Nitrogenous fertilizers- Manufacturing process and properties of major nitrogenous fertilizers

A commercial fertilizer is defined as a material containing at least one of the primary nutrients in assemble or available form to plants in known amounts.

Nitrogenous Fertilizers

Nitrogenous fertilizers are chemical substances that contain the nutrient element nitrogen in absorbable form by plants chiefly as ammonium (NH_4^+) or nitrate (NO_3^-) or which yield these from after conversion.

Classification of nitrogen fertilizers

Classification

On the basis of chemical forms of nitrogen, nitrogen fertilizers are classified into following groups :

I. Nitrate Fertilizers :	
(i) Potassium nitrate (KNO_3)	13% N.
(ii) Calcium nitrate [$Ca(NO_3)_2$]	15% N.
(iii) Sodium nitrate ($NaNO_3$)	16% N.
II. Ammonium Fertilizers :	
(i) Ammonium sulphate [$(NH_4)_2SO_4$]	20.5% N.
(ii) Ammonium chloride (NH_4Cl)	25% N.
(iii) Ammonium phosphate ($NH_4H_2PO_4$)	11% N.
(iv) Diammonium phosphate [$(NH_4)_2HPO_4$]	18% N.
(v) Anhydrous ammonia (NH_3)	82% N.
III. Ammonium and Nitrate Fertilizers :	
(i) Ammonium nitrate (NH_4NO_3)	33.5% N.
(ii) Calcium ammonium nitrate	20.5% N.
(iii) Ammonium sulphate Nitrate	26% N.
IV. Nitrogenous Solutions :	
(i) Aqua ammonia	20% N.
(ii) Ammonia urea solution	35-36% N.
(iii) Ammonia-ammonium nitrate solution	35-50% N.
(iv) Ammonia-ammonium nitrate-urea solution	37-49% N.
(v) Non-ammonia-ammonium nitrate-urea solution	32% N.

Origin and reserves:

1) Nitrogen reserves on the earth are abundant. The earth's atmosphere consists of nearly 80 percent of nitrogen by volume.

2) Deposits of natural nitrates present in vast areas in CHILE and PERU of pacific coast of South America even up to 30 feet .The nitrogen containing salt of these deposits are called chile salt peter.

3) Bulk of the nitrogenous fertilizers are produced synthetically from atmospheric N via ammonia synthesis. Though plants are surrounded by atmospheric nitrogen (N_2). They can not split this highly stable molecule and convert it into utilizable forms under normal pressure and temperature conditions. But this splitting (splitting of N_2) can be done only by certain microorganisms in the presence of specific enzymes.

4) Production of N fertilizers from atmospheric nitrogen requires energy i.e., for producing 1 kg Nitrogen in the form of fertilizer it requires 40,000 Kilo Joules of energy.

Production of nitrogen fertilizers

Nitrogen fertilizers are produced by binding atmospheric nitrogen [N_2] by any one of the following process.

1. Ammonia synthesis by Haber –Bosch process
2. Calcium cyanamide synthesis
3. Nitrate synthesis by arc-gap process

Nitrogen fertilizers are produced essentially via ammonia synthesis with ammonia being further processed in to various nitrogenous fertilizers.

The other two processes could not economically compete with the Haber and Bosch process.

Manufacturing process:

Ammonia:

The production of ammonia (NH_3) a simple compound of hydrogen and nitrogen is the basis for nitrogen industry. The first full scale ammonia plant was established in 1913 by FRITZ HABER and CARP BOSCH at OPPAU, Germany for Badische, Anilin and SODA –FABRIC A.G (BASF). The process is called Haber –Bosch process.

In the Haber –Bosch process the reaction between molecular atmosphere nitrogen and hydrogen, the hydrogen is obtained by dissociation of water, or from natural gas etc., takes place at a pressure of 200 atmospheres and a temperature of 550 ^{0}C.

$$N_2\,(g) + 3H_2\,(g) \xrightarrow[550^0C]{200\ atm} 2NH_3\,(g)$$

Synthesis of ammonia being an exothermic reaction produces heat so, that production of N_2 and H_2 requires large quantities of energy. As such production of ammonia is mainly a energy problem.

Raw materials:

Besides atmospheric air being the source of N_2, the other raw material used as a source for H_2 in the manufacture of ammonia include water, natural gas, naphtha, fuel oil or heavy petroleum fractions, coal and coke oven gas.

Water:

The electrolysis of water to generate H_2 requires an electric power of 4.40 to 6.00 K.W/m^3 of water. This method is adopted wherever abundant supply of electricity is available and cheep. Only one fertilizer plant at NFL (Nangal Fertilizer LTD.,), Bakranangal (Punjab) uses this process in India.

Natural gas:

The composition of natural gas varies with location. About 64 % of ammonia produced in the world is from natural gas. Natural gas is a mixture of gases viz., methane, ethane, butane, propane, pentane and CO_2 etc., of all these gases methane constitutes major portion varying 74 to 94 per cent by volume. Higher the concentration of methane lower will be C:H ratio requiring smaller purification unit.

Naphtha:

The light distillate fraction of petroleum with a maximum boiling point (B.P.) of 215 ^{0}C is called Naphtha, which is produced during the refining of crude oil .Naphtha contains hydrocarbons such as a) paraffin (79%) b) Olefins (1.0%) c) Naththanes (14 %) d) aromatics (6%). It has C:H ratio by weight around 5.48. About 75% of nitrogen produced in India utilizes NAPHTHA.

Fuel oil (or) Heavy petroleum products :

Fuel oil contains various products obtain from primary distillation and cracking of crude oil. Example: low sulphur heavy stock (LS HS) and heavy sulphur heavy stock (HS HS). Any of these fractions can be used to produce hydrogen gas.

Coal :

Coal contains hydrogen gas varying from 4.5 to 6.0 % by weight and carbon 79 to 85% by weight, besides sulphur to the extent of 0.3 to 6.0% depending on the location of this natural resources. Fertilizer plant at Ramagundam (Andhra Pradesh) is based on coal gasification to produce hydrogen.

Coke oven gas: Coke oven gas consists of gases (%) H_2 (52.6), CH_4 (28.9), CO (7.5) CO_2 (3.5) and produced during coal carbonization in steel industry.

Manufacturing process of Ammonia:

The process of ammonia synthesis involves four successive steps viz.,

1. Gasification
2. Conversion of CO to produce H_2
3. Gas purification
4. Synthesis

The first three steps are beyond the scope of the course.

Ammonia [or gaseous ammonia] :

Ammonia synthesis is carried out at elevated temperature of 550 ^{0}C and pressure of 200 atmospheres by passing N_2 and H_2 mixture (1:3 mole ratio) over an activated iron oxide catalyst. This process is carried out in a typical NH_3 synthesis reactor. It is a steel cylinder of 80-140 cm diameter and 10-18 meters height, provided with a catalyst container which helps for dissipating the heat expelled.

$$N_2\,(g) + 3H_2\,(g) \xrightarrow[550^0C]{200\ atm} 2NH_3\,(g)$$

(Over the activated catalyst)

Physical properties of ammonia:

1. Ammonia is a colour less gas with a pungent odour, when concentrated, it is toxic to humans and plants. But it is a plant nutrient and in dilute form is harmless to humans
2. One kg of ammonia contains 0.82 kg of nitrogen at 10 ^{0}C the gas exerts a pressure of 34.10 kg /inch ^{2} while the pressure at 38 0C is 89.50 kg / inch ^{2}. It is stored in steel or plastic tanks that can with stand the pressure of 120.4 kg / inch ^{2}.
3. Ammonia is handled on liquid under pressure and is released as a gas through an ammonia resistant hose into the soil. Copper and brass fittings reacts with ammonia and should not be used.
4. Ammonia contains 82 per cent nitrogen by weight.99.5 per cent nitrogen fertilizers are made from ammonia .It is the cheapest N-fertilizer to manufacture.
5. Ammonia is soluble in water up to 30% by weight .This gives a low pressure solution containing 24 per cent nitrogen called AQUA AMMONIA**.**
6. Ammonia is weak alkali. Ammonia and aqueous ammonia both being alkali (basic),the immediate effect of addition to soil is to raise the soil pH to above 9.0 in the zone of application .
7. Ammonia reacts with clay, organic matter and soil moisture. In warm aerated soil, microorganisms convert the applied ammonia to soluble nitrates after few days. The nitrate ions thus formed combine with Ca^{2+}, Mg^{2+} and K^{+} and moves towards the growing root or percolating water. Thus, the final effect of ammonia is to reduce the basicity of the soil and to increase concurrently the soil acidity. One kg nitrogen applied as ammonia will require 1.8 kg of lime for neutralization.

Aqua ammonia [or aqueous ammonia] :

Manufacturing process:

It is the addition of anhydrous ammonia to water. The operation requires facilities for proportioning the flow of water and ammonia. Cooling is required to remove heat of absorption and measuring the concentration of aqua ammonia.

Physical and chemical properties of aqua ammonia:

1. Aqua ammonia is colour less solution with pungent odour, normally containing 20 % N. One liter of water can dissolve 700 liters of ammonia at 20 ^{0}C.
2. It is a non pressure solution which contains no free ammonia.

3. It can be handled and stored without the use of high pressure tanks and equipment.

Ammonia application to soil

The system consists of

1. Nursery tank
2. Ammonia application
3. Ammonia transferring system to till the applied from nursery tank and
4. Tractor to pull tank.

- Ammonia is applied at 8" depth in the soil just below the tillage zone
- Hot compressed NH_3 is stored in the nursery tank
- Anhydrous NH_3 expands in the converts and doing so, it freezes, separating the liquid ammonia from vapour
- The liquid ammonia flows due to gravity through hoses and gas in the soil.

Manufacturing process and properties of Ammonium sulphate, urea and CAN

(1) AMMONIUM SULPHATE [$(NH_4)_2$ SO_4]:

Introduction:

It is the oldest synthetic fertilizer. The production of Ammonium sulphate is related largely to the production of steel, a coke consuming process.

Manufacturing process:

I. By product Process
II. Gypsum process
III. Neutralization process

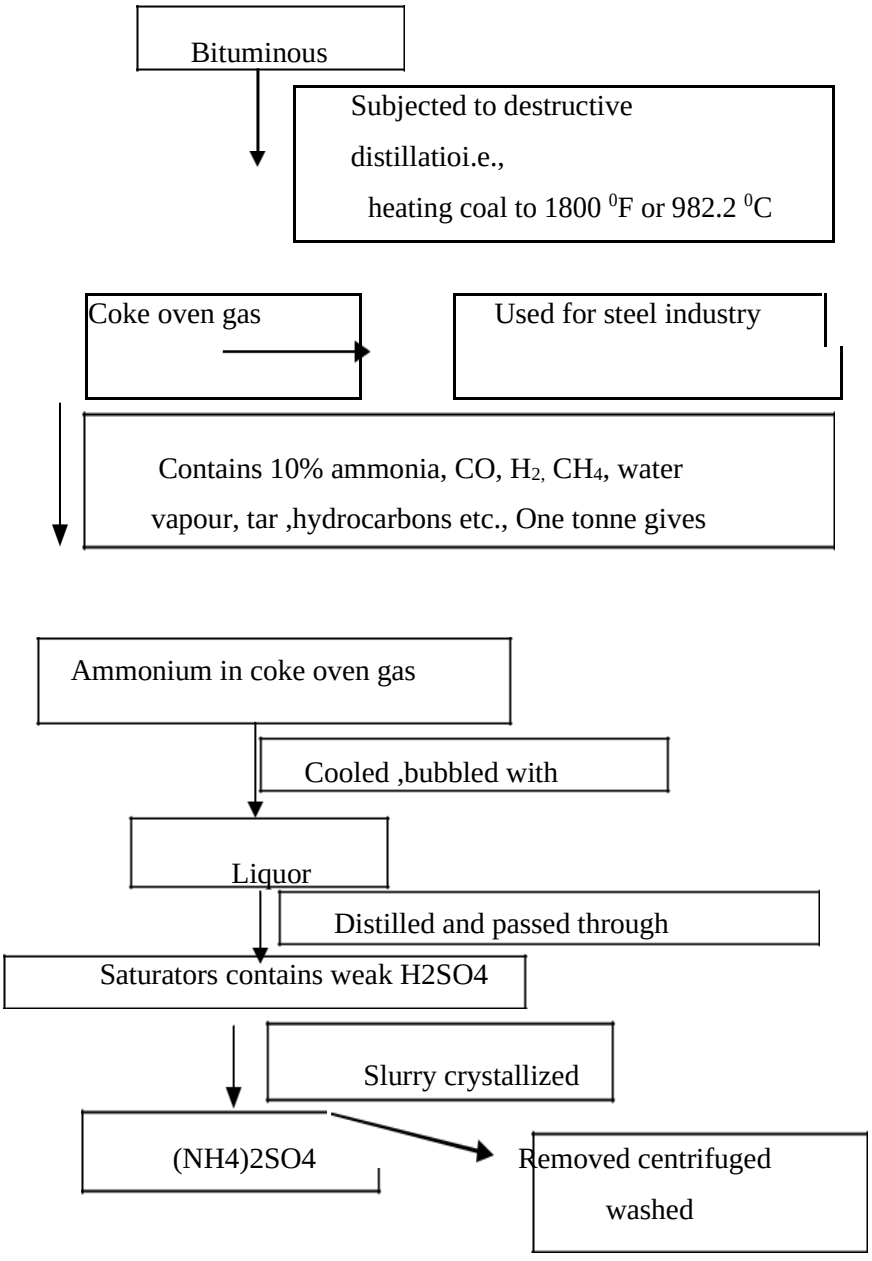
By product process: [Raw materials Coal and Sulphuric acid]

In iron and steel production when bituminous coal is subjected to destructive distillation i.e., heating coal to 1800 ^{0}F (982.2 ^{0}C) in the absence of air, coke is obtained which is used for iron and steel industry. During this process coke oven gas is evolved which contains 10 per cent.

Ammonia by volume, besides the admixtures like CO, H_2 CH_4, water vapour finely divided tar particles and hydrocarbons etc., One tonne of coal burnt yields about 2-3 kg of ammonia. This coke oven gas is cooled and bubbled through water, when liquor ammonia is formed, which is

distilled and passed into saturators containing weak H_2SO_4. Ammonium sulphate $[(NH_4)_2SO_4]$ crystals are formed in the saturators are removed centrifuged, washed and drained. Reaction: $2NH_3$ (g) $+H_2SO_4 \rightarrow (NH_4)_2\ SO_4$ (salt) Energy 67.71K.cal/k.

Flow diagram



II. Neutralization process: [Raw materials NH_3 and H_2SO_4]

In this process, gaseous ammonia produced in **Haber and Bosch** process is directly neutralized with sulfuric acid to produce ammonium sulphate. The chemical reaction is exothermic.

Reaction: $2NH_3$ (g)+H_2SO_4(liquid) → $(NH_4)_2SO_4$ (salt) +67.710 k.cal /gram mole

Neutralization of ammonia by sulphuric acid takes place in reactor and the resultant slurry is transferred to crystallizer, where the heat of neutralization is advantageously utilized to evaporate the water in the slurry. Ammonium sulphate crystals are taken out from the bottom of the reactor and centrifuged. The crystal growth is regulated by air flow, time and temperature.

III. Gypsum process or leuna process: [**Raw materials**: **NH_3 ,CO_2 and Gypsum)**

In this process anhydrous ammonia is absorbed in water in a tank and CO_2 is pumped at 5 atmospheres. The resulting Ammonia carbonate is made to react with Gypsum (Calcium dihydarate; $CaSO_4$ $2H_2O$) suspended with water on double decomposition reaction, ammonia sulphate and calcium carbonate are formed. The calcium carbonate being insoluble, precipitated out, the ammonium sulphate solution is filtered out, and crystallized by evaporation.

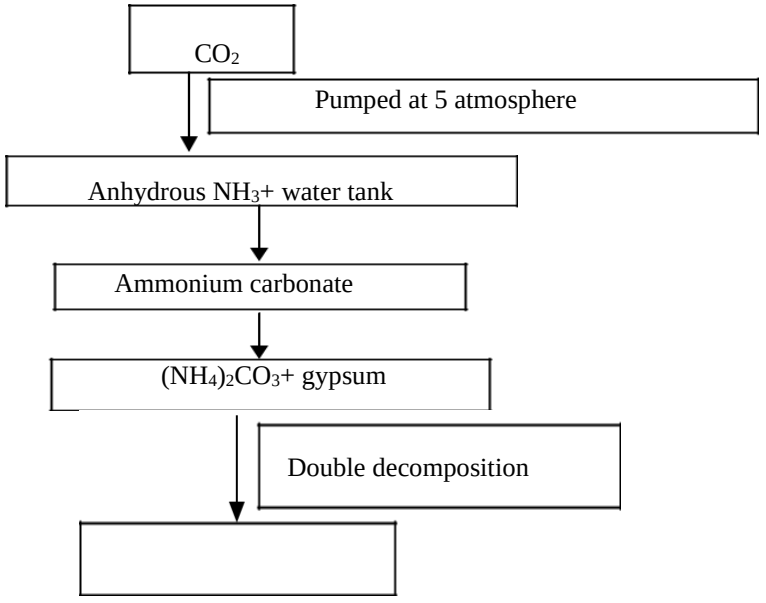
Reactions: NH_3 +H_2O⇋ NH_4OH + 8.32K.Cal/g.mole

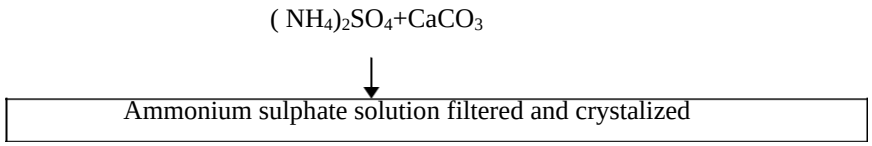
2 NH_4OH +CO_2 → $(NH_4)CO_3$ + H_2O +22.08 K Cal /g.mole

$(NH_4)CO_3$ + $CaSO_4$ $2H_2O$ ⇋$(NH4)_2SO_4$ + $CaCO_3$ +2 H_2O+ 3.9K Cal/g.mole

Advantage of this process over other processes

1. In countries where sulphur supplies are meager and natural resources of gypsum are present ammonium sulphate can be produced without purchasing sulphur from abroad.
2. The by product $CaCO_3$ could be utilized for the manufacture of Calcium Ammonium Nitrate (CAN). Flow diagram





Physical properties:

1. It is white crystalline salt, but commercial product has light yellow to grey colour with free flowing character.
2. Thiocyanates when present are toxic to plants**.**
3. No problem in handling and storage ,if it contains some powdered material ,it cakes (stored in polythene bags)
4. Bulk density of $(NH_4)_2 SO_4$ is 876.60 kg /m^3

Chemical properties:

1. Ammonium sulphate fertilizer contains 20.6 per cent N and 23.45per cent sulphur (It is a acid producing fertilizer)
2. Soluble in water at ordinary temperatures. Solubility at 0 ^{0}C is 70.60g/100 grams of water and at 100 ^{0}C is 103.80 grams /100 grams of water.

It has free acidity (pH =5.0) of 0.025 per cent by weight .One kg of N applied as Ammonium sulphate fertilizer required 5.1 kg of lime for neutralization.

(2) CALCIUM AMMONIUM NITRATE (CAN):

Calcium ammonium nitrate in one of the major straight N - fertilizer produced in India .It is also called as Lime Ammonium Nitrate.

Raw materials:

1) Ammonia 2) Nitric acid 3) Limestone or Dolomite 4) Soapstone (essentially magnesium silicate)

Manufacturing process:

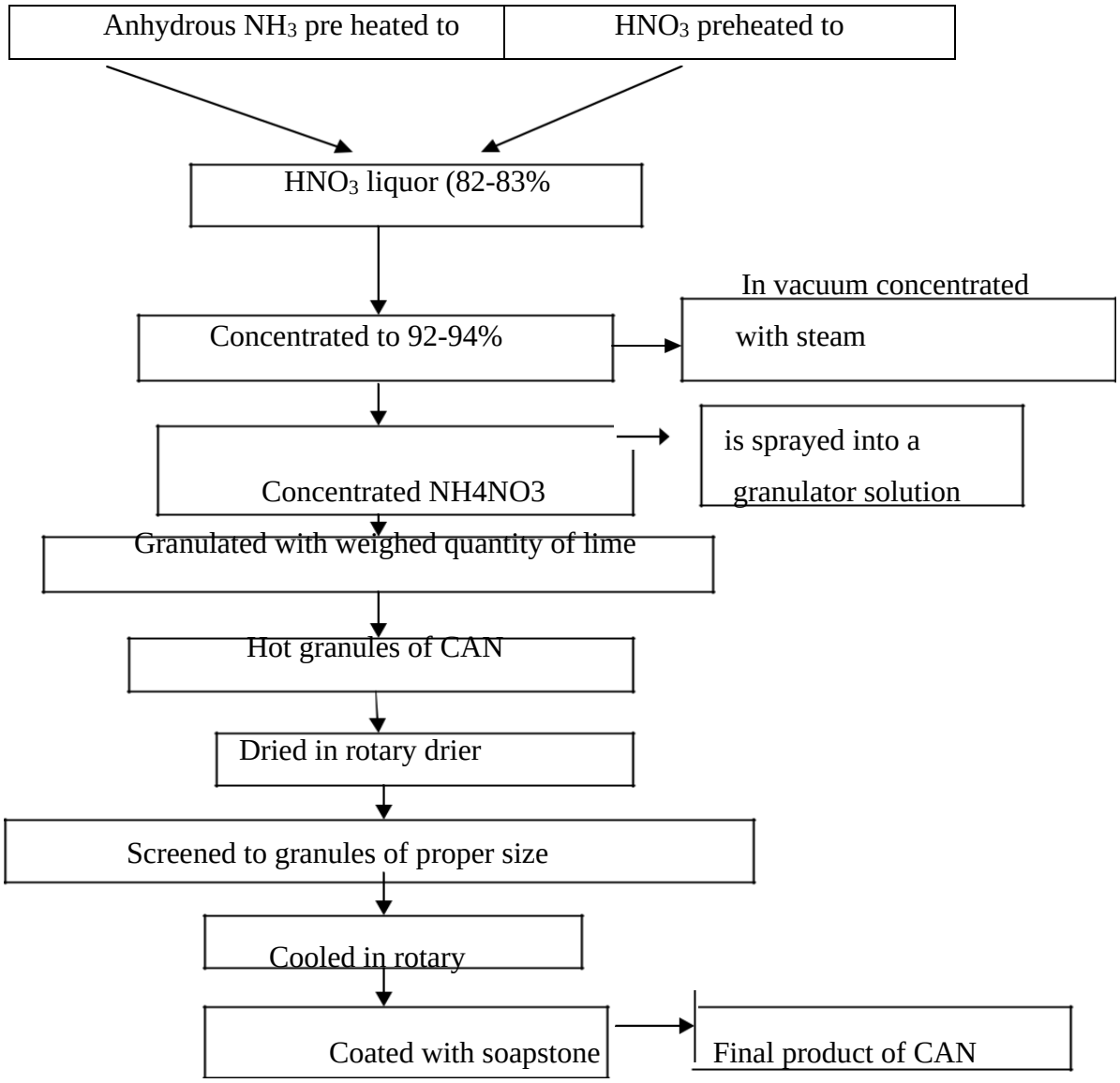
Anhydrous ammonia and nitric acid are heated to 85 ^{0}C and 65 ^{0}C respectively by means of a steam vapour in a neutralizer, when ammonium nitrate liquor of 82 to 83 percent concentration is obtained .It is further concentrated to 92 to 94 per cent by heating with steam in a vacuum concentrator and stored in a tank.

NH_3 (g) +HNO_3 (liquid) → NH_4NO_3 (liquid) + 26 K.cal./g.mole The concentrated ammonium nitrate solution is(92-94 %) sprayed in a granulator fed with the weighed quantity

of lime stone powder, when hot granules of Calcium ammonium nitrate are obtained .They are dried in a rotary drier by hot air and later screened to obtain the granules of proper size .They are cooled in a rotary cooler by air , and coated with soap stone dust (Talc) in a coating drum. The final product is a mixture of calcium carbonate and ammonium nitrate.

$NH_4NO_3 + Ca\ CO_3 \rightarrow NH_4NO_3\ CaCO_3$

Flow diagram:



Physical properties:

1. CAN is an easy flowing granular material (size 1 to 4 mm)

2. Addition of calcium carbonate (lime powder) during the manufacture of CAN improve handling character and reduced the explosive and hygroscopic nature of ammonium nitrate.

Chemical properties:

1. CAN contains 25 per cent nitrogen with equal quantity of each NH_4^+ and NO_3^- forms of nitrogen (12.5% and 12.5%)
2. It is a neutral fertilizer and leaves neither acidic nor basic residues on soil application
3. It contains 8.1per cent of calcium and 0.5per cent by weight of calcium nitrate
4. It is readily soluble in water

(3) UREA [Carbamide ($NH_2CO\ NH_2$)]:

Urea or carbamide as it is sometimes called "non-ionic" nitrogen compound used as a fertilizerfor crops and also as protein supplement in the feed of ruminants (farm animals).

1. It is the most important N-Fertilizer constituting nearly 91 per cent of the total production of nitrogen in India.
2. The major reason for its rapid growth is its very high nutrient content (46% N).

Raw materials: 1) Ammonia and 2. Carbon dioxide

Fwholer (German chemist), first prepared urea in the year 1828 [Commercial production started in 1922] by isomerizaiton of ammonia cyanate. Since then numerous processes have been developed for the synthesis of urea. All commercial processes are based on the dehydration of ammonia carbamate. The chemical reaction is follows.

$$2NH_3 + CO_2 \xrightarrow[2500\text{-}3500\ \text{Psi}]{180\text{-}200\ ^0C} \underset{\text{(Ammonium carbamate)}}{NH_4CO_2\ NH_2} \longrightarrow \underset{\text{(Urea)}}{NH_2\ CO\ NH_2} + H_2O$$

[Psi: Pressure in pounds per square inch]

Manufacturing process

Liquid ammonia and carbon dioxide gas are pumped continuously into a reactor maintained at temperature ranging 180-200 ^{0}C and pressure ranging 2500 to 3500 Psi. The reaction is exothermic. The reaction product, is a mixture of urea, ammonia, carbon dioxide, ammonium carbamate and water. The mixture then flows in to a carbamate strippers, where liquid phase of urea, water containing small quantities of ammonium carbamate, ammonia and gaseous phase of ammonia, carbon dioxide and water vapour are separated. The aqueous urea

solution contains around 70-80 per cent urea .It may be used directly in various nitrogen solutions, but must be concentrated to produce solid urea.

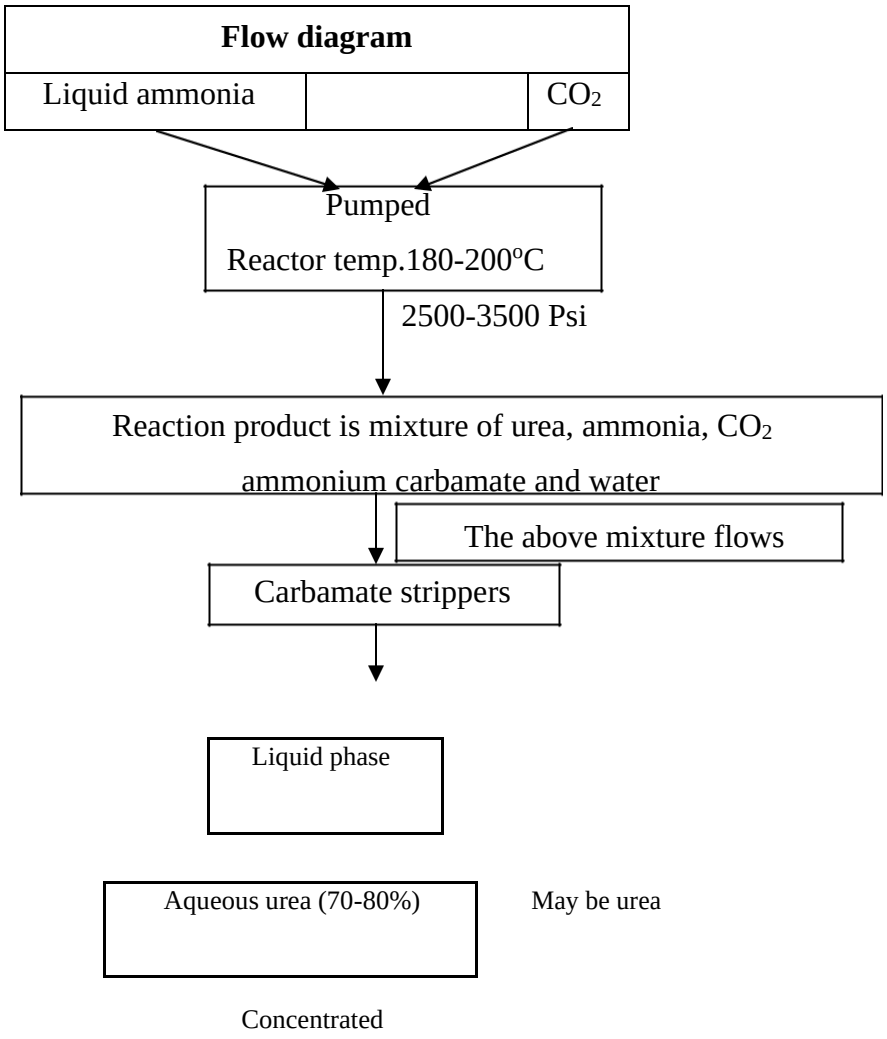
Biuret:

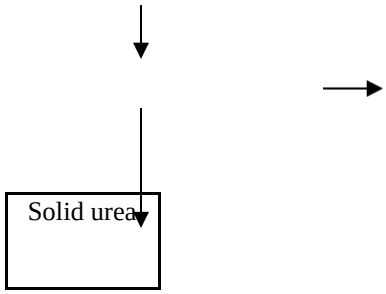
When concentrated urea solution is exposed to elevated temperatures i.e., greater than 100 ^{0}C during evaporation in prilling process biuret is formed by mixing of two urea molecules ,which is toxic to plants. At a temperature of above 100 0C

$$NH_2CO_2NH_2 + NH_2CO_2NH_2 \longrightarrow NH_2\text{–}CO\text{-}NH\text{-}CO\text{-}NH_2 + NH_3$$

Urea Urea Biuret

The urea solution concentrated to 99.70 to 99.80 percent in a vacuum evaporation and is finally dried by spraying in to a tower where it is solidifies in the form of prills (or) granules





Physical properties:

1. White organic compound with low bulk density i.e., 0.7 kg /L
2. It is a solid fertilizer usually granulated to (1 to 2 mm)
3. Having specific gravity of 1.335

Chemical properties:

1. Synthetic protein, organic compound, richest source of N (46%) in amide form among solid N fertilizers
2. Soluble in water and solubility is 100 g /100 g of water at 20^0C
3. Biuret content is about 1.5 per cent by weight
4. It is identical to urea found in animal urine.

What happens when urea is applied to soil

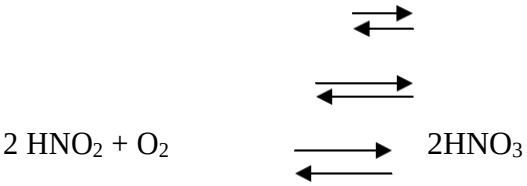
Conversion of urea in to ammoniacal and nitrate form is complete in about a week. As such it is advisable to apply urea three to four days before sowing of any field crop. Loss of nitrogen by leaching is less.

Urea is less acidic compared to ammonia sulphate. Since application of 100 kg urea leaves acidity, which requires 80 kg of $CaCO_3$ to neutralize it .Plants are capable of absorbing most of the nutrients through their leaves. Being very soluble and highly concentrated urea is most suitable fertilizer for spraying in the form of weak solution **(**3 to 6 %).

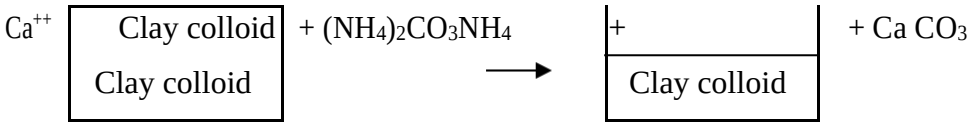
Urea is easily hydrolyses to ammonia soon after its application to the soil in the presence of urease enzyme by micro organisms and is converted to ammonium carbonate and then by microbial oxidation into ammonium and nitrate and these forms are absorbed by plant. Some of the ammonia and nitrate formed is lost due to leaching, volatilization and denitrification and these losses are responsible for the low recovery of urea by rice which is generally 40-50 per cent or even less.

$NH_2\ CO\ NH_2 + 2H_2O \rightarrow (NH_4)_2CO_3$

$(NH_4)_2CO_3 + 3O_2 \rightarrow 2\ HNO_2 + 3H_2O + CO_2$



Urea being converted in to ammonium carbonate, the following reaction occur in the soil.



Calcium carbonate is in soluble in water and therefore its loss is minimum.

Urea is gaining importance as nitrogenous fertilizer because of the following reasons.

Urea was first produced in India at SINDHRI (BIHAR**)** during 1959-60. At present urea is producing nearly 50 different locations in India.

1. High nitrogen content 44 to 46 per cent
2. Good physical condition
3. Less cost per unit of nitrogen in production, storage and transportation
4. Less acidic residual effect as compared to ammonium sulphate
5. Suitable for foliar application
6. Lack of corrosiveness
7. Agronomic value equal to other nitrogenous fertilizers
8. The biuret content exceeds 1.5 %, it is toxic to plants.

Mode of action of N fertilizers in soils or reactions of fertilizers in soils

1. Urea (Refer fate of applied urea in soil)

2. Nitrate (NO_3^-) N fertilizers when applied to soil

1. Nitrate fertilizers raise the pH of the soil .These are superior in highly acid soil
2. Nitrate fertilizes are immediately effective and as such are specially suited for top dressing
3. These are also suitable for moderately to slightly acidic soils
4. Loss through leaching of Nitrate from soil are unavoidable but can be limited by precise N-fertilization

3. Ammoniacal N fertilizers [NH_4^+]

1. It is soil acidifier .It superior to neutral to very slightly alkaline soil.
2. Application of NH_4^+ Fertilizers to alkaline soils (pH =7.5) resulting in losses of gaseous ammonia .For this reason there are generally inferior in alkaline soils.
3. These are moderately quick in action. It becomes more mobile in the soil only after conversion to NO_3
4. Soil acidification through some N-fertilizers *viz*., Ammonium sulphate, urea ,brings about changes in soil reaction(pH). It is advantageous in soils with high pH, since contain trace elements are better mobilized through acidification.
5. NH_3 has fungicidal action against normal fungi in the soil.

4. Amide form (urea)

In general N fertilizers are very rapid in action in soils .Salt damage to crops occur due to heavy application of N fertilizers, which effects the absorption of water and mineral nutrients. Fertilizers can act effectively only when soil has optimum structure and soil reaction.