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AN EVALUATION OF RECENT ADVANCES IN THE USE
OF ANHYDROUS AND AQUEOUS AMMONIA OVERSEAS AND
THEIR APPLICATION IN NEW ZEALAND HORTICULTURE.

A thesis submitted in partial fulfilment of the requirements for the National Diploma

in Horticulture

in New Zealand.

bу

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INTRODUCTION

The object of this study is to evaluate recent advances in the use of anhydrous and aqua ammonia as nitrogenous fertilisers, with emphasis on the prospects and needs there are for their usage in New Zealand. There is at present a large dependence on New Zealand made organic and imported artificial fertilisers which are mostly low analysis materials. These nitrogenous fertilisers, with their low nitrogen content, have a high cost per pound of nitrogen. Anhydrous and aqua ammonia are high analysis materials whose use could prove worthwhile in this country on the grounds of economy and practicability. An appraisal of these prospects would appear to offer advantages in the development of horticulture (and agriculture) in New Zealand.

Part I deals with the aspects of nitrogen in the soil and in plants. This introduces the trends in nitrogenous fertilisers and usage of the various forms, particularly anhydrous and aqua ammonia. Also dealt with is the history of nitrogenous fertilisers.

Part II illustrates the usage of ammonia as a fertiliser. The manufacture, use for crops, equipment and basic economics are discussed, with a view to demonstrating that anhydrous and aqua ammonia fertilisers have been shown to be both efficient and very economical fertilisers overseas.

Part III deals with the position in New Zealand.

The types of nitrogen fertilisers used and the economic aspects of their usage. Prospects for anhydrous and aqua ammonia in New Zealand are looked at.

In conclusion the general findings are summarised and recommendations are made with a view to future needs in New Zealand for anhydrous and aqua ammonia. This thesis attempts to tentatively answer the question, "Is there a place for anhydrous and aqua ammonia fertiliser in New Zealand, and what action should be taken to examine this subject more closely".

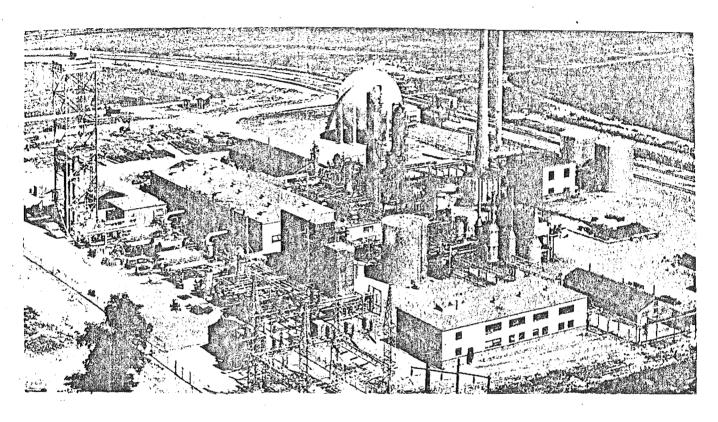


PLATE I
A typical Anhydrous Ammonia production plant where Nitrogen from the air and Hydrogen from a fuel are united to form the 82% N fertiliser.

(Reprinted from Anhydrous Ammonia Handbook) (Anon (1))

PART I

NITROGEN AND THE PLANT

PART I

CHAPTER 1

THE NEED FOR NITROGEN BY PLANTS

Research work over the years has indicated that nitrogen is the most critical food element and is in fact, a primary structural unit for all living matter. It is essential for all animal and plant protein, chlorophyll and numerous other compounds (Anon (1) 1965). This has resulted in the amount of nitrogen utilised by crops to be as great or greater than any one of the other fifteen essential elements.

Although the atmosphere contains 78% of this essential element, it is not easy for the plant to obtain a ready supply. It is important to provide nitrogen in an available form to the plant and a review of the best way to solve this and supply nitrogen in the most economical way appears necessary.

The first questions to be asked in a consideration of nitrogen metabolism are:-

- 1. What nitrogenous substances can be assimilated by plants?
- 2. What are the pathways involved in the assimilatory process? (Webster 1959).

There are four main sources of nitrogen in the soil:-

- 1. Organic
- 2. Ammonium
- 3. Nitrate
- 4. Molecular

Green plants obtain their nitrogen only from the soil. except in the case of legumes which make use of symbiotic nitrogen from nitrogen fixing bacteria in their roots. is characteristic of the lower orders of plant life such as certain fungi like Endomyces and Phycomyces, various bacteria and species of unicelluar plant life like Euglena, solely on organic nitrogen. Other fungi like Mucor and Rhizopus and some bacteria can utilise organic and ammonium nitrogen. Certain bacteria and blue green algae can utilise all four forms of nitrogen whilst most bacteria, fungi, algae and higher plants use all but molecular nitrogen since this form of nitrogen is insoluble (Webster 1959). Although all forms, except molecular nitrogen are utilised by these higher plants with which we are mainly concerned, there is frequently a marked preference for one form of nitrogen. Many species are reported to grow better with nitrate and ammonium combined than with one alone. No plant is known to require both ions separately, but their simultaneous use avoids changes in acidity, due to preferential absorption of a single ion (McKee 1962).

For the purpose of this study it is necessary to look more closely only at the first three sources of nitrogen and their consequent metabolism for plant utilisation.

METABOLISM OF ORGANIC NITROGEN COMPOUNDS

Amino acids and urea are the main forms of organic compounds which can be absorbed by plants, most other organic compounds being poor sources of nitrogen (Webster 1959).

The value of organic nitrogen substances is a function of how easily they can be broken down into ammonia, or of the efficiency with which they can be incorporated into the normal metabolic cycles of the plant.

METABOLISM OF AMMONIA

This has been studied using ¹⁵NH₃. Webster (1959) reports that this isotope was shown to be incorporated into amides, amino acids, and proteins by Vickery et al in 1940. Further experiments showed that glutamic and aspartic acids become highly labelled with ¹⁵N from ¹⁵NH₃ and that glutamate, aspartate, their amides and alanine are the major products of ammonia uptake. However although ammonia is the primary material for the building of amino acids, the uptake from the soil is in general quite small in comparison with the uptake of nitrates. This is primarily because ammonia tends to be held on the soil colloids and organic matter, while nitrates which are very soluble occur mostly in the soil water.

Many species of plants, when grown in sand or solution cultures (under suitable conditions) develop as well or better when supplied with ammonium salts as when supplied with nitrates (Meyer et al 1965). This is not surprising since the nitrogen in ammonium compounds is in a highly reduced form similar to that found in amino acids and related compounds. Meyer et al goes on to say that in certain types of soils, ammonium compounds are the chief form of nitrogen which is available to plants. This is apparently true of certain soils in the northern hemisphere such as the acid podsolic soils and of many uncultivated soils in the southern areas of the United States of America. soils contain little nitrate, but considerable quantities of ammonium compounds and plants in these areas apparently depend on ammonium compounds for their source of nitrogen.

METABOLISM OF NITRATE NITROGEN

Nitrate is the principal form in which nitrogen is assimilated from the soil. The absorbed nitrate is rapidly reduced through the molybdenum containing enzyme, nitrate reductase (Webster 1959). Normally plants only contain relatively small amounts of nitrate as it is rapidly reduced as soon as it enters the plant. However under certain conditions plants accumulate relatively large amounts of nitrate in their tissues without any toxic effects.

Subsequently this accumulated nitrate is utilised in the nitrogen metabolism of the plant. Plants sometimes exhibit acute symptoms of nitrogen deficiency whilst they still contain quite large quantities of nitrates. Although such plants have been able to absorb nitrates, metabolic conditions within the plant have been such that they have been unable to utilise them in the formation of nitrogenous organic compounds (Meyer et al. 1965).

The first step in the utilisation of nitrates by plants is their reduction to nitrites. Plants can also use nitrites as a source of nitrogen, as shown by solution culture experiments (Meyer et al,1965). However, nitrites are seldom if ever an important source of nitrogen for plants in nature being only an intermediate stage in the reduction of nitrates. Nitrites are further reduced to ammonia, perhaps through the intermediate steps of hyponitrous acid and hydroxylamine (Meyer et al,1965).

The ammonium ions and some of the carbohydrates synthesised in the leaves are built up into amino acids mainly in the green leaf itself but some transamination does occur in roots. This source of amino acids is then built up into protein as the leaf enlarges, and this in turn produces a greater photosynthetic area for the production of more carbohydrates. The resulting nitrogen therefore not only allows conversion of carbohydrates to proteins, protoplasm and cell wall material, but also allows leaf growth. (Russell 1961).

With an ample supply of nitrogen leaves are greener and more succulent, as there is a greater proportion of protoplasm to cell wall. Excessive nitrogen can produce plants with large thin leaves which are more susceptable to attack by insects and fungi or unfavourable weather. Conversely plants grown under low nitrogen conditions tend to be paler and small, the leaf cells are small and thick walled and the leaves in consequence are harsh and fibrous.

Crops grown for their carbohydrate content such as root crops and cereals, benefit from the effect of a greater leaf area. On the other hand leafy crops like cabbages and lettuce respond directly, and have a high nitrogen requirement.

Examples of nutrient requirements for various crops indicate that nitrogen in general is needed in quite large amounts (Minard 1964).

Crop	Yield per Acre			Nutrients removed in lbs. element per acre		
			N	P	K	
Early potatoes	7	tons	76	12	105	
Carrots	12	11	107	20	105	
Celery	8	11	116	20	149	
Onions	12	tt	71	16	60	
Cauliflower	20	ff.	178	31	185	
Savoy cabbage	14	11	223	33	185	
Lettuces	10	tt	47	8	89	
Tomatoes	16	Ħ	98	12	119	
Spinach	8	tt	85	14	74	
Rhubarb	28	11	228	64	334	

Many young plants tend to absorb ammonium nitrogen preferentially over nitrate nitrogen (Murphy and Schrader 1965). This phenomenon is due in part to the fact that young plants do not possess the enzyme systems necessary to convert nitrate nitrogen to the ammonium form. Azaleas, laurel, and other plants that require a low-lime soil are examples of plants which readily absorb ammonium compounds. Some plants such as lowland rice even prefer ammonium compounds to nitrates.

Allison (1966) states that ammonia is regularly found in plants but accumulates appreciably only where lack of carbohydrates delays assimilation. Both ammonia and hydrocyanic acid gasses have been identified, but the loss of ammonia as a gas is probably not great as it is not formed in large amounts and may be absorbed back into the soil.

Nitrogen has been shown to be of major importance for plants and to be essential for the building up of plant protoplasm. Increasing knowledge about crop requirements and forms in which nitrogen occurs in the soil has led to greater world-wide usage of nitrogenous fertilisers.

Crop plants mostly obtain their nitrogen in the form of nitrates, but owing to high solubility, nitrates are easily leached from soil. It is therefore important to recognise the form in which the nitrogen fertiliser is applied since it will have a bearing on plant uptake and loss from the soil. These factors

are mostly controlled by soil conditions which lead to differing reactions. An understanding of the nitrogen balance in soil will therefore assist in deciding the appropriate nitrogen fertiliser and this is commented on in the next chapter.

CHAPTER 2

ASPECTS OF THE BEHAVIOUR OF NITROGEN IN THE SOIL

THE NITROGEN BALANCE

Under virgin conditions in temperate soils, the nitrogen content approaches an equlibrium value, the magnitude of which depends primarily upon climate, vegetation and the physical characteristics of the soil (Ensminger L.E. and Pearson R.W.1950). However as soon as land is cultivated a new set of conditions is established and the equlibrium level of soil nitrogen drops much lower. Soil nitrogen is in a dynamic state since there is continual interchange in and out of, and within the soil of the various forms of nitrogen. This series of reactions is collectively known as the "Nitrogen Cycle" (as depicted in Fig.I.)

ORGANIC NITROGEN IN THE SOIL

As described in Chapter 1, organic nitrogen is one of the principal reservoirs of nitrogen in the soil. The organic matter in the soil consists of plant and animal remains which are in varying stages of decay. Organic nitrogen is an important factor in fertility of a soil since it affects physical and chemical properties. Decomposition of organic nitrogen in soil produces humus.

Humus

Nitrogen in humus is mostly combined with lignin-type

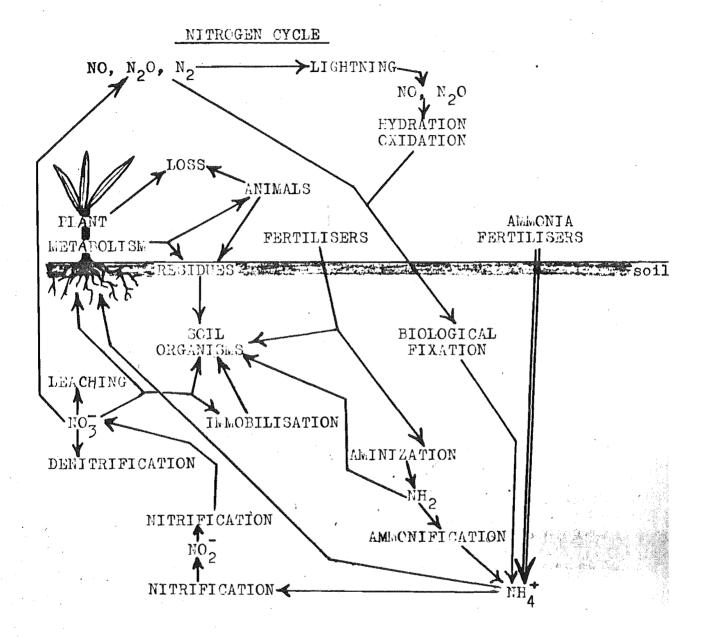


Figure I.

residues in the form of lignin protein complexes. Newly synthesised humus bears little or no resemblance to the original organic matter source, and it consists mostly of remains and by-products of micro-organisms. Humus is a dark amorphous colloidal material. It has a high capacity to absorb water and cations, and forms stable complexes with metal ions and also with clays. It is thus important in initial fixing of ammonia when added to soil as a fertiliser. Humus confers a low plasticity to clay soils and improves water holding capacity of clay and sandy soils. Humus has a high cation exchange capacity which gives it important buffering powers, thus the content of humus will help reduce the effect of adding strongly alkaline fertilisers like ammonia.

Nitrogen in organic compounds, such as amino acids and proteins, is subject to complex changes as it is broken down to humus by micro-organisms. Proteins are converted into various decomposition products and finally some of the nitrogen appears in the nitrate form. Even then it is allowed no rest, as it is either used by micro-organisms and higher plants, or is removed in drainage, or is lost by volatilisation. Nitrogen in the soil is in a continual state of flux. The mobility of nitrogen is very great, rivalling carbon in its ease of movement (Buckman and Brady 1964).

The overall process of mineralisation, which is conversion of organic nitrogen to nitrate nitrogen, can be divided into two parts. ammonification and nitrification.

Ammonification

This is the process in which organic nitrogen is broken down by heterotrophic bacteria, and as depicted in the diagram of the nitrogen cycle (Fig.1), it provides a natural source of ammonium ions. Ammonification is of importance here as it provides a means for release of nitrogen which has been locked up by immobilisation of nitrates.

Nitrification

Nitrification is the conversion of ammonium ions to nitrate, the most highly oxidised form of nitrogen in soil. Murphy and Schrader (1965) state that there are eight possible nitrogen compounds between ammonium and nitrate in the nitrification process, since ammonium has to lose eight electrons. The main recognised intermediate is nitrite. The oxidation of ammonium to nitrite is quite separate from that of nitrite to nitrates since a different set of micro-organisms is involved in each case. The bacteria responsible for the oxidation of ammonium to nitrite belong to the genera Nitrococcus spp. and Nitrisomonas spp. These micro-organisms are tolerant of high pH's and free amnonia. Nitrobacter spp.are autotrophic bacteria which oxidise the nitrite and are much more sensitive to high pH's and free ammonia in soil. The oxidation of nitrite to nitrate usually occurs at a faster rate than ammonium ions to nitrite but an accumulation of sizeable amounts of ammonia in alkaline soils will tend to limit the action

of the <u>Nitrobacter spp</u>. and sometimes cause a nitrite build-up. Although nitrite can be readily utilised by many micro-organisms it is very toxic to higher plants when present in the soil in high concentrations. Nitrite can also combine with the soil organic fraction to form stable organic nitrogen complexes and various nitrogen gases. These nitrogen gases are often toxic to growing tissues and in addition are a possible mechanism of nitrogen loss to the atmosphere.

Non-Symbiotic Nitrogen Fixation

Non-symbiotic nitrogen fixation is carried out by algae, fungi and bacteria. This is supplemented by ammonia added in rainfall which amounts to approximately five pounds per year, per acre on average in New Zealand. Addition of non-symbiotic nitrogen is of the greatest importance where there are low organic matter levels in the soil. This process is often described as Azofication, because a major part of the fixation is due to the Azotabacter group of bacteria (Buckman and Brady 1964).

These organisms are not directly associated with higher plants and obtain their nitrogen from the air while using soil organic matter as a source of energy. The amount of nitrogen put into soil by this free fixation process is dependent on such factors as the supply of readily available energy material, supply of available nitrogen and pH. In soils high in available nitrogen little or no nitrogen is added by this means (Ensminger and Pearson, 1950).

Symbiotic Nitrogen Fixation

The accumulation of nitrogen in New Zealand soil due to its predominantly pastoral mode of farming is greatly dependent on symbiotic nitrogen fixation. Rhizobia bacteria in the nodules of legumes are able to fix atmospheric nitrogen. Symbiotic fixation of nitrogen is dependent on factors such as aeration, available nitrogen, moisture and the amount of active calcim in the soil (Ensminger and Pearson, 1950). Other factors such as the need for molybdenum and the strain of Rhizobium are also important.

Buckman and Brady (1964) state that nitrogen fixed by nodule organisms can go in three directions. Firstly it can be absorbed and utilised by the host plant. Secondly the nitrogen can pass into the soil itself, either by excretion or more probably by a sloughing off of the roots and especially of their nodules. The crop growing in association with the legume may therefore benefit, as in a pasture with clover and grass. Lastly, when the land is ploughed and the legume is turned over, nitrogen will be released when decomposition occurs. Since these residues usually have a low carbon-nitrogen ratio their nitrogen may swing through the nitrogen cycle with remarkable ease and may quickly appear in the ammoniacal and nitrate forms.

Symbiotic nitrogen fixation has less significance in cropping soils. The incorporation of legumes in a rotation has long been a recognised practice in growing vegetables. However with

specialised growing procedures it is often not economic to grow a legume on the land with much regularity, and nitrogen is then applied in the form of fertilisers. Continual cropping will tend to deplete organic matter in the soil and there is usually quite heavy demands on the nitrogen supply as well as other nutrients. Decline of soil nitrogen in cropping soils can also be accounted for by crop removal and erosion and by other factors, which are examined in the following chapter.

CAUSES OF LOSS OR SHORTAGE OF NITROGEN IN THE SOIL

Leaching

Leaching is the downward movement and consequent loss of nutrients in soil drainage water. Leaching is the main source of nitrogen loss in field soils and is nearly all as nitrate, while loss of ammoniacal nitrogen in this way is small (Allison, 1966). When rainfall is sufficient nitrate in upper horizons of the soil is diluted and moves to lower regions.

Burns and Dean (1964) state that there are many factors affecting loss of nitrate by leaching in soil. The most important of these are:-

- 1. Soil porosity.
- 2. Amount and movement of water.
- 3. Cations associated with the nitrate radicle.
- 4. Physical placement.

- 5. Amount of nitrogen added.
- 6. Temperature.
- 7. Microbial activity.

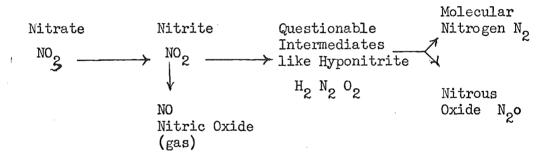
Loss of nitrates in soil drainage water has an important bearing on anhydrous ammonia application since anhydrous ammonia will undergo nitrification when applied when the soil temperature is above 55°F. This renders the nitrogen susceptible to leaching in the form of nitrate. On the other hand, if nitrogen is applied as ammonia in late autumn or winter, little or no nitrogen is converted to nitrate due to low temperatures, and, as a result there is less leaching of nitrogen. Leaching is a greater problem in light soils and in high rainfall areas.

Loss by Denitrification

Denitrification is the biological reduction of nitrite and nitrate. Both of these radicles are changed to gaseous products such as nitrous oxide or molecular nitrogen. There is a resulting reduction in the overall nitrogen content in the immediate environment of the denitrifying organisms. Ammonia as such cannot undergo the process of denitrification. This process is carried out by anaerobic bacteria which generally use oxygen as a hydrogen acceptor, but may also use nitrate as substitutes (Allison, 1966). Denitrification is most likely to occur when there is a shortage of oxygen. It occurs to the greatest extent under conditions of high soil moisture, but it may also occur on finer textured soils

where moisture content is below field capacity. Under common field conditions denitrification is probably second only to leaching as a source of nitrogen loss in the soil. High temperatures, low oxygen supply, waterlogged conditions and a neutral or too high pH tend to enhance the denitrification process (Murphy and Schrader, 1965).

Denitrification



Under most soil conditions nitrous oxide is the gas lost in largest amounts. With a pH above 7 loss by elemental nitrogen is also important and below pH 6 there are increasing amounts of nitric oxide lost to the atmosphere (Buckman and Brady, 1964).

Loss by Ammonia Volatilisation from the soil

The loss of nitrogen from soils as ammonia is likely to be of greater consequence than has been supposed in the past (Buckman and Brady, 1964). This is principally due to changes in nitrogen sources and farm practices. Allison (1966), attributes the main causes of this increased loss (in the United States of America) to

greater use of nitrogen fertilisers, use of anhydrous and aqua ammonia instead of ammonium salts and to the extensive use of urea which is readily hydrolysed by urease to ammonia. Ammonia volatilisation is of particular importance on soils low in organic matter and clay, since ammonia is only sparingly fixed by these soils components, and will either be given off into the atmosphere or remain in soil water. Loss of ammonia will also be greater when it is not covered or sealed properly at application, or when simply applied to the surface.

Biological Immobilisation.

Biological immobilisation affects higher plants most significantly when there is a high carbon to nitrogen ratio and as a result the micro-organisms in the soil take it up and convert it to organic forms in the microbial tissue. Murphy and Schrader (1965) term this process "microbial denitrification". A large supply of carbohydrates in soil represents a large food supply and energy source to micro-organisms and under favourable conditions a tremendous multiplication of their numbers takes place. This causes a temporary standstill in the nitrification process until the supply of energy is reduced. When this occurs the microbe population drops and there will then be some ammoniacal nitrogen released. When the carbon nitrogen ratio in temperate climate soils is approximately 25, the ammonium nitrogen is converted on a large scale into various proteins by the metabolic activities of

of micro-organisms. As the C/N ratio drops to about 15 these organisms begin to die, and the nitrogen contained in their cells is converted back to ammonium nitrogen by the process of ammonification. The addition of ammonia to soil as opposed to bulky manures greatly reduces any possibility of a shortage of nitrogen occurring due to biological immobilisation.

CHAPTER 3

NITROGEN AS A FERTILISER

HISTORY OF NITROGENOUS FERTILISERS.

Since the beginning of recorded history man has sought to increase the yield of his crops by the addition of substances to the soil. Even in primitive cultures man noticed that grass grew better where animals defacated or urinated, and thus he developed simple manuring techniques. Records of ancient Chinese civilisation, as well as early Greek and Roman writings, refer to the use of animal manure to fertilise the ground (Ensminger and Pearson, 1950). Long before the birth of Christ, Egyptians applied the deposits of the Nile to their poorer lands. The early discoverers of America observed that certain Indian tribes ritually placed a fish in each planting hill with several kernels of corn (Anon (1) 1965). For the most part, these primitive practices were passed on from generation to generation. Farming was an art and there was no science attached to these practices.

About one hundred years ago, agricultural learning and procedures started moving from the alchemy of the dark ages towards the scientific approach of today. In the 1840's a German chemist, Justus von Liebig, perceived that plants grew in relation to their intake of certain chemical substances from soil and air. This was one of the most significant beginnings to the scientific approach

of supplying plant nutrients by fertilisers. Another person of importance in the early days was the English chemist, Humphrey Davey, who in 1813 theorized that unproductive land must be deficient in one or more elements of the soil and these deficiencies could be determined by chemical analysis. Again in the 1840's, John Bennet Lawes, on his estate in Rothamstead, England, conducted trials to find the major elements required by plants. He and his associate J.H. Gilbert, produced basic evidence that nitrogen, phosphorus and potassium are of foremost importance in crop fertilisation (Anon (1) 1965).

As knowledge of plant nutrient requirements was gradually built up, materials containing these elements were used by farmers to improve their crops. Bulky animal manures and crop refuse were first used. Following this, minerals were mined in order to utilise natural supplies of potash, phosphate and nitrogen to fertilise the ground. Salt petre from deposits in India and nitrate of soda from extensive fields in Chile were used as nitrogen fertilisers.

In spite of the vastness of these deposits, a need was recognised to obtain usable nitrogen compounds from the air. Over every square inch of soil there are about 12 pounds of this element - about 20 million tons over every square mile. Yet this is uncombined, and insoluble, nitrogen which is not available to plants (Anon (1) 1968)

The discovery and process of the manufacture of ammonia from

the air is described in Part 2, Chapter 1, under the title of
Manufacture of Ammonia. The development of large scale ammonia
production started a new era, as ammonia is the primary or raw
material for the manufacture of a large number of fertilisers.

It is thus used in the production of ammonium nitrate, sodium
nitrate, nitrophosphates, sulphate of ammonia, ammonium sulphates,
urea, nitrogen solutions and aqua ammonia. The use of these and
other artificial nitrogen fertilisers has increased steadily,
while usage of bulky manures has decreased, except in intensive
growing of crops such as in horticulture.

NITROGEN MATERIALS

Natural organic materials like animal manures and composts supplied about 90% of the American domestic consumption of commercial fertiliser nitrogen in 1900, but less than 2% in 1956.

After 1940, a year in which by-product ammonium sulphate and Chilean nitrate together furnished about 60% of fertiliser nitrogen, synthetic ammonia products rapidly gained dominance; they accounted for about 87% (1,685,000 short tons) of fertiliser nitrogen in 1955-56 (Jacob,1959). The use of organic fertilisers like blood and bone is still prominent in New Zealand and this is discussed in Part 3.

Ammonium Sulphate

Ammonium sulphate in the United States of America was first made from ammonia which came from by-product sources, chiefly coke ovens. In 1945 more than 90% of its manufacture was from coke ovens

but by 1957 it had dropped to 47% and manufacture from synthetic ammonia has increased correspondingly. Spent waste and reclaimed acids from various industrial operations are also used for a large amount of the ammonium sulphate manufactured from synthetic ammonia. As with other fertiliser materials, resistance to caking in storage and ease of application in the field are important requirements of ammonium sulphate, both of which may be markedly influenced by the size and shape of the crystals.

Ammonium sulphate continued until 1959-1960 as the largest single nitrogen material produced in the world (Nelson, 1965).

It is still the leading source of nitrogen in Asia, Africa, Oceania, but in Europe and North and Central America it has been replaced by ammonium nitrate which has a higher nitrogen content.

Approximately one third of the total nitrogen output of Russia is ammonium sulphate, compared with about two thirds from ammonium nitrate. The main disadvantages of ammonium sulphate as a fertiliser are its low N content and the acid reactions that it produces in soils.

Nitric Acid

Nitric acid is mainly used in the production of fertilisers
by conversion into ammonium nitrate products, sodium nitrate and
other materials. It is produced by oxidation of ammonia under
pressure with the aid of a platinum - rubidium catalyst, followed
by absorption of the nitric oxides under practically the same pressure

World production of nitric acid is increasing rapidly, primarily to meet the needs of rapid expansion in ammonium nitrate production, (Jacob, 1959).

Fertiliser grade Ammonium nitrate.

Before the second world war use of solid ammonium nitrate as a fertiliser was confined mostly to mixtures of ammonium nitrate with calcium carbonate, limestone or dolomite, and to combinations of ammonium nitrate with ammonium sulphate and potassium chloride. In 1943, the ammonium nitrate from ordnance and industrial plants in the United States of America and Canada became available for use as a fertiliser but the product was initially unsuitable due to its tendency to absorb water. Once these difficulties were overcome, fertiliser grade ammonium nitrate (33.5%N) rapidly gained the dominant position among the solid nitrogen materials for direct application in the United States of America.

The most commonly used method of manufacturing ammonium nitrate in the United States of America is by prilling or spray granulation. The treatment of granular ordnance type materials with a petrolatum mixture and an anticoking agent involved several problems in the early stages of ammonium nitrate usage, and was responsible for the Texas City explosion of 1947.

There has been a sharp increase in world production and use of ammonium nitrate, now exceeding that of sulphate of ammonia. The United Kingdom doubled its production in the nine years starting 1957-1958, while ammonium nitrate is the principal source of

fertiliser nitrogen in the majority of European countries with the exception of Italy, Portugal, Spain and the United Kingdom, which favour ammonium sulphate (Nelson, 1965).

Urea

Fertiliser urea is marketed as the nearly pure solid, containing approximately 45 per cent nitrogen, and as solutions with ammonia and/or ammonium nitrate, both forms of which are used in mixed fertilisers for direct application. In 1948 consumption of urea fertiliser in United States of America was 3,490 short tons and this rose to 467,359 short tons by 1966 (Harre, 1967).

Urea was initially made by hydrolysis of calcium cyanamide but it is now commonly made by the reaction of ammonia with carbon dioxide under pressure. Research has been made in the formation of complexes between urea and other materials in order to decrease the hygroscopicity of urea. Present practice in the processing of solid urea for fertiliser commonly involves its conversion into pellets by spraying a concentrated solution at elevated temperature. These conditions favour the formation of biuret, a compound which has toxic effects on some plants under certain conditions. It is formed by reaction of urea with its decomposition product isocyanic acid, but this has been reduced to less than 1 per cent in recent urea manufacture (Nelson, 1965). Biuret became a problem with foliage sprays on plants like citrus.

In New Zealand biuret content is not a problem due to the high purity of urea used.

Urea hydrolyses to ammonium carbonate in soil. The reaction being catalysed by the enzyme urease which is produced by most bacteria, actinomycetes, fungi and crop residues. Large quantities of ammonia may be evolved along with the ammonium carbonate.

Nelson (1965) states that the free ammonia produced could cause plant damage and, because the pH will be raised, could inhibit nitrite oxidation.

Urea has had a rapid rise in popularity in the last decade due to its high N content, effectiveness as a nitrogen source and the substantial drop in price since 1962. Its high N content gives it a distinct advantage over ammonium sulphate. World production of urea has risen from 198,000 short tons in 1950 to 5,290,000 by 1963, and was expected to double by 1966 (Nelson, 1965).

Urea Formaldehyde Materials

These materials when correctly made, have low solubility in water and are capable of releasing nitrogen to crops over extended periods of time. Urea formaldehyde is marketed under trade names such as Nitroform, Uramite and Ureaform. Ureaform is principally used on greenhouse crops and turf, as a consituent of mixed fertiliser in the United States of America.

When properly prepared, urea formaldehyde has mole ratios ranging from 1.2 to 1.4 and then exhibits the desired characteristics of low solubility, slow release of nitrogen and high nutrient value.

Products having higher ratios behave much like urea itself, whereas the urea formaldehyde resins are of little or no value as fertilisers.

Urea formaldehyde was initially made in the United States of America in mixtures by ammoniating with an urea solution. They are now made from solid urea, a liquid concentrate and formaldehyde.

A third commercially practiced method involves treating mixtures containing solid urea with a solution supplying formaldehyde and free ammonia.

Urea formaldehyde has been used mostly in United States of America, however it is manufactured in France and Russia. A reported 15,000 short tons were used in the United States of America during 1961, largely in speciality lawn, garden and turf fertilisers (Nelson, 1965).

Nitrogen Solutions

Nitrogen solutions are those materials (other than anhydrous and pure aqua ammonia) that are liquid fertilisers with nitrogen as their main constituent. Examples of those used in the United States of America are as follows (Adams et al, 1965):-

Non Pressure Solutions	Total N %				
Aqueous solutions of nitrogen products	8.5 to 37.6				
Low Pressure Solutions					
Ammonia / ammonium nitrate solutions	31.8 to 44.8				
Ammonia / urea solution	21.0				
Ammonia / ammonium nitrate / urea solutions	36.9 to 44.0				

In 1961 - 62 these solutions accounted for 38 per cent of the domestic consumption of liquid fertilisers in the United States and six per cent of the nitrogen materials used directly (Adams et al. 1965).

Nitrogen solutions require simpler storage and application equipment than anhydrous ammonia, since it does not have to meet high pressure requirements. The most common solutions are those containing ammonium nitrate or urea or both, and all are generally of a lower price per unit of nitrogen than solid forms of similar nitrogenous fertilisers. In 1957 the number of nitrogen solutions available in the United States of America was 53, but by 1960 the number had increased to 99. (Adams et al, 1965).

Low pressure solutions are characterised by the presence of free ammonia, 4.3 to 49 per cent by weight. They are used principally for the manufacture of mixed fertilisers, but also have a use in direct application. Non-pressure solutions are principally used for direct application. Choice of a solution for a particular purpose and area involves, among other things, consideration of its vapour pressure and salting-out temperature. The vapour pressure varies from a gauge pressure of 3 psi with the lowest low pressure solution to 144 psi with the highest pressure solution at 104°F. (Adams et al. 1965).

The salting out temperature is the temperature at which crystals begin to form in the liquid and this will cause equipment

failure. Solutions with high salting-out temperatures cannot be recommended for use during cold weather unless they are diluted to prevent salting-out.

Nitrogen solutions are corrosive, particularly when they contain ammonium nitrate. Aluminium equipment is preferred but addition of ammonium thiocyanate as a corrosion inhibitor will permit use of carbon steel (Nelson, 1965).

Custom or contract application is a major factor in distribution of nitrogen solutions in the United States of America. Many American farmers, because of high cost of machinery and labour, prefer to have the materials custom applied rather than invest in labour and application equipment.

FERTILISER DEVELOPMENTS IN THE UNITED STATES OF AMERICA.

The importance with which nitrogenous fertilisers have come to be regarded can be illustrated by reference to statistics from the United States of America (De Geus, 1967):-

$\underline{\mathtt{Year}}$	Short tons	of elements used	as fertilisers
	N	P	K
1935 - 39	371, 236	287,820	311,313
1960 - 61	3,030,788	1,163,837	1,799,882
1964 - 65	4,605,442	1,552,832	2,347,620

Although fertiliser usage has risen generally, there is a very strong swing towards increased use of nitrogen fertilisers.

This is illustrated by the relative amounts of N: P: K used, which have changed from 1: 1: 1 in 1935 - 39 to roughly 9: 3: 5

in 1964-65 in America. The expectations for plant nutrient consumption by 1980 in the United States of America, which were made by the Tennessee Valley Authority, are:-

Nitrogen 10,000,000 tons (N)

Phosphorus 2,262,000 tons (P)

Potash 4,482,000 tons (K)

Harre (1967) described the usage of nitrogen in the United States of America as follows:-

"Nitrogen consumption in the United States increased to 5,326,303 short tons in 1966 from 4,638,538 in 1965, an increase of 14.8 per cent. Nitrogen now accounts for more than 43 per cent of all plant nutrients used and is expected to increase to 46 per cent by 1970. Direct application materials were almost 70 per cent of the 1966 total, a jump from 68.7 per cent in 1965. (This increase is depicted in Figure II).

Anhydrous ammonia for direct application continued its rapid growth with a 25.3 per cent increase in 1966. This material now represents 43 per cent of all direct application materials used. Use of nitrogen solutions increased 19.6 per cent and aqua ammonia 22 per cent.

The use of solid nitrogen materials for direct application increased at a slower rate, with solid ammonium nitrate showing a 12 per cent increase and solid urea 9 per cent. Urea now

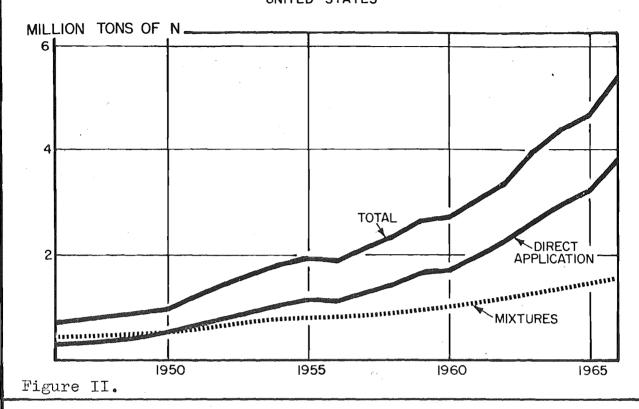
accounts for 17 per cent of the solid direct application nitrogen market, compared with 6 per cent in 1956."

I. Table of usage of nitrogen fertiliser in the U.S.A. 1964-65 (De Geus, 1967)

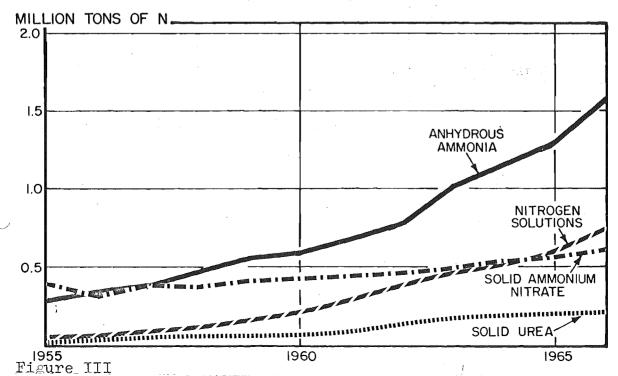
	Short tons N.	Percentage of total
Mixtures	1,456,866	31.6
Anhydrous ammonia	1,268,686	27.5
Nitrogen solutions	592,216	12.9
Aqua ammonia	146,874	3.2
Ammonium nitrate	550,207	11.9
Ammonium nitrate limestone	35,294	0.8
Ammonium sulphate	161,848	3.5
Ammonium phosphates	111,778	2.4
Sodium nitrate	48,575	1.1
Urea	193,713	4.2
Natural organics	18,511	0.4
Other nitrogen materials	20,841	0.5
Total	4,605,442	100.0

Thus recent years have seen a marked revolution in the nitrogen fertiliser industry. Changes in the United States of America have occurred not so much from the introduction of new materials (anhydrous ammonia was used commercially in the mid-1930's) but in greatly expanded production and consumption, the changing importance of the different nitrogen materials, sources used in

NITROGEN CONSUMPTION UNITED STATES



CONSUMPTION OF NITROGEN AS STRAIGHT MATERIALS UNITED STATES



manufacture, and in improvements of manufacturing processes.

Whilst anhydrous ammonia has increased in importance in America, it is still largely unused in other countries. Thus the nitrogen industry is expanding rapidly with the greatest advance in the United States of America. According to Nelson (1965), world consumption of nitrogen can be expected to double between 1960 and 1970, the percentage increase being in the nutritionally deficient countries.

Recent Developments in the Use of Anhydrous and Aqua Ammonia.

The following figures demonstrate the great increase in use of the principal nitrogenous fertilisers for direct application in the United States of America (Harre, 1967):-

		N in short t	ons	
<u>Material</u>	<u>1955</u>	% of total	1966	% of total
Anhydrous ammonia	290,337	25.1	1,606,872	43.0
Nitrogen solutions	38,362	3.3	712,445	19.1
Ammonium nitrate	375,318	32.5	610,715	16.4
Urea	30,973	2.6	211,615	5.7
Aqua Ammonia	46,617	4.0	200,814	5.4
Other materials	375,388	32.5	391,915	10.4
Total	1,156,995	100.0	3,734,376	100.0

From the table above and Figure III it can be seen that anhydrous ammonia in the United States of America is now the major nitrogen fertiliser having risen from 25 to 43 per cent of all direct application materials used. Furthermore the use of anhydrous

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ammonia appears to be increasing faster than other nitrogenous fertilisers. The use of aqua ammonia is also increasing although overall consumption is not nearly as great as anhydrous ammonia. Figure III also demonstrates trends in the United States of America of the use of liquid and gaseous nitrogen materials.

Anhydrous ammonia has also been used in several European countries, in particular France, and Denmark where anhydrous ammonia comprises 2% and 20% of nitrogen fertilisers used respectively.

The English farmer is now generally accepting anhydrous ammonia and there are now many firms doing contract work in England and other parts of the British Isles. Van Burg (1967) states that in 1964

East Germany applied 0.6 per cent of its nitrogen as ammonia and Czechoslovakia 3.5 per cent in 1963.

Landy (1968) reports that interest in anhydrous ammonia generally is growing considerably in Australia. At the moment most of the usage is confined to New South Wales and Queensland, while there is some use on a limited scale in both Victoria and Western Australia. Aqua ammonia has been used for several years on sugar cane in Queensland. Anhydrous ammonia has been used on a range of crops which will be discussed in Part II, Chapter 5.

PART II

2

ANHYDROUS AND AQUA AMMONIA AS A NITROGENOUS FERTILISER

CHAPTER 1

MANUFACTURE OF AMMONIA

In Part I it has been shown that nitrogen has become, and is still becoming an element of major importance for crop yield improvement. Its importance has led to new developments in efficiency of application of nitrogen and the new techniques using anhydrous and aqua ammonia have come into prominence over the last decade. The use of these materials is dependent upon the effective production of the basic constituent, ammonia. Therefore an appraisal of this material now becomes necessary.

Extensive commercial manufacture of ammonia has been achieved by only three of the numerous methods that have been proposed for chemical fixation of atmospheric nitrogen and these are:-

- 1. The electric arc process.
- 2. The cyanamide process.
- 3. The synthetic ammonia process.

1. The Arc Process.

The arc process involving the direct union of nitrogen and oxygen to form nitrogen oxides was first used on a commercial scale in Norway in 1905 (Jacob, 1959). However this process did not prove economic and it was abandoned in 1939. Study has continued, however, of methods for directly combining nitrogen and oxygen, especially as regards replacement of the electric arc by other sources of heat.

Recent sources of heat which have been investigated are solar heat and the use of nuclear energy.

2. Cyanamide Process.

The cyanamide process was first begun in about 1906 and has been mostly confined to Europe and Japan. Nitrogen is fixed by reaction with calcium cyanamide (Jacob, 1959). Production in the western hemisphere is largely restricted to a large plant situated in Canada.

3. Synthetic Ammonia or Haber-Bosch Process.

The first large scale plant for manufacture of ammonia by the union of nitrogen with hydrogen at elevated temperature and pressure was established at Oppau in Germany in 1913. A scientist named Fritz Haber managed to synthesize small amounts of ammonia in his laboratory by forcing nitrogen to combine with hydrogen. A chemical engineer called Carl Bosch, then developed facilities for mass production of ammonia. This method has since become known as the Haber-Bosch process after these two men who developed it. The process involves the presence of a catalyst and marked the beginning of a commercial process that now furnishes most of the world supply of fertiliser nitrogen. (Jacob, 1959).

An economical source of hydrogen is a major consideration in the location of a synthetic-ammonia plant.

Hydrogen may be obtained from the following:

- 1. Electolysis of water.
- 2. By processing carbonaceous materials such as coal, wood, charcoal, petroleum, and natural gas.
- 3. From gases resulting as by-products of certain industries, especially coke manufacture and petroleum processing.
- 4. As a by-product of the electrolytic process for caustic soda and chlorine.

Much the greatest production of hydrogen for synthetic ammonia before World War II, was based on hydrogen produced from coke by the water gas reaction. By 1950 however, about 52 per cent of production was based on coke, 43 per cent on natural gas and 5 per cent on hydrogen by-products from caustic soda chloring cells. By 1957 about 69 per cent of hydrogen production was based on natural gas, 12 per cent on oil refinery gas and only 9 per cent on coke in the United States of America. Coke oven gas is an important source of hydrogen for ammonia synthesis in Europe (Jacob, 1959).

The production of ammonia can be described as the base point of the manufacture of nitrogen fertilisers. The ammonia gas is utilised in three main ways.

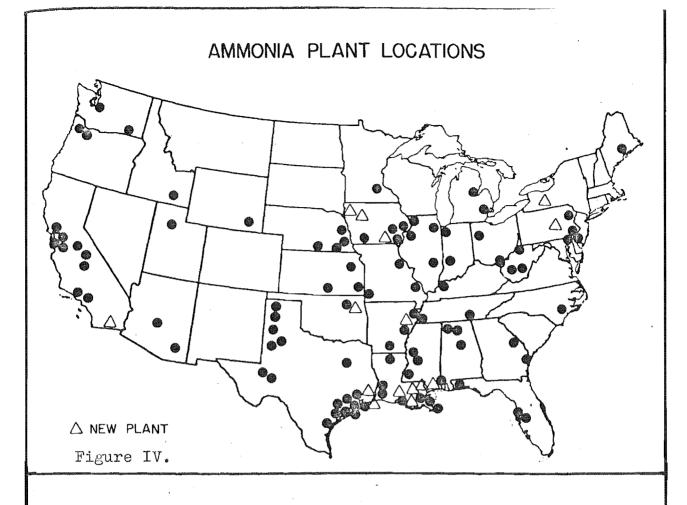
1. It is liquified under pressure to produce anhydrous ammonia. Anhydrous ammonia can be used on its own as a fertiliser or it can be mixed in fertilisers to form materials like ammoniated superphosphate.

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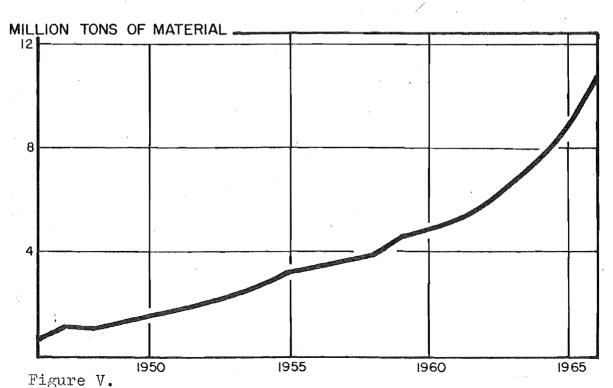
- 2. Aqua ammonia can be produced by dissolving ammonia gas in water. Aqua ammonia can be used on its own or can be used in the manufacture of nitrogen solutions or other nitrogen carriers like urea and ammonium nitrate.
- 3. Another use of ammonia gas is production of other inorganic nitrogen fertilisers. For example addition of sulphuric acid to ammonia is used in the manufacture of sulphate of ammonia, while combination with phosphates produces materials such as ammonium phosphate and nitrophosphates (Buckman and Brady, 1964). WORLD DISTRIBUTION OF AMMONIA PLANTS

The United States of America has shown the greatest rise in production of synthetic ammonia and will most likely continue this trend. The total capacity for the production of ammonia for all purposes, on the 1st January, 1967, was estimated at 12,156,000 short tons of ammonia. This figure is estimated to rise to 17,851,000 short tons of ammonia in 1968, (Harre 1967). There are approximately 100 plants for the production of synthetic ammonia in the United States alone, as can be seen in Figure IV, and the rapid rise in ammonia production is depicted in Figure V.

The importance of ammonia as a raw material has been appreciated in other countries apart from the United States of America. The following countries built plants between 1945 and 1958 - Brazil, India, Columbia, Egypt, Finland, Iceland, Israel, Mexico, Pakistan, Peru, Phillipines, Portugal, South Korea, Taiwan, Trinidad, Turkey, Venezuela and Jugoslavia.







From 1950 to 1955 Canada was the principal supplier to the United States of nitrogen fertilisers based on synthetic ammonia. The production of nitrogen as synthetic ammonia rose from 370,000 short tons in 1939 to 1,258,000 short tons in 1947. In this time an increase from 7 to 19 plants occurred due to the impetus of In 1950 to 1957 there was an increase from the Second World War. 22 to 56 plants and the capacity rose from $1\frac{1}{2}$ million to 4 million The tremendous expansion of synthetic short tons of nitrogen. ammonia plants in the world kept growing and by 1963 there were some 278 synthetic ammonia plants in operation and another 43 were under construction. These plants accounted for over 80% of the world's production of fertiliser nitrogen. The remaining 20% was produced from coke oven gases, by the cyanamide process and a small amount from natural materials, (Nelson, 1965).

The building of synthetic ammonia plants in Australia is of particular significance to New Zealand. There are at present two plants which are fully operative, one in Sydney, which has a capacity of about 100 tons of ammonia per day, and one in Brisbane which has a 150 tons per day capacity. These were started in mid-1964 and 1966 respectively. There are also plants due to start in late 1968 in Perth, Brisbane and Newcastle with proposed capacities of 330, 600 and 600 tons per day respectively. It appears therefore that there will be a ready source of ammonia in bulk in Australia and the price should lower as production and usage increase.

In conclusion it can be seen that ammonia is largely produced by direct synthesis of elemental nitrogen and hydrogen. It is also produced in small quantities as a by-produce from coke manufacture. It is produced in New Zealand for example at the Wellington and Auckland gas works but will never be available from these sources in large enough quantities for commercial fertiliser usage. On the other hand, there are several synthetic ammonia plants in Australia.

Since most inorganic nitrogen fertilisers are manufactured from anhydrous and aqua ammonia its production is important in economic manufacture of these fertilisers as well as for direct application.

CHAPTER 2

PROPERTIES OF AMMONIA

ANHYDROUS AMMONIA

Chemical Properties

Ammonia is a compound made up of nitrogen with three parts hydrogen, i.e. NH₃. The term "anhydrous ammonia" means free of water. Anhydrous ammonia is highly soluble in water and forms aqua ammonia (ammonium hydroxide) as shown in the following equation:-

$$^{\mathrm{NH}_3} + ^{\mathrm{H}_2\mathrm{O}} \longrightarrow ^{\mathrm{NH}_4\mathrm{OH}}$$

Most of the common metals are not affected by dry ammonia, but the presence of moisture will cause ammonia to react rapidly with copper, brass, zinc (galvanised equipment) and many alloys, especially those containing copper. Iron and steel are not affected by moist ammonia, and equipment made of these materials can be used with both anhydrous and aqua ammonia.

Physical Properties

Anhydrous ammonia is a liquifiable gas which is handled in commerce in a liquid form. Though its density varies with temperature, it weighs 5 pounds per gallon at 80°F. Ammonia gas is less than two thirds as heavy as air, and when released into air, rises quickly unless brought down by air currents. It has a gauge pressure of 74 psi at 50°F.

One cubic foot of liquid expands to approximately 850 cubic feet of vapour.

Boiling point at 1 atmosphere (vaporisation poi	nt) -28°F.
Melting point at 1 atmosphere	-107.9°F.
Critical temperature	271.4°F.
Critical pressure	1,657 p.s.i
Vapour density at - 28°F. 1 atmosphere	0.0555 lb/cu.ft
Liquid density at - 28°F. 1 atmosphere	42.57 lb/cu.ft
Specific volume of vapour at 32°F. 1 atmospher	ce 20.78 cu.ft/lb
Range of explosive ammonia - air mixtures	16 - 25% NH ₃ by volume
Ignition temperature (iron bomb)	1.204°F.
Specific heat, (1 atmosphere 60°F)	0.52B.R.U./16/
Solubility in water at 1 atmosphere depends of temperature:-	
32°F.	0.899g. NH ₃ /g water
68°F.	0.518g. NH3/g water
104°F.	0.338g. NH ₃ /g.water
140°F.	0.238g. NH ₃ /g.water
Specific gravity of the gas (air = 1.00)	0.588
Specific gravity of the liquid (water = 1.00)	0.617
Vapour pressure at o°F.	15.7 p.s.i
Vapour pressure at 70°F.	114.1 p.s.i
Vapour pressure at 100°F	197.2 p.s.i
Vapour pressure at 130°F	315.6 p.s.i
Vapour pressure at 150°F.	418.4 p.s.i

Toxicity of Ammonia

Adams et al (1965) described the critical gaseous ammonia concentrations for humans.

II. Table - Ammonia Toxicity

Ef	fects on unprotected worker	Concentration parts per million		Exposure period
1.	Least detectable odour	50)	Permissible for
2.	No adverse effects for average unprotected worker	100)	8 hour working day.
3.	Causes irritation of the throat	400)	Ordinarily no serious results following
4.	Causes irritation of the eyes	700)	infrequent exposure (less than 1 hour)
5.	Causes convulsive coughing	g 1720		No exposure permissible (may be fatal after short exposure - less tha half an hour).
6.	Causes respiratory spasm, strangulation, asphyxia	5000		No exposure permissible, rapidl fatal.

Care must be taken when handling ammonia gas for it is very soluble and will readily dissolve in the perspiration of the body (Adams et al, 1965). It can cause caustic burns which vary in severity with the length of exposure. A two per cent concentration is generally the maximum tolerated by the skin for more than a few seconds as ammonia causes freezing due to the evaporation of the liquid.

Persons working with ammonia should wear suitable protective clothing, including as masks, rubber gloves and other rubber clothing. A person overcome or burned by ammonia should be placed under the care of a doctor. Immediate artificial respiration should be carried out if the person has been asphixiated. The symptoms resulting from exposure to ammonia gas may be nausea, vomitting, pain in the abdomen and throat, weak and rapid pulse, convulsions, burning of the eyes and coughing.

Aqua Ammonia

Aqua ammonia is a colourless liquid with the same pungent odour as anhydrous ammonia.

The general properties of aqua ammonia are listed as follows:-

0 fra-t	
Ammonia content	25.0%
Nitrogen content	20.6%
Salting out temperature	103°F.
Calcium carbonate equivalent per 100 lb.material	37.1
Vapour pressure (gauge) at 60°F.	-9 p.s.i
104 ⁰ F	2 p.s.i
120 ⁰ F	8 p.s.i
Specific gravity at $60^{\circ}F$	0.911
Weight of solution per gallon at $60^{\circ}F$	7.60 pounds
Weight of nitrogen per gallon at $60^{\circ}F$	1.56 pounds
Volume per 100 pounds of nitrogen at 60°F	64.1 gallons

CHAPTER 3

BEHAVIOUR, DISTRIBUTION AND EFFECTS OF AMMONIA IN THE SOIL

Soil application of anhydrous ammonia takes advantage of the rapid expansion of the liquid to a gas and its high affinity for water. Several chemical processes begin as soon as ammonia (NH_Z) is injected into the soil (Murphy and Schrader, 1965):-

Firstly there is the conversion of amnonia gas into ammonium ions (NH₄). In practise the liquid flows into the soil where it is deposited at a depth of about 6 inches. On release it expands to a gas, spreads out in the soil and dissolves immediately in soil moisture forming ammonium hydroxide, which then dissociates into hydroxyl and ammonium ions.:-

$$NH_3$$
 + H_2O \longrightarrow $NH4OH$ \longrightarrow OH + NH_4^{\dagger} Ammonium Hydroxyl Ammonium Hydroxide Ions Ions

Ammonia also forms ammonium ions in contact with acid clay particles and with humus and organic compounds:-

Thus in the process of conversion from NH_3 to NH_4^{\dagger} , the ammonia molecules accept hydrogen ions (H †) from a soil source and become

positively charged ammonium ions. The formation of ammonium ions converts ammonia gas, which is toxic to living matter, to a form which can be utilised by soil micro-organisms and higher plants.

The next process is adsorption, whereby ammonium ions, formed with the initial reactions with water, clay and organic matter attach themselves to soil mineral particles. Ammonia may be absorbed on soil colloids by a variety of reactions. The reactions are extremely important from the standpoint of fertiliser usage for two reasons:-

- The adsorption itself prevents loss of ammonia molecules to the atmosphere and so preserves it in the soil for plant and microbial use.
- 2. Some of the adsorption mechanisms convert ammonia gas directly to the ammonium form.

Adsorption of ammonia occurs due to physical and chemical reactions.

1. Chemical Adsorption

This occurs when ammonium ions become bonded to clay particles due to electronegative attraction. Ammonis is converted into ammonium ions prior to, or simultaneously with chemical adsorption, since ammonia has to be in this positively charged form before bonding to the specific sites on clay particles can take place. Ammonium ions held in this way are considered to comprise the soil's exchangeable ammonium supply. Buckman and Brady (1964) state that

the ammonium ion is about the same size as the potassium ion and therefore both are subject to fixation by similar minerals. Illite and related clays have a significant ammonia fixing capacity. In this form nitrogen is not subject to rapid oxidation but may slowly become available to plant roots. Chemical reactions tend to hold ammonia very strongly and they may be represented by the following equation:-

2. Physical Adsorption

Physical adsorption is characterised by weaker bonds between the ammonia and the clay, than occur in the chemical reactions. Physical adsorption takes place only where there is a positive pressure of ammonia in the soil. As soon as the pressure of ammonia in the gaseous phase is reduced, the physically adsorbed ammonia will return to the gaseous form and diffuse through the soil where it may react with soil water, clay, organic matter or perhaps volatilise into the atmosphere.

Physical Adsorption of Ammonia

Anon (3) (1966) stated that ammonium adsorption by the soil was dependent on the following factors:-

- 1. Soil texture.
- 2. Soil structure.
- 3. Moisture content of the soil.
- 4. pH of the soil.
- 5. The organic content of the soil.

Soil Texture

Soils of heavier texture will have a greater capacity to hold ammonia than lighter soils, since those with more clay will have a higher cation exchange capacity and thus will have more exchange sites to hold ammonium ions. At very high rates a low cation exchange capacity could limit the ability of the soil to hold ammonia, however this does not become a problem at lower rates.

Soil Structure

Poor soil structure influences the ability of a soil to hold ammonia as it can limit the spread of gas in the soil. There will be more ammonia retained in a well-structured clay than there will be in an impervious clay since gas spreads further when soil has good tilth. The fact that ammonia can spread further in the soil brings it into contact with more cation exchange sites. However the level of exchangeable bases (Ca, Mg, Na, K.) already present determines the amount of physical and chemical adsorption which takes place.

Soil Water

Although ammonia is very soluble in water it is not essential to have a high moisture content in the soil (Anon (1) (1966). The clay and organic matter content of the soil are of much greater significance. The main problem in dry soils is holding the ammonia in the soil for the short time that is needed for it to become attached to clay or organic matter. Dry soils may be cloddy and may not seal properly, but if they are dry and in good physical structure, dry soils will actually hold more ammonia than moist soils. Anon (1966 (1)), proposes that the best soil moistness for ammonia retention in the soil is between 15 - 18% moisture content (Field capacity being 23% moisture content in clay soils).

Parr and Papendick (1966 (1), 1966 (2), 1967), carried out a series of pot trials in which they examined the adsorption of ammonia in soils of varying moisture content. They came to the conclusion that air dry and oven dry soils will hold more ammonia than soils of higher moisture content. However in the most recent trials they concluded that soil moisture content at time of ammonia application is not a critical factor in the retention of ammonia by soil, but that it is important in providing adequate physical soil conditions to insure rapid and complete closure of the injection channel.

The pH of the Soil

In theory acid soils should adsorb more ammonia than neutral soils since there are more available hydrogen ions to combine with ammonia to form ammonium ions. In practice, however, ammonia is

effectively absorbed at normal commercial rates of application even by soils containing free calcium carbonate (Anon, 1966. (1)). For conversion of ammonia in the soil in the process of nitrification, a pH of 6.5 to 7.0 is optimal for the best bacterial action (Beers, 1966).

The Organic Matter Content of the Soil.

As indicated in Part I, Chapter 2, organic matter plays a key part in the nitrogen cycle in soil. Smith & Case (1966), state that approximately 50% of ammonium ions retained in soils are contained in organic matter. This is due to the available surface area and the number of cation exchange sites being greater weight for weight in organic matter than in clay minerals. Of the ammonia adsorbed by organic matter at least 75% is in a form readily available to plants (Anon, 1966 (1)).

The Importance of Rate of Nitrification

The speed of nitrification, i.e. the time that it takes for ammoniacal nitrogen in soil to be oxidised to nitrate nitrogen has an important bearing on the application of ammonia fertilisers to soils. Nitrification is most rapid when the soil temperature is between 65 to 90°F. Outside this range micro-organisms become less active until nitrification is considered to cease when the soil temperature falls to 32°F. or below. This is made use of in America by the application of ammonia in autumn. If temperatures are low enough, nitrification will not occur during winter and thus nitrogen can be safely held in the soil ready for spring sown crops.

Nitrate nitrogen would be much more susceptable to loss from the soil (as discussed later). Nitrification is often rapid at the end of a dry summer and in warm moist conditions of spring.

Conversely, nitrification will often be reduced when there are high crop residues in the soil and when it is too dry or very wet.

Other factors which can affect the rate of nitrification are the supply of nutrients, particularly calcium, soil pH, soil aeration and chemical ammonium retention in soil (Murphy and Schrader, 1965).

DISTRIBUTION AND EFFECTS OF AMMONIA APPLICATION IN THE SOIL

Patterns of Distribution in the Soil.

Parr and Engibous (1965) stated:-

"It has been shown that immediately following injection of anhydrous ammonia into soil, high concentrations of ammonia and ammonium ions are retained in a localised, horizontal cylindrically shaped zone with diameter ranging from 1 to 3 inches depending on the rate of application, soil texture, soil organic matter and soil moisture."

This means that there will be an area of very high ammonia concentration which is toxic to micro-organisms in that area. As a result of this, the retention zone can remain partially sterilised for several weeks. If conditions are suitable, nitrification begins at the periphery of this area and gradually the concentration of ammonia is reduced.

Ammonia in concentrated zones in the soil will take up to eight weeks to completely nitrify under good nitrifying conditions.

Thus if conditions are optimal nitrogen remains in soil as ammonia and is not leached out as nitrates nor lost by dentrification (Beers, 1966).

Blue and Eno (1954), found that in sandy soils with rates of 58, 115 and 258 pounds per acre of ammonium nitrogen, ammonia accumulated in zones from 2 to 8 inches wide, depending on the soil moisture content. Most of the ammonia was usually concentrated in a three inch zone even at the highest rate. Papendrick and Parr, (1966), carried out detailed greenhouse pot trials which demonstrated that most of the ammonia from a single 680 mg injection of ammonium-nitrogen was subsequently found to be within a 5 cm radius around the injection point. They also found that the order of retention observed within a 3 cm radius around the injection point was:-liquid ammonia in moist soil greater than gaseous ammonia in moist soil, greater than liquid ammonia in air dry soil, greater than gaseous ammonia in air dry soil.

McIntosh and Frederick (1958), injected anhydrous ammonia by field application into sandy clay loam, at rates of 60 and 120 pounds of ammonium nitrogen per acre. In summer they found that ammonium nitrogen decreased from a maximum of 1300 to 1200 ppm. (pH 9.5) at the centre, to less than 200 ppm. (pH 8.0) in the area about $1\frac{1}{2}$ inches from the centre of the retention zone. After two weeks maximum concentration of ammonium nitrogen was 800ppm. (pH 9.8) in the centre to less than 100ppm. (pH 7.0) in the area about two inches away from the centre of the retention zone. Thus the high

concentration of ammonia in soil during summer application falls off quickly to low levels of ammonia nitrogen within a month. They concluded that the falling concentration is due in part to the diffusion of ammonia from the application zone, and in part to nitrification of the applied ammonia. McIntosh and Frederick, (1958) also stated that autumn applications made in America when soil temperatures are declining, will remain as ammonia until the temperature rises above 40°F. in the spring.

It is therefore important to apply anhydrous ammonia at the right depth in the soil to reduce volatilisation losses. particularly important in neutral and alkaline soils where it is essential to release ammonia at not less than 6 inches below the soil surface. This depth is sufficient to prevent loss to the atmosphere from the retention zone and subsequent movement out of this A good understanding of the retention of ammonia in soil is important from the agronomic point of view to avoid damage to seedlings or seeds at planting and to be aware of the persistence of the retention zone so that injection will not be made too close to plants and ammonia levels will not be toxic when plant roots reach this area in the soil. Tillage of soil in close proximity to the retention zone should be avoided and injection should be carried out when the soil is in good physical condition to avoid losses, (Parr and Engibous, 1967).

Effect on Nitrification and Acidity in the Soil

Duisberg and Buehrer (1954), applied anhydrous ammonia to soil and studied the effects on nitrification and oxidation products within the plants. They found that pH showed a pronounced drop in the first few days, even though concentrations of the various forms of nitrogen remained constant. As nitrification proceeded the pH value levelled off, nitrite rose to a peak on about the tenth day and ammonia levels steadily fell whilst nitrate levels rose. The nitrification process is probably completely inhibited within the retention zone where the concentration of ammonia is usually about 30ppm. However in the field nitrification proceeds towards the centre of this area from the periphery. Therefore nitrifiers gradually reduce the concentration of ammonia centripetally until all of it is utilised. (Eno et al, 1955).

The application of ammonia to soil causes a sudden rise in pH, however as nitrification proceeds the pH value drops. The overall effect is to lower the pH of the soil. The initial rise in pH can be as high as 9.5, depending on soil type (Adams et al, 1965).

Continual use of ammonia may lower soil pH but this can be easily corrected by liming. Lowered pH has become a major problem in certain soils in the United States of America, where the pH of the subsoil has dropped rather low due to continual deep injection of ammonia.

Effect on Fungi and Micro-organisms in the Soil

Eno and Blue (1954) and Eno et al. (1955) carried out trials to study the effect of ammonia on the microbiological population in soil. Numbers of nematodes, fungi and bacteria were measured in the retention zone after a normal rate of approximately 600 ppm ammonia was applied. It was found that the nematode population was reduced to 0.6% of its original level and fungi to 4.9%. The numbers of bacteria and actinomycetes increased after a period of three days. After the first day it was found that the numbers of nematodes, fungi and bacteria were reduced, but this was only temporary in respect of the bacteria. It was also noted that toxic effects were restricted to a three inch zone around the point of injection. It was found that ammonia acted as quite a strong fungicide since the effect on fungi lasted for at least 38 days. It was concluded that from a total population standpoint these effects are not likely to permanently disturb the ecological balance in soil.

Other Effects

The application of ammonia to soil can also affect the availability of nutrients in soil. Ammonia tends to increase the availability of phosphorus and potassium in soil, while levels of readily available calcium are reduced (Stanley and Smith, 1956). However total exchangeable calcium in soil is not greatly affected and the magnitude of these effects is not very great.

In some cases nutrient release by ammonia is an unexpected

bonus in its use (Anon 1965 (1)). The presence of high concentrations of ammonia in a localised area can also cause a partial breakdown of soil organic matter for a short period after application, (McDowell and Smith, 1958). High concentrations of ammonia will inhibit seed germination and subsequent growth of plant roots in the region of high ammonia levels (Duisberg and Buehrer 1954).

CHAPTER 4

METHOD OF APPLICATION

Application of anhydrous and aqua ammonia generally requires more complex equipment than that used for the application of other fertilisers since ammonia is mostly applied by sub-surface application. Such methods are only possible effectively, under the conditions outlined in the previous chapter, particularly with reference to texture and structure of soils. A less common but important use of anhydrous ammonia is by surface application in irrigation water. This method has gained prominence in the United States of America and in Australia.

EQUIPMENT FOR SUB-SURFACE APPLICATION

The basic ammonia application equipment consists of a high pressure tank, a metering device, a distributor manifold and injection times. There are numerous variations on this basic design, but three main types are used: the tractor mounted, a trailing unit, and a semi-mounted unit supported by both tractor and trailing unit.

Examples of applicators are shown in Plates II, III, IV and V.

Pressure Tank

There are two types of tank used overseas for the storage of anhydrous ammonia. Firstly there are non-refrigerated pressure vessels, commonly referred to as pressure tanks, where ammonia is stored at atmospheric temperature and pressure. Secondly, there

are also refrigerated tanks where ammonia is stored at relatively low pressures. High pressure tanks are used with application equipment and are designed for pressures of 50 psi.

They are hydrostaticly tested (in U.S.A) at time of manufacture to about one and a half times the designed tank pressure. Thus, a pressure tank with a designed pressure of 250 psi would be hydrostaticly tested to 375 psi (Anon (1) 1965). All metal equipment which comes in contact with ammonia is preferentially made out of steel or iron. Most common metals are not affected by ammonia, but the presence of moisture will cause ammonia to react rapidly with copper, brass, zinc (galvanized equipment) and many alloys, especially those containing copper (Adams, 1965). Most tanks are cylindrical with rounded ends. On many tanks being used for the application of these materials overseas, fittings are screwed into threaded holes in welded-on plates which are called "island bars". On mobile tanks mounted fittings are commonly protected by metal guards which surround them. Basic fittings are shown in Figure VI. These fittings are used to ensure that the pressure and level of the liquid in the tank is fully known, and that it can be emptied with complete safety.

Two different types of arrangement of the valves are shown in the diagram. The bleed valves are used to remove liquid or vapour via a hose or larger valve before disconnecting; they can also be used to indicate when the tank has been filled to the 85% level.

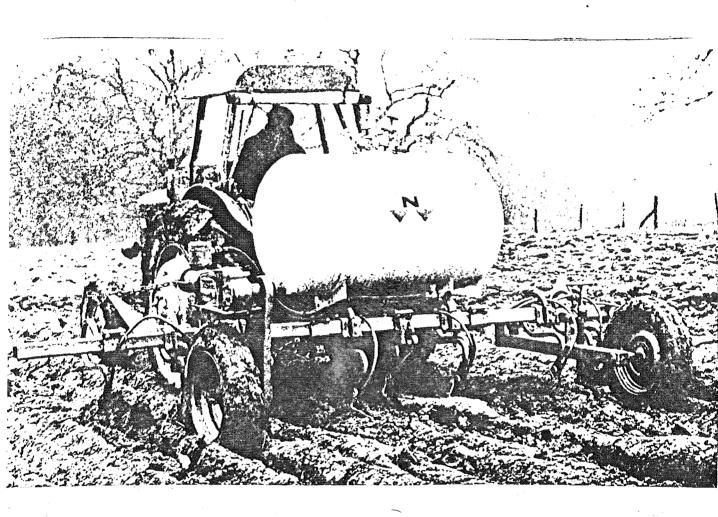


PLATE II

Anhydrous ammonia applicator tank mounted on a cultivator unit for application to ploughed land.

(Reprinted from Direct Nitrogen Limited).

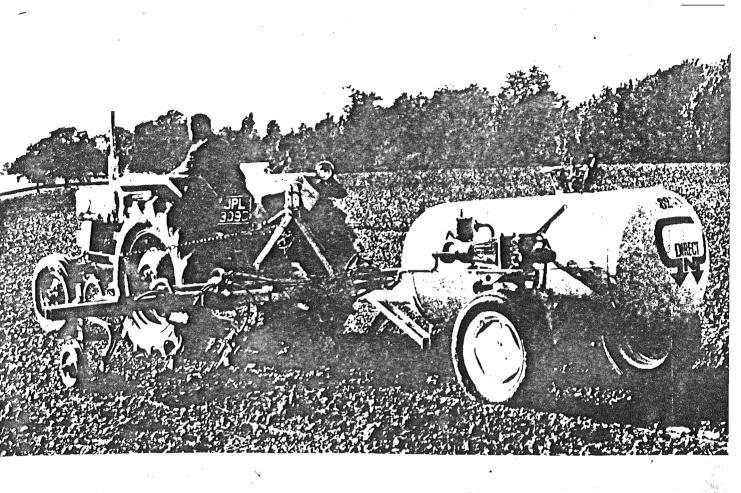


PLATE III

A supply tank of Anhydrous Ammonia towed by a tiller unit. (Reprinted from Direct Nitrogen Limited).

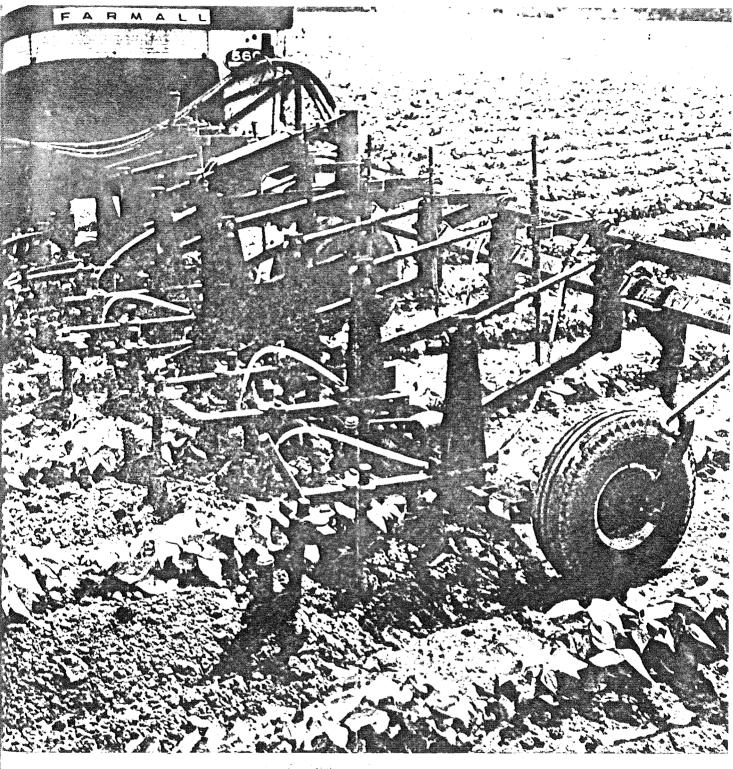


PLATE IV

Row Crop Application.
(Reprinted from American Vegetable Grower) (Anon (6)).

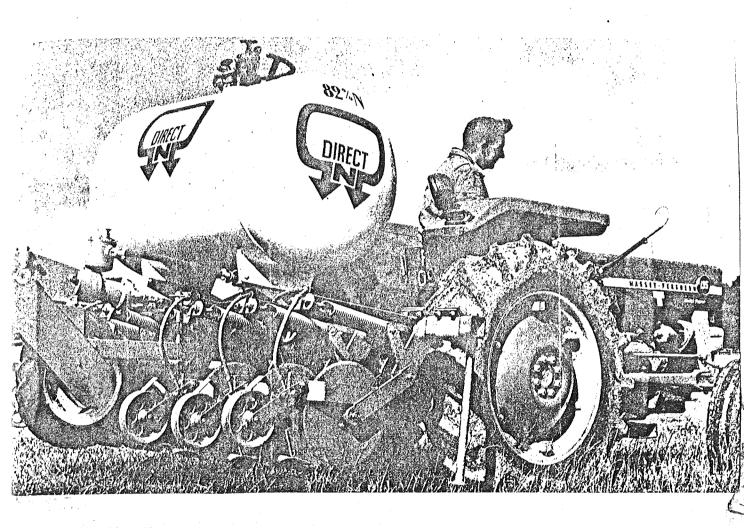


PLATE V

A grassland anhydrous ammonia applicator.

(Reprinted from Direct Nitrogen Limited).

Thermometers may also be used on tanks where the density of ammonia needs to be computed.

Ammonia Flow Regulators

The next basic part of an ammonia applicator is the metering device. The accurate application of anhydrous ammonia requires it to be metered either as a liquid or a gas. However, mixtures of these two states will cause errors in measurement and application. In practice ammonia is measured as a liquid, and the devices currently used can be divided into to types:

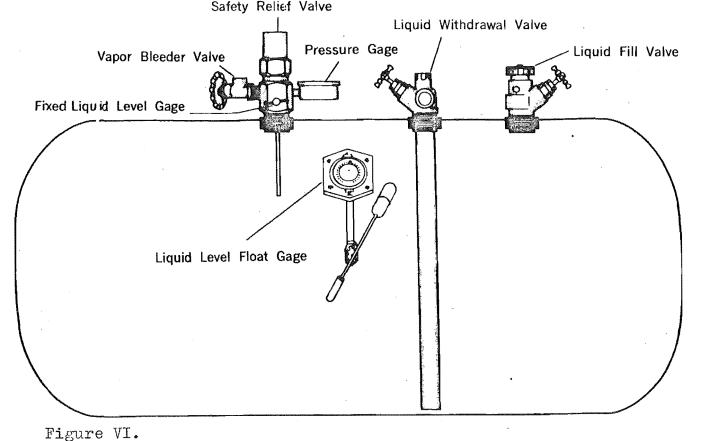
- 1. Pressure
- 2. Pump

1. Pressure System

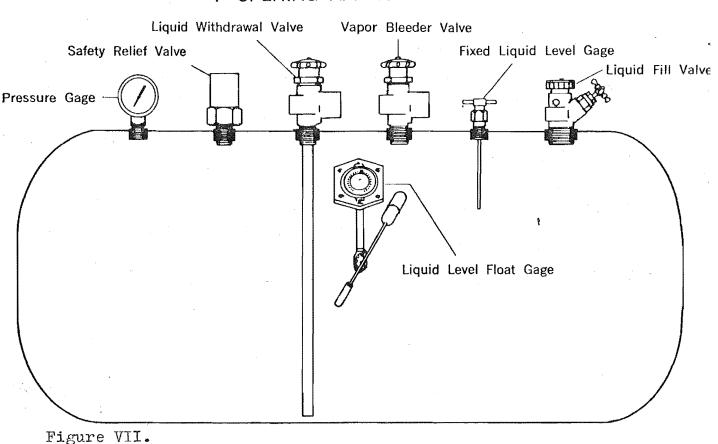
The amount of liquid delivered by the pressure system per linear foot of travel of the distributor is dependent on (Adams, 1965):

- (i) gauge pressure of the contained liquid.
- (ii) orifice size
- (iii) Static Line pressure.
 - (iv) speed of the applicator rig.

A uniform pressure and a constant speed of travel are necessary to maintain a uniform rate of application. Hedman and Turner (1954) studied the effect on application of various vapour to liquid mixtures and of adiabatic expansion from saturated to liquid ammonia. They correlated the density variations with changes in pressure with different initial pressures and stressed the



4 - OPENING APPLICATOR TANK



7 - OPENING APPLICATOR TANK

importance of maintaining a constant fluid density. They also came to the conclusion that ammonia flow rate is principally controlled by the following four factors - rate of application, tool bar width, application speed, and ammonia pressure.

There are three types of pressure regulators:

- (1) Orifice or needle valve.
- (2) Adjustable pressure type.
- (3) Variable orifice regulators.
- (1) The orifice or needle-valve type are the simplest type of regulating device but they do not compensate for changes in tank pressures. Thus different sized orifices must be substituted, or the needle valve adjusted, for each pressure change or when another output rate is wanted.
- (2) With the adjustable pressure types the pressure of the ammonia within the regulator, against fixed output orifices, determines the amount of ammonia injected. This type is more accurate than the previous one.
- (3) Variable orifice regulators depend on control by a single built-in variable orifice. Settings are made on gauges on the regulator bodies. This eliminates the need for calculations which are required in other pressure regulating devices.

2. Pump System

Ammonia metering pumps are the most accurate means of controlling application rate. This consists of a variable stroke

displacement pump and heat exchanger. The metering pump is driven from the rear axle of the tractor or from one of the wheels of a trailer applicator with length of stroke controlling amount of liquid entering the distributor manifold. This system must be equipped with a heat exchanger to prevent liquid vaporising and entering the metering cylinder. Length of the pump stroke is adjustable to raise or lower the output and the number of strokes per foot of travel can be varied using different drive-gear ratios. After a desired rate of application has been calibrated for a ground-driven displacement pump the rate per acre is fairly constant regardless of the speed of travel or variations due to uneven ground.

The principal disadvantages of this system are the relatively high initial cost and the expense of annual servicing which is an essential requirement of this type of equipment (Adams, 1965, Anon (a) 1965).

The principles governing application of anhydrous ammonia to soil are also applicable to aqua ammonia. Solutions are forced into the distributor manifold and through applicators by air compressors or solution pumps driven by a power takeoff or geared to the drive wheel of the tractor. A pressure regulating valve is required when using a compressor. This valve should be placed between the compressor and the solution tank to maintain a constant pressure in the solution tank regardless of the quantity of solution

and changes of temperature in the system but there is usually a certain amount of pulsation irrespective of which pump is used. A wide variety of pumps working on the tractor power take-off, such as centrifugal, disphragm, gear, piston and roller are used. Uniform application rates are difficult with these pumps as it is necessary to have a constant ground speed.

DISTRIBUTOR MANIFOLD

The distributor manifold provides an equal amount of liquid/ gas mixture, to the individual times. Hose nipples or combination nipple-orifices are screwed into the outlet holes.

Injection Tines

These are the actual soil injection parts of the applicator which resemble knife coulters on a plough. There are several applicator knife designs from the conventional, thin evenly sloping type, to backswept and chisel-faced modifications. They are attached to a tool bar and cut into the soil to allow the applicator tube to discharge ammonia at the required depth. The applicator tube consists of a small metal pipe welded to the back of each tine and through which the liquid/gas mixture passes. A sealing device follows the tine and covers in the knife cut, thus reducing vaporisation losses. There are many types of sealers, such as packer feet, rod coverers and press wheels.

SURFACE APPLICATION

Both anhydrous and aqua ammonia can be used in irrigation water, and in addition diluted solutions of aqua ammonia have been applied

with sprinklers to increase foliar absorption. However, care must be taken to ensure that there is a low concentration to avoid leaf burn.

Adams (1965) states that application of pressure liquids in surface irrigation water needs careful design since on soils with high infiltration rates an excessive quantity of nitrogen may be found close to the water inlet. With anhydrous ammonia it may also be necessary to add sodium hexametaphosphate to prevent objectionable deposits of calcium carbonate on pipes and valves when hard water is used.

Anhydrous ammonia is metered from cylinders under its own pressure. Cylinders are laid horizontally on the ground adjacent to head ditch or standpipe. The ammonia from a single cylinder or in a manifold connecting two or three cylinders is measured into the irrigation water through a hose connected to the metering orifice. The rate of flow through the orifice is controlled by orifice size and ammonia pressure which is regulated, in turn, by a control valve.

Application of aqua ammonia to surface irrigation water also requires little equipment for the solution can be added using gravity. Adams (1965) states that in the United States of America tanks with extensible legs are carted to the site and set up in their raised positions. A manually-operated control valve regulates flow of aqua ammonia through a rubber hose into the irrigation water. Atmospheric pressure is maintained in the tank by venting it to the

air and nitrogen losses through the aperture are negligible.

These mobile trailer tanks can be used for both anhydrous and aqua ammonia.

LOSSES DURING SUB-SURFACE APPLICATION

Losses during sub-surface application are primarily due to vaporisation although nitrogen salts in aqua ammonia exert no vapour pressure and are not subject to loss. One of the first essentials, particularly with sub-surface application, is to have efficient leak-proof equipment while adequate sealing of the knife cut made by the times on an applicator rig is equally important. It has already been stated in the previous chapter that sub-surface application is most efficient when soil is in good physical condition. For example, it would be hard to seal ammonia in soil with a dry lumpy seedbed.

LOSSES DURING SURFACE APPLICATION

Surface application is subject to greater evaporation losses than sub-surface application, particularly if the soil has a low infiltration rate. Adams (1965) points out that a wide range of nitrogen losses when ammonia is applied to irrigation water have been recorded. He quotes workers who have estimated evaporation losses as being negligibly small to one who quoted losses exceeding 26% under conditions of high water temperature and very low soil permeability. Losses from irrigation water can be minimised by irrigating in cool humid weather, maintaining a concentration not over 110 ppm of ammonia, and keeping the exposed surface of flowing

water to a minimum by reducing the turbulence of the water and by using narrow but deep ditches (Adams, 1965).

Butler and Smith (1962) made a comprehensive study of ammonia losses using surface application from both tandom discs and mouldboard plough equipment. They reported that losses with a mouldboard plough were reduced to an acceptable level with a plough depth of 6 inches or more, a hose length of 3 feet running behind each plough body, and a lateral hose position of 4 to 8 inches from the furrow wall. Distribution was also found to be excellent for both types of machinery for rates up to 500 lb. of ammonia per acre. They stated that 90% of ammonia loss with both types of equipment occurred in the first 30 minutes and 97% within an hour of application, and that as a general rule on silt or silty clay if no ammonia could be seen rising then losses from tillage application should be less than 1%.

Storage

The pressure tank and its construction requirements was discussed when the applicator tank was described earlier in this chapter. In the United States of America anhydrous and aqua ammonia are required by farmers in spring and autumn. Ammonia plants, to keep running efficiently, produce ammonia all through the year and therefore storage is an important factor in usage of anhydrous and aqua ammonia.

Anhydrous ammonia is usually stored at the producer plant in

large spherical refrigerated tanks. These are called "Hortonospheres", have a capacity of several hundred thousand gallons and have moderately low working pressures. As ammonia vaporises within the sphere a compressor draws off the vapour, compresses it into a liquid and returns it to the sphere. Insulated spheres are used in some cases and ammonia is maintained at a temperature of -28°F. with a vapour pressure equivalent to 6 inches of water. Some producers store anhydrous ammonia in batteries of 30,000 gallon pressure tanks. Still others convert anhydrous ammonia to aqua ammonia and store it in low-pressure tanks. Plate VI shows a bulk dealer's plant where Hortonospheres, bulk tanks, and nurse tanks are visible, and Plate VII shows filling of an applicator tank from a nurse tank.

In United States of America storage of anhydrous and aqua ammonia at bulk distribution centres is usually be means of 15 - 30,000 gallon pressure tanks or in batteries of tanks with a 6,000 gallon capacity. The next smaller forms of storage are portable trailer or nurse tanks and farm storage tanks. Trailer tanks commonly have a 500 to 1,000 gallon capacity. Aqua ammonia can be stored in low pressure vertical tanks. Applicators can vary from 10 gallon to 750 gallon trailer rigs.

Transportation

Ammonia is transported by road, rail and water in the United States of America. A vast fleet of railway tankers carrying up to

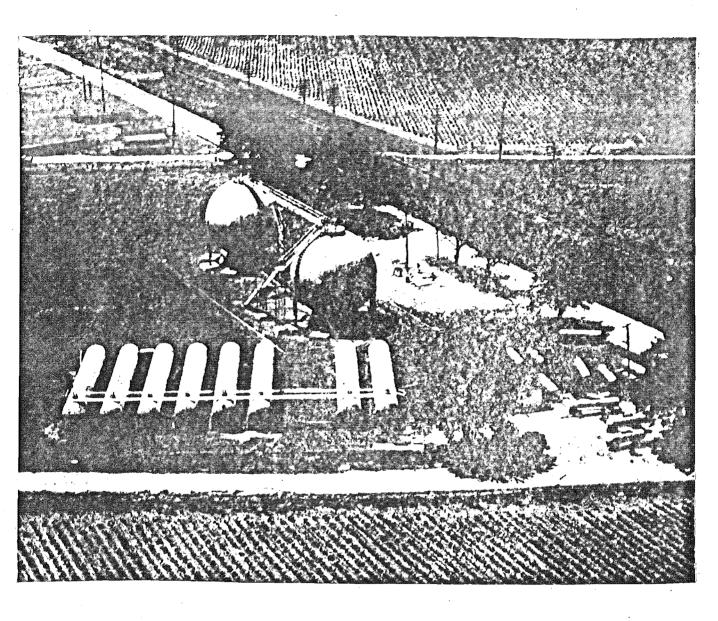


PLATE VI

Three types of Anhydrous Ammonia storage tanks are seen in this view of a bulk terminal. The 2 round tanks, centre, are Hortonospheres; the cylinders, left foreground, are 30,000 gallon pressure tanks; the trailer tanks, right foreground, are 1,000 gallon nurse tanks.

(Reprinted from Anhydrous Ammonia Handbook) (Anon (1)).

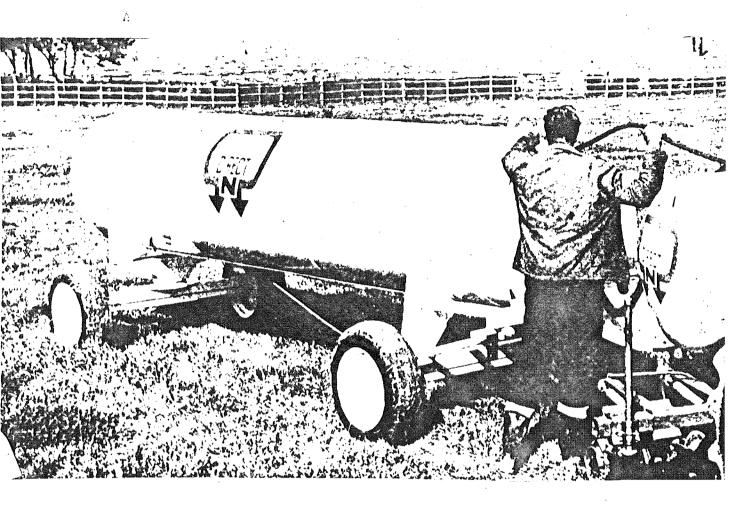


PLATE VII

The nurse tank is used to transport ammonia from the storage tanks to the farm and, as shown above, is used as a refill source for the applicator feed tanks.

(Reprinted from Direct Nitrogen Limited).

10,000 gallons or 25 to 26 tons of ammonia under high pressure is used each year to transport anhydrous ammonia from producer to distributor. These tankers, referred to as "tank cars" are one of the major means of transport in the United States of America.

Sea transport is used by several producers in the United States. (Adams (1965) states that the first use of an ocean tanker was in 1953 when aqua ammonia was carried from California to Hawaii. Inland waterways are also utilised - making use of barges. This is a very economical method since one barge may carry 6 tanks with a total of 400,000 gallons of anhydrous ammonia.

Road transport from producer to distributor centre and thence to farmer is also of major importance in the United States of America and in Britain. Road transport is used for movement of large articulated trucks with capacities from 6,000 to 9,000 gallons in the United States, Britain and Australia.

Equipment for small scale Trial Work

There have been very few laboratory or glasshouse studies of anhydrous (or aqua) ammonia although it has become the leading source of N for direct application to soils in the United States of America (Parr and Papendick, 1966 (1)). However, in recent years apparatus for dispensing small quantities of anhydrous ammonia for laboratory and glasshouse work (Papendick and Parr, 1965), Papendick and Parr, 1966) and (Parr and Papendick, 1967) has been developed

at the Tennessee Valley Authority in the United States of America.

A British company has also developed a hand-operated device for accurate placement of small quantities of liquefied ammonia (Anon (10), 1968). This hand-operated device consists of a 4 lb. cylinder with a hose coupling connected to a hand-operated lance or injecting probe.

CHAPTER 5

CROP RESPONSES TO AMMONIA FERTILISERS

EARLY USAGE AND HISTORY OF TRIAL WORK

More than a century ago Liebig suggested the possibility of using ammoniacal liquors from coal gas plants as a source of fertiliser nitrogen. Adams (1965) reports usage of ammonical solutions on grassland in the 1840's - both in Scotland and in England. Anon (1) (1965) reports that early workers such as Maze in France about 1898 and Prianischnikow, a Russian, about 1900, had successfully experimented with ammonia as a fertiliser but their work was overlooked. In 1908 the Haber-Bosch process for synthetic ammonia production was first initiated and although it was soon developed on a commercial scale, use of anhydrous ammonia as a fertiliser was still a long way off, and increasing ammonia production was largely utilised for military and industrial purposes.

J.O. Smith, of the Mississipi Delta Branch Experimental Station, first used anhydrous ammonia by direct application in 1930 (Anon (1), 1965). Smith used a small ammonia cylinder on a plough pulled by a mule. However, this work waited another fifteen years before general commercial adoption.

Agricultural progress and the economic climate in the United

States of America was not ready for nitrogen fertilisation as a basic

farming practice, except in a few intensive cropping areas.

The most significant early step in the use of anhydrous ammonia in agriculture and horticulture came in 1932 when it was first applied in irrigation water (Anon (1), 1965). This work was extended to the point where water application of anhydrous ammonia was a substantial commercial business on the West Coast of the United States of America by the mid 1930's. Adams (1965) states that study of soil injection of anhydrous ammonia was begun in California shortly after application of this fertiliser in irrigation water had gained acceptance. Injection into soil proved feasible, and the first commercial application was made in California in 1939. Direct application of anhydrous ammonia was limited until supplies became plentiful after World War II.

LABORATORY WORK

In the United States of America Jackson and Chang (1947) carried out one of the first laboratory experiments. They used 800 ml. beakers, containing 1 kgm. of soil, to study the retention of anhydrous ammonia. Stanley and Smith (1956) described the use of stainless steel laboratory equipment to study the effect of soil moisture and depth of application of anhydrous ammonia. They reported that movement of ammonia within soil was least when the soil was of a good tilth. They also noted that there was a slight effect on availability of nutrients such as potassium, phosphorus and calcium. Sohn and Peech (1958) studying retention of anhydrous ammonia in glass bottles filled with soil found that in many cases

organic matter accounted for 50% of the ammonia retention.

Papendick and Parr (1965 and 1966) developed equipment for laboratory and glasshouse trial work at Tennessee Valley Authority in the United States of America. They followed this work up with a study of agronomic efficiency of ammonia using three glasshouse pot experiments in which they found that corn appeared to be remarkably resistant to high levels of anhydrous ammonia although some reduction of yield occurred due to root damage (Parr and Papendick (1) 1966). Their next studies involved an investigation into the effect of ammonia concentration and soil moisture on retention, which was discussed in Chapter 3, part 2 (Parr and Papendick (2), 1966). The distribution of ammonia, which was also discussed in Chapter 3, part 2, was examined in experiments at the Tennessee Valley Authority and related to agronomic efficiency of anhydrous ammonia (Parr and Papendick, 1967; and Engibous, 1967). An interesting new development in the study of anhydrous ammonia has been the development of anhydrous ammonia-Parr and Papendick (3) (1966) described sulphur solutions. trials with corn kn which these solutions compared favourably with other forms of sulphur fertiliser. Scott and Tisdale (1965) state that numerous compounds are quite soluble in anhydrous ammonia: the metal ammonium salts of copper and zinc, zinc nitrate, zinc oxide, elemental sulphur and elemental white phosphorus. They also state that while many more substances are soluble in ammonia it is

apparent from the examples given that the value of anhydrous ammonia as a fertiliser may be increased if techniques for dissolving and applying certain plant nutrients in this solvent can be developed.

PRACTICAL USES IN GRASSLAND AND CROPPING

Trials in America, notably in Mississipi, indicate that in years with average rainfall ammonia is just as efficient a fertiliser as ammonium nitrate: while in dry years ammonia is more effective. However, work done in Denmark and England has shown that anhydrous ammonia was inferior to materials like sulphate of ammonia (Van Burg and Van Brakel, 1965), Cook, 1966), Jameson, 1959), and Hunter and Jarvis (1953-54). It was found in Denmark that nitrolime gave much higher yields and that the effectiveness was partly dependent on having very thin times (Van Burg et al. 1967). Jeater (1966), in England, found that the action of agua ammonia was very slow and that the yields on pasture were 4 - 20% lower than those obtained from equivalent amounts of solid fertiliser. Also in England, Webber (1957) experimented with gas liquor which is a crude form of ammonia liquid with 1 - 4% N. Gas liquor was sprayed on the surface and as a result care was needed with applicators and weather conditions to avoid scorching. Webber found that grass yields were 75% or less of those obtained for sulphate of ammonia. Jameson (1959) and Tod and Simpson (1956) also found, in England, that gas liquor depressed yields by comparison with other nitrogen fertilisers. Andrews (1956) reports that anhydrous amnonia compared very favourably with other sources of nitrogen in American trials.

Wheat, Oats and Barley

Andrews (1956) reported on a large number of preliminary trials which were carried out in America. Although variable results did emphasise the importance of applying fertiliser ammonia at the right time and when soil microbes are able to carry out nitrification on this ready source of ammonia. In general, the use of anhydrous ammonia was fully as effective as ammonium nitrate in promoting growth of these crops. Adams, et al. (1965) mentions other workers who have found that anhydrous ammonia substantially increased yields, and in other cases where it was equally effective.

In England Jameson (1959) found that winter wheat responded equally well to anhydrous and also to aqua ammonia as it did to other solid nitrogen fertilizers. Jeater (1966) also found, in England similar results with spring barley but in the case of winter wheat the results were not as good because it was considered ammonia was applied too late.

Potatoes, Sugar Beet and Kale

The area of potabes in New Zealand during the 1965-66 season was 24,434 acres (Anon (7) N.Z. Yearbook, 1967). In trials in England Jeater (1966) found that ammonia applied during potato planting gave equal yields to soil nitrogen fertilizers but later application of ammonia gave reduced yields by comparison. Andrews (1956) states that in trials carried out in America in 1954 by Lorenze irrigation of aqua ammonia gave much lower yields than the use of sulphate of

ammonia. Andrews also reports that anhydrous ammonia on potatoes compared favourably with calcium ammonium nitrate, and, in Denmark, was superior to sulphate of ammonia.

Van Burg (1967) reported on trials which he carried out in the Netherlands between 1936 and 1966. In the 1965 season much higher yields from potatoes and also sugar beet were obtained with anhydrous ammonia rather than conventional fertilizers. trials were carried out in 1966, on 3 soil types using these two crops, and it was found that injecting ammonia 1 - 3weeks rather than 5 - 9 weeks before sowing or planting was much more satisfactory. Van Burg found that increasing nitrogen improved yields using conventional fertilisers but yields were depressed by increasing rates of anhydrous ammonia. Spacing of injectors was also examined by Van Burg. It was noted that very uneven stands of potatoes developed when the injectors were 90 cms apart, but at 60 cms the difference was not great, compared with control plots. Van Burg also reported on trials in which Oats, Spring Wheat, Potatoes and Sugar Beet were grown. It was found that anhydrous ammonia gave higher yields overall than conventional fertilisers. Autumn application of anhydrous ammonia was shown to be of value only when winters were cold as opposed to moist warm or mild winters when nitrification occurred and the fertiliser was consequently leached down into lower soil horizons.

Other workers in Denmark and England found in trials that anhydrous ammonia compared favourably with other nitrogenous

fertilizers for use with kale, sugar beet and potatoes (Mulder, 1953. Hunter and Jarvis, 1953-54, and Jameson, 1959).

Maize

Maize is now quite an important crop in New Zealand, and in the 1965-66 season, 13,920 acres were grown (Anon (7) 1967. Eighty per cent of these crops are grown on the east coast of the North Island, and it is also gaining in importance in Northland (Dunne, 1967). Maize requires about 160 lb. of nitrogen per 100 bushels of crop. This is higher than the potassium and phosphorus requirements which are 40 and 125 respectively (Graham, 1967).

In North Carolina nitrogen is considered to be the most limiting factor for producing corn. Corn yields can increase by about one bushel for each 2 lb. of nitrogen applied within the general ranges of response to nitrogen. It has been found in North Carolina that there were no differences in sources of nitrogen for corn when each was properly applied. However the residual or carry-over effect upon the acidity of the soil must be considered in long-term use of each fertiliser (Krantz and Chandler, 1954).

Other work by Chandler in North Carolina has shown that anhydrous ammonia and aqua ammonia are fully as effective as solid forms of nitrogen in promoting growth of corn. Andrews (1956) carried out large numbers of tests to compare anhydrous ammonia with materials like ammonium nitrate. For example, he found that when anhydrous ammonia was applied at 4 to 5 inches depth and ammonium nitrate was applied on the surface of the soil as early side dressing, the

increase of yield was 7 bushels for ammonium nitrate and 10 bushels for anhydrous ammonia. The inferiority of surface applied ammonium nitrate is attributed to lack of sufficient rain to leach it into the root zone. On average, anhydrous ammonia was slightly superior to ammonium nitrate for both pre-planting and side dressing. The thirteen tests carried out by Andrews on side-dressing also showed a slight superiority for anhydrous ammonia. The rate of application was 32 lb. of nitrogen per acre in these tests. Andrews also refers to a number of trials carried out in Delaware, Florida and Michigan and other areas in the United States where it has been shown that anhydrous ammonia is an equivalent or better fertiliser for corn than other conventional nitrogen materials.

Maize is a crop which is well suited to fertilisation with anhydrous ammonia since it has a high nitrogen requirement, a long growing season over the summer months and has wide row spacings. Since most maize crops are grown in a localised area in New Zealand it may be possible that there is a potential for contract application of anhydrous or aqua ammonia provided that an economic source of ammonia can be found. Large crops of sweet corn which are grown for processing could also be within the range of this technique. Maize growing in these East Coast, North Island, areas has already become quite highly mechanised.

Other Horticultural Crops

Andrews (1956) reports that anhydrous ammonia compared favourably with ammonium nitrate for french beans, cabbage, tomatoes

and sweet potatoes. He found that in order to avoid damage to young plants a six-inch depth of application, and placement about five inches to the side of the plants was preferable. Andrews also refers to trials in Michigan where it was found that ammonium nitrate was slightly superior to anhydrous ammonia for cabbage. Though the differences were not large, the data suggested early application of anhydrous ammonia to vegetable crops to ensure that the nitrogen is in the form of nitrates early in the season. Other work in Virginia showed also that it is important to apply anhydrous ammonia earlier than, say, ammonium nitrate.

Lorenzo et al.(1955) carried out trials on a range of vegetable crops shown in Table III:-

III Table: Response of crops to Nitrogenous Fertilisers

Yield assessed with Sulphate of Ammonia as a base level of 100.

Nitrogen Source	lbs. N per acre	Radish	Radish	Spinach	Peas	Cabbage	Lettuc	e Onion
Anhydrous)	60	73	81	71	94	51	57	76
Ammonia)	120	89	87	96	81	91	51	86
Aqua)	60	91	93	87	101	88	80	71.
Ammonia }	120	78	81	80	92	78	55	37
Sulphate)	60	123	103	91	101	86	96	104
of) Ammonia)	120	100	100	100	100	100	100	100

These trials were carried out on a fine, sandy loam in which risk of injury was quite high and indicate that damage can severely reduce yields, particularly in sensitive crops like onions.

Lorenzo et al. made the observation that aqua ammonia is chiefly a gas in water and that the concentration of ammonia ions in solution at one time is very small. The ionization constant of ammonia is very small, 1.8×10^{-5} at room temperature, while sulphate of ammonia ionizes much more and the ammonium ions dominate.

They concluded that application of ammonia should be deeper and further from the plant than solid less concentrated fertilisers. However not all crops are equally injured and plants like sweet corn are much more tolerant to close placement.

J. Landy (1968) reports that although anhydrous ammonia has been largely used for wheat crops in New South Wales, Australia, a large amount has also been used in irrigation on cotton, sorghum, maize and horticultural crops. In Landy's opinion anhydrous ammonia is much more useful as a fertilizer under irrigation than when applied directly to soils because such areas allow for high application rates - thus cutting the unit cost of the fertiliser and irrigation, and also offering a stable outlet from year to year.

The use of anhydrous and aqua ammonia on vegetables in the United States of America is now common, particularly for those crops with a high nitrogen requirement (Balser, 1968; Anon (1) (1965). An examination of the importance of liquid nitrogen fertilisers was shown in a survey carried out amongst vegetable growers in the United States (Anon (6) 1966). The survey reported that usage of these materials was quite variable but in many

areas where dry fertilisers are used there is now a trend towards liquid nitrogen fertilisers. Anhydrous and aqua ammonia is used on a wide range of crops and this varied from State to State. For example, in Pennsylvania liquid nitrogen fertilisers are of particular importance on canning tomatoes, while in other areas sweet corn, potatoes, green beans, peppers, snap beans and peas are fertilised in this way. While the use of liquid nitrogen is limited in some areas the survey showed that in California the trend to increased use of nitrogen is occurring in all vegetable cropping.

Finally, it was stated that the most significant trends in the United States of America are towards bulk handling of fertilisers and contract application.

The only crops in the United States which are not generally given ammonia are the quick growing vegetables like lettuce when planted in the winter since soil temperatures are so low that nitrification is inhibited and nitrate is not made available fast enough. Another of the rare exceptions is strawberries where, with limited nitrogen use, there is little reason to use ammonia. (Luckhardt, 1968).

Anhydrous ammonia has thus proved an excellent nitrogen material for vegetables in the United States of America. For best results proper depth and sidewise placement of the material is highly important. Application in the desired position in the bed - either by combination bedding and ammonia injection - side dressing, or

irrigation application is therefore highly desirable. Anhydrous ammonia is also an accepted fertiliser for all orchard crops in America. Direct soil injection in the middle of orchard rows, or application in irrigation water, is satisfactory for cultivated orchards. Where an orchard is kept in permanent sod and the roots grow just under the soil surface, direct injection of ammonia may be impossible without damage to roots. Work is being done in United States of America to develop applicators for these conditions (Anon (1) 1965).

Thus there is a trend towards greater use of ammonia fertilisers in the United States and overseas. This has become particularly apparent in certain areas in U.S.A where anhydrous ammonia is being used increasingly on vegetable crops. Trials indicate that horticultural crops will, in general, respond to anhydrous and aqua ammonia just as well as to other conventional nitrogenous fertilisers.

CHAPTER 6

THE ECONOMICS OF AMMONIA USE

The main features that distinguish the economics of anhydrous and aqua ammonia from other conventional solid nitrogen materials is the distribution of costs. The cost of producing anhydrous ammonia is less than any other synthetic nitrogen fertiliser as it is one of the raw materials required for manufacture of other nitrogen fertilisers. Adams et al. (1964) in table IV below demonstrate the competitive price of the two ammonia fertilisers in the United States of America:

Table IV

F.O.B. Price of Chemical Nitrogen Fertilisers - 1964	Price per ton Us \$	Price per pound N US cents
Anhydrous ammonia 82 per cent N	84.00	5.1
Aqueous ammonia 24.4 per cent NH3	87.00	5.3
Ammonium nitrate 33.5 per cent N	70.00	10.4
Sulphate of ammonia 21 per cent N	32.00	7.6
Nitrogen solutions	1.69	8.5
Sodium nitrate	44.00	13.7
Urea 45 per cent N	83.00	9.2

Nelson, (1965), gives the following rough cost index of the contained nitrogen in different carriers at producing plants in the United States of America using 1963 prices:-

Anhydrous ammonia	1.0
Aqueous ammonia	1.03
Pressure type nitrogen solution	1.18
Non-pressure type nitrogen solution	1.48
Solid bagged fertiliser	1.87 - 2.46

Macadam and Noonan (1965) quoted 1964 prices for various nitrogen fertilisers in Australia:

<u>Fertiliser</u>	Cost per ton Aust. £.	Per cent nitrogen	Cost per pound of N
Sulphate of ammonia	29	20.5%	1/3
Calcium ammonium nitrate	39	20.5%	1/8 ¹ / ₃
Urea	52	46%	1/0
Anhydrous ammonia	****	82%	1/1

The cost of the individual nitrogenous fertilisers is far from being the only one to consider and the cost of the nitrogen applied to the soil rather than its f.o.b price is of prime importance to the farmer. It has been pointed out that the cost of anhydrous and aqua ammonia is quite low, however storage and handling, equipment and application costs are much higher. Since anhydrous ammonia is a liquified gas under pressure, operators must be experienced and follow all safety requirements. The cost of the nitrogen applied to the soil will therefore include the f.o.b price, freight, handling charges, cost of storage, a reasonable dealer mark up and cost of application.

Since the cost of anhydrous and aqua ammonia is low while the cost of getting ammonia from the producer and applying it is high, it will require to be applied on a certain minimum number of acres to become economic. The following figures demonstrate 1949 costs of applying 56 pounds of nitrogen per acre on 50 acres (Adams et al. 1965):-

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Items of Cost	Anhydrous ammonia US\$	Ammonium <u>nitrate</u> US\$
Storage and handling	62.49	9.33
Application	71.27	44.08
Material	246.50	327.25
Total costs	380.26	380.66
Costs per acre	7.60	7.61
Costs per pound of nitrogen	0.136	0.136

These figures demonstrate that 56 pounds of nitrogen per acre in the United States of America, derived from anhydrous ammonia or ammonium nitrate, can be applied to 50 acres of cropland for 13.6 cents per pound. The importance of this is that if rates or acreage or a combination of these are increased, then anhydrous ammonia will become more economic. Under 1949 price relationships in the United States, 56 pounds of nitrogen per acre in the form of anhydrous ammonia could be applied to 850 acres for 10.2 cents per pound of nitrogen. The corresponding cost if ammonium nitrate was applied to 850 acres at the same rate, would be 12.9 cents, (Adams et al, 1964).

The cost of materials in each case constituted 86 per cent for anhydrous ammonia and 90 per cent for ammonium nitrate. The total cost for custom application of anhydrous ammonia at the rate of 100 pounds of nitrogen per acre was estimated at only slightly more (\$10.30) than the purchase price of the equivalent nitrate (Adams et al. 1964).

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Adams et al.(1964), also reported on a study which was carried out in Iowa, United States, to compare the cost of farmer-applied solid and liquid forms of nitrogen fertilisers. The study was based on fixed costs associated with the application equipment and storage facilities and such variable costs as the acreage fertilised, rate of fertilisation, cost of fertiliser, labour, and tractor power. Figure VIII illustrates the relationship between total cost per acre and acres fertilised at a rate of 50 pounds of nitrogen per acre.

Adams et al. drew the following conclusions from this work:-

- 1. A farmer with a 5-row applicator and a 550 gallon storage tank applied 50 pounds of nitrogen as ammonia per acre, on approximately 56 acres as economically as the same amount of a solid source of nitrogen was applied with a 12-foot distributor.
- 2. The cost of applied ammonia per acre was less than the cost of solid fertiliser when applied on more than 56 acres or when both were applied at higher rates.
- 3. The break-even acreage for a farmer without a storage tank was about 30 acres.

- 4. The break-even acreage for the farmer using non-pressure and low pressure solutions were approximately 185 acres if he had no storage tank, and 260 acres if he had a 550 gallon storage tank.
- 5. At a nitrogen application rate of 100 pounds per acre, anhydrous ammonia was applied for less per acre than solid nitrogen materials even on small acreages. This high application rate lowers the break-even acreages for non-pressure and low pressure solutions to 50 acres if the farmer has no tank and to 80 acres if a 550 gallon storage tank has been purchased.
- 6. Contract or custom application of anhydrous ammonia was 90 cents per acre less than for nitrogen solutions.
- 7. Nitrogen solutions can be custom applied on a small acreage at rates of 50 pounds of nitrogen per acre at a lower cost than the solid form can be applied with farmer ownedd equipment
- 8. At a rate of 100 pounds of nitrogen per acre, average contract costs per acre for anhydrous ammonia were less than the cost of farmer application up to about 120 acres.

 A comparable figure for the non-pressure and low pressure solutions was about 320 acres.

Luckhardt (1968) provided the following table which was compiled by farm advisors in California:-

Acres injected	Without Farmer Storage Either aqua or anhydrous ammonia	With Farmer Aqua . ammonia	Storage Anhydrous ammonia
	US \$ per acre	US \$ per a	acre
300	2.80	3.50	6.30
500	2.30	2.70	4.30
700	2.10	2.40	3.60
1000	1.90	2.20	3.00
2000	1.80	1.90	2.30
3000	1.75	1.85	2.10

(100 lbs. N/acre, 45 days per year use of kit and nurse equipment)

The principal point that these figures illustrate is that the farmer must have a large acreage to economically justify owning storage equipment. Comparing contract application with farmer storage and using aqua ammonia, the extra costs of having his own equipment is 70 cents per acre when 300 acres are injected, but when 3000 acres are treated the difference is only 10 cents per acre. Similarly, comparing contract application and farmer storage, the corresponding differences fall from \$3.50 to 35 cents for these acreages.

It can therefore be seen from overseas work on the economics of anhydrous and aqua ammonia usage, that rate of application, total

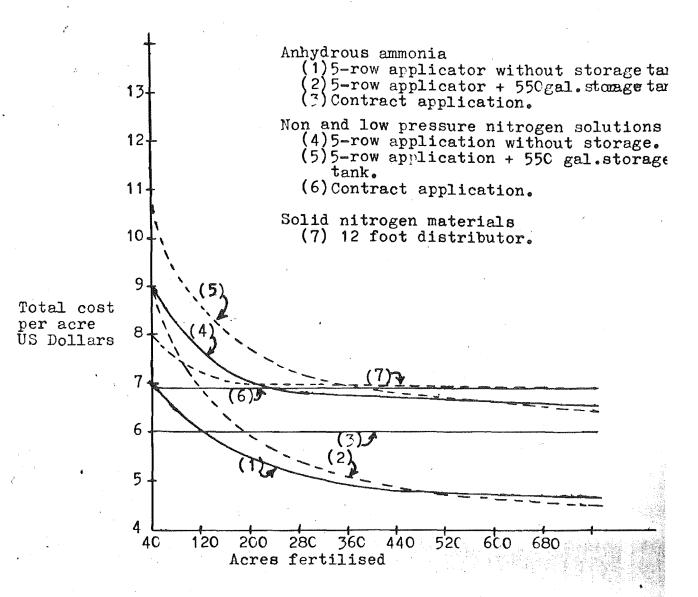


Figure VIII — Total cost per acre of applying 50 pounds of nitrogen in liquid and solid forms.

acreage to be fertilised, comparisons between contract application and farmer storage must all be taken into account when looking at application costs and the comparative price of conventional solid nitrogen materials.

PART 3

ANHYDROUS AND AQUA AMMONIA IN NEW ZEALAND

CHAPTER 1

NITROGEN FERTILISER USAGE IN NEW ZEALAND

CROPPING PRACTICES IN NEW ZEALAND

The pastoral nature of New Zealand's agriculture is well known; there are 19\frac{3}{4} million acres of sown grassland plus 12 million acres of tussock grassland. On the other hand there were in 1965-66 2,701,141 acres of arable crops grown (Anon (7) 1967). This gives a pasture to arable ratio of about 11.5: 1. In the United States of America, there were 1,120,158,000 acres occupied by farms of which 313,446,000 acres were cropped in 1959. Assuming that most of the non-cropped land is pasture then the pasture to arable ratio in the United States of America is about 2.7: 1. The main point arising from these figures is that the pastoral to arable ratio in New Zealand is very much higher than it is in the United States of America.

The total area of crops in New Zealand has increased from 2,378,997 acres in 1961-62, to 2,701,141 acres in 1965-67 (Anon (7) 1967). This indicates that cropping is at least keeping its significance and may possibly be on the increase. Vegetable growing accounts for 2 - 3% of the total cropping land with 40% of holdings under 10 acres. This is in direct contrast to America where emphasis is on specialisation on large areas with few crops.

The trend towards extensive crop production has become apparent in New Zealand over the last few years particularly with crops where mechanisation is possible, such as potatoes, peas, beans, sweet corn, tomatoes, carrots, cabbages and onions. There has also been a trend to crops with higher gross margins, and farmers in particular have looked to crops like onions for higher net returns. It is under this system of growing, using large acreages but few crops, that anhydrous and aqua ammonia could play an important part, helped perhaps by contract application.

One particular aspect of specialised vegetable growing is the production of process vegetable crops. The acreage of these crops has increased from 16,357 acres in 1961-62, to 18,287 acres in 1965-66 (Anon (7) 1967). The consumption of processed vegetables in New Zealand is one of the highest in the world at 26 lb. per head compared with United States of America at 11 lb. per head. Thus the growing of process vegetables is an important and enlarging aspect of vegetable cropping, and along with specialised growing of fresh vegetables lends itself to contract application of anhydrous and aqua ammonia. There is a trend to diversify away from traditional cropping and many new crops like sunflowers, rice and soya beans are being tried. The first commercial crop of sorghum was grown in Gisborne this season and this has a similar nitrogen requirement to maize. The potential of large areas like the Canterbury Plans has hardly been exploited for intensive cropping.

Comparative Usage of Nitrogen Fertilisers

Anon (8) (1967) gives the following figures for fertiliser usage in New Zealand (in thousands of tons):-

	1958-59	1965-66	% Increase
Sulphate of ammonia	10.0	15.9	59
Nitrate of Soda	0.4	3.7	82
Organic fertilisers	32.2	37.3	15.8
Total phosphates	878.5	1656.8	88.7
Total potashes	55.6	150.4	169.5
Total of all fertilisers (N P & K)	976.7	1864.1	90.4

The table above indicates that nitrogenous fertilisers are only a very small portion of the total fertilisers used, and, in fact, they have fallen in seven years from around 4% to 3%. There has been a marked stress on use of phosphatic fertilisers in New Zealand such that importance of nitrogenous fertilisers and their potential value in many instances has not been given the attention it deserves. Legumes are used almost exclusively for the building up of nitrogen in pasture and phosphatic and potash fertilisers dominate the increased use of fertilisers over this period. Nitrogen fertilisers, of which organic materials predominate, have only played a small part in the increased usage.

The use of nitrogenous fertilisers in horticultural crops is well established and there is a wide range of materials available.

It is noticeable that organic fertilisers account for the largest part of nitrogen fertilisers used in New Zealand. This was 65.6% of the nitrogen fertiliser used in 1965-66 and although home gardens must account for quite a large amount, these high-cost low-analysis nitrogenous materials clearly do not justify their dominant role, as will be shown in the next chapter.

Nitrogenous fertilisers used in horticulture vary from materials containing only nitrogen to those that contain phosphorus, potassium and minor elements combined with nitrogen. The most commonly used artificial nitrogenous fertiliser is sulphate of ammonia (four times the tonnage of any other), even though it has a strong acid reaction in soil and the fact that it contains only 21 per cent nitrogen. Organic materials like blood and bone, and bone flour contain less than 10 per cent nitrogen but usually contain phosphorus in addition. There are small amounts of amnonium nitrate and calcium nitrate used in New Zealand, and an even smaller but growing tonnage of urea. differs from the overseas trend of much greater use of high nitrogen analysis fertilisers. The economic aspects of this will be discussed in the next chapter. Combined fertilisers have become popular in New Zealand and examples of these are Nitrophoska, Ammophos and Rustica. The range of nitrogen in these mixtures, however, is not great since none of them contain more than 20 per cent nitrogen.

CHAPTER 2

ECONOMICS OF NITROGEN FERTILISERS IN NEW ZEALAND

Having examined the current use of nitrogenous fertilisers and their relationship to cropping practices in New Zealand, the economic aspects should be looked at next. The source of nitrogen fertilisers for New Zealand, and the comparative costs with anhydrous and aqua ammonia is of prime importance in this study.

Imports of Nitrogen Fertilisers

Most of the artificial nitrogen fertilisers used in New Zealand are imported. The total nitrogenous fertilisers imported into this country for the year ending 1960 amounted to 16,676 tons (Anon (8) 1967). This has since risen to 25,168 tons for 1965-66. The following figures were obtained from the Statistics Department, (Anon (9) 1968) for the year ending June, 1967:-

Fertiliser	Tons	Current Domestic Value	Principal Suppliers	
Ammonium nitrate	996	48,772	West Germany United Kingdom	55% 25%
Ammonium Sulphate	12,738	416,666	West Germany Japan Netherlands	35% 30% 20%
Calcium nitrate	1,853	45,804	Belgium & Lux. West Germany	44% 50%
Calcium Cyanamide	5	214	Japan	100%
Natural Sodium		,		
Nitrate	2,600	91,402	Chile	98%
Urea	1,289	88,628	West Germany	41% 24%
Other kinds of N				
Fertiliser	7,279	310,228	West Germany	39%
			U.S.A	18%
			Belgium & Lux.	16%
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Total:	26,760	\$1,001,716		

The total current domestic value for all types of fertilisers including phosphatic and potash fertilisers imported into New Zealand for this period was \$4,861,460. By comparing this figure with the total imports of nitrogenous fertilisers it can be seen that the latter account for nearly 25 per cent of the total value of fertiliser imports.

<u>Fertiliser Costs</u>

Farming in many countries which were initially pastoral has been encouraged to diversify into mixed cropping by the use of subsidies on fertilisers.

Nitrogen fertilisers are not subsidised in New Zealand while in countries like Britain and Australia costs of these materials are effectively lowered by this method. Anon (6) (1967) gives the following subsidies for England:-

<u>Fertiliser</u>	% N	Subsidy per ton
Nitrate of Soda	16	£4.14.8
Sulphate of Ammonia	21	6. 4. 3
Nitro chalk	21	6. 4. 3
Nitra shell	26	7. 13. 10
Bone Meal	4	none
Hoof and Horn	13	none

Pickering (1967) states that five years ago Australians were using one unit of nitrogen to 15 units of phosphate. Today they are using one to ten. He also reports that the Australian Government since late in 1966 has paid a bounty of \$80. a ton for nitrogenous fertilisers and this was undoubtedly another reason for the increased usage in Australia. Five years ago the only nitrogen used in Australia was on horticultural crops but now it is used on wheat, cotton, sugar cane, rice, grain, sorghum and winter pastures. Pickering (1967) reports that imports of urea into Australia rose from 9111 tons in 1958-59 to 47,810 tons in 1963-64 and that there is a positive upsurge in the use of nitrogenous fertiliser in that country. This does not appear to have occurred in New Zealand and this may be accounted for by several reasons;

the lack of subsidies, a smaller proportion of arable farming, and the lack of fierce competition, promotion and advertising amongst fertiliser companies.

Wild (1960) states that New Zealand soils are as a rule richer in nitrogen than are those of England; the average content of soils of the chief arable districts in New Zealand is 0.25% as compared with 0.15%, which is the average of some typical fertile soils in England. This is accounted for by the milder conditions in New Zealand which allow faster nitrification under similar moisture regimes. Probably the most significant factor in the low use of nitrogenous fertilisers in New Zealand is the overall pastoral nature of the agriculture in this country and the traditional method of allowing legumes to supply nitrogen to pastures. Nitrogen must be used carefully and in no way can it be considered in the same light as phosphatic fertilisers. Pickering (1967) summarises the position in Australia by saying that nitrogen there is on the increase subject to the three limiting factors of management, moisture and finance.

Evaluation and Cost Comparison of Nitrogen Fertilisers

When examining the costs of fertilisers it is important to compare them on a 'Unit Basis'. In this case the cost per lb of nitrogen is used as a standard for comparison. The cost per lb. of nitrogen allows an evaluation on the basis of active ingredient and is made up from the following:-

Cost per lb. of nitrogen = $\frac{\text{Price ex Store per ton}}{\text{lb. of N per ton x 2240 lb/ton}}$ x $\frac{100}{1}$

% N-P-K	Price to farmer (ex store) (bagged)	Price per 1b. N
21-0-0	\$55.70	12 c.
46-0-0	\$100.70	10 c.
7-7-0	\$64.	41 c.
21-0-0	\$64.25	13.7 c.
16-0-0	\$65.50	18 c.
82-0-0	-	25 c.
82-0-0	-	20 c.
82-0-0	- .	34 c.
82-0-0	\$184.41/ton	10 c
	N-P-K	% farmer (ex store) (bagged) 21-0-0 \$55.70 46-0-0 \$100.70 7-7-0 \$64. 21-0-0 \$64.25 16-0-0 \$65.50 82-0-0 -

This costing applies to a farm situated up to and including 20 miles from the static tank. Thereafter the price increases at the rate of 15 cents/ton/mile.

Application costs of anhydrous ammonia in Australia (Landy, 1968) are as follows:-

Broadacres - \$1 per acre
Row crops - \$2 " "
Rice - \$1.40 per acre

The price per 1b. of nitrogen for various fertilisers gives only an approximate indication of the various unit prices. Perhaps the most important feature of these prices is that blood and bone has much the highest price per lb. of nitrogen although this can be partially offset by the phosphorus content. As stated in the previous chapter, organic fertilisers accounted for 65.6% of the total use of nitrogen fertilisers in New Zealand in the 1965-66 season, yet it can be seen from the figures for blood and bone that organic materials have a very high cost per lb. of nitrogen. appears, therefore, that greater use of fertilisers with a lower cost per lb. of nitrogen would be worthwile. This is probably an important factor accounting for the trend towards more concentrated nitrogen fertilisers, with a low cost per lb. of nitrogen, in countries like the United States of America. It can be seen from the table of fertiliser prices that the cost per lb. of nitrogen in blood and bone, which is the principal nitrogen fertiliser being used, is even greater than that for anhydrous ammonia imported in 95 lb. cylinders from Australia.

A significant feature of imports of nitrogen fertilisers into New Zealand is the large tonnage of sulphate of ammonia imported. Yet this material contains only 21% nitrogen and is therefore costly to import per lb. of nitrogen. It is also noticeable that sulphate of ammonia comes principally from Europe and Japan. This is in direct contrast to urea which is a high analysis material (46% N) but only a small tonnage is imported each year from Japan.

Anhydrous ammonia on the other hand is an 82% nitrogenous material which could come directly from Australia but bulk or refrigerated tanks would be needed for shipment of large quantities. A feature of anhydrous ammonia is that once large enough quantities are being used then the very low cost per lb. of nitrogen will offset the cost of specialised shipment, storage and application. In this way anhydrous ammonia has become the most economical nitrogen fertiliser in America.

The price of anhydrous ammonia even if imported from Australia is clearly competitive with that of other nitrogen fertilisers. The position is even stronger in Australia where prices of solid fertilisers are comparatively greater. For example sulphate of ammonia, in Australia is 11.1 cents per lb. of nitrogen ex factory, not ex store (Landy, 1968).

The case for manufacture of anhydrous ammonia in this country needs urgent examination if New Zealand is to venture into extensive crop production.

PART 4

CONCLUSIONS

CONCLUSIONS

The need for nitrogen has been established as an essential but variable major element for the growth of plants. Nitrogen can be absorbed in the ammonium form in preference to nitrate and has the advantage of being strongly held on soil colloids against leaching until conditions are suitable for growth. Thus anhydrous and aqua ammonia can be applied in autumn for spring crops. In addition these liquid fertilisers have been shown to have a potential for carrying other nutrients like sulphur and may have scope as herbicide and therapeutant carriers.

As the use of nitrogenous fertilisers increases the economics of methods of nitrogen application become more important. Overseas it has been shown that nitrogen from anhydrous ammonia per unit of N. is by far the most economic means of supplying nitrogen to the plant if areas or rates are sufficiently great. Consequently a great increase in the use of this material has occurred in all fields of agriculture and horticulture with much success. Anhydrous and aqua ammonia are however virtually unknown and untested in New Zealand.

In New Zealand fertiliser use has largely involved only phosphorus and potassium applications, while nitrogen has been supplied through N. fixation in clover nodules. As a result nitrogen fertilisers are largely organic sources or relatively low analysis inorganic forms such as sulphate of ammonia.

If New Zealand is to maintain its position as an agricultural nation and diversify into a wider range of primary products it must develop the most favourable economic climate for export. Increased yields and lower costs of production must take their part in this, and greater and more efficient use of nitrogen has been shown to be an important part of this development.

In New Zealand there must be a strong trend away from the expensive organic sources of nitrogen to more economic sources of inorganic nitrogen. The production of cheaper electricity from hydro-electric power schemes has increased the feasibility of an ammonia plant in this country. However if this development is not currently possible then only nitrogen fertilisers of the highest concentration should be imported and then from the closest sources. Such fertilisers are not sulphate of ammonia at 21%N or Urea at 46% but the highly concentrated forms of anhydrous ammonia at 82%N.

There is no doubt that both agronomically and economically anhydrous and possibly aqua ammonia offer very great possibilities for New Zealand agriculture and horticulture. The next step is to demonstrate these advantages effectively under New Zealand conditions.

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REFERENCES

- ADAMS, J.R. et al. 1965. Liquid nitrogen fertilisers for direct application. U.S. Dept. Agric. Handbook. 198. 46p.
- ALLISON, F.E. 1966. The fate of nitrogen applied in soils. Adv. Agron.18: 219-258.
- ANDREWS, W.B. 1956. Anhydrous ammonia as a nitrogenous fertiliser. Adv. Agron. VIII: 61-125.
- ANONYMOUS (1) 1965. Agricultural ammonia handbook. Agric. Ammonia Inst. Tenn. 92p.
 - (2) 1965. Fertilising with anhydrous ammonia. Oklahoma State Univ. Circ. E-759. 8p.
 - (3) 1966. Notes on the use of anhydrous ammonia as a fertiliser. Agric. News. Agric. Anhydrous Ammonia Ltd. England. 8p.
 - (4) 1966. Ten facts to help you get more mileage from anhydrous ammonia. Monsanto Company Publication, Missouri. 4p.
 - (5) 1966. Trends in fertilisers and fertiliser application. Am. Veg. Grow. 14 (5): 13-15.
 - (6) 1967. Market Reports. Fertil. Feed Stuffs. J.65 (16): 579-583.
 - (7) 1967 New Zealand official yearbook. 72nd issue. Govt. Printer, Wellington. 1171p.
 - (8) 1967 Statistical review of fertilisers in New Zealand 1965-66 Dept. Agric., Wellington. 22p.
 - (9) 1968 Pers. Comm. Stats. Dept. Christchurch.
 - (10) 1968 Pers. Comm. Direct Nitrogen Limited.
- AYRES, A.S. & Humbert, R.P. 1956 Nitrification of aqua ammonia and ammonium sulphate in Hawaiian soils in relation to pH. Rep. Hawaiian Sug. Technol. 15: 22-26.
- BALSER, R.L. 1968 Pers. Comm. Gulf Oil Co. U.S.A.
- BEERS, Z.H. 1966 Soils hold lots of ammonia for crop use. Agric. Ammonia Inst. Tenn. 4p.

- BLUE, W.G. & ENO, C.F. 1954 Distribution and retention of anhydrous ammonia in sandy soils. Proc.Soil Sci. Soc.Am. 18: 420-424.
- BAERGER, J. 1962 Maize production and the manuring of maize. Conzett & Huber, Zurich. 315p.
- BUCKMAN, H.O & BRADY, N.Z. 1964 The nature and property of soils. 6th ed. Macmillan, Washington. 567p.
- BURNS, G.R. & DEAN, L.A. 1964 The movement of water and nitrate around bands of sodium nitrate and glass beads. Proc. Soil Sci. Soc. Am. 28: 470-484.
- BUTLER, B.J. & SMITH, M.R. 1962 Anhydrous ammonia losses and distribution in tillage application. Trans. Am. Soc. Agric. Engrs. 5 (2): 231-234,239.
- CAMPBELL, J.A. 1950 Anhydrous ammonia as a source of nitrogen for cabbage, tomatoes and beans. Proc.Am.Soc. hort. Sci. 56: 253-256.
- COOKE, G.W. 1956 Soils and fertilisers. Jl Roy. agric. Soc. 117: 113-129.
 - 1966 Soils and fertilisers. Jl. Roy. agric. Soc. 127: 128-145.
- DE GEUS, I.R.J.G. 1967 Developments in the fertiliser field in the United States of America. Stikstof.
- DUISBERG, P.C. & BUEHRER, T.F. 1954 Effect of ammonia and its oxidation products on rate of nitrification and plant growth. Soil Sci. 78: 37-49.
- ENGELSTAD, O.P. & LERMAN, G.L. 1966 Fertiliser nitrogen and its role in crop yield levels. Agron. J. 58: 536-539.
- ENO, C.F. & BLUE, W.G. 1954 The effect of anhydrous ammonia on nitrification and the microbial population in sandy soils. Proc. Soil Sci. Soc. Am. 18: 178-181.
 - et al 1955 The effect of anhydrous ammonia on nematodes, fungi, bacteria and nitrification in some Florida soils. Proc. Soil Sci. Soc. Am. 19: 55-58.
- ENSMINGER, D.E. & PEARSON, R.W. 1950 Soil Nitrogen. Adv. Agron. 2: 81-111.

- GOLDFIELD, E.D. 1966 Statistical abstract of the United States. 87 Amer.ed. U.S. Dept. Commerce Bur. Of Census. U.S. Govt. Print. Office. Washington. 1039p.
- GRAHAM, G.J. 1962 Maize, a crop that needs forethough. J.Agric.N.Z. Dept. Agric. 115 (5): 15-19.
- HARDLING, R.B. et al. 1963 Leaching and gaseous loss of nitrogen from non tilled Californian soils. Californian Citrograph. 8p.
- HARRE, E.A. 1967 Fertiliser trends for 1967. Tenn. Valley Author. Alabama. 83 p.
- HEDMAN, C.L. & TURNER, A.E. 1954 Application of anhydrous ammonia fertiliser. Agric. Engng. 35: 801-807.
- HOPKINS, D.F. et al. 1963 High pressure injection of anhydrous ammonia. Trans. Am. Soc. Agric. Engrs. 6 (3): 343-356.
- HUNTER, F. & JARVIS, G.F. 1953-54 Ammonia Gas as a fertiliser. Agriculture, Lond. 60: 275-277.
- JACKSON, M.L. & CHANG, S.C. 1947 Anhydrous ammonia retention by soils, as influenced by depth of application, soil texture, moisture content, pH value and tilth. J.Am. Soc. Agron. 39: 623-633.
- JACOB, K.D. 1959 Fertiliser production and technology. Adv. Agron. XI: 234-312.
- JAMESON, H.R. 1959 Liquid nitrogenous fertilisers. J.Agr. Sci., Camb. 53 (3): 333-338.
- JEATER, R.S.L. 1966 Liquified ammonia in agriculture. Agriculture, Lond. 73: 542-547.
- KRANTZ, B.A. & CHANDLER 1954 Fertilise corn for higher yields.
 Bull. N.Carol. Agric. Exp. Stn. 366. 20p.
- LANDY, J.M. 1968 Pers. comm. I.C.I.A.NZ. Australia.
- LORENZO, O.A. et al. 1955 Liquid nitrogen for onions on sandy loam soils. Proc. Am. Soc. hort. Sci. 65: 296-306.
- LUCKHARDT, R.D. 1968 Per. Comm. Collier Carbon Chem. Corp. of U.S.A.

- MACADAM, R.D. & NOONAN, J.B. 1965 Anhydrous ammonia a new nitrogenous fertiliser. Agric. Gaz. N.S.W. 76: 71-77.
- McDOWELL, L.L. & SMITH, G.E. 1958 The retention and reactions of anhydrous ammonia on different soil types. Proc. Soil Sci. Soc. Am. 22: 38-42.
- McINTOSH, T.H. & FREDERICK, L.R. 1958 Distribution and nitrification of anhydrous ammonia in a Nicollet sandy clay loam. Proc. Soil Sci. Soc. Am. 22: 402-405.
- McKEE, H.S. 1962 The sources of nitrogen for plants. Clarendon Press. Oxford. 728 p.
- MAYER, B.S. et al. 1965 Introduction to plant physiology. Photolitho. Frome, Somerset. 541p.
- MINARD, H.R.G. 1954 Nutrient requirements of vegetable crops. J. Agric. N.Z. Dep. Agric. 108 (2): 115-117.
- MULDER, E.G. 1953 Investigations on the agricultural value of nitrophosphate and anhydrous ammonia. Proc. Fertil. Soc. (Lond.) 25: 1-43.
- MURPHY, L.S. & SCHRADER, L.L. 1965 Transformation of ammonia in the soil, p5-1 to 5-10. In Anhydrous ammonia agronomy workshop, Tennessee.
- NELSON, L.B. 1965 Advances in fertilisers. Adv. Agron. 17: 1-84.
 - & HAUCK, R.D. 1965 Nitrogen fertilisers, progress and problems. Agric. Sci. Rev. (3): 38-47.
- PAPENDICK, R.I. & PARR, J.F. 1965 Retention of anhydrous ammonia by soil: I. Methodology and experimental considerations. Soil Sci. 100 (3): 182-191.
 - - - 1966 Retention of anhydrous ammonia by soil: III. Dispensing apparatus and resulting ammonia distribution. Soil Sci. 102 (3): 193-201.
- PARR, J.F. & ENGIBOUS, J.C. 1965 Patterns of ammonia distribution in the soil, p4-1 to 4-8. <u>In</u> anhydrous ammonia agronomy workshop, Tennessee.
 - - - 1967 Distribution patterns of ammonia in the soil. Agric. Ammonia News. 17: 62-65.

- PARR, J.F. & PAPENDICK (1) 1966 A greenhouse evaluation of the agronomic efficiency of anhydrous ammonia. Agron. J.58: 215-219.
 - - - (2) 1966 Retention of anhydrous ammonia by soil: II. Effect of ammonia concentration and soil moisture. Soil Sci. 101 (2): 109-119.
 - - - (3) 1966 Agronomic effectiveness of anhydrous ammonia-sulphur solutions. Soil Sci. 101 (4): 336-345.
 - - 1967 What happens to ammonia in the soil.
 Agric. Ammonia News. 16: 64-67.
- PICKERING, W. 1967 Nitrogen fertilisers. Aust. Country Mag. May Ed.
- RUSSEL, E.W. 1966 Soil conditions and plant growth. 9th ed. Jarrold, Norwick. 688p.
- SCOTT, W.C. & TISDALE, SL 1965 Ammonia sulphur solutions for agriculture. Anhydrous Ammonia Symposium. 15p.
- SMITH, G.E. & CASE, N.L. 1965 Crop response to anhydrous ammoni; p6-1 to 6-5. In anhydrous ammonia agronomy workshop, Tennessee.
- SOHN, J.B. & PEECH, M. 1958 Retention and fixation of ammonia by soils. Soil Sci. 85: 1-9.
- STANLEY, F.A. & SMITH, G.E. 1956 Effect of soil moisture and depth of application on retention of anhydrous ammonia. Proc. Soil Sci. Soc. Am. 20: 557-567.
- TOD, H. & SIMPSON, K. 1956 Ammonia liquor as a nitrogenous fertiliser. J. Sci. Fd. Agric. 7: 511-516.
- VANBURG, P.F.J. & VAN BRAKEL, G.D. 1965 The fertiliser value of anhydrous ammonia on permanent grassland. Stikstof.(9):28-36.
 - - - 1967 The agricultural value of anhydrous ammonia on arable land: Experiments 1963-66.

 Neth.N. Tech. Bull. 3. 39p.
 - - - et al. 1967 The agricultural value of anhydrous ammonia on grassland: experiments 1963-65. Neth.N. Tech. Bull. 2. 31p.

- VAN DER BOON, I.R.J. 1963 Nitrogen fertilisers in horticulture. Stikstof.
- WEBBER, J. 1957 Experiments on the use of gas liquor. Agriculture, Lond. 63(12): 571-574.
- WEBSTER, G.C. 1959 Nitrogen metabolism in plants. Row, Peterson & Co. Evanston, Illinois. 152p.
- WILD, L.J. 1960 Soils and manures in New Zealand. Whitcombe and Tombs, New Zealand. 174p.