US06DCHE27

UNIT – IV

CHEMICAL ASPECT OF FERTILIZERS

Compiled by Dr M M Moreker

Man has developed many facilities to live a comfortable and stable life. Many things are required for living. These things are usually obtained from nature. Most of the things are based on chemistry.In the 20th century use of things these become necessary for daily life has increases to a great extent. As a result there has been a basic change in chemistry and importance of chemistry is ever increasing. In modern times, life has become easy with all necessary amenities available by industrial growth.Chemistry and chemical sciences have contributed a great deal for this.

Basic chemicals necessary for human life are found in food, protection and housing with important chemicals like fertilizers, polymers, drugs, dyes, biochemical etc.

The increase in production of food grains requires sunlight,Fertilizers, water and protection of crops. The repeated cultivation in a farm decreases the fertility of soil due to decrease in the nutrients needed for the growth of plants. The major nutrients are nitrogen, phosphorous and potassium. Moreover iron, cobalt, calcium, magnesium, etc. are necessary in trace amounts.Generally soil contains enough trace elements, whereas major necessary elements are added to the soil in the form of NPK chemical fertilizers. India manufactures fertilizers like ammonium sulphate, urea, potassium nitrate, diammonium phosphate (DAP) etc.

NEED FOR FERTILIZERS :

After repeated cultivation a stage is however reached when the soil becomes less productive if supply of the above mentioned nutrients is not provided.Thus,"In order to make up this deficiency certain elements in the form of their compounds have to be added to the soil to make it reproductive. These substances are known as fertilizers."

Fertilizers :

" **Fertilizers** are the substances which are to be added to the soil in order to remove the deficiency of essential elements required by the plant. "

OR

" **Fertilizers** are those substances which must be added to the soil in order to remove the deficiency of essential elements required for plant growth. "

OR

" **Fertilizers** are chemical substances supplied to the crops to increase their productivity. "

The need of fertilizing a land is therefore three fold:

a) To supplements what has been eaten up by the plants.
b) To supply them an additional tonic and good food so that they may grow more health and produce a better yield.
c) To maintain the pH of the soil in the vicinity of 7–8 and hereby optimum growth and health.

PLANT NUTRIENTS :

plants,like human being and animals requirefood for their growth and development. The food of plants is composed of certain chemical elements, known as **plant nutrients**or **plant food elements.**

About 35 elements such as carbon, hydrogen, oxygen, Nitrogen, phosphorus, potassium, Calcium, magnesium, Sulphur, manganese, molybdenum,copper,boron,zinc, iron,chlorine, sodium, silicon, aluminium, cobalt, iodine, rubidium, strontium, nickel, chromium, arsenic, bromine, gallium, lanthanum, lithium, lead, vanadium, yttrium, zirconium, and selenium have been regarded for nutrition for plants.

Out of these, **sixteen elements** have been considered **essential** for plant growth and development. These sixteen elements are namely carbon, hydrogen , oxygen, Nitrogen, phosphorus, potassium, Calcium, magnesium, Sulphur, manganese, molybdenum,copper,boron,zinc, iron, chlorine. **(C, H, O, N, P, K, Ca, Mg, S, Mn, Mo, Cu, B, Zn, Fe, and Cl)**

Out of these three **carbon, hydrogen** and **oxygen** are derived from air and water and so these are called **natural nutrients.**

The remaining **thirteen elements** are supplied by the soil.

These may be **classified** as:

a) **Primary nutrients:**
   Nitrogen, phosphorus and **potassium** are consumed in large quantities by the plants and therefore, they are called **primary nutrients**.
b) **Secondary nutrients:**
   Calcium, magnesium and **Sulphur** which occur to a limited extent in soil for plant growth are called secondary nutrients.
c) Micro nutrients:
   These include **manganese, molybdenum, copper,boron,zinc, iron** and**chlorine**.
   These required by plants only in minute quantities are called **micro nutrients.**

The primary and secondary nutrient elements collectively known as **major plant nutrients.**

The nutrients which are used by the field crops in very small quantities are known as **micro nutrients**or**minor plant nutrients.** They are also known as **trace elements** because they are required in trace quantities. They are, however, as important for the plant growth as the major elements in plant nutrition.

Several other elements such as rubidium, strontium, chromium, nickel, and arsenic have been found to stimulate the growth of certain plants or to have certain beneficial effects at very low concentration and often under specific conditions. Hence these elements are often called as **potential micronutrients** or **beneficial elements**.

PLANT NUTRIENT FUNCTIONS:

N – Nitrogen: Soil take's up the nitrogen in the form of ammonium or nitrate ions and forms amino acids with carbon compounds in the complex chemical system in the plant. These amino acids are then converted into proteins and enzymes. Proteins thus formed make part of the protoplasm, while enzymes act as catalysts for various reactions taking place in the plants. Nitrogen is also a special constituent of the chlorophyll without which photosynthesis is not possible.

P – Phosphorus: It has been found that certain high energy phosphate bonds are involved in the respiratory and photosynthetic processes. These bonds transfer energy in some of the plants metabolic processes without which the plant cannot live. The need of phosphorus is also necessary for the health of plant. It is a constituent of nucleic acids, phytins and phospholipids. It is also found in seeds and fruits. The phosphorous has also been found to contribute to the formation of the reproductive parts in the early life of the plant.

K – Potassium: It is essential for healthy growth of plants. Formation and movement of carbohydrates in plant is contributed by potassium and a deficiency of potassium quickly reduces the carbohydrate contents.

Ca – Calcium: Calcium acts as a plant nutrient and also as a soil amendment to correct soil acidity.It is found as a plant constituent in the cell walls of leaves in the form of calcium pectate. Calcium is closely associated with the growth of the flowers and a deficiency of calcium also prevents normal development of buds and tips, calcium is a structural component of chromosomes.

Mg – Magnesium: Magnesium acts as a carrier of phosphate and therefore, plays an important part in the formation of phospholipids and in the synthesis of nucleoproteins. Magnesium is also a mineral constituent of chlorophyll and makes up 2.7% of the weight of chlorophyll. Several photosynthetic enzymes present in chlorophyll require magnesium as an activator.

S – Sulphur: It is present in many proteins in the form of cysline and methionine which contain 26.7 and 21.5% Sulphur respectively. A deficiency of Sulphur decreases the plant growth accompanied by extensive yellowing of green parts.

B – Boron: It is required by plants in extremely small amounts. Its function is difficult to understand but accumulation of carbohydrates and water soluble amino compounds in plants efficient in boron suggests that boron is of some importance in protein synthesis.

Fe – Iron: Iron is necessary for the synthesis of chlorophyll, but it is not a constituent of chlorophyll. Iron is used by the plant in some of its respiratory enzyme systems, especially catalyze cytochrome and peroxidase. A deficiency of iron causes leaves to turn white and growth to cease. Iron deficiency is noted in the growth of citrus and in crops such as soyabeans and peanuts.

Zn – Zinc: It is believed to be involved in enzyme system in the plant, particularly carbonic anhydrase and carboxylase. Zinc functions in enzyme systems which are necessary for important reactions in plant metabolism. Zinc is associated with iron and manganese for the synthesis of chlorophyll.

Mn – Manganese: Manganese is an essential constituent of chlorophyll and also for the formation of oils and fats. Manganese also influences the uptake and utilization of other nutrients in the plants.It is an essential factor in photosynthesis, nitrogen metabolism and respiration. It is found in active region of the plant and acts, as an oxidizing agent for iron.Deficiencies of manganese usually occur in organic soils and in alkaline or highly acidic soils.

Cu – Copper: Copper is associated with some of the plant enzyme systems, such as polyphenol oxidase and ascorbic acid oxidase. Deficiencies are generally associated with organic soils. Copper is capable of acting as electron carrier in enzyme systems which bring about oxidation reduction systems in plants.

Mo – Molybdenum: It has also been proposed to be associated with the functioning of one or more of the plant enzyme systems, especially nitrate reducing enzymes. Molybdenum has been found to enhance the symbiotic nitrogen fixation as well as protein synthesis. It also regulates activities of various enzymes.

Cl – Chlorine: It is the most recent addition to the essential nutrient list. It has been observed that the deficiency of chlorine can cause chlorosis (yellowing of green plants). Chlorine in small amounts also stimulates growth of crops like barley, alfalfa and tobacco.

ESSENTIAL REQUIREMENTS OF FERTILIZER:

Every compound containing nitrogen or phosphorus or calcium or potassium cannot be used as a fertilizer.
The chief requisites of fertilizer are:

1) The element present in the compound must be easily available to the plant.
2) The substance must be soluble in water
3) By rain water, fertilizer must be converted into a form which can be easily assimilated by the plant.
4) The compound must be stable so that it is available for a long time to the growing plant.
5) It should not be injurious to plants. (It should not be a poison for plant.)
6) It should able to maintain the pH of the soil in the vicinity of 7 to 8. (It should able to correct acidity of the soil.)
7) It should be cheap. (It should not be a very costly.)

FERTILITY OF THE SOIL :

Virgin soil: A virgin soil may be regarded as a portion of the soil or land in which plants have not grown for a long time. Since the elements present in it have not been used up by the plants as food, it is always fertile and a good crop may be yielded by making use of it.
Exhausted soil : Exhausted soil is an unproductive soil and may be regarded as asoil on which crop and after crop, especially of the same variety have been raised. The plantskeep on absorbing the same elements from the soil and hence the soil becomes impoverished.

There are three important factors which affect the fertility of a soil.

1) The amount of fixed nitrogen,
2) Nitrogen, phosphorous, potassium and other minerals salts,
3) pH value of the soil.

SYMPTOMS OF DEFICIENCY:

The nature of symptoms depends upon:

1) The degree of deficiency,
2) The type of the crop and
3) The nature of the soil.

Some examples are given below:

a) **Nitrogen:** Deficiency of nitrogen reduces plant vigour and the leaves become light green or yellowish green.

b) **Phosphorus:**Deficiency of phosphorus causes poor root growth, delayed ripening, stunted growth etc. These are very important in cotton, tobacco and potato crops.
c) **Potassium:**Deficiency of potassium is responsible for causing small white, yellow or reddish brown spots on the leaves following by the browning of the leaf edges.
d) **Iron:**Deficiency of iron causes the leaves to lose green colour.
e) **Magnesium:**Deficiency of this is responsible to cause the yellowing or redding of the tips and margins of the leaves.
f) **Calcium:**It causes a distorting of new leaves.

CLASSIFICATION OF FERTILIZERS:

Fertilizers are classified as direct or indirect fertilizers according to their agrochemical nature.

a) **Direct fertilizers:** Direct fertilizers are those which contain the nutrient elements in the form of compounds which are directly assimilated by plants.Examples are: super phosphates, nitrates and other ammonium compounds.
   Direct fertilizers are classified as phosphatic nitrogenous, potash, magnesium etc, according to the nutrient element present in them.
b) **Indirect fertilizers:** Indirect fertilizers are those substances which are added to the soil in order to improve its chemical, mechanical or biological properties. Ground dolomite and limestone, used to decrease soil acidity and gypsum used to improve the properties of soils with a high salt content are the examples of indirect fertilizers
c) **Complete fertilizers:**There are fertilizers which provide all the essential elements (nitrogen, phosphorus, potassium etc.), to the soil, guano is a classic example of a complete fertilizer.
d) **Incomplete fertilizers:**These can provided only one or two essential elements to the soil. For example KNO_3, ammonium phosphate etc.
e) **Mixed fertilizers:**These are prepared by mixing appropriate quantities of ammonium salts, superphosphates and potassium salts etc. they may supply more than one essential element.

According to the number of basic nutrient elements such as phosphorus, nitrogen and potassium in them fertilizers are classified as **simple fertilizers**, containing only one nutrient element or **double or triple fertilizers**, containing two or three elements respectively.
The **triple fertilizers** are also called **complete fertilizers** because they contain all the principal nutrient elements nitrogen, phosphorus and potassium.

Micro fertilizers are those which contain the elements such as boron, manganese, zinc and copper. These fertilizers are required in very small amounts to stimulate the plant growth.

Fertilizers containing several nutrient elements and obtained by mechanical mixing of various fertilizers are known as **mixed fertilizers.**

Fertilizers containing several nutrient elements which are produced by chemical reactions are known as **complex fertilizers.**

Fertilizers are classified as**water soluble** or **soluble in soil acids** according to their solubility in the moisture in the soil. All nitrogenous and potash fertilizers are soluble in water. These fertilizers are readily assimilated by plants, but they are quickly washed out of the soil by surface water.Most phosphates are the fertilizers soluble in soil acids. They are dissolved much slower, but are retained in the soil much longer.

Fertilizers are classified as **physiologically acid**, **physiologically alkaline** or **physiologically neutral**, according to their physiological effect on the soil to which they are added. The physiological neutral fertilizers do not change the pH of the soil.

According their form or physical properties, fertilizers are subdivided into **powder form** and **granulated form**. Granulated fertilizers are less hygroscopic and they do not cake during storage. They are not subjected to weathering after being introduced into the soil and are retained by the soil for a longer time, that is,they are not washed out quickly by rains. Moreover, granulated fertilizers can be added to the solid using fertilizer machines or seed drills.

SOURCE OF FERTILIZERS :

Fertilizers can be obtained from natural and artificial sources.

Two sources of fertilizers are: (1) Natural (2) Artificial

- **Natural fertilizers:**

Natural Organic Fertilizers :

a) **Plant matter:** Oil cakes from cotton seed meal, linseed meal and caster cake belong to this class contains 7%, 5.5% and 6% of nitrogen respectively.
b) **Farmyard manures:**A typical farmyard manure consists of cow dung, sheep dung and human excretions.
c) **Animal matter:**Powdered dry fish and red dry blood from the slaughter house are important nitrogenous fertilizers
d) **Guano:**Guano is a classic example of complete fertilizer and it is a mixture of birds excrements, fish refuge and fish hones.

Natural Inorganic Fertilizers :

a) **Chile saltpeter:** $NaNO_3$
b) **Rock phosphates:**Finely divided rock phosphate, although insoluble in water weathers rapidly and may be used directly
c) **Potassium salts:** Natural potassium sources are wood ash (containing 5–6% potash) and waste materials of sugar beet crops.

- **Artificial fertilizers:**

Natural organic and inorganic fertilizers are not sufficient to make the soil productive. As the natural fertilizers cannot completely meet the demand, the artificial fertilizers are to be manufactured.

These may be studied under three groups according to nature of the element.

Nitrogenous fertilizers

Important commercial nitrogenous fertilizers are nitrates of sodium, calcium and potassium, ammonium sulphate, calcium cyanamide, ammonium nitrate and urea.

AMMONIUM NITRATE :

Ammonium nitrate is a very important nitrogenous fertilizer because of its high nitrogen content (33%), the simplicity and cheapness of its manufacture, and its valuable combination of quick acting nitrate and slower-acting ammoniacal nitrogen.

Its tendency to cake on storage reduced its acceptability at first but proper granulation, the addition of antihygroscopic agents, and better packaging have largely remedied this problem.

Most commercial and many military explosives contain cheap ammonium nitrate as the major explosive ingredient.

Ammonium nitrate is difficult to detonate, but when sensitized with oil or mixed with other explosive materials, it can be detonated with a large booster-primer.

Ammonium nitrate mixtures are “permissible”, that is, permitted for use in coal mines where combustible vapors may be encountered.

The use of explosives in mines and quarries provides a large and continuing market.

Amatol is a mixture of TNT and granular ammonium nitrate (AN). This is the major conventional military explosive.

On explosive decomposition, ammonium nitrate (AN) rapidly and violently decomposes to form elemental nitrogen.

$$NH_4NO_3 \rightarrow 2N_2 + 4H_2O + O_2$$

Under different conditions, i.e. at 200 – 260°C, it is safely decomposed to form the anesthetics nitrous oxide. This is the commercial method of preparation.

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

Ammonium nitrate is made by reacting nitric acid (made by oxidizing ammonia) with ammonia.

$$NH_{3\,(g)} + HNO_{3\,(aq)} \rightarrow NH_4NO_{3\,(aq)} \quad \Delta H = -86.2 \text{ kJ}$$

If properly proportioned and preheated, the reaction can be run continuously to produce molten ammonium nitrate containing very little water (1 to 5%) which can be formed into small spheres (prills) by dropping the reaction product through a shot tower or into flakes by cooling it on belts or drums.By fluidized bed treatment; it is possible to obtain a dry granular material as product.Batch processes have also been used, but the labor and equipment costs are prohibitive.

Figure shows a typical flowchart.

Manufacture:
Ammonium Nitrate:

Ammonium nitrate is most important nitrogenous fertilizer.

1	Percentage of nitrogen	3.5%
2	Solubility, g/100g. water 32°F	118
	212°F	843
3	Melting point °C	170.4

Raw materials:

The raw materials for ammonium nitrate are ammonia and nitric acid and both of these usually produced at the same installation.

Method of production:

There are three important methods of producing ammonium nitrate:

a) Crystallization
b) Flaking
c) Prilling

Prilling:

A modem ammonium nitrate prilling plant consists of the following operations:

a) **Neutralization:**
Heated ammonia vapour (obtained by Haber's process) and 60–80% nitric acid (prepared by the oxidation of ammonia) are introduced at the base of a neutralizer tower operating under a pressure of 3–5 atmospheres and through which neutralized solution is recycled.
The neutralization reaction is exothermic and gives a high yield.

$$HNO_3 + NH_3 \rightarrow NH_4NO_3 \quad \Delta H = 20.6 \text{ k.cals}$$

b) **Evaporation:**
Solution obtained from the neutralizer contains about 83% NH_4NO_3. This solution is allowed to pass through a heater supplied with steam for the neutralizer. The heated solution from the heater is then passed to a vacuum evaporator when its concentration is increased to about 95%.

c) **Prilling:**
The concentrated solution is now sprayed into prilling tower.
The falling solution in the tower is cooled by an ascending current of air.
The prilling towers are quite high, up to 185 ft. The solution is sprayed through spray nozzles in such a manner that the liquid breaks up into drops of uniform and adequate size.
The prills solidify sufficiently as they reach the bottom of the tower.
They must be handled carefully until they are dried.

d) **Drying and finishing:**
It is very difficult to dry the prills of ammonium nitrate because it is deliquescent in nature. The drying temperature must be low to avoid melting.
Various methods of drying are available. In one method, the material is cooled to below 90°F and the remaining moisture is removed in a second dryer.

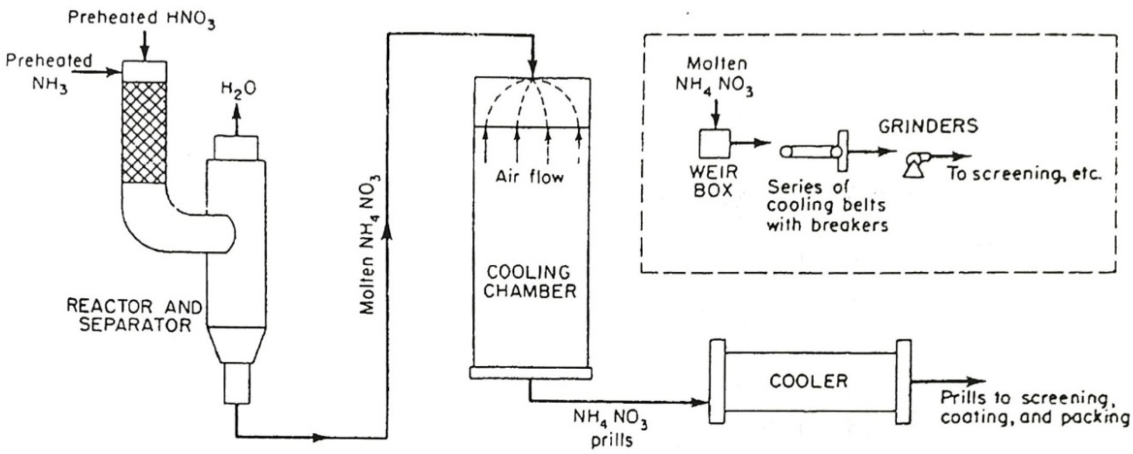

Fig. 3.5. Simplified flowchart for the Stengel process for ammonium nitrate manufacture. *(Commercial Solvents Corp. and L. A. Stengel.)*

In another method, known as short tower prilling, ammonium nitrate solution concentrated to about 99.5% rather than the usual 95% is prilled in the usual way in a short tower, making use of the fact that strong solution solidifies faster.

The last trace of water may be removed by the process of evaporation than removing it in dryers.

AMMONIUM SULPHATE :

Ammonium sulfate, which has little tendency to cake on storage, was accepted by farmers long before ammonium nitrate was made noncaking.

Originally it was made by using sulfuric acid to scrub by-product ammonia from coke-oven gas and much is still produced in this manner.

However, most ammonium sulfate is now made by reaction between synthetic ammonia and sulfuric acid.

Production is about 2.3×10^6 t/year with about 20% from by-product ammonia. Where sulfur for sulfuric acid is at a premium, for example at Sindri India a process based on gypsum and carbon dioxide from combustion is used:

$$(NH_4)_2CO_{3\,(aq)} + CaSO_4 2H_2O_{(S)} \rightarrow CaCO_{3(s)} + 2H_2O + (NH_4)_2SO_{4\,(aq)}$$

Anhydrite can also be used.Some ammonium sulfate is also obtained as a by-product of caprolactum (for nylon – 6) manufacture.

Manufacture:

Ammonium sulphate :
Properties:

Properties of fertilizer grade ammonium sulphate are given in the following table.

1	Percent of nitrogen	20 – 21%
2	Solubility g/100gH_2O	
	32°F	70.6
	212°F	103.8
3	Melting point °C	513°C

AMMONIUM SULPHATE FROM GYPSUM OR ANHYDRITE ($CaSO_4 2H_2O$) :

A new method, which is used at Sindri in India, consists in passing a concentrated aqueous solution of ammonia down a tower, packed with aluminium rings against a current of CO_2so as to form ammonium carbonate.

$$2NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2CO_3$$

Ammonia is manufactured by Haber process and CO_2 is manufactured by heating lime stone.

$$CaCO_3 \rightarrow CaO + CO_2$$

Now proper proportion of finely ground gypsum or anhydrite is fed into the aqueous solution of ammonium carbonate in large tanks, whereby calcium carbonate is precipitated gradually as a result of double decomposition.

$$(NH_4)_2CO_3 + CaSO_4 \rightarrow (NH_4)_2SO_4 + CaCO_3$$

CO_2 and NH_3 are passed until all the gypsum is converted into $CaCO_3$.The resulting $CaCO_3$ is separated by filtration and the ammonium sulphate solution is evaporated and crystallised in vacuum. $CaCO_3$ is used as a raw material for the manufacture of cement.

ACTION OF $(NH_4)_2SO_4$AS FERTILIZER :

Ammonium sulphate reacts with lime present in the soil to form ammonium hydroxide which is oxidized by air with the help of nitrosifying bacteria into nitrous acid.
The latter is then converted into nitrites.
The nitrous acid and nitrites also undergo oxidation by means of air in presence of nitrosifying bacteria and form nitric acid and nitrates.
The bases present in the soil react with nitric acid to form potassium and calcium nitrate etc.
Most of the plants take up nitrogen in the form of these soluble nitrates.

UREA :

Urea is in many ways the most convenient form for fixed nitrogen.

It has the highest nitrogen content available in a solid fertilizer (45 – 47 %).

It is to produce as prills or granules and easily transported in bulk or bags with no explosive hazard.

It dissolves readily in water.

It leaves no salt residue after use on crops and can often be used for foliar feeding.

In addition to fertilizer use it is used as a protein food supplement for ruminants, in melamine production as an ingredient in the manufacture of resins, plastics, adhesives, coatings, textile antishrink agents and ion-exchange resins.

It is an intermediate in the manufacture of ammonium sulfamate, sulfamic acid and phthalocyanines.

Annual production in the United States is very large, 6.4×10^6 t at \$150 to \$160 per metric ton in 1982.

Two reactions are involved in the manufacture of urea.

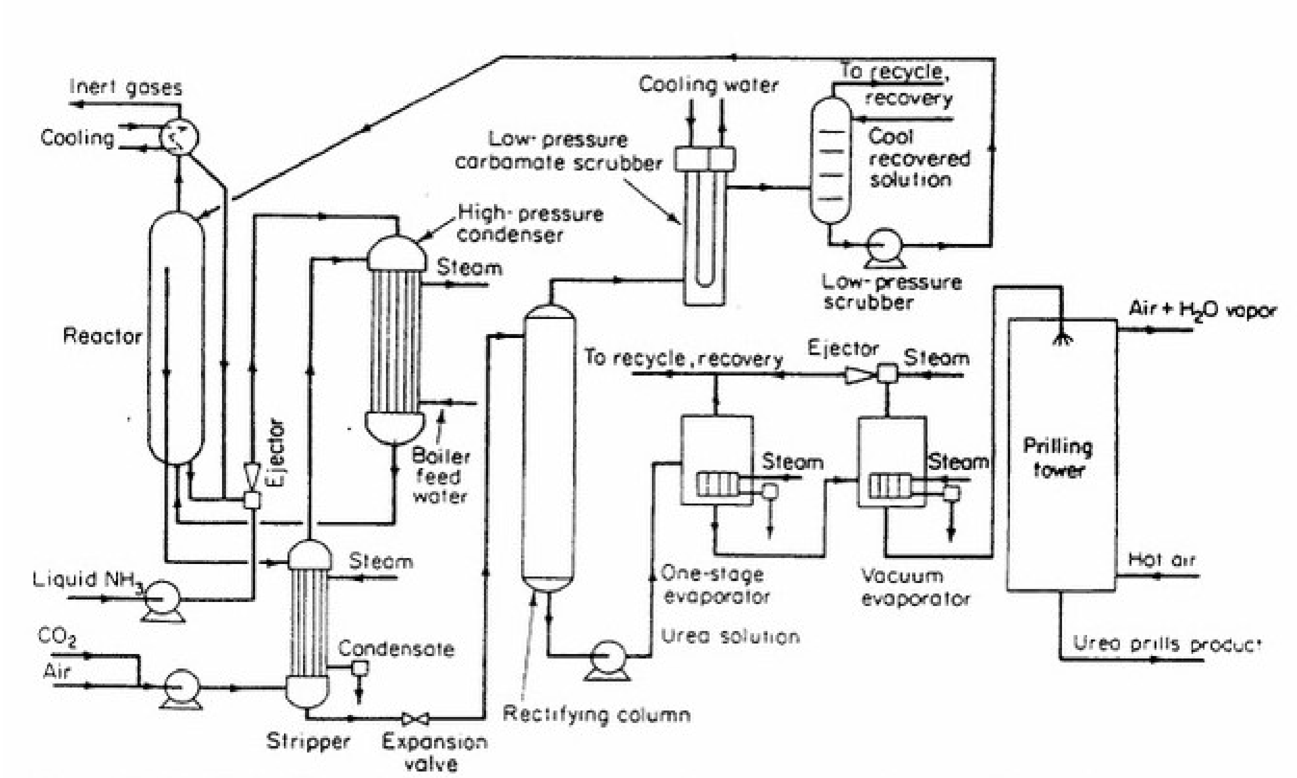

Fig. 3 .6. Simplified flow chart, Stamicarbon urea stripping process. *(Stamicarbon and M. W. Kellogg Co.)*

Urea occupies the third place among the world's solid nitrogenous fertilizers, but it is the highest in nutrient concentration because, if pure, it contains nearly 45–47% nitrogen.

The most important properties of fertilizer grade urea are given in the following table.

PROPERTIES OF FERTILIZER GRADE UREA

1	Nitrogen percentage	45%
2	Solubility g/100 ml H_2O at 25°C	119
3	Melting point	132.7°C

Manufacture:

Urea can be manufactured by passing liquid CO_2 and liquid NH_3 in a silver lines special, autoclave when ammonium carbamate is formed.

The latter is heated at 130–135°C under about 35 atmospheric pressure to get urea.

The conversion is about 40% urea remains in the aqueous solution.

The resultant charge is passed into another vessel and steam is introduced.

$$2NH_3 + CO_2 \rightarrow NH_2COONH_4$$

$$\underset{\text{Ammonium Carbamate}}{NH_2COONH_4} \rightarrow \underset{\text{Urea}}{NH_2CONH_2} + H_2O \qquad \Delta H = +6.3 \text{ k cals}$$

Since the rate determining step is endothermic, the overall reaction should be favored by a rise in temperature.

But conversion of NH_2COONH_4 to NH_2CONH_2 actually records increasing yield upto about 170°C and above it, it fails.

Temperature above 200°C in a 180–200 atm. unit is not conductive, because it promotes corrosion, and favours biuret formation (a side reaction) at the cost of urea.

$$\underset{\text{Urea}}{2NH_2CONH_2} \rightarrow \underset{\text{Biuret}}{NH_2 - CO - NH - CONH_2} + NH_3$$

Action of urea as fertilizer :

Urea is first hydrolysed by soil water to NH_3 and CO_2.

Then, nitrosification of NH_3 takes place by nitrosomonas and nitrosococcus bacteria and nitrites are formed.

Nitrification of nitrites is brought about by nitrobactor bacteria to form nitrates utilized by the plants in the soil.

$$NH_2CONH_2 + H_2O \rightarrow CO_2 + 2NH_3$$

$$2NH_3 + 3O_2 \xrightarrow{\text{BACTERIA}} 2NO_2^- + 2H_2O + 2H^+ + \text{ENERGY}$$

$$2NO_2^- + O_2 \xrightarrow{\text{BACTERIA}} 2NO_3 + \text{ENERGY}$$

CALCIUM AMMONIUM NITRATE

Calcium nitrate contains 15.5% nitrogen and its manufacturing process involved reaction of lump limestone with concentrated nitric acid, addition of ammonia to neutralize excess of acid, evaporation of the resulting solution, and prilling or flaking the melt.

The resulting product is a double salt, $5Ca(NO_3)_2NH_4NO_3$ called calcium ammonium nitrate and is more useful than the single salt calcium nitrate.

Calcium ammonium nitrate contains 19% nitrogen and is manufactured in India particularly at Nangal(Punjab).

Ammonium nitrate is first prepared by the reaction of ammonia (obtained by oxidation of ammonia) as described earlier.

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

Ammonium nitrate so obtained contains some unreacted nitric acid which is neutralized by adding calcium carbonate (obtained as a byproduct in the manufacture of ammonium sulphate).

On cooling grain of calcium ammonium nitrate separate out.

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

$$CaCO_3 + 2\,HNO_3 \rightarrow Ca(NO_3)_2 + CO_2 + H_2O$$

$$CaCO_3 + NH_3 + 3HNO_3 \rightarrow Ca(NO_3)_2 + NH_4NO_3 + CO_2 + H_2O$$

The granules of calcium ammonium nitrate are finally coated with thin layer of soap stone powder, which acts as a protective coating and prevents the absorption of moisture during storage and transportation.

CO_2 is obtained as a byproduct.

AMMONIUM PHOSPHATE :

(a) MonoammoniumPhosphate:

Monoammonium phosphate is prepared by the action of sulphuric acid on a mixture of calcium phosphate and ammonium sulphate. As a result, monoammonium phosphate is formed along witha slurryof $CaSO_4$. The prohpate is separated from the slurry and crystallised to get fine crystals of monoammoniumphoaphate containing about 12% nitrogen and 50% P_2O_5.

$Ca_3(PO_4)_2 + (NH_4)_2SO_4 + 2H_2SO_4 \rightarrow 2NH_4H_2PO_4 + 3CaSO_4\downarrow$
Monoammonium phosphate
Monoammonium phosphate can also prepared by treating anhydrous ammonia with phoaphoric acid with a P_2O_5 content of 40–42% at a controlled pH of 5.6 in a tank. 90% neutralization takes place through the exothermic reaction.

$$NH_3 + H_3PO_4 \rightarrow NH_4H_2PO_4 + \text{ x cals}$$

The slurry from the neutralizer is spread over a revolving drum fitted with water absorption device.

The cakes of monoammonium phosphate thus formed are dried, disintegrated, cooled, screened and packed.

Ammonium phosphate is best suited for all crops and soils.It is readily soluble in water and so becomes available to crops readily. It is slightly acidic in nature.

The acidity developed by application of 100 lbs of ammonium phosphate requires 86 lbs of $CaCO_3$ to neutralize the acidity.

Ammonium phosphate is well suited for use in calcareous and alkaline soils.

(b) Diammonium Phosphate:

It is prepared by continuous process in which anhydrous ammonia gas and almost pure phosphoric acid are passed into saturated mother liquor containing monoammonium phosphate.

The temperature is kept at about 60–70°C and pH about 6.0.The heat of reaction vaporizes water from the liquor and crystals of pure diammonium phosphate are formed.

These are centrifuged, washed and dried.

Diammonium phosphate can also be prepared by taking the slurry from the neutralization tank for the preparation of monoammonium phosphate into a second water cooled neutralizer.

Here it is allowed to react with anhydrous NH_3. The unreacted NH_3 is taken out for neutralization of a second lot of monoammonium phosphate.

Rest of the process is similar to the preparation of monoammonium phosphate.

$$NH_4H_2PO_4 + NH_3 \rightarrow (NH_4)_2HPO_4$$

Diammonium phosphate

This fertilizer is better in nitrogen but poor in phosphorus.

(a) Triammonium Phosphate:

Similarly, triammonium phosphate can also be prepared.

$NH_3 + H_3PO_4 \rightarrow NH_4H_2PO_4$

Monoammonium phosphate

$2NH_3 + H_3PO_4 \rightarrow (NH_4)_2HPO_4$
Diammonium phosphate

$3NH_3 + H_3PO_4 \rightarrow (NH_4)_3PO_4$
Triammonium phosphate

NORMAL SUPERPHOSPHATE :

Phosphate manure can be taken up by the plants in soluble form.When tricalcium phosphate in the form of bone meal or rock phosphate powder (main source of P_2O_5) is applied to the soil,$Ca_3(PO_4)_2$ is slowly converted into $Ca(H_2PO_4)_2$ in the soil through the agency of acids present in the soil and then the soluble phosphate is taken up by the plants.In order to avoid the slow transformation, rock-phosphate is transformed quickly into soluble phosphate, which is then applied to the soil.This artificially prepared mono calcium phosphate, $Ca(H_2PO_4)_2$ is known as **superphosphate**.

Commercial superphosphate is a mixture of mono calcium phosphate and crystalline calcium sulphate, $Ca(H_2PO_4)_2 + CaSO_4 \cdot 2H_2O$. it contains about 16% P_2O_5.

The soluble calcium phosphate prepared by treating rock phosphate with sulphuric acid is called **superphosphate**.

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 2H_2O \rightarrow Ca(H_2PO_4)_2 + 2CaSO_4 2H_2O$$

Normal superphosphate is manufactured by mixing equal quantities of powdered phosphate rock and chamber acid (sp. Gr. 1.45–1.60) into a cast iron mixer M provided with a stirring mechanism.The mass is stirred for about 5 minutes and then it is allowed to remain for a day.P_1 and P_2 are openings which lead to the respective pits from the mixer M. The temperature rises to about 100–110°C as the reaction is exothermic.A mixture of fumes consisting of HF (from calcium fluoride), SiF (from calcium fluoride and silica) and CO_2 (from lime stone) are evolved.These gases make the material porous.

As the reaction proceeds, the mixture stiffens and ultimately sets to a solid mass. Successive charges from the mixer are introduced to the pits A_1 or A_2 until it is full and then it is allowed to stand for some days. When it has become perfectly dry, it is dug out of the pit and meanwhile the second pit is filled. The gases from the mixture and pits are washed by spraying water in two successive towers. The resulting hydrofluoric acid solution is then neutralized easier by sodium carbonate or sodium fluoride and finally treated with washed sand to from Hydrofluosilicic acid(Hexafluorosilicic acid$H_2[SiF_6]$).

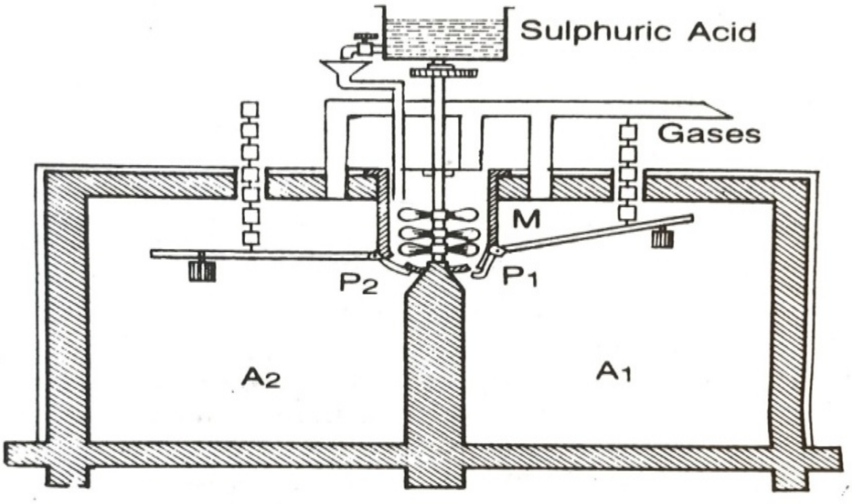

Fig. 6. Manufacture of super phosphate.

The latter is further neutralized with sodium carbonate to form sodium silico fluoride (Na_2SiF_6) or with magnesium to form magnesium silico fluoride ($MgSiF_6$).The product is used without further treatment other than breaking it up to the desired size. The main reaction is:

$$Ca_{10}(PO_4)_6F_2 + 7H_2SO_4 + 3H_2O \rightarrow 3Ca(H_2PO_4)_2\ 3H_2O + 7CaSO_4 + 2HF$$

Na_2SiF_6 or $MgSiF_6$ are useful by products.

Raw materials:

A fairly high grade of phosphate rock is required to make super phosphate that contains 20% available P_2O_5.Rock containing 33.5% or more P_2O_5 is normally used.Strong sulphuric acid (93–98%) is used in most plants.

Properties:

a) Superphosphate normally contains 5–8% moisture after curing. Low moisture contents help in reaching the general objective of 20% available P_2O_5 contents.
b) Hygroscopicity is quite low, the critical relative humidity at 86°F is 94%.
c) Bulk density for non-granular and granular material, ranges from about 50 to 70 lb/ft^3 respectively.

TRIPLE SUPERPHOSPHATE :

Triple superphosphate or concentrated superphosphate contains about 44–47% P_2O_5 content, which is nearly three times as high as in normal superphosphate.It can be manufactured by the action of 78% phosphoric acid (containing 52–54% P_2O_5) on finely powdered calcium phosphate or phosphate rock containing about 32.5–33% P_2O_5 content. The manufacturing procedure is quite similar to that of normal superphosphate. The reaction mixture is allowed to stand for about 3 months to make the reaction complete.The grey solid mass thus obtained is crushed to powder.

$$Ca_3(PO_4)_2 + 4H_3PO_4 \rightarrow 3Ca(H_2PO_4)_2$$

Triple superphosphate is essentially an impure mono-calcium phosphate, made by the following reaction.

$$Ca_{10}(PO_4)_6F_2 + 14H_3PO_4 + 10H_2O \rightarrow 10CaH_4(PO_4)_2\ 10H_2O + 2HF$$

The properties of triple superphosphate depend upon the type of rock and acid used for production and on the granular or nongranular nature the product. **Granular triple superphosphate** is usually prepared by the following methods:

a) In **wet and dry method** granulation is carried out by treating the crude product with water and steam in a rotary drum, followed by drying and screening.
b) In **slurry granulation method**, rock is mixed with relatively weak acid (38–40% P_2O_5) in a series of tanks.The resulting slurry is then mixed with excess of dried recycled granules in a paddle mixer, called blunger. The coated granules thus obtained are dried and screened.
c) In another **granulation process**, acidulations as well as granulation are carried out simultaneously in a rotary drum. Preheated acid, phosphate rock and recycled fines are mixed in the drum and then granulated with steam. The resulting product is cooled screened and cured.

Properties of granular triple superphosphate depend on the type of process by which it is manufactured.

(Mixed Fertilizers)

NPKFERTILIZERS :

A mixed fertilizer is one which is prepared by mixing three major plant nutrients, namely nitrogen, phosphoric acid and potash in suitable proportion. It may be made either at home or in factories by mixing the constituent fertilizer in correct proportion.

The modern trend is towards the production of mixed fertilizers containing nitrogen, phosphorus and potash. Such a fertilizer is called NPK fertilizer.

Example of NPK fertilizers are ammonium sulphate, phosphate and potash (KCl) combination.

This mixed NPK fertilizer can be preparedby taking anhydrous liquid ammonia, phosphoric acid (25–30% P_2O_5), sulphuric acid (93–98%) and potash (KCl) as raw materials. The manufacture involves three neutralization tanks.

The acid mixture and anhydrous ammonia are allowed to react, as a result of which 80% neutralization takes place.

The exothermic reaction boils the liquid producingslurry that is taken into second neutralizer for further ammonization and finally to the third neutralizer for final treatment furnishing a diammonium salt.

The slurry from the third neutralizer is mixed with calculated amount of potash (KCl) to get NPK fertilizer of proper grade.

It is passed through a granular, dried in hot air at about 140–150°C, screened and packed.

$$NH_3 + H_3PO_4 \rightarrow NH_4H_2PO_4$$

$$NH_3 + NH_4H_2PO_4 \rightarrow (NH_4)_2HPO_4$$

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)2SO_4$$

POSITION OF FERTILIZER IN INDIA:

The growth of the chemical fertilizer industry in India is largely reflected in the growth of the fertilizer corporation of India.

The corporation was formed on 1st January, 1961.

At that time there were only two operating units, one at Sindri and other at Nangal. Later on With the addition of three more plants (Trombay, Gorakhpur and Namrup), the corporation has five operating units with as aggregate production capacity of 3,85,000 tons of nitrogen per year and produced more than 50% of the country's fertilizers.

The rapid growth of the corporation is evident from the fact that in 1960–61 when it came into existence. It was producing 68,400 tonnes of nitrogen where as in 1971-1972, its production has increased to 3, 85,000tonnes of nitrogen and 36,000tonnes of P_2O_5 by 1973.

Later on two more plants at Durgapur and Barauni, as well as Namrup expansion were established with the production capacity in terms of nitrogen was nearby 8,29,000 tonnes.

There are more than 57 large and 64 medium and small fertilizer production units under the India fertilizer industry. (May, 2015).

Some units are located at Trombay, Sindri, Sindri, Gorakhpur, Namrup, Namrup expansion, Durgapur, Brauni, Trombay expansion, Sindrirationalisation, Talcher, Ramangundam, Haldia.

The main products manufactured by the fertilizer industry in India are phosphate based fertilizers, nitrogenous fertilizers, and complex fertilizers.

Production of fertilizer-N in India increased from 0.1 million tons (Mt) in 1960–61 to 13.5 Mt in 2015–16. The number of urea manufacturing units currently being 30.

QUESTION BANK

MCQ :

(1)	How many elements have been considered essential for plant growth and development ?			
	(a) 16	(b) 15	(c) 17	(d) 14
(2)	Carbon, hydrogen and oxygen are derived from air and water and so these are called __________ nutrients.			
	(a) primary	(b) secondary	**(c) natural**	(d) micro
(3)	Nitrogen, phosphorus and potassium called ____________ nutrients.			
	(a) primary	(b) secondary	(c) natural	(d) micro
(4)	Calcium, magnesium and Sulphur are called ___________ nutrients.			
	(a) primary	**(b) secondary**	(c) natural	(d) micro
(5)	Elements which required by plants only in minute quantities are called _________ nutrients.			
	(a) primary	(b) secondary	(c) natural	**(d) micro**
(6)	The primary and secondary plant nutrient elements collectively known as _____ plant nutrients.			
	(a) major	(b) minor	(c) micro	(d) trace
(7)	The nutrients which are used by the field crops in very small quantities are known as -			

	______ plant nutrients.			
	(a) major	(b) minor	**(c) micro**	(d) trace
(8)	Soil take's up the _______ in the form of ammonium or nitrate ions			
	(a) phosphorus	(b) potassium	(c) calcium	**(d) nitrogen**
(9)	Deficiency of _______ reduces plant vigour and the leaves become light green or yellowish green.			
	(a) phosphorus	**(b) nitrogen**	(c) potassium	(d) calcium
(10)	Deficiency of ______ causes the leaves to lose green colour.			
	(a) iron	(b) zinc	(c) magnesium	(d) calcium
(11)	A deficiency of ______ causes leaves to turn white and growth to cease.			
	(a) zinc	(b) calcium	**(c) iron**	(d) magnesium
(12)	Deficiency of _____ is responsible for causing small white, yellow or reddish brown spots on the leaves following by the browning of the leaf edges.			
	(a) Zinc	(b) copper	(c) Molybdenum	**(d) potassium**
(13)	Deficiency of ______ is responsible to cause the yellowing or redding of the tips and margins of the leaves.			
	(a) Zinc	(b) copper	(c) Molybdenum	**(d) magnesium**
(14)	The nutrient elements in the form of compounds which are directly assimilated by plants is known as __________ fertilizers.			
	(a) direct	(b) indirect	(c) complete	(d) incomplete
(15)	______ fertilizers are those substances which are added to the soil in order to improve its chemical, mechanical or biological properties.			
	(a) Direct	**(b)Indirect**	(c) Complete	(d) Incomplete
(16)	______ fertilizers which provide all the essential elements to the soil.			
	(a) Direct	(b) Indirect	**(c) Complete**	(d) Incomplete
(17)	______ fertilizers can provide only one or two essential elements to the soil.			
	(a) Direct	(b) Indirect	(c) Complete	**(d) Incomplete**
(18)	To dry the prills of ammonium nitrate is very difficult because ammonium nitrate is _________ in nature.			
	(a) amorphous	**(b) deliquescent**	(c) sublimating	(d) None of these
(19)	Ammonium sulphate reacts with lime present in the soil to form ______.			
	(a) ammonium hydroxide	(b) ammonium nitrite	(c) ammonium nitrate	(d) None of these
(20)	_________ is the molecular formula of ammonium carbamate.			
	(a) $C_2H_6N_2O_2$	**(b) $CH_6N_2O_2$**	(c) $C_2H_4N_2O_2$	(d) $C_2H_6N_2O$
(21)	The acidity developed by application of 100 lbs of ammonium phosphate requires _________ lbs of $CaCO_3$ to neutralize the acidity.			
	(a) 82	(b) 76	**(c) 86**	(d) 78
(22)	Commercial superphosphate is a mixture of ______ calcium phosphate and crystalline calcium sulphate.			
	(a) mono	(b) di	(c) tri	(d) None of these

Short Questions :

(1) Define : Fertilizers, Plant Nutrients
(2) Give the classification of plant Nutrients.
(3) What is the function of plant Nutrient nitrogen / phosphorus / calcium / magnesium / iron ?
(4) What are the essential requirements of fertilizers ?
(5) Give the classification of fertilizers.
(6) What are the sources of natural organic fertilizers?

(7) Give the action of ammonium sulphate as a fertilizer.
(8) Give the action of urea as a fertilizer.
(9) How will you prepare triammonium phosphate.
(10) What are the properties of normal super phosphate ?
(11) How will you prepare Granular triple superphosphate ?
(12) What is NPK fertilizers ?

LongQuestions :

(1) Define plant nutrients. Discuss the function of plant nutrients.
(2) Discuss the classification of fertilizer.
(3) Describe the manufacturing process of ammonium nitrate.
(4) Discuss the manufacturing process of urea and also write action of urea as fertilizers.
(5) Explain manufacturing process for normal super phosphate.