

SOME STUDIES ON UREA WHEN ADDED TO SOILS OF DIFFERENT TEXTURES

Thesis for Degree of M. S. Jesse Davis Romaine

1925

THESIS

agriaultural chounsta

NEER ALLED TO SOLDS OF

LIEFERST TEXTURES

A THESIS

SUBWITTED TO

THE GRADUATE PACULTY

сf

THE MICHIGAN STATE COLLEGE

of

AGRICULTURE AND APPLIED SCIENCES

Су

Jesse D. Homaine.

In Partial Bulfillment for the Degree of

MASTER OF SCIENCE

June 5, 1925,

THESIS

,

•

The writer taxes this opportunity to express his appreciation for many helpful suggestions hade by Dr. M. M. MeCool and other members of the Soils Department during the course of these experiments.

.

## SOME STUDIES ON URLA WHEN ADDED TO SOIDS OF DIFFERENT

### TEXTURES.

#### T#IPOLIONI%T

Inere is a marked tendency in Agricultural practice toward the use of more concentrated, and of greater quantities of fertilizers. In the search for concentrated plant food carriers, uses naturally came under consideration as it has long been known to exist naturally and artificially, has a high Nitrogen content, and is easily enanged to other compounds.

Urea has the empirical formula of N2E4CO, usually written as CO(ND2)2, and is frequently celled Carbanide. It carries 45.6% dirrogen or of 6% Ammonia, which is double the about of Ammonia carried by Ammonia, Sulphate, the most concentrated Nitrogen carrier in common use as a fertilizer. As marketed by a German firm it is guarenteed to carry 45% Nitrogen. It is thus prepared commercially quite free from impurities. It is moderately hygroscopic and readily soluble in all proportions in which it would be added to the scil.

#### HISTORICAL

Considerable work has been done with prea on soils in the field and in pots in Germany and other European Countries. It is only puring the last several years that any work has been reported in this country from the viewpoint of using it as a fertilizer.

Coleran (12)\* recorted that the addition of .7e\* of

\* Reference is made by numbers in parenthesis to Literature Cited, at end of paper. urea to the soil retarded nitrification therein.

Tacke (42) found that uses as good as Sodium Ni-trate on a number of crops.

Easelhoff (17), however, found that it was slightly inferior to Sodium Mitrate, in an extensive, five years' test with a number of crops on several soils.

Stutzer (42) in another five years' test in East Prussia said that uses was as good as Sodium Mitrate on all crops and was even better on topecco. On cets a greater recovery of Mitrogen from uses than from Sodium Mitrate was secured.

Mappen (16) which that uses made from Lime-Mitrogen, or Calcium Cyanamide, was slightly superior to Sodium Mitrate. The only narm that may occur is the possibility of the presence of Dicyanodiamide, which may be formed in this process of manufacture.

Gerlach (15) reported that wroa gave as good results as any other of the Nitrogen carriers studied.

Schneidawind ( $37, 5\epsilon$ ), in several articles, wrote that urea was as good as any other Nitrogen carrier, except in the case of **a** top dressing on rice, where it gave the poorest results of any of the carriers.

Mitscherlich, von Sauchers, and Iffland (88) reported also that urea was as good as any of the Mitrogen carriers studied.

benmermenn (21), in an extensive and comprehensive set of experiments, showed that it was practically as good as any of the Nitrogen carriers, in both pot and field work.

Eokorny (5) said that unea gave good results when serving as a source of ooth Mitrogen and Carbon for green plants.

von Knierien (19) wrote that urea gave the best results of any of the Aitrogen carriers used, the experiments being carried out on several soils with potatoes and beets.

Polo (34), with pot experiments, found that area gave very good results, compared with the other Nitrogen carriers. Synthetic area was especially poor, though. (In the light of later work this toxicity may have been due to the presence of plant poisins which are now known to be produced as a by-product in some synthesizing processes.) van Barrsveld (16) stated that urea gave as good results as Ammonium Chloride, as a fertilizer. Somever, it leached from Java soils in greater quantities than Ammonium Chloride did, and in about the same quantities as Sodium withate.

In this country the most extensive experiments reported with uses more by Allison, Staham, and McGuetrey (1). They used breaksingly and in combination, along with a great number of other withogen carriers in field tests, comparing their relative efficiencies. These experiments were conducted through several years, with outcoments and corn. They summarize their results as follows:

"Urea seems to be as readily available as Sodium Nitrate and equally as good in all respects as any other material used. Since urea is an excellant material physically and leaves neither a basic nor acid residue in the scil it should prove to be an almost ideal Nitrogen carrier for all types of soils."

Allison, Vliet, Skinner and Reid (2) also reported the results of some greenhouse experiments in which they found that unce gave about the same results as Sodium Nitrate, Ammonium Sulphate, Ammonium Nitrate, Calcium Nitrate, and Ammoniated Superphosphate.

NcCuinn (30) showed that there is no harm to the germination and early growth of several crops when urea is in direct contact with the seeds.

Lipman and McLean (23) reported that unde congared with other Nitrogen carriers in pots was as good as any, if Dicyandiamid wore not present.

The above reports agree fairly well as to the relative value of usea as a plant food carrier, it being as good as any under most conditions. The limiting factor in its use at present is the high price caused by the lack of a cheap method of manufacturing it from cheap materials. As before mentioned a Jorman firm is selling it in this country in small quantities, chiefly as a fertilizer for gerden use. Werner (44) reviews the principal methods used at present to produce urem on a commercial scale. He also suggests that its proparation from Ammonia and Carbon Monoxide in the presence of a catalyst might be developed into an economical method of manufacture. Krase and Gadiy (20) have worked out a method for its synthesis which they think has commercial possibilities. Their method consists briefly in heating Ammonium Carbangte at 150° C. for four hoars under a pressure of 80-120 atmospheres. According to them the price of Ammonia will largely determine the price of the urea produced. Lipman and MoLean (18) outline a method by which commercial fertilizer urea may be made. The essential feature is the treating of Calcium Cyanamide with Sulphuric Acid as follows:

 $3CaCN_2 + 3H_2SO_4 + H_2O = CO(NH_2)_2 + C_2H_4N_4 + 3CaSO_4$ The CO(NH\_2)\_2 is the urea, while the C\_2H\_4N\_4 is Dicyandiamid. It will be noticed that the basis of all of these methods of preparation is the electrolytic fixation of Nitrogen, either as Ammonia or Calcium Cyanamide. When this is worked cut on an economical and large scale, and this is gradually being done, urea should become available as a commercial fertilizer.

As montioned in the preceding paragraph, one of the products in some of the present commercial processes for manufacturing urea is Dicyandiamid. As pointed out by Kappen (14) and Lipman and MeLean (23), this substance is quite narmful to plants. Cowie (13) states that even in very small quantities it is toxic and also inhibits the ammonifying bacteria in their action. McGuinn (30) showed that dicyandiamid apparently did not seriously affect the germination of seeds, but was toxic to later growth. He did not get such toxic effects as Cowie described. Unless it were present in quantities greater than 10%, it did not affect the value of urea as a fertilizer. The dicyanamid storged nitrification, which result was also the opposite to that secured by Cowie. Lipman and McLean (23) say, however, that the urea now on the market contains very little dicyandianid, as the manufacturers are careful to remove as much of it as possible.

## EXFERIMANTAL WORK

The work for this paper is divided into four main divisions or series. The first series is preliminary in nature. It shows the results of making several very large applications of urea to a Coloma Fine Sand and determining the Nitrates produced, reaction and concentration of the soil solution from time to time. The second series reports the results of making moderate applications of urea to a Fox Sandy Leam and a Miami Silt Leam, determining at intervals the Nitrates produnced, reaction and concentration of the scil solutions. The third series was suggested by the results of the first series and shows the amounts of Annonia that might be liberated when urea is added to different soils in various ways and ancunts. In the fourth series, the influence of leaching on the reaction of several scils previously treated with urea is reported, and also the residuary effects of such treatments on the soil reactions.

## SFRIFS 1

## Large Applications of Urea to Coloma Fine Sand

In this series, large applications of urea were made to a Coloma Fine Sand. The surface soil from a cropped area which had not received fertilizer recently was used, so as to secure material rather low in Nitrates. The scil was sifted through a sieve with openings about three millimeters square, and made up to optimum moisture content by thereughly mixing the required ancunt of water with the soil. In case urea was added it was dissolved in the water with which the soil was to be moistened, thus insuring a uniform distribution of the material throughout the soil. The soils were put in pint jars and kept in the dark at a temperature of 20-25°C. Every two or three days the soils were removod from the jars and serated very thoroughly. Moisture was added as needed to keep the soils at the optimum moisture content.

The following treatments were used, each one being run in duplicate:

1-	Chec	k. No	o urea	addec	1.			
2-	. 5%	urea,	based	uron	dry	weight	cť	scil.
3-	1.0%	urea,	11	11	11	11	Ħ	"
4_	2. 5%	urea,	H	11	u	11	11	11
5-	5.0%	urea,	11	Ħ	ti	11	Ħ	11

These treatments are far in excess to the ancunts that would be applied to the soil in the field, but it was the object to determine the upper limit for the use of the material. A botter idea of the magnitude of the application may be had by considering that the smallest treatment above, or the .5%, is equivelent to sixteen tons of Nitrate of Soda per acre six inches of soil. It might be stated that all of these treatments proved to be too heavy for the proper functioning of the soil organisms.

At the beginning of the experiment, and at the end of 4, 11, 22, 29, and 36, days, each jar was sampled, care being taken to secure as representative a sample as possible. The Hydrogen-ion concentration, the Nitrate content, and the total concentration of the soil solutions were determined on these samples.

> A- Ammonification and Nitrification of Urea in Coloma Fine Sand.

Nitrates in the soil were determined by the colorimetric method as cutlined by Schreiner and Failyer (39), with a few modifications. The equivelent of 30 grams of dry soil was weighed and put in a shaker bottle. 3 c.c. of a normal solution of Copper Sulphate and enough water to make a total of 150 c.c. were added. This would then make a 1 to 5 aquecus extract of the soil. The samples were shaken for twenty minutes and then .6 gram of Magnesium Carbonate and .24 gram of Calcium Hydroxide were added. The bottles were then shaken for one minute to secure a thorough mixing of the chemicals throughout the soil. The flocculent material was then allowed to settle, a clear su-

· · · ·

pernatent liquid being secured almost immediately except in the case of the very fine soils, or those strongly alkaline. The solutions were decanted through filter papers, which would remove any particles still in suspension. The Nitrates were then determined as described in the aforementioned publication. They are reported as parts per million in the 1 to 5 extract, the average of quadruplicate determinations being given. The results for the Colona soil are given in Table 1. Many of the extracts from the treatel soils were colored, apparently due to the alkaline condition of the soil, and the figures may be higher than they should be. The solutions from the check soils were perfectly clear.

Table 1 - Nitrates in parts per mislion in 1 to 5 extract. Coloma Fine Sand.

Treat.	0 Days	11 Days	22 Days	29 Days	36 Days
Check.	3.9	9.1	16.5	28.1	18.2
.5% urea	3.9	2.7	2.3	2.4	2.4
1.0% "	3.9	2.1	1.8	2. 5	2.6
2.5% "	3.9	2.6	. 2. 9	3.1	4.2
5.0% "	3.9	2.6	2.3	2.7	2.9

The determinations made at the end of four days were lost, as the Nitrate samples were destroyed.

The check soil increased in its Nitrate content until 29 days, after which it fell off. The increase can probably be accounted for by the conditions of moisture, heat, light and aeration being made optimum for biological activity. The soil was rather dry when taken from the field because of a lack of rainfall. The decrease at the end is a little harder to account for, but may be due to the development of many organisms and the depletion of readily available organic matter, in which case the organisms would possibly consume the Nitrates faster than they could be produced.

All the urea treatments reduced the amounts of Nitrates present in the soil solutions. As before explained, even the small amounts shown are probably too high. Apparently the urea added to the soil has not been nitrified, and has even caused the Nitrates of the soil to be lowered. In order to give a satisfactory explanation of this it will be necessary to explain some of the biological processes that take place with urea in the soil.

When urea is added to a soil it is done so with the idea that it will ammonify and nitrify, eventually producing Mitrates for plant food. The first step, or ammonification, is the changing of the urea to Ammonium Carbonate. This cayinge can be brought about by bacteria and molds, probably by several species of the former. These organisms accomposite this by means of an enzyme called Urase, which is described by Warshall as a Zymase (31). The reaction, according to Rahn, in Marshall's Microbiology (31), is :

 $(NH_2)_2CO + 2H_2O = (NH_4)_2CO_3 + 14.3$  calories. The organisms thus secure their energy from the process, not using free Oxygen for the purpose. This possibly accounts for the results of Christensen (10,11), who found that the process can go on without the presence of any other organic substance. Fhelps, in Marshall (31), states that the organisms are anacrobic, but Rahn (35) states that they require some Oxygen for certain of their life processes, even though they appear to be a facultative aerobic organism. Littauer (25) did some work which would tend to show that they do not need much Oxygen. He found that an excess of moisture did not retard the breaking down of urea in the soil.

The formation of the Ammonium Carbonate from usea is very rapid. This had been shown by Lipman (24) and Lochnis (26). After the material is ammonified it is probably nitrified in the usual manner.

Returning to the data on the Nitrates in Table 1 and the notes taken during the course of the experiment, some interesting things are spen. Two days after the experiment was **beg**un, strong fumes of Ammonia were given off from the .5% and 1% treatments when the soils were acrated. The urea must have ammonified to an extent sufficient to saturate the soil moisture and the absorptive capacity of the soil for the gas. Of course this soil probably had a low absorptive capacity, owing to its low clay and colloidal content. The observations of previous investigators, that urea is quickly broken down, were certainly being born out. The check soil had no Ammonia coming off, and neither did the 2.5% or 5% treatments. As the experiment continued the two lower treatments continued in giving off more or less Ammonia and liter the 2.5% treatment also gave it off. The 5% treatment did not give off very much at any time, compared to the amounts given off by the other treatments.

Unfortunately, the Ammonia given off was not determined and the observations were made simply on the relative strengths of the funes that could be smelled coming off, a rather rough method of determining Ammonia, to say the least. As the experiment continued, the .5% and 1% treatmonts did not seem to give off so much gas as at first. This may have been due either to the complete ammonification of the urea or to the succumbing of the organisms. When the experiment was about half way through, the Ammonia that would come from some of the jars was so strong that it was exceedingly unpleasant for the person aerating the soils.

Some doubt was expressed concerning the probability of this action being biological rather than strictly chemical or catalytic in nature. The question as to whother organisms could live in an atmosphere so strong in ammonia and a solution so highly concentrated justified this doubt. However, if this action were chemical rather than bio-chemical, by the law of mass action, the 5% treatment should react the most quickly and produce the most **A**mmonia. What actually happened was just about the opposite of this. The 5% treatment produced the least Ammonia of any and the .5% and 1% treatments reacted the most quickly, apparently producing the most Ammonia. These facts are more easily explained from a biological than from a chemical standpoint. In the case of the 5% treatment, the concentration of the

-9-

. .

.

· · · · ,

• •

• ,

• • .

.

scil solution was very great, so that the organisms might have been killed or rendered inactive to a large extent, thus not producing great amounts of Ammonia. The frequent acration and consequent removal of excess Ammonia from the other treatments a parently allowed the organisms to live for a while at least. Willar (32) has shown that the ammonifying organisms can function in soil solutions quite ecceentrated. He did not work with solutions quite so concentrated as some of these in this experiment, but he showed that the inhibiting concentrations varied with the materials added to the solution. He did not work with urea, but it is possible that the inhibiting concentration for this material is quite high. He points out that other factors than the total concentration of the soil solution may be limiting.

There was no nitrification, probably because of the killing of the nitrifying organisms. They possibly could not tolerate the conditions of high concentration and alkalinity. with a lack of Oxygen, as were present in the treated soils. The fact that the check or no treatment scil produced nitrates is proof that the soil had at least some nitrifying power. The lowering of the nitrates in the treated soils is ressibly due to assimilation by organisms in their life processes, without nitrification going on much to restore them to the soil solution. It is recognized that the above statements may not fully and adequately explain all of the observed facts, but they serve the purpose better than any other that were considered. The data secured in connection with the Mitrate determinations go far to explain the results secured from determining the Hydrogen-ion concentrations and also the total concentrations of the soil solutions.

> B - Effect of Applications of Urea on Reaction of Coloma Fine Sand.

The Hydrogen-ion concentrations were determined electrometrically by means of the Quinhydrone electrode, as described by Billmann (4). The results from these determinations were frequently checked roughly by the use of Soiltex, as described by Spurway (41). Comparatively close results were secured by the two methods. Two determinations were made on the samples of soil from each jar, and as the jars were in duplicate, four readings were made on each treatment. Very close agreements were secured among the readings, and the averages of the four readings are reportin Table 2. As is the general custom, the values are given in terms of pH, rather than as the actual Hydrogen-ion concentration.

Table 2 - pH Values for Colona Fine Sand.

Treat.	0 Days	4 Days	11 Days	22 Days	29 Days	36 Days
Check.	6.92	6.68	6.25	5.93	5.85	5.95
.5% urea	8.01	8.94	9. <b>1</b> 5	8.21	8.12	7.85
1.0% "	8. 58	9.01	9.17	8.47	8.33	8.04
2.5% "	8.17	8.99	ટ <b>. 99</b>	8 <b>.67</b>	8.51	8.19
5.0% "	7.99	8.67	8.60	8,36	8.04	7.61

The very alkaline figures are possibly not exactly correct, although good checks were secured from the quadruplicate determinations. However, the Guinhydrone electrode is not supposed to give accurate results at such high pH values. The figures could not be checked against the Hydrogen electrode as the great amount of Ammonia present seemed to throw it off when an attempt was made to use it.

The urea tends to make the soil more alkaline as larger amounts are added to it, as will be seen by examining the column headed O Days. This represents the reaction of the soil immediately after the urea is added. As the soil was about neutral to begin with, the urea threw it over to the alkaline side. This is natural, as a tenth melar sclution of the material added had a pH of 7.35, while a nearly saturated solution of it had a pH of 8.77. The largest application made was almost a saturated solution of the urea.

The check soil became more acid until 22 days, after

which it remained about constant in reaction. It happens that this coullibrium is reached at the same time that the scil solution reaches its greatest concentration. This is considered at present to be merely a coincidence, as the cther scils studied did not show this relationship. The reasons for the increased acidity of the soil are probably the nitrification of organic matter, producing Nitric Acid, and bringing into solution more of the slightly soluble acid silicates. As before mentioned, when the soil was brought from the field, it was after a period of dry weather. As it was made more moist in the laboratory. it would tend to have more of these slightly scluble acid silicates in its sclution. After these materials saturate the soil solution an equilibrium is reached and the acidity of the soil would remain the same.

Treating the soil with urea made it quite alkaline. This is not surprising since, as before mentioned, ammonia was produced in large quantities. In fact the PH value of the soil is considered to be an index to the amounts of Anmonia formed in this experiment. The pH would be highest when the greatest amounts of Anmonia would be noticed coming from the soils. The 5% treatment, where very little Ammonia could be noticed coming off, always had the lowest alkalinity of any of the treated soils. During the course of the experiment the alkalinity reached a high point and then decreased. This was probably due to the loss of Ammonia by volatilization. The results of the determinations of the total concentration of the soil solution bear this cut.

C - Effect of Applications of Urea on the Concentration of the Soil Solution. Coloma Fine Sand.

The concentration of the soil solution was determined by the freezing point method as devised by Bouyouces and McCool (6,7). The equivalent of 20 grams of dry soil was weighed out, put into a freezing tube and made up to 70% moisture content. This high medisture content was used so as to secure more accurate results. Thus the figures can only be considered from a relative standpoint, and cannot be taken as absolute concentrations of the soil solution. The actual concentration of the soil solution would probably be represented by a depression several times that securel. The results are reported as the depression of the freezing point below that of water, in degrees Centigrade. The averages of duplicate determinations are given.

Table 3 - Freezing Point Depressions in Degrees C. Coloma Fine Sand.

Treat.	0 Days	4 Days	11 Days	22 Days	29 Days	38 D <b>a</b> js
Check.	0.000	0.008	0.020	0.043	0.018	0.022
.5% ures	a 0.066	0.290	0.297	0.224	0.133	0.097
1.0% "	0.353	0.796	0.600	0.408	0.230	0.213
2.5% "	0.537	1.063	1.510	1.109	1.161	1.150
5.0% "	0.992	1.247	1.921	2.139	1.931	2.030

In the case of the untreated or check soil, the concentration of the soil solution increased up to 22 days, after which it decreased and then became constant. This is somewhat similar to results reported by Wheeting (38). . Working with a number of soils, he found that they had a maximum depression of the freezing point, after which the depression decreased. It took longer for his soils to reach the maximum point, but he used heavier soils than the one used here. He found that, in general, it took heavier soils longer to reach their maximum depression than it did sandy soils.

Ine addition of usea to the soil increased the concentration of material in the soil solution more or less in propertion to the amounts added. In all of the treatnents during the course of the experiment a maximum concentration of the soil solution, or depression of the freezing point, was secured. This did not occur at the same time in all of the treatments. However, after the maximum was reached, the depression did not recede and become constant, as in the case of the check treatment. They kept going down as long as the experiment continued. This rise and fall may have been due to the rate and amount of the production of Ammonia. There is some correlation between the freezing point depressions and pH values in the .5%, 1%, and 2.5% treatments, the highest pH occurring at about the same time as that of the greatest depression of the freezing point. Toward the end of the end of the experiment, when the pH was lower, and the oder of Ammonia coming from the soils was much less, the depression of the freezing point was also much less.

The facts that the soil solutions did not keep constant after reaching the maximum, but received, and that the ammonia noticed coming off at this time was much less, indicate that either ammonification was not going on very fast or was being removed. The Nitrate determinations show that it was not being nitrified and the freezing point determinations show that it, or something else, was going out of solution. Since the pH was lowering at the same time, it would point to the less of Ammonia from the solution. The following is a possible explanation of how this took place.

When the Ammonia volatilized it saturated the soil solution and the absorptive capacity of the colloids, after which it was given off into the atmosphere. It thus set up more or less of a pressure in the closed atmosphere of the jar. According to Henry's law, which states that t the concentration of the dissolved has is directly proportional to that in the free space above the liquid, the sclubility of the Ammonia in the soil solution would be increased the more Ammonia there was produced. This extra amount dissolved would probably not have time to go off before the freezing point determination was made and would therefore influence it. When the production of Ammonia stopped, the pressure of this gas in the soil atmosphere would be lowered, due to the frequent aeration of the soil. Some of the dissolved Ammonia would now some from the soil solution in order to reostablish the equilibrium of the gas between the solution and the air in the jar. This would coour at each abration of the soil and might easily become appreciable in time, thus accounting for the lowering of

the concentration of the soil solution. Of course, the Ammonia might have disappeared due to biological action. This may have caused it to have been synthesized into organic compounds that were more or less insoluble. This explanation would take care of all of the observed phenemona. The results as secured may have been due to a combination of these actions, and possibly others also.

The data of the 5% urea treatment are interesting. It will be recalled that very little Ammonia was noticed volatilizing from this soil. However, a reaction must have been going on as the freezing point changes considerably during the course of the experiment. Since the depression increases at first, the urea must have been breaking down into compounds of a greater number of mole, or else it was affecting the solubility of the soil, either before or after breaking down. No club was found to show what this action might have been.

Conclusions - Series 1

From the experiments on the Coloma Fine Sand the following general conclusions may be drawn:

1- Urea added to this soil was ammonified very rapidly, although if exceedingly large applications were made, a point was reached where ammonification would not go on.

2- Nitrification would not go on appreciably when urea was added to this soil in large quantities, the smallest application made here being too great for this process.

3- Aumonification can go on unler conditions in which nitrification will not take place. Thus the soil's ammonifying power is not necessarily an index to its nitrifying ability.

## SERIES 2

Moderate Applications of Urea to Fcx Sandy Leam and Miami Silt Leam.

Based upon the results of the preliminary work with

the Coloma soil, a new series of experiments was begun. For this work two agriculturally important soils were used, a Fox Sandy Loam and a Miami Silt Loam. Both soils had been cropped the summer previous to the fall in which they were taken, the Fox soil to corn and the Miami soil to cats. The surface soil to a depth of about four inches was taken, the surface dobris always being removed previous to the sampling.

Urea was added at the rates of 83.3 pounds, 166.6 pounds, 333.3 pounds, 666.6 pounds and 1333.3 pounds per acre six inches of soil. An acre six inches was considered as two million pounds of dry soil. The treatments of the two soils were the same, except that the Fox soil received 66 pounds of urea instead of 83.3 pounds for the lowest application.

The treatments given can also be considered on another basis. A drill usually mixes the fertilizer through about one and a half inches of soil. Therefore the treatments listed above, divided by four will represent the conditions present when these amounts per acre are added to the soil by a arill. The following table shows these relationships.

Lbs. NaNO3 per acre 6" equive lent to urea addel.	Actual Lbs. - urea added per acre 6"	Lbs. NaNO3 per acre 1 1/2" e- qual to urea added (drill)	Actual Lbs. urea added to drill depth (1 1/2)
0 - Check	0.0	0.0	0.0
250	83.3	62.5	20.8
500	166.6	125	41.6
1000	333, 3	250	83.3
2000	666.6	500	166.6
4000	1333.3	1000	333.3

All the figures in any horizontal line refer to one treatment as run in the following series of experiments. Thus, while the figures in the first two columns may soom to be rather large, the last two columns show that they represent conditions frequently occurring in the soil. Nitrate of Soda is commonly drilled at the rate of 125 and 250 pounds per acre, and the data secured for the 166 and 333 pound treatments are also data for these drilled treatments. The pounds of uses added are here expressed in terms of equivelent amounts of Nitrate of Soda so as to give a better idea of the anounts added. These figures also show the relative concentrations of Nitrogen in the two captiers.

Of course, the relationships in the proceeding paragraphwould not hold for any length of time in a well moistened soil. Medocl and Wheeting (27) and Wheeting (46) have shown that the movement of soluble salts in the soil solution is moderately rapid, especially at moisture contents as used here. A rain would also tend to remove these relationships, owing to the high solubility of the under. No data are available concerning the absorption of the material by the soil, but if it were absorption of the material by the soil, but if it were absorbed to an appreciable extent, it would cause the above relationships to persist longer. van Harreveld (12) has shown that under leaches readily from the soils of Java, but that does not necessarily mean that such will be the case for soils in this country.

The general procedure and methods of making determinations were the same as previously described for the Colona soil, in the first Series. The soils were made to and kept at optimum moisture content and the urea was added to the soil by dissolving it in the water to be added to the soil. Frequent and thorough aeration was given to the soils, and the samples for the nitrate, ability and freezing point determinations were taken at about the same intervals. The experiments were not run simultaneously, however, the Fox soil being started about two weeks before the Miami soil. In both cases a check or no treated soil was run for comparison, and all treatments were run in duplicate.

A - Nitrification Studies in Fox and Miami Soils. The results of the Nitrate determinations are given in Tables 4 and 5, for the 1 to 5 extracts from the two soils. The average of quadruplicate determinations is given in parts per million, based upon the extracted solution, for each treatment.

Table 4 - Nitrates in 1 to 5 aqueous extract of Fox Santy Loam. (parts per million.)

Treat	0 Days	5 Days	11 Days	22 Days	40 Days
Check,	11.8	17.3	24.7	29.5	33.0
66 # urea	11.8	20.7	33.7	42.2	47.4
166 ≱ "	11.8	26.8	55.7	60.8	66.4
333 <b>* "</b>	11.8	31.4	74.4	82.2	91.8
666 * "	11.8	39.1	103.1	188.8	1-10.0
1333# "	11 <b>.</b> ö	ə <b>1.</b> 2	182.0	191.4	181.4

Table 5 - Mitcates in 1 to 3 aqueous extract of Miami Silt Loam. (parts per million)

Treat.	0 Days	3 Jara	10 <u>Days</u>	17 Days	37 Days
Check.	13.6	28.0	45.2	43.5	58.2
83 # urea	13.6	41.6	54.2	59.7	58.2
166 🗯 "	13.6	42.6	64.0	64.0	73.4
333 🗍 "	13 <b>.</b> ö	42.6	93.2	6.83	93.8
666 <b>* "</b>	13.6	47.1	105.8	106.7	94.1
1333* "	13,6	50.0	172.6	188.2	228.6

It will be noticed that the soils were rather low in nitrates at the beginning, and there was about the same amount in each. Examining the results of the check soils above will show that the nitrate content increased in both soils, but it increased about 50% more in the Miani soil than in the Fox. Biological processes had probably been low in each previous to taking the samples from the field, due to dry weather. On making conditions optimumfor bacterial action, the Miami soil showed that it had more potential nitrifying power, probably due to a combination of circumstances, among which may be higher organic content, more plant and bacterial food elements, and less acid reaction. These soils treated with usea gave increases in nitrate content and the larger the treatment, the greater the amount of nitrates formed. This shows that nitrification was going on in all of the soils, and that apparently some of the usea was being nitrified. As the experiment continued the Nitrates continued to increase, with a few exceptions, and these were possibly due to experimental error. After forty days the nitrates were still increasing. No regular determinations were made after this, due to a lack of material, but determinations made a month later in connection with some other work, showed that the nitrates were still slowly increasing. The results are not given as it is felt that they may not be exactly comparable to these given in Tables 4 and 5.

In order to study the rate and amount of nitrification from anothor angle, other tables were worked from Tables 4 and 5 above. These are given in Tables 6 and 7 and were secured by subtracting the nitrates present in the check soil from these present in the treated soils. This is really taking for granted that the amount of nitrification of the crianic matter in the check scil will be the same as the amount of nitrification of the criginal organic matter in the treated soils, the expess of nitrates being assumed as coming altogether from the urea added. It is readily admitted that such is not necessarily the case. It is to be more or less expected that the addition of the urea to the soil, especially if in large quantities, would affect its microcreanic population, both in kinds and numbers. The results, however, bring out some interesting points, and show in part whether the above assumption was justified.

In the last column, headed theoretical maximum, the figures were secured by calculating the amount of nitrates that would be formed if all of the urba added had its Nitrogon changed to nitrates.

Considering first the results from the Fox soil in Table 6, it will be seen that the increased rates of adding urea caused greater increases in nitrates over check. However, this increase in nitrates in the larger treatments is not proportional to the increase in the applications of urea. The applications double each time while the increases do not, except in the cases of the two lower treatments. The 166 pound treatment is two and a half times the 66 pound treatment, and the increases over check in nitrates in these treatments follow this ratio closely. As the experiment continues the increases over check become greater, as a rule indicating that the nitrification of the urea is gaining in momentum.

Table 6 - Increase of Nitrates over Shock. 1 to 5 Extract. Fox Sandy Leam. (p.p.m.)

Treat.	5 Days	11 Days	22 Days	40 Days	Theoretical
Check.	17.3	24.8	29.6	33.0	Maximum.
66 # ur9a	<b>3.</b> 4	8. 9	12.0	14.4	14.5
100 # "	9.6	31.0	31.3	33.4	36.4
333 🗚 "	14.1	49.8	52.7	58.7	72.9
666 ¥ "	21.9	78.3	109.3	112.9	145.8
<b>1</b> 333 <b>*</b> "	34.0	107.3	161.9	148.4	291.6

Table 7 - Increase of Nitrates over Check. 1 to 5 Extract. Wigmi Silt Logm. (p.p.m.)

Treat.	3 Days	10 Days	17 Days	37 Days	Theoretical
Check.	28.0	45.2	43.5	58.2	Maximum.
83 # urea	13 <b>.</b> ö	9.0	16.2	00 <b>.0</b>	18.2
166 # "	14.6	13.8	20.5	10.2	36 <b>.</b> 4
333 🗚 "	14.6	48.0	45.1	37.6	72.9
066 ¥ "	19.1	60.6	63.2	32.9	145.8
1333# "	22.0	127.4	144.7	170.4	291.6

Comparing now the total nitrates possible from the urea, shown in the last columns of Tables 6 and 7, with the increases in Nitrates over check at the end of the experiment, in maxt to the last columns, it will be seen that they are the same for the lowest treatments in the Fox soil

in Table 6. As the treatments increase, the divergences between the figures increase. Thus the two lowest applications have produced the theoretical maximum amount of nitrates over check soil within the time of this experinent. This would tend to show that all of the urea added in these treatments had been nitrified. However, this is only deduction, and there is the possibility that the original soil organic matter was nitrified to a preater extent in the treated soils than in the untreated soil, the figures for the increases over the check soil not represnting nitrates produced from urea alone. The fact that the larger treatments cause a falling off in the approach to the maximum of nitrates produced over check that is possible, tends to show that the original soil organic matter is not nitrified to such an extent as it is in the untreated soil. This fact, coupled with the many experiments reperted on the ease of the ammonification and nitrification of urea would indicate that the increase of nitrates over these in the untreated soil represents usea nitrified and leads to the conclusion that all the urea added was nitrified in the soils receiveing the two lowest applications. It will be recalled from the last paragraph that these two treatments maintainel the ratio of their increases over check fairly constantly.

As before stated, if the urea is going to have an effect on the nitrification of the original soil organic matter, that effect should s on up most strongly in those soils receiving the heaviest applications. The falling off of the heavy treatments in the approach of the excess nitrates to the maximum would indicate that there was an effect of the urea on the soil, not noticed particularly in the two lowest treatments, but increasingly marked in the heavier treatments.

The falling cff in the increase of nitrates in the cases of the heavy applications may be due to:

1- A lower percent of the added uses being nitrified in the heavy treatments, as ecupired with the lighter.t The length of time of the experiment would probably have quite an influence on this point. The longer the experiment runs, the greater the percent of the aided unca that should be nitrified.

2-Less of the original soil organic matter being nitrified in the heavy treatments. If the organisms could use usea as a source of energy, it would be reasonable that theywould use less of the comparatively unavailable soil organic matter. If this is true, the results in Tables 6 and 7 do not show all of the nitrates produced from the heavy additions of usea to the soil.

3- A greater consumption of the nitrates after they are produced, due to the much greater production of organisms, caused by the addition of the urea to the soil. The final result is probably a combination of all of the above three points.

Turning now to the results for the diami soil in Table 7, the lack of regularity in the data makes interpretation more difficult. Considering first the lowest application, it will be notleed that the increase over check at one time was practically up to the maximum, after which it dropped down to nothing. In this case, and in all cases where the increase over check decreases from one time to the next. it shows that nitrification has been soins on faster in the check soil than in the treated soil, or else the nitrates are being consumed in the treated soils. This condition harrens quite frequently in the case of the Miami scil. while it happened only once in the case of the Fox soil. Of course, the nitrification of the urea was put to a harder test in the Biami soil than in the Fox, as shown by the preater amount of Nitrates produced in the check soil of the former. The Miami soil ressibly had a dreater amount of easily nitrifiable organic matter in it. If it were due to the greater nitrifying power of the Miami scil, the increase of nitrates over those in the untreated soil should be the same as that of the Fox soil. With one exception, the Fox soil produced greator increases over check then the Miami soil. However, the General trend of the results from the Wiami soil is the same as those from the Wox soil.

E - Effects of Applications of Urea on Boaction of Fox Sandy Leam and Miami Silt Leam.

The pH determinations are reported in Tables 8 and 9. They are the average of quadruplicate samples run separately. The last set of determinations for the Miami soil had to be discarded, as one of the electrodes was found to a have had an error in it, after the work was finished.

Table 8 - pH Values of Fox Sandy Loam.

Treat.	o Days	5 Days	11 Days	22 Days	40 Days
Cheek.	5.27	4.65	4.80	4.79	4.69
66 🕷 urea	5. 52	4.73	4.84	4.79	4.49
166 🗚 "	5.84	4.78	4.72	4.83	4.40
333 🐇 "	e.00	4.85	4.45	4.47	4.17
සිබිසි 🛊 🕛	5.90	5.13	4. č1	4.05	3.80
1333# "	6.05	5.75	4.66	4.21	3.75

Table 9 - pH Values fo Miani Silt Leam.

Treat.	0 Days	3 Days	10 Days	17 Days
Check.	5.40	5.41	5.32	5.43
83 # urea	5.56	5.41	5.20	5.41
166 🐐 "	5.84	5.31	5.34	5.36
333 🗍 "	5.67	5.42	5.30	5.21
666 🐇 📲	5.72	5.52	5.17	5.07
1333# "	2. 33	5, 90	5.15	4.60

It will be noticed that in both soils the addition of urea tended to make them less acid, as was the case in the Oclona Scil. Both soils had pH values that wore rather low for the average of these types. This may have been due to their rather dry condition/when taken from the field, and they were not used for some time after that, although they were not allowed to become air dry. Bost and Fieger (36) have shown that drying soils lowered their pH value we little, and remaining them still further reduced the rH. Storing in the moist condition also caused an increase

 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .
 .

•

in acidity according to their results. These factors should be considered when interproting the data.

The Fox energy soil, in Table 8, tended to become more acid during the ocurse of the experiment, but the charge is not great. The kiami soil changed very little in the check or no treatment jars, being gradically constant. A possible explanation of this will be given later. In the treated soils, after the first day they all tended to beeome more acid as the experiment continued. The heavier the treatment, the nighter was the initial gF and the lower was the final gH. There somed to be some correlation between the total mitrates produced and the gH of the soil. As a rule, the more mitrates there were produced, the lower would be the gH value. This may be explained by examining , the following general relation for the mitrification of urea:

 $\frac{\text{CC(NE}_2)_2}{(\text{ME}_4)_2} + \frac{2}{10} \frac{\text{H}_20}{10} = \frac{(\text{ME}_4)_2}{200_3}$  $\frac{(\text{ME}_4)_2}{10} + \frac{2}{10} \frac{10}{10} + \frac{2}{10} \frac$ 

Thus a strong and a wook apid are formed as the rosult of the process. Those would etteck the soil bases to scale extent, probably, and be partly neutralized, but this process in itself would tend to lower the pH of the soil. Spurway (40) has shown they treating soils with strong acids causes weak actus to be split off, and this would tend to lever the pH of the soil. Of Sourse, if plants were growing on this, they would remove the nitrate radicle more duickly than the base, so that in time the soil reaction should eche partly back toward the original value, if no leacning occurs. The acidity caused by the nitrification of urea is not peculiar to this material, but would coour with any nitrified material. The acidifying effects of the nitrification of Amerium Sulphate are much prostor, as the second seid preduced with this material is Sulphurie, which is ruch strenger then the Cerbonic Acid formed from urea.

As before mentioned, the Missi shock soil did not e change much in reaction during the course of the experi-

ment, while the Fox scil became more acid. However, the Miami soil produced more nitrates and was less acid to bebin with. Peth of these things should make the Miami seil change more than the Fox scil. Equal amounts of urea added to both soils caused the Fox soil to change more in initial reaction than the Miami. During the course of the experimont. the Miasi scil did not change in reaction as much as the fox scil, jet, as a rule, the Miani scil produced more nitrates. Thus in all cases, with equal treatments, the Wiami soil did not change in reaction as much as the Fox scil dil. This is probably due to the buffering action being strongerin the Riami soil. This soil is a silt leam and contains a high percentage of silt and clay, while the Fox Sendy Loam is low in silt and elay.. The silt and elay are the parts of the soil which are supposed to contain most of the buffering meterials, and this would account for the stronger buffer action in the Miami scil. Arrhonius (3) states that the processes tending to make the fine rarticles of the scil also build up the buffer effect of the scil. Bradfield (8) states that the buffer action of a scil is some direct function of its colloidal content.

C - Effects of Applications of Urea on the Concentration of the Soil Solution. Fox Sandy Loam and Miemi Silt Loam.

The concentration of the soil solution in terms of the depression of the freezing point is given in Tables 10 and 11 for each of the treatments of the two soils. The figures are the averages of duplicate determinations. It should be remembered that the real soil solution was not used for these determinations, but it was diluted in order to secure greater accuracy. The results are not absolute, but only relative. The actual concentration would be represonted by a depression probably much greater than that given below, in each case.

The depression of the freezing cint in the check soils increased at first, after which it stayed practically constant. This is schewhat different than what was observed in the case of the Colona soil, in which a maximum deprossion and then a receiving of the depression was secured. This might possibly be due to the fact that the Pox and Miami soils for finer in texture and thus do not reach the maximum point so soon. Wheeting (45) found that the finer textured soils usually required longer to reach their maxinum depression than the coarser soils. It was not until after thirty or forty days that he secured the maximum depressions in soils of textures comparable to those in this experiment. It would look as if these soils had not run long enough to have passed their maximum concentration in the solution.

Table 10 - Freezing Feint Depressions, Degrees Centigrade. Fox Sandy Lean.

Treat.	0 Days	5 Days	11 Days	22 Days	40 Days
Chock.	C.001	0.011	0.009	0.013	0.016
66 🖠 ur	ea C.014	0.010	0.021	0.021	0.024
166.4 "	0.014	0.017	0.027	0.028	0.035
333 * "	0.010	C.023	0.037	0.041	0.055
666 🐇 📲	0.019	0.028	C.019	0.068	0.022
1333# "	0.040	0.040	0.075	0.025	0.107

Tablo 11 - Froezing Point Depressions, Degroes Centigrado. Miazi Silt Leam.

Treat.	0 Dafa	3 Days	10 Days	17 Dajs	37 Days
Check.	0.010	0.015	0.028	0.027	0.026
E3 * urea	0.013	0.025	0.035	0.038	0.044
166 🗚 "	0.013	0.026	0.040	0.039	0.051
333 🐐 "	0.017	0.028	0.052	0.057	0.066
666 * "	0.021	0.035	0.062	0.062	0.072
1333# "	0.026	0.038	0.100	0.120	0.134

As the experiment progressed, the treated scils gave greater depressions and the scils receiving the heaviest applications had the greatest depressions. This is quite natural since the metorial added and also the nitrates formed would tend to lower the freezing point. There is a fairly good and regular correlation between the total nitrates and the depressions of the freezing points. The urea itself depressed the freezing points, as will be seen in the column headed O Days in Tables 10 and 11. However, the results are irregular and do not seem to indicate much. except that the depressions are not proportional to the material added. It would look as if there was some absorction without replacement, or else precipitation. In the Fox scil in Table 10, after the first addition, the degreesion does not change much until the largest application is made, when it increases considerably. The absorptive capacity of the scil was possibly not exceeded by the lower applications, but was by the largest application. In the Miami scil (Table 11) there is a slow but gradual increase in the depression. This may be due to the urea itself or to absorption with replacement. However, no definite conclusions can be drawn from the few and irregular data secured.

Tables 12 and 13 show the increases in freezing point depressions over check. The results in the Check line are the actual depressions secured. The figures in the columns below represent the amount in degrees Centigrade below the check at which the solutions froze. These figures show the relative effects the uses additions actually had on the soil solution. The effects may have been direct or indirect, but they are quite appreciable in most cases.

Table 12 - Increase of Freezing Foint Depressions Below Check. Fox Sandy Loam. (Degrees C.)

Treat.	0 Days	5 Lays	11 Days	22 Dajs	40 Days.
Check.	0.001	0.011	0.009	0.014	0.016
65 # urea	0.013	0.000	0.013	0.007	0.008
166 🕻 "	0.013	0.006	0.018	0.015	0.019
333 🐇 "	0.009	0.013	0.029	0.028	0.040
666 # "	0.018	0.017	0.040	0.055	0.066
1333# "	0.038	0.030	0.066	0.081	0.021

Uneek.	Miami Silt	Leam Sci	1. (Deg	rees Cent	igrale.)
Preat.	0 Days	3 Days	10 Days	17 Days	37 Days
Check.	6.010	0.015	0 <b>.</b> 028	0.027	0.026
83 # ur	ea 0.003	0.010	0.00.	0.(09	0.018
166 🟄	0.003	0.011	0.012	0.012	0.025
333 🛊 🛛	0.007	0.013	0.024	0.030	0.040
666 #	0.011	C.020	0.034	0.035	0.046
<b>1</b> 333¥ - 1	" 0 <b>.</b> 016	0.023	0.072	0.003	<b>0.1</b> 08

Table 13 - Increase of Freezing Foint Depressions Below

In the lighter treatments, the increased depressions below check did not vary much, while the heavier treatments caused the increased depressions below check to become greater. There was some correlation between the increase of nitrates over check and the increase of freezing point depression below check, but it was not very close or well defined.

The theoretical increase of freezing point depression below check was calculated using the increased amount of nitrates over check as the material that would cause the depression. For this purpose, figures were chosen from results where all of the uroa had apparently been nitrified. so that none of the urea would be present to affect the depression. The nitrates were assumed to be in the form of Calcium Nitrate and completely dissociated, which was probably the case in the weak soil solution. However, even on this basis, the theoretical depression is very much less than the observed depression. This is not so strange when it is considered that the nitrification process, with its production of a strong and a weak acid, and the subsequent salts, probably affects the solubility of quite a few of the soil constituents. Another indication that material other than the nitrates was causing the increased freezing point depressions was the fact that occasionally the increase on nitrates over check would drop off without the increase of freezing point depression falling off. Also, when the total nitrates would fall off, the total depression

-28-

of the freezing point would not be lowered.

Conclusions - Series 2

The results from the preceding experiments have let to the following general conclusions:

1- Urea added to scils at rates up to 1833 pounds per acres six inches, is realily nitrified.

2- The nitrification of the added upoa is apparently rather complete in the smaller applications, but falls off considerably in completeness in the larger applications.

3- The nitrification process apparently causes an increase in the acidity of the soil, at least for a time, the increase being more or less correlated with the amount of nitrification.

4- The addition of urea causes an increase in the concontration of the soil solution, the effect being greater the more urea that is added and the longer the time after the application, at least up to forty days.

SERIES 3.

Studies on Volatilization of Ammonia Upon Applying Urea to Coloma, Fox, and Miami Soils.

Another series of experiments was begun based upon lines suggested by the results secured with the Colona scil in Series 1, where great amounts of Ammonia were given off by the applications of very large amounts of usen to the scil. It was desired to ascertain whether the usea would volatilize Ammonia when added in quantities comparable to applications made in the field. If such would be the case, it would be a serious limiting factor in its use. No Ammonia was noticed coming from the Fox and Miami scils in Series 2, but more definite and exact information on this question was desired.

A - Volatilization of Ammonia From Coloma Soil.

For this purpose, Coloma Fine Sand similar to that

used in Series 1, was placed in jers, given the desired treatments, and any Ammonia volatilized determined by drawing the soil air through standard acid. The air was first drawn through dilute Sulphuric Acid to remove any Ammonia that might have been in it. It then went through two bottles of distilled water, in order to thoroughly wash it. The water bath also served to increase the percent of water vapor in the air, and thus greatly lowered the arying influence of the aspirations on the soils. By means of glass tubing, the air entered the jar of soil at the bottom, and was drawn off at the top of the jar, thus insuring a thorcugh aeration of the soil. After leaving the soil, the air was drawn through tenth normal Sulphuric Acid. The Sulphuric Acid was titrated with tenth normal Pctassium Hydroxide to determine the amount of acid that had been neutralized by Ammonia. The aspirations were conducted every two or three days, and the air was drawn slowly cothrough the scil for one hour at each aspiration. Muen nct being aspirated, the jars were closed tightly and they were always kept out of the direct light, more or less in the dark.

The experiment was allowed to run for two and a half nceks, after which it was than down and the nitrates determined in 1 to 5 aquecus extracts of the soils. When the urea was to be added and mixed through the soil, it was disscived in the water used to make the scil up to optimum moisture content. In the case of the top dressing treatment, the area of the jar was calculated and the percentage of an acre determined. The pounds of urea that were to be applied per acre were multiplied by this percontage, which gave the actual weight of the urea to be put on the soil in the jar. The top drossing was made at the rate of 1333 pounds of urea per acro, which is the eguivelent of two tens of Nitrate of Soda per acre. This figure is rather high for a top drossing, but it was used in order to secure an ancunt that could be spread uniformly over the surface and also in order to secure more positive results, if any were to be secured. The treatments mixed through the soil were: 83 pounds of urea per acre six in-

. . . .

 ches cf soil (equivelent to 250 pounds of Scdium Nitrate), 166 pounds of urea (equivelent to 500 pounds of Scdium Nitrate), 666 pounds of urea (equivelent to 2000 pounds of Scdium Nitrate), and 1333 pounds of urea (equivelent to 4000 pounds of Scdium Nitrate). Two jars had no urea added, serving as a check. All of the treatments were run in duplicate.

Table 14 gives the results of this experiment, the figures being the averages of duplicates. The numbers are the cubic centimeters of tenth normal Ammonium Sulphate formed at each aspiration. These were secured by subtracting the cubic centimeters of tenth normal Fotassium Hydroxide necessary to neutralize the acid, from twenty-five, the number of cubic centimeters of tenth normal Sulphuric acid used.

Table 14 - Amounts of Ammonia Volatilized, Expressed as c.c. of .1% (NH4)2504, and Nitrates produced. Coloma Soil.

Treat.	1 Day	2 Days	5 Days	7 Days	10 Days
Check.	0.00	0.00	0.00	0.00	0.00
83 # urea	0.00	0.22	0.00	0.00	0.02
166 ≱ "	lost	0.00	0.00	0.00	0.32
666 * "	0.00	0.00	0.00	0.02	0.0.
<b>13</b> 33¥ "	0.00	0.(0	0.00	0.12	0.30
1233# "	0.00	0.00	0.(0	0.QO	0.58
top dress.					NO3 prod.
Treat.	12 Days	14 Days	17 Days	Totals	F. F. M.
Check.	0.00	0.00	0.00	0.00	17.8
83 * urea	0.00	0. CO	0.00	0.24	42.1
166 # "	0.05	0.23	0.32	0.94	38.1
ರೇರೆ 🖇 "	0.00	0.00	0.00	U. 02	72.7
1333# "	0.00	0.00	0.45	0.07	22.9
1333≱ "	0.00	0.65	0.60	1.83	17.0
top dress.					

It will be seen that the results are not very conclusive owing to small differences and many irregularities. The top dressing treatment appeared to be volatilizing some

Ammonia toward the end of the experiment, although not a great deal was being produced. The 166 pound treatment also seemed to be giving off some Ammonia quite regularly toward the end of the experiment. The 666 round treatment did not give off any Ammonia to speak of, while the 1353 pound treatment mixed in. gave off some. although not as much as the 166 pound treatment. These irregularities make it difficult to draw any definite conclusions except that the amounts of Ammonia given off are not very great at any one time, or even in the aggregate. It can be seen that the figures in any one case are not large, and might be due in part at least, to experimental error. The results from the top drossing are the only ones that might be called at all significant, and even these should be treated with circumspection. Locking at the total amount of Ammenia produced without considering the sizes of the numbers that go to make up these totals is liable to give misleading conclusions. The total amount of Ammonia given off was never more than a small fraction of the Nitrogen added in the urea.

However, by comparing the last two columns in Table 14, which give the total Ammonium Sulphate produced and the nitrates in the 1 to 5 aqueous extract at the end of the experiment, respectively, an interesting apparent correlation is noticed. The greater the amount of nitrates produced, the lower the volatilization of Ammonia. This correlation holds fairly well through-out the whole experiment. This is a logocal result, since the more rapid the nitrification, the less will be the tendency for Ammonia to accumulate in the soil. No explanation can be offered as to why some treatments gave this rapid nitrification and others did not. It does not appear to be correlated with the amount of urea added, and with the exception of this, conditions were as uniform as possible in all the jars.

> B - Volatilization of Ammonia From Fox and Miami Scils.

Another experiment was run in the same sories, using

Fox Sandy Loam and Miami Silt Loam soils similar to those used in Series 2. The general plan of the experiment was kept the same as in the Coloma experiment, except that here some of the intermediate treatments were chitted. Another difference was the use of 20 c.c. of Standard acid instead of 25 c.c., but this does not affect the results.

The following treatments were used:

1- Fox scil - Chesk, no additions made.

2- Fex seil - unea added as a tep dressing at rate of 1333 rounds per acre.

3- Fox soil - urea added at rate of 1333 pounds per acre six inches of soil, and mixed in.

4- Miami soil - Cheek, no additions made.

5- Miani scil - urea added at rate of 1333 pounds per acre, as a top dressing.

6- Eiami scil - urea added at rate of 1333 pounds per acre six inches of scil and mixed in. The treatments were run in duplicate, the average of them being reported in Table 10 as before.

The data for the Fox soil in Table 15 show that much greater regularity existed than in the case of the Ocloma or Miami soils. The top dressing showed regular volatilization of Ammonia, the total amount being slightly higher than was secured for the Ocloma soil. None of the other results from this experiment are of any great significance. While there is evidence of some volatilization in the case of the Fox soil with 1333 pounds of urea mixed in, and also with the top dressing of the Miami soil, yet it is felt that the results are not regular or large enough to warrent drawing conclusions from them.

Here again there is a correlation in both soils between the total amount of Ammonium Sulphate produced and amount of Nitrates produced. In both soils the top drossings volatilized more Ammonia and produced less Nitrates, while the applications incorporated into the soils volatilized less Ammonia and produced more Nitrares.

Table 15 -	Amounts	cf Anac	nia Volati	lized, Fx	prossed us c	. 3.
cf .1N (NH4	)2304, 3	and Nitr	ates Frod	uced. "c	x and Miami	
			5011S.			
Treat.	2 Days	5 Days	7 Days	9 days	11 Days	
Fox Scil						
Check	0.00	0.00	0.00	0.00	0.00	
1333¥ urca Top Dress.	0.32	0.14	0.46	0.34	0.36	
1333∦ urea Mixod in.	6.00	0.10	0.12	0.38	0.00	
Hiami Scil						
Check.	0.00	0.00	0.00	$\Omega_{\bullet} \cup \mathbb{Q}$	0.00	
1333¥ urea. Top Dress.	0.00	0.0.	0.10	0.00	. 0. 26	
1333# urea Nixed in.	0.00	0.00	0.10	0.02	0.00	
		_			NU3 prod.	
	14	Days	16 Days	Total	5. F. m.	
Fcx Soil						
Check.	0.	. 00	0.00	0.00	16 <b>.</b> 3	
1333 # urea Top Dress.	0,	32	0.20	2.14	trace	
1333 # uroa Mixed in.	0.	02	0.00	0.62	6n. 7	
Wiami Soil						
Sheck.	0.	, 00	0.00	0.00	32.0	
1333% urea Top Press.	0.	22	0.00	0.62	30.8	
1333# urca Mixed in.	0.	. 00	0.00	6.17	88.9	

Conclusions - Series 3

No definite conclusions can be drawn from the volatilization work, owing to discrepencies and small differences, but the following indications are given:

1- Top dressing with large applications of urea may cause a loss of Annonia by volatilization, if conditions are damp. The loss will probably hot be very great. Attention is called to the fact that the conditions in this series of experiments are not really comparable to a top dressing in the field. They are similar only in that the material is on top of the soil in both cases. In the field the surface of the soil is usually such that the urea would not be acted on much by the organisms, owing to the lack of moisture and sterilizing action of the sun's rays. In this series the surface of the soil was moist and in the dark, so that bacterial action could take place there. In the field, the urea would probably not be broken down until it was washed into the soil, so it is thought that there is not much danger of an appreciable loss of Ammonia from surface applications.

2- The urea in the scil may volatilize a little Ammonia, but the loss will not be much, if any, according to the results secured here.

SEFIES 4

## Residual Fffects of Applications of Urea, and of Leaching on the Reaction of Fox and kiami Soils.

The last series of experiments conducted was an attempt to study the residual effects on the soil reaction of the application of urea. More this purpose, Mox Sandy Lean and Miami Silt Leam soils, before described, which had been treated with various amounts of urea, were leached several times with distilled water and the reaction or pH istormined.

The soils were the same as these used in the second series of experiments on the nitrification and effects of urea in the soil. They had been running three months when this work was done on them. 20 grams of any soil, or its equivalent, were weighed out and spread over a filter paper in a ten centimeter Euchner funnel. The soil was then washed four times with distilled water. The first washing was 50 c.c., the second was 150 c.c., the third was 50 c.c., and the last was 50 c.c. Each leachate was saved and a sample of the soil taken after each washing. The pH value was then determined by the Quinhydrone electrode on each of the solutions and soil samples, as well as on the original soil. The washed soils were then placed in Erlenmyer flasks and kept for ten days, after which time the the pH values were again determined. The moisture during this ten days was slightly above optimum in the soils, but well below saturation. The work was done with duplicate jars, and the data are presented in Tables 16 and 17, the figures being the everages of the duplicates.

Locking at the data for both soils, it will be seen that each washing tends to make the soil and the extract obtained from the soil less acid. This would indicate that the material causing the acidity is leachable. The first 50 c.c. of leaching usually removes more of the acid components than the latter leachings, as measured by means of the increase in pH over that of the soil before leaching. The second leaching of 150 c.c. usually increases the the pH to some extent, but the two additional leachings of 50 c.c. each do not change the pH of the soil very much. There is usually a tendency for the soil to become higher in pH in the last two leachings, but the differences are, in most gases, within the experimental error.

Comparing the pH values of the Miami soil after the last loaching (Table 17), it will be seen that the intermodiate treatments with usea loft the soil about neutral. The highest and lowest treatments and the check soil were left slightly acid. The lowering of the pH of the check soil by the last losehing is possibly due to an error in sampling. This might easily occur then it is considered that the water may not go through all of the soil in the same amount, thus not leaching all of the soil in the same amount. However, in an attempt to secure as representative a sample as possible, the sample for the pH reading Was taken from several places on the paper.

In the case of the Fox soil, the pH values of all of the soils after leaching were about the same, although there was a tendency for the heavily treated soils to be slightly more acid than the other treatments. The Fox soils did not become neutral neutral as did many of the Miami soils after leaching (Table 18). This may be due to the greater initial acidity of the Fox soils, although the pH values of the soils do not increase very much in the last two

Table	10 -	ĘΗ	Values	cf	Sci	.ls	and	Let	achir	gs.	Fcx	Soil.
Treats	ent	Cri Sci	ginal 1	1s Tasi	t. h.	2nd Was	h.	3rc Waa	i. sh.	4th Tes	h.	Week Lat Later
Gheck. Scil Extrac	et	5.	59	5.8 6.	85 10	5. 6.	98 31	6. 6.	03 46	6. 6.	11 53	6.14
66 ∦ Zoil Extrac	urea et	5.	52	5.9 6.	95 15	6. 6.	02 29	6. 6.	19 43	6. 6.	16 41	6.14
166 % Scil Extrac	urea et	5.	33	5.) 6.(	85) 07	5. ő.	61 23	5. 6.	99 , 41	6. 6.	14 67	6.09
233 ¥ Scil Extrac	urea et	J.	25	5.' 6.:	71 2 <b>7</b>	б. 6.	03 22	6. 6.	<b>1</b> 2 53	6. 6.	12 73	6.09
666 * Soil Extrac	urea et	4.	83	5. 5.	31 86	อ. ห.	68 02	5. 6.	.78 19	5. 6.	92 22	5, 51
1333# Scil Extrac	uroa et	4.	58	5.( 5.(	0 <b>1</b> 83	5. 6.	68 00	5. 6.	66 14	5. 6.	79 17	5, 27
Table	17 -	pH \	aluos	cf .	Scil	.3 3	nd I	eac	ehing	js.	Miani	Scil.
Check Soll Extrac	et	E.	74	5. 5.	99 88	6. 6.	70 33	6. 6.	80 37	б. б.	48 56	6.77
83 Soil <sup>#</sup> Extrac	urea et	5.	67	6. 3.	29 2 <b>1</b>	б. Б.	อีก 19	6. 6.	<b>44</b> 24	6. 6.	58 31	7.04
163 ¥ Scil Extrac	urea et	6.	22	6. ( 6. )	62 26	6. 6.	91 67	7. 6.	. <b>1</b> 8 . 74	7. 6.	27 79	7.15
333 ∮ Soil Extrac	urea et	ô.	24	6. ( 6. (	54 02	7. 6.	01 64	ö. 6.	88 76	7. ć.	07 65]	6, 96
666 # Scil Extrac	urea et	6.	09	6. ; 6. ;	50 26	6. 6.	93 48	6. 6.	94 72	ö. 6.	93 9 <b>1</b>	6.91
1333¥ Soil Extrac	urea et	ē.	51	5.8 5.8	92 93	ต์. ชั.	45 00	б. Б.	55 14	6. 6.	64 17	6, 37

		•	-	•			•
		-					
		_				•	
	.`			•			
				•			
		,					
	-			•			
			•	•			
		•					
				•			
•		·					
			•	• • •			
					•		
				•	-	、	
	•	•	• •		•		
					•		
					•		
					•		
		•	•				
		•	•		•		
					٢		

· · · ·

leachings. This would indicate that an equilibrium is being approached, and the neutral point may not be reached by the Fox soils even with much greater washings. The neuvier treatments with unce caused the soil to have a much lower pH value before leaching began. After the soils were leached, this difference was reduced, showing that washing tended to make the differently treated soils more alike.

The above results from this experiment agree well with some data recently published by Crowtner (14). He also found that leaching soils with water tended to reduce their Hydrogen-ion concentration, and that the amount of reduction was increased by increasing the amount of washing. Even with a soil that was alkaline to begin with, washing increased the alkalinity. He states:

"The increase in pH value of the soil after extraction is not the result of the removal of a definite amount of water soluble acid, because no amount of this order can be determined by titration of the percolate, and the change due to the removal of a certain amount of the soluble material is greater than that due to the addition of an equal amount to the soil."

Considering the pH values of the extracts from the soils in Tables 16 and 17, one thing is very noticable, namely, the extract from the Miami soil is nearly always more acid than the soil is after the extraction is made. The opposite is true in the case of the Fox soil, where the extract is nearly always less acid than the soil after being extracted. No wholly satisfactory explanation can be offered for this, but a possible reason for these apparently contradictory results is offered.

The pH values of the extracts from the two soils do not vary nearly so much as do the pH values of the two soils themselves. It has been shown by Bradfield (8,9) and MeCool and Wheeting (29) that colloids extracted from soils are acid. It is quite probable that many colloids were leached out of the soils in securing the extracts, as the latter were cloudy. These colloids may be largely respensible for the reaction of the extract, and thus account for both of the soils producing extracts that are acid. The results of WeCcol and Wheeting (29) show that the pH of the colloids from the surface horizon is about the same in the three soils they studied. If it is true that the colloids in the surface horizon of soils in the same locality do not differ a great deal from each other, this might account for the similarity in the pH values of the extracts from the two soils, even the soils varied somewhat in reaction. The surface horizon was used in these studies.

The facts that the colloids are acid and that they are probably removed to some extent from the soil by leaching, led to the idea that this may account for the rise in pH of the soil when leached with water. It would soom reasonable that the removing of an acid constituent from the scil would be the cause of the lowering of its acidity. Melocl and Wheeting (28,29, unpub. data) have found contradictory results on this point. At one time they found that the removal of the colloids lowered the acidity of the soil. However, in some later work they found that the removal of the colloids sometimes left the soil more acid, even though the colloids were more acid than the scil. This is very difficult to explain at present. Owing to these contradictory results, a definite statement cannot be maie that the removal of the colloids is what caused the soil to become less acid on being leached. However, there are indications that this may be part of the cause.

Examining new the figures secured by determining the pH of the soils after being extracted with water and left to stand ten days (last column Tables 15 and 17), it will be seen that , in general, no great changes have taken place. The results are more or less irregular and in the Miami 83 # treatment an exception is noted. Here the pH has jumped a great deal and is up with the other treatments. The most heavily treated soil became slightly more acid on standing. Here the acid producing factors apparently are still at work after the soil has been leached. In the case of the soils in which the  $r^{H}$  did not change, the acid producing factors were either removed or rendered inactive for at least ton days by the leaching.

Conclusions - Series 4

The following general conclusions may be arawn from this series of experiments:

1- Leaching a soil with water tends to make it less acid, possibly due in part to the removal of the acid soil colloids.

2- The first leachings are more acid than the latter leachings.

3- After being leached, the soils tended to stay the same, except in the case of the heaviest treatments, where they became more acid on standing.

#### GENERAL DISCUSSION

The large amounts of Ammonia formed in the first Series, without the subsequent formation of nitrates shows that ammonification stulies are not necessarily a true indication of the availability of the materials to the plants. assuming that they use nitrates as the main source of Nitregen. It has been assumed by some that nitrification follows along after attribution at about the same rate, and that measuring one will also neasure the other. This may usually be the case, but it has been shown above that nitrification does not always necessarily follow after anmonification has taken place. Lipman and Burgess (22) have also brought this fact out, where they found that high nitrification was not necessarily correlated with high ammonification, working with several organic organic Nitrogen carriers in several soils. As will be seen by comparing Series 1 and 2, the conditions unlor which the tests are conducted would have some influence on the results obtained. The large applications of urea did not tomom nitrates after fadming Ammonia, while the smaller applications all friched nitrates.

The applications of urea as made in the first series could not be made in the field to a soil of this texture. since much of its nitrogen would be lost as ammonia. However, there are other factors which might tend to limit its use before amounts comparable to these would be used. The law of diminishing returns would probably be one of the first factors limiting its use, even though the price of t the material was comparatively low. Another factor is the question of whether rlants would live in a soil solution as concentrated as that of these experiments. This exceriment does serve to show that there is a biological limit above which uses cannot be applied with the expectation cf securing nitrates. It would be interesting to see whether the limiting concentrations for plant growth would be reached before the limit for complete biological activity would be reached.

When added in amounts comparable to and slightly in excess of amounts of nitrogenous fertilizers now used, urea proved to be entirely satisfactory as a nitrogen carrier. judging by the nitrates produced and considering only that phase of the requirements of a good nitrogen carrier. Since the smaller applications of the urea were apparently completely nitrified, and the larger ones were not, it would appear as if the quickost and greatest returns per dollar scent on the material would be secured from smaller applications at one time. This does not necessarily mean that the material unnitrified during the course of this experiment will not later become available or nitrified. The very rapid nitrification of urea should be considered when applying it to crops such as the grains, where an excess of nitrates early in the growing period may weaken the rlant.

A general characteristic of all of the tables is that the lighter applications reacted more quickly in the soil than did the heavier applications. The large amounts of material added second to be more or loss of a shock to the soil, the effects of which had to be overcome before the advantageous results of the heavier treatments would be noticable. After the shock was over\_come, the more heavily treated soils would usually forge ahead of the soils with smaller applications, although as a rule not in proportion to the extra amounts added. In some cases, where the applications were very heavy, these offects would nover be wholly overcome.

## SUMLARY

A Colona Hine Sand was treated with urba in amounts ranging from .5% to 5% the weight of the soil. These were kept at optimum moisture and frequently aerated. From time to time the nitrates, Hydrogen-ion concentration, and total concentration of the soil extract were determined, on the various treated and untreated soils. The results showed that urea was ammonified very quickly, but was not nitrified. In the 5% treatment, very little ammonification apparently took place. With the exception of the check and 5% treated soils, ammonification was so great that ammonia was given off in large quantities from the soils.

The soil was made alkaline by the addition of the urea and subsequent formation of ammonia. A period of maximum alkalinity was reached, after which it decreased. The concontration of the soil solution was increased by the treatments according to both the size of the treatment and the length of the experiment. A period of maximum concentration was reached, after which it declined. There was some correlation between the time of maximum alkalinity and concontration, indicating that the increased concentration of the soil solution was probably due in part at least to the ammonia formed.

A Fox Fine Sanly Loam and a Miami Silt Loam were run in the same way, the treatments ranging from no urea added to 1333 pounds per acre six inches of soil. The nitrates increased in every treatment the longer the experiment ran. The larger the amount of urea added to the soil, the more hitrates there were formed, but the increased nitrates were not in proportion to the extra amounts of urea added. In only the two smallest additions was there an indication that all the urea added was nitrified in the time of the experiment. The acidity of the soil increased more or less with the time of the experiment and the amount of urea added. This means that the more nitrates there were produced the more the acidity increased.

The concentration of the soil solution increased with the addition of urea and during the time of the experiment. This means that the more hitrates there were produced, the more concentrated the solution became. However, the increased componentration was not all due to the extra hitrates produced, in and of themselves, although they possibly indirectly exuspidit.

The Goloma, Fox and Miami soils wore treated with urea as a top dressing of 1333 pounds per acre, also with urea mixed in the soil at rates up to 1333 pounds per acre six incles. They were aspirated from time to time and any ammonis given off was determined. The results were Unconclusive but indicate that urea mixed with the soil in the amounts used did not cause ammonia to be lost by volatilization in any appreciable amounts. The top dressings of the Fox and Coloma soils lost ammonia, while that of the Miami soil lost little if any. The acre mitrates there were produced, the less ammonia there was volatilized.

Fox and Wiami soils that had urea added in amounts ranging from none to 1333 pounds per acre six inches, and kept three menths, were leached with water. Four leachings were made and the pH values of the extracts as well as of the soils before and after each extraction were determined. The washed soils were wept for ten days after which the pH was again determined.

The results show that the soils became less acid with each leaching, although the greatest changes as a rule were brought about by the first two leachings. With the exception of the heaviest treatments, washing the soils caused the different treatments in each soil to become about alike in pH. The lowered acidity of the soils from washing is thought to be partly due to the washing out of some of the acid colloids from the soil. The extracts from the Miami soil were usually more acid than the extracted soils, the opposite being the case with the Fox soil. Thus the extracts from the two soils were closer in pH than were the soils themselves. This is thought possibly to be due to the colleils in the extracts from the soils being nearly alive. The extracts from the soils being nearly alive. The extracts from the soils became less acid with each leaching. After standing for ten days, the extracted soils did not change much in pH, except that the most heavily treated soils became more acid.

## LITERATURE CITED

- Allison, F. E., Braham, J. M., and Memartrey, J. C.
   Field experiments with nitrogenous fertilizers. U.
   B. Dept. Agr. Bul. 1180. (Jan. 22, 1924)
- 2- Allison, F. E., Vliet, E.B., Skinner, J. J., and Boin, F. Greenhouse experiments with atmospheric nitrogen fertilizers and related compounds. Jour. Agr. Res. v. 20, no.9, pp.971-976. (May 31, 1924)
- 3- Arrhenius, U. The potential acidity of soils. Soil Sci. v.14, pp. 223. (1922)
- 4- Biilmann, E.

On the measurement of hydrogen-ion concentrations in soil by means of the quinhydrono electrode. Jour. Agr. Sci. v.14, no.2, pp.232-239. (1924)

5- Bokorny, T.

Urea and some other sources of nitrogen for green plants. Fflueger's Arch. Physicl. v.172, pp.468-498. (1918) in Exp. Sta. Ros. v.45. p.519.

6- Bouyoucos, G. J., and McCool, M. M. The freezing point method as a new means of measuring the concentration of the soil solution directly in the soil. Michigan Tech. Bul. 24. (1915)

7- Bouyouces, G. J., and MeCcol, M. M. Further studies of the freezing point bowering of

scils. Michigan Tech. Bul. 31. (1916) 8- Bradfield. R. The nature of the acidity of the colloidal clay of acid scils. Jour. Mmer. Chem. Soc. v.45, no.11, p. 2669. (1923) 9- Bradfield. R. The chemical nature of a colloidal clay. Missouri Res. Bul. 60. (1923) 10- Christensen, H. R. On the influence of humus material in urea decomposition. Jentbl. Baxt.2 Abt.27, no.13-16, pp.336-362. (1910) in Exp. Sta. Rec. v.23, r.722. 11- Christensen, H. R. On the influence of humus substances on the decomposition of urea into ammonia. Tidschr. Landbr. Planteavl.17, no.1, pp.79-109. (1910) in Exp. Sta. Rec. v.24, p.523. 12- Coleman. L. C. Investigations on nitrification. Contbl. Bakt.2 Abt.20, no.12-14. (1908) in Exp. Sta. Rec. v.20. c.518. 13- Cowie. G. A. Decomposition of Cyanamide and dieyanodiamide in the soil. Jour. Agr. Sci. v.9, part 2, p.113. (1919) 14- Crowther. E. M. Studies of soil reaction III, The determination of the hydrogen-ich concentration of soil suspensions by means of the hydrogen electrode. Jour. Agr. Sei. v.15, part 2, pp.201-221. (April, 1925) 15- Gerlach, The action of new nitrogenous fertilizers. Mitt. Deut. Landw. Gesell.31, no.7, pp.90-93. (1916) in Mxp. Sta. Rec. v.35, p.325. 16- van Harreveld, C. H. Absorption and leaching of the nitrogen when urea and ammonium chloride are applied as fortilizors.

Lako, Archiv, vccr de Suikerindustrie in Mederlandisch India, no.8 Soerabaja. (1924) in Int. Rev. cf Sei. and Prac. Agr. ns. v.2, nc.4, p.857. (1925) 17- Haselhoff, E. Experiments with nitrogeneus fortilizers. Landw. Vers. Stat. v.84, nc.1-2. (1914) in Exp. Sta. Rec. v.31, p.518. 18- Kappen, H. Fertilizer experiments with transformation products of line-nitrogen. Landw. Vers. Stat. v.86, no,1-2. (1915). in Mxr. Sta. Rec. v.34, p.25. 19- von Knieriern, J. Fertilizer experiments with different new nitrogencus fertilizers. Witt. Deut. Landw. Gesell. v.37, nc.43, p.654. (1922). in Exp. Sta. Rec. v.48, p. 721. 20- Krase, N. W., and Gaddy, V. L. Synthesis of urea from ammonia and carbon dioxile. Jour. Indus. and Eng. Chem. v.14, nc.7, pp.611-616. (1322)21- Lemmernann.O. Investigations on different fertilization questions. Arb. Deut. Laniw. Jesell. nc.297. (1919) in Exr: Sta. Rec. v. 44. p. 317. 22- Ligman, C. B., and Burgess, P. S. Ammenifiability versus nitrifiability as a test for the relative availability of nitrogenous fertilizers. Soil Sei. v.3, p.63. (1912). 23- Ligman, J. G., and McLean, H. C. The agricultural value of some of the newer nitrogencus fortilizors. Amer. Fertilizer, v.62, no.4, pp. 23-28. (Feb. 21, 1923) 24- Ligman, J. G., et al. Report of the soil chemist and bacteriologist. New Jersey Sta. kept. 1908, pp.91-147. 25- Littauer, F.

-46-

Decomposition of urea in soil. Zeitschr. Fflanzenornachr. u. Duengang. v.3, nc.3, Wiss. pp.165-179. (1924) in Exp. Sta. Bee. v.51, r.818. 26- Loehnis. F. Contribution to the knowledge of mitrogen basteria. Centbl. Bakt.2 Abt.14, no.18-20, pp.582-604. (1905) in Exp. Sta. Rec. v.17, p.447. 27- McCcol. M. M., and Mheeting, L. C. Movement of soluble salts through soils. Jour. Agr. Res. v.11. nc.11. rc.531-547. (Dec. 10,1917) 28- MaCool M. M., and Wheeting, L. C. The influence of the removal of colloids on some soil properties. Soil Sci. v.18, no.2, pp.99-102. (1924) 29- McCocl. M. M., and Wheeting, L.C. Studies on the colloidal material of certain soil profiles in Michigan. Rept. Fifth Ann. Neet. Amer. Scil Survey Assoc. Bul.d, v.2, pp.122-126. (1924) 30- Meduinn, A. F. The action of dicyandiamid and guanyl prea sulphate cn plant growth. Scil Ssi. v.17, no.6, pp.487-500. (June, 1924) 31- Marshall, C. E. Microbiology. 2nd. ed. rov.& enl. F. Blakiston's Son & Bo. Philadelphia. (1917) 32- Millar, C. E. Relation between biological activities in the presonce of various salts and the concentration of the scil solution in different classes of soil. Jour. Agr. Ros. v.13, nc.4, rp.213-223. (Apr. 22, 1918) 33- Eitschorlich, E. A., von Sauchen, S., and Iffland, F. Experiments with various nitropenous fertilizers. Jour. Landw. 66, no.3, pp.187-198. (1918) in Exp. Sta. Rec. v. 41, L.22. 34- Popp, M. Fot fertilizer experiments with new nitrogenous fertilizers. Mitt. Deut. Lanix. Gesell. v.31, nc.4,

.

· . . . . . . . .

· · · · · · ·

· · · · · ·

pp.54-57. (1916) in Exp. Sta. Rec. v.35, p.518. 35- Rahn. U. The bacterial activity in soil as a function of grain size and moisture content. Michigan Tech. Bul. 16. (1,12)Br-Rest, C. U., and dieger, E. A. Effect of drying and storage upon the hydrogen-ion concentration of soil samples. Soil Sci. v.16, no.2, pp.121-126. (Aug., 1923) 37- Senneiderini. Field experiments on the action of new forms of nitrojen. Mitt. Deut. Lanew. Gesell. v. 31. no. 2. rr. 16-20. (1916) in Exp. Sta. Rpc. v.35. p.427. 38- Schneidewind. Results of further nitrogen experiments. Landw. Wehnschs. Saensen. v.20, nc.16, pp.153-155. (1918) in Exp. Sta. Sec. v. 42, p. 624. 29- Schreiner, C., and Failyer, G. H. Sclerimetric, turbidity, and titration methods asod in soil invostigations. U. S. Bar. Soils Bul.31 (1906). 40- Sturway, C. H. Studies on active bases and excess acids in mineral scils.. Michigan Tech. Bul. 57. (1923) 41- Spurway, C. H. Soiltex method for soil reaction. Coment, Mill and Quarry, June 5, 1923. 42- Stutzer, A., et al. Pive years' fertilizer experiments in East Prussia. Arb. Deut. Landw. Gesell. no.258. (1914) in Exp. Sta. Res. v.31, p.821. 43- Tacke, B. The action of certain now nitrogenous fertilizers on sandy and neer seils. Mitt. Ver. Peerd. Meerkultur Deut. Reiche. v.32, nc.23, p.411 (1914) inn Exp. Sta. Rec. v.33, p.25.

44- Werner, E. A.

The Chemistry of urea. Monobiographs on biochemistry. Longmans, Green, & Go. London. (1923)

45- Whoeting, L. C.

Some physical and chemical properties of several soil profiles. Michigan Tech. Bul.62. (1924)

46- Wheeting, L. C.

Certain relationships between added salts and the moisture of scils. Soil Sci. v.12, nc.4, pp.287-299. (Apr., 1925)

# RECUL USE DILL.

2

\_\_\_\_\_

