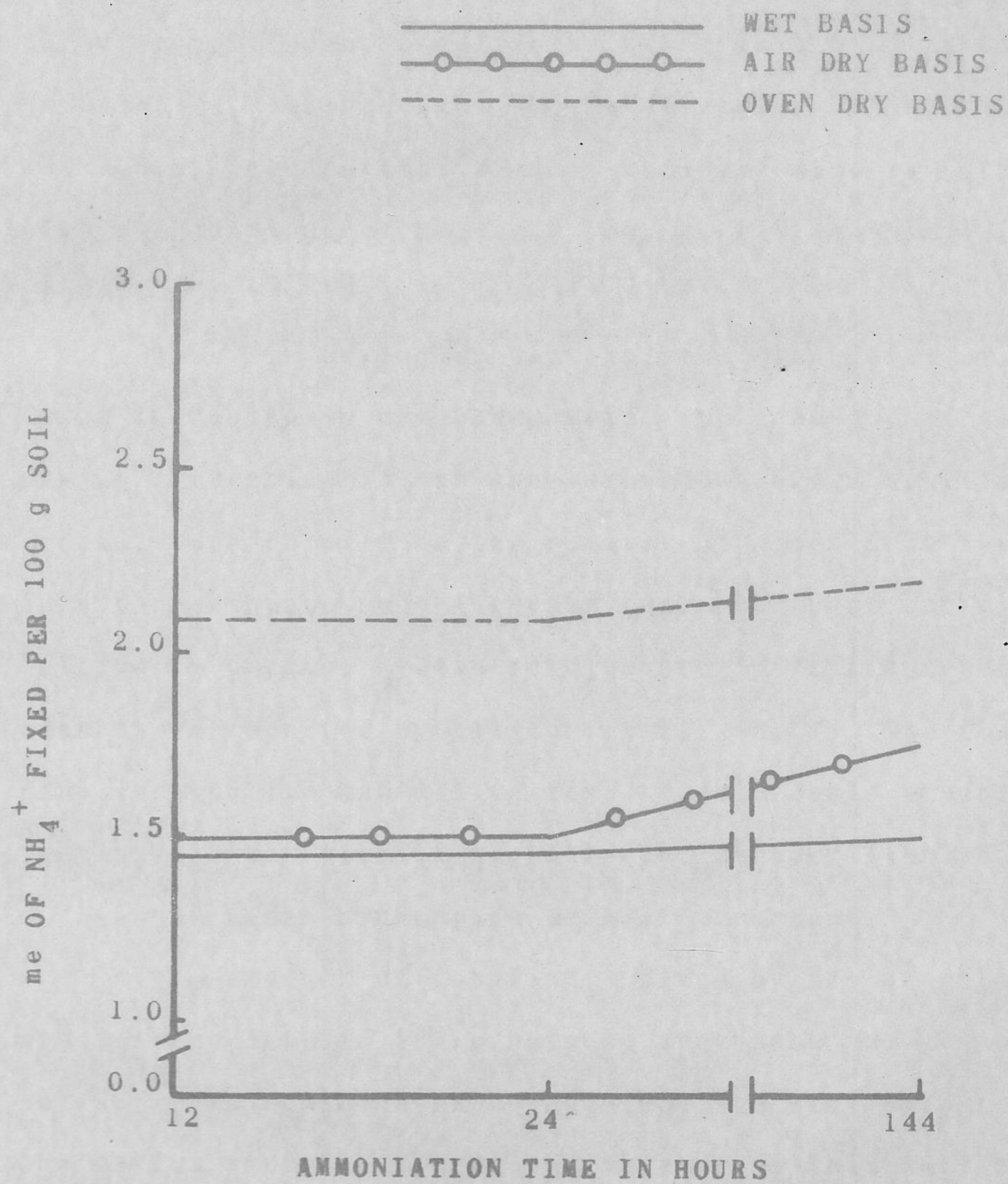


Figure 6. Effect of ammoniation time on the fixation of ammonium by the brown soil under different conditions.

under wet, air dry, and oven dry conditions. The percentage fixation in the brown soil ranged from 84 to 99 percent, under the different conditions, after 12 and 24 hours of ammoniation when based on the total ammonium fixed after 144 hours. The results of this soil are also in agreement with the findings of McIntosh (35, p. 113) and Nommik, and Leggett (35, p. 18).

Upon air drying or heating, the quantities of  $\text{-NH}_4^+$  fixed increased in the brown soil. This effect of air drying or heating in the non-calcareous brown soil is probably due chiefly to the removal of water from the interplaner spaces and increase contraction of the mineral lattice by drying. These results are in fair agreement with those reported by Allison et al. (3, 7), who found that vermiculite and illite fixed considerable amounts of  $\text{-NH}_4^+$  under wet conditions while the montmorillonite fixed more  $\text{-NH}_4^+$  after air drying or heat treatment.

The amounts of total  $\text{-NH}_4^+$  fixed by the brown soil are intermediate in value between the black and the gray soils. This would be expected since the clay content and the cation exchange capacity (Table 2) of this soil were also intermediate.

The foregoing results indicated that  $\text{-NH}_4^+$  fixation may be of practical importance in these soils. Substantial amounts of added  $\text{-NH}_4^+$  may be fixed if it is mixed with the soil under field conditions. Frequently, under some

conditions, crops may fail to assimilate as large a percentage of added  $\text{-NH}_4^+\text{-N}$  as of added nitrate. The combining of the  $\text{-NH}_4^+$  with the clay minerals into a non-exchangeable form may furnish a partial explanation to this fact (2).

Presumably the fixed  $\text{-NH}_4^+$  would be released eventually, but studies of various workers (3, 4, 7, 15) have shown that the availability of fixed  $\text{-NH}_4^+$  to biological systems is less than an equivalent amount of soluble or exchangeable  $\text{-NH}_4^+$ . If nitrifying bacteria are unable to oxidize fixed  $\text{NH}_4^+$  it is unlikely that the crops could utilize it.

#### Some Factors Affecting Ammonium Fixation

The quantities of ammonium fixed in soils, in the laboratory depend upon the conditions employed for the fixation. Therefore, a knowledge of the effects of certain conditions, necessary for non-biological fixation of ammonium, is desirable. The results reported in the following sections show the effect of some factors on the ammonium fixation in the soils.

Influence of cations and glycerol: The calculated fixed ammonium values in Tables 8 and 9 depended upon the kind of the cation employed for replacement of the "readily exchangeable ammonium". In general, N NaCl removed more adsorbed ammonium than did N  $\text{CaCl}_2$ . The amounts of adsorbed

Table 8. Removal of exchangeable ammonium by  $N CaCl_2$  and the levels of fixed ammonium left in the soils, under different conditions, based on ammoniation period of 144 hours.

Soils	me of $NH_4^+$ per 100 g								
	Wet basis			Air dry basis			Oven dry basis		
	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>
Black I <sup>x</sup>	54.64	53.52	1.12	53.24	52.12	1.12	52.87	51.81	1.06
II <sup>x</sup>	54.28	53.04	1.24	53.58	52.50	1.08	52.53	51.45	1.08
Average	54.46	53.28	1.18	53.41	52.31	1.10	52.70	51.63	1.07
Gray I <sup>x</sup>	23.74	23.06	0.68	22.40	21.84	0.56	21.45	20.85	0.60
II <sup>x</sup>	23.79	23.11	0.68	22.36	21.80	0.56	22.40	21.87	0.53
Average	23.76	23.08	0.68	22.38	21.82	0.56	21.92	21.36	0.56
Brown I <sup>x</sup>	39.97	38.36	1.61	39.97	38.28	1.69	39.21	37.61	1.70
II <sup>x</sup>	39.65	38.26	1.39	39.31	37.60	1.71	39.43	37.71	1.72
Average	39.81	38.31	1.50	39.64	37.94	1.70	39.37	37.66	1.71

<sup>x</sup> Soils I and II refer to low level (2 ppm) and high level of  $NH_4^+$  (1.22 ppm), respectively, applied to the soils before planting.

<sup>xx</sup> Exch. = Exchangeable.

<sup>++</sup> The fixed  $NH_4^+$  was calculated by subtracting the exchangeable- $NH_4^+$  from the total- $NH_4^+$ .

Table 9. Removal of exchangeable ammonium by N NaCl and the levels of fixed ammonium left in the soils, under different conditions, based on ammoniation period of 144 hours.

Soils	me of $\text{NH}_4^+$ per 100 g								
	Wet basis			Air dry basis			Oven dry basis		
	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>
Black I <sup>x</sup>	54.64	53.56	1.08	53.24	52.20	1.04	52.87	51.87	1.00
II <sup>x</sup>	54.28	53.16	1.12	53.58	52.50	1.08	52.53	51.45	1.08
Average	54.46	53.36	1.10	53.41	52.35	1.06	52.70	51.66	1.04
Gray I <sup>x</sup>	23.74	23.14	0.60	22.40	21.88	0.52	21.45	20.95	0.50
II <sup>x</sup>	23.79	23.15	0.64	22.36	21.82	0.54	22.40	21.88	0.52
Average	23.76	23.14	0.62	22.38	21.85	0.53	21.92	21.41	0.51
Brown I <sup>x</sup>	39.97	38.41	1.56	39.97	38.37	1.60	39.31	37.63	1.68
II <sup>x</sup>	39.65	38.15	1.50	39.31	37.61	1.70	39.43	37.69	1.74
Average	39.81	38.28	1.53	39.64	37.99	1.65	39.37	37.66	1.71

<sup>x</sup> Soils I and II refer to low level (2 ppm) and high level of  $\text{NH}_4^+$  (122 ppm), respectively, applied to the soils before planting.

<sup>xx</sup> Exch. = Exchangeable.

<sup>++</sup> The fixed- $\text{NH}_4^+$  was calculated by subtracting the exchangeable- $\text{NH}_4^+$  from the total- $\text{NH}_4^+$ .

ammonium removed by  $\underline{\text{N}}$  KCl were the least.

The results in Table 8 show that the average values of the fixed ammonium in the black soil, on wet, air dry, and oven dry bases were 212, 198, and 192 ppm, respectively, when the adsorbed ammonium was removed with  $\underline{\text{N}}$   $\text{CaCl}_2$ . The corresponding figures for the gray soil were 122, 100, and 100 ppm. The average quantities of ammonium fixed in the brown soil were 270, 306, and 376 ppm on wet, air dry, and oven dry bases, respectively.

Table 9 gives the data of fixed ammonium in the soils when the exchangeable ammonium was removed with  $\underline{\text{N}}$  NaCl. The average quantities of the ammonium fixed in the black soil on wet, air dry, and oven dry bases were 198, 191, and 187 ppm, respectively. The average values of the fixed ammonium in the gray soil were 111, 95, and 91 ppm on wet, air dry, and oven dry bases, respectively. The corresponding values for the brown soil were 275, 295, and 307 ppm.

Table 10 gives the difference between the quantities of fixed ammonium left in the soil when the different cations were used to remove the adsorbed ammonium. It is evident from the results that the quantities of fixed ammonium left in the soils depended upon the cation employed to remove the adsorbed ammonium.  $\underline{\text{N}}$   $\text{CaCl}_2$  removed about 52, 47, and 46 percent more  $\text{NH}_4^+$  from the black soil on wet, air dry, and oven dry bases, respectively, than

Table 10. Difference between the quantities of fixed ammonium left in the soil when the different cations were used to remove exchangeable ammonium<sup>+</sup>.

Soils	Difference of cations	me of $\text{NH}_4^+$ per 100 g		
		Wet basis	Air dry basis	Oven dry basis
Black	K - Ca	1.29	0.99	0.91
	K - Na	1.37	1.03	0.94
	Ca - Na	0.08	0.08	0.03
Gray	K - Ca	0.10	0.03	-0.03
	K - Na	0.16	0.06	0.02
	Ca - Na	0.06	0.03	0.05
Brown	K - Ca	0.01	0.05	0.39
	K - Na	-0.02	0.10	0.39
	Ca - Na	0.03	0.05	0.00

<sup>+</sup> The values of the fixed  $\text{NH}_4^+$  for  $\text{K}^+$ ,  $\text{Ca}^{++}$  and  $\text{Na}^+$  were taken from tables, 6, 8, and 9, respectively.

did N KCl. N NaCl removed about 55, 49, and 48 percent more  $\text{NH}_4^+$  than did N KCl from the black soil, on wet, air dry, and oven dry bases, respectively. The difference between the amounts of  $\text{NH}_4^+$  removed by N  $\text{CaCl}_2$  and N NaCl (Table 10) showed that the N NaCl removed approximately 6, 3, and 3 percent more  $\text{NH}_4^+$ , on wet, air dry, and oven dry bases, respectively, than did N  $\text{CaCl}_2$ .

The trend of the results with the other two soils, using the same cations, was the same, except that in the case of the brown soil the quantities of the adsorbed ammonium removed by N  $\text{CaCl}_2$  and N NaCl, on oven dry bases were the same. Also the amounts of fixed ammonium increased in the various stages from wet to oven dry conditions in the non-calcareous brown soil, while it decreased in the two calcareous soils (black and gray). The reason for the decrease was the volatilization of ammonium upon drying.

These results (Tables 6, 8, 9) show that the soils have the property of adsorbing large quantities of ammonium ion and holding it in a form that is not removed by N KCl (Table 6). This fixed ammonium is, however, removed to a slight extent by N NaCl (Table 9) and to a still less extent by N  $\text{CaCl}_2$  (Table 8). The explanation of this phenomenon is given below.

The expansion of the lattice along the C axis and its hydration properties vary with the cation adsorbed and



largely determine the ease of removal of the fixed ammonium. Potassium produces a contracted lattice and hence is unable to replace ammonium, which produces the same type of lattice. On the other hand calcium and sodium expand the lattice along the C axis. This is mainly due to the hydration properties of calcium and sodium which can adsorb more shells of water around their respective nuclei than potassium, which hydrates only slightly. When  $\text{Ca}^{++}$ , and  $\text{Na}^+$  attain bigger sizes, on entering the interplanar space of the mineral lattice, they cause expansion of the lattice along the C axis and, therefore, can replace the fixed ammonium to some extent.

These results are in fair agreement with those reported by Allison et al. (3, 4) and Allison and Roller (5, 6) who found that N NaCl removed the largest portion of  $\text{NH}_4^+$ , whereas N KCl removed the least. The corresponding values with N  $\text{CaCl}_2$  were intermediate.

Table 11 gives the data pertaining to the removal of adsorbed ammonium by N  $\text{CaCl}_2$  plus 10 percent glycerol and the subsequent quantities of fixed ammonium left in the soils. The average quantities of fixed ammonium left in the black soil, after removing the adsorbed ammonium with N  $\text{CaCl}_2$  plus 10 percent glycerol, were 192, 188, and 185 ppm on wet, air dry, and oven dry bases, respectively. The corresponding values for the gray soil were about 110, 99, and 92 ppm. The values of the fixed ammonium in the brown

Table 11. Removal of exchangeable ammonium by  $\text{N CaCl}_2$  plus 10 percent glycerol and the levels of fixed ammonium left in the soils, under different conditions, based on ammoniation period of 144 hours.

Soils	me of $\text{NH}_4^+$ per 100 g								
	Wet basis			Air dry basis			Oven dry basis		
	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>
Black I <sup>x</sup>	54.64	53.62	1.02	53.24	52.20	1.04	52.87	51.85	1.02
II <sup>x</sup>	54.28	53.16	1.12	53.58	52.52	1.06	52.53	51.49	1.04
Average	54.46	53.39	1.07	53.41	52.36	1.05	52.70	51.67	1.03
Gray I <sup>x</sup>	23.74	23.12	0.62	22.40	21.86	0.54	21.45	20.93	0.52
II <sup>x</sup>	23.79	23.19	0.60	22.36	21.80	0.56	21.49	20.99	0.50
Average	23.76	23.15	0.61	22.38	21.83	0.55	21.47	20.96	0.51
Brown I <sup>x</sup>	39.97	38.47	1.50	39.97	38.37	1.60	39.31	37.67	1.64
II <sup>x</sup>	39.65	38.21	1.44	39.31	37.77	1.54	39.43	37.83	1.60
Average	39.81	38.34	1.47	39.64	38.07	1.57	39.37	37.75	1.62

<sup>x</sup> Soils I and II refer to low level (2 ppm) and high level of  $\text{NH}_4^+$  (122 ppm), respectively, applied to the soils before planting.

<sup>xx</sup> Exch. = Exchangeable.

<sup>++</sup> The fixed- $\text{NH}_4^+$  was calculated by subtracting the exchangeable- $\text{NH}_4^+$  from the total- $\text{NH}_4^+$ .

soil were 264, 282, and 291 ppm on wet, air dry, and oven dry bases, respectively.

Table 12 gives the data of adsorbed ammonium removed by  $\underline{\text{N}}$   $\text{CaCl}_2$  plus 20 percent glycerol and the subsequent quantities of fixed ammonium left in the soils. By comparing the average values of the fixed ammonium in Tables 11 and 12 it can be observed that there was no considerable difference between the quantities of fixed ammonium left when  $\underline{\text{N}}$   $\text{CaCl}_2$  plus 10 percent glycerol and  $\underline{\text{N}}$   $\text{CaCl}_2$  plus 20 percent glycerol was used to remove the adsorbed ammonium.

Table 13 and 14 show the data of exchangeable and fixed ammonium when  $\underline{\text{N}}$   $\text{NaCl}$  plus 10 percent glycerol and  $\underline{\text{N}}$   $\text{NaCl}$  plus 20 percent glycerol were employed to remove the adsorbed ammonium. It can be seen from the average values of the fixed ammonium that there was no considerable difference between the results when  $\underline{\text{N}}$   $\text{NaCl}$  was used alone (Table 9) or in combination with glycerol.

These results showed that the calcium plus glycerol expanded the mineral lattice more than did calcium alone where as the sodium plus glycerol expanded the mineral lattice to the same extent as did sodium alone.

From the foregoing results it can be concluded that the different cations or cations plus glycerol removed different amounts of adsorbed ammonium and hence the quantities of ammonium fixed also varied with the cation.

Table 12. Removal of exchangeable ammonium by  $N CaCl_2$  plus 20 percent glycerol and the quantities of fixed ammonium left in the soils, under different conditions, based on ammoniation per 144 hours.

Soils	me of $NH_4^+$ per 100 g								
	Wet basis			Air dry basis			Oven dry basis		
	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>
Black I <sup>x</sup>	54.64	53.60	1.04	53.24	52.24	1.00	52.87	51.81	1.06
II <sup>x</sup>	54.28	52.20	1.08	53.58	52.52	1.06	52.53	51.51	1.02
Average	54.46	53.40	1.06	53.41	52.38	1.03	52.70	51.66	1.04
Gray I <sup>x</sup>	23.74	23.13	0.61	22.40	21.88	0.52	21.45	20.91	0.54
II <sup>x</sup>	23.79	23.16	0.62	22.36	21.82	0.54	22.40	21.84	0.56
Average	23.76	23.14	0.62	22.38	21.85	0.53	21.92	21.37	0.55
Brown I <sup>x</sup>	39.97	38.43	1.54	39.97	38.37	1.60	39.31	37.69	1.62
II <sup>x</sup>	39.65	38.21	1.44	39.31	37.73	1.58	39.43	37.79	1.64
Average	39.81	38.32	1.49	39.64	38.05	1.59	39.37	37.74	1.63

<sup>x</sup> Soils I and II refer to low level (2 ppm) and high level of  $NH_4^+$  (122 ppm), respectively, applied to the soils before planting.

<sup>xx</sup> Exch. = Exchangeable.

<sup>++</sup> The fixed- $NH_4^+$  was calculated by subtracting the exchangeable- $NH_4^+$  from the total  $NH_4^+$ .

Table 13. Removal of exchangeable ammonium by N NaCl plus 10 percent glycerol and the amounts of fixed ammonium left in the soils, under different conditions, based on ammoniation period of 144 hours.

Soils	me of $\text{NH}_4^+$ per 100 g								
	Wet basis		Air dry basis		Oven dry basis				
	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>	Total	Exch. <sup>xx</sup>	Fixed <sup>++</sup>			
Black I <sup>x</sup>	54.64	53.60	1.04	53.24	52.20	1.04	52.87	51.84	1.03
II <sup>x</sup>	54.28	53.22	1.06	53.58	52.50	1.08	52.53	51.46	1.07
Average	54.46	53.41	1.05	53.41	52.35	1.06	52.70	51.65	1.05
Gray I <sup>x</sup>	23.74	23.12	0.62	22.40	21.90	0.50	21.45	20.97	0.48
II <sup>x</sup>	23.79	23.14	0.65	22.36	21.84	0.52	22.40	21.88	0.52
Average	23.76	23.13	0.64	22.38	21.87	0.51	21.52	21.42	0.50
Brown I <sup>x</sup>	39.97	38.43	1.54	39.97	38.39	1.58	39.31	37.63	1.68
II <sup>x</sup>	39.65	38.15	1.50	39.31	37.69	1.62	39.43	37.71	1.72
Average	39.81	38.29	1.52	39.64	38.04	1.60	39.37	37.67	1.70

<sup>x</sup> Soils I and II refer to low level (2 ppm) and high level of  $\text{NH}_4^+$  (122 ppm), respectively, applied to the soils before planting.

<sup>xx</sup> Exch. = Exchangeable.

<sup>++</sup> The fixed- $\text{NH}_4^+$  was calculated by subtracting the exchangeable- $\text{NH}_4^+$  from the total- $\text{NH}_4^+$ .

Table 14. Removal of exchangeable ammonium by N NaCl plus 20 percent glycerol and the levels of fixed ammonium left in the soils, under different conditions, based on ammoniation period of 144 hours.

Soils	me of NH <sub>4</sub> <sup>+</sup> per 100 g								
	Wet basis		Air dry basis		Oven dry basis				
	Total	Exch. xx	Fixed <sup>++</sup>	Total	Exch. xx	Fixed <sup>++</sup>	Total	Exch. xx	Fixed <sup>++</sup>
Black I <sup>x</sup>	54.64	53.62	1.02	53.24	52.20	1.04	52.87	51.85	1.02
II <sup>x</sup>	54.28	53.22	1.06	53.58	52.48	1.10	52.53	51.47	1.06
Average	54.46	53.42	1.04	53.41	52.34	1.07	52.70	51.66	1.04
Gray I <sup>x</sup>	23.74	23.14	0.60	22.40	21.86	0.54	21.45	20.95	0.50
II <sup>x</sup>	23.79	21.21	0.58	22.36	21.84	0.52	22.40	21.92	0.48
Average	23.76	23.17	0.59	22.38	21.85	0.53	21.92	21.43	0.49
Brown I <sup>x</sup>	39.97	38.45	1.52	39.97	38.39	1.58	39.31	37.63	1.68
II <sup>x</sup>	39.65	38.15	1.50	39.31	37.69	1.62	39.43	37.73	1.70
Average	39.81	38.30	1.51	39.64	38.04	1.60	39.37	37.68	1.69

x Soils I and II refer to low level (2 ppm) and high level of NH<sub>4</sub><sup>+</sup> (122 ppm), respectively, applied to the soils before planting.  
 xx Exch. = Exchangeable.  
 ++ The fixed-NH<sub>4</sub><sup>+</sup> was calculated by subtracting the exchangeable-NH<sub>4</sub><sup>+</sup> from the total-NH<sub>4</sub><sup>+</sup>.

Effects of time and drying: The effects of time and drying on the fixation of ammonium have already been discussed under the subheading "total ammonium fixing capacity of the soils".

Total Ammonium Fixation of the Calcareous  
Soils when the Carbonates were Destroyed  
Before and After Ammoniation

Table 15 gives the data of total ammonium fixed by the two calcareous soils, black, and gray, when the carbonates were destroyed with  $\underline{N}$  HCl in the presence of  $\underline{N}$  KCl and then the soils were saturated with  $\underline{N}$   $\text{NH}_4\text{Cl}$ . It can be seen from the results that: firstly, quantities of fixed ammonium, under wet conditions, were less than those reported in Table 6. Secondly, the amount of fixed ammonium had increased, in both the soils, after air drying or heat treatment. However, even after air drying or heating, the values of fixed ammonium were less than those obtained, under wet conditions, when the carbonates in the soils were destroyed after saturating with  $\underline{N}$   $\text{NH}_4\text{Cl}$  (Table 6). The reason for this is explained below.

As the mechanism of fixation of potassium ion,  $\text{K}^+$ , and ammonium ion,  $\text{NH}_4^+$ , is the same (10, 49), therefore, it is possible that potassium occupied the fixation sites when the soils were suspended in  $\underline{N}$  KCl to destroy the carbonates. Hence the ammonium fixing capacity of the soils was reduced. It may be concluded from these results that

Table 15. Ammonium fixing capacity of the calcareous soils after destroying the carbonates in the presence of  $\underline{N}$  KCl, under different conditions, based on ammoniation period of 144 hours.

Soils	Condition employed	me of $\text{NH}_4^+$ per 100 g					
		Total	KCl exch. <sup>x</sup>	Fixed <sup>xx</sup>	Total	NaCl exch. <sup>x</sup>	Fixed <sup>xx</sup>
Black	Wet basis	52.24	50.28	1.96	52.24	50.34	1.90
Gray	"	21.96	21.38	0.58	21.96	21.44	0.52
Black	Air dry basis	52.48	50.38	2.10	52.48	50.48	2.00
Gray	"	22.06	21.42	0.64	22.06	21.50	0.56
Black	Oven dry basis	52.60	50.38	2.22	53.04	50.86	2.18
Gray	"	22.14	21.46	0.68	22.14	21.54	0.60

<sup>x</sup> Exch. = The exchangeable  $\text{NH}_4^+$  was extracted with  $\underline{N}$  KCl; and  $\underline{N}$  NaCl.  
<sup>xx</sup> The fixed- $\text{NH}_4^+$  was calculated by subtracting the exchangeable- $\text{NH}_4^+$  from the total- $\text{NH}_4^+$ .



if, in practice, ammonium and potassium fertilizers are applied together, then, of course the fixation of each of the individual fertilizer should be less as compared to the individual application of each fertilizer.

Table 16 gives the data of total ammonium fixing capacity of the two calcareous soils when the soils were ammoniated after destroying the carbonates with  $\underline{\text{N}}$  HCl in the presence of  $\underline{\text{N}}$   $\text{CaCl}_2$ . The results show that the amounts fixed in the black soil, under all the conditions employed, were more than those reported in Tables 6 and 15. The cation used was  $\text{Ca}^{++}$  and the behavior of  $\text{Ca}^{++}$  to expand the mineral lattice is well known. Therefore, it is possible that this phenomenon resulted in more fixation of ammonium. As the gray soil was highly calcareous (Table 2), therefore, the effect of calcium was not evident in this case.

Table 17 gives the data of ammonium fixation when the carbonates in the calcareous soils were destroyed by  $\underline{\text{N}}$  HCl before ammoniation. The results indicate that the values of fixed ammonium in most of the cases were almost the same as given in Table 16. This would be expected since the soils were calcareous thus the exchangeable cations on the complex were  $\text{Ca}^{++}$  and since the amount of HCl used was limited only to destroy the carbonates. Therefore, the results of the soils reported in Tables 16 and 17 were almost identical.

The destruction of the carbonates either before air

Table 16. Ammonium fixing capacity of the calcareous soils after destroying the carbonates in the presence of  $\text{N CaCl}_2$ , under different conditions, based on ammoniation period of 144 hours.

Soils	Condition employed	me of $\text{NH}_4^+$ per 100 g			
		Total	KCl exch. <sup>x</sup>	Fixed <sup>xx</sup>	Total NaCl exch. <sup>x</sup> Fixed <sup>xx</sup>
Black	Wet basis	52.95	51.44	2.52	53.96 51.52 2.44
Gray	"	23.60	22.84	0.76	23.60 23.01 0.59
Black	Air dry basis	54.02	51.44	2.58	54.22 51.70 2.52
Gray	"	23.66	22.88	0.78	22.86 22.18 0.68
Black	Oven dry basis	53.98	51.34	2.64	53.98 51.40 2.58
Gray	"	23.22	22.44	0.78	23.22 22.52 0.70

<sup>x</sup> Exch. = The exchangeable  $\text{NH}_4^+$  was extracted with  $\text{N KCl}$ ; and  $\text{N NaCl}$ .

<sup>xx</sup> The fixed- $\text{NH}_4^+$  was calculated by subtracting the exchangeable- $\text{NH}_4^+$  from the total- $\text{NH}_4^+$ .

Table 17. Ammonium fixing capacity of the calcareous soils when the carbonates were destroyed before ammoniation, under different conditions, based on ammoniation period of 144 hours.

Soils	Condition employed	me of $\text{NH}_4^+$ per 100 g			
		Total	KCl exch. <sup>x</sup>	Fixed <sup>xx</sup>	Total NaCl exch. <sup>x</sup> Fixed <sup>xx</sup>
Black	Wet basis	53.66	51.21	2.45	53.66 51.25 2.41
Gray	"	22.88	22.14	0.74	22.88 22.32 0.56
Black	Air dry basis	53.75	51.20	2.55	53.75 51.25 2.50
Gray	"	22.84	22.08	0.76	22.84 22.20 0.64
Black	Oven dry basis	53.68	51.06	2.62	53.68 51.08 2.60
Gray	"	22.88	22.10	0.78	22.86 22.16 0.70

<sup>x</sup> Exch. = The exchangeable  $\text{NH}_4^+$  was extracted with  $\text{N KCl}$ ; and  $\text{N NaCl}$ .

<sup>xx</sup> The fixed- $\text{NH}_4^+$  was calculated by subtracting the exchangeable- $\text{NH}_4^+$  from the total- $\text{NH}_4^+$ .

drying (wet conditions) or after air drying resulted in a pH value around 7 (Table 18). This illustrates that the amount of HCl used was only sufficient to destroy the carbonates and there was no excess HCl to acidify the soil system.

Table 18. pH values of the calcareous soils, under different conditions, after ammoniation period of 144 hours.

Soils	pH			
	After air drying in the presence of carbonates	After air drying followed by carbonates destruction	Wet condition followed by carbonates destruction	After destroying carbonates followed by air drying
Black	8.0	6.8	7.0	7.0
Gray	8.1	6.9	7.0	6.9

A comparison of Table 17 and 19 indicated that destroying the carbonates before ammoniation resulted in slightly less fixed ammonium than destroying the carbonates after ammoniation. However, further work is needed since the differences were small.

Table 19. Ammonium fixation of the calcareous soils when the carbonates were destroyed after ammoniation then air dried or heated, based on ammoniation period of 144 hours.

Soil	Condition employed	me of $\text{NH}_4^+$ per 100 g			
		Total	KCl exch. <sup>x</sup>	Fixed <sup>xx</sup>	Total NaCl exch. <sup>x</sup> Fixed <sup>xx</sup>
Black	Air dry basis	53.72	51.10	2.62	53.72 51.20 2.52
Gray	" "	22.77	21.99	0.78	22.77 22.09 0.68
Black	Oven dry basis	53.78	51.10	2.68	53.78 51.20 2.58
Gray	" "	22.82	22.02	0.80	22.82 22.06 0.76

<sup>x</sup> Exch. = The exchangeable  $\text{NH}_4^+$  was extracted with N KCl; and N NaCl.

<sup>xx</sup> The fixed- $\text{NH}_4^+$  was calculated by subtracting the exchangeable- $\text{NH}_4^+$  from the total- $\text{NH}_4^+$ .

Ammonium Fixation of the Clay and  
Silt plus Sand Fractions  
of the Soils

It has been established by the various workers (2, 10, 14) that the clay minerals of the soil are mainly responsible for the ammonium fixation. Little evidence is available with respect to ammonium fixation in the silt and sand fractions of the soils.

The data (Table 20) show that considerable amount of  $\text{NH}_4^+$  were held in the silt plus sand fractions of the soils. In general the amounts of ammonium fixed by soil I, in all the cases, were less than the amounts fixed by soil II. Different levels of application of the ammonium fertilizer may account for this difference (Table 1). On the percentage basis, the silt plus sand fractions of the black, gray, and brown soils fixed about 34, 44, and 45 percent, respectively, of the total ammonium fixed by the whole soils.

The fixed ammonium held on the silt plus sand as a percentage of the total fixed ammonium in the whole soil was calculated as follows:

1.  $\text{me of total NH}_4^+$  fixed by the silt plus sand fractions =  $\text{me of NH}_4^+$  fixed by the silt plus sand fraction per 100 g of silt plus sand X percentage of the silt plus sand in the sample.

Table 20. Original fixed ammonium on the clay and silt plus sand fractions of the soils.

Soil	me of $\text{NH}_4^+$ per 100 g				% of total fixed $\text{NH}_4^{+xx}$				
	Clay fraction		Silt + sand fractions		On clay + sand		On silt + sand		
	Total	Exch. <sup>††</sup>	Fixed	Total	Exch. <sup>††</sup>	Fixed	Total	Exch. <sup>††</sup>	
Black I <sup>x</sup>	3.72	2.64	1.08	1.78	1.34	0.54	69.36	33.30	102.66
II <sup>x</sup>	4.82	3.30	1.52	2.25	1.47	0.78	70.18	34.90	105.08
Gray I <sup>x</sup>	2.77	2.39	0.38	0.92	0.70	0.22	56.70	42.45	99.65
II <sup>x</sup>	2.89	2.35	0.54	1.10	0.78	0.32	57.75	45.75	103.50
Brown I <sup>x</sup>	3.78	2.89	0.89	1.38	0.74	0.64	54.02	44.15	98.25
II <sup>x</sup>	4.32	3.07	1.25	1.78	0.70	1.08	55.71	45.92	101.63

<sup>x</sup> Soils I and II refer to low level (2 ppm) and high level of  $\text{NH}_4^+$  (122 ppm), respectively, applied to the soils before planting.

<sup>xx</sup> Based on the data of Tables 2 and 3 (after destroying the carbonates in case of calcareous soils)<sup>†</sup>

<sup>††</sup> The exchangeable- $\text{NH}_4^+$  was extracted with N KCl.

2. Percent of the total  $\text{NH}_4^+$  fixed by the silt plus sand fraction = me of total  $\text{NH}_4^+$  fixed by the silt plus sand fractions of soil X 100 / me of  $\text{NH}_4^+$  fixed by the whole soil.

The calculations for the clay fraction were made in the same way.

Table 21 shows the total ammonium fixing capacity of the clay, and silt plus sand fractions of the soils under different conditions. In general, it can be seen that the amounts of ammonium fixed per 100 g of clay or silt plus sand were different in the different soils. This can be attributed to the different kinds and amounts of ammonium fixing minerals in the different soils.

The results (Table 21) indicated that all the fractions of the calcareous soils fixed maximum amounts of ammonium under the wet conditions and the least on oven drying. But the non-calcareous brown soil fixed the maximum amounts on oven drying the soils fractions. The reasons for this trend of these soils have been explained under the subheading "total ammonium fixing capacity of the soils".

It is noteworthy that on the percentage basis the clay fraction of the black soil fixed more ammonium than did the clay fraction of the gray and the brown soils, under all the conditions. The clay fraction of the gray, and the brown soils, on percentage bases, fixed almost the



Table 21. Total ammonium fixing capacity of the clay, and silt plus sand fractions of the soils after saturating with  $\text{N NH}_4\text{Cl}$ , based on ammoniation period of 144 hours, under different conditions.

Soil Basis	me of $\text{NH}_4^+$ per 100 g						% of total fixed $\text{NH}_4^{xx}$		
	Clay fraction			Silt + sand fractions			On clay	On silt + sand	On clay + sand + silt
	Total	Exch. <sup>x</sup>	Fixed	Total	Exch. <sup>x</sup>	Fixed			
Black Wet	68.78	65.42	3.36	46.72	45.04	1.68	69.10	33.44	102.54
Gray "	34.42	33.44	0.98	16.52	15.94	0.58	55.96	42.56	98.52
Brown "	56.72	55.96	1.76	30.72	29.40	1.32	54.57	46.49	101.06
Black Air dry	70.04	67.18	2.86	45.82	44.56	1.26	69.52	31.05	100.57
Gray "	33.76	32.98	0.78	16.58	16.13	0.45	56.61	43.56	100.17
Brown "	57.12	55.00	2.12	31.84	29.39	1.45	56.68	44.05	100.73
Black Oven dry	68.12	65.80	2.32	45.68	44.44	1.24	68.00	30.80	98.00
Gray "	34.16	33.46	0.70	16.12	15.72	0.40	56.70	43.20	99.90
Brown "	56.92	53.27	3.65	32.16	29.51	2.65	55.09	45.48	100.57

x Exch. = The exchangeable  $\text{NH}_4^+$  was extracted with  $\text{N KCl}$ .  
 xx Based on the data of Tables 2 and 6.

same amounts. But the silt plus sand fractions of the black soil, on percentage bases, fixed the least amounts and the brown soil the maximum. The values of the fixed ammonium, on the percentage basis, in the silt plus sand fractions of the gray soil were intermediate. However, no explanation to this differential behavior of the clay and silt plus sand fractions of the soils, can be given unless the soil separates are mineralogically analysed.

#### Nitrogen Fertilization and Ammonium Fixation

Ammonium fixation could be an important factor in plant nutrition particularly when soils high in vermiculite, illite and montmorillonite are fertilized with ammonium fertilizers such as ammonium sulfate and ammonium nitrate. Various studies (2, 3, 15) on ammonium fixation have shown that plow sole application of these fertilizers, may not always lead to the expected crop yields the first few years. Larger increase in yields might be expected from ammonium fertilizers applied to soils higher in kaolinites since they fix little ammonium than to those where ammonium fixing minerals are abundant.

The practical significance of  $\text{NH}_4^+$  fixation by the soil mineral fraction remains to be determined. Whether such fixation is considered "good" or "bad" must depend on the circumstances involved and the point of view in each situation. Young and Cattani (59) reported that among the

other things one must recognize the increasing tendency (a) to farm subsurface horizons following land levelling, deep plowing and erosion, and (b) to observe residual carry over of applied nitrogen. Since deep plowing and effects of erosion are commonly observed in Lebanon, this problem is of considerable importance. However, it would seem that the mineral  $\text{NH}_4^+$  fixing property of soils should not be overlooked in attempting to understand low first year recovery of applied nitrogen on some soils.

## V. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

Studies on ammonium fixation of calcareous and non-calcareous soils of Lebanon were conducted, during the year 1965-66, in the Division of Soils and Irrigation of the American University of Beirut. The objectives of these studies were to evaluate the amounts of original fixed ammonium present in the soils and to determine the total ammonium fixing capacity of these soils. The studies also included the effect of some factors on the fixation of ammonium and the role of the clay and the silt plus sand fractions in the fixation of ammonium.

The original fixed ammonium in the soils was determined by the HF method. In the case of the calcareous soils fixed ammonium was determined after destroying the carbonates with  $\underline{\text{N}}$  HCl in the presence of  $\underline{\text{N}}$  KCl.

Total ammonium fixing capacity of the soils was determined by saturating the soils with  $\underline{\text{N}}$   $\text{NH}_4\text{Cl}$ . The exchangeable ammonium was removed by  $\underline{\text{N}}$  KCl and determined, on an aliquot, by distillation with MgO. Fixed ammonium was then determined by digesting the soils with  $\underline{\text{N}}$  HF:  $\underline{\text{N}}$  HCl.

Ammonium fixing capacity of the calcareous soils was determined when ammoniation was done both before and after

destroying the carbonates.

The clay and the silt plus sand fractions of the soils were separated by dispersing the soils in dilute  $\text{Na}_2\text{CO}_3$  solution followed by centrifugation. The original fixed ammonium and the total ammonium fixing capacity of these soil separates, after saturating with  $\text{N NH}_4\text{Cl}$ , were determined by the HF method.

The presence of the carbonates in the soils resulted in considerably less recovery of the fixed ammonium. Thus, the quantities of ammonium fixed in the black soils, before removing the carbonates, were 0.61 me per 100 g in the low  $\text{NH}_4^+$  level soil and 0.92 in the high  $\text{NH}_4^+$  level soil, while the corresponding values after removing the carbonates were 30 and 20 percent higher, respectively. Similarly, the quantities of ammonium fixed in the two highly calcareous gray soils, before removing the carbonates, were 0.12 me per 100 g in the low ammonium level soil and 0.23 in the high ammonium level soil. The corresponding values after removing the carbonates were 142 and 74 percent higher, respectively. These results suggest the importance of removing the carbonates before making a quantitative estimate of the fixed ammonium. The reason for this is that when the carbonates are present, a considerable amount of HF is inactivated by forming insoluble  $\text{CaF}_2$ .

The total ammonium fixing capacity of the black soil ranged from 1.98 to 2.47 me per 100 g of soil. The quantities of ammonium fixed in the gray soil ranged from

0.53 to 0.78 me per 100 g of soil. The lowest and the highest values in the brown soils were 1.51 and 2.10 me per 100 g of soil, respectively. The levels of the fixed ammonium in the soils were determined under wet, air dry, and oven dry bases.

All the soils investigated fixed considerable amounts of ammonium under the wet condition. Air drying or heating to 50°C resulted in the loss of ammonium in the calcareous soils. The lower recovery of the fixed ammonium was possibly due to the greater loss of ammonium by volatilization rather than to the entrapment of ammonium in the collapsed lattice. However, when the carbonates were destroyed before ammoniation, there was an increase in the ammonium fixation of the calcareous soils upon air drying and heating compared to the decrease of ammonium fixation when the carbonates were not destroyed. This increase resulted due to the lattice collapse of the minerals. The ammonium fixation also increased in the non-calcareous soil on drying, because the mineral lattice tended to collapse and caused more entrapment of the ammonium.

The rate of fixation of ammonium by all the soils investigated was rapid. The fixation in the various soils was about 85 to 99 percent complete after 12 hours of ammoniation when based on the total ammonium fixed after 144 hours of ammoniation.

Removal of the exchangeable ammonium from the soils, under the laboratory conditions, with different cations and with cations plus glycerol gave different values for the fixed ammonium. The order of replacement of adsorbed ammonium was  $\text{Na}^+ > \text{Ca}^{++} > \text{K}^+$ . Therefore, the quantities of fixed ammonium left in the soils were highest when N KCl was used to remove the exchangeable ammonium and the lowest when N NaCl was used. This is explained by the fact that  $\text{K}^+$  produces a contracted lattice while  $\text{Ca}^{++}$  and  $\text{Na}^+$  expand the mineral lattice.

Calcium plus 10 percent glycerol and  $\text{Ca}^{++}$  plus 20 percent glycerol removed more exchangeable ammonium from the complex than did  $\text{K}^+$ ,  $\text{Ca}^{++}$  or  $\text{Na}^+$  alone. Sodium plus 10 percent glycerol and  $\text{Na}^+$  plus 20 percent glycerol gave almost the same values of fixed ammonium as with Na alone. This suggested that the  $\text{Ca}^{++}$  plus glycerol expanded the mineral lattice more than either cation without the glycerol while the Na plus glycerol expanded the lattice to the same extent as with the Na alone.

Removing the carbonates in the presence of N KCl, before ammoniation, resulted in the reduction of the ammonium fixing capacity of the calcareous soils. But there was an increase in the ammonium fixing capacity when the carbonates were destroyed in the presence of N  $\text{CaCl}_2$ . Since potassium ions are fixed by the same mechanisms as ammonium ions, it is possible that the  $\text{K}^+$  occupied the fixation

sites and hence reduced the ammonium fixing capacity of the soils. The effect of the  $\text{Ca}^{++}$  is to expand the mineral lattice and, therefore, the treatment with calcium resulted in more fixation of ammonium.

Considerable amounts of the fixed ammonium were held in the silt plus sand fractions of the original soils. The silt plus sand fractions of the black soils, receiving low level of ammonium, contained about 33 percent of the total ammonium fixed by the whole soil. The silt plus sand fractions of the high level ammonium black soil fixed 35 percent. The silt plus sand fractions of the low and high ammonium gray soils fixed about 42 and 46 percent of the total ammonium fixed by the whole soil, respectively. The corresponding figures for the brown soils were about 44 and 46 percent.

The total ammonium fixing capacity of the clay and the silt plus sand fractions of the various soils depended upon the conditions employed for fixation. On the percentage bases, the silt plus sand fraction of the black, gray, and brown soils fixed about 31, 43, and 45 percent of the total ammonium fixed by the whole soil, respectively. This indicated that the coarse fractions of these soils play a very active role in the inactivation of  $-\text{NH}_4^+$ .

In conclusion it is suggested that in the case of the calcareous soils the carbonates should be destroyed before making a quantitative estimate of the fixed  $\text{NH}_4^+$ .



A large percentage of the ammonium nitrogenous fertilizers may become fixed. This fixation may result in decreased yield response to applied ammonium nitrogenous fertilizers. It was found that the black, gray, and brown soils fixed 46, 16, and 41 percent of the applied  $\text{NH}_4^+$ . Under such conditions it may be advisable that the nitrate form of the nitrogenous fertilizers may be applied for high efficiency. Further work is needed on the rate of nitrification of fixed- $\text{NH}_4^+$  because relatively little has been reported.

Further studies are suggested to determine the effect of carbonates on the fixation of  $\text{NH}_4^+$ .

The silt plus sand fractions of the soils fixed considerable amounts of  $\text{NH}_4^+$ . This indicated that the  $\text{NH}_4^+$  fixing minerals were present in the silt plus sand fractions. It is suggested that the mineralogical analyses on these soil separates should be carried out to confirm the presence of  $\text{NH}_4^+$  fixing minerals.

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