Availability of nonexchangeable potassium and ammonium to plants and microorganisms

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AVAILABILITY OF NONEXCHANGEABLE POTASSIUM AND AMMONIUM TO PLANTS AND MICROORGANISMS

by

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A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Soil Fertility

Approved:

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INTRODUCTION

K occurs in soils in water-soluble, exchangeable, and nonexchangeable forms. Furthermore, these various forms are generally regarded as being in a state of chemical equilibrium, and, for this reason, removal or addition of any form results in a displacement of the equilibrium. Plants absorb K from both the exchangeable and water-soluble forms, and with cropping these forms tend to become depleted below the equilibrium levels with the result that nonexchangeable K is released to exchangeable and water-soluble forms. The K-supplying power of a soil during cropping depends upon its ability to release K. Thus, an understanding of the factors affecting the rate and magnitude of this release is needed.

NH₄ behaves like K in that it may be fixed and released from soils by a similar mechanism. Since it is now evident that some native fixed NH₄ occurs in soils, and that NH₄ added as a N fertilizer may be fixed, an understanding of the NH₄ release process is also needed.

It has been observed that the presence of fixable cations (K or NH₄) blocks the chemical replacement of fixed NH₄ in soils and clay minerals by nonfixable cations like Na. Since NH₄ and K are fixed by the same mechanism, it may be expected that the chemical extraction of K would also be blocked by the presence of fixable cations in the extracting
solution. The release of nonexchangeable K or fixed NH$_4$ to a form that is available to plants or nitrifying bacteria depends upon the chemical replacement of these cations from their fixed position. Thus, the release and availability of nonexchangeable or fixed K and NH$_4$ should also be affected by the presence or addition of fixable cations.

The objectives of this study were to determine the effect of K on the availability of fixed NH$_4$ to nitrifying bacteria, and to determine the effect of added NH$_4$ and/or K on the release and availability of nonexchangeable soil K to plants. The development of suitable methods for determining these effects was, however, an essential part of this study.
LITERATURE REVIEW

Forms and Equilibrium of Potassium and Ammonium in Soils

Different terms have been used to categorize soil K into various forms based on the severity of the chemical treatment needed to extract it from the soil. Peech and Bradfield (58) proposed that the forms of K be thought of as: nonexchangeable ⇔ exchangeable ⇔ water-soluble. Nonexchangeable K is that remaining in the soil after the exchangeable and water-soluble forms have been extracted with a neutral salt solution.

It is now known that some of the soluble K added to a soil may be changed to the nonexchangeable form. This K is commonly referred to as fixed K. Thus, the nonexchangeable K may be thought of as being composed of fixed K and lattice or native K. Barshad (16) used "native K" to denote K that has never been disturbed from its naturally occurring position in the crystal lattice of K-bearing minerals. Many agronomists had reasoned in this manner even before Wiklander (79) expressed equilibrium among the forms of K as:

lattice ⇔ fixed ⇔ exchangeable ⇔ water-soluble.

The above equilibrium expressions are now generally accepted even though the transformation from lattice to water-soluble K may take a considerable period of time as compared
to the time required for many chemical reactions to reach equilibrium. If one regards the expression by Wiklander (79) as a chemical equilibrium, then any factor responsible for decreasing water-soluble K should result in a displacement of the other three forms toward the water-soluble form. This has been termed K release. Contrariwise, any factor causing an increase in water-soluble K greater than the equilibrium value should result in a displacement of some of the water-soluble K to the nonexchangeable form. This has been termed K fixation.

A number of different methods have been utilized to increase or decrease water-soluble K in studying the equilibrium conditions of soil K. Long- and short-time cropping experiments have been conducted which cause a decrease in the water-soluble K due to absorption by plants (17, 21, 23, 24, 27). The water-soluble and/or exchangeable forms have been removed by chemical extractions and the soil then has been allowed to reequilibrate (1, 20). The same phenomenon has been studied by precipitating water-soluble K and maintaining an equilibrium gradient that would favor release of the other three forms (42). A shift in equilibrium which would result in K fixation has been observed when soluble K salts were added to soils (40, 46, 76, 79).

It has been suggested that NH₄⁺ and K ions are fixed in soils and clay minerals by the same mechanism (50, 70). This
is based on the fact that there is a linear relationship between the quantity of NH\textsubscript{4} and K fixed and the previous fixation of one decreases the fixation of the other (47, 70). This fixation relationship is due to the similar size of the NH\textsubscript{4} and K ions (56). Because the ions are fixed by the same mechanism, their release might be expected to be somewhat similar.

Chemical Release of Potassium and Ammonium

Once it had been shown that cations may be fixed by soils and clay minerals, attention was directed toward factors affecting the release of fixed cations.

Barshad (16) reported that in vermiculite, and to some extent in soils, all of the adsorbed NH\textsubscript{4} was found to be replaceable with Li, Na, Mg, Ca, or Ba, but only a fraction was replaceable with K, Rb, or Cs. He also reported that replaceability of adsorbed K followed a somewhat similar pattern. The differences in the replaceability of adsorbed cations was explained as resulting from their accessibility to the replacing cations, which in turn depends upon the expansible nature of the crystal lattice interlayer space. Barshad further stated that ions in a contracted-type layer lattice are replaceable only by those cations that, when adsorbed, cause the layers of the crystal lattice to expand. It was recom-
mended that the difference in NH₄ replaced from two NH₄ saturated soil samples when distilled with NaOH and KOH, respectively, be taken as a measure of the fixation capacity of the soil for NH₄ or K. It was not inferred that K be determined by distillation, but, since NH₄ and K are fixed to about the same extent, once the NH₄-fixing capacity has been determined, this value may be taken as the K-fixing capacity also.

Bower (19) found that leaching soils of semiarid regions with 0.5 N NaCl removed more NH₄ than did leaching with 0.5 N KCl. Based on the cation-replacing mechanism proposed by Barshad (16), this would be expected since Na is a hydrated cation and should result in expansion of the clay mineral lattice.

Allison et al. (4) reported that considerably lower NH₄-fixation values are obtained if 1 N CaCl₂ is used to extract NH₄-saturated soils than if 1 N KCl is used. Thus, due to the method of calculating fixed NH₄, this merely means that the CaCl₂ solution extracted more adsorbed NH₄. Studies by Allison and Roller (5) showed that when soils were NH₄-saturated and leached with various reagents, 1 N NaCl removed the largest portion of the NH₄, whereas 1 N KCl removed the least. The corresponding results with 1 N CaCl₂, 1 N MgCl₂, and 0.05 N HCl were intermediate and similar. As compared to leaching with KCl, the NH₄-fixing capacity of a soil as determined by the difference between NaOH and KOH distilla-
tion gave results that were too low for NH$_4^+$-saturated soils that had been heated and too high for unheated soils. The authors concluded that fixed NH$_4^+$ can best be defined as that NH$_4^+$ not removed by extraction with 1 N KCl. The distillation procedure has also been reported as being unsatisfactory for determining fixed NH$_4^+$ on NH$_4^+$-saturated bentonite variously treated (6).

Hanway et al. (38) found that by distilling in NaOH solutions, fixed NH$_4^+$ in NH$_4^+$-saturated vermiculite and bentonite was completely released. K in the solutions blocked this release of NH$_4^+$, and if more than 2 K ions per 100 Na ions were present, no fixed NH$_4^+$ was released from vermiculite. With smaller amounts of K present, the amount of fixed NH$_4^+$ released decreased as the K/Na ratio in solution was increased. In an equilibrium salt extraction, small amounts of either fixable ion, NH$_4^+$ or K, in the solution prevented the release of fixed NH$_4^+$. However, 10 K ions per 100 Na ions in NaCl were not as effective as 2 K ions per 100 Na ions in the NaOH distillation. More NH$_4^+$ was released where KCl was added to the NaOH solution than where it was added directly to the vermiculite sample prior to adding the NaOH. This led the authors to suggest that the K must be adsorbed by the vermiculite before it is effective in blocking NH$_4^+$ release. The difference due to the method of adding K decreased as the K/Na ratio increased.
Hanway and Scott (36) reported that, with NH$_4^+$-saturated soil samples, added K blocked the release of fixed NH$_4^+$ in soils by NaOH distillation. Because fixed NH$_4^+$ values were about the same whether determined by the Kjeldahl method or alkaline distillation, the authors stated that the K blocking effect due to the native soil K did not occur in the alkaline distillation determination because the soluble and exchangeable K were removed when the soils were initially NH$_4^+$-saturated.

Merwin and Peech (54) leached four widely different New York soils with successive portions of 0.5 N acetate solutions and found that the amount of K extracted by the different cations decreased in the following order: Na > H > NH$_4^+$ > Mg > Ca > Ba. The NH$_4$Ac gave a clear-cut separation of the exchangeable K. That is, K was released readily by the NH$_4$Ac and further leaching gave only a slight release of K. Today, leaching with neutral 1 N NH$_4$Ac is generally regarded as the standard procedure for measuring exchangeable K.

Bray and DeTurk (20) leached exchangeable K by use of 0.1 N HCl, stored the soil moist, and determined K release 6 months after the original exchangeable K had been removed. There was good agreement between original exchangeable K and that released during the storage period. In other studies soils were heated at 200° C. for 6 days with the result that soils medium to low in exchangeable K fixed some of the
original or added K, while those originally high in exchangeable K tended to release K.

Freezing and thawing increased exchangeable K in about 2/3 of the soils studied by Fine et al. (28), while in some cases a fixation of K resulted, and in others there was no change. Bentonite had K applied and was then dried so as to fix K. Exchangeable K was removed and the bentonite was frozen and thawed 10 times. CaCl₂ and NaCl were added to the clay and it was concluded that an excess of CaCl₂ or NaCl present during freezing inhibited release of fixed K, but NH₄Ac and NH₄Cl enhanced K release. When no excess salt was present, the effect of NH₄⁺ and Ca was about the same. NH₄⁺-saturated bentonite, nontronite, Putnam clay, and montmorillonite released K on freezing and thawing, but illite fixed K. It is somewhat surprising that excess CaCl₂ or NaCl inhibited K release more than NH₄⁺. However, since the exchangeable K originally present was extracted by the same cation that was added in excess, the Na no doubt removed more K than the NH₄⁺. If this were the case then the NH₄⁺-saturated soil might be expected to release more K than the Na-saturated soil.

Seatz and Winters (65) added K to soils and noted the release when H or Ca was the complementary ion. At the highest rate of K application the complementary ion had little effect on the release of K, but at the lower rates more K was
recovered where Ca, rather than H, was the complementary ion. Merwin and Peech (54) found that K release by the whole soil or the clay fraction was greater in the presence of Ca than in the presence of H as the complementary ion.

Evans and Simon (27) saturated 3 Wisconsin soils with H or NH₄ and reported that the cumulative amounts of K removed by repeated extractions with 0.5 N HCl were less when NH₄-saturated. Between leachings the soil samples were dried for 24 hours at 80°C, moistened to field capacity, and incubated at room temperature for 48 hours. For the NH₄-saturated soils, 0.5 N HCl extracted more K than 1 N NH₄Ac.

Scott et al. (64) added salts or HCl to field-moist soils, dried the soils, and determined the release of K. Soils that normally released K on drying showed net fixation when enough KCl was added to the moist soil. With lesser amounts of KCl, fixation and release were observed in the same drying sequence. The release of K was reduced when NH₄Cl, NaCl, or HCl was added to the soil prior to drying, with NH₄Cl being the most effective. CaCl₂ had little or no effect on the quantity of K released by drying. No explanation was offered by the authors as to why NaCl or HCl should decrease the release of K on drying. Their investigation did not involve removal of the original exchangeable soil K as contrasted to the work by Evans and Simon (27).
Biological Studies on Potassium Release

A number of long- and short-time cropping experiments have been conducted, and the amount of K absorbed by the plants has been determined (13, 14, 17, 21, 23, 27, 31). In many cases, the K absorbed by the plants was greater than the original exchangeable K, thus, some originally nonexchangeable K was absorbed by the plants. The quantity of nonexchangeable K released to plants has generally been calculated by the following expression:

\[
\text{Nonexchangeable K released} = \text{Exchangeable K after cropping} + \text{K in the plants} - \text{K added} - \text{Exchangeable K before cropping.}
\]

Bear et al. (17) conducted a greenhouse study in which soil samples taken from the A horizon of 20 New Jersey soils were cropped with alfalfa. After 7 successive harvests of alfalfa, where no K was added, the nonexchangeable K released was as high as 195 pounds of K for one soil while another soil fixed 133 pounds of K per acre. Of the other 18 soils, 5 fixed K and 13 released K from the nonexchangeable form. With 166 pounds of K added per acre the quantity of nonexchangeable K released was reduced, and many of the soils that released K when no K was added then fixed K.

Chandler et al. (23) reported that upon continuous greenhouse cropping with Ladino clover the exchangeable K of the soils decreased very rapidly at first and then more gradually.
until a certain level was reached. At this level, the K-supplying power of the soil was determined largely by the rate at which the nonexchangeable K was converted in the exchangeable form. That is, the exchangeable K tended not to decrease below this certain value.

Attoe (13) grew 7 successive greenhouse crops of oats in soils receiving 0 to 1350 pounds of K per acre. Although up to 56% of the K applied in the 50 and 150 pound rates was fixed, the recovery ranged from 92 to 98% of that applied. The author suggested that the fixation of K is distinctly a beneficial process, because the fixed K is not subject to leaching but serves as a reservoir from which the supplies of the exchangeable or available forms are replenished when depleted.

According to Gholston and Hoover (31) more than 50% of the K removed by 8 successive crops of millet was released from the nonexchangeable form. Exchangeable K in the soils decreased with cropping. Evans and Simon (27) reported that 4 Ohio soils varied greatly in the amount of nonexchangeable K released to 25 harvests of alfalfa during a 36-month period. The nonexchangeable K released ranged from 41 to 232 pounds per acre.

Attoe and Truog (15) grew oats and corn in soil in which exchangeable K had or had not been removed. Corn absorbed 34.2 pounds of K per acre from the unextracted soil as
compared to 14.1 pounds from the extracted soil, while the oats absorbed 30.2 and 8.4 pounds per acre from the respectively treated soils.

Biological Studies on Ammonium Release

Chaminade and Drouineau (22) found that not all of the NH$_4^+$ added to soils was absorbed by plants and that NH$_4^+$ accumulated in the fixed form. Of 171 soil samples studied by Fraps and Sterges (29), 32 nitrified less than 60% of the added NH$_4^+$ even though nitrifying organisms were added. Addition of phosphates increased the nitrifying capacity of most of these soils, and of the several forms of phosphate tested, monopotassium phosphate gave the greatest increase in nitrification.

Bower (18) prepared samples of two soils in such a manner that they contained either fixed or exchangeable NH$_4^+$. Nitrification and the availability of the two forms to plants was determined. Regardless of the form of NH$_4^+$ supplied, nitrification practically ceased after 14 days incubation. At this time 78 and 87% of the exchangeable NH$_4^+$ but only 13 and 28% of the fixed NH$_4^+$ supplied was nitrified. A moist surface soil supplied nitrifying bacteria for the nitrification studies. Barley plants grown for 17 days on inoculated soils recovered 14 and 25% of the fixed NH$_4^+$ supplied, but where no
inoculum was added the maximum recovery was only 10%. The recovery of exchangeable NH$_4^+$ by barley from soils not inoculated was 75%. When inoculated, the percentages of fixed NH$_4^+$ recovered by barley plants agreed closely with the maximum percentages of nitrification obtained in the nitrification studies.

Regardless of the temperature and moisture conditions used under which fixation occurred, Allison et al. (2) found that usually less than 10% of the fixed NH$_4^+$ in a Harpster soil was nitrified during periods of 6 to 16 weeks incubation. NH$_4^+$ added, after the fixation capacity of the soil had been satisfied with K, was nitrified to an extent of 80 to 100%, whereas if the fixation capacity was not satisfied before adding NH$_4^+$ only 60 to 80% was nitrified. The authors noted that NH$_4^+$-saturated soils leached with KCl, so as to contain only fixed NH$_4^+$, did not nitrify satisfactorily. Even when most of the K was removed from the K-saturated soils by Ca and Mg, nitrification was frequently erratic. The soils containing Ca and Mg were then leached with a mineral nutrient solution and nitrification studies were conducted. The 200 ml. of nutrient solution used to leach 100 g. of soil contained 115 mg. of K as well as numerous other nutrient elements.

Having studied the Harpster soil from Iowa, Allison et al. (4) extended their study to several representative soils of the United States. NH$_4^+$-saturated soils were leached with
either CaCl\(_2\) or KCl to remove exchangeable NH\(_4\). The KCl-leached soils were treated in the same manner as the Harpster soil (2) in order that they be suitable for nitrification studies. Nitrification of fixed NH\(_4\) during a 2-month period varied between 5 and 24\%, being lowest for soils containing vermiculite and highest for those containing montmorillonite, with illite-containing soils intermediate. NH\(_4\)-saturated soils leached with CaCl\(_2\) instead of KCl resulted in greater nitrification. This was explained as being due to the expansion and contraction of the clay lattice by Ca and K, respectively. Also, it was again shown that satisfying the fixation capacity of the soil before adding NH\(_4\) resulted in greater nitrification. Other studies by Allison et al. (3) showed that millet grown in the greenhouse absorbed only 7 to 12\% of the fixed NH\(_4\) supplied. It was pointed out that slightly higher nitrification values were obtained when the soils did not come in contact with high concentration of K salts.

Allison et al. (7) also reported that in two samples of natural vermiculite, fixed NH\(_4\) was nearly as available to nitrifying bacteria as was that in (NH\(_4\))\(_2\)SO\(_4\). With a third sample of vermiculite the availability was only 11 to 16\%. They concluded that the cation exchange capacity of the vermiculites was not an important factor in determining the rate of release of fixed NH\(_4\) to the nitrifying bacteria. As reported
by Allison and Roller (6), average nitrification of NH$_4^+$ fixed in 6 montmorillonites was 37% where CaCl$_2$ was the extractant, and 29% where KCl was first used and then enough CaCl$_2$ leaching to reduce the K content below the "toxicity limit". In this study, the soil used as inoculum had a final leaching with nutrient solution which contained K and other elements.

Aomine and Higashi (9) found that when NH$_4^+$ was added to soils the availability of the NH$_4^+$ to plants differed for different soils. Rice plants recovered 76 to 88% of NH$_4^+$ added to soils and 90% of that added to sand. Wheat plants recovered 53 to 78% of the NH$_4^+$ added to 4 soils. The availability of NH$_4^+$ added to vermiculite was about 60% for rice plants and 30% for wheat plants. A nutrient solution containing K and other elements was added to the soil after NH$_4^+$ was added and before being cropped. Total nitrogen content of vermiculite particles, after two crops were grown, revealed higher N contents where NH$_4^+$ had been added as compared to where no NH$_4^+$ was added.

Nitrification, that took place in 77 days, of NH$_4^+$ added to five soils and one vermiculite was investigated by Aomine and Higashi (10). Nitrification practically ceased after 4 weeks, but the rate of nitrification differed among soils. In 4 soils, nitrification of added NH$_4^+$ was 67 to 75%, but in a soil which fixed very little NH$_4^+$, nitrification was 100%. The nitrification of NH$_4^+$ added to vermiculite was only 40%,
and this value was almost reached after 3 weeks. The authors concluded that exchangeable NH$_4^+$ is easily nitrified, but fixed NH$_4^+$ is difficult to nitrify in most cases.

Recently, Nomnrik (55) added NH$_4^+$ to a high-fixing soil and observed that only 8 to 26% of the fixed NH$_4^+$ was nitrified in 6 months. With 5 other soils no greater than 15% of the fixed NH$_4^+$ was nitrified after 150 days of incubation. In comparing the fertilizing effect of NH$_4^+$ and NO$_3^-$ nitrogen to oats, it was found there was no difference in the quantity of N absorbed by the plants. However, if large amounts of K were added to the soil simultaneously with NH$_4^+$, the plants could not utilize the fixed NH$_4^+$.

Legg and Allison (48) added NH$_4^+$ to a high-fixing subsoil and a non-fixing surface soil and found there was no difference in the quantity of N absorbed by sudangrass. Thus, the loss of NH$_4^+$ fertilizer through fixation was evidently not of importance even though the former soil sample was a "high fixer".

Effect of K on Nitrification in Soils

Vandecaveye (75) studied the effect of K on nitrification from a Carrington soil by adding 100 mg. of (NH$_4^+$)$_2$SO$_4$ to 100 g. air-dry soil, moistening the soil, and then incubation for 30 days at 25°C. When added with manure and lime there
was no consistent effect of K on nitrification of added NH$_4^+$, but, when only K and NH$_4^+$ were added, the increase in NO$_3^-$ over the check was 12, 28, and 32% for 100 pounds of KCl and K$_2$SO$_4$ and 200 pounds kainit per acre, respectively. The K treatments which increased nitrification also resulted in decided increases in citrate-soluble and water-soluble K. This showed the author that there existed a definite relationship between bacterial activities and the citrate-soluble and water-soluble K. The results in general agreed closely with the observations of Renoult (61) and Stoklasa (71) who pointed out that K salts promote the growth and activities of nitrifying organisms.

Harper and Boatman (39) added NH$_4^+$ to moist Iowa soils and noted that a higher percentage of added NH$_4^+$ was nitrified in 28 days at the lower rates of NH$_4^+$. Air drying soils before adding NH$_4^+$ did not seem to affect nitrification if the same physical condition was secured after the soils were re-moistened as that in the moist soil. With 3 Iowa soils receiving no NH$_4^+$, drying increased nitrification in 2 of the soils and decreased nitrification in the other. K fertilization did not produce any significant changes in nitrification.

Houghland (41) concluded that, in general, nitrification of NH$_4^+$ added to soils decreased as the concentration of K increased. Smith and Dean (67) applied 100, 200, and 500 pounds of KCl per acre to 2 Iowa soils and found that nitrification
was stimulated at first by additions of KCl but was depressed sometime after 4 weeks. Nitrate analyses were made after 4 weeks and 5 months incubation. Turk (73) reported that P and K additions caused a slight increase in nitrate production on both limed and unlimed soil.

Mack and Haley (52) added KCl, K₂SO₄, and K₂CO₃ to soil, and their data indicate that at the end of 7 weeks, nitrification was about 36% less than the control, but after 10 weeks incubation there were no significant differences. In soils treated with NH₄, nitrate production was greater in every case for the soils receiving K. In every case, K₂CO₃ caused a greater rate of nitrification than either KCl or K₂SO₄.

Laboratory experiments, by Hahn et al. (33), employing somewhat higher amounts of fertilizers than are commonly used in field practice indicated that phosphorus had little or no influence on the nitrifying capacity of the soils studied, but KCl significantly reduced nitrification when applied in amounts greater than 400 pounds per acre. In another report, Hahn (32) discussed the inhibiting effect of KCl on nitrification and concluded that Cl was the responsible ion. KCl did not reduce NO₃ accumulation when the water content of the soil was greater than 66% of the water holding capacity, but inhibition was great at 50% of the water holding capacity. He stated that no satisfactory explanation had been found of
how soil moisture and KCl interacted in affecting soil nitrification.

Ammonium and Potassium Absorption by Plants

One of the factors known to affect cation absorption by plants is the concentration of other nutrient elements in the soil or nutrient solution. According to Pierre and Bower (58), plant analysis data have led to the theory that ions present in very high concentration in the nutrient medium depress the absorption of other ions of like charge. This theory in various modified forms has been referred to as the theory of ion antagonism.

Following the theory of ion antagonism, one might expect the use of \( \text{NH}_4^+ \) to result in lower K uptake by plants as compared to when \( \text{NO}_3^- \) is employed as the source of nitrogen. This has been studied by biological investigators to a considerable extent, and many of the results reported are somewhat contradictory. Much of this contradiction may, no doubt, arise from differences in techniques employed to study the phenomenon.

The influence of the degree of saturation by soil colloids on the nutrient intake by plants has been studied by Jenny and Ayers (44). They reported that in clay suspensions small amounts of \( \text{NH}_4^+ \) ions on the colloidal particles seemed
to stimulate the intake of K by excised barley roots, but as soon as the degree of K saturation fell below 60% (NH$_4^+$ saturation greater than 40%), the absorption of K reached a very low level. The authors (44, p. 456) stated, "this sharp decline of K consumption from NH$_4^+$-K-clay, however, is not only a consequence of exchangeability but is also conditioned by physiological processes of the roots, since in the mixtures of KCl and NH$_4$Cl the roots behave in a very similar manner. In place of K the roots gained considerable amounts of nitrogen, which might have impaired the absorptive capacity for potassium." For a given level of K in solution, the percentage of the total K absorbed by the excised barley roots decreased with high levels of added NH$_4^+$. However, small amounts of added NH$_4^+$ increased K uptake from solution culture.

Ames and Gerdel (8) added NaNO$_3$ or (NH$_4^+$)$_2$SO$_4$ to soils 10 days before mixing with sand and planting 100 wheat seeds. On practically all the soils receiving (NH$_4^+$)$_2$SO$_4$, the weights of dry matter were less than for plants grown on soils receiving no NaNO$_3$ or (NH$_4^+$)$_2$SO$_4$. However, K uptake by the plants was about the same as where NaNO$_3$ was added. For soils that had received KCl and lime in previous fertility studies, addition of NaNO$_3$ as well as (NH$_4^+$)$_2$SO$_4$ reduced K uptake.

Arnon (11) transferred 7-day-old barley seedlings, which had been grown in tap water, into nutrient solutions where
they were allowed to grow 5 weeks. One nutrient solution had \((\text{NH}_4)_2\text{SO}_4\) added, while the other had \(\text{Ca(NO}_3\text{)}_2\). The proper adjustment of the culture solution, with respect to aeration and certain minor elements, made it possible to produce \(\text{NH}_4\)-plants not inferior to \(\text{NO}_3\)-plants. Later, Arnon (12) reported that \(\text{NO}_3\)-plants had a higher percent Ca, Mg, and K but a lower P percent than the \(\text{NH}_4\)-plants. Similar results on \(\text{NH}_4\) decreasing K uptake by plants have been reported by Wadleigh and Shive (77).

Wimer (80) reported that additions of K reduced the N and P content of corn stover. Shibuya and Saeki (66) found that uptake of K by plants was greater from soils receiving \(\text{NO}_3\) as compared to \(\text{NH}_4\). Tyner and Webb (74) reported that \((\text{NH}_4)_2\text{SO}_4\) had a depressive effect on the percent K occurring in the sixth corn leaf.

In contrast to some of the above findings, Dastur and Winfred (25) found \(\text{NH}_4\) was a better source of N than \(\text{NO}_3\). Thorne (72) observed that \(\text{NaNO}_3\) gave slightly higher corn yields than \((\text{NH}_4)_2\text{SO}_4\).

It was reported by Lipman and Blair (51) that \(\text{NaNO}_3\) gave the greatest yield of corn on unlimed soils, but \((\text{NH}_4)_2\text{SO}_4\) gave greater yields on limed soils. In their study, all soils received liberal applications of a K fertilizer. Along this same line, Prianischnikow (59) showed that in sand culture with a neutral solution, \((\text{NH}_4)_2\text{SO}_4\) gave better plant growth,
but in acid solution NaNO$_3$ gave better results. Increased concentration of Ca ions in the nutrient solution increased the efficiency of NH$_4^+$ but had the opposite effect on NO$_3^-$. Clark (24) observed that plants grown in NO$_3$ and NH$_4^+$ solutions made about the same growth but did it at different pH values. Espino and Esticko (26) indicated that solutions containing both NH$_4^+$ and NO$_3^-$ gave the best results.

Potassium Requirement of Bacteria

K is required for most biological growth processes. However, in many cases, the exact function of K in the living cell is still unknown.

Rahn (60) reported that there is considerable evidence that most of the gram-negative bacteria thrive well without K. He based his statement on the results presented in a rather extensive literature review and his own findings.

Rahn grew organisms in a medium which consisted of 1.88 g. of NH$_4$Cl, 1.0 g. of Na$_2$HPO$_4$·12H$_2$O, 0.2 g. of CaCl$_2$, and 50 g. of glucose per liter. To this medium, increasing amounts of KCl were added, from 2.6 to 520 ppm. To be certain of not transferring any K with bacteria, new cultures with and without K were inoculated from the culture without K. After making a number of transcultures into K-free media, Rahn (60, p. 399) stated, "The gram-negative bacteria inves-
tigated so far, with the exception of *Rhizobium*, can grow without potassium. At least they develop to large numbers in media made from analyzed C. P. chemicals in glass containers, and addition of potassium salts does not greatly increase the crop. Gram-positive bacteria develop in such media only after addition of potassium salts."

In 1957, Lester (49) recrystallized inorganic constituents, from 50% aqueous ethanol, to prepare a medium for studying the K requirements of bacteria. The medium consisted of 3.5 g. of $\text{NaN}_2\text{HPO}_4\cdot4\text{H}_2\text{O}$, 8.2 g. of $\text{Na}_2\text{HPO}_4$, 2.0 g. of citric acid$\cdot\text{H}_2\text{O}$, 0.2 g. of $\text{MgSO}_4\cdot7\text{H}_2\text{O}$, 0.01 g. of $\text{CaCl}_2$, 1.0 ml. of a trace element solution, 10 mg. of nicotinamide, and 5 g. of glucose per liter. K was added, in some cases, at a concentration of 78 ppm. as the chloride.

Growth of all species of bacteria studied was poor without K and was markedly enhanced by K. From his study, Lester (49, p. 428) stated, "the data which have been presented indicate that for continued growth potassium or rubidium is an obligate requirement for many, and probably all, species of bacteria." Rubidium generally served as a good substitute, but cesium was a poor substitute.

Lester pointed out that the growth obtained by Rahn (60) in the absence of added K might have been due to the presence of small amounts of K in the medium, or to carry over of K in the bacteria used as inoculum. Lester also indicated that
the small amount of growth without added K in his own study might have been due to K from the glassware.
MATERIALS AND METHODS

The vermiculite samples were obtained from the Zonolite Company, Evanston, Illinois. The samples included a high and low exchange capacity ore from South Carolina and high exchange-capacity ore from Montana. The samples will be referred to as Montana High, South Carolina High, and South Carolina Low. The samples were ground in a Christy-Norris laboratory hammer mill to pass a 1/64-inch screen.

Samples of Wyoming (Volclay) bentonite, mined in the Black Hills region of Wyoming and South Dakota, were supplied by the American Colloid Company. Illite (Goose Lake Grundite) was supplied by Illinois Clay Products Company. The bentonite and illite samples were already finely divided and were used without further grinding.

Clarion and Marshall soil samples, taken from the 0 to 6 and 18 to 24-inch depth, were obtained from sites designated as Iowa Number 4 and Iowa Number 34, respectively, of the regional K Project. Fayette soil samples, from the 12 to 18 and 36 to 48-inch depth, were taken from Clayton County, Iowa. All the soil samples were taken field moist, passed through a 3/16-inch screen, and stored in plastic bags until used.

$\text{NH}_4^+$-saturated samples were prepared by placing the materials on a Buchner funnel and leaching with either neutral 1
*NH₄Ac or 1 *NH₄Cl. The materials were then washed with 70% methanol or distilled water until the leachate gave a negative test with Nessler's reagent or AgNO₃.

Fixed NH₄ in the NH₄-saturated materials was determined by the difference between total and exchangeable NH₄. Total NH₄ was determined by Kjeldahl analysis (43), and exchangeable NH₄ was determined by KOH distillation. The KOH distillation consisted of distilling the NH₄-saturated materials in 400 ml of 0.1 N KOH for approximately 2 hours. The released NH₃ was trapped in a measured amount of 0.1 N HCl, and the excess acid was titrated with 0.1 N NaOH. All NH₄ determinations were made in duplicate, and due consideration was given to appropriate blank controls.

NO₃, in the nitrifying system, was determined quantitatively by the phenoldisulfonic acid method as outlined by Hanway and Heidel (35), beginning in their procedure where the soil extract has been obtained. K determinations were made with a Perkin-Elmer 520 flame photometer with Li as the internal standard.

The development of suitable methods for determining the availability of nonexchangeable K and fixed NH₄ was one of the objectives of this investigation. Thus, the specific methods used and their experimental justification are presented later with the experiments in which they were applied.
Fixable cations (K and NH$_4^+$) block the chemical extraction of fixed NH$_4^+$ from soils and clay minerals. K and NH$_4^+$ appear to be fixed by similar mechanisms, thus, their chemical extraction should be governed by the same factors. In this event the chemical displacement of fixed K should be blocked by the presence of fixable cations (NH$_4^+$ and K).

The water-soluble and exchangeable forms of soil K are readily available to plants, but as these forms are depleted plants rely on the release of K from the nonexchangeable form. This release of K involves the replacement of nonexchangeable K by other cations. Therefore, the release of K should be governed by the same factors that determine the chemical extraction of nonexchangeable K.

Much of the nonexchangeable K in soils is either added K that has been fixed or naturally occurring lattice K in micaceous minerals. The K fixed by micaceous minerals and the lattice K in these minerals are both located in interlayer positions, therefore, their chemical extraction should be somewhat comparable. The release of nonexchangeable K is thus probably affected by the presence of fixable cations like K and/or NH$_4^+$.

The objective of this study was to determine if added
NH₄ and/or K do affect the availability of nonexchangeable soil K to plants because of their effect on the release of this form of K.

NH₄ added to soils may be nitrified to NO₃. In this event the blocking effect of NH₄ would be eliminated. Therefore, it was necessary to determine the release of nonexchangeable K to plants under conditions that minimized the nitrification of added NH₄. There is a lag period from the time NH₄ is added to soils until rapid nitrification occurs, thus, the short-time cropping technique proposed by Stanford and DeMent (68) appeared to be a suitable method for determining the release of nonexchangeable soil K with a minimum of interference from nitrification. Since this cropping method has been used previously only with P, it was necessary to determine if plants grown under these conditions would absorb appreciable quantities of K if it were present in an available form.

In this study the measurement of the effect of added NH₄ and/or K on the release of nonexchangeable soil K will rely partially on the absorption of K by plants, therefore, any factor which might affect K absorption per se must be given due consideration. NH₄ has been reported to reduce K absorption by plants from sand and nutrient culture (12, 77). Thus, if K absorption should be reduced in soils which had had NH₄ added, the investigator would not be able to state specifi-
cally if the reduction was due to some physiological effect or whether NH$_4^+$ blocked the release of nonexchangeable K such that K was not available for absorption. The effect of added NH$_4^+$ on K absorption from sand culture was thus determined, in order that the effect of NH$_4^+$ added to soils might be properly evaluated without interaction between the physiological effect on K absorption and the blocking effect on the release of nonexchangeable soil K.

Soluble K added to the sand provided information as to the quantities of K that might be absorbed by the plants during the short-time cropping period. Also, the short-time cropping technique was applied to soils with or without added K to evaluate its suitability for determining the release of nonexchangeable soil K.

After conducting experiments to determine the suitability of the short-time cropping technique, the technique was then used with surface and subsoil samples to determine the effect of added NH$_4^+$ and/or K on the release of nonexchangeable K. The effect of the order of adding NH$_4^+$ and K to soil samples was also determined.

**Short-Time Cropping Technique**

The bottoms were cut from 12-ounce cottage cheese cups, and the cups were placed on a plastic sheet that was on a
greenhouse table. To each cup were added 350 g. of acid-washed (0.1 N HCl), dry quartz sand and 20 kernels of single-cross hybrid seed corn. An additional 200 g. of sand was used to cover the seeds, after which all cups received 100 ml. of distilled water. The cups were then covered with paper to reduce evaporation until the seedlings emerged from the sand. Distilled water and a K-free nutrient solution were added during the growing period. The nutrient solution contained 70.9 mg. of CaHPO₄, 494.4 mg. of MgSO₄·7H₂O, 217 mg. of FeSO₄·7H₂O, 1.0 mg. of H₃BO₃, 6.0 mg. of MnSO₄·2H₂O, and 4.0 mg. of ZnCl₂ per liter. Nitrogen as Ca(NO₃)₂ was added separately and periodically during the growing period. In all of the experiments except the sand-culture experiment, a total of 150 mg. NO₃-N was added to each cup.

Eight days after planting each cup was thinned to 15 plants. The plants removed in the thinning process were kept for total K analysis. The plants were grown in the sand for 10 days without any K being added. Analysis of plant tops showed that they contained less than 1% K at this time. The mat of roots below the sand at this time is shown in Figure 1. On the 10th day quantities of sand or field-moist soil equivalent to 100 g. (oven-dry basis) were added to cups with bottoms intact. The soil or sand received various treatments as described in the individual experiments. The bottomless cups containing the sand and growing corn plants were placed
Figure 1. Upper: The root mat of K-deficient corn plants grown in sand-culture for 10 days

Middle: Placing the root mat of K-deficient plants in contact with soil

Lower: Intensive root development in the soil after 10 days of root-soil contact
inside the cups containing the soil or sand, Figure 1. Since only 100 g. of soil or sand was used, a good contact between the mat of roots and the soil or sand was assured by placing the bottoms cut from the first cups into the second cups before the soil or sand was added to the latter cups. Paraffin was added so as to form a water-tight seal at the top of the artificial bottom. This seal prevented solution from getting between the artificial and true bottom of the cup.

The corn plants were harvested 5 or 10 days after the roots were brought in contact with the soil or sand, i.e., 15 or 20 days from the time of planting. The plant "tops" were removed by cutting the plants at the surface of the sand. In the experiments with soils, the roots were cut at the soil-sand junction. The roots from the sand ("roots in sand") were washed relatively free of sand with distilled water. There was such a mat of roots in the soil (Figure 1) that it was not deemed feasible to separate the roots from the soil. The "soil plus roots in soil" was thus treated as a unit. In the sand-culture experiment no division was made in the roots. That is, the roots from the sand in which the seeds were germinated and the roots from the 100 g. of sand placed in the second cup were left intact and washed relatively free of sand. In this case the "roots in sand" represents the entire root system.

Exchangeable K in the moist "soil plus roots in soil"
was determined by shaking the entire sample of soil and roots for 1 hour with 200 ml. of NH₄Ac and leaching with an additional 250 ml. of NH₄Ac solution. Exchangeable K in the moist soil before cropping was also determined by this same procedure. The harvested plant "tops" were oven dried for 48 hours at 65° C. and weighed. Total K in the "tops" was determined by dry ashing at 425° C., adding 0.1 M HCl, filtering, and analyzing the filtrate for K. The plants removed in the thinning process were placed with the "roots in sand" and the total K was determined in the same manner as for the "tops". Dry weight yields were not taken for the "roots in sand" because with limited washing some sand remained on the roots.

In each experiment some of the cups with plants growing in the sand were carried through the entire growing period without being brought in contact with soil and without adding K. The total K determined in the "tops" and in the "roots in sand" of these plants gave a measure of the K introduced by the seed or by impurities in the sand. This K will be referred to as "K added by seed". Frequently, 20 seeds, equal to the number used in each cup, were analyzed for total K, but the values obtained were essentially the same as those obtained from the "tops" plus "roots in sand" at the end of the cropping period. This indicated that there was no other source of K during the growing period, except that contained in the seeds originally.
The quantity of nonexchangeable soil $K$ released during the short-time cropping period was calculated by the following expression:

Nonexchangeable $K$ released = $K$ in "tops" + $K$ in "roots in sand" + exchangeable $K$ in "soil plus roots in soil" after cropping − exchangeable $K$ in soil before cropping − "$K$ added by seed" − $K$ added as $K_2SO_4$.

For some of the experiments, some of the terms in the above expression are zero. In view of the way nonexchangeable-$K$-release values are calculated, negative values would mean that some of the original exchangeable $K$ in the soil before cropping, and/or $K$ added by the seeds, and/or $K$ added as $K_2SO_4$ were converted to the nonexchangeable form during cropping.

It was necessary to first determine if the plants would absorb appreciable quantities of added $K$ during the relatively short absorption period and to determine the effect of added $NH_4$ on the uptake of readily available $K$. Thus, a short-time cropping experiment was conducted with 100 g. of sand added to the second cups and with different levels of $NH_4$ and $K$ added to the sand.

Other investigators have reported that $NH_4$ reduces $K$ absorption by plants in sand or nutrient culture. It was deemed possible that the effect of $NH_4$ on $K$ absorption might be reduced if an excess of $NO_3-N$ was always present with the $NH_4-N$. 
Therefore, various levels of NO₃⁻N were also used in this present experiment.

Sixty ml. of water containing the desired quantity of (NH₄)₂SO₄, K₂SO₄, and 1/3 or 2/5 of the total NO₃⁻N was added to the 100 g. of sand, in the cups with the bottoms intact, just prior to placing the roots of the 10-day-old plants in contact with the sand. For the 2 lowest levels of NO₃⁻N, 1/6 of the total added was applied on the 7th, 9th, 14th, and 19th day from the time of planting, while with the highest NO₃⁻N level 1/5 of the total was added on the same days with none being added on the 19th day. The quantities of NO₃⁻N and K added were based on preliminary experiments conducted by the author. The plants were harvested 10 days after being placed in contact with the sand. The average values obtained with two replications are given in Table 1.

The quantity of total K absorbed increased with increasing K additions, and most of the added K was recovered even at the 60-mg. addition. This indicates that during the short-time period of cropping, the plants will absorb large quantities of K if available.

At each K level the 150-mg. NO₃⁻N addition resulted in higher yields of plant "tops" than the 300 and 417-mg. additions, and at the 150-mg. NO₃⁻N addition the yield of "tops" increased with increasing additions of K. Furthermore, at a given K level the yield was not affected by higher additions
Table 1. Potassium content and yield of corn plants grown in sand culture with various levels of added nitrate, potassium, and ammonium. (Per cup)

<table>
<thead>
<tr>
<th>Treatment (mg.)</th>
<th>Tops</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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<tr>
<td></td>
<td></td>
<td>dry wt.</td>
<td>K</td>
<td>K</td>
<td>K</td>
<td>Total K in roots</td>
<td>Total K in plants</td>
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<td>NO$_3$-N</td>
<td>NH$_4$-N</td>
<td>K</td>
<td>yield (g.)</td>
<td>(mg.)</td>
<td>(%)</td>
<td>(mg.)</td>
<td>(mg.)</td>
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</tr>
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<td>18.09</td>
<td>75.04</td>
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of NH₄-N at the 150-mg. NO₃-N level, whereas the yield was decreased at the 417-mg. NO₃-N level when 38.8 mg. of NH₄-N was added. For the latter case the plants showed signs of burning around the margin of the leaves. The two highest levels of NO₃-N were obviously too high for the best plant growth, as reflected in the decreased yield of the "tops", irrespective of whether NH₄-N was also added.

The "tops" contained only 0.52% K with 0 K added, and the percent K increased with increasing additions of K. At the 60-mg. K addition the "tops" contained almost 2% K. At a given level of added K the percent K in the "tops" increased with increasing additions of NO₃-N, but this increase was due more to a decrease in yield than to an increase in K in the "tops". At a constant NO₃-N and K level, the percent K was not affected by the level of NH₄-N added.

The total K absorbed by the plants increased with increasing additions of K, and at the 150-mg. NO₃-N level the total quantity of K absorbed was not affected by the level of NH₄-N. However, at the two highest levels of NO₃-N the total K absorbed was reduced, especially at the highest level of NH₄-N.

It is concluded from the sand-culture experiment that the 150-mg. NO₃-N level gave the best plant growth, and, at this level, total K absorbed by the plants was not affected by the levels of NH₄-N used. Because of these results, the
150-mg. NO$_3$-N level was used in the experiments which follow.

A short-time cropping experiment was then conducted with 100-g. samples of soil to determine if native K in the soil and K added to the soil would be absorbed by the plants. Either 0 or 25 mg. of K as K$_2$SO$_4$ was added to 100-g. moist samples of Clarion and Marshall surface and subsoils, and the samples were then cropped. The soil samples were placed in cups with bottoms intact, and the K was added in sufficient water to allow thorough mixing with the soil by stirring. The roots of 10-day-old corn plants were placed in contact with the soil, and the plants were harvested after being in contact with the soil either 5 or 10 days. The experiment consisted of two replications, and the results are given as averages in Table 2.

There was greater absorption of K by the plants where K was added to the soil samples, and this indicates the plants will absorb greater quantities of K, if available, than the soils would normally supply under these cropping conditions. As would be expected, the plants absorbed more K with the 10-day cropping period than with the 5-day period.

The soils differed in regard to the quantities of K absorbed by the plants, and in some cases the quantity of K in the plants grown in soil was less than in the check. Furthermore, the difference between the quantity of K absorbed with 0 and 25 mg. of K added is less than 25 mg. These phenomena
Table 2. Absorption of potassium by corn plants grown on soil, with or without added K, for 5 or 10 days. (Per cup with 100 g. soil)

<table>
<thead>
<tr>
<th>Soil</th>
<th>K added (mg.)</th>
<th>K in plant tops + &quot;roots in sand&quot; (mg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5 days</td>
</tr>
<tr>
<td>Sand</td>
<td>0</td>
<td>20.87</td>
</tr>
<tr>
<td>Marshall 0 to 6 in.</td>
<td>0</td>
<td>27.05</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>45.50</td>
</tr>
<tr>
<td>Clarion 0 to 6 in.</td>
<td>0</td>
<td>25.99</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>46.11</td>
</tr>
<tr>
<td>Marshall 18 to 24 in.</td>
<td>0</td>
<td>21.56</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>33.62</td>
</tr>
<tr>
<td>Clarion 18 to 24 in.</td>
<td>0</td>
<td>17.46</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>36.26</td>
</tr>
</tbody>
</table>

are related to differences in the K-supplying power and fixation of added K by the soils, and they will be discussed in the experiments which follow.

In regard to the results from both the sand and soil experiments, it is concluded that the short-time cropping technique is satisfactory for determining the effect of added NH₄ and/or K on the release of nonexchangeable soil K. It is also proposed that the short-time cropping technique may prove useful for assessing the K-supplying power of soils and for studying equilibrium conditions among the various forms of K present in soils.
Effect of Added Ammonium

The short-time cropping technique was used to determine the effect of added NH$_4^+$ on the release of nonexchangeable soil K in samples of surface soils. Either 0, 7.8, 19.4, 38.8, or 76.6 mg. of NH$_4^+$-N, as (NH$_4$)$_2$SO$_4$, was added to cups containing 100-g., moist samples of either 0 to 6-inch Marshall or Clarion soil. The NH$_4^+$ was added in sufficient water to allow thorough mixing with the soil sample when stirred. Ten-day-old corn plants growing in sand were placed on the soil and the plants were harvested 10 days later.

NO$_3^-$-N was added periodically during the 20-day period, and the total quantity supplied was 150 mg. of N per cup. The experiment was conducted with four replicates, and the effect of added NH$_4^+$ on the release of nonexchangeable soil K is illustrated graphically in Figure 2.

The average quantities of nonexchangeable K released by 100-g. samples of soil when 0, 7.8, 19.4, 38.8, and 77.6 mg. of NH$_4^+$-N were added were 21.82, 16.44, 11.56, 4.96, and 0.12 mg. for the Marshall soil and 5.19, 4.74, 3.55, 0.91, and -1.44 mg. for the Clarion soil, respectively. It is apparent from these results that added NH$_4^+$ caused a decrease in the quantity of nonexchangeable K released. This effect became more pronounced as the level of NH$_4^+$ added increased, until at the highest NH$_4^+$-N level, essentially no release of K occurred.
Figure 2. Nonexchangeable K released during a 10-day cropping period from Marshall and Clarion surface soils with NH₄ added.
In regard to previous knowledge concerning chemical extraction, the inhibiting effect of NH$_4^+$ on the release of nonexchangeable soil K is in line with what would be expected. That is, the presence of a fixable cation blocks the release of a fixed cation.

At the highest NH$_4^+$-N rate in the Clarion soil sample, some K was fixed, i.e., there was less K extracted from the plants and soil at the end of the cropping period than there was at the beginning. This may be due to fixation of some of the initial exchangeable K during cropping, or it may be that K introduced in the seeds was lost to the soil sample and fixed. Jenny and Overstreet (45) reported that barley roots lost 32% more K when in a nutrient solution containing 0.33% NH$_4^+$-clay than when the roots were kept in water.

The Clarion and Marshall soil samples differed in regard to the quantities of nonexchangeable K released with 0 NH$_4^+$-N added. At this NH$_4^+$-N level, the Clarion sample released 104 pounds and the Marshall sample released 436 pounds per acre, even though the quantity of exchangeable K before cropping was 254 and 221 pounds per acre, respectively. Thus, this difference between the K-supplying power of the two soils could not have been evaluated from the quantities of exchangeable K present before cropping. The strong exploitation of soil K by the plants suggests that the short-time cropping technique may provide a relatively rapid method for
assessing the K-supplying power of soils.

More of the results from the above experiment are given in Table 3. The yields of "tops" were slightly less for the Clarion than for the Marshall sample, and for both samples of soil the yields were unaffected by added NH₄ except at the 77.6 mg. NH₄-N level. The total K and the percent K in the "tops" were higher for the Marshall than for the Clarion sample, and these K values decreased with increasing additions of NH₄ for both soils. In no case was the percent K in the "tops" very high, and the decrease in the yield of "tops" at the highest NH₄-N level was undoubtedly the result of the very low percent K.

The exchangeable K values for "soil plus roots in soil" are lower than the initial exchangeable K, thus, exchangeable K in the soil was reduced by cropping. As mentioned earlier, no attempt was made to separate the roots from the soil sample because of the matted condition, and, since these roots contained K, the exchangeable K values for the soil samples alone after cropping would be even lower than those given.

The exchangeable K values for "soil plus roots in soil" after cropping decreased with increasing rates of NH₄-N, particularly in the Marshall sample. This decrease could be due to a decrease in the quantity of exchangeable soil K and/or a decrease in the quantity of K in the roots in the soil. However, because of the consistent reduction in the percent K
Table 3. Yield and potassium content of plant tops, and exchangeable potassium after 10-days cropping, with various levels of ammonium added to Marshall and Clarion 0 to 6 inches soil samples. (Per cup with 100 g. soil)

<table>
<thead>
<tr>
<th>NH₄-N added (mg.)</th>
<th>Plant Tops</th>
<th>K in &quot;soil plus roots in soil&quot; after cropping (mg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry wt. (g.)</td>
<td>K (mg.)</td>
</tr>
<tr>
<td>Marshall</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>2.71</td>
<td>31.5</td>
</tr>
<tr>
<td>7.8</td>
<td>2.73</td>
<td>27.7</td>
</tr>
<tr>
<td>19.4</td>
<td>2.70</td>
<td>23.8</td>
</tr>
<tr>
<td>38.8</td>
<td>2.63</td>
<td>18.6</td>
</tr>
<tr>
<td>77.6</td>
<td>2.46</td>
<td>14.8</td>
</tr>
<tr>
<td>Clarion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>2.59</td>
<td>19.8</td>
</tr>
<tr>
<td>7.8</td>
<td>2.57</td>
<td>19.6</td>
</tr>
<tr>
<td>19.4</td>
<td>2.63</td>
<td>18.8</td>
</tr>
<tr>
<td>38.8</td>
<td>2.57</td>
<td>17.1</td>
</tr>
<tr>
<td>77.6</td>
<td>2.32</td>
<td>14.1</td>
</tr>
</tbody>
</table>

*The exchangeable K in the soils before cropping was 11.06 and 12.69 mg. per 100 g. for the Marshall and Clarion, respectively.

in the "tops" with increasing levels of NH₄-N and because the roots might be expected to follow the same general trend, the decrease in the K values for "soil plus roots in soil" for Marshall, in Table 3, are probably due to a decrease in the quantity of K in the roots in the soil sample. This conclusion is supported by the observation that a smaller decrease in the quantity of exchangeable K in the "soil plus roots in soil" was associated with a smaller decrease in the percent
K in the "tops" for the Clarion soil sample.

The effect of added NH$_4^+$ on the release of nonexchangeable K from moist, 18 to 24-inch Marshall and Clarion soil samples was determined in a separate experiment. The plants were harvested after being in contact with the soil samples for 5 and 10 days, and the rates of NH$_4^-$N used were 0 and 38.8 mg. per 100 g. soil. Otherwise, the experimental procedure was the same as for the surface samples. This experiment was carried out with two replicates.

As given in Table 4, in the absence of added NH$_4^+$ the Marshall subsoil sample released nonexchangeable K to the plants, but the Clarion sample did not. In fact, some of the originally exchangeable K and/or K introduced by the seeds were fixed by the Clarion subsoil sample. The quantity of K released by the Marshall sample increased with time of cropping, but there was little change with the Clarion sample.

When NH$_4^+$ was added the release of nonexchangeable K by the Marshall sample was largely inhibited, and with only 5-day cropping a slight amount of K fixation occurred. There was no effect of NH$_4^+$ added to the Clarion sample, but none would be expected since no release occurred even without NH$_4^+$ added.

As was the case with the surface samples (Table 3) the Marshall subsoil sample released more nonexchangeable K than the Clarion subsoil sample with no NH$_4^+$ added. Thus, using
Table 4. Release of nonexchangeable potassium from Marshall and Clarion subsoils during 5- and 10-day cropping periods with or without added NH$_4$. (Per cup with 100 g. soil)

<table>
<thead>
<tr>
<th>Soil*</th>
<th>NH$_4$-N (mg.)</th>
<th>Nonexchangeable K released (mg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 days</td>
<td>10 days</td>
</tr>
<tr>
<td>Marshall 18 to 24 in.</td>
<td>0 38.8</td>
<td>3.21 -1.09 5.88 0.40</td>
</tr>
<tr>
<td>Clarion 18 to 24 in.</td>
<td>0 38.8</td>
<td>-0.93 -1.23 -1.50 -0.67</td>
</tr>
</tbody>
</table>

*The exchangeable K in the soils before cropping was 2.30 and 2.31 mg. per 100 g. for the Marshall and Clarion, respectively.

The short-time cropping technique, the Marshall soil had a greater K-supplying power than the Clarion soil when no NH$_4$ was added even though the quantity of exchangeable K before cropping was about the same for the two soils. However, at high rates of added NH$_4$ there was little difference in the K-supplying power of the two soils because neither released much K with the cropping technique used. Therefore, when determining the K-supplying power of soils, due consideration should be given to the form of N added. Many studies made by other investigators may be difficult to properly evaluate, even though longer cropping periods may have been used than was the case in this study, because the form of N used was not specified (13, 14, 31, 69).
Effect of Added Potassium

Ten-day-old corn plants, grown in sand, were placed on 100-g. samples of soil to which had been added either 0 or 25 mg. of K as K₂SO₄. Soil samples from both the 0 to 6 and 18 to 24-inch depths of the Marshall and Clarion profiles were used, and the experiment included two replications. The plants were harvested after being in contact with the soil sample either 5 or 10 days, and the results are given in Table 5.

Table 5. Release of nonexchangeable soil potassium from Marshall and Clarion surface and subsoils samples during 5- and 10-day cropping periods with or without added potassium. (Per cup with 100 g. soil)

<table>
<thead>
<tr>
<th>Soil</th>
<th>K added</th>
<th>Nonexchangeable soil K released (mg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(mg.)</td>
<td>5 days</td>
</tr>
<tr>
<td>Marshall 0 to 6 in.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>4.44</td>
<td>14.75</td>
</tr>
<tr>
<td>25</td>
<td>1.06</td>
<td></td>
</tr>
<tr>
<td>Clarion 0 to 6 in.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.62</td>
<td>4.80</td>
</tr>
<tr>
<td>25</td>
<td>-0.28</td>
<td></td>
</tr>
<tr>
<td>Marshall 18 to 24 in.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>3.21</td>
<td>5.88</td>
</tr>
<tr>
<td>25</td>
<td>-9.06</td>
<td>-2.61</td>
</tr>
<tr>
<td>Clarion 18 to 24 in.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-0.93</td>
<td>-1.50</td>
</tr>
<tr>
<td>25</td>
<td>-4.06</td>
<td></td>
</tr>
</tbody>
</table>
Nonexchangeable K was released by all of the soil samples except the Clarion subsoil, when no K was added. Furthermore, the amount of K released increased with the time of cropping. Contrariwise, the Clarion subsoil sample fixed more K with the 10-day cropping period, but the results of later experiments were not in agreement with this particular result although they did support the other trends. When K was added to soils that normally released K, there was a decrease in the amount of nonexchangeable K released. In some cases, as with the Marshall subsoil sample, there was fixation of K instead of release. Fixation of K was increased with K added to the Clarion subsoil sample, which fixed K even if no K$_2$SO$_4$ was added.

It appears that added K, like NH$_4^+$, inhibits the release of nonexchangeable soil K. In the case of NH$_4^+$, this effect has been discussed in terms of the blocking effect of a fixable cation on the release of another fixed cation. In the case of added K the effect is the same, but, since the added and released cations are both K, it may be more easily interpreted in terms of the mass-action effect.

There is an equilibrium distribution among the watersoluble, exchangeable, and nonexchangeable forms of K in soils, and, when the water-soluble and exchangeable forms are depleted by cropping the nonexchangeable K is released. This accounts for the increase in the amount of nonexchangeable K
released with increased periods of cropping. If soluble K is added to soils there will be a tendency for K to shift in the other direction, i.e., K will be fixed instead of released as was the case in the Marshall subsoil sample with 25 and 0 mg. of K added, respectively. The results of this experiment are in agreement with the observation that subsoils tend to fix added K, such that it is not available to plants, more than surface soils.

For samples from a given soil, there was considerable difference between the quantities of nonexchangeable K released by surface and subsoil samples with the surface samples giving the greater release. This indicates the need for investigating more than the surface samples when attempting to determine the K-supplying power of a soil or when studying soil-plant relationships in general, since a large proportion of a plant's root system may be located in the subsoil. The importance of K distribution and behavior throughout the soil profile has recently been discussed by Hanway and Scott (37).

As has already been discussed, the Marshall soil samples released more K than the Clarion samples when no K was added. It is now apparent that this is also true with K added.

Effect of Added Ammonium and Potassium

After having studied the effect of added NH₄ and K on the release of nonexchangeable soil K when applied singly, an
investigation was made, in which 100-g. samples of moist soil received 25 mg. of K and either 0 or 38.8 mg. of NH$_4$-N, to determine the effect of adding both cations. In one case, K was added with sufficient water to allow thorough mixing with the soil, the soil was dried to about the field-moist state with the use of an electric fan, and the desired rate of NH$_4$-N was then mixed with the soil. The other case consisted of adding the desired rate of NH$_4$-N with water, stirring, drying to the field-moist state, and then adding the 25 mg. of K. Thus, the two cases differed in that the order of adding the NH$_4$ and K was reversed.

Ten-day-old corn plants were placed in contact with the soil sample, and the plants were harvested 10 days later. The experiment consisted of four replications, and surface and subsoil samples from the Marshall and Clarion profiles were used. The results of the experiment are given in Table 6.

A treatment in which neither K or NH$_4$ was added to the soil was not included in this experiment, but it has already been shown that the addition of K alone decreased the release of nonexchangeable soil K as compared to when no K was added (Table 5). Thus, the nonexchangeable K values for the treatment in Table 6 in which only K was added may be assumed to be lower than the values that would have been obtained if a 0 K-0 NH$_4$ treatment had been included in the present study.
Table 6. The effect of ammonium on the release of nonexchangeable potassium during a 10-day cropping period, by Marshall and Clarion soil samples when potassium was also added. (Per cup with 100 g. soil)

<table>
<thead>
<tr>
<th>NH₄-N added (mg.)</th>
<th>K added (mg.)</th>
<th>Nonexchangeable K released (mg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Marshall</td>
<td>Clarion</td>
</tr>
<tr>
<td></td>
<td>0 to 6 in.</td>
<td>18 to 24 in.</td>
</tr>
<tr>
<td></td>
<td>0 to 6 in.</td>
<td>18 to 24 in.</td>
</tr>
<tr>
<td>0</td>
<td>25</td>
<td>10.34</td>
</tr>
<tr>
<td>38.8</td>
<td>25</td>
<td>0.84</td>
</tr>
<tr>
<td>38.8</td>
<td>25</td>
<td>1.89</td>
</tr>
</tbody>
</table>

\(^a\)NH₄ added after K.

\(^b\)NH₄ added before K.
When NH$_4^+$ was also added to the soil sample, but after the K had been added, there was a further reduction in the quantity of K released by samples that still released K when 25 mg. of K was added. That is, the NH$_4^+$ reduced the quantity of nonexchangeable K released beyond what has been observed where K was added alone. Apparently the effect was just additive to that of the added K. In the case of the subsoil samples that exhibited a small amount of K fixation at the end of the cropping period when only K was added, the amount of K fixed was markedly increased when NH$_4^+$ was added after the K. It is evident that these samples of soils fixed appreciable amounts of the 25 mg. of added K and that added NH$_4^+$ inhibited its subsequent release during the cropping period.

When NH$_4^+$ was added before the K, there was a decrease in the quantity of K released by the samples that released K with only 25 mg. of K added. In these samples there was little difference in the quantities of K released irrespective of whether K or NH$_4^+$ was added to the soil sample first. In the case of the subsoil samples that did not release K but instead fixed some of the 25 mg. of K added, there was little effect of NH$_4^+$ if added before the K. However, since there was no release of K from these samples even with no NH$_4^+$ added, the added NH$_4^+$ could not be expected to exhibit a blocking effect. If enough NH$_4^+$ were added to satisfy all the fixation capacity of the soil samples before K was added, a decrease
in fixation of subsequently added K could be expected. This apparently did not occur in this experiment.
NITRIFICATION OF FIXED AMMONIUM IN CLAY MINERALS
AND SOILS AS AFFECTED BY POTASSIUM

The availability of fixed NH$_4^+$ in soils and clay minerals to nitrifying microorganisms has been studied rather extensively. In general it has been observed that only a small part of the fixed NH$_4^+$ is nitrified. In most of these experiments, considerable amounts of K could have been present because of the techniques used. As mentioned earlier, Hanway and Scott (36) and Hanway et al. (38) have shown that the chemical extraction of fixed NH$_4^+$ in soils and clay minerals is blocked by the presence of K in the extracting solution. Thus, it was considered possible that the low nitrification of fixed NH$_4^+$ was also due to this blocking effect of K.

NH$_4^+$ that is fixed by clay minerals is located between the layers of the crystal lattice. Furthermore, the lattice containing fixed NH$_4^+$ is contracted, and the space between the layers does not exceed a few angstroms. *Nitrosomonas* bacteria, which oxidize NH$_4^+$ to NO$_2^-$, are oval in shape and about 15,000 Å long and 10,000 Å wide (53). It is apparent that these bacteria are too large to enter between the lattice plates. Therefore, NH$_4^+$ fixed between the lattice plates must be replaced by some cation like Na that will produce an expanded lattice before it will be positionally available for nitrification. Since K inhibits the chemical
replacement of fixed NH₄⁺ by other cations, it is expected that it will consequently inhibit the nitrification of this NH₄⁺.

The objective of this study was to determine the effect of added K on the release and subsequent nitrification of fixed NH₄⁺ from soils and clay minerals. Because nitrification was to be studied as a function of added K, it was first necessary to determine if nitrification of available NH₄⁺ would occur when low amounts of K were present. Thus, the minimum level of K at which nitrification of NH₄⁺ from (NH₄)₂SO₄ would occur without K being a limiting factor was determined. Then, using a nitrifying system that contained this minimum level of K, the nitrification of fixed NH₄⁺ in various samples of soils and clay minerals was determined with as little interference from the blocking effect of K as possible. By adding known increments of K to these nitrifying systems, the effect of K on the nitrification of fixed NH₄⁺ was investigated.

Developing a Nitrifying Culture in a Low-Potassium System

An active nitrifying culture was obtained by adding a 25-g. sample of moist garden soil to a 500-ml. flask which contained 250 ml. of a buffered high-K nutrient solution. The nutrient solution contained 0.325 g. of MgSO₄·7H₂O, 5.100 g.
of \( \text{Na}_2\text{HPO}_4 \), 1.411 g. of \( \text{K}_2\text{HPO}_4 \), 1.000 g. of \((\text{NH}_4)_2\text{SO}_4\), 1 drop of a 10% \( \text{FeCl}_3 \) solution, and 50 ml. of soil extract per liter. The soil extract was prepared by autoclaving a 1,000-g. sample of Ida soil, 1 g. of \( \text{CaCO}_3 \), and 1 liter of distilled water for 30 minutes at 15 pounds pressure. The soil extract was then filtered until practically colorless. The flask was fitted with a two-hole rubber stopper, and the nitrifying system was incubated at room temperature and aerated continuously by passing a stream of water-saturated air through a capillary tube placed in the solution. Nitrification of the added \( \text{NH}_4 \) was followed by measuring the initial \( \text{NO}_3 \) content and then measuring the \( \text{NO}_3 \) content periodically.

The above nitrifying system contained \( \text{K} \) added in the nutrient solution as well as \( \text{K} \) added by the soil. A reduction in the \( \text{K} \) content and soil particles was made by transculturing. When rapid nitrification was evident and most of the added \( \text{NH}_4 \) had been nitrified, 10 ml. from the nitrifying system was transferred into 120 ml. of low-K nutrient solution which was the same as the high-K solution except no \( \text{K}_2\text{HPO}_4 \) was added. The analyses of the reagent-grade chemicals used in the preparation of this low-K nutrient solution did not indicate the presence of \( \text{K} \). Thus, the \( \text{K} \) in the low-K nutrient solution was mainly that added by the soil extract. The transculturing process was repeated until the nitrifying system had no visible traces of soil particles,
and the K content was reduced to that present in the low-K nutrient solution. The minimum K level obtained was thus determined by the K added to the nutrient solution by the soil extract. This K level varied slightly from one batch of nutrient solution to another but was generally less than 0.6 ppm.

There was a lapse of time between the individual nitrification experiments conducted, thus, the same batch of active nitrifying culture could not be used as inoculum for them all. Instead, an active nitrifying culture, in a clear low-K nutrient solution, was maintained by transculturing into fresh low-K nutrient solution whenever the NH$_4^+$ was depleted. Prior to conducting each experiment, a large enough batch of the nitrifying culture was prepared so that all treatments in the same experiment would receive inoculum from the one batch of culture. In each case, the nitrifying culture was not used as inoculum until all of the NH$_4^+$ in it was nitrified as indicated by a negative Nessler test. Thus, no NH$_4^+$ was introduced with the inoculum. Also, the nitrifying culture was used as inoculum as soon as the NH$_4^+$ was depleted so that the inoculum from different batches of culture would be as comparable as possible.

During the preparation of the low-K nitrifying culture, it was apparent that the nitrifying bacteria were nitrifying the NH$_4^+$ added with the nutrient solution even though the K
level was very low. Before this culture could be used to study the effect of added K on the nitrification of fixed NH$_4^+$ in soils and clay minerals, however, it was necessary to establish that the nitrification of available NH$_4^+$ would not be affected by the addition of K. That is, it was necessary to determine if the K level in the low-K nutrient solution was adequate for the nitrification process per se.

Nitrification experiments, in which a low-K nitrifying culture was used as inoculum, were carried out in duplicate by adding to a 300-ml. flask: 115 ml. of low-K nutrient solution that contained no NH$_4^+$, 5 ml. of distilled water or K$_2$HPO$_4$ solution, 5 ml. of an (NH$_4^+$)$_2$SO$_4$ solution, and 10 ml. of inoculum. Thus, the total volume was 135 ml. of solution per flask. The NO$_3^-$ content of each flask was determined soon after adding the inoculum, and the flasks were then incubated at room temperature and aerated. The solutions in the flasks were sampled periodically during the incubation period, and NO$_3^-$ determinations were made on the samples in order to follow nitrification of the added NH$_4^+$.

The nitrification of NH$_4^+$, supplied as (NH$_4^+$)$_2$SO$_4$, in the low-K nutrient solution was determined and compared with the nitrification of NH$_4^+$ in the same nutrient solution to which 300 ppm. K was added. An analysis of the low-K nutrient solution showed that only 0.40 ppm. K was present. The results of this experiment are presented in Figure 3 where the
Figure 3. Nitrification of NH$_4^+$, supplied as (NH$_4^+$)$_2$SO$_4$, in nutrient solutions containing 0.40 and 300 ppm.
percent nitrification of the added NH$_4$ is plotted against time of incubation.

Most of the added NH$_4$ was nitrified within 2 weeks of incubation, and there was no difference between the two K levels in regard to the percent nitrification. Apparently, there was enough K present at the 0.40 ppm. level for nitrification to proceed normally. The fact that there was only about 90% recovery of the NH$_4$-N as NO$_3$-N may partially be due to incorporation of N in microbial tissue.

There is disagreement in the literature as to the K requirement of bacteria, and, in the case of the nitrifying bacteria, there is a deficiency of information on the subject. The previous experiment shows that 0.40 ppm. K is adequate for nitrification. It was possible, however, that this amount of K could have an effect on the nitrification of fixed NH$_4$, and it was necessary to know if nitrifying cultures containing even less K could be developed.

The soil extract was the source of the K in the low-K nutrient solution used in the previous experiment. The following nutrient solutions, containing less than 0.40 ppm. K were prepared by omitting or diluting the soil extract.

Solution number

1-- 0.325 g. of MgSO$_4$·7H$_2$O, 5.100 g. of Na$_2$HPO$_4$, 1 drop of a 10% FeCl$_3$ solution, and 50 ml. of soil
extract per liter. (K content 0.17 ppm.).

2— 500 ml. of solution 1 and 500 ml. of solution 6 per liter. (K content 0.09 ppm.).

3— 333 ml. of solution 1 and 667 ml. of solution 6 per liter. (K content 0.06 ppm.).

4— 333 ml. of solution 1 and 667 ml. of solution 5 per liter. (K content 0.35 ppm.).

5— 0.325 g. of MgSO₄·7H₂O, 5.100 g. of Na₂HPO₄, 0.222 g. of Ca(HPO₄)₂, 1 drop of a 10% FeCl₃ solution per liter, and 1 ml. of a 100 ppm. K solution per liter. (K content 0.14 ppm.).

6— same as solution 5 except no K solution was added. (K content 0 ppm.).

Solution 1 was prepared in the same manner as the previously used low-K nutrient solution, but the soil extract apparently contributed less K. No soil extract was added in the preparation of solutions 4 and 5, thus, Ca(HPO₄)₂ was added to supply Ca. The K values of solutions 1 and 5 were determined with a flame photometer using solution 6 as a standard that was assumed to contain 0 ppm. K. The K values for solutions 2, 3 and 4 were then calculated from the values of solutions 1 and 5.

Nitrification experiments were conducted with these nutrient solutions, with 14.76 mg. NH₄ as (NH₄)₂SO₄ added per flask. Nitrifying bacteria were provided by adding 10 ml. of
inoculum per flask, from a nitrifying culture grown in a nutrient solution comparable to solution 1. Thus, all flasks contained some K, because K was transferred, in solution and in the bodies of the nitrifying bacteria, with the inoculum. To further dilute this K, inoculum was taken from the solutions at the end of the first nitrification cycle and transferred to respective fresh nutrient solutions which had NH added, and nitrification was carried through a second cycle. The nitrification results obtained in the first and second cycles are presented in Figures 4 and 5, respectively.

It is evident that K affects nitrification, and the quantity of K required for nitrification is low. There was little difference in the amount of nitrification that occurred with the 0.44 and 0.35 ppm K levels, but below these K levels nitrification was decreased. Nitrification at the 0.44 and 0.35 ppm K levels (Figures 4 and 5) was comparable to nitrification that occurred with 300 ppm K (Figure 3).

Nitrification with the highest K levels was about the same in both cycles, but, with the 0 and 0.06 ppm K nutrient solutions, nitrification was practically nil in the second cycle and was much less than in the first cycle. Evidently, enough K was transferred in the inoculum to allow some nitrification to occur in the first cycle, but in the second cycle the K had been diluted to a level such that nitrification was negligible.
Figure 4. First cycle study on nitrification of NH$_4^+$, supplied as (NH$_4$)$_2$SO$_4$, in nutrient solutions containing various low levels of K
Figure 5. Second cycle study on nitrification of NH₄⁺, supplied as (NH₄)₂SO₄, with inoculum from the first cycle study added to nutrient solutions containing various low levels of K.
K affects the rate as well as the amount of nitrification. With the highest K levels, there was a lag period of about 6 days and then nitrification was very rapid until most of the added $NH_4^+$ was converted to $NO_3^-$. The time of the lag period increased as the K level decreased. The characteristic lag period for the nitrifying bacteria has been observed and discussed by others (30, 62).

Nitrification in the 0 ppm. K nutrient solution was low in both the first and second cycles. To determine if the nitrifying bacteria were dead or just inactive due to a K deficiency, 30 ml. of inoculum from these flasks, at the end of the second cycle, was added to flasks containing 100 ml. of solution 5 (0.44 ppm. K) with $NH_4^+$ added. The nitrification results obtained in this experiment are given in Figure 6.

There was a lag period of about 13 days after which nitrification increased rapidly. This lag period was about twice as long as the lag period for the comparable solution in the first and second cycles. Only about 80% of the added $NH_4^+$ was nitrified, but at the end of the experiment a Nessler test indicated that no $NH_4^+$ was present. The $NH_4^-$N not recovered as $NO_3^-$N evidently was incorporated with microbial tissue.

The results of these experiments indicate that K is required by the bacteria responsible for the nitrification
Figure 6. Nitrification of $\text{NH}_4^+$, supplied as $(\text{NH}_4)_2\text{SO}_4$, with inoculum from 0 ppm. K flasks of second cycle study added to nutrient solution containing 0.44 ppm. K
process. Furthermore, the nitrifiers appear to be able to persist in an inactive state if K is limiting and become active if K is again supplied. Because of the small quantity of K necessary for nitrification, it would appear that the quantity of K in soils would probably never be low enough to limit the nitrification process per se.

Ammonium-Saturated Vermiculites

By leaching samples of vermiculite until NH$_4^+$-saturated, as was done in this study, soluble and exchangeable K should be at a minimum. The vermiculite samples contained considerable amounts of nonexchangeable K, probably because of biotite that is present, but it was assumed that most of this K would remain in a nonexchangeable form during the nitrification experiment. Thus, by using inoculum from a nitrifying culture that contained 0.55 ppm. K, it was possible to study the nitrification of fixed NH$_4^+$ in vermiculite at a low K level and to evaluate the effect of K on the nitrification of fixed NH$_4^+$ by adding known amounts of K.

Samples of NH$_4^+$-saturated vermiculite were prepared, and the values for total, exchangeable, and fixed NH$_4^+$ are given in Table 7. Exchangeable NH$_4^+$ constituted only 3 to 6% of the total, and these quantities should be readily nitrified regardless of the level of added K.
Table 7. Total, exchangeable, and fixed ammonium in ammonium-saturated vermiculites

<table>
<thead>
<tr>
<th>Vermiculite</th>
<th>NH₄⁺ extracted (me. per 100 g.)</th>
<th>Fixed NH₄ (me. per 100 g.)</th>
<th>Exchangeable NH₄ (% of total)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kjeldahl (total)</td>
<td>KOH distillation (exchangeable)</td>
<td></td>
</tr>
<tr>
<td>Montana High</td>
<td>65.03</td>
<td>4.18</td>
<td>60.85</td>
</tr>
<tr>
<td>South Carolina High</td>
<td>79.46</td>
<td>2.92</td>
<td>76.54</td>
</tr>
<tr>
<td>South Carolina Low</td>
<td>39.57</td>
<td>1.29</td>
<td>38.28</td>
</tr>
</tbody>
</table>
Nitrification experiments, consisting of two replicates, were conducted with the NH$_4^+$-saturated samples by adding to a 300-ml flask: 115 ml. of low-K nutrient solution that contained no NH$_4^+$, 5 ml. of distilled water or K$_2$HPO$_4$ solution, 14.76 mg. of NH$_4^+$ added as NH$_4^+$-saturated vermiculite or as 5 ml. (NH$_4$)$_2$SO$_4$ solution, and 10 ml. of low-K inoculum. The flasks which received the NH$_4^+$-saturated samples had 5 ml. of distilled water added so as to provide 135 ml. of total solution per flask. The quantity of NH$_4^+$ added per flask was constant, and, since the NH$_4^+$-saturated vermiculites differed as to the total quantity of NH$_4^+$ present per gram, it was necessary to add different quantities of the NH$_4^+$-saturated materials. Since it has been shown (38) that the order of adding K and the replacing cations affects the blocking effect of K in chemical extractions, the various components were always added in the order listed. The NO$_3^-$ content of each flask was determined soon after adding the inoculum, and the flasks were then incubated at room temperature and aerated. The solution in each flask was sampled periodically during the incubation period and NO$_3^-$ determinations made in order to follow the nitrification of added NH$_4^+$. The nitrification results obtained with the various vermiculite samples are given in Figures 7, 8, and 9 where the percent nitrification of added NH$_4^+$ is plotted against days of incubation. When 0 K was added, practically all the NH$_4^+$ in the vermiculite was
Figure 7. Nitrification of $\text{NH}_4^+$ in $\text{NH}_4^+$-saturated South Carolina High vermiculite as affected by the level of added $K$ in the nutrient solution
Figure 8. Nitrification of NH$_4^+$ in NH$_4^+$-saturated Montana High vermiculite as affected by the level of added K in the nutrient solution
NITRIFICATION OF ADDED NH₄ (%)

TIME OF INCUBATION (DAYS)

0 ppm. K
100 ppm. K
200 ppm. K
300 ppm. K
Figure 9. Nitrification of $\text{NH}_4^+$ in $\text{NH}_4^+$-saturated South Carolina Low vermiculite as affected by the level of added $\text{K}$ in the nutrient solution
The graph illustrates the nitrification of added NH₄⁺ (%). It shows the time of incubation (days) on the x-axis and the nitrification (% of added NH₄⁺) on the y-axis. The graph includes lines for different potassium concentrations:

- 0 ppm. K
- 100 ppm. K
- 200, 300 ppm. K

The lines indicate an increasing trend with time, suggesting a higher nitrification rate with increased potassium concentration.
nitrified. Since 98% of the NH\textsubscript{4} was nitrified in the 0 K treatment, apparently not enough of the native nonexchangeable K was released at any time during the nitrification period to affect nitrification of the remaining NH\textsubscript{4}. Likewise, the small amount of K in the low-K nutrient solution and in the inoculum did not affect the nitrification of the fixed NH\textsubscript{4} in the vermiculite. Allison et al. (7) found that NH\textsubscript{4} in two samples of vermiculite was nearly as available to nitrifying bacteria as was that in (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}, but in a third sample the availability was only 11 to 16%.

It is apparent that addition of K inhibited the nitrification of NH\textsubscript{4} in the three vermiculites. More than the exchangeable NH\textsubscript{4} in the Montana High and South Carolina High vermiculites was nitrified when there was 300 ppm. K present. Therefore, some of the fixed NH\textsubscript{4} was released even at the highest K level used. In the case of the South Carolina Low vermiculite, little more than the exchangeable NH\textsubscript{4} was nitrified at the 200 and 300 ppm. K levels, i.e., no fixed NH\textsubscript{4} was released. The difference among the minerals, in regard to the effect of added K on the release and subsequent nitrification of fixed NH\textsubscript{4}, can be seen more readily in Figure 10 where the nitrification, after 21 days' incubation, has been plotted against the ratio of fixable/non-fixable cations in the nitrifying system. The nutrient solution contained 8.26 me. of Na and 0.30 me. of Mg which would tend to replace the
Figure 10. Nitrification of NH$_4^+$ in NH$_4^+$-saturated vermiculites as affected by the ratio of fixable to non-fixable cations in the nutrient solution.
Thus, the ratio of fixable to non-fixable cations was $\text{me. K}/(\text{me. Na} + \text{me. Mg})$. Only the added K was used in this calculation. The K in the low-K nutrient solution and any K released from the vermiculite were assumed to be negligible, thus, the calculated ratio was zero when no K was added.

Nitrification of $\text{NH}_4^+$ in the vermiculites decreased as the me. K/(me. Na + me. Mg) ratio increased, but added K did not affect nitrification when $\text{NH}_4^+$ was supplied as $(\text{NH}_4)_2\text{SO}_4$. The nitrification of available $\text{NH}_4^+$ was not decreased by the added K, but the nitrification of fixed $\text{NH}_4^+$ in vermiculite was decreased. It is obvious that the vermiculites are different in regard to the effect of added K on the availability of fixed $\text{NH}_4^+$ to nitrification. The reason for this difference is not apparent.

Since nitrification converts released $\text{NH}_4^+$ to $\text{NO}_3^-$, $\text{NH}_4^+$ displaced by the Na or Mg did not accumulate in the nutrient solution during the incubation period. The latter statement is based on the fact that all treatments gave a negative test with Nessler's reagent at the end of the incubation period. Thus, the nitrifying system may be considered to be comparable to a chemical extraction of $\text{NH}_4^+$ by alkaline distillation, in that only K was blocking the release of the fixed $\text{NH}_4^+$.

Hanway et al. (38) reported that in alkaline distillations essentially no fixed $\text{NH}_4^+$ was released from a Montana
vermiculite when the K/Na ratio exceeded 0.02, but in a NaCl extraction some fixed NH$_4^+$ was released at a ratio of 0.10. They stated that this difference was probably due to the effect of pH. The present experiment would be somewhat comparable to the NaCl extraction, in regard to pH, because the pH of the nutrient solution was 8.1 and about 7 before and after nitrification, respectively. Also, the Montana High vermiculite released some fixed NH$_4^+$ and it was nitrified at a ratio as high as 0.10.

**Partially-Ammonium-Saturated Vermiculite**

If the NH$_4^+$ in NH$_4^+$-saturated vermiculite is extracted by leaching with a 1 N NaCl solution, it is observed that the remaining NH$_4^+$ becomes increasingly difficult to extract as the leaching process is continued. It is possible that the NH$_4^+$ ions located near the edge of the vermiculite particle are removed first, thus, the NH$_4^+$ ions remaining must be replaced from fixed positions farther in the interior of the crystal lattice. On the other hand, NH$_4^+$ ions between lattice layers may be fixed with different tenacities and are removed accordingly. Thus, the remaining NH$_4^+$ ions would be those that are fixed more strongly. In either case, it might be expected that K would block the release of fixed NH$_4^+$ to different degrees depending on the degree of NH$_4^+$. 
saturation. The objective of this study was to determine the effect of K on the nitrification of NH\textsubscript{4} in vermiculite at different degrees of NH\textsubscript{4} saturation.

Partially-NH\textsubscript{4}-saturated vermiculite may be prepared by leaching NH\textsubscript{4}-saturated samples so as to remove part of the NH\textsubscript{4}, or samples may be prepared by merely adding NH\textsubscript{4} to vermiculite. Both of these methods were used in obtaining partially-NH\textsubscript{4}-saturated vermiculite samples for use in this study.

Partially-NH\textsubscript{4}-saturated South Carolina High vermiculite was prepared by leaching NH\textsubscript{4}-saturated samples with 1 N NaCl so as to remove part of the NH\textsubscript{4}. The excess chloride was removed by washing with 70% methanol, and the samples were then air dried. The total and fixed NH\textsubscript{4} remaining on these samples were determined, and the results are given in Table 8. Other samples of partially-NH\textsubscript{4}-saturated vermiculite were prepared by adding quantities of NH\textsubscript{4}, equivalent to that remaining on the above samples, to Na-saturated vermiculite. The NH\textsubscript{4}, as (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}, was added in sufficient water to allow thorough mixing with the vermiculite, and the material was then air dried. Fixed NH\textsubscript{4} was calculated as the difference between the quantity of NH\textsubscript{4} added and that removed by KOH distillation, and the results are given in Table 9. For simplicity of reference the two groups of partially-NH\textsubscript{4}-saturated samples will be referred to as "leached" and
Table 8. Ammonium released by Kjeldahl analysis and KOH distillation from NH₄⁺-saturated and partially-NH₄⁺-saturated South Carolina High vermiculite prepared by "leaching"

<table>
<thead>
<tr>
<th>NH₄⁺ released as determined by:</th>
<th>Fixed NH₄⁺</th>
<th>NH₄⁺ saturated</th>
<th>Exchangeable NH₄⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>(me./100 g.)</td>
<td>(me./100 g.)</td>
<td>(%)</td>
<td>(% of total)</td>
</tr>
<tr>
<td>Kjeldahl</td>
<td>KOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>79.46</td>
<td>2.92</td>
<td>76.54</td>
<td>100.0</td>
</tr>
<tr>
<td>30.50</td>
<td>2.32</td>
<td>28.18</td>
<td>38.4</td>
</tr>
<tr>
<td>3.11</td>
<td>0.46</td>
<td>2.65</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Table 9. The release of NH₄⁺ by KOH distillation when NH₄⁺ was "added" to Na-saturated South Carolina High vermiculite

<table>
<thead>
<tr>
<th>NH₄⁺ added</th>
<th>NH₄⁺ released by KOH</th>
<th>Fixed NH₄⁺</th>
<th>Exchangeable NH₄⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>(me./100 g.)</td>
<td>(% of exchange capacity)</td>
<td>(me./100 g.)</td>
<td>(me./100 g.)</td>
</tr>
<tr>
<td>79.46</td>
<td>100.0</td>
<td>11.44</td>
<td>68.02</td>
</tr>
<tr>
<td>30.50</td>
<td>38.4</td>
<td>4.15</td>
<td>26.35</td>
</tr>
<tr>
<td>3.11</td>
<td>3.9</td>
<td>1.20</td>
<td>1.91</td>
</tr>
</tbody>
</table>
From Tables 8 and 9 it is apparent that, with both methods of preparing the partially-NH$_4^+$-saturated samples, a greater percent of the total NH$_4^+$ was exchangeable as the percent NH$_4^+$ saturation decreased. The NH$_4^+$-saturated sample contained only 4% exchangeable NH$_4^+$, whereas the exchangeable NH$_4^+$ values were greater than 4% for the partially-NH$_4^+$-saturated samples. These results are not in agreement with those of Bower (19) and Nommik (55), who reported that the percent of the added NH$_4^+$ fixed decreased as the quantity of NH$_4^+$ added increased. However, in the present study the percent NH$_4^+$ saturation varied inversely with the percent Na saturation, therefore, when the exchangeable NH$_4^+$, in the partially-saturated samples, was determined by KOH distillation, Na was also present and could act as a replacing cation. Thus, the exchangeable values would be expected to be higher the more Na that was present.

The exchangeable-NH$_4^+$ values for the "added" samples, Table 9, are higher than the values obtained with the "leached" samples, Table 8. That some of the NH$_4^+$ remained in the soluble form in the former samples is evident because 14.4% was exchangeable when NH$_4^+$ equivalent to 100% saturation was added, whereas only 4% was exchangeable in the 100%-NH$_4^+$-saturated "leached" sample.

"Leached" samples were added in sufficient quantity to
provide a constant rate of 7.38 mg. of NH₄ per flask, and a
nitrification experiment was conducted in the same manner
as described for the NH₄-saturated vermiculites. Since the
samples differed in regard to the percent NH₄ saturation,
0.5149, 1.3412, and 13.1377 g. of 100%, 38.4%, and 3.9%- 
NH₄-saturated vermiculite, respectively, were added to separate flasks. Other flasks in the nitrification experiment contained the same quantities of Na-saturated vermiculite, and 7.38 mg. of NH₄ per flask was added in 20 ml. of an 
(NH₄)₂SO₄ solution, after which the samples were air dried. The percent nitrification is plotted against weeks of incubation in Figure 11.

Nitrification was decreased with 100 and 300 ppm. K added, but there was little effect of K at the lower rates. At the 300 ppm. K level, the percent nitrification was less than the exchangeable NH₄, except for 100%-NH₄-saturated "leached" sample and the comparable "added" sample. It is not known why the percent nitrification should be less than the percent exchangeable NH₄ unless it is due to the possibility that the chemically determined exchangeable-NH₄ values might be high, because the samples were partially-Na-saturated. This fits the concept of the discussion given earlier for the results presented in Tables 8 and 9.

During the first 4 weeks of incubation and at the three lowest K levels, the rate of nitrification was less for the
Figure 11. Nitrification from partially-$NH_4^+$-saturated South Carolina High vermiculite as related to K level, percent $NH_4^+$ saturation, and method of preparing the samples.
3.9%-NH₄⁺-saturated samples than for the other samples. However, at the end of the incubation periods, the percent nitrification was usually about the same for all samples with the three lowest K levels. At the two highest K levels, the final percent nitrification was greater for the 3.9%-NH₄⁺-saturated samples than for the others, with the exception of the "added" sample that received NH₄⁺ equivalent to its exchange capacity.

The percent nitrification was greater for the "added" samples than for the "leached" samples. This would be expected, because, as has already discussed, the percent exchangeable NH₄⁺ was greater for the former samples.

The quantity of K in solution was determined at the end of the incubation period. The quantity of K adsorbed or released by the samples of vermiculite was calculated as the difference between the K added at the beginning of the incubation period and the K present in solution at the end of the incubation period. The percent nitrification and K adsorbed by the vermiculite are plotted against K added for the 3.9%- and 38.4%-NH₄⁺-saturated samples in Figures 12 and 13, respectively.

As discussed previously, the percent nitrification was less with increasing additions of K and was greater from the "added" samples than from the "leached" samples. Adsorption of K by the vermiculite increased with increasing additions.
Figure 12. Nitrification from 3.9%-$\text{NH}_4^+$-saturated South Carolina High vermiculite as related to $K$ adsorbed by the vermiculite
Figure 13. Nitrification from 38.4%-NH₄⁺-saturated South Carolina High vermiculite as related to K adsorbed by the vermiculite
of K, and the quantity of K adsorbed was greater for the "leached" samples than for the "added" samples. Thus, the "leached" samples adsorbed the greater quantity of K and the percent nitrification was less from these samples than from the "added" samples. It can be stated that, in general, the percent nitrification was inversely proportional to the quantity of K adsorbed by the vermiculite.

The milligrams of K added and adsorbed per gram of vermiculite were less for the 3.9%-NH₄⁺-saturated samples (Figure 12) than for the 38.4%-NH₄⁺-saturated samples (Figure 13). Since the percent nitrification was about the same for the two groups of samples but at different rates of added K, it is concluded that the quantity of K required to block the release of fixed NH₄⁺ decreases as the degree of NH₄⁺ saturation decreases.

Bentonite and Illite

With no K added most of the NH₄⁺ in vermiculite is nitrified even though 95% of it is fixed against chemical extraction by KOH distillation. Vermiculite is a trioctahedral micaceous mineral, whereas montmorillonite and illite are dioctahedral minerals and are more common in soils. Allison et al. (3) have reported low nitrification of fixed NH₄⁺ in these latter minerals. Thus, an experiment was conducted
with the two dioctahedral minerals to determine the nitrification of fixed NH$_4^+$ under controlled low K conditions and to determine the effect of added K.

Bentonite does not fix much NH$_4^+$ under moist conditions or on drying at 110° C. When NH$_4^+$-saturated bentonite is heated at higher temperatures, however, it does fix appreciable amounts (63). Bentonite containing fixed NH$_4^+$ was prepared by heating NH$_4^+$-saturated bentonite at 350° C. for 24 hours. Illite also does not fix much NH$_4^+$ if it has not been previously treated to remove K. Nevertheless, the illite used in this experiment was merely NH$_4^+$ saturated and heated at 110° C. for 24 hours.

Fixed NH$_4^+$ in these clays was calculated as the difference between the quantity of NH$_4^+$ extracted by Kjeldahl analysis (total) and KOH distillation (exchangeable), and the results are given in Table 10. The bentonite fixed more than 50% of the NH$_4^+$, whereas the illite fixed only about 7% of the total NH$_4^+$ present.

Nitrification experiments were conducted by the usual procedure, and the low-K nitrifying culture which was used as inoculum contained 0.5 ppm. K. Enough of the NH$_4^+$-saturated clays was added so as to provide 14.76 mg. of NH$_4^+$ per flask, and the quantity of K added was varied between 0 and 300 ppm.

The nitrification results obtained with bentonite are
Table 10. Ammonium released by Kjeldahl analysis and KOH distillation from NH₄⁺-saturated bentonite and illite

<table>
<thead>
<tr>
<th>Clay</th>
<th>NH₄⁺ released by:</th>
<th>Fixed NH₄⁺</th>
<th>Exchangeable NH₄⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(me./100 g.)</td>
<td>(me./100 g.)</td>
<td>(% of total)</td>
</tr>
<tr>
<td></td>
<td>Kjeldahl</td>
<td>KOH</td>
<td></td>
</tr>
<tr>
<td>Bentonite</td>
<td>50.44</td>
<td>24.68</td>
<td>25.76</td>
</tr>
<tr>
<td>Illite</td>
<td>15.19</td>
<td>14.18</td>
<td>1.01</td>
</tr>
</tbody>
</table>

given in Figure 14. Nitrification in the (NH₄⁺)₂SO₄ treatment was only 83% in this experiment, whereas in other experiments it was approximately 90%. It is not known why the recovery of added NH₄⁺ was not greater in the (NH₄⁺)₂SO₄, because no NH₄⁺ was present in solution at the end of the experiment according to the Nessler test. With 0 ppm. K added, the nitrification of NH₄⁺ in the NH₄⁺-saturated bentonite was 10% less than in the (NH₄⁺)₂SO₄. Thus, all of the fixed NH₄⁺ was not nitrified in the bentonite even in the absence of added K. Nitrification decreased with increasing K additions, and with 300 ppm. K slightly less than the exchangeable NH₄⁺ was nitrified. Thus, no fixed NH₄⁺ was released and subsequently nitrified when 300 ppm. K was added.

In the vermiculite experiments, nitrification was greater in the NH₄⁺-saturated clay with 0 ppm. K added than in the (NH₄⁺)₂SO₄ treatment. With the bentonite, however, nitrifica-
Figure 14: Nitrification in NH$_4^+$-saturated bentonite with various levels of added K in the nutrient solutions
Nitrification of added NH₄⁺ (%)

Time of Incubation (Days)

- (NH₄)₂SO₄
- 0 ppm K
- 100 ppm K
- 200 ppm K
- 300 ppm K
tion was only 72% with 0 ppm. K added, and this is considerably less than what occurred in the \((\text{NH}_4\text{)}_2\text{SO}_4\).

The nitrification results obtained with the illite samples are given in Figure 15. Nitrification in the \((\text{NH}_4\text{)}_2\text{SO}_4\) treatment was 88.5% and this is about what was obtained in other experiments with the exception of the bentonite. Like the bentonite, nitrification was less, even with 0 ppm. K added, when \(\text{NH}_4^+\) was supplied in \(\text{NH}_4^-\)-saturated illite than when supplied as \((\text{NH}_4\text{)}_2\text{SO}_4\). In fact, recovery of \(\text{NH}_4^-\text{N}\) as \(\text{NO}_3^-\text{N}\) was less than the quantity of exchangeable \(\text{NH}_4^+\) in the illite. Nitrification was only slightly affected by added K, and this effect was rather inconsistent. However, the effect of K would not be expected to be very great since only about 7% of the total \(\text{NH}_4^+\) in the \(\text{NH}_4^-\)-saturated illite was fixed.

In view of these results obtained with bentonite and illite, further experiments were conducted with these clays to learn more about their behavior and to learn why they behaved differently from vermiculite with no K added.

Illite samples containing fixed \(\text{NH}_4^+\) were prepared in several ways. Since heating is known to release nonexchangeable K from some minerals, some of the heated samples, comparable to those used in the preceding experiment, were leached with 1 M NaCl so as to remove any K that might have been released during the heating process. Excess chloride was removed by washing with distilled water, and the samples
Figure 15. Nitrification in $\text{NH}_4^+$-saturated illite with various levels of added K in the nutrient solutions
were kept in a moist condition until used in a nitrification experiment. This leaching with NaCl also removed some of the exchangeable NH\textsubscript{4}⁺, therefore, a greater percent of the remaining NH\textsubscript{4}⁺ would be expected to be fixed. In this event, the effect of added K on the nitrification of fixed NH\textsubscript{4}⁺ should be easier to evaluate.

Other illite samples were degraded by removing K with sodium tetraphenylboron. The illite samples were heated at 70° C. for 5 days in 2 N NaCl with sodium tetraphenylboron added periodically. The K replaced from the illite by Na was precipitated by the tetraphenylboron. This K precipitate was removed and the clay NH\textsubscript{4}⁺ saturated by leaching with an aqueous solution containing 50% acetone and 1 N with respect to NH\textsubscript{4}⁺Cl. Excess acetone and chloride were removed by washing with 70% methanol, and the illite was then air dried and heated at 110° C. for 24 hours. Some of these degraded NH\textsubscript{4}⁺-saturated samples were then leached with NaCl. The excess chloride was removed with water, and the samples were kept in a moist state until used in nitrification experiments.

Natural illite samples were K-saturated by leaching with 1 N KCl, and the excess chloride was removed by washing with 70% methanol. The samples were then air dried and later used in nitrification studies with NH\textsubscript{4}⁺ supplied as (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}.

The quantities of the various forms of NH\textsubscript{4}⁺ in the dif-
ferent samples were determined by Kjeldahl analysis (total) and KOH distillation (exchangeable), and these results are given in Table 11. Fixed NH$_4^+$ was calculated as the difference between total and exchangeable. The NH$_4^+$-saturated natural illite had 7% of the total NH$_4^+$ fixed, but after leaching with NaCl 53% of that remaining was fixed.

The sodium tetraphenylboron degradation treatment increased the amount of NH$_4^+$ adsorbed by the illite. Similar results obtained by Hanway (34) led him to suggest that this was indirect evidence that K had been displaced from the illite. With this increase in total NH$_4^+$, there was an increase in both the fixed and exchangeable NH$_4^+$. Leaching the degraded NH$_4^+$-saturated illite with NaCl removed exchangeable and fixed NH$_4^+$ but more of the exchangeable, thus, the percent of the total NH$_4^+$ remaining that was fixed increased.

NH$_4^+$ was added as either NH$_4^+$-illite or (NH$_4^+$)$_2$SO$_4$ at the rate of 3.52 mg. of NH$_4^+$ per flask, and a nitrification experiment was conducted in the usual manner. (NH$_4^+$)$_2$SO$_4$ was added to flasks which contained no illite or illite which was K saturated to prevent any fixation of the added NH$_4^+$. The results of nitrification with time are given in Figures 16 and 17, and the total nitrification in 28 days is given in Table 12. The K content of the nutrient solution was determined at the end of the incubation period, and these values are given in Table 12 also.
Table 11. Ammonium in variously treated illite samples

<table>
<thead>
<tr>
<th>Treatment</th>
<th>NH$_4^+$ (me. per 100 g.)</th>
<th>Fixed NH$_4^+$ (% of total)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Totala</td>
<td>Exchangeable</td>
</tr>
<tr>
<td>K-saturated</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NH$_4^+$-saturated, heated at 110° C.</td>
<td>15.19</td>
<td>14.18</td>
</tr>
<tr>
<td>NH$_4^+$-saturated, heated at 110° C., NaCl leached, and kept moist</td>
<td>3.90</td>
<td>1.85</td>
</tr>
<tr>
<td>Degraded, NH$_4^+$-saturated, heated at 110° C.</td>
<td>22.74</td>
<td>17.05</td>
</tr>
<tr>
<td>Degraded, NH$_4^+$-saturated, heated at 110° C., NaCl leached, and kept moist</td>
<td>3.89</td>
<td>0.58</td>
</tr>
</tbody>
</table>

*aThe K-saturated illite contained 4.45 me. of total NH$_4^+$ per 100 g. This quantity has been deducted from the total-NH$_4^+$ values for all of the treatments, thus, total NH$_4^+$ in the K-saturated illite is given as zero.
Table 12. Nitrification in 28 days from variously treated illite samples with or without K added

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Soluble K (ppm.)</th>
<th>Exchangeable NH₄⁺ (% of total)</th>
<th>Nitrification (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>added</td>
<td>final</td>
<td></td>
</tr>
<tr>
<td>No illite</td>
<td>0</td>
<td>0.17</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>304</td>
<td>-</td>
</tr>
<tr>
<td>K-saturated</td>
<td>0</td>
<td>224</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>496</td>
<td>-</td>
</tr>
<tr>
<td>NH₄⁺-saturated, heated at 110°C.</td>
<td>0</td>
<td>14.5</td>
<td>93.4</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>275</td>
<td>93.4</td>
</tr>
<tr>
<td>NH₄⁺-saturated, heated at 110°C.</td>
<td>0</td>
<td>11.1</td>
<td>47.4</td>
</tr>
<tr>
<td>NaCl leached, and kept moist</td>
<td>300</td>
<td>210</td>
<td>47.4</td>
</tr>
<tr>
<td>Degraded, NH₄⁺-saturated, and</td>
<td>0</td>
<td>14.0</td>
<td>75.0</td>
</tr>
<tr>
<td>heated at 110°C.</td>
<td>100</td>
<td>104</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>316</td>
<td></td>
</tr>
<tr>
<td>Degraded, NH₄⁺-saturated, heated</td>
<td>0</td>
<td>34</td>
<td>14.9</td>
</tr>
<tr>
<td>at 110°C., NaCl leached, and</td>
<td>100</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>kept moist</td>
<td>300</td>
<td>74</td>
<td></td>
</tr>
</tbody>
</table>

*The treatments which did not have NH₄⁺ added as NH₄⁺-illite had NH₄⁺ added as (NH₄)₂SO₄.*
Figure 16. Nitrification of NH₄ in variously treated samples of natural illite
NITRIFICATION OF ADDED NH$_4$ (%) vs TIME OF INCUBATION (DAYS)

- (NH$_4$)$_2$SO$_4$
- K-ILLITE, (NH$_4$)$_2$SO$_4$
- NH$_4$-ILLITE, 110°C
- NH$_4$-ILLITE, 110°C, NaCl LEACHED

- 0 ppm. K
- 300 ppm. K
- 0, 300 ppm. K
Figure 17. Nitrification of NH$_4$ in variously treated samples of degraded illite
NITRIFICATION OF ADDED $\text{NH}_4^+$ (%)

TIME OF INCUBATION (DAYS)

- $0, 300$ ppm K
- $0$ ppm K
- $300$ ppm K
- $100$ ppm K

- K-ILLITE, ($\text{NH}_4)_2\text{SO}_4$
- DEGRADED $\text{NH}_4$-ILLITE, $110^\circ\text{C}$
- DEGRADED $\text{NH}_4$-ILLITE, $110^\circ\text{C}$, NaCl LEACHED

- $0$ ppm K
- $100$ ppm K
- $300$ ppm K
Nitrification was essentially the same when \((\text{NH}_4)^+\text{SO}_4\) was added to flasks containing no illite as when added to flasks containing K-saturated illite (Figure 16). But again as in the previous illite experiment, nitrification was less when \text{NH}_4 was supplied as \text{NH}_4^-\text{illite} than when supplied as \((\text{NH}_4)^+_\text{SO}_4\). The K-saturated illite should not fix the added \text{NH}_4 and should be a suitable check for all the illite treatments. Under these conditions the \text{NH}_4 was readily nitrified, thus, the presence of the illite per se had little effect. The lower nitrification in the \text{NH}_4^-\text{saturated illite} must be due to unavailability of the \text{NH}_4 in illite to nitrification even though the K was as low as 0.4 ppm.

A comparison of nitrification in the \text{NH}_4^-\text{saturated natural (Figure 16) and degraded (Figure 17) illite shows that nitrification was about the same, with 0 ppm. K added, even though 6.6 and 25\% of the \text{NH}_4 was fixed (Table 12), respectively. That is, nitrification in both the natural and degraded \text{NH}_4^-\text{saturated illite was less than in the K-saturated illite with \((\text{NH}_4)^+_\text{SO}_4\) added, but the amount of this decrease was not related to the quantity of fixed \text{NH}_4.

Added K reduced nitrification 6.7 and 22\% in the \text{NH}_4^-\text{saturated natural and degraded illite samples, respectively. These reductions are comparable to the quantities of fixed \text{NH}_4 in these samples, thus, these data would indicate that the decrease in nitrification caused by added K is due to
the unavailability of fixed NH\textsubscript{4}. If this is true then there was less nitrification of NH\textsubscript{4} in the NH\textsubscript{4}-saturated illite treatment than in the (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} treatment, at the 0 ppm. K level, because part of the NH\textsubscript{4} was unavailable to nitrification for some reason other than the fixed NH\textsubscript{4} being unavailable.

The illite was only partially-NH\textsubscript{4}-saturated after the NH\textsubscript{4}-saturated sample had been leached with NaCl. As a result a larger percent of the remaining NH\textsubscript{4} was fixed, and it was anticipated that the blocking effect of K on the nitrification of fixed NH\textsubscript{4} would be more readily observed. With no K added, nitrification was low in both the natural and degraded samples which had been leached with NaCl. The results obtained for the natural illite samples are not readily explained, because nitrification was much less than the exchangeable NH\textsubscript{4} and nitrification increased with added K.

Added K decreased nitrification in the degraded samples, which had been leached with NaCl, but the decrease was not comparable to the amount of fixed NH\textsubscript{4}. Nitrification in these samples at 300 ppm. K was approximately equal to the quantity of exchangeable NH\textsubscript{4}, and this would be expected if K was exhibiting its maximum blocking effect on the release and subsequent nitrification of fixed NH\textsubscript{4}. Thus, the lack of the difference in nitrification between the 0 and 300 ppm. K levels to be equal to the amount of fixed NH\textsubscript{4} is due to all
the NH$_4^+$ not being nitrified at the 0 ppm. K level. K analysis of the nutrient solution, with 0 ppm. K added, showed 34 ppm. K to be present in the degraded NaCl-leached sample at the end of the incubation period (Table 12). Thus, nonexchangeable K was released from the illite during the period of nitrification, and enough K was apparently released to partially block the release of fixed NH$_4^+$ from the partially-NH$_4^+$-saturated illite samples. This K released from the illite tended to mask the observed effect of added K.

With the exception of the natural illite which was leached with NaCl, these results with illite indicate that K blocks the nitrification of fixed NH$_4^+$, but for some reason all the NH$_4^+$ is not nitrified even with no K added. The latter was explained as being due to the blocking effect of the K released from the degraded partially-NH$_4^+$-saturated samples, but this is probably not the case with the NH$_4^+$-saturated natural and degraded samples because only 4.5 and 14.0 ppm. K were in solution at the end of the incubation period, respectively.

Bentonite samples containing fixed NH$_4^+$ were prepared in several ways. The treatments used and the amount of the various forms of NH$_4^+$ in the bentonite samples are given in Table 13.

NH$_4^+$-saturated bentonite fixed less than 1% of the total NH$_4^+$ when heated to only 110° C., whereas more than 50% was fixed when heated at 350° C. The total NH$_4^+$ in the bentonite was reduced when the samples were heated at 350° C., because
Table 13. Ammonium in variously treated bentonite

<table>
<thead>
<tr>
<th>Treatment</th>
<th>NH₄⁺ (me. per 100 g.)</th>
<th>Fixed (% of total)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td>Exchangeable</td>
</tr>
<tr>
<td>K-saturated</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NH₄⁺-saturated, heated at 110° C.</td>
<td>76.97</td>
<td>76.67</td>
</tr>
<tr>
<td>NH₄⁺-saturated, heated at 350° C.</td>
<td>50.44</td>
<td>24.68</td>
</tr>
<tr>
<td>NH₄⁺-saturated, heated at 350° C., NH₄Cl leached, kept moist</td>
<td>73.77</td>
<td>58.18</td>
</tr>
<tr>
<td>NH₄⁺-saturated, heated at 350° C., titrated to pH 7.5, kept moist</td>
<td>48.10</td>
<td>34.30</td>
</tr>
<tr>
<td>NH₄⁺-saturated, heated at 350° C., titrated to pH 7.5, NaCl leached, kept moist</td>
<td>17.28</td>
<td>6.20</td>
</tr>
</tbody>
</table>
NH₃ is volatilized from the bentonite at this temperature (63). When NH₃ is volatilized from clay minerals by heating, a H ion remains on the exchange site previously occupied by NH₄⁺. Since this H may affect the quantity of fixed NH₄⁺ and its availability to nitrification, it was removed in various ways. In one case, the 350°C-heated bentonite was leached with 1 N NH₄Cl. This leaching with NH₄Cl apparently removed most of the H since the total NH₄⁺ was about equivalent to that in the NH₄⁺-saturated sample which had been heated at only 110°C. However, this NH₄Cl-leached sample contained less fixed NH₄⁺ than the 350°C-heated sample that was not leached with NH₄Cl after heating. This difference may be due to the fact that the former sample was kept moist after the NH₄Cl leaching.

A sample of the 350°C-heated bentonite was also titrated to pH 7.5 with NaOH to neutralize any H that might have been present. The titrated sample contained less fixed NH₄⁺ than the NH₄⁺-saturated sample which had only been heated at 350°C. Part of this difference may be due to Na being present in the former sample and its effect on determining exchangeable NH₄⁺ by KOH distillation, as discussed previously for the partially-NH₄⁺-saturated vermiculite samples. Also, part of the decrease in the quantity of fixed NH₄⁺ in the titrated sample may be due to the sample being moistened during the titration and kept moist prior to the KOH distillation.
The quantity of fixed NH$_4^+$ in the NH$_4$Cl-leached and titrated samples was about the same, and this indicates that the decrease in the fixed NH$_4^+$, in both these samples, was due to the moistening.

Bentonite which was NH$_4^+$-saturated, heated at 350° C., titrated to pH 7.5, NaCl leached, and kept moist had less total and fixed NH$_4^+$ than comparable samples which were not leached with NaCl, but a greater percent of the total was fixed in the former sample.

NH$_4^+$ was added as either NH$_4^+$-bentonite or (NH$_4^+$)$_2$SO$_4$ at the rate of 14.76 mg. of NH$_4^+$ per flask, and a nitrification experiment was conducted in the usual manner. (NH$_4^+$)$_2$SO$_4$ was added to flasks which contained either no bentonite or bentonite samples which were K-saturated so as to prevent any fixation of added NH$_4^+$. The results of nitrification with time of incubation are given in Figures 18, 19, 20, and 21. Total nitrification in 28 days is given in Table 14 along with the K content of the nutrient solution at the end of the incubation period.

There was essentially no difference in nitrification when (NH$_4^+$)$_2$SO$_4$ was added to flasks containing no bentonite as compared to flasks containing K-saturated bentonite (Figure 18). This, as was the case with K-saturated illite, indicates that when no NH$_4^+$ was fixed there was no effect of the bentonite per se on nitrification. Nitrification in the NH$_4^+$-
Figure 18. Nitrification of $\text{NH}_4^+$ in $(\text{NH}_4)_2\text{SO}_4$, K-saturated, $\text{NH}_4^+$-saturated-$110^\circ\text{C}$, and $\text{NH}_4^+$-saturated-$350^\circ\text{C}$ bentonite samples with different levels of added K in the nutrient solutions.
Figure 19. Nitrification of NH$_4^+$ in NH$_4^+$-saturated bentonite samples, which were heated at 350° C. and then variously treated, when no K was added to the nutrient solutions.
Figure 20. Nitrification of NH$_4^+$ in NH$_4^+$-saturated bentonite samples heated at 350° C. with different levels of added K in the nutrient solutions.
Graph showing the nitrification of added NH₄⁺ (%). The x-axis represents time of incubation (days) ranging from 0 to 28, and the y-axis represents the percentage of nitrification (%). The graph includes data for different conditions:

- K-BENT., (NH₄)₂SO₄
- NH₄-BENT., 350°C
- NH₄-BENT., 350°C, NH₄Cl leached

Lines indicate different potassium concentrations:

- 0 ppm. K
- 0 ppm. K
- 300 ppm. K
- 300 ppm. K

The graph shows increases in nitrification over time for all conditions.
Figure 21. Nitrification of NH$_4$ in NH$_4$-saturated bentonite samples heated at 350° C. and titrated to pH 7.5 with different levels of added K in the nutrient solutions.
0, 300 ppm. K

0 ppm. K

300 ppm. K

K-BENT., (NH₄)₂SO₄

NH₄-BENT., 350°C, TITRATED, NaCl LEACHED

TIME OF INCUBATION (DAYS)

NITRIFICATION OF ADDED NH₄(%)
<table>
<thead>
<tr>
<th>Treatmenta</th>
<th>Soluble K (ppm.)</th>
<th>Exchangeable $\text{NH}_4^+$ (% of total)</th>
<th>Nitrification (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>added</td>
<td>final</td>
<td></td>
</tr>
<tr>
<td>No bentonite</td>
<td>0</td>
<td>0.17</td>
<td>-</td>
</tr>
<tr>
<td>K-saturated</td>
<td>300</td>
<td>301</td>
<td>-</td>
</tr>
<tr>
<td>$\text{NH}_4^+$-saturated, dried at 110° C.</td>
<td>0</td>
<td>1</td>
<td>99.6</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>268</td>
<td></td>
</tr>
<tr>
<td>$\text{NH}_4^+$-saturated, dried at 350° C.</td>
<td>0</td>
<td>0.8</td>
<td>48.9</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>242</td>
<td></td>
</tr>
<tr>
<td>$\text{NH}_4^+$-saturated, dried at 350° C., $\text{NH}_4\text{Cl}$ leached, kept moist</td>
<td>0</td>
<td>0.4</td>
<td>78.9</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>281</td>
<td></td>
</tr>
<tr>
<td>$\text{NH}_4^+$-saturated, dried at 350° C., titrated to pH 7.5, kept moist</td>
<td>0</td>
<td>1.1</td>
<td>71.3</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>273</td>
<td></td>
</tr>
<tr>
<td>$\text{NH}_4^+$-saturated, dried at 350° C., titrated to pH 7.5, NaCl leached, kept moist</td>
<td>0</td>
<td>2.4</td>
<td>35.9</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>188</td>
<td></td>
</tr>
</tbody>
</table>

aThe treatments which did not have $\text{NH}_4^+$ added as $\text{NH}_4^+$-bentonite had $\text{NH}_4^+$ added as $(\text{NH}_4)_2\text{SO}_4$. 
saturated, 100°C-heated bentonite sample was only slightly lower than the check, i.e., the K-saturated sample with \((\text{NH}_4\text{)}_2\text{SO}_4\) added. This \(\text{NH}_4\) saturated sample had less than 1\% of the \(\text{NH}_4\) fixed, thus, high nitrification would be expected. There was very little difference between the 0 and 300 ppm K levels in the 3 treatments above (Table 14) thus, the curves for these treatments in Figure 18 represent both the 0 and 300 ppm K levels. Nitrification in the \(\text{NH}_4\) saturated bentonite sample heated at 350°C was less, even with 0 ppm K added, than the check. About 50\% of the \(\text{NH}_4\) in the former sample was fixed, thus, only a portion of this fixed \(\text{NH}_4\) was available for nitrification, as was the case in the experiment presented earlier for this same sample of \(\text{NH}_4\) saturated bentonite.

Nitrification was about the same in the \(\text{NH}_4\) saturated, 350°C-heated sample as in a comparable sample which was leached with \(\text{NH}_4\text{Cl}\) after heating, but both were less than the check (Figure 19). This occurred despite the fact that the former sample had more than twice as much fixed \(\text{NH}_4\) as the latter sample (Table 13). These data would indicate that there is an amount of fixed \(\text{NH}_4\) which is unavailable to nitrification, but fixed \(\text{NH}_4\) in excess of this amount is available for nitrification with 0 ppm K added. Titrating the sample which had been heated at 350°C resulted in less nitrification than the sample which was only heated. Leaching
the titrated sample with NaCl caused a further reduction in nitrification, but this would be expected since a higher percent of the NH$_4^+$ was fixed (Table 13). In both titrated samples, no fixed NH$_4^+$ was available for nitrification.

Added K reduced nitrification in both of the NH$_4^+$-saturated samples heated at 350°C. and a comparable sample which was leached with NH$_4$Cl after heating (Figure 20), but the reduction was less in the latter sample. Since with 0 ppm. K added only the exchangeable NH$_4^+$ was nitrified in the NH$_4$Cl-leached sample, added K would not be expected to reduce nitrification to a great extent. However, added K did reduce nitrification below the exchangeable NH$_4^+$ in this sample, and it is not apparent as to why this should occur.

Nitrification was reduced in both of the titrated samples with K added (Figure 21). This reduction occurred despite the fact that not all of the exchangeable NH$_4^+$ was nitrified with 0 ppm. K added. However, this might be explained by the fact that the exchangeable-NH$_4^+$ values reported in Table 14 may be high because of the presence of Na in these samples and its effect on the quantity of NH$_4^+$ extracted by the KOH distillation.

The small quantity of K released from the bentonite, with 0 ppm. K added, does not appear to be high enough to account for the fact that not all of the NH$_4^+$ in the NH$_4^+$-bentonite samples was nitrified even in the absence of added
K, Table 14. Also, the H in the heated bentonite is not responsible, because the titrated samples gave no greater nitrification than the samples that were not titrated. It is still not apparent from this study why with no K added, the fixed NH$_4^+$ in bentonite samples is not as available to nitrification as fixed NH$_4^+$ in vermiculite.

Soils

Nitrification of NH$_4^+$ in soils has been studied rather extensively. One aspect that has received attention recently is the availability of fixed NH$_4^+$ in soils to nitrification. Since it is known that soils may fix added NH$_4^+$, loss of NH$_4^+$-N fertilizer could occur if it is fixed in an unavailable state. In general, it has been reported that fixed NH$_4^+$ in soils is relatively unavailable to nitrification. Bower (18) reported that with two soils only 13 and 28% of the fixed NH$_4^+$ was nitrified after incubating for 14 days. Allison et al. (2) found that usually less than 10% of the fixed NH$_4^+$ in a Harpster soil was nitrified during periods of 6 to 16 weeks of incubation. K present in the soils could possibly be responsible for the low nitrification obtained, since it is now known that K inhibits nitrification of fixed NH$_4^+$ in clay minerals. Thus, exploratory nitrification studies were conducted with soils containing fixed NH$_4^+$ to evaluate this pos-
Nitrification studies were first conducted with air-dried, NH$_4^+$-saturated soil samples. Soil samples from the 18 to 24-inch depth of the Marshall and Clarion profiles were used, because it is known that subsoil samples fix more NH$_4^+$ than surface samples (4). Also, there is less organic matter present in the subsoil samples to influence the determination of total and exchangeable NH$_4^+$ present. The samples were NH$_4^+$ saturated, and total NH$_4^+$ was determined by distilling in 400 ml. of 0.1 M NaOH for 2 hours. Other samples were distilled in KOH to determine the exchangeable NH$_4^+$. Fixed NH$_4^+$ was calculated as the difference between these values. It is known that the values for total NH$_4^+$ are probably low (5). Nevertheless, the Marshall and Clarion NH$_4^+$-saturated samples contained a total of 17.6 and 13.3 me. NH$_4^+$ per 100 grams, and 4.1 and 7.8% of the total NH$_4^+$ was fixed, respectively.

Nitrification of NH$_4^+$ in these NH$_4^+$-saturated samples was determined by the same procedure as used in the previous experiments. To determine the effect of added K, 0 and 300-ppm. K treatments were used. Nitrification of NH$_4^+$ supplied as (NH$_4^+$)$_2$SO$_4$ served as a check. In each case, 14.76 mg. of NH$_4^+$ was used per flask. The nitrification results obtained are shown in Figure 22.

Less nitrification occurred in the Clarion than in the Marshall samples, but the nitrification in both soil systems
Figure 22. Nitrification of NH$_4^+$ in NH$_4^+$-saturated Marshall and Clarion 18 to 24-inch soil samples with different levels of added K in the nutrient solutions
The graph shows the nitrification of added NH$_4$\(^+\) (%). The x-axis represents time of incubation (days), ranging from 0 to 21 days. The y-axis represents the nitrification percentage, ranging from 0 to 100%.

Key to the graph:
- (NH$_4$)$_2$SO$_4$ represented by triangles (Δ)
- Marshall represented by circles (○)
- Clarion represented by circles (●)

Lines with markers indicate different potassium (K) levels:
- 0 ppm K (solid line)
- 300 ppm K (dashed line)
- 0,300 ppm K (dotted line)

The graph illustrates the effect of different potassium levels on the nitrification of added NH$_4$\(^+\) over time.
was less than in the \((\text{NH}_4\text{)}_2\text{SO}_4\) treatment. When K was added there was 6% less nitrification in the Marshall but no change in the Clarion samples. These differences observed were thus small and inconsistent between soils. It is evident from this experiment that the availability of fixed \(\text{NH}_4\) and the effect of added K cannot be readily observed in the presence of the large amount of exchangeable \(\text{NH}_4\). In general, however, it appears that less nitrification can be expected in soils than in \((\text{NH}_4\text{)}_2\text{SO}_4\) even with 0 ppm. K added. An effect of added K is also indicated.

Soil samples containing fixed \(\text{NH}_4\) can be prepared by simply adding a known quantity of \(\text{NH}_4\). Fixed \(\text{NH}_4\) is then calculated as the difference between that added and that removed by KOH distillation. Soil samples which had no \(\text{NH}_4\) added serve as blanks in the KOH distillation determinations. This method is particularly useful in surface soil samples because of the absence of an established method for determining fixed \(\text{NH}_4\) in the presence of large amounts of organic matter. Also, with this method, naturally occurring exchangeable and soluble K which is present could affect nitrification of the fixed \(\text{NH}_4\), whereas with \(\text{NH}_4\)-saturated samples these forms of K are removed by the leaching process. Experiments were conducted with soil samples that fixed added \(\text{NH}_4\) to determine if low nitrification of added \(\text{NH}_4\) occurs under these conditions because of fixation.
NH₄⁺ was added to 10-g. samples of moist Fayette 12 to 18-inch soil at the rate of 9.34 me. NH₄⁺ per 100 g., after which the soil was air dried, and the exchangeable NH₄⁺ was determined by KOH distillation. Of the NH₄⁺ added, 0.89 me. of NH₄⁺ per 100 g. or 9.5% was fixed.

Nitrification experiments were conducted with the Fayette samples for a period of 35 days with 0 and 500 ppm. K added. Flasks were included which contained soil samples that received no added NH₄⁺, and the results are given in Figure 23. With both of the K levels there was an initial gain in NO₃⁻-N and then a decrease, with the 500 ppm. K level giving the greatest decrease. The negative values mean that some of the NO₃⁻-N added as inoculum or originally present in the sample had disappeared. The subsoil sample would be expected to have a low rate of ammonification and subsequent nitrification. Thus, the NO₃⁻-N disappearance is evidently due to the incorporation of N in microbial tissue. The NO₃⁻-N content of these flasks was used as blanks in calculating the percent of the added NH₄⁺ nitrified in the flasks which received NH₄⁺.

The results of nitrification when NH₄⁺ was added to the samples are given in Figure 24. Recovery of NH₄⁺-N as NO₃⁻-N was as great when added to the soil samples as when supplied as (NH₄)₂SO₄ with 0 ppm. K added. Nitrification in the soil samples was reduced about 6% in the 500 ppm. K level as compared to the 0 ppm. K level. Thus, it appears that some of
Figure 23. $\text{NO}_3^-\text{-N}$ content in Fayette 12 to 18-inch soil samples during incubation with no $\text{NH}_4^+$ added and with different levels of added K in the nutrient solutions
Figure 24. Nitrification of $\text{NH}_4^+$ added to moist 12 to 18-inch Fayette soil samples with different levels of added K in the nutrient solutions. ($\text{NH}_4^+$ was added at the rate of 9.34 me. per 100 g.)
the fixed NH$_4^+$ was nitrified at this high K level, because 9.5% of the added NH$_4^+$ was fixed.

While there is no established method of determining naturally fixed NH$_4^+$ in soils it is generally believed that some is present in some soils. When soils are dried some nonexchangeable K is released, and there may also be an increase in exchangeable NH$_4^+$ by a similar process. Thus, it seems likely that drying a soil might increase nitrification in the soil since more NH$_4^+$ would be available. On the other hand, K released by drying would inhibit the release of fixed NH$_4^+$, and this would decrease nitrification.

A nitrification experiment was conducted with soils to evaluate the effect of drying on naturally occurring NH$_4^+$ and the effect of the nonexchangeable K released on the nitrification of fixed NH$_4^+$. Samples of Clarion and Marshall 0 to 6-inch, Marshall 18 to 24-inch, and Fayette 36 to 48-inch soils were treated as follows and used in this experiment: (a) soil sample kept in field-moist state, (b) sample heated at 110° C. for 24 hours, (c) field-moist sample leached with CaCl$_2$ and kept moist, (d) field-moist sample leached with CaCl$_2$, 10 me. NH$_4^+$ added per 100 g., and kept moist. The soils were CaCl$_2$ leached by placing 200-g. samples on a Buchner funnel, leaching with 2 l. of 1 N CaCl$_2$, and washing with water until free of chloride. The CaCl$_2$ leaching was done so as to remove the exchangeable and soluble K and to determine if this
would result in greater nitrification due to increased availability of native or added NH$_4^+$ that was fixed. Nitrification of NH$_4^+$ in treatment (c) was determined with 0 and 300 ppm. K added, whereas treatment (a) and (b) had 0 ppm. K added. Ten-gram soil samples were used per flask. The results of nitrification experiments conducted with samples receiving treatments (a), (b), and (c) are given in Figures 25, 26, 27, and 28.

Nitrification was greater in the surface samples than in the subsoil samples. The surface samples contain more organic matter than the subsoil samples, thus, the results are in agreement with what would be expected since ammonification would undoubtedly be greater in the surface soil samples.

Except for the moist and CaCl$_2$-leached Marshall 18 to 24-inch sample, the subsoil samples exhibited a disappearance of NO$_3^-$-N. N was evidently incorporated in microbial tissue. No consistent effect was observed with the four soil samples in regard to drying, removing K by leaching with CaCl$_2$, or adding K.

In treatment (d) NH$_4^+$ was added as 20 ml. of (NH$_4$)$_2$SO$_4$ solution, and the soil samples were then allowed to sit 10 hours before beginning the nitrification experiment. Both subsoil samples fixed 14% of the added NH$_4^+$, whereas the Clarion and Marshall 0 to 6-inch samples fixed 7 and 5%, respectively, of the 10 me. NH$_4^+$ added per 100 g. of soil.
Figure 25. Nitrification in variously treated samples of Clarion 0 to 6-inch soil with no NH₄ added

Figure 26. Nitrification in variously treated samples of Marshall 0 to 6-inch soil with no NH₄ added
CLARION 0-6 IN.

- MOIST, 0 ppm. K
- OVEN DRY, 0 ppm. K
- CaCl\textsubscript{2}-LEACHED, 0 ppm. K
- CaCl\textsubscript{2}-LEACHED, 300 ppm. K

TIME OF INCUBATION (DAYS)

NO\textsubscript{3}-N (PPM. SOIL BASIS)

MARBULL 0-6 IN.

- MOIST, 0 ppm. K
- OVEN DRY, 0 ppm. K
- CaCl\textsubscript{2}-LEACHED, 0 ppm. K
- CaCl\textsubscript{2}-LEACHED, 300 ppm. K

TIME OF INCUBATION (DAYS)

NO\textsubscript{3}-N (PPM. SOIL BASIS)
Figure 27. Nitrification in variously treated samples of Marshall 18 to 24-inch soil with no NH$_4^+$ added.

Figure 28. Nitrification in variously treated samples of Fayette 36 to 48-inch soil with no NH$_4^+$ added.
The nitrification results obtained with the soil samples that received treatment (d) are given in Table 15. The soil samples all gave nitrification curves similar to those shown in Figure 29 for the Clarion 0 to 6-inch sample. The quantity of NO$_3$ produced in the CaCl$_2$-leached samples which received no NH$_4$ was deducted from the NO$_3$ produced from the samples that received NH$_4$ in calculating the percent nitrification of added NH$_4$.

In every case where NH$_4$ was added to the soil samples, nitrification was less where K was added as compared to the 0 ppm K level. However, the slight reduction in nitrification due to added K (generally about 4%) was less than the quantity of NH$_4$ fixed, particularly in the subsoil samples. Despite the fact that up to 14% of the total NH$_4$ was fixed in the subsoil samples, nitrification of added NH$_4$ appears to be fairly complete because nitrification was as great in the soil samples as in the (NH$_4$)$_2$SO$_4$ treatment. These results indicate that there is little loss of added NH$_4$ through fixation, at least in these soils.
Table 15. Nitrification in 28 days in CaCl₂-leached soil samples with NH₄ and 0 and 300 ppm. K added

<table>
<thead>
<tr>
<th>Soila</th>
<th>K added (ppm.)</th>
<th>Nitrification of added NH₄ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>90.5</td>
</tr>
<tr>
<td>0</td>
<td>300</td>
<td>91.8</td>
</tr>
<tr>
<td>Clarion 0 to 6 in.</td>
<td>0</td>
<td>95.5</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>93.0</td>
</tr>
<tr>
<td>Marshall 0 to 6 in.</td>
<td>0</td>
<td>95.1</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>90.8</td>
</tr>
<tr>
<td>Marshall 18 to 24 in.</td>
<td>0</td>
<td>93.2</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>90.6</td>
</tr>
<tr>
<td>Fayette 36 to 48 in.</td>
<td>0</td>
<td>93.5</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>89.6</td>
</tr>
</tbody>
</table>

Flasks which received no soil had NH₄ added as (NH₄)₂SO₄.
Figure 29. Nitrification in CaCl₂-leached, 0 to 6-inch Clarion soil samples with 10 me. of NH₄ added per 100 g.
TIME OF INCUBATION (DAYS)

NITRIFICATION OF ADDED NH$_4$ (%)
SUMMARY AND CONCLUSIONS

A short-time greenhouse cropping technique was utilized to determine the effect of added NH$_4^+$ and/or K on the release and availability of nonexchangeable soil K to plants. The technique was particularly suitable in that the corn plants absorbed relatively large quantities of K, if available, during the 5- and 10-day cropping periods, nitrification of added NH$_4^+$ was limited by the time factor, and NH$_4^+$ did not affect the absorption of soluble K by the plants.

Moist surface samples of the Marshall and Clarion soils differed considerably in regard to the quantity of nonexchangeable K released during cropping with no NH$_4^+$ or K added. Likewise, the Marshall and Clarion subsoil samples differed with respect to each other, and they also differed in respect to the surface samples. The Marshall soil released more nonexchangeable K, in both the surface and subsoil samples, than the Clarion. The Clarion subsoil sample released no nonexchangeable K.

The soil samples that released large amounts of K with no NH$_4^+$ added gave very little release with high levels of NH$_4^+$ added. Added K also decreased the quantity of nonexchangeable K released, and in some cases much of the added K was fixed. The effect of NH$_4^+$ is a blocking phenomenon, while with K, the effect may be considered in terms of mass action.
The effect of NH₄ and K on the release of nonexchangeable K was additive when both cations were added to the same soil sample. The order of adding the NH₄ and K is important. If NH₄ is added before K, less of the K is fixed and more is available for absorption by plants. If K is added before NH₄ the K is fixed and the NH₄ prevents its release.

The availability of NH₄ fixed in clay minerals and soils to nitrifying bacteria as affected by added K was investigated. This was done by adding the NH₄-materials to a buffered nutrient solution, which was inoculated with nitrifying bacteria cultured in a low-K solution, and measuring the NO₃ content periodically during the incubation period. During the course of this investigation the effect of K on the nitrification process per se was determined.

Nitrification of NH₄, supplied in (NH₄)₂SO₄, occurred to about the same extent in nutrient solutions containing 0.40 and 300 ppm. K, but, at K levels less than 0.35 ppm., nitrification was limited. Nitrification in a solution near 0 ppm. K was negligible after a series of transcultures had been made to further dilute any K added by the original inoculum. However, the nitrifying bacteria, in these flasks which showed low nitrification, were not dead but merely inactive under the conditions of extremely low K, because, upon addition of K, nitrification occurred to about the same extent as if ample K had always been present. Because of
the small quantity of K required for the nitrification process, the quantity of K in soils is probably always adequate for nitrification.

The NH$_4^+$ in samples of three NH$_4^+$-saturated vermiculites, that contained about 95% of the total NH$_4^+$ in the fixed form, was as available for nitrification as was that in (NH$_4^+$)$_2$SO$_4$, with low-K levels. However, the release and subsequent nitrification of the fixed NH$_4^+$ was decreased with K added, but nitrification in the (NH$_4^+$)$_2$SO$_4$ treatment was not affected. This decrease in nitrification was so pronounced in some of the vermiculites that with 300 ppm. K only slightly more than the exchangeable NH$_4^+$ was nitrified. Furthermore, the effect of K was related to the ratio of fixable (K) to non-fixable (Na and Mg) cations, and it was observed that the nitrification of fixed NH$_4^+$ decreased as the ratio of fixable to non-fixable cations increased. Because soluble NH$_4^+$ was nitrified and did not accumulate in the nitrifying system, the decrease in nitrification is attributed to K preventing the non-fixable cations from replacing the NH$_4^+$ from its fixed position in the crystal lattice.

Nitrification of NH$_4^+$ in partially-NH$_4^+$-saturated samples of vermiculite was also decreased by the presence of K. In the first few days of incubation, nitrification was slower as the degree of NH$_4^+$ saturation decreased, but the recovery of NH$_4^+$-N as NO$_3^-$-N was about the same, irrespective of the
degree of $\text{NH}_4^+$ saturation, after 6 weeks of incubation. The percent nitrification of $\text{NH}_4^+$ added in the vermiculite samples was inversely related to the $K$ adsorbed per gram of vermiculite. The effect of a given quantity of adsorbed $K$ on nitrification increased as the degree of $\text{NH}_4^+$ saturation decreased.

$\text{NH}_4^+$-saturated samples of bentonite (heated at $350^\circ C$) and illite (heated at $110^\circ C$) behaved differently from the vermiculite samples in that all the fixed $\text{NH}_4^+$ was not nitrified even in the absence of added $K$, and, with illite, nitrification was less than the exchangeable $\text{NH}_4^+$. The low nitrification that occurred was not due to the effect of the clay minerals per se, because $(\text{NH}_4^+)_2\text{SO}_4$ in the presence of the $K$-saturated minerals was nitrified to the same extent as $(\text{NH}_4^+)_2\text{SO}_4$ in the absence of the clay minerals. Like the vermiculite samples though, added $K$ decreased the amount of nitrification that occurred in the $\text{NH}_4^+$-saturated illite and bentonite samples. Leaching the $\text{NH}_4^+$-saturated samples removed some of the $\text{NH}_4^+$ and resulted in a greater percent of the remaining $\text{NH}_4^+$ being fixed. Because of this, the percent nitrification in the partially-$\text{NH}_4^+$-saturated samples was less than in the $\text{NH}_4^+$-saturated samples.

Degrading illite samples with the use of sodium tetraphenylboron, before saturating with $\text{NH}_4^+$, resulted in an increase in the percent of the total $\text{NH}_4^+$ which was fixed. Nitrification was about the same in the natural illite samples...
as in the degraded samples, but added K decreased nitrification more in the latter samples.

Bentonite samples which were NH\textsubscript{4} saturated and then heated at 110° C. fixed very little NH\textsubscript{4}, and the NH\textsubscript{4} was available for nitrification. The difference between the availability of NH\textsubscript{4} to nitrification in these samples and those heated at 350° C. does not appear to be related to the H ions formed or to the nonexchangeable K that may be released during heating.

The nonexchangeable K released by the illite during the incubation period may account for the low nitrification obtained in the absence of added K. This does not appear to be the case with the bentonite samples, because very little nonexchangeable K was released.

In a limited study with soils, the effect of K on the nitrification of fixed NH\textsubscript{4} was difficult to evaluate because of the small quantity of fixed NH\textsubscript{4} that was present. It appears, however, that the blocking effect of K on the release and subsequent nitrification of fixed NH\textsubscript{4} occurs in soils also.

Nitrification of native NH\textsubscript{4} was greater in surface samples than in subsoil samples. One subsoil sample had less NO\textsubscript{3}-N present at the end of the incubation period than at the beginning. Ammonification was evidently very slow, and, apparently, NO\textsubscript{3}-N was incorporated into the bodies of microor-
ganisms. There was no consistent effect on nitrification irrespective of whether moist, oven-dry, or CaCl₂-leached samples were used. Added K did not consistently affect nitrification of native NH₄ in the CaCl₂-leached samples.


3. ________, ________, and ________. Availability of fixed ammonium in soils containing different clay minerals. Soil Sci. 75: 373-381. 1953.


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