

AMMONIA UTILIZATION AND SYNTHESIS

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History and Occurrence of Ammonia

Ammonia is formed when animal matter decays, and since it has a characteristic odor it has been known from the earliest times. Ammonium chloride--the compound formed from ammonia and hydrochloric acid--was known to Egyptians. Its ancient name, Sal ammoniac, from which the word ammonia is derived, is said to have been given to the salt in honor of the Egyptian sun god Ammon. In the middle ages, ammonia gas was made by distilling the horns of harts and was supposed to be very valuable as a medicinal agent. It was called spirits of hartshorn, a name by which it was called until very recently when it was used in medicine. The alchemists obtained ammonium chloride by evaporating a mixture of urine and salt to dryness and heating to a high temperature.

Priestley, in 1774, first isolated ammonia as a gas as the result of heating ammonium chloride with lime. He collected the gas over mercury. Many of Priestley's most important discoveries were due to the fact that he used mercury in his pneumatic system instead of water. He isolated it in this way for the first time. Three industrial processes have been developed during the past 165 years for fixation of atmospheric nitrogen. These three are (1) the electric arc process for the production of nitric acid, (2) the process for manufacturing calcium cyanamide and (3) the process for reacting H with atmospheric N to form ammonia.

The cyanamide process for N fixation dates back to 1895-1898 when the Germans, Frank and Caro patented the reaction

between calcium carbide and N to form calcium cyanamid. Synthesizing ammonia by the reaction between H and atmospheric N is the basis for the nitrogen fertilizer industry today. Beginning in 1884 Le Chatlier stated his principle of mobile equilibrium which helped clarify the theoretical basis for ammonia synthesis. Between 1904 and 1908 the German chemist Fritz Haber and others produced nitrogen through a wide range of temperature and pressure. A major obstacle was overcome when Alwin Mittash of Bodische Anilin and Soda Fabrik A-G developed an iron-base catalyst for promoting the reaction between H and N at a temperature below 1,000°F. Until recent years coal or coke was the major raw material used to produce the H required for ammonia synthesis. Since 1945 all new ammonia plants use natural gas, oil or naphtha.

Ammonia

Formula NH_3	Boiling point -33.4°C
Weight of 1 l. at 0°C and 760 mm	Melting point -77.7°C
Density of liquid at -34.4°C	Solubility in water at 0°C and 760 mm 89.9g in 100 cc
per cubic centimeter	Critical temperature 132.4°C
Density of 28 per cent solution at 15°C 0.90	Critical pressure 11.5 atm
Density of 6 per cent solution at 15°C 0.94	Vapor pressure of liquid at 25°C 9.9 atm
	Heat of vaporization 327.1 Cal per gm

The chemistry of ammonia is of the greatest importance because of its significance in the growth and decay of living things. The farmer fertilizes his fields with ammonia salts, and later when he eats the grain or vegetables he has grown, he

obtains the nitrogenous material which through digestion and assimilation becomes a part of his flesh. Since the supply of ammonia furnished by nature is limited, the chemist has devised ways of converting the nitrogen of the air into this important product, he has triumphed over what appeared at first to be insurmountable difficulties in his endeavor to make out of the inexhaustible supply of air and water a substance that can be used as a plant food when the supply of natural occurring nitrogen fertilizers is exhausted.

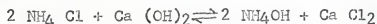
Since ammonia is produced as the result of the decay of refuse organic matter, its presence in undue amounts in natural water is evidence of contamination. As a consequence, in examining a water supply to be used for drinking purposes, the amount of ammonia present is always determined; the results obtained guide the chemist in his decision as to its potability and may lead to the discovery of sources of contamination which can be removed.

The physics of ammonia serves mankind in another important way. The gas can be readily liquefied through pressure alone; the resulting liquid, boiling at a very low temperature, absorbs a large amount of heat when it passes into the gas ~~and~~ state. Its latent heat of vaporization is very high. These characteristics have been utilized in making machines for the production of low temperature. By the use of ammonia we can make ice anywhere in unlimited quantity or keep a warehouse cold for the storage of perishable food materials. This use of ammonia has had a marked effect on the health of people and has revolutionized the economics

of food production. Refrigerator cars and cold storage warehouses have become a necessity in modern civilization with the growth of large cities.

Preparation of Ammonia

The commercial source of ammonia was formerly ammonium salts, and the gas was prepared from these by the action of a base; ammonium chloride and calcium hydroxide are commonly used in the laboratory. As the result of this reaction, which is one of double decomposition, ammonium hydroxide is first formed and then decomposes into ammonia and water. The equations for the reaction are as follows:



The reaction is brought about by the use of solid substances which contain only a trace of water, because ammonia is very soluble in water. The gas is collected in the laboratory by downward displacement of air.

Synthetic Ammonia

It has been known for many years that ammonia is formed when electric sparks are passed through a mixture of nitrogen and H. The behavior of nitrogen with hydrogen under these circumstances is quite different from that of oxygen. A single spark is all that is required to cause the union of the entire amount of oxygen, provided enough hydrogen is present, the reaction propagates itself through the entire mass. We could synthesize water from oxygen

and hydrogen in any desired quantity if it were necessary. With nitrogen, however, only the gases in the immediate vicinity of the flame unite, and the mixture has to be sparked for a long time to get appreciable quantities of ammonia.

Why Ammonia Soaks up Heat

These questions and answers give a clear picture of what happens to liquid refrigerant and how it does its work while being changed from one pressure to another by a compressor.

The kinds and meanings of refrigeration in a few simple explanations.

1--The term, one ton of refrigeration

The American Society of Refrigerating Engineers defines the standard commercial "ton" of refrigeration as the transfer of 200 BTU per min., or 12,000 BTU per hour. It is the basis of all refrigeration calculations, for cold storage, air conditioning, ice making, etc.

2--What happens to ammonia as it passes through an expansion valve?

When ammonia passes through an expansion valve, it expands because it passes from a higher to a lower pressure. As pressure drops, boiling temperature falls, and some or all of the ammonia, depending on conditions, changes from liquid to gas.

A drum of ammonia at 70°F shows a pressure of 114 psi .9°F if it has previously been stored in a cooler place; boiling takes place until it reaches 70°F and a pressure of 114 psi.

3--What is the specific heat of ammonia? And how does such heat affect the use of this liquid as a refrigerant.

Specific heat is actually a ratio, but the term is used to indicate the quantity of heat needed to raise one pound of a substance one °F, or to lower one pound the same amount. Specific heat varies with temperature.

Generally speaking, when the ratio between latent heat and specific heat of the liquid is large, it is an ideal refrigerant.

Liquid ammonia is in this class, its specific heat is 1.129 at 70°F, and that of its gas at constant pressure corresponds to 86°F, is 0.4011. Ammonia refrigerant serves to convey heat away from some substances that we wish to cool or freeze. When liquid ammonia expands from a higher to a lower pressure in an evaporator coil, we have to remove some of the heat content.

4--What is the meaning of the term latent heat when applied to ammonia?

Latent heat is the number of BTU that must be applied to and absorbed by ammonia to change it from liquid to gas. If a quantity of liquid ammonia is just at its boiling point (-28°F at atmospheric pressure), each pound must absorb 589.3 BTU before it will change to a gas. This quantity is not a fixed quantity, but varies with pressure and temperature.

5--What is sensible heat when used in speaking of ammonia?

Sensible heat, applied to ammonia shows up as temperature registered on the ordinary thermometer. The term, used without considering other factors, simply indicates whether ammonia is hot or cold--as we think of these terms in everyday life. It is not a measure of total heat or BTU for ammonia.

6--What is pressure-temperature relationship of ammonia in a closed cylinder?

Pressure of ammonia in a closed cylinder increases with its temperature--slowly at low temperatures, but rapidly at high temperature.

7--Critical temperature

Critical temperature is 280°F for ammonia. At this temperature latent heat becomes zero, and the heat content of the liquid and the vapor is the same.

Assimilation of Ammonia

For most plants ammonia and nitrates in the soil serve as sources of nitrogen; only a few are able to assimilate atmospheric nitrogen.

One of the source of the soil ammonia is the decomposition of animal excreta and plant remains by micro-organisms, a process known as ammonification. Ammonifying organisms contain active enzymes which rapidly break down proteins, amino acids and other nitrogen-containing substances. The first step in the degradation of proteins is their hydrolysis to amino acids by proteases followed by deamination of the amino acids to give ammonia.

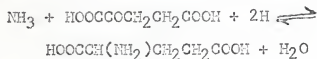
Amino acids may also be decarboxylated under anarobic conditions to give an amine and carbon dioxide. The amine may be further broken down to carbon dioxide and ammonia.

Ammonia in the soil is either absorbed by plant roots or oxidized to nitrites and nitrates by nitrifying bacteria. Future

studies on the enzyme system which participate in the biological fixation of nitrogen will make it possible not only to understand the nature of this extremely important process, but will also indicate new ways of improving the industrial synthesis of ammonia. At present this process requires high temperature and pressure, but in the cells of nitrogen-fixing micro-organisms it occurs very efficiently under ordinary conditions of temperature and pressure.

Winogradskii Hypothesis and Nitrogen Fixation by Nodule Bacteria

The chemistry of nitrogen fixation by nodule bacteria is not completely known. In the hypothesis put forward by Winogradskii it is assumed that ammonia is the primary product and that it reacts with glutaric acid to form glutamic acid.



The glutamic acid then combines with another molecule of ammonia to form glutamine. The pattern of nitrogen fixation is probably the same in both freeliving organisms and nodule bacteria.

Conversion of Ammonia into Amino Acids

Ammonia reacts with keto-acids to form amino acids. Kostychev considered that this was the principle way in which amino acids were synthesized in the plant. In the presence of alanine dehydrogenase pyruvic acids react with ammonia to give alanine.



The reaction proceeds in two stages. Ammonia and the keto acid react to give an amino acid.



The amino acid is subsequently reduced by



Enzyme preparations (glutamate dehydrogenase) have been obtained from yeasts, bacteria and higher plants which catalyse the formation of glutamic acid from

-keto glutaric acid

Ammonia (acid) plants

Enzymes occur in higher plants which catalyse the deamination of phenylalanine and tyrosine to give ammonia and the corresponding unsaturated aromatic acids. Barley, lucerne, peas and rice contain a phenylalanine deaminase that converts phenylalanine into ammonia and cinamic acid.

Barley also contains an enzyme that breaks down tyrosine into P-coumaric acid and ammonia.

What happens to the ammonia formed in deamination?

Free ammonia is usually present in higher plants in only trace amounts. At higher concentrations it is toxic to living tissues. If there is an adequate carbohydrate reserve, ammonia will be used to form amino acids from keto acids.

Ammonium Carbamate

Large amounts of ammonia are formed in the soil by the breakdown of urea from farmyard manure and sewage, because of the activities of urobacteria. Ammonium carbonate may be formed in addition to ammonia.

Ammonia Blood Levels

Free ammonia is extremely toxic and never accumulates in living cells or surrounding media. Only traces of ammonia (0.1 to 0.2 mg per 100 ml) are found in human blood.

Ammonia is excreted as such only when there is an abundance of water for its rapid removal. This excretion takes place in the marine invertebrates and in all fresh water animals, whether vertebrate or invertebrate.

Energetics of Ammonia Formation

Most deamination reactions produce a certain amount of heat, but there is no gain in ATP. In poikilotherms the production of heat may be thought of as a useless by-product of metabolism. Useful energy appears in other forms, particularly in the pyrophosphate bond of ATP.

Ammonia Metabolism

The production of deaminated carbon residues for the citric acid cycle was discussed in the previous section. This is a small part of the story of nitrogen metabolism. There are several other ways in which the NH_2 group may be moved about and, although sometimes excreted, they more frequently enter an extremely labile

nitrogen pool and become part of the synthetic and regulatory machinery.

Ammonia Poisoning

Sulfate of ammonia is an excellent fertilizer for many crops, but fumes of free ammonia are poisonous even at very low concentrations. In hothouses ammonia may sometimes be released from fresh manure, and in such cases the fumes may cause a bleaching of the edges in the lower leaves of cucumber plants. Damage may also be caused to seedlings, dark green or blackish leaf spots may appear on tomato plants and the leaf stalks of begonias may become soft and easily snapped. Contamination of CO₂ gas with a small amount of free ammonia may lead to damaged foliage when cylinders of carbon dioxide are used in hothouses. White variegation of the leaves may appear in tomato seedlings that have received an overdose of cheshnut compound.

Extent of damage

The extent of the damage depends on various internal factors; it is worse in bright light, less severe in shaded plants and at night. Well-nourished plants growing well suffer less than weak ones. In all cases the green leaf tissue is most affected and the flowers the least. Susceptibility to damage by ammonia fumes also depends partly on internal factors. Plants with weak acid cell sap (p_H over 5) have their growth retarded by one part of ammonia in 7-8,000 parts of air, whereas plants with very acid sap (p_H under 5) are uninjured by such small quantities.

When ammonia is used in a freezing plant, leakage of fumes may damage fruit and onion in cold storage.

Ammonia Scorching

Ammonia fumes from fresh manure may scorch leaves, causing white to brown withered spots to appear, especially along the edges of the lower leaves. These become dome-shaped, for a leaf surface continues to grow while the scorched margins do not. Scorching of this kind may somewhat check growth but is not particularly harmful when confined to the lowest leaves.

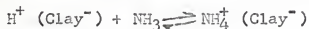
Ammonia Interactions with Soil Minerals

The mechanism of adsorption of ammonia by minerals ranges from chemical reactions which bind the ammonia very strongly to physical adsorption where it is bound very weakly, with a complete gradation of adsorption energies within these extremes. As soon as the pressure of ammonia in the gaseous phase becomes low, the physically adsorbed ammonia will go back into the gaseous form and diffuse through the soil until it can react chemically with a mineral or organic matter surface or is possibly lost to the atmosphere.

Mechanisms of Ammonia Adsorption on Minerals

The ammonium form (NH_4^+) has a positive electrical charge, and is thus attracted by the negative electrical charge of the soil minerals. It enters into ordinary cation exchange reactions in the same manner as metal cations such as Ca, Mg, K, etc.

Formation of the ammonium ion proceeds when ammonia can react with a proton (H^+). Thus an acid soil, or minerals having exchangeable hydrogen ions on the cation exchange complex may provide the necessary protons for ammonium ion formation.



The ammonia may also react with protons arising from hydroxyl groups associated with silicon on the edges of clay minerals or in amorphous material in the soil.



Retention of NH_3 by Soil

Ammonia is retained in the soil by a number of mechanisms, including chemically sorbed or exchangeable ammonium (NH_4^+), fixed NH_4^+ , ammonia (NH_3) that reacts chemically with soil organic matter, and physically sorbed ammonia. The equipment and methodology presented here permit a more realistic evaluation of the total ammonia retention capacity of a soil because all of the various mechanisms of retention are accounted for.

$$\text{NH}_3 \text{ retained by soil} = \text{NH}_3 \text{ applied} - \text{NH}_3 \text{ removed}$$

Results of Laboratory Studies

The ammonia retention capacities of soils have previously been characterized by discrete or fixed numerical values; however, the laboratory studies have revealed that such values may be rather arbitrary unless a suitably long period is allowed for desorption of excess and weakly sorbed ammonia. Ammonia retention by soils appears to be a dynamic characteristic that depends not only on soil properties but also on the experimental conditions used.

It is interesting that more ammonia is ultimately retained by air-dry and oven-dry soils than by the moist systems. The probable explanation here is that water and ammonia molecules compete for the same sorption and reaction sites in soil, particularly when only small amounts of water are present.

Results of Greenhouse Studies

Preliminary greenhouse experiments have shown anhydrous ammonia to be quite comparable to other fertilizers as a source

of nitrogen for corn. However, additional studies are in progress to ensure a thorough evaluation of the agronomic efficiency of anhydrous ammonia.

Soil moisture at the time of anhydrous ammonia injection had little effect on yield of dry matter and nitrogen uptake by corn plants, although a small but consistent increase in yield was observed when high levels of anhydrous ammonia were applied to moist rather than air-dry soils.

Organic Matter Interactions

When ammonia is applied to soil very little movement occurs unless the soil is coarse in texture. Physical and chemical reactions cause part or all of the ammonia to be retained near the point of application. Ammonium ions can also undergo exchange reactions with cations located within the structure of clay minerals. This ammonium cannot be removed by leaching with potassium salt solution and is said to be "fixed". In addition ammonia reacts reversibly with organic matter, in which case stable organic nitrogen complexes are formed which must be decomposed by microorganisms before the nitrogen becomes available to plants.

Reaction of Ammonia with Organic Matter

1--Retention in Exchangeable form

Organic matter treated with anhydrous or aqueous ammonia in a closed system will lose considerable ammonia on evacuation, or through diffusion on exposure to the atmosphere.

Organic matter and organic soils exhibit cation retention capacities which are high in relation to those of mineral soils. Ammonia reacts with carbons, and possibly other acidic groups present in the organic fraction to form salts which might be termed "ammonium humates" in the immediate vicinity of an ammonia injection band.

Extraction of ammonia-treated soils by various solutions has shown that considerable ammonia originally retained against leaching with dilute acid or salt solution can be removed by more prolonged extraction procedures.

Extraction of fixed ammonium from Slaten Featy
muck with HCl Solution

Normality of HCl	Total N	Fixed NH ₃ -N	Total N extracted	Fixed NH ₃ -N extracted
	Ppm	Ppm	%	%
0.1	2,690	205.0	12.1	46.8
1.0	780	47.9	3.5	10.9
2.0	481	18.1	2.2	4.1
3.0	319	6.4	1.4	1.5
6.0	399	4.6	1.8	1.0
Total	4,669	282.0	21.1	64.4

2--Chemical Fixation

The capacity of soil organic matter and related materials to retain ammonia in non exchangeable form has been known for more than 35 years. Mattson and Koulter--Andersson conducted an extensive series of experiments with various forms of litter and humus which established that ammonia fixation involves simultaneous oxidation of the organic material through uptake of atmospheric oxygen, and that the ammoniated complex is very stable toward acids.

Ammonia fixation has been found to be p_H dependent increasing as p_H increases above the neutral point. Injection of ammonia into soil produces an alkaline reaction in the injection zone with the highest p_H along the line of injection and a steep p_H gradient outward from that line.

Factors Affecting Fixation

1-- p_H

Auto-oxidation of organic matter, induced by high p_H , was essential for ammonia fixation.

2--Oxygen

The presence of oxygen is not essential to ammonia fixation. In agricultural practice some degree of autoxidation of soil organic matter occurs when ammonia is applied, whether or not it is essential to fixation.

Effect of Oxygen on Ammonia Fixation by some Phenolic Compounds

Compounds	Fixation without O_2	Fixation with O_2
	moles N/mole	
	0	0
2,6-dimethoxyphenol	0	0
3,5-dihydroxytoluene	0	0.077
hydroquinone	0	0.69
pyrogallol	0	0.79

Application of Ammonia

Six key questions

1--How deep should ammonia be placed into the soil?

The depth that ammonia should be placed in the soil depends on several factors, including the rate of application, spacing of knives, soil moisture, type of soil and the crop being fertilized.

When the soil is in good condition, ammonia can be injected as shallow as three inches without any of the ammonia escaping into the air. It has been proven, however, that an application of from eight to ten inches influences the development of deep roots which are capable of extending further downward to take advantage of sub-soil moisture and plant foods.

With these factors in mind, it is recommended that side-dress ammonia be applied at least six inches deep and up to 10 to 12 inches to obtain the greatest efficiency. It is logical that if high rates of application are made on 40-inches spacing of knives, a deep application must be made so that the ammonia can come in contact with a higher amount of the soil mass for fixation to the clay, organic matter and soil moisture. Deep placement insures that nitrogen is available in the zone where plant roots feed and where soil moisture is available for maximum root growth. If the soil is not in top condition, sealers should be used to prevent ammonia loss.

2--How late in the season can you side-dress?

The choice between early side-dressing and late side-dressing

depends generally on such things as whether some nitrogen has been applied as a starter fertilizer, the residual nitrogen level of the soil, the availability of anhydrous ammonia and of course, weather factors. The single most important factor to consider is the amount of root damage done by the ammonia knife in pruning the roots.

Corn can generally be side-dressed until it becomes too high for use of the application equipment. Corn responds well to side-dressing from early stages until it becomes too high.

Cotton should be side-dressed as early as possible after plants emerge. Fruiting of cotton is a continuous process and begins at an early stage of plant growth. Early nitrogen applications insure the needed vitality for a plant to continue to grow, produce new fruit and mature older fruit throughout the growing season.

One agronomist used this rule of thumb: do not side-dress corn after the corn is $2\frac{1}{2}$ feet high or when the plants lap the middle of the rows. Cotton must be side-dressed from the time it emerges until it is 45 days old. Another agronomist pointed out that the earlier side-dressing can be done, even starting to follow the planter tracks, the better it is. Later in the season, when the plants are two to three feet tall, some of the roots will stretch across the row and be subject to pruning by knives. But it is always better to prune a few roots and bend a few stalks than to allow the crop to starve for nitrogen.

3--How much ammonia can be side-dressed?

The quantity of anhydrous ammonia, which can be effectively

applied to the soil as a side-dress, depends on the exchange capacity of the soil, organic matter content with reference to the organic acid, and the moisture content of the soil. If the soil is too dry, quantities in excess of 100 pounds of nitrogen on 40-inch rows may escape from the application zone because of the dryness and fluffiness of the soil. This is a physical problem associated with back pressure of the ammonia vaporizing in the soil. If soils are too wet, the problem is of closing the applicator knife opening with some kind of disc or slide-closing device. The kind and per cent of soil clay content determines the ammonia holding capacity in the application zone. Farmers shooting for optimum yields of corn are now using as much as 125 to 150 pounds of nitrogen per acre side-dressed. A good rule of thumb is to use $1\frac{1}{2}$ pounds of nitrogen per bushel of expected corn yield. The average rate for normal 36 to 40-inch rows of solid cotton is from 80 to 100 pounds of nitrogen per acre. Applications up to 150 pounds of nitrogen per acre have been used successfully when the skip row pattern was utilized. On long-growing crops, such as cotton and corn, any amount of nitrogen that is needed in growing a good, profitable crop can be applied as a side-dressing if it is applied early in the growing season to give it ample time to be taken up by the plant and be ready for use during the fruiting period. If the soil is very sandy, then smaller amounts should be applied in any one band. Additional injection shanks can be added in order to apply the amount needed without applying too much in one band. Heavier soils obviously can hold more ammonia.

4--How close to the row can ammonia be applied side-dress?

Generally, the distance from the growing crop that ammonia can be applied side-dressed depends upon the type of crop and its stage of development.

One good advantage of applying anhydrous ammonia side-dress is that it can be applied with exact relationship to the crop row. Side-dressed ammonia will give satisfactory results when applied directly in the middle between rows of crops like cotton and corn. Applying the ammonia in the middle, leaves the widest margin of error for the tractor driver.

Careful consideration should be given to the root development--the smaller the crop, the less the roots have extended, and the closer to the row the knife can be allowed to travel. Generally, corn and grain sorghums should have the ammonia applied mid-way between the rows which would give the maximum distance from the growing plants. For cotton and other crops which produce a root system that spreads out only a few inches laterally, it is usually necessary to space the knives closer to the row or root systems of the plant. For vegetable crops with compact root systems, or in the case of root crops such as beets, onions, carrots and others, it is best to place the ammonia on each side of the row and about six to eight inches away from the row. In no case should the ammonia be side-dressed closer than five to six inches to the row. The primary consideration in side-dressing ammonia in relationship to row distance is that considerable root pruning damage can occur if side-dressing is made too close to the plant.

5--How does side-dressing fit into a minimum tillage program?

In minimum tillage systems, it is customary to apply fertilizers, including ammonia, pre-plant or at planting time. In cases where adequate amounts of nitrogen have not been applied and the prospects for greater crop yields are in view, side-dressing can be recommended.

Minimum tillage will create a problem for the application of side-dressed ammonia. It is obvious that the best ammonia applications are made where crop residues have been chopped and where a good seed bed has been prepared. If the ammonia applicator is equipped with a good, sharp rolling coulter or other equipment which will pass through the crop residue and not disturb the depth or penetration of the ammonia shank, the use of ammonia fits into the minimum tillage program very well. Side-dressed ammonia will fit into the minimum tillage system the same as it does where conventional cultivation is practiced.

6--Are there any special techniques involved where narrow (28-inch or 30-inch) rows are used?

Side-dressing of crops having narrow row spacings can be achieved easily with conventional equipment. It will be necessary for the ammonia applicators to be adjustable to travel between the narrow rows. Such an adjustment will probably come on the tool bar and axle-frame connection. Also, the wheels must be adjustable for the various row spacings to allow them to travel between the rows. Usually it is recommended to split the rows, allowing the knife to travel halfway between the rows. The operator with his tractor may have some trouble getting through

his fields, especially when the corn approaches knee high or the leaves touch in the middle, for the wheel can catch the leaves and break the stalks. Slippage from the tractor resulting in damage to the crop is often experienced when any mechanical cultivation follows narrow row cropping. The driver must be alert and move his equipment at a slower rate through the field on narrow row crops. Normally, a complete herbicide program is used in narrow row agriculture.

Application in Irrigation Water

Anhydrous or aqua ammonia may be accurately metered into irrigation water, and this procedure has been shown to be an effective means of supplying it even though losses by volatilization can be appreciable. Because of volatilization losses, application of ammonia through sprinkler irrigation systems is not usually recommended or widely practiced. However, at low rates of application it may at times prove feasible.

In surface irrigation systems, ammonia is usually applied at rates to give less than 100 ppm ammonium -N in the water. Thus, a single application may provide up to about 80 pounds of N per acre. Many row crops, trees, and vines are successfully fertilized through ammonia in the irrigation water. The practice is often used to provide supplemental N, especially on coarse-textured soils. Among the major row crops, corn, cotton, and potatoes are probably most often fertilized with ammonia in the irrigation water.

In report from the irrigated sections on the West Coast,

most ammonia applied is injected into the soil. In Southern California and Arizona, about one-third of the ammonia is applied in irrigation water on growing crops. If the crop is in beds or on hills, this procedure would be called side-dressing, and if the crop is planted flat, then a water application would be considered top-dressing. From six to eight inches is the usual side-dressing depth of application when ammonia is injected.

Anhydrous Ammonia as a Nitrogen Fertilizer

Anhydrous ammonia contains the highest percentage of nitrogen of any nitrogenous fertilizer currently on the market. It is stored under pressure as a liquid, and its application in the field requires the use of high-pressure tanks and metering devices. Bulk storage at atmospheric pressure, which has only recently come into use, requires refrigerating equipment to liquify the ammonia gas volatilized but does not depend on the construction of high pressure tanks. Because no further processing is needed after its manufacture, ammonia can be offered to the grower at a very attractive price. Much of this material is custom applied so that the farmer does not have to purchase his own high-pressure tanks and equipment for on-the-farm handling and storage of this product. Anhydrous ammonia may be applied directly to the soil by injection through tubes running down the rear of a blade-type applicator. In some areas, notably the irrigated areas of the west, ammonia is applied by metering into irrigation water.

Because it is a gas at atmospheric pressure, some anhydrous ammonia may be lost to the above-ground atmosphere during and after application. Factors associated with this loss are the physical condition of the soil during application, soil texture and moisture content, and depth and spacing of placement. If the soil is hard or full of clods during application, the slit behind the applicator blade may not close fully, and some of the released ammonia will escape to the atmosphere.

Ammonical Sources

The following ammonical compounds are used as sources of fertilizer nitrogen:

Average Composition of some Common Chemical Sources of Fertilizer Nitrogen

Sources	N %	F ₂ O ₅ %	K ₂ O%	CaO%	MgO%	S%
Ammonium sulfate	20.5	----	----	----	----	23.4
Anhydrous ammonia	82.2	----	----	----	----	----
Ammonium chloride	28.0	----	----	----	----	----
Ammonium nitrate with lime (ANL)	20.5	----	----	10.0	0.7	.6
Ammoniated ordinary superphosphate	4.0	16.0	----	23.0	5.0	10.0
Mono ammonium Phosphate	11.0	48.0	----	2.0	.5	2.6
Diammonium Phosphate	18.0	54.0	----	----	----	----
Ammonium phosphate Sulfate	16.5	20.0	----	----	----	----
Calcium nitrate	15.5	----	----	27.0	2.5	----
Calcium cyannamide	22.0	----	----	54.0	----	0.2
Potassium nitrate	13.4	----	44.2	0.5	0.5	0.2
Sodium nitrate	16.0	----	----	----	----	----
Urea	46.0	----	----	----	----	----
Urea-Sulfur	40.0	----	----	----	----	10.0

Principal N fertilizers: N Content, USA average
price per ton, and calculated cost per pound
of N, 1964

Product	Nitrogen Content %	Product Price/ton \$	Cost/lb. N
Anhydrous ammonia	82.0	124.00	7.6
Ammonium nitrate	33.5	72.20	11.8
Ammonium sulfate	20.5	52.60	12.8
Nitrate Soda	16.2	60.00	18.5

Handling of Ammonia

Anhydrous ammonia is a gas under normal temperature and pressures, but it is easily compressed to a liquid and usually is handled in industry as a liquid under pressure in a closed or gas tight system.

Storage tanks

Tanks for storing anhydrous ammonia can be divided in two classes, high pressure (non refrigerated) and refrigerated. Refrigerated tanks can be further divided into two general classes, medium pressure (40 to 70 PSig) and atmospheric storage (cryogenic) tanks.

Methods of transferring ammonia

- 1--vapor compressors to produce a pressure differential between vessels
- 2--Liquid pumps

Safety Equipment

Anhydrous ammonia can be handled safely by using proper equipments

- 1--an approved ammonia type gas mask with refill container
- 2--rubber gloves
- 3--rubber boots
- 4--rubber slicker or rubber pants and jacket
- 5--first aid kit (ammonia type)
- 6--shower or 60-gal open top drum of water

Nitrogen Requirements of Crops

Supplying the nitrogen needs of crops in amounts to achieve optimum quantity and quality of product is an elusive goal.

Total Nitrogen Requirements of Crops

N requirement is defined as the minimum amount of this element in the above ground portion of the crops associated with maximum production.

Corn

Several studies depicting the course of dry matter production and nutrient uptake for corn from early stages of growth to maturity are reported in literature. In only one instance were varying rates of N fertilizer employed. In other cases a single level of fertility was established, an exception being Hanway's study involving variations in crop rotation system and general fertility level. Although corn is grown largely for its grain, substantial acreages are for silage. The amount of N needed to produce a given yield of grain is of primary interest to the grower.

Maximum Corn Yields and Corresponding
Total Yields of N

Estimated from experiments
receiving varying amounts
of N fertilizer

Soil type and location	Year	N		N-uptake		
		Applied lb/acre	Grain bu/acre	lb/acre	lb/bu	
Ruston S.1 Poplarville, Mississippi	1956	150	87	099	1.15	
	1957	100	43	64	1.49	
	1958	150	75	102	1.36	
	1959	200	75	111	1.50	
Huston Clay Brooksville, Mississippi	1950	125	62	56	0.90	
	1957	150	90	138	1.53	
	1959	200	78	116	1.50	
Cecil S.1 Watkinsville, Georgia	1957	40	102	115	1.13	
	1958	120	110	135	1.23	
	1959	200	137	145	1.06	
Greenville S.1 Thorsby, Alabama	1950	125	96	137	1.43	
	1958	150	102	187	1.83	
	1959	200	109	152	1.39	
Tifton S.1 Tifton, Georgia	1958	90	112	124	1.11	
	1959	130	84	147	1.75	
Leon F.S. floriide	10,000*	1959	370	75	96	1.29
	15,000*	1950	500	92	140	1.50
	20,000*	1950	500	108	145	1.36
Tilden F.S.1 State College, Mississippi	4,000*	1946	100	67	98	1.46
	12,000*	1946	140	84	130	1.55

* Stalks/acre

Forage Grasses

During the last decade, a number of comprehensive field experiments have been conducted on N fertilization of high yielding tropical and sub-tropical grasses. Fewer experiments applicable to the present study have been reported for the temperature regions. Reasonable approximations of maximum yield of dry matter and associated N uptake were obtained from free-hand curves relating total yields of dry matter and N to rate of N applied.

The summary of results for various tropical grasses given in the table below directs attention to the high levels of N fertilizer required to achieve maximum yield.

Nitrogen uptake Associated with Estimated Maximum Yield of Various Tropical Grasses

Grass	Reference	Harvest interval days	N applied lb/acre	Dry matter ton/acre /year	N in dry matter lb/ton	Remark
Guinea	59	40	800	13.8	36	2 yr. average
	60	45	800	16.0	38	2 yr. average
	33	50-60	800	20.9	36	2 yr. average
	60	60	900	17.4	34	2 yr. average
	59	60	800	16.4	32	2 yr. average
	59	40	1200	23.0	28	2 yr. average
Pangola	58	30	600	10.0	44	2 yr. average
	58	45	600	11.9	36	2 yr. average
	33	50-60	800	9.5	38	2 yr. average
	58	60	800	15.5	36	2 yr. average
	17	*	480	3.2	38	1955 3 harvest
	17	*	320	4.4	48	1956 4 harvest
Bahia	17	*	480	4.8	42	1957 3 harvest
	18	30-40	600	10.4	40	1957 irrigated
	17	*	120	2.5	44	1953 2 harvest
	17	*	240	5.0	46	1954 5 harvest
	17	*	300	3.6	42	1955 4 harvest
	17	*	300	3.4	42	1956 3 harvest
	17	*	240	3.5	42	1957 3 harvest

*harvested when best plots were 18 inches tall

Sugar Cane

Interest in the problem of N requirement of the sugar crops in its present context began with the studies by Stanford and Ayres on N fertilization of sugar cane in Hawaii. A major problem appeared to be that of minimizing overapplication to reduce losses of sugar and waste of fertilizer. Field experiments comparing varieties of sugar cane fertilized with different levels of N were conducted on the major irrigated sugar cane soils. Yields of millable cane, total dry matter, and sugar were determined for each soil treatment and variety.

Golden and Ricard found the average amount of N in the tops and roots of sugar cane grown in Louisiana to be 4.2 lb/ton of millable cane.

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AMMONIA UTILIZATION AND SYNTHESIS

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Importance of ammonia as a source of nitrogen cannot be over-emphasized for plants from the decomposition of organic matter and various synthetic forms of NH_4 -fertilizer. Besides its use as a source of plant food, it has also other industrial uses, eg. refrigeration, and synthesis of different salts which are in use in a number of industries. It is readily soluble in water, and it is easily available to plants. There are various forms of ammonium fertilizers that are synthesized in large amounts. The important ones are ammonium nitrate, ammonium sulfate, urea, anhydrous ammonia, ammonium phosphate and ammonium phosphate nitrate. Uses of various forms of ammonium fertilizers depend on economic advantages, availability to plants, ease of application, concentrations, and lastly their residual effect on the soil.

The synthesis of NH_3 involves gas preparation, carbon monoxide conversion, gas purification and finally the Haber process is widely used. This process involves the direct combination of hydrogen and nitrogen, with proportion three to one, under high pressure in the presence of a catalyst. This reaction is exothermic, and according to the Le Chatlier's principle, the yield of ammonia at equilibrium is less at a high temperature than at low temperature.

The various changes that take place in the soil after the application of NH_4 -fertilizer are ammonium interaction with soil minerals and organic matter. Ammonium has a positive charge and is attracted by the negative electrical charges of soil minerals. It enters into ordinary cation exchange reactions in the same

manner as metal cations. Formation of ammonium ion proceeds when ammonia can react with a proton (thus an acid soil, or minerals having exchangeable hydrogen ions on the cation exchange complex may provide the necessary protons for NH_4 -ion formation).

Ammonium is retained in the soil by a number of mechanisms including chemically sorbed, or exchangeable NH_4^+ , fixed NH_4^+ , NH_3 that react chemically with soil organic matter, and physically sorbed NH_3 . There is physical and chemical interaction, between NH_3 and soil organic matter. Once an NH_4 -organic matter complex is formed, then only micro-organisms can release NH_3 to the soil solution.

The nitrogen requirements for different crop species have been very well worked out as evident from the literature. There are differences in the N-requirements between species, varieties and stages of growth.