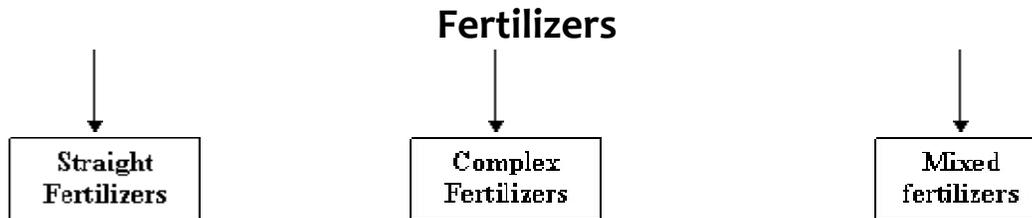


# Lecture 7: Classification of chemical fertilizers; Classification, Composition, synthesis and properties of straight nitrogenous fertilizers

## CLASSIFICATION OF FERTILIZERS



**1. Straight fertilizers:** Straight fertilizers are those which supply only one primary plant nutrient, namely nitrogen or phosphorus or potassium. e.g. Urea, ammonium sulphate, potassium chloride and potassium sulphate.

**2. Complex fertilizers:** Complex fertilizers contain two or three primary plant nutrients of which two primary nutrients are in chemical combination. These fertilizers are usually produced in granular form. e. g. Diammonium phosphate, nitrophosphates and ammonium phosphate.

**3. Mixed fertilizers:** are physical mixtures of straight fertilisers. They contain two or three primary plant nutrients. Mixed fertilisers are made by thoroughly mixing the ingredients either mechanically or manually.

Fertilisers can also be classified based on physical form:

1. Solid
2. Liquid fertilizers



### I. Straight fertilizer

Straight fertilizers are chemical substances that contain only one nutrient element in absorbable form by plants. The straight fertilizers include 1) Nitrogenous, 2) Phosphatic and 3) Potassic fertilizers.

## A. NITROGENOUS FERTILIZERS

Nitrogenous fertilizers are chemical substances that contain the nutrient element nitrogen in absorbable form by plants chiefly as ammonium ( $\text{NH}_4^+$ ) or nitrate ( $\text{NO}_3^-$ ) or which yield these from after conversion .

### Classification of mineral nitrogen fertilizers

S.No.	Chemical Form of Nitrogen	Fertilizer	Chemical formula	N Content (%)
1	Ammonium [ $\text{NH}_4^+$ ]	a) Gaseous ammonia	$\text{NH}_3$	82
		b) Ammonia water	$\text{NH}_3, \text{NH}_4\text{OH}$	24
		c) Ammonium sulphate	$(\text{NH}_4)_2\text{SO}_4$	21
2	Nitrate [ $\text{NO}_3^-$ ]	a) Calcium nitrate	$\text{Ca}(\text{NO}_3)_2$	16
		b) Sodium nitrate	$\text{NaNO}_3$	16
		c) Ammonium sulphate nitrate	$(\text{NH}_4)_2\text{SO}_4 + \text{NH}_4\text{NO}_3$	26
3	Ammonium + Nitrate [ $\text{NH}_4^+$ ] + [ $\text{NO}_3^-$ ]	a) Ammonium nitrate	$\text{NH}_4\text{NO}_3$	35
		b) Calcium ammonium nitrate	$\text{NH}_4\text{NO}_3 + \text{CaCO}_3$	25
4	Amide [ $-\text{NH}_2$ ]	a) Urea	$\text{CO}(\text{NH}_2)_2$	46
		b) Calcium cyanamide	$\text{CaCN}_2$	22

## Synthesis and properties of nitrogenous fertilizers

### AMMONIA

Ammonia synthesis is carried out at elevated temperature of  $550^\circ\text{C}$  and pressure of 200 atmospheres by passing  $\text{N}_2$  and  $\text{H}_2$  mixture (1:3 mole ratio) over an activated iron oxide catalyst. This process is carried out in a typical  $\text{NH}_3$  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.

### Physical and chemical properties of ammonia:

- 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

- One kg of ammonia contains 0.82 kg of nitrogen at 10 °C the gas exerts a pressure of 34.10 kg /inch<sup>2</sup> while the pressure at 38 °C is 89.50 kg / inch<sup>2</sup> .It is stored in steel or plastic tanks that can withstand the pressure of 120.4 kg / inch<sup>2</sup> .
- 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 react with ammonia and should not be used.
- 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.
- Ammonia is soluble in water up to 30% by weight .This gives a low pressure solution containing 24 per cent nitrogen called AQUA AMMONIA.
- Ammonia is weak alkali.

### **Aqua ammonia [or aqueous ammonia]**

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:**

- Aqua ammonia is colourless solution with pungent odour, normally containing 20 % N. One liter of water can dissolve 700 liters of ammonia at 20 °C.
- It is a low pressure solution which contains no free ammonia.
- It can be handled and stored without the use of high pressure tanks and equipment.

### **AMMONIUM SULPHATE [(NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub> ]**

#### **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

#### **I. 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 °F (982.2 °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<sub>2</sub>, CH<sub>4</sub>, 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<sub>2</sub>SO<sub>4</sub>. Ammonium sulphate [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>] crystals are formed in the saturators, are removed, centrifuged, washed and drained.

**Reaction:**  $2\text{NH}_3(\text{g}) + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4(\text{salt})$  Energy 67.71K.cal/kg

## II. Neutralization process: [Raw materials NH<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>]

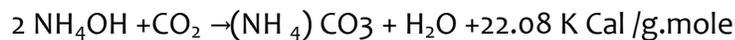
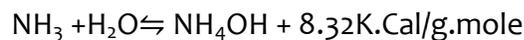
In this process, gaseous ammonia produced in **Haber and Bosch** process is directly neutralized with sulfuric acid to produce ammonium sulphate. The chemical reaction is exothermic.

**Reaction:**  $2\text{NH}_3(\text{g}) + \text{H}_2\text{SO}_4(\text{liquid}) \rightarrow (\text{NH}_4)_2\text{SO}_4(\text{salt}) + 67.710 \text{ k.cal /gram mole}$

## III. Gypsum process or leuna process: [Raw materials : NH<sub>3</sub>, CO<sub>2</sub> and Gypsum ]

In this process anhydrous ammonia is absorbed in water in a tank and CO<sub>2</sub> is pumped at 5 atmospheres. The resulting ammonia carbonate is made to react with Gypsum (Calcium dihydrate; CaSO<sub>4</sub> 2H<sub>2</sub>O) 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:



### Properties of ammonium sulphate

#### Physical properties:

- It is white crystalline salt, but commercial product has light yellow to grey colour with free flowing character.
- Thiocyanates when present are toxic to plants.

- No problem in handling and storage ,if it contains some powdered material ,it cakes (stored in polythene bags )
- Bulk density of  $(\text{NH}_4)_2 \text{SO}_4$  is  $876.60 \text{ kg /m}^3$

#### Chemical properties:

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

### 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:

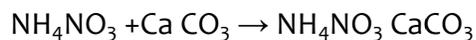
1)Ammonia 2) Nitric acid 3) Limestone or Dolomite 4) Soapstone(essentially magnesium silicate)

#### Manufacturing process:

Anhydrous ammonia and nitric acid are heated to  $85^\circ \text{C}$  and  $65^\circ \text{C}$  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.



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.



### Physical properties:

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

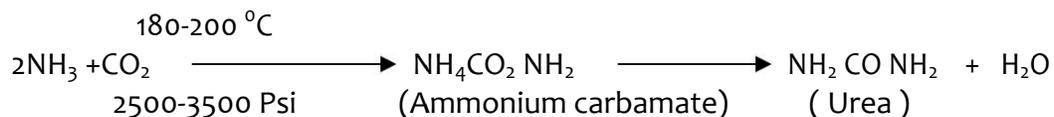
- CAN contains 25 per cent nitrogen with equal quantity of each  $\text{NH}_4^+$  and  $\text{NO}_3^-$  forms of nitrogen (12.5% and 12.5%)
- It is a neutral fertilizer and leaves neither acidic nor basic residues on soil application
- It contains 8.1per cent of calcium and 0.5per cent by weight of calcium nitrate
- It is readily soluble in water

### UREA [Carbamide ( $\text{NH}_2\text{CO NH}_2$ )]

Urea or carbamide as it is sometimes called "non-ionic" nitrogen compound used as a fertilizer for crops and also as protein supplement in the feed of ruminants (farm animals). It is the most important N-Fertilizer constituting nearly 91 per cent of the total production of nitrogen in India.The major reason for its rapid growth is its very high nutrient content (46% N).

**Raw materials:** 1) Ammonia and 2. Carbon dioxide

All commercial processes of urea production are based on the dehydration of ammonium carbamate .The chemical reaction is follows.



[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 °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 °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 oC



The urea solution concentrated to 99.70 to 99.80 per cent 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:

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

### Chemical properties:

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