

**ACHARYA N.G.RANGA AGRICULTURAL UNIVERSITY  
RAJENDRA NAGAR, HYDERABAD**



**MANURES , FERTILIZERS AND AGRICULTURAL CHEMICALS**

**Course No. : SSAC 321**

**Credits: 2+1 = 3**

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**Lecture :1** Introduction- Definition , difference between manures and fertilizers-Classification of manures (Bulky & Concentrated) with suitable examples. Importance of manures in soil fertility management

The word “Manure” is originated from the French word “MANOEUVRER” which refers to “work with soil” .The word Manure is also originate from Latin word “Manu” (hand) and operate( to work).

#### **Manure:**

Manures are the substances which are organic in nature, capable of supplying plant nutrients in available form , bulky in nature having low analytical value and having no definite composition and most of them are obtained from animal and plant waste products.

Formerly, the word in use was “DUNG ”in English (at present fertilizer). It is derived from the old German word “TUNG” meaning storage pit covered with manure for protection of soil against cold .From Tung “TUNGEN is derived (to cover ) and then dung (fertilizer ) as the cover .

The corresponding English word “Fertilizer” which is now accepted internationally in view of the old English word DUNG was derived from Latin word “Fertil” .

#### **Fertilizer:**

A fertilizer can be defined as a mined or manufactured material containing one or more essential plant nutrients in potentially available forms in commercially valuable amounts.

#### **Differences between manures and Fertilizers:**

S.No.	MANURES	FERTILIZERS
1	Organic in nature	Inorganic in nature
2	Slow acting	Quick acting
3	Having low analytical value	Having high analytical value
4	Having no definite chemical composition	Having definite chemical composition
5	Obtained from plant , animal and human resources	Mined or manufactured
6	Improves physical properties of soils	Don't improve the physical properties of soils
7	Supply almost all major, minor and micronutrients.	Supply one or very few plant nutrients.
8	Derived from French word 'MANOEUVRER' to work with soil	Derived from Latin word Fertil ( means Fertile )
9	Bulky in nature	Non-bulky in nature

**Manuring:** Manuring is the process of increasing the productive capacity of land by adding plant foods to the soil in different forms.

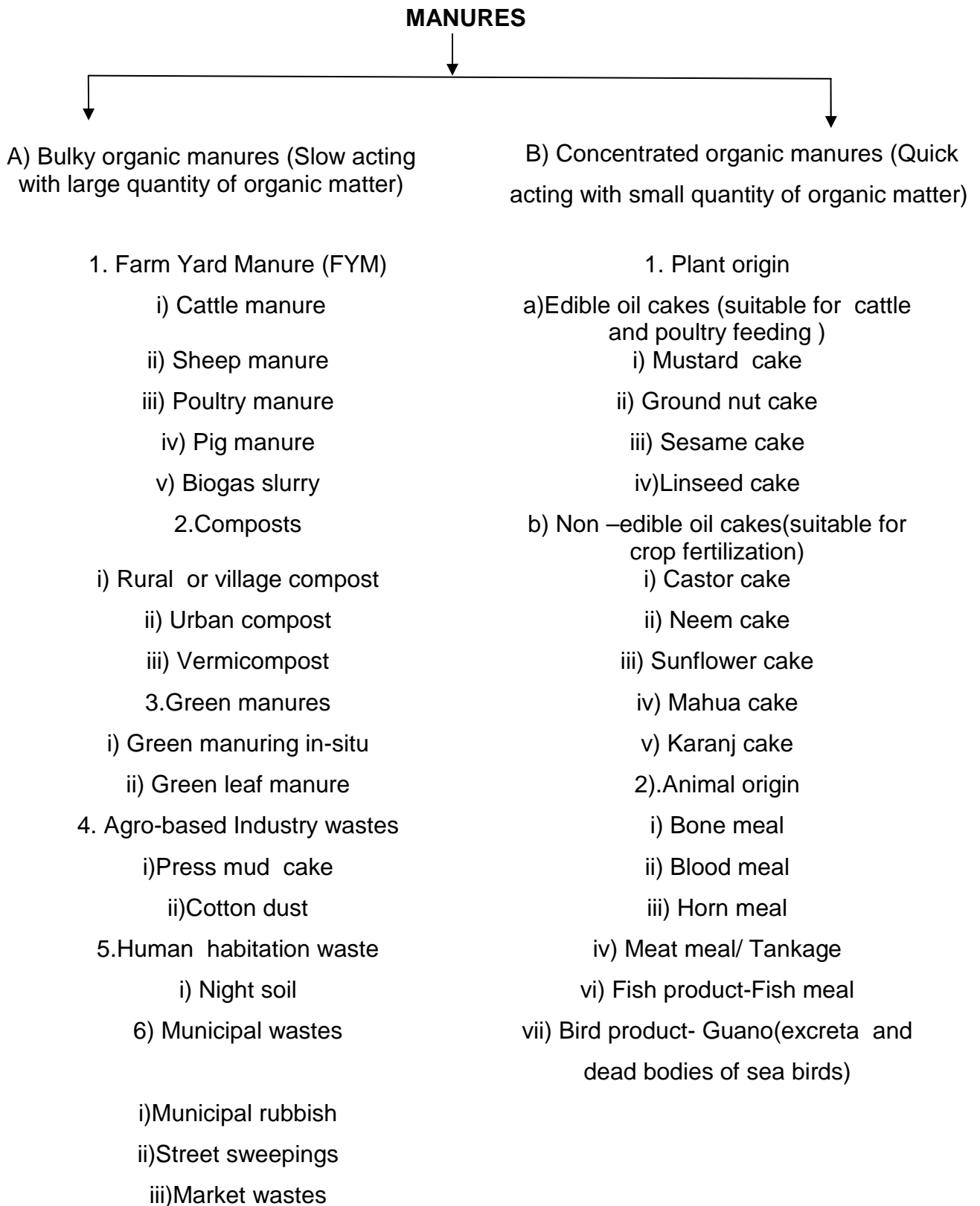


## Classification of Manures and fertilizers with examples

I. Classification of Manures

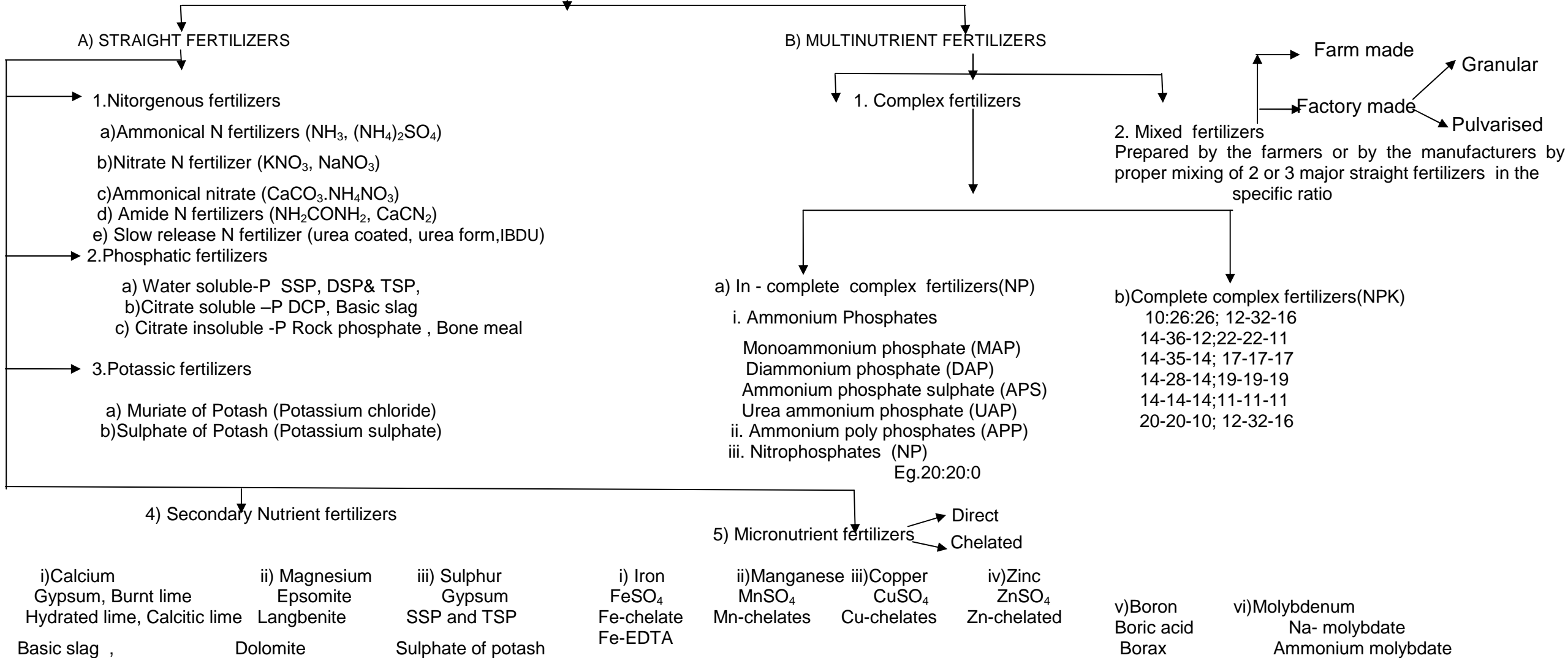
II. Classification of Fertilizers

I. Classification of Manures :



## II. CLASSIFICATION OF FERTILIZERS

### FERTILIZERS



## IMPORTANCE OF MANURES IN SOIL FERTILITY MANAGEMENT

### A) Bulky organic manures:

The bulky organic manures are organic in nature and required in huge amounts. All these bulky organic manures are bulky in nature and supply i) plant nutrients in small quantities and ii) organic matter in large quantities. Eg. FYM, Composts, Green manures, Sewage sludge. Of the various bulky organic manures FYM, Compost and Green manures are widely used. The effect of bulky organic manures on soils is three fold.

- I. Since these manures contain plant nutrients, they have direct effect on plant growth like any other commercial fertilizer. Bulky organic manures contain nutrients in small quantities, therefore large quantities of these are needed. Besides the major nutrients, they also contain traces of micro-nutrients
- II. Bulky organic manures increase organic matter content and hence improve the physical properties of soil. This effect is very important in case of most of our arable land. Such manures increase the humus content of soil and consequently water holding capacity of sandy soils also increased and the drainage of clayey soils is improved.
- III. Bulky organic manures provide food for soil microorganisms. This increases the activity of microbes which in turn help to convert unavailable plant nutrients into available form.

Organic manures have been the traditional means of improving soil fertility. The organic matter that is applied through organic manures has very complex effect on soil and on plant growth. The main effects are

### Effect of organic matter on soil properties:

- I. Improvement of soil physical properties
  - 1) Improvement of soil structure
  - 2) Improvement of water holding capacity
  - 3) Improvement of soil aeration
  - 4) Reduction of soil loss through erosion
- II. Improvement of chemical properties
  - 1) Supply of essential plant nutrients in balanced ratio
  - 2) Slow release of nutrients
  - 3) High residual value
- III. Improvement of biological activity
  - 1) Stimulation of soil fauna and flora

**B Concentrated organic manures:**

Like bulky organic manures, these organic manures contain plant nutrients and considerable amount of organic matter. They have direct effect on plant growth. Nitrogen content is higher in concentrated organic manures and varied from 2.5 per cent in mahua cake to 7.9 per cent in decorticated safflower cake. In addition to nitrogen all the oil cakes contain  $P_2O_5$  (0.8 to 2.9 %) and  $K_2O$  (1.2 to 2.2%) since they contain nitrogen in relatively large quantities ,they are usually classified as organic nitrogenous manures . By virtue of this high nitrogen content they enrich the nitrogen status of soil.

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**Lecture : 2** Bulky organic manures –Preparation of FYM –Methods of collection and storage.

### **A. Bulky organic manures**

**Definition:** Bulky organic manures are those materials of plant and /or animal origin, which when added to the soil have tendency to decrease bulk density and to increase soil volume ,thus providing better physical conditions for plant growth especially in coarse textured soils and also provide essential nutrients in smaller quantities than the chemical fertilizers .

#### **Characteristics of bulky organic manures:**

1. Organic materials are relatively poorer in concentration of plant nutrients
2. These materials possess wider C:N ratio and C:S ratios and so supply energy needed for microorganisms
3. The mineral nutrients that are available in the organic materials become available to plants after mineralization.
4. Judicious combination of organic and inorganic manures is quite essential to maintain fertility status. Examples : 1.FYM, 2.Composts, 3.Green manures, 4.Pouderette, 5.Biogas slurry, 6.Sewage or sludge, 7.Molasses and 8.Vermicompost

#### **I. FARM YARD MANURE (Cattle manure)**

**Definition:** The physical composition of cattle manure is called Farm Yard Manure, which consists of dung and urine of cattle and the litter, a bedding material like hay, straw used for cattle

Cattle manure is slow acting, bulky organic and however is a low analysis fertilizer, obtained from dung and urine of farm animals mixed with litter and other miscellaneous farm wastes.

#### **Constituents of FYM:**

- A. Dung:** The dung is a solid excreta voided by farm animals, which represents the undigested and non-digestible portion of the animal feed. Besides, it is also admixed with digestive juices, tissues of alimentary canal, microbial cells etc., The percentage of moisture varies from 70-80 per cent.
- B. Urine :** The liquid excreta of farm animals, which is composed essentially of the by products of nitrogen metabolism of farm animals .It also consists of 90 per cent water with small amounts of urea, hippuric acid, sulphates of sodium and potassium and also chlorides and phosphates of Ca, Mg ,K and Na etc.,
- C. Litter :** Litter is a variable mixture consisting of straw , leaves , stems used as bedding material for cattle during their rest and eventually absorbs the urine and adds carbonaceous matter in the manure to facilitate decomposition .

### **Quality and composition of FYM:**

The quality of manure and chemical composition in particular is highly variable as the following factors affect the product.

1. Kind of animal
2. Age and condition of the individual animal
3. Quality and quantity of feed consumed
4. Kind of litter used
5. Collection and
6. Storage of manure

#### **1) Kind animal:**

The quality of manure depends on the class of manure .viz., cattle ,horse manure. With in the same class ,quality varies according to the kind of animal , such as milch cattle, dry cattle ,work cattle ,breeding bulls etc., By and large the dung and urine from animals , which assimilates less (little ) for their maintenance and production will provide better quality manure .

#### **2) Age and condition and individual animal:**

Growing animals ,milch cattle ,pregnant or carrying cattle utilize much of the ingredients in the feeds for building up their growing bodies ,milk production and for the development of the embryo[ calf] .Old or adult animals kept on light work or no work utilize little from feeds and as such, most of nitrogen is voided through urine and dung. Eventually, the adult old cattle provide better manure.

#### **3) Quality and quantity of feed consumed:**

Nutritious and protein rich feeds like oil cakes enriches the nitrogen content to the resulting manure than the bulky feeds like straw and green grass. Animals fed on concentrated feeds yield better quality manure.

#### **4) Kind of litter used:**

The quality of manure depends to a considerable extent on the nature of litter used. Remnants of leguminous hays (*Bhusa* ) give richer manure than usual straws.

#### **5) Collection of manure:**

The method adopted for collection of dung, urine and litter primarily decide the quality of manure as the loss of nutrients particularly nitrogen occurs from the time urine and dung are voided by cattle .The quality of manure depends upon the methods of collection viz., Byre, Lose box and Dry earth systems

##### **a. Byre system :**

Cattle are stalled in a shed with a non absorbent floor provided with necessary slope towards the urine drains. The urine that flows into the drains is collected into a covered tank .From where it is periodically removed and sprinkled on the manure stored in a covered pit .The urine which is an important component of FYM can be properly stored (conserved) in this system. The perfect cleanliness and hygienic conditions of the stalls as well as cattle can be maintained in this system.

**b. Dry earth system :**

The floor of the cattle shed is well rammed and compacted .Layers of fine sand ,red earth of loamy soil are spread as an absorbent for urine .The wet portions are properly covered with dry layers or any of the above materials and once a week the surface layer is removed and dumped in the manure pit. Available saw dust , paddy husk , groundnut shell, paddy winnowed dust would serve the purpose very well compared to the earth absorbents. This system is popular and extensively adopted in rural parts being cheap, convenient and practicable under the existing rural conditions in India.

**6) Storage of Manure:**

Method of storage of manure influences the quality of manure to a large extent. During storage the manure undergoes fermentative changes, decomposition which leads to losing its original structure and shape . There are three methods of storage viz., pit method and heap method and covered pit method.

**A. Pit method ( Below ground level) :**

In this method, the manure is stored in a pit with non –absorbent bottom and sides. The pit is provided with a bund at the rim of the pit to prevent the surface run-off of waters during rainy season .The dimensions of the pit can be variable depending on the quantity of dung ,urine and litter produced on the farm per day .The losses also occur in this method due to exposure to sun and rain ,but it is relatively a better method than the heap method.

**B. Heap method (Above the ground level) :**

This is the most common method adopted in Indian villages . Manure is heaped on the ground preferably under the shade of a tree. Ideal procedure is to dump the dung first and to cover it with litter soaked urine .This is further covered with a layer of litter /ash / earth to prevent the loss of moisture and to avoid direct exposure to sun .It is also desirable to put up a small bund around the base of the heap to protect against surface run-off washing out the manurial ingredients .It is beneficial to cover the exposed portion of the heap with Palmyra leaves or any other available material.

The maximum losses of nutrients occur in this method of storage, resulting in poor quality manure. Direct exposure to the vagaries of climate such as sunshine and rainfall causes looseness and dryness of manure, which hasten the losses of nutrients and rapid oxidation of organic matter.

**C. Covered pit method :**

Of all the methods described, it is the best method .In this method, the bottom and sides of the pit are made non-absorbent by granite stone lining. The pit is also provided with a bund of 1½ feet height to prevent surface flow of water (Rain water) and a suitable cover by way of roofing with locally available materials like Palmyra or phoenix leaves etc., organic matter and nutrient losses can be effectively controlled in this method of storage in order to obtain better quality manure [FYM: 0.68 % N- 0.5%P – 1 % K].

### **Improved methods of handling farm yard manure**

It is practically impossible to check completely the loss of plant nutrients and organic matter during handling and storing of FYM .However, improved methods can be adopted to reduce such loss. Considerably, they are.

#### **A) Trench method of preparing FYM:**

This method has been recommended by **C.N.Acharya** .The manure preparation should be carried in trenches of suitable size ,say 20-25 feet length , 5-6 feet breadth and 3-3.5 feet depth .All available dry litter and refuse from the farm and the houses should be heaped up near the cattle shed and portions of litter mixed with earth if available should be spread in the shed in the evening @2.26 kg per animal for the absorption of urine .The litter should be localized in the areas where urine generally drops and soaks into the ground. Every morning the urine soaked litter and dung should be well mixed and then taken into the manure trench .A section of 3 feet length of the trench from one end should be taken up for filling with daily collection of refuse from cattle shed. When the trench is filled to the height of 1.5 to 2.0 feet above ground level, the top is made dome shaped and plastered with cow dung mixed with soil. The manure becomes ready for about three months .By this time the next 3 feet length of the trench being filled up. .Generally 2 such trenches would be needed for three to four cattle. It is possible to prepare by this process 250-300 cubic feet of manure (3 to 5 tones or 10-12 cart loads) per animal. The FYM should be enriched by addition of super phosphate @ 30-40 kg per trench before application to fields. The content of nitrogen is at least 0.7 to 0.8 % N on the fresh weight basis or 1.4 to 1.6 % N on dry weight basis.



**Lecture : 3** Losses of nutrients from FYM during collection and storage-Ways to minimize these losses

### LOSSES OF NUTRIENTS FROM FYM DURING COLLECTION AND STORAGE

There are two types of losses of FYM, which are as follows.

#### A. Losses during handling

#### B. Losses during preparation and storage

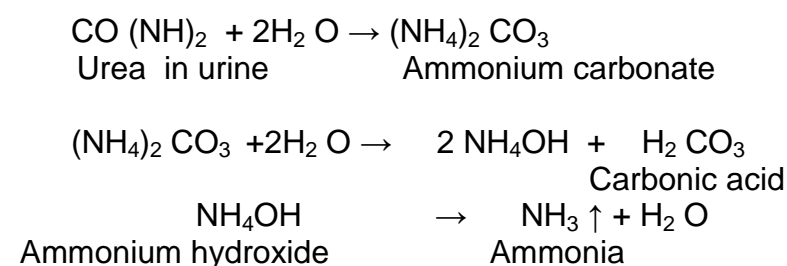
##### A. Losses during handling :

FYM consists of two original components such as i) dung (solid portion) and ii) urine (liquid portion) which are subjected to different losses in different ways.

Both the components contains N, P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O. Approximately, half of nitrogen and potash in dung and other half in urine .Whereas nearly all the phosphorus (96%) in the solid portion. To conserve N, P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O, it is most essential that both the parts of cattle manure are properly handled and stored

i) Losses of dung: Dung is a valuable manure. Still larger portion is dried in dung cakes and burnt as fuel .Besides this large portion of cattle excrements is dropped out side the cattle shed, when the animals are grazing on the uncultivated lands. This can be used for preparation of FYM.

ii) Losses of urine: Urine contains nitrogen and potassium in large portions. But there is no good method of preserving the urine in our country. In our country most of the cattle sheds have un cemented or *kachha* floor and the urine gets soaked in the soils of *kachha* floor of the cattle shed and the large quantities of nitrogen are thus lost through the formation of gaseous ammonia as follows .



##### B. Losses during preparation and storage :

Cow dung and other farm wastes are collected daily and these are accumulated in manure pit in open space for months together .The manure remain exposed to sun and rain during this period .Due to this effect the nutrients are lost in following ways .

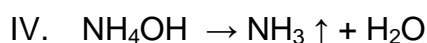
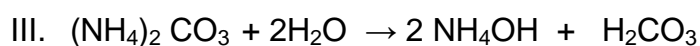
##### i) By leaching :

Nutrients of manures are water soluble and these are liable to get washed by rain water .The leaching loss of nutrients will vary with the surface exposed ,the intensity of rain fall and the slope of the surface on which manure is heaped .The leaching loss may be prevented by erecting a roof over the pit .

ii) By volatilization :

During storage, the urine and dung are decomposed and considerable amount of ammonia is produced. The ammonia combines with carbonic acid to form ammonium carbonate and bicarbonate, which are rather unstable and gaseous ammonia may be readily liberated and passes into atmosphere as indicated in the following equations.

I. Urea and other nitrogenous compounds in urine and dung by microbial decomposition liberates  $\text{NH}_3$  (Ammonia)

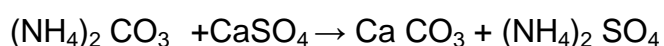


### Ways to minimize these losses from FYM during handling

- 1) Adopt trench method as suggested by C.N.Acharya for handling of dung and urine
- 2) Use of Gobar gas plant: 50 % of dung is made dung cakes and burnt as fuel for cooking. The use of cow dung in gas plant produces a combustible gas, methane used as fuel gas which, is an improved method of handling FYM.
- 3) Adopting covered method of storing FYM : Nutrients losses can be effectively controlled by this method
- 4) Adoption of BYRE system in collection of FYM
- 5) Proper field management of FYM : During spreading of FYM in the field in small heaps leads to loss of nutrients from it. It is advisable to spread the FYM before ploughing.
- 6) Use of chemical preservatives :

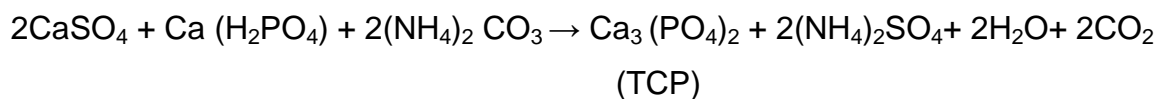
Chemical preservatives are added to FYM to decrease nitrogen losses. To be most effective, the preservatives are applied in the cattle shed to permit direct contact with the liquid portion of excreta or urine. This has to be done because the loss of nitrogen from urine starts immediately.

Commonly used preservatives are 1) Gypsum 2) Super phosphate. It is recommended that 450 g to 900 g of super phosphate should be applied per day per animal in the cattle shed. Super phosphate should be applied in places where animal pass urine. The reaction of gypsum with ammonium carbonate (intermediate product from decomposition of urea present in urine) is



With this reaction ammonium carbonate is converted to  $(\text{NH}_4)_2 \text{SO}_4$ . As long as manure is in moist, no loss of ammonia will occur but if dried the chemical reaction is reversed and loss of ammonia may occur. Use of gypsum also prevents the bad smell caused by production of ammonia in the cattle sheds. As such in Indian conditions use of gypsum to decrease N loss does not offer practical solution.

Super phosphate has been extensively used as a manure preservative. Since ordinary superphosphate contains up to 50 to 60 per cent gypsum besides mono calcium phosphate. The reaction with ammonium carbonate is given below



In this reaction, tricalcium phosphate is formed which does not react with ammonia sulphate when manure becomes dry as such there is no loss of ammonia.

### **STRAW:**

Straw is sometimes left on the field as waste product from the harvest. It is useful as organic fertilizer especially on farms without live stock. Although straw contains few nutrients, it yields decomposable organic matter (Eg. Cellulose). Fertilization with straw thus supplies energy [1 kg straw = 12 Kilo Joules energy], but mainly improves the structure of medium and heavy soils. The nutrient contents of straw vary but are small in any case viz., 0.5 % N – 0.1 % P – 1 % K and dry matter of 85 %. The C:N ratio is very large about 100:1. This may cause inhibition of decomposition because the microbes lack in nitrogen, [Compensating supplies of N about 1% of the quantity of straw] is thus required.

**Lecture : 4** Compost and rural composting –Different methods of composting including the starters and raw materials.

## II. COMPOST

Dry and fresh plant tissues and also animal wastes can be introduced directly into or on the soil. They are then decomposed at varying speeds, but have only slight and sometimes detrimental effects and bring about scarcely any substantial soil improvement. Process known since antiquity make it possible to convert such wastes into useful agents for soil improvement i.e., compost.

The word compost is derived from the Latin word “COMPONERE” to mean put together.

**Compost** : Compost is a product of decomposition of plant and animal wastes with various additives. The compost had the largest variation of all organic material ranging from neglected garbage dumps to carefully composted and treated substances with high fertility.

**Composting** : Composting is a process of converting organic matter into manure in a short time by accelerating fermentation process under controlled conditions is called composting.

The organic material that is usually handled for composting are waste vegetative material such as spoiled straw, peanut hulls, saw dust, dried leaves etc., stubbles, chilli plants, cotton stalks, tobacco stems, weeds, municipal rubbish etc., according to availability.

**The following basic rules are important for the production of good quality compost:**

1. The purpose of composting is to convert organic matter into growth promoting substances, for sustained soil improvement and crop production.
2. The organic matter is partially decomposed and converted by microbes. These microbes require proper growth conditions, for their activity. i.e moisture content : 50 % and 50 % aeration of total pore space of the composting material. This is achieved through stacking and occasional turning over. Microbes also need sufficient nitrogen for synthesizing their body cells [the optimum C:N ratio of the composting material is 20:1 to 30:1]
3. Soil microorganisms constitute sufficiently to the decomposition of organic matter through their continuous activities. The majority of these soil animals provide optimal conditions in their digestive track for their synthesis of valuable permanent humus and stable soil crumbs. A typical compost earthworm is *Eisenia foetida*.
4. Certain additives accelerate the conversion and improve the final product. The materials such as lime, earth, gypsum, rock phosphate act as effective additives. The addition of nitrogen (0.1 to 1 %) is important in case of large C:N ratio of the composting material. Addition of lime (0.3 to 0.5 %), if sufficient lime is not present. The preparation of compost takes 2-3 months. The composition of compost varies with in wide limits.

The following average values are rough estimates

**Composition of compost (Rough)**

S.No.	Constituent	Percentage
1	Dry matter	30-50
2	Organic matter	10-15
3	N	0.3
4	P	0.1
5	K	0.3

**Methods of composting**

The process of composting was first initiated in England during the period of First World War (1914 -1918).

The various systems of composting are

1. ADCO process (Agricultural Development Company )
2. Activated compost process
3. Indore process
4. Bangalore process
5. Coimbatore process
6. Rain -water compost
7. Rural compost
8. Urban compost
9. Mechanical compost and
10. Vermicompost

1. ADCO process :

Agricultural Development Company was initiated, [A private concern operating at Harpenden, England] developed by **Hutchinson, H.B and Richards , E.H.** during 1914-1918, at Rothamsted Experimental Station , England .

Materials needed:

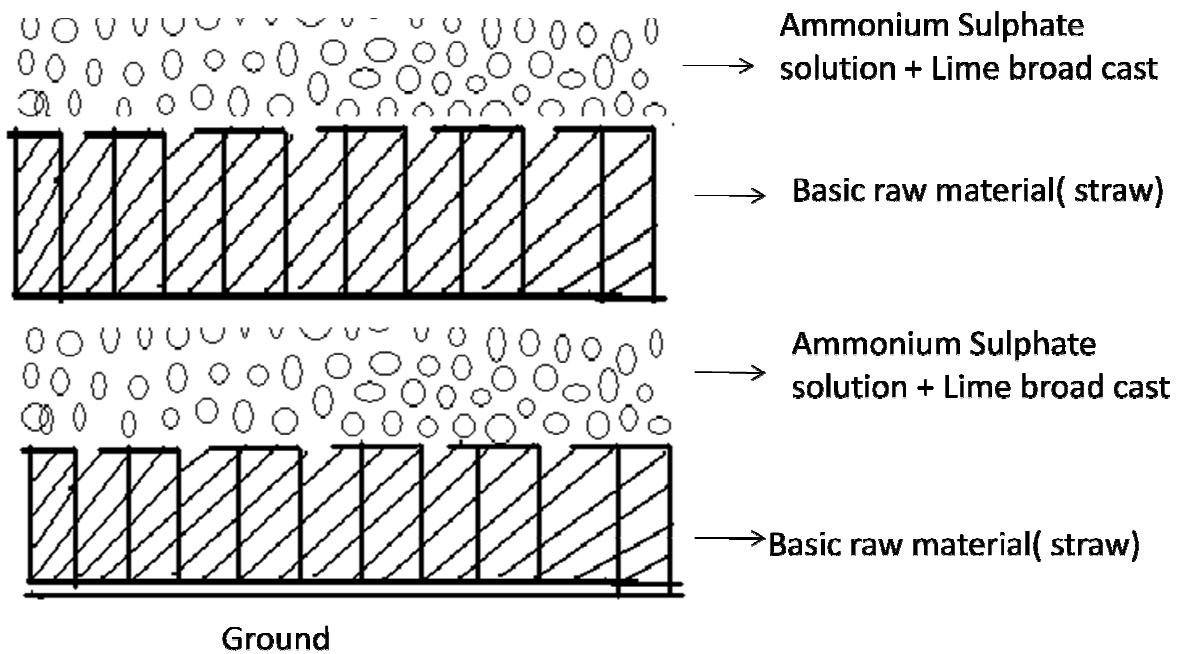
1. Straw and other wastes -Basic raw material )
2. Ammonium sulphate/Ammonium phosphate /Super phosphate/Muriate of potash  
Ground limestone/ urea - Starters

Procedure:

The basic raw material straw is spread in layers and sprinkled over with a solution of ammonium sulphate. Then powdered lime stone is applied as broadcast. Then another straw layer is put on. The piling of the layer is continued till a decent heap of convenient height is built up. After about 3 months of fermentation the resulting material is similar to FYM and hence called “synthetic FYM”

The ADCO process was patented and concentrated starters were put in the market with the trade names of ADCO accelerator and ADCO complete manure with full direction for their use.

Fig.1



## 2. Activated compost process:

This method was developed by **Fowler and Ridge in 1922** at Indian Institute of Science, Bangalore

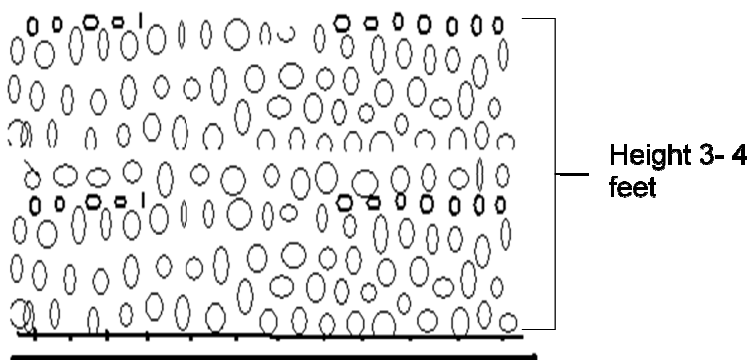
Materials needed:

1. Basic raw materials ( Straw and farm wastes )
2. Starters : a) Cow dung b) Urine c) Night soil d) Sewage and sludge

Procedure:

In this process the basic raw material for composting straw and other farm wastes is treated with mixture of cattle dung and urine as decoction . So that every portion of mass comes in contact with the inoculants(dung + urine ) and fermentation takes place evenly . On piling up in a heap of 3 feet or 4 feet height and turning over from time to time, keeping moist with dung and urine decoction,very high temperatures attained. When the temperatures begin to drop at the end of one week. The volume of the material gets reduced . further quantity of the basic material is added onto the heap. About 25 % of the new materials should be added at one time and thoroughly mixed with starters (dung +urine decoction) at intervals as before. If properly carried out, the compost will be ready in 5-6 weeks .Night soil and sewage and sludge are also used as starters in this method.

Fig.2



### 3. Indore process :

This process is developed in India by **Howard and Ward** at the Indian Institute of plant Industry, Indore

- Materials needed: a) Straw or organic farm wastes as basic raw materials  
b) Cattle dung as starter (urine, earth and wood ashes)

#### Procedure :

A compost pit of dimensions of 30 x 14 x 3 feet with sloping sides (narrow at bottom and at wide surface) is prepared and the raw material is spread in layers of 3" thickness. A mixture of urine, earth, and wood ashes is sprinkled and this is followed by 2" layer of dung. The pit is filled up this way until the material occupies a height of 3 feet above the ground level . As air can conveniently penetrate only to a depth of 1.5 to 2.0 feet extra aeration has to be provided, which is done by means of artificial vents (holes) of 4" diameter pipe for every 4 feet length of the pit. The pit is watered twice a day i.e., morning and evening with rose can. The material is turning over 3 times, i.e.,

First – at the end of the first fort night

Second – at the end of the second fort night

Third – when the material is two months old in the process of composting.

#### Observations:

##### I. After 10 days of composting the following things happens

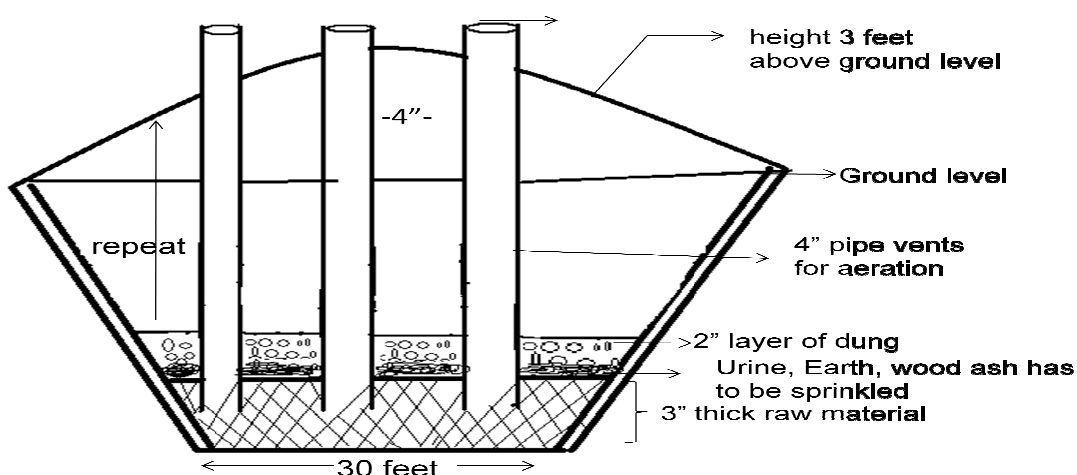
- A. Synthesis of humus begins i.e., development of fungi and the height of the material is reduced by half
- B. Check anaerobic decomposition, as indicated by the foul smell and fly breeding
- C. If there is an anaerobic decomposition ,turn over material for proper aeration
- D. If insufficient fermentation, hasten by watering the material.

##### II. At the end of two months

- A. Fungal activity is over
- B. Materials become dark
- C. Now the bacterial aeration takes place
- D. Stock the material on the ground after 2 months .So 25 % of additional free nitrogen will be fixed from atmosphere.

Compost is ready by 3-4 months .One cattle pair produced 50-60 cartloads per year.

Fig:3



#### 4. Bangalore process [ Aerobic and anaerobic process] :

This process of composting was developed by **Dr.C.N.Acharya** in the year 1949.

1. Basic raw material used : Any organic material
2. Starters or inoculants : FYM or mixture of dung and urine or litter [Undecomposed]
3. Additives : Bone meal or oil cakes , wood ash

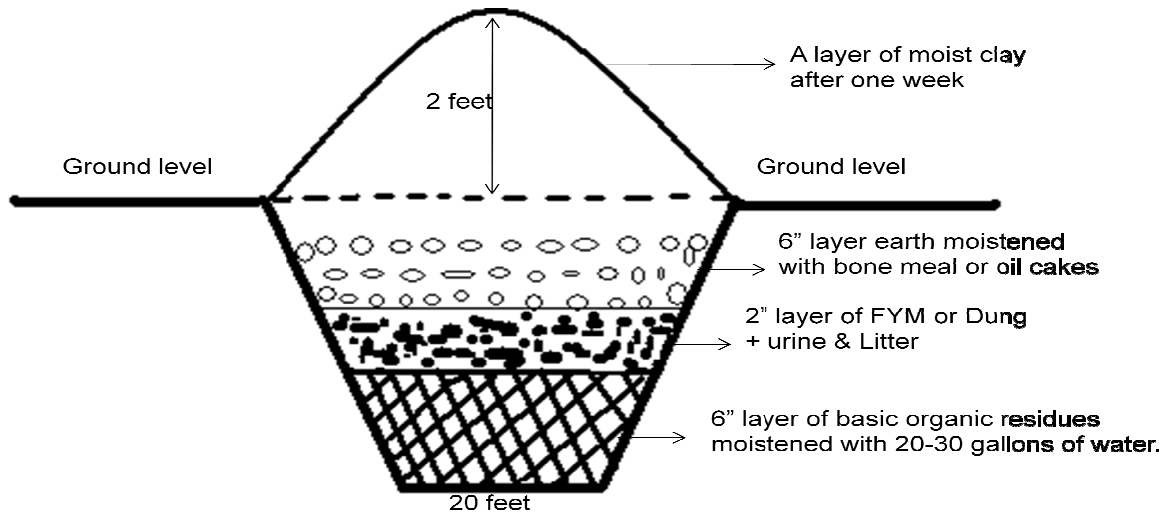
Procedure [Pit size: 20 x 4 x 3 feet]:

The basic raw material is spread in a pit of 20 x 4 x 3 feet dimensions to a depth of 6 " layer, moistened with 20-30 gallons of water if the material is dry .Over this FYM or preferably a mixture of dung, urine and litter (un-decomposed) from the cattle shed is placed as a layer of 2" thickness. It is again covered on the top with a layer of earth to a thickness of 6 " .It is beneficial to mix the earth with bone meal or oil cakes ,wood ash etc., to improve manurial value of the compost .The piling of layers is continued till the heap raises above the ground level to a height of 2 feet , .Then the heap is kept open for one week to facilitate aerobic decomposition . Later the heap is plastered with a layer of moist clay for anaerobic fermentation to occur .Fissures , or cleavages (cracks ) that occur in the clay layer , have to be sealed off periodically .The compost will be ready in 4-5 months period starting from the day of preparation .This process is called as aerobic and anaerobic decomposition of compost .



In this process the basic raw material is not so well decomposed as in the other methods .But organic matter and N contents are well conserved .The number of turnings are reduced .The out turn of the compost is relatively greater and cheapest process .

Fig :4



#### 5. The coimbatore process:

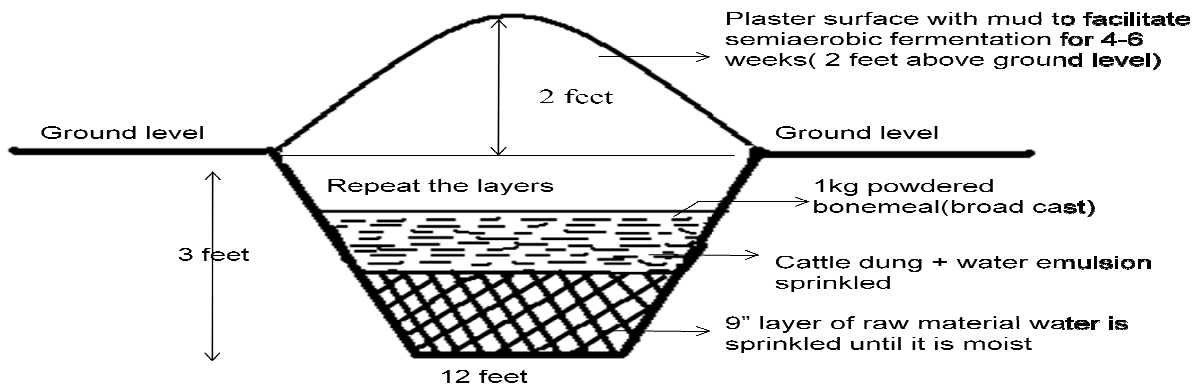
1. The basic raw materials: Raw organic matter
2. Starters : Powdered bone meal and cattle dung and water emulsion prepared by mixing

Dung in water @ 5-10 kg dung in 5 to 10 liters water.

Procedure [Pit: 12 x 6 x 3 feet]:

The basic raw material loosely spread [Pit: 12 x 6 x 3 feet] to a depth of 9" and water is sprinkled till the entire material is moist. Then about one kg of powdered bone meal is broadcasted uniformly above the layer and above this an emulsion of 5-10 kg of fresh cattle dung in 5-10 liters of water is applied .Repeat this process until a heap 2 feet above ground level is formed .Then the entire exposed surface area of heap is plastered with mud to facilitate semi-aerobic fermentation which would takes place for above 4-6 weeks depending upon the nature of the raw material .After 4-6 weeks ,the mud plaster is removed to permit aerobic fermentation . If the heap has sunk unevenly which is a sign of defective fermentation, the material is reheaped after forking and moistened .The decomposition is complete in 3-4 months and is fit for application to the field.

Fig.5



### 3. Rain watered compost:

In dry areas where it is difficult to obtain water for watering, the composting can be done with the aid of rain fall.

The compost heap is built up as usual before the rains set in. The turnings are given during the rainy period at the end of rains the material will be ready for application. About 400 mm rain fall received in 3-4 months is considered sufficient.

**Lecture : 5** Methods of preparation of rural and urban compost. Mechanical compost plants –their advantages over conventional composting –Vermicomposting

#### 4. Rural compost :

Compost prepared using farm organic wastes and fresh dung and /or urine soaked earth as starter is called as Rural Compost. This is within the reach of farmers, as they can individually prepare the compost in their farm sheds.

##### Procedure:

Composting can be done in a pit size of 3 x 6 x 3 feet size located on an elevated place. Even length and width are adjustable depending upon the raw material available .Keep the sides of the pit slanting .When a number of pits are dug, keep 12 feet gap between the pits for facilitating turnings .Locate the compost pits away from the civilians areas.

Basic raw material: 1) Green succulent, non-woody and non-fibrous material (12"thick)  
2) Dry materials like sugarcane trash, stubbles etc., (3" thick)

Starter : Dung and water

Neutralizing agents for organic acids: Bone meal is preferred to ash as it provides Ca and also phosphate, which are desirable constituents in the final product.

##### Procedure:

The organic material is spread in layers .The thickness depends upon compostability of materials. Green succulent non-woody materials can be laid in 12 " layer while tough woody materials like sugarcane trash and stubbles are spread in 3" layer .Bone meal or ash is sprinkled in a thin layer over the material to provide the base for neutralizing organic acids produced during the decomposition .Dung and water is then sprinkled over the layer . Dung functions as starter while the water provides the moisture. The layers are thus built up to a height of one foot above the ground level .It is desirable to cover the surface of the heap with a layer of earth .Periodically watering is done .

##### Precautions:

- 1) Over watering creates anaerobic decomposition.
- 2) Turnings are necessary to hasten the aerobic decomposition
- 3) After turning the compost must be re-heaped and covered
- 4) Use the compost immediately
- 5) It is to be preserved by providing suitable cover
- 6) The compost will be ready by three months to one year depending upon material (Sugarcane trash –late )

### 5. Urban compost:

Compost prepared by local bodies, municipalities, corporations etc., with their output of street sweepings, municipal rubbish etc., as organic matter using night soil as starter is called urban compost

Methods of urban composting:

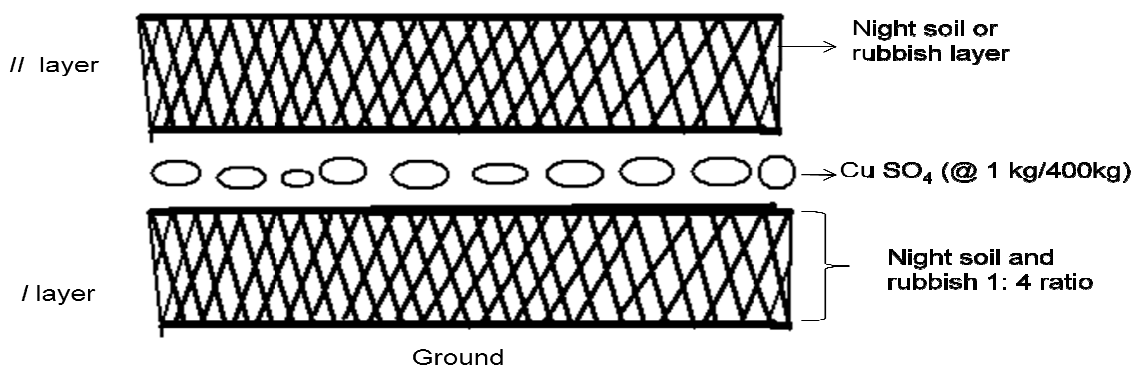
#### I. Method of urban composting :

Using municipal or town rubbish as basic raw material and night soil as starter. Sprinkling of copper sulphate powder between layers will put down the offensive odour due to putrefactive fermentation of the material, yielding foul smelling organic compounds called Mercaptans.

#### II. Method of composting :

Night soil and rubbish are mixed in 1:4 ratio. Copper sulphate is added between layers at the rate of one kilogram for every 400 kg of the mixture and the mixture is raked up to heaps of convenient size.

Fig :6



The heaps are moistened and raked up for every fortnight and rebuilt. During the period of two months, the manure will be ready for use. The product is dry and powdery, free from foul smell.

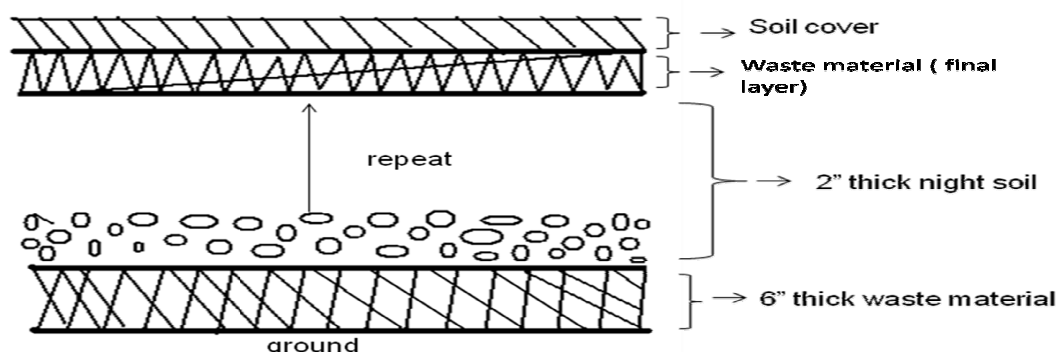
#### III. Method of composting :

Town refuse is heaped into a pit of dimensions of 8 x 4 x 4 feet. A groove measuring 6x1 x 1 feet is made at the top in the centre and is filled up with night soil and covered over with refuse. Heap is moistened daily with sullage water and raked up once a week. For six weeks by which the decomposition process would be complete and the product would be ready for use as manure.

#### IV. Method of composting :

The layer of waste material of 6" thick and night soil 2" thick are altered; the final top layers will be the waste material. The heap is covered by 9" thick layer of soil. The material will be ready in about five months.

Fig:7



#### 6. Mechanical compost :

In big cities like Delhi, Bombay, Calcutta (kolkata) while disposing the urban wastes, face innumerable problems such as cost , land , labour for composting operations , involving human contact with filthy and obnoxious materials with a result mechanical composting is undertaken .mechanical composting can be undertaken at a central location and in small compact area .it is only mechanized composting which may prove effective in not only serving as a means of disposal of urban wastes but also of providing the country with large quantities of organic matter .

The advantages of Mechanical composting

1. Sanitary control with odour control device
2. Operational convenience, both in dry and wet seasons
3. Efficient recovery of discarded materials like metal ,glass etc.,
4. High quality manure in a short period
5. Eliminates large anaerobic decomposition
6. Reduces preparation cost @ 10% for every tonne
7. Economically, cheaper than chemical fertilizers

Israel built up largest compost plant in the world at TEL-AVIV. It is designed to cope up with all domestic refuse from TEL-AVIV i.e., 500 tonnes in one shift of 8 hours .

Second biggest plant is in Bangkok

Economics: One tonne compost contains 13 kg N , 11 kg  $P_2 O_5$  and 11 kg  $K_2 O$  ,which is equivalent to 65 kg ammonium sulphate , 66 kg single super phosphate and 22 kg muriate of potash

#### 7. Vermicompost technology :

An emerging technology for recycling of crop residues and other organic solid wastes is the utilization of earthworm technology to convert them into vermicompost.

Definition of vermicomposting:

Vermicomposting is a method of making compost, with the use of earthworms, which generally live, in soil eat biomass and excrete it in digested form. This compost is generally called vermicompost or Wormicompost.

Definition of Vermiculture:

Vermiculture means scientific method of breeding and rising earthworms in controlled conditions.

### Vermitechnology:

Vermitechnology is the combination of vermiculture and vermicomposting. Thus, earthworms can be used in the following areas.

1. For development of arable soils, turnover of soil, break down of plant organic matter aeration and drainage
2. For production of useful products like vermifertilizer and worm tissue for animal feed.
3. For maintenance of environmental quality and monitor of the environment for soil fertility, organic and heavy metal non-biodegradable toxic material pollution.

### Vermiculture industry or vermicompost preparation:

1. Basic raw material: Any organic material generated in the farm like bhusa, leaf fall etc.,
2. Starter: Cow dung, Biogas slurry, or urine of cattle
3. Soil animal: Earth worms (Species: *Eisenia foetida*)

### Favourable conditions of earth worms in the composting material:

- A. pH: Range between 6.5 and 7.5
- B. Moisture: 60-70% of the moisture below and above range moderately of worms taking place
- C. Aeration: 50% aeration from the total pore space
- D. Temperature: Range between 18 °C to 35 °C

### Procedure:

It is mostly prepared in either pit or heap method. The dimensions either heap or pit are 10 x 4 x 2 feet. The length and width can be increased or decreased depending on the availability of material but not the depth because the earth worms activity is confined to the 2 feet depth only.

1<sup>st</sup> layer: bedding material of 1" thick with soft leaves

2<sup>nd</sup> layer: 9" thick organic residue layer finely chaffed material

3<sup>rd</sup> layer: Dung + water equal mixture of 2" layer.

Continued the layer up to pile to ground level protect the worms against natural enemies like ants, lizards, snakes, frogs, toads etc., Maintain proper moisture and temperature by turnings and subsequent staking. At the day of 24<sup>th</sup>, 4000 worms are introduced in to the pit [1m<sup>2</sup> =2000 worms] without disturbing the pit by regular watering the entire raw material will be turned into the vermicompost in the form of worm excreta. The turn over of the compost is 75% [the total material accommodated in the pit is 1000 kg; The out turn will be 750 kg]

Harvesting of the vermicompost from the pit:

Stop watering before one week of harvest . All the worms spread across the pit come in close and penetrate each other in the form of ball in 2 or 3 locations .Heap the compost by removing the balls and place them in a bucket ,then the material is sieved in 2 mm sieve , the material passed through the sieve is called as vermicompost which is stored in a polythene bags [ Note : Vermicomposting is done under thatched roof to protect worms against rain and sun ]

Nutrient composition of vermicompost

S.No.	Nutrient	Content
1	Organic carbon	9.15 to 17.98 %
2	Total nitrogen	1.5 to 2.10 %
3	Total phosphorus	1.0 to 1.50 %
4	Total potassium	0.60 %
5	Ca and Mg	22.00 to 70.00 m.e / 100 g
6	Available S	128 to 548 ppm
7	Copper	100 ppm
8	Iron	1800 ppm
9	Zinc	50 ppm

Besides the above nutrients the vermicompost also contains following enzymes

➤ Enzymes : Protease ,Lipase ,Amylase , Cellulose

Source: Kale (1983) in Vermicompost published in Agro bios Vol.I, No.XI, April, 2003 Edited by Purohit, S S

Conversion rates:

1000 earth worms may convert 5 kg waste material per day

1000 worms weighs about a kilogram

Advantages of composting over direct application:

1. There will be no immobilization in compost because of narrow C:N ratio
2. Application is easy, because the compost is humified and have a structure of crumb and granular.
3. It is hygienic, pathogens and weeds seeds are destroyed.

Advantages of direct application:

1. No loss of nutrients
2. It improves physical properties better than compost on soil application.

**Differences between Aerobic and anaerobic decomposition**

<b>S.NO.</b>	<b>Aerobic decomposition</b>	<b>Anaerobic decomposition</b>
1	This takes place in the presence of oxygen	This takes place in the absence of oxygen
2	CO <sub>2</sub> is produced	Methane gas is produced
3	High water content is required	Less water content is required
4	Organic matter conserved is around 50-60 %	Organic matter conserved is around 75 %
5	Around 25-50 % N is lost	20 % nitrogen is lost and more N is conserved
6	Temperature built up is more .Hence , pathogens weed seeds are killed	Pathogens are only killed due to antibiotics.
7	More labour is required for turnings and watering	Less labour is required
8	Time taken for decomposition is 3-4 months	Time taken is 5-6 months

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#### **IV. GREEN MANURING**

**Green manuring:** Green manuring can be defined as the growth of a crop for the specific purpose of incorporating it into soil while green, or soon after maturity with a view to improving the soil and benefiting subsequent crops or Practice of ploughing or turning in to the soil un decomposed green plant tissues for the purpose of improving physical condition as well as fertility of the soil

**Objectives of green manuring:**

- i. Increasing organic matter content of soil
- ii. Maintain and improve soil structure
- iii. Reduce the loss of nutrients ,particularly nitrogen
- iv. Provide a source of nitrogen for the following crop
- v. Reduce the soil loss by erosion

**Types of green manuring:**

The practice of green manuring is adopted in various ways in different states of India to suit soil and climatic conditions. Broadly speaking, the following two types of green manuring can be differentiated.

**Classification of Green manuring:**

classified into two groups as

**I. Green manure *in situ***

**II. Green leaf manuring**

**I. Green manuring *in situ*:**

In this system, green manure crops are grown and buried in the same field which is to be green-manured, either as a pure crop or as intercrop with the main crop. This is most common green manure crops grown under this system are sunnhemp (***Crotalaria juncea***), daincha (***Sesabania aculeata***), Pillipesera (***Phaseolus trilobus***) and guar (***Cyamopsis tetragonoloba***)

The green manure crops are mostly legumes, which are fast growing and yield substantial succulent vegetation. There is little or no preparatory cultivation. Sowing is effected by broad cast adopting a heavy seed rate. Green manuring can be safely adopted for irrigated and irrigated dry crops viz., rice, sugarcane, tuber crops, vegetables and orchards. In case of dry crops it is unsafe because of limiting moisture. But when rains are sufficient and evenly distributed green manuring could be followed even under rain fed conditions when the rain fall is above 900 mm (Application of lime is suggested to neutralize organic acids that are formed during decomposition (Bone meal preferred))

**Green manure crops:****1. Sunnhemp ( *Crotalaria juncea* ) :**

- i) It is a unique crop possessing ,fiber ,fodder and green manurial value with nutrient composition of 2.3 % N, 0.2 % P and 1.4 %K
- ii) It can be raised beneficially for irrigated dry conditions
- iii) Under high rain fall conditions it is grown in dry lands
- iv) Grown in medium fertile soils
- v) Seed rate is 45 kg ha<sup>-1</sup>
- vi) Green matter yield 9-17 tonnes ha<sup>-1</sup>

**2. Daincha ( *Sesbania aculeata* ) and ( *Sesbania speicosa* )**

- i) They are erect growing deep rooted crops and useful to open soil and improve drainage in heavy soils.
- ii) Nutrient composition(%) [ 3.5N,0.3P and 1.0K]
- iii) These crops are grown on heavy soils
- iv) They are non fodder crops and non palatable
- v) They correct sodic soils specially *S. spaciosa* as it is less woody and less fibrous ,which gives heavy foliage and easily decomposable
- vi) Seed rate 30 kg ha<sup>-1</sup>
- vii) Yield 5 tonnes ha<sup>-1</sup>
- viii) Seeds require scarification for easy germination (Scarification means lightly pounding with sand).

**3. Indigo ( *Indigofera tinctoria* ):**

- i) Slow growing, deep rooted drought resistant crop
- ii) It is not relished by cattle
- iii) Can be grown in fruit gardens and plantations during non –monsoon
- iv) Seed rate is 20 kg ha<sup>-1</sup>
- v) Yield is 5 tonnes ha<sup>-1</sup>

**4. Wild indigo ( *Tephrosia purpurea* )**

- i) It is suited for hard coarse gravelly textured soil and poor soils.
- ii) It is used as a green leaf manure also
- iii) Self grown crop when sown once
- iv) Suitable for unirrigated orchards like mango, sapota
- v) Nutrient composition (%) crop : 1.8N , 0.1 P and 0.3 K ; leaf : 3.2 N, 0.1 P and 1.2 K

**5. Pillipesara ( *Phaseolus trilobus* )**

- i) Regular green manure , minor pulse crop and fodder crop ( triple purpose crop )
- ii) Popular green manure crop for black and alluvial soils
- iii) It has good ratooning capacity
- iv) The crop could be incorporated in to the soil after two cuttings for fodder
- v) Yield : 3-5 tonnes ha<sup>-1</sup>
- vi) Seed rate : 35 kg ha<sup>-1</sup>

vii) Chemical composition (%): 3 N, 0.1 P and 0.3 K

### 6. Horse gram (*Dolichus biflorus*)

It is suitable as green manure crop for poor and hard soils. It can also withstand drought. Seed rate is 35 kg ha<sup>-1</sup> and yield a green matter of 3.5 tonnes ha<sup>-1</sup>

### II. Green leaf manuring:

Green leaf manuring refers to turning into the soil green leaves and tender twigs collected from shrubs and trees grown on bunds, waste lands and near by forest areas. The common shrubs and trees used are Glyricidia, Sesbania speciosa, Karanj (*Pongamia pinnata*) etc.,

Plants used as a source of green leaf manure are as follows

S.NO.	Scientific name
1	<i>Aeschynomene aspera</i>
2	<i>Azolla filiculoides</i>
3	<i>Azolla pinnata</i>
4	<i>Calotropis gigantea</i>
5	<i>Cassia auriculata</i>
6	<i>Cassia siamea</i>
7	<i>Cyamopsis tetragonoloba</i>
8	<i>Ipomea carnea</i>
9	<i>Glyricidia maculate</i>
10	<i>Leucaena leucocephala</i>
11	<i>Pongamia glabra</i>
12	<i>Sesbania rostrata</i>
13	<i>Sesbania cannabina</i>
14	<i>Tephrosia purpurea</i>
15	<i>Tinctonia diversiflora</i>

### Advantages of green manuring (*in situ*):

1. Green manure crops can be chosen to suit the soil, season, water facility and cropping pattern
2. Reduces expenditure on collection and transportation of green leaf
3. It is easy to incorporate the green manure crop in right time
4. It reduces the loss of nitrogen from the soil

### Limitations of green manure crops (*in situ*)

1. There must be sufficient time available for growing the green manure crop, nearly 2-3 months
2. Extra expenditure has to be incurred for growing green manure crop
3. Some of the green manure crops are of fodder value, they are liable for cattle tress pass
4. They are susceptible for pests and diseases as such they may harbour them as alternate hosts.
5. Need timely rainfall or irrigation etc., for growing
6. Seeds may not be available in time

**Advantages of green leaf manuring**

1. All the quantity of green leaf applied is entirely an addition to soil –neither the moisture nor nutrients are utilized from the soil
2. There is no fear of spread of pests and diseases
3. It can be adopted at any time irrespective of the season

**Limitations of green leaf manuring:**

1. The green leaf is not available every where except in forest regions and waste lands
2. Green leaf which ever is available has to be used without choice
3. Green leaf may not be available sufficient quantity in all seasons
4. Extra expenditure on collection and transport has to be incurred

**Criteria for green manure crop**

1. Capacity to fix atmospheric N in good amounts in symbiosis with micro organisms
2. Plethorcity of vegetative growth (heavy foliage)
3. Succulent vegetation with limited fibrous material
4. Deep root system to open the soil-for recycling of nutrients
5. Short duration with maximum and faster vegetative growth.

**Advantages of leguminous crops:**

Legumes have the capacity to fix nitrogen and generally decompose more easily than others . Legumes come up better in poor soils where non –leguminous may fail to put satisfactory growth.

Organic materials act as binding agents :

Organic materials acts as binding materials for holding soil particles as aggregates. There are three groups of binding agents as identified by TISDELL and OADES (1981)

1. Transient binding agents : These are plant and microbial products, rapidly decomposed , having more polysaccharides. They are produced by plant roots as mucigel or by bacteria as extra cellular components
  2. Temporary binding agents : Fine plant root and fungal hyphae, mycorrhizal hyphae .They accumulate in soil over a period of time and persist for months or even years
  3. Persistent binding agents : Microbially resistant humic polymers derived from decomposition of plant residues, bacterial cells and fungal hyphae associated with Fe and Al in soils
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**Lecture: 7** Definitions of penning, sewage, sullage, sludge and poudrette .Concentrated organic manures – oil cakes, blood meal, bone meal, horn meal, fish meal, meat meal & Guano

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### V.PENNING

**Penning:** Keeping the boven animals (cattle and sheep) in the fallow land after the harvest of the last crop, throughout day /and or night provided with suitable food and shelter.

**Types of penning: There are two types of penning**

#### I. Cattle penning

#### II. Sheep penning

##### I. Cattle penning :

Keeping the cattle in the fallow land after harvest of the last crop, throughout day and night by providing them suitable food and shelter is called cattle penning .It is an ideal practice of collection and storage of dung and urine directly in the field .Urine is absorbed by soil while dung and litter are incorporated in situ . Losses in storage and collection are avoided by penning. Cattle are shifted from one field to other field once in 2-3 days for covering the maximum area . The dung and urine are uniformly spread and ploughed in it. The period congenial for cattle penning varies from 3-6 months i.e., from January –June or March to May depending on the extent of non cropping period.

Cattle penning is largely done for seedbeds of rice, root crops, sugarcane, vegetable etc., which require very heavy manuring. It is one of the oldest practice followed in India .About 800-1000 cattle per acre are penned which would be equivalent to 10-15 tonnes of cattle manure per acre [Composition (%): 0.5 N, 0.25P and 0.5K].

##### II. Sheep penning :

It is a popular practice followed in drier regions of Andhra Pradesh .Flocks of sheep and goats are penned in the fields during nights and allowed to graze during day time .The flocks are frequently disturbed during nights to increase droppings as they tend to void droppings when disturbed .The sheep penning is generally adopted for cash crops like vegetables, tuber crops, chillies and sugarcane .

Penning about 2000 heads per acre is the common practice. Sheep and goat manure are relatively lower in moisture content and higher in nutrient value than cattle manure .Average nutrient composition (%) of sheep and goat manure 1.93 N , 0.6 P and 1.90 K .

Some of the other organic (bulky) manures are obtained from the solid excretions from piggery, poultry and Human excreta (Night soil)

- I. Pig manure: It is collected in dry state stored and extensively used whenever it is available for rice, banana, and vegetables .The percent nutrient composition is 3.7 N,1.4 P and 0.3 K.
- II. Poultry manure: It has been become popular consequent to the rapid growth of poultry industry .It is used for extensive cropping such as rice, sugarcane and chillies .The percent nutrient composition of poultry manure is 0.9 N,0.8P and 0.5K.

**III. Night soil:** Human excrements both of solid and liquid material put together constitute Night soil. It is a rich source of N and P than cattle dung.

S.No.	Nutrient	Human excreta nutrients supply(kg /person /year)	Relative values in terms of cattle dung (kg /cow /year )
1	N	4.7	2.9
2	P <sub>2</sub> O <sub>5</sub>	1.1	0.8
3	K <sub>2</sub> O	1.0	2.3

## VI. POUDRETTE

It is the product obtained from night soil without any admixture of other organic waste materials . Night soil is spread in thin layers over which copper sulphate and soil are lightly spread .The mass is periodically raked up and re-spread till dry .It is called poudrette .When it is properly prepared looks like a reddish loamy soil and in dry, powdery and devoid of offensive smell .

Night soil digestion: CPHERI (Central Public Health and Engineering Research Institute), Nagpur is working on night soil digestion, it provides

- i) In offensive sludge with undiminished fertilizer value
- ii) Gas and electricity for rural areas

Night soil can be digested in a 230 sq .feet (6.5m<sup>3</sup>) digester without any fly or odour nuisance in an unheated open tank with manual stirring

Design criteria for night soil digester

- A. Capacity : 3-6 m<sup>3</sup>
- B. Raw night soil : water : 2:3
- C. Gas yield : 3 m<sup>3</sup>/100 persons
- D. Calorific value : 5558 K.Cal/ m<sup>3</sup> gas
- E. Horse power generated for 100 persons : 2.0
- F. Manurial value on dry basis (%): 3-5 N, 2 to 4.4 P<sub>2</sub>O<sub>5</sub> and 0.7 to 1.9 K<sub>2</sub>O

The sludge in the night soil digester is removed in a week or two .The sludge can be spread on a drying bed of 3-5m<sup>3</sup> /100 persons where it can dry and be removed for use as manure .

The composition of gas(%): 65 CH<sub>4</sub> , 34 CO<sub>2</sub> and 1 others on volume basis. Gas is used for running pump sets and street light lamps.

The supernatant liquid from the digester is mixed with garbage and compost and used as manure.

Full scale night soils digester exists in Ernakulam in Kerala state is capable of serving 20,000 people .One of the best village organization viz., Koroda Gram Panchayat in Maharastra has installed for night soil digestion where lavatories were constructed in such a way that night soil can be directly taken to a centrally located digester.

## VII SEWAGE AND SLUDGE

### SEWAGE:

Sewage refers to the used up water from towns and cities collected through a drainage system. It consists of solid and liquid excreta and liquid wastes from kitchen and bath rooms. It also contains animal vegetable and mineral matter in suspension, solution and colloidal state. It is the mineral matter that makes the purification difficult.

**SEWERAGE:** Sewerage is the pipe system that carries the sewage for disposal

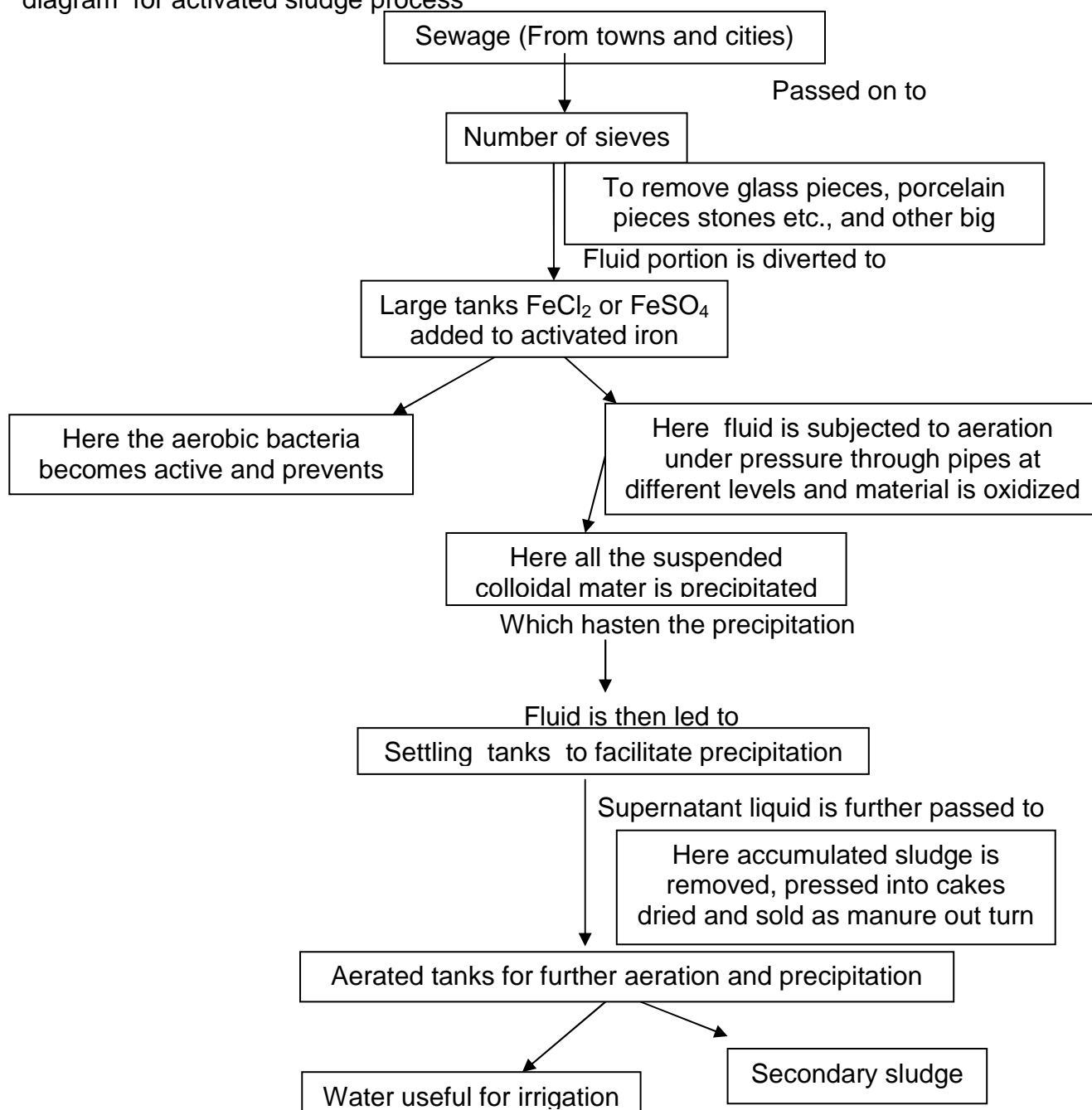
**SULLAGE:** Is the water drained from the kitchens, bathrooms and drainage water of the streets (open canal)

**EFFLUENT:** It is the clear supernatant liquid obtained after aeration during sedimentation process in the septic tanks of the activated sludge process. It is fit for irrigation and rich in N.

**SLUDGE:** Sludge is the sediment that settles down in the activated sludge process. It is dark and powdery material with good manurial value.

### ACTIVATED SLUDGE PROCESS

In this process, the sewage is diverted outside the town or city and processed. There is specially constructed plant consisting of series of tanks fitted with pipes at different levels and the compressors to pump air under pressure. The following is a flow diagram for activated sludge process



Out turn of the sludge is 15 per cent of entire sludge handled. Manurial value is 3.5% N- 1.0%  $P_2O_5$  - 0.5 to 1.0 %  $K_2O$

**Advantages:**

1. Maintain proper sanitary conditions
2. Large quantities of manure and water useful for irrigation
3. Generates good income to the local bodies
4. Avoids pollution of adjoining rivers and seas.

**B. CONCENTRATED ORGANIC MANURES**

**I. BONE MEAL :**

Bone meal is a white to whitish material produced by treating the bones obtained in abattoirs (Slaughter houses) .The bones are dried, crushed, degreased and cleaned to obtain bone grist .Finely ground ,it serves as an organic N- P fertilizer.

**Deamination:** It is a process of removal of proteins from the grist which yields deaminated bone meal. It is also referred as steamed bone meal .

Bone meal is a P-fertilizer of organic origin i.e., it contains  $Ca_3 (PO_4)_2$ . It has 1.0 to 2.0 per cent N and 10-13 per cent P .In general young bones contain less P and more nitrogen than older bones .

Bone meal has some residual effect. Rice and other cereals and other orchard crops respond well to its application . It is particularly useful for soils high in Fe and Al content and applied along green manures with advantage prior to sowing or planting. It can be used for crops rather indiscriminately without fear of salt damage (burning ) unlike chemical fertilizers.

**II. HORN MEAL :**

Horn powder, horn grist or horn chips can be obtained depending on the degree of crushing and collectively termed as horn meal .This is a slow acting fertilizer of Nitrogen containing 14 per cent N.

About 3-4 kg horn and hoof material can be obtained from each animal .Horn and hoof meal manufactured in India annually to the extent of 14,000 tones provided horns and hoofs of all the dead animals are collected and processed .

Horn and bone meal mixed fertilizers yield organic N-P depending on their composition (N from Horns and P from Bones)



### III. BLOOD MEAL/ BLOOD POWDER :

Blood is collected from abattoirs (slaughter houses ) dried and ground. Two types of dried blood are manufactured.

- i) Red product: It is obtained by drying the blood with super heated steam and hot air.
- ii) Black product: It is obtained by evaporating the liquid blood over sand bath subjected to higher temperatures .It is evenly causes the loss of N and causes Charring.

Both red and black products are spread on the concrete floor covered with a net and allowed to sundry . This powder is used as manure

#### Characteristics:

- 1) Blood meal absorbs moisture on exposure to atmosphere
- 2) Of all the protein organic manures, dried blood has the highest availability of N and given a rating of 80 (i.e.,) it is 80 per cent as efficient as the inorganic N fertilizer in providing the nitrogen to the crop.
- 3) An adult bovine (cow, buffalo /ox) gives 15 kg where as sheep or goat yields 1.5 kg of dried blood.
- 4) About 30-40 kg of dried blood is obtained from 100 kg fresh blood.
- 5)The principal component of blood is N .Which is 10-14 % in slow acting form.

### IV. MEAT MEAL :

It is also referred as TANKAGE obtained from rejected carcasses (meat products) mostly meat and waste products such as leather scrap, feather,wool etc., .These materials are cooked in steel tanks under pressure of 2 to 7 kg / cm<sup>2</sup> for 30-90 minutes. Addition of sulphuric acid (0.5%) facilitates hydrolysis at low temperature . It is dark brown and fluffy material . It contains 7 %N , 1 to 5 % P and 3 to 10 % K . Tankage has the rating of 60 per cent .

### V. FISH MEAL :

The non-edible fish, fish carcasses and offels (parts of butchered animal) are used to prepare fish meal .Such material are crushed or powdered after drying .The oil is generally removed before the meal is ground and facilitate easy decomposition .It is quick acting fertilizer suitable for all crops on all soils .It contains 7 to 8% N ,2 to 3 % P<sub>2</sub>O<sub>5</sub> -and 0.2 to 0.5 % K<sub>2</sub>O

### VI. GUANO:

The name Guano is originated in PERU, from the word "HAUNO" to mean manure. GUANO is a product of sea bird (Pelican, Gannets, and Albatrosses) excrement covered over long periods and occurring in natural deposits. These birds live on islands with no rain or vegetation along with the pacific ocean coasts of PERU and CHILE and feed on abundant fish in the sea .These deposits may also have the excrements of turtles and seals together with the remains of dead bodies of birds ,bone, feather,

sand and gravel etc., guano deposits are up to 60 meters thick, however only central layer has a higher N-content. Guano has a colour varying from grey to dark brown, physical characters vary with the age, nature of deposit and amount of foreign material. It contains 8 to 15 % N and 2 to 3 % P. The chemical constituents are mainly ammonium oxalate and ammonium phosphate as well as calcium phosphates. There are important admixtures besides 2-4 % K.

Raw guano is some times processed into guano fertilizer by acid decomposition with sulphuric acid. This is called peru guano: 6+12+2 (N+ P<sub>2</sub>O<sub>5</sub>+ K<sub>2</sub>O). Guano also occurs elsewhere as "cane fertilizer" produced by bats.

## VII. OIL CAKES :

After removal of oil from seeds, the residue is made into cakes. Oil cakes are used as organic fertilizers as they are rich source of organic nitrogen in protein form. In addition to N, small amounts of P, K and micronutrients. Oil cakes are classified into two groups viz.,

- i) **Edible oil cakes:** Suitable for cattle and poultry feeding and also as a manure /fertilizer but not economical Eg. Groundnut, Gingelly cakes etc.,
- ii) **Non –Edible oil cakes:** Suitable for crop fertilization. Eg. Castor cake, neem cake etc.,

Edible oil cakes serve as fertilizers, but their use is restricted due to economic reasons. Composition of oil cakes are variable. Oil cakes are quick acting organic manures. The decomposability increases with decrease in oil content. They nitrify in about 30-45 days on addition to the soil. The rate of decomposition can be hastened by grinding the oil cakes into fine powder and thorough mixing with the soil.

### 1) Castor cake :

It is also called as castor pomace. It is the ground residue of beans from which oil has been extracted. It is poisonous to animals and used only as fertilizer. It is a by-product in the manufacture of castor oil. It contains 5 to 6 % N, 1 % P<sub>2</sub>O<sub>5</sub> and 1.0 % K<sub>2</sub>O. It has got a rating of 75 per cent.

### 2) Neem cake :

Neem cake is prepared by crushing the neem seed (with shells) in expellers and oil is separated. Neem tree is regarded as a "village dispensary" by virtue of its medicinal and antiseptic value. Neem cake is useful for cash crops mainly due to insect repellent or insecticidal properties owing to the presence of residual bitter and sulphur. Comparatively it contains higher N. It cannot be used as a cattle feed due to its bitter taste.

**Chemical composition of neem cake**

<b>S.No.</b>	<b>Constituent</b>	<b>Content (%)</b>
1	Organic matter	84.5
2	Moisture	9.9
3	Carbohydrates	17.5
4	Protein	36.2
5	Fiber	11.7
6	Oil	18.2
7	Ash	6.8
8	N	5.8
9	P	0.46
10	K	1.12

Neem cake has also been used as coating material over urea super granules as the former is reported to improve the fertilizer efficiency of soil applied urea .



**BIOGAS PLANT:****Working principle:**

When dung or any other organic materials is fermented in absence of air, the combustible gas methane is produced.

In biogas plant, the fermentation is carried out in a brick lined well which is filled with dung made in to liquid slurry with water. This is then covered with an iron drum introduced upside down in the well which serves to cut off air and provide the necessary conditions for fermentation .The gas is produced in the form of bubbles inside the drum which gradually fills up and begins to float and rise .The gas is then taken through a wheel cock on the top of the drum and led to the kitchen by pipes and burned through suitable burners . The gas production is maintained by adding 50 kg fresh dung daily through a funnel pipe which carries the slurry to the bottom of the well. The spent slurry (biogas slurry) over flows from the top of the well and collects in a pit where it is periodically removed and added to the compost.

**Pre –requisites for setting up a gas plant**

1. A minimum of 45 kg dung should be available to operate the gas plant of 60 cubic feet (2 m<sup>3</sup>) capacity. Medium size cow, buffalo or bullock yield 10 kg fresh dung and roughly 5 animals are needed.
2. Night soil can also be used. Sixty (60) adults are needed for the above plant .This is normally possible in case of hotels, hostels ,public lavatories etc.,
3. Normally the distance between gas plant and place where gas is to be used should be with in 20 meters (Kitchen to gas plant ).
4. Besides cattle dung and night soil, piggery and poultry droppings if available in sufficient quantities can also be utilized.
5. The gas plant should be located in open space in order to receive maximum possible sunshine to ensure better fermentation and gas production.

**Advantages of biogas plant:**

1. The cow dung when processed through the gas plant yields enough gas (combustible gas) for cooking lightening and good quality manure (methane free manure).
2. The manure obtained from biogas plants has higher content of nitrogen (1.5 %) as against 0.75percent found in FYM.
3. The thermal efficiency of cow dung bunt for fuel in usual manner is around 11 per cent while it is 60 per cent when burnt in properly designed burners.
4. Biogas digest is very rich in humus content
5. The manure is free from offensive odour
6. It helps in improving the sanitation by preventing fly and mosquito breeding.

**III. BIO-GAS SLURRY:** Biogas slurry is also used as bulky organic manure produced from bio-gas plant.

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**Lecture: 9** Commercial fertilizers – Classification with examples –Nitrogenous fertilizers- Manufacturing process and properties of major nitrogenous fertilizers viz., Ammonia

In this chapter mineral or chemical or inorganic fertilizer, their manufacture including the chemical reactions involved, physical and chemical properties are described. These chemical fertilizers are also called as commercial 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.*

**Elements essential for plant growth:**

Macronutrients: N, P, K, Ca, Mg and S

Micronutrients : Fe , Zn ,Cu ,Mn , Mo, B ,Cl, etc.,

Primary nutrients: N, P and K

Secondary nutrients: Ca, Mg and S

The mineral fertilizers are produced in plants (Industries or Factories) varying in size from a simple operation run by a few people with modest investment to huge plants involving heavy involvement requiring hundreds of trained personnel. The technologies are complex.

**Classification of fertilizers refer page no : 3**

**A. STRAIGHT FERTILIZERS :**

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.

**1. 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 .

**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 ( $\text{N}_2$ ).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  $\text{N}_2$ ) 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<sub>2</sub>] by any one of the following process.

- i) Ammonia synthesis by Haber –Bosch process
- ii) Calcium cyanamide synthesis
- iii) 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.

### Classification of mineral nitrogen fertilizers

S.No.	Chemical Form of Nitrogen	Fertilizer	Chemical formula	N Content (%)
1	Ammonium [NH <sub>4</sub> <sup>+</sup> ]	a) Gaseous ammonia	NH <sub>3</sub>	82
		b) Ammonia water	NH <sub>3</sub> , NH <sub>4</sub> OH	24
		c) Ammonium sulphate	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	21
2	Nitrate [NO <sub>3</sub> <sup>-</sup> ]	a) Calcium nitrate	Ca(NO <sub>3</sub> ) <sub>2</sub>	16
		b) Sodium nitrate	Na NO <sub>3</sub>	16
		c) Ammonium sulphate nitrate	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> +NH <sub>4</sub> NO <sub>3</sub>	26
3	Ammonium +Nitrate [NH <sub>4</sub> <sup>+</sup> ]+[NO <sub>3</sub> <sup>-</sup> ]	a) Ammonium nitrate	NH <sub>4</sub> NO <sub>3</sub>	35
		b) Calcium ammonium nitrate	NH <sub>4</sub> NO <sub>3</sub> +CaCO <sub>3</sub>	25
4	Amide [-NH <sub>2</sub> ]	a) Urea	CO(NH <sub>2</sub> ) <sub>2</sub>	46
		b) Calcium cyanamide	CaCN <sub>2</sub>	22

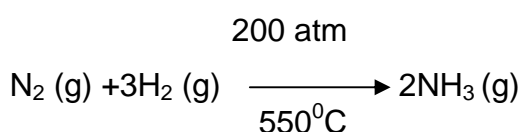
**Note :** For the sake of convenience ,the list of mineral fertilizers also include urea, an organic compound which yields mineral N after conversion in the soil .

### Manufacturing process:

#### AMMONIA:

The production of ammonia (NH<sub>3</sub>) 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 °C .



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.

**i) Water :**

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

**ii) 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.

**iii) Naphtha :**

The light distillate fraction of petroleum with a maximum boiling point (B.P.) of 215 °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) Naphthenes (14%) d) aromatics (6%). It has C:H ratio by weight around 5.48. About 75% of nitrogen produced in India utilizes NAPHTHA.

**iv) 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.

**v) 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

**Vi) Coke oven gas :** Coke oven gas consists of gases (%) H<sub>2</sub> (52.6), CH<sub>4</sub> (28.9), CO (7.5) CO<sub>2</sub> (3.5) and produced during coal carbonization in steel industry.

**Manufacturing process of Ammonia:**

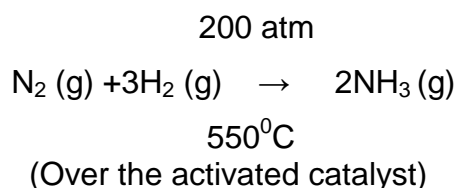
The process of ammonia synthesis involves four successive steps viz.,

1. Gasification
2. Conversion of CO to produce H<sub>2</sub>
3. Gas purification
4. Synthesis

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

**I. AMMONIA [or gaseous ammonia] :**

Ammonia synthesis is carried out at elevated temperature of 550 °C and pressure of 200 atmospheres by passing N<sub>2</sub> and H<sub>2</sub> mixture (1:3 mole ratio) over an activated iron oxide catalyst. This process is carried out in a typical NH<sub>3</sub> 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 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 °C the gas exerts a pressure of 34.10 kg /inch<sup>2</sup> while the pressure at 38 0C is 89.50 kg / inch<sup>2</sup> .It is stored in steel or plastic tanks that can with stand the pressure of 120.4 kg / inch<sup>2</sup> .
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  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^+$  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 .

## **II. 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 °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  $\text{NH}_3$  is stored in the nursery tank
  - Anhydrous  $\text{NH}_3$  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.

**Lecture : 10** Manufacturing process and properties of Ammonium sulphate, urea and calcium ammonium nitrate.

### III. AMMONIUM SULPHATE $[(\text{NH}_4)_2\text{SO}_4]$ :

#### Introduction:

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

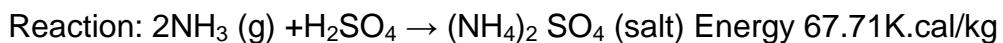
#### Manufacturing process:

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

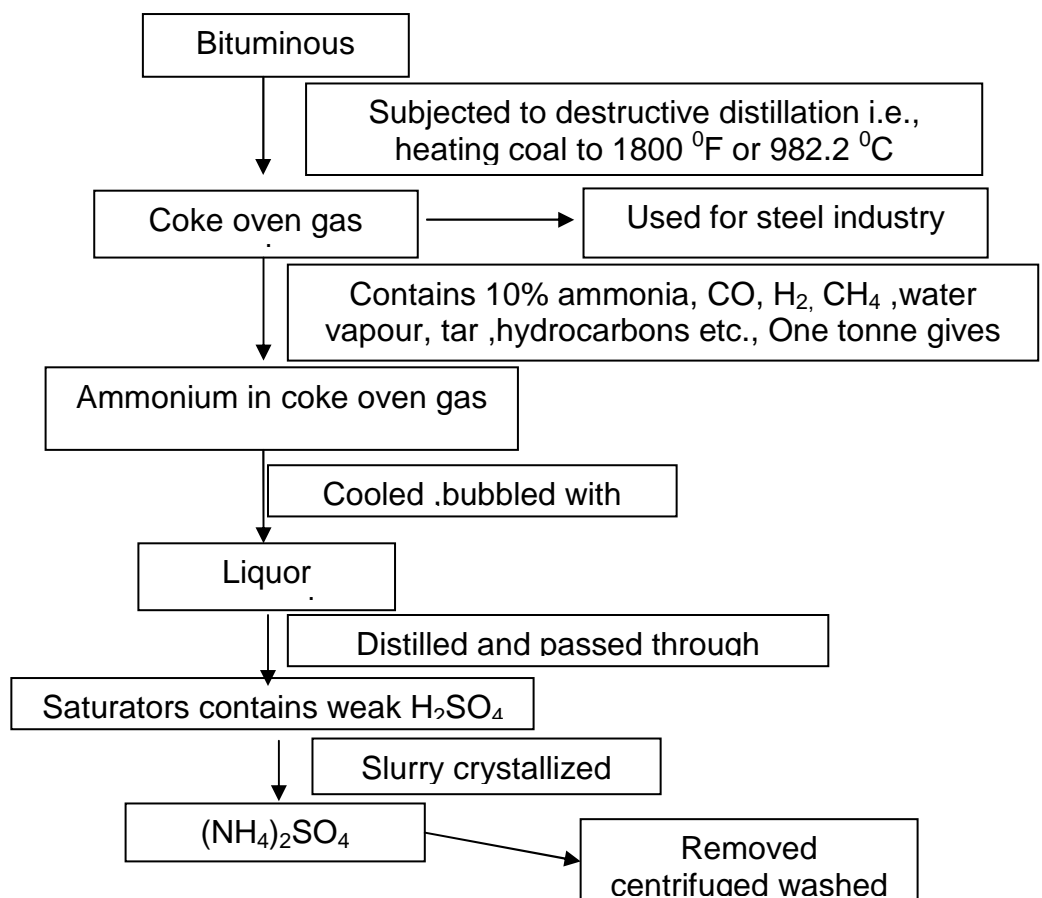
#### I. By product process : [Raw materials Coal and Sulphuric acid ]

In iron and steel production when bituminous coal is subjected to destructive distillation i.e., heating coal to  $1800^\circ\text{F}$  ( $982.2^\circ\text{C}$ ) 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  $\text{CO}$  ,  $\text{H}_2$   $\text{CH}_4$  ,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  $\text{H}_2\text{SO}_4$  .Ammonium sulphate  $[(\text{NH}_4)_2\text{SO}_4]$  crystals are formed in the saturators are removed centrifuged ,washed and drained.



Flow diagram



## 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.

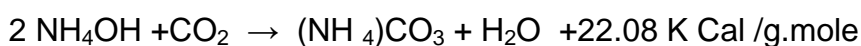
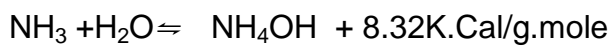


Neutralization of ammonia by sulphuric acid takes place in reactor and the resultant slurry is transferred to crystallizer, where the heat of neutralization is advantageously utilized to evaporate the water in the slurry. Ammonium sulphate crystals are taken out from the bottom of the reactor and centrifuged.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

## III. Gypsum process or leuna process: [Raw materials : NH<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.

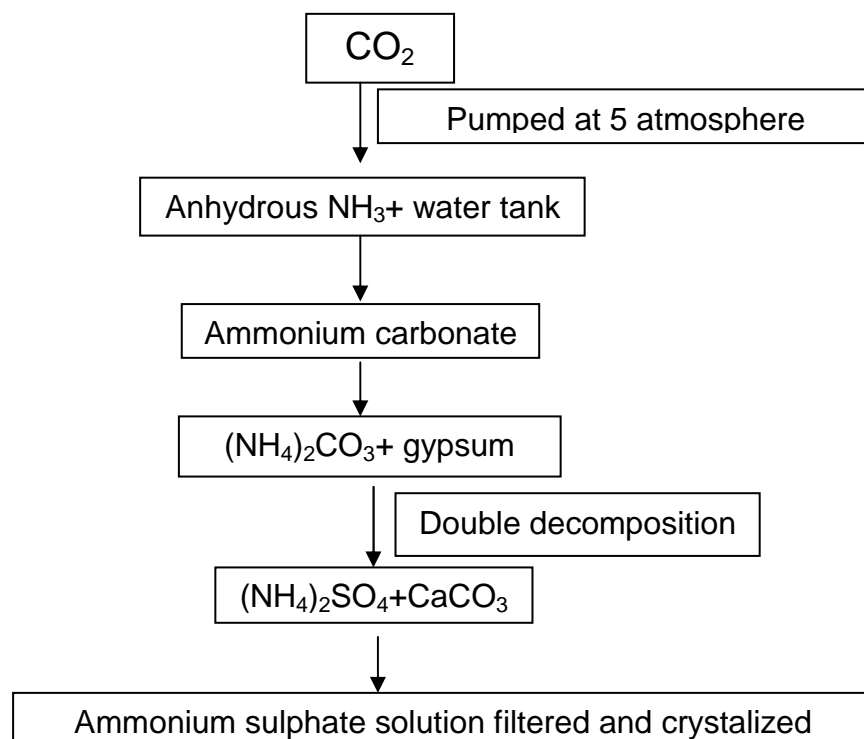
Reactions:



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<sub>3</sub> 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  $(\text{NH}_4)_2 \text{SO}_4$  is  $876.60 \text{ kg /m}^3$

**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  $0^\circ\text{C}$  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

**IV. 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:**

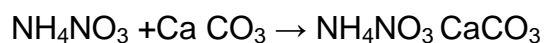
1)Ammonia 2) Nitric acid 3) Limestone or Dolomite 4) Soapstone(essentially magnesium silicate)

**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.

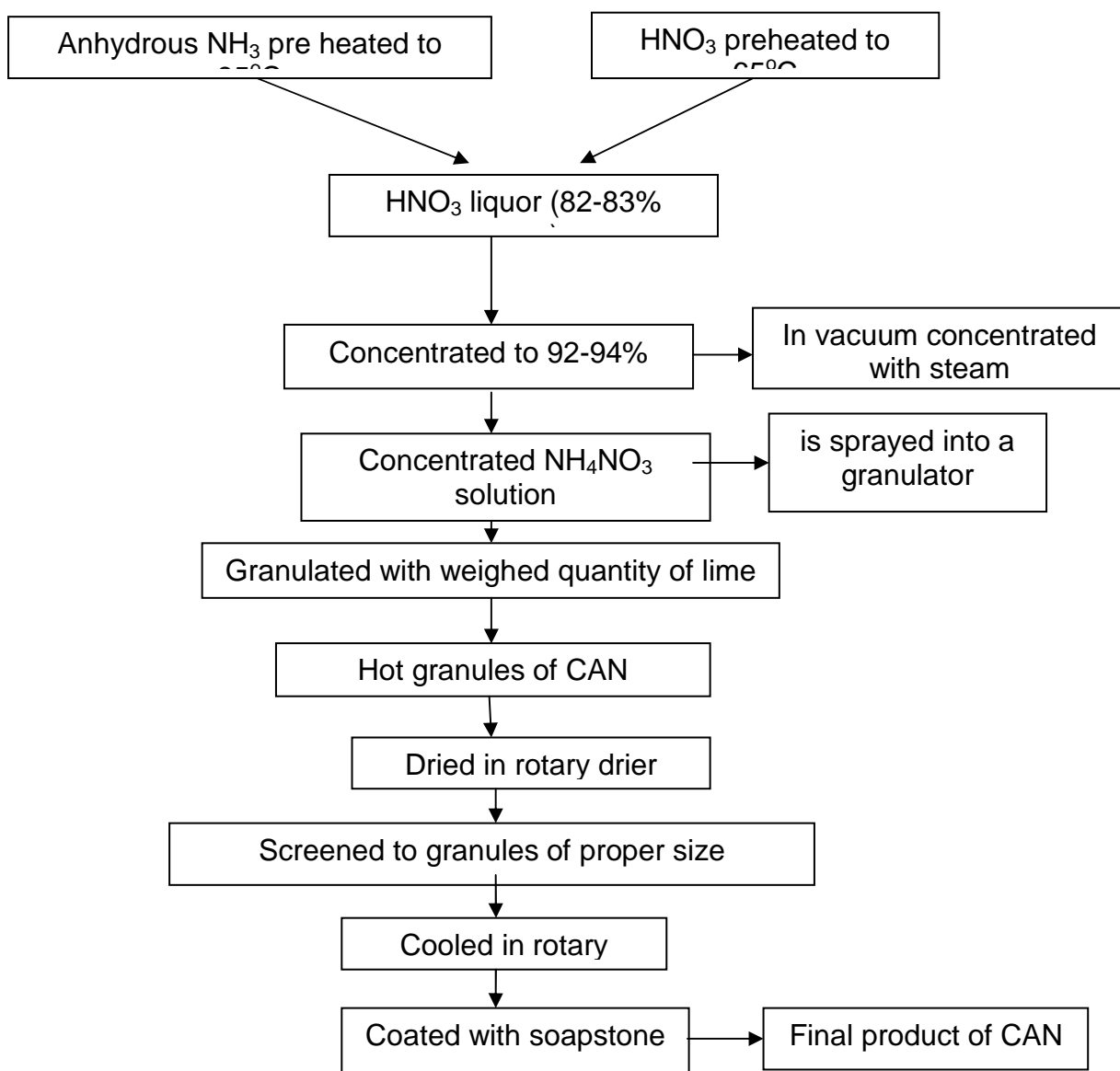
**Physical properties:**

3. CAN is an easy flowing granular material (size 1 to 4 mm )
4. 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  $\text{NH}_4^+$  and  $\text{NO}_3^-$  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 8.1 per cent of calcium and 0.5 per cent by weight of calcium nitrate
4. It is readily soluble in water

Flow diagram:

**V. UREA [Carbamide (NH<sub>2</sub>CO NH<sub>2</sub>)] :**

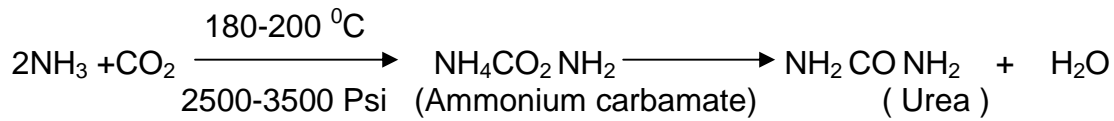
Urea or carbamide as it is sometimes called "non-ionic" nitrogen compound used as a fertilizer for crops and also as protein supplement in the feed of ruminants (farm animals).

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

**F.WHOLER** (German chemist), first prepared urea in the year 1828 [Commercial production started in 1922] by isomerization 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.



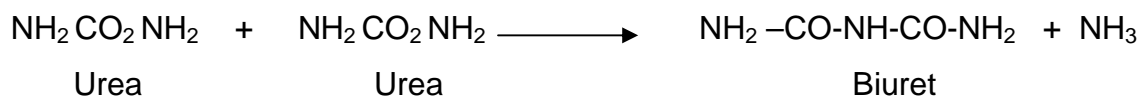
[Psi: Pressure in pounds per square inch]

### Manufacturing process

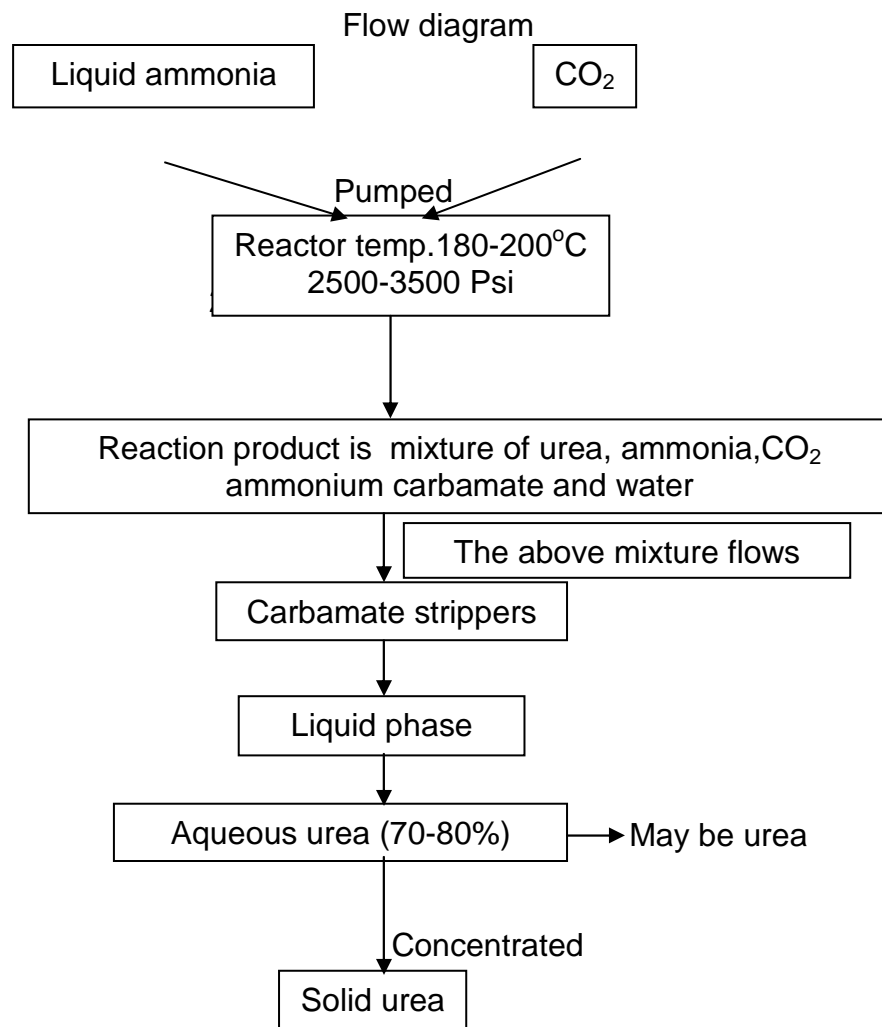
Liquid ammonia and carbon dioxide gas are pumped continuously into a reactor maintained at temperature ranging 180-200 °C and pressure ranging 2500 to 3500 Psi .The reaction is exothermic .The reaction product , is a mixture of urea , ammonia, carbon dioxide , ammonium carbamate and water .The mixture 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 °C



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:**

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:**

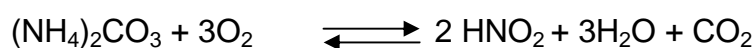
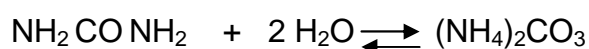
1. Synthetic protein, organic compound, richest source of N (46%) in amide form among solid N fertilizers
2. Soluble in water and solubility is 100 g /100 g of water at 20°C
3. Biuret content is about 1.5 per cent by weight
4. It is identical to urea found in animal urine.

**What happens when urea is applied to soil**

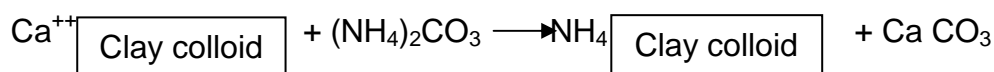
Conversion of urea in to ammoniacal and nitrate form is complete in about a week. As such it is advisable to apply urea three to four days before sowing of any field crop . Loss of nitrogen by leaching is less.

Urea is less acidic compared to ammonia sulphate .Since application of 100 kg urea leaves acidity, which requires 80 kg of CaCO<sub>3</sub> 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.



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.
-



**Lecture:11** Phosphatic fertilizers –Rock phosphate –Uses – Occurrence, types and properties. Manufacturing process and properties of SSP, TSP and Basic slag

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## PHOSPHATIC FERTILIZERS

Phosphate fertilizers are chemical substances that contain the nutrient element phosphorus in the form of absorbable phosphate ions (anions) or that yield such phosphate anions after conversion

Origin and reserves:

The raw material of P-fertilizers are essentially rock phosphates from phosphate deposits, phosphate ores and other P compounds. The deposits of phosphate rock exist in nature because of the low solubility of the compounds present. The composition of rock phosphates consists of various apatites (Calcium phosphate) which are partly of magmatic and partly of organogenic origin.

**Magma :** Weathering and decomposition of primary minerals

**Organogenic :** Bones, Teeth of animals, Guano deposits result in the formation of apatites.

**Large deposits of rock phosphates occur in**

- i) North Africa (Morocco, Algeria, Tunisia) in the form of organic crystalline phosphate, especially in a soft earth, finely crystalline form known as gafsa phosphates.
- ii) USA (eg. Florida apatite) in the form of pebbles.
- iii) USSR in the form of hard earth, coarsely crystalline kola apatite

In India phosphate rock deposits have been found in Udaipur in Rajasthan and Mussoorie in Uttaranchal. Some deposits occur in Singbhum district (Bihar), Jhabhua district (M.P), Visakhapatnam district (AP), Tiruchanapalli (TN).

**Production of phosphate fertilizers**

Mineral P-fertilizers are obtained by chemical treatment or fine grinding of phosphates found in nature. Soft earth rock phosphates require grinding whereas hard earth raw material require chemical treatment. This is accompanied by

- 1) Thermal methods
- 2) Chemical methods using  $H_2SO_4$  or other acids
- 3) Combination of above two methods [1 and 2 methods]

## Classification of phosphatic fertilizers

Phosphatic fertilizers were classified by two ways .They are

- I. Classification of phosphatic fertilizers based on relative solubility of phosphate
- II. Classification of phosphatic fertilizers based on the form in which orthophosphoric acid or phosphoric acid is combined with calcium.

### I. Classification of phosphatic fertilizers based on relative solubility of phosphate :

Based on the relative solubility, the phosphatic fertilizers are classified into following three types

- A) Water soluble phosphorus fertilizers
- B) Water insoluble but citrate soluble phosphorus fertilizers
- C) Water and citrate insoluble phosphorus fertilizers

A) Water soluble phosphorus fertilizers : Phosphorus in these fertilizers is present in water soluble form. P is present in the form of monocalcium phosphate  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ . This form of P is generally regarded as the most readily available to plants.

1. Single super phosphate (16-18%  $\text{P}_2\text{O}_5$ )
2. Double super phosphate (32 %  $\text{P}_2\text{O}_5$ )
3. Triple super phosphate (46-48%  $\text{P}_2\text{O}_5$ )
4. Higher content or concentrated super phosphate
5. Ammonium phosphate ( 20% N and 20%  $\text{P}_2\text{O}_5$ )

These fertilizers are suitable for neutral to alkaline soils and should be applied at the time of sowing. Immediately after application , phosphorus gets converted into insoluble dicalcium phosphate. Hence the P fertilizers containing water soluble P should be applied in granulated form rather than powdered form. Contact between soil and fertilizers should be reduced. Hence pocketing of fertilizers is beneficial than broad casting. Under acidic conditions, water soluble phosphoric acid gets converted into an available iron aluminium phosphates.

B) Water insoluble but citrate soluble phosphorus fertilizers : Phosphorus present in these fertilizers is soluble in 2% citric acid or neutral normal ammonium acetate solution. P is present as dicalcium phosphate  $\text{Ca}_2\text{H}_2(\text{PO}_4)_2$  /  $\text{CaHPO}_4$

1. Basic slag (14 to 18%  $\text{P}_2\text{O}_5$ )
2. Dicalcium phosphate (34-39 %  $\text{P}_2\text{O}_5$  )
3. Raw and steamed bone meal ( part of the  $\text{P}_2\text{O}_5$  soluble in citric acid ) – suitable for acid soils and lateritic soils

The fertilizers of this group are particularly suitable for the acidic soils, because with low pH citrate soluble phosphoric acid gets converted into monocalcium phosphate or water soluble phosphate, and there is less chance of phosphate getting fixed as iron and aluminium phosphate. Contact between soil and fertilizer should be more to solubilize the citrate soluble P present in the fertilizer. Hence they should be applied as broadcast to increase contact with soil.

C) Water and citrate insoluble phosphorus fertilizers : Phosphorus present in the fertilizer is not soluble both in water and citrate solution containing insoluble phosphoric acid or tri calcium Phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ )

- 1) Rock phosphate (20 to 40 %  $\text{P}_2\text{O}_5$ )
- 2) Raw bone meal (20 to 25%  $\text{P}_2\text{O}_5$ )
- 3) Steamed bone meal (22%  $\text{P}_2\text{O}_5$ )

These fertilizers are very well suited for acidic soils or organic soils, which require large quantities of phosphatic fertilizers to raise the soil fertility. They should be applied as broadcast to facilitate intimate contact with soil. They should be applied one month before taking up the crop so that insoluble-P gets solubilized by the time of sowing of crop.

## II. Classification of phosphatic fertilizers based on the form in which orthophosphoric acid or phosphoric acid is combined with calcium.

The phosphatic fertilizers can be classified broadly into three groups, depending on the form in which orthophosphoric acid or phosphoric acid is combined with calcium. They are:

1. Ortho phosphates Eg. MAP, DAP, UAP, SSP, Nitro phosphates
2. Polyphosphates Eg. Ammonium poly phosphate, Potassium poly phosphate
3. Metaphosphates Eg. Ammonium meta phosphate, Potassium meta phosphate

**Available Phosphorus** : The sum of the water soluble and citrate soluble values is taken as an estimate of the fraction of the total P which is available to plants.

**Total phosphorus** : The total P is the sum of the available and citrate insoluble fractions. It is determined by treating a sample of the original material with strong acids and analyzing the solution for phosphates.

**Manufacturing processes, physical and chemical properties of the following four phosphatic fertilizers are described in detail below :**

- I. Ground rock phosphate
- II. Single super phosphate
- III. Triple super phosphate
- IV. Basic slag

## I. Ground Rock Phosphate :

The World phosphate industry is based essentially on deposits of rock phosphate – a fluoride bearing complex of calcium phosphates. The content of rock is usually expressed in terms of its tricalcium phosphate  $[\text{Ca}_3(\text{PO}_4)_2]$  equivalent.

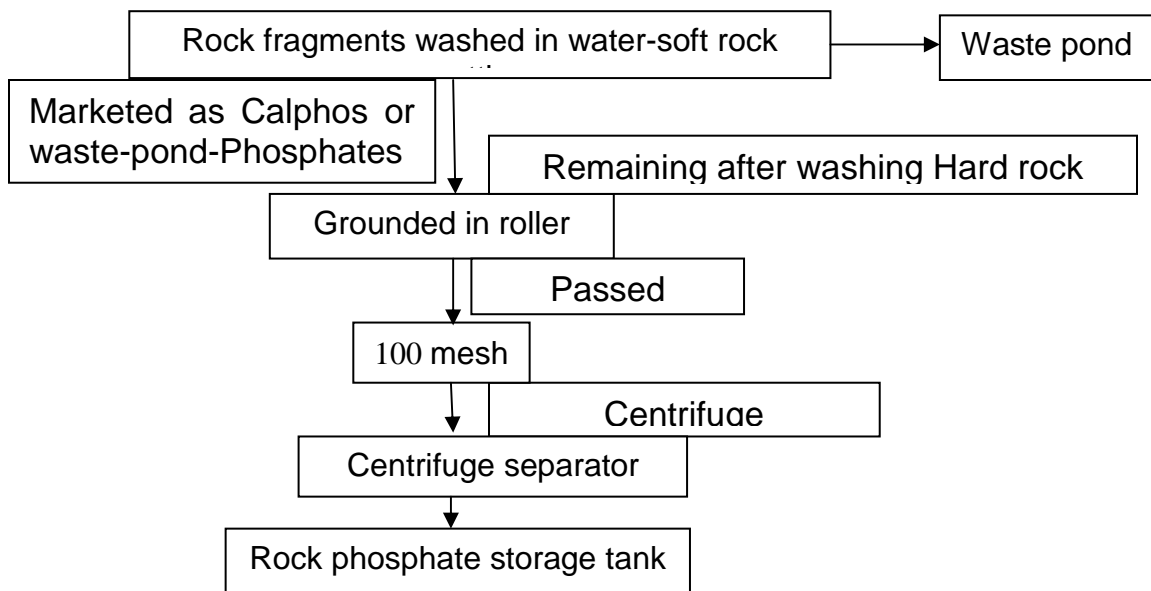
Four kinds of rock phosphate are recognized viz., 1) soft rock phosphate 2) Hard rock phosphate (Hard earth) 3) Land pebble phosphate 4) River pebble phosphate .

The exposed rock phosphates are washed with water into the waste ponds, where soft rock phosphates (soft earth) settle out with clay and other impurities .The fractions remaining after washing i.e., hard phosphate rock , land pebble phosphate are ground to pass to through 0.14 mm sieve (100 mesh screen ) either in a roller mill or ball mill and the resultant rock phosphate powder is carried out a centrifugal separator by means of an air blower .The product is discharged into a storage tank . The plant (industry) can grind about 50 tonnes of phosphate rock per hour .Previously waste ponds containing soft phosphates and clay material is marketed under trade names in USA viz., Colloidal phosphates ,mineral colloids ,Calphos and phos-cal-oids .These products are known in the fertilizer industry as waste-pond phosphates.

### Physical and chemical properties:

- 1.The fine powder of phosphate rock is known as float to mean un acidulated ground rock phosphate
- 2.The mineral in phosphate rock is apatite which has the general formula  **$[\text{Ca}_{10}(\text{PO}_4)_6(\text{F}, \text{Cl}(\text{OH})_2(\text{CO}_3)_2]$**
3. Contain about 10-16 % P and varying amounts of lime (7-10%  $\text{Ca CO}_3$ ) and, silica fluoride [3-4% F] iron and aluminum as impurities.
4. It has no practically water soluble phosphates ( $10^{-7}$  molar P), but less than 30% of P is soluble in 2.0% citric acid solution.
5. Waste pond phosphates contain 7-9 % P out of which 1 to 2 % phosphate rock is soluble in 1 N neutral ammonium acetate.

## FLOW DIAGRAM

**Action of rock phosphate on acid soils:**

When finely ground rock phosphate is applied to acidic soils or to soils containing high percentage of organic matter, Carbonic and nitric acids present in the soil act on rock phosphate, which is containing tricalcium (unavailable) and convert unavailable phosphate to mono calcium phosphate or water soluble phosphate which is easily available to growing plants. It has been observed reactions in the following manner.



[Rock Phosphate [ Carbonic acid ] → [Mono calcium phosphate]  
Containing  
no fluoride] [Available]

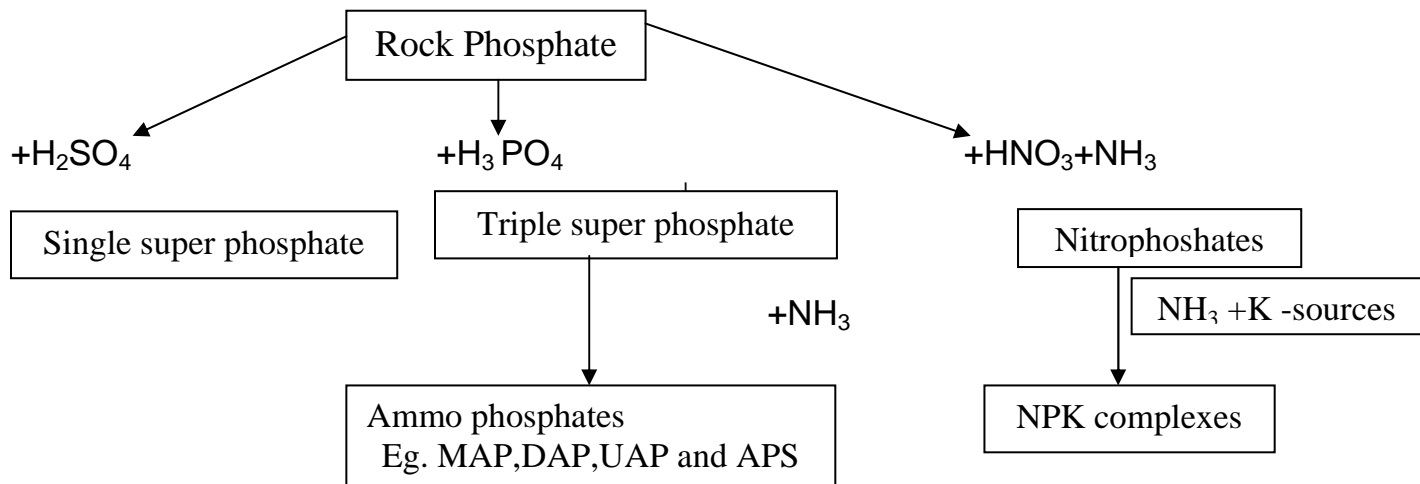


In general ground rock phosphate should be applied in large quantities of 500 to 1000 kg per hectare once in three years, but should not be applied in small quantities every year. It should be thoroughly mixed in the top soil with country plough or disc harrow.

Strongly acidic soils are most suitable for direct application of rock phosphates. Such areas are found in whole Kerala, Shimoga, Mysore, parts of Assam, Bihar, Mussorie rock phosphate and Purulia rock phosphate have been recognized by ICAR for direct application.

### Direct uses of rock phosphate [ R.P]

- 1) Around 90% of rock phosphate is used in the manufacturing of phosphatic fertilizers :

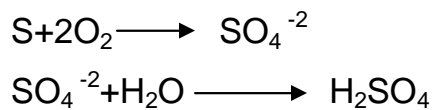


- 2) Direct use of Rock Phosphate [ R.P] is mainly for acid soils. Acidic soils contain acids which react with rock phosphate yield monocalcium phosphate (MCP) ,which is available to plants .

### Use of Rock phosphate as direct application depends on the following factors:

- Soil reaction** : Not applied in neutral and alkaline soils
- Dose and time of application** : It should be applied in large quantities once in 5-6 years ,it should be finely ground
- Plant Species**: R.P. is useful for calcium loving plants like legumes .It should be applied for long duration commercial crops.
- Soil organic matter** : Can be applied in soils containing higher amounts of organic matter because acids are produced during decomposition , then the tricalcium phosphate(TCP ) is converted to mono calcium phosphate (MCP) .
- Organic manures**: R.P can be applied along with un decomposed organic materials like green manures because during decomposition acids are secreted .
- Phosphocompost**: Applying rock phosphates along with phosphorus solubilizing bacteria with or without sulphur and sulphur oxidizing bacteria. During the decomposition process of plant and animal sources (residues) is called phosphor compost . Acids produced during composting convert TCP to MCP.

- g) Phosphate solubilizing bacteria:** When RP is applied to neutral soils, it is applied with phosphorus solubilizing bacteria.
- h) Fertilizers:** It can be applied along with acid producing fertilizers. It is also applied along with the SSP, because MCP produces  $H_3PO_4$  which in turn converts TCP in R.P to MCP.
- i) Biosuper :** Super phosphate produced by biological organisms . Application of R.P. along with sulphur or without sulphur oxidizing bacteria .



In this process sulphur get oxidized to sulphate and which, forms  $H_2SO_4$ , which will be helpful in acidulation of Rock phosphate. Phosphate fertilizers are those fertilizers which contain  $PO_4$  ion in plant absorbable form or which yield on conversion.

#### **I. NORMAL (Or) ORDINARY (OR) SINGLE SUPER PHOSPHATE [16%P]:**

Super phosphate is a term used in reference to phosphates of which is in a form readily available to plants

Single super phosphate is the oldest artificially produced fertilizer and its manufacture dates back to 1842, when **LAWES J.B** prepared for the first time in ENGLAND by treating Rock phosphate with sulphuric acid.

#### **Manufacture process of single super phosphate**

**Raw materials: 1) Phosphate rock 2) Sulphuric acid**

Single super phosphate is (SSP) is manufactured by mixing gravimetrically equal parts of

sulphuric acid (75%) and rock phosphate of 0.14 mm [100 mesh seive]

There are two methods of preparation of SSP viz.,

- i. Den process**
- ii. Continuous rock phosphate acidulation process**

#### **i. Den process:**

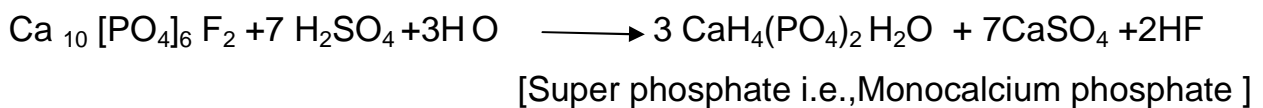
Weighed quantities of Rock phosphate(0.14mm) and sulphuric acid (75% ) are mixed in a mixer, capable of handling 40-50 tonnes per hour, are allowed to react for about a minute and the resultant slurry is dumped in to a compartment known as DEN [100-300 tonnes capacity ] . In a few hours the reaction goes to completion .Water ,carbon dioxide ,fluorine ,volatilize away resulting in the reduction in the bulk of the material by retaining the material in the Den becomes a hard block and removal is accomplished by means of

mechanical excavators equipped with revolving knives which cut into the block and the disintegrated SSP is stored for 2 to 6 weeks to cure and attain the desired physical condition .

## ii. Continuous rock acidulation process:

This is a popular and latest process in which acidulation of rock phosphate with sulphuric acid is done continuously in mixer provided with indigenous metering ( $\text{H}_2\text{SO}_4$ ) and weighing (RP) devices. The mixer is agitated for 2-3 minutes and is then discharged into an endless conveyer belt on which it solidifies .The belt conveyer moves the blocks of hardened super phosphate towards a revolving cutter which disintegrate the material .It is then transferred to a storage bin and stored for 2-6 weeks to cure and attain the desired physical condition .

The chemical reaction (Exothermic) involved in both processes are same as represented below



Three points are suggestive of the above equation viz.,

- 1) Phosphate originally present as apatite is converted into water soluble Monocalcium phosphate
- 2) The by-product reaction is gypsum which is initially mixed with the monocalcium phosphate
- 3) The reaction releases toxic hydro fluoric acid gas

## Physical properties of SSP:

- 1) SSP is in granular form has bulk density  $961.10 \text{ kg m}^{-3}$  and is easy to handle
- 2) SSP is also available in powder form, it is not free flowing and being slightly hygroscopic has a tendency to cake . Hydration of monocalcium phosphate may be the cause for hardening SSP .It has grey colour and an acidic odour.
- 3) Free acid in the SSP, will usually rot the jute fiber bags and hence the fertilizer has to be stored in polythene lined gunny bags or polyethylene bags.

## Chemical properties of SSP:

- 1) SSP has 2/5 Mono calcium phosphate and 3/5 Gypsum by weight
- 2) SSP manufactured in India consists of two grades viz., Grade I: 16%  $\text{P}_2\text{O}_5$  % or (7%P) by weight of water soluble  $\text{P}_2\text{O}_5$  and Grade II: 14%  $\text{P}_2\text{O}_5$  or (6%P) by weight of water soluble  $\text{P}_2\text{O}_5$  .



- 3) SSP also contains 21.0% calcium, 12% sulphur and traces of micronutrients .Obviously it contains more sulphur (12%) than phosphorus (6 to 7%).
- 4) SSP has a pH of about 3.0

## II. TRIPLE SUPER PHOSPHATE (TSP-contains 46 % P<sub>2</sub>O<sub>5</sub>):

Factors for its popularity:

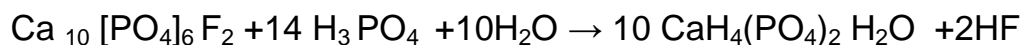
Its high plant nutrient content and its capacity to react with NH<sub>3</sub> in the production of multinutrient fertilizers .The 'prefix' 'TRIPLE' was first used when SSP contained 16 % P<sub>2</sub>O<sub>5</sub> and TSP contained three times as much as 48% P<sub>2</sub>O<sub>5</sub> .

### Manufacturing process:

#### Raw materials :

1. Rock phosphate
2. Phosphoric acid

TSP is obtained by acidulating finely ground phosphate rock (0.14 mm) with phosphoric acid .



The method of manufacture is called CONE MIXER PROCESS.

The phosphate rock (100 mesh) is mixed with phosphoric acid (75%) in a cone mixer in the acid –rock ratio (expressed as eh mole ratio of total P<sub>2</sub>O<sub>5</sub> to CaO in the acidulate) of 0.91 to 0.95. The resultant slurry is then fed to a belt conveyer [as already described in case of SSP. An extended curing period of about 30 days is required for the reaction to complete, for attaining described physical condition]

### Physical properties of TSP:

- 1) TSP in powdery form is not free flowing , has a tendency to form lumps on storage . However, the granulated product has excellent handling and storage characters and is free flowing .
- 2) It has bulk density 800-881 kg m<sup>-3</sup>
- 3) TSP is to be packed in polyethylene lined jute bags or multi wall paper bags to prevent rotting due to free phosphoric acid .

### Chemical properties of TSP:

- 1) The main phosphate compound present in TSP is monocalcium sulphate.
- 2) It contains 46% total P<sub>2</sub>O<sub>5</sub> by weight and 36.8% minimum by weight of water soluble P<sub>2</sub>O<sub>5</sub>
- 3) It has 3% free phosphoric acid
- 4) TSP also contains 12 to 16% of calcium and 1.0 to 2.0 % of sulphur.

### III. BASIC SLAG [(CaO)<sub>5</sub> P<sub>2</sub>O<sub>5</sub> SiO<sub>2</sub>]:

Basic slag is a by product of steel industry . It also called as "Thomas slag" named after the inventor of the production process ,the English metallurgist, **THOMAS (1877)**. Millions of tonnes of "slag" have been used as a source of P in European Agriculture .

#### **Manufacturing process:**

Iron ores contains several impurities and phosphorus is one . Elimination of phosphorus is essential for obtaining high quality steel. Steel with over 2 % P is brittle .

Basic slag or Thomas slag is produced by open - hearth process.

In this process, the iron ore and lime are heated by means of producer gas in an open hearth . Fluorspar a mineral [ Natural calcium fluoride ] is added at the rate of 3.4 kg per tonne of lime to reduce viscosity of the slag. When the mixer becomes red hot, the lime melts and unites with acid impurities including phosphoric acid. The resulting compounds containing Ca, P ,Si , Mg and Mn are lighter than iron ore and as such rise to the surface of the molten mass and are poured off as slag . After the slag is cooled, become hard massive block .It is crushed and ground to a fine powder .

#### **Physical properties of slag:**

- 1) Heavy ,dark brown powder, ground and pass through 100 mesh sieve
- 2) Has relatively higher density than any other fertilizer material
- 3) It is likely to solidify when exposed to moisture.

#### **Chemical properties of phosphatic fertilizers:**

- 1) The basic slag is a double silicate of phosphate and lime
- 2) The slag obtained from Indian steel industry contain only 3-8 % P<sub>2</sub>O<sub>5</sub> .Being low in P<sub>2</sub>O<sub>5</sub> having highest viscosity ,it is not popularly used in Indian agriculture.
- 3) Being low in P<sub>2</sub>O<sub>5</sub> it is currently enriched with rock phosphate and marketed as pelophos which on analysis contains 11.0 % citrate soluble and 5.0% water soluble P<sub>2</sub>O<sub>5</sub>
- 4) It is alkaline in reaction and has neutralizing effect equal to 70% CaCO<sub>3</sub> equivalent .

**Lecture: 12** Potassic fertilizers –Mineral sources –Manufacturing process and properties of Muriate of Potash and sulphate of potash -Mode of action of N, P and K fertilizers in soils or reactions of fertilizers in soils

### POTASSIC FERTILIZERS

The Latin / German word for the element with symbol K is " **Kalium** ". It is derived from the Arab word " **el-kali** " means **ash (Potash in English , Potassic in French)**.

The term potash generally refers to any salt used to provide fertilizer potassium . In early days, potassium carbonate was produced from solutions leached from wood ashes evaporated in iron pots, hence term potash meaning "pot ashes" .

The crude potassium salts ( K-minerals with impurities ) were found in the processes of drying up of sea water in former ocean basins which occur largely during the permian period some 200 million years ago .The sea water salts crystallized in the order of solubility i.e., (common salt ) NaCl, strata are overlain by K-minerals . In course of time they were covered by many geological strata and converted to a hard rock . Crude potassium salts are thus natural sea water minerals .

Potassium content of earth crust is 2.40 % ,whereas the content of phosphorus is only 0.11% .Potassium reserves are large .The large deposits of potassium salts are in North America (Canada,USA) , USSR, West Germany ,East Germany and France in that order .The important potash minerals of the world occurring as deposits and their chemical composition are given

#### Principal potash minerals of the world

S.NO.	Mineral	Chemical formula	Approx. Content of K (%)
1	Carnallite	KCl MgCl <sub>2</sub> 6H <sub>2</sub> O	14.1
2	Kainite	KCl Mg SO <sub>4</sub> 3H <sub>2</sub> O	15.7
3	Langbeinite	K <sub>2</sub> SO <sub>4</sub> 2 Mg SO <sub>4</sub>	18.8
4	Nitre	KNO <sub>3</sub>	38.6
5	Polyhalite	K <sub>2</sub> SO <sub>4</sub> MgSO <sub>4</sub> 2CaSO <sub>4</sub> 2H <sub>2</sub> O	12.9
6	Sylvite	KCl	52.4
7	Sylvinite	KCl NaCl	29.4

All the fertilizers potassium viz., KCl and K<sub>2</sub>SO<sub>4</sub> used in India is imported as on today. Recently Geological Survey of India has reported the occurrence of K-deposits in Leh (Jammu and Kashmir) and Bikanir (Rajasthan) which await commercial exploitation . Potassium schoenite a double salt of K<sub>2</sub>SO<sub>4</sub> and Mg SO<sub>4</sub> obtain from salt bitterns is recently being produced on a pilot scale at Bhavanagar (Gujarat).

## Manufacturing processes of potassic fertilizers

Two types of potassium fertilizers are widely produced in India

- I. Potassium chloride ( Muriate of potash)
- II. Potassium sulphate (Sulphate of potash )

### I. **POTASSIUM CHLORIDE (KCl) [MOP] :**

Potassium chloride is popularly known as muriate of potash [MOP] .The term muriate is derived from muriatic acid ,a common name for hydrochloric acid(HCl) .It is the most important K-fertilizer used directly or in conjunction with P and N fertilizers.

#### **Raw materials:**

##### **1. Sylvinite (or) brine**

Unlike phosphate rock , K mineral salts do not require heat or strong acid treatment as they are water soluble.

Potassium chloride is recovered, from sylvinite adopting either of the two processes viz.,

##### **1. Crystallization process**

##### **2. Flotation process**

##### **1. Crystallization process :**

**Principle:** Crystallization process employed in separating potassium chloride from sodium chloride (Sylvinite: KCl .NaCl) is largely dependent on their different solubilities in hot (100 °C) and cold (20 °C) water . The solubility of KCl increases rapidly with a rise in temperature whereas the solubility of NaCl varies very slightly .

Cool brine (20 °C) saturated with both the salts is heated to (100 °C) and passes over the finely ground sylvinite ore, when KCl rich brine solution is obtained .It is cooled by vacuum evaporation which produces KCl crystals, which are centrifuged , washed ,dried and packed .The filtrate (brine rich NaCl) is recycled for treating fresh ore.

##### **2. Flotation process:**

Separation of potassium chloride from its ore by mineral flotation is widely practiced allover the world relative to the crystallization process.

**Principle:** Flotation is a separation process in which a solid treated with a selective agent is suspended in an aerated aqueous liquid. The treated solid adheres to the bubbles of air, and the froth is floated off the suspension. Non floating material is removed as pulp. The sylvinite ore is a mixture of interlocked crystals of potassium chloride and sodium chloride plus small quantities of clay and other impurities.

**Raw material : Sylvinite ore**

Sylvinite ore is ground to a particle size of 10 mesh

- ❖ Pulped in a saturated NaCl-KCl brine and scrubbed (Centrifuge) to disperse clay and other impurities .
- ❖ The resultant slurry is thus deslimed in spiral classifiers to remove finely divided clay slimes.
- ❖ Desliming or removal of clay is the most important step since these material consume large quantities of flotation reagents.
- ❖ The deslimed slurry relatively free of clay is treated with binding agents such as starch or mannogalactan gums
- ❖ The reagents used for sylvinite flotation is a mixture of primary aliphatic amine salts derived from beef tallow ,which selectively film the sylvinite particle so that they will float
- ❖ The conditioned slurry is carried to flotation cells where air is drawn into the slurry.
- ❖ The air bubbles attach themselves to the reagent treated sylvinite particle in the pulp causing them to float to the surface as froth ,which is mechanically skimmed off by paddles
- ❖ The concentrate rich in KCl is further purified by sending it to cleaner cells to remove residual NaCl
- ❖ The MOP is separated from brine by centrifuging and drying in rotary driers ,screened to a desirable particle size and finally sent for product storage

**Physical properties of MOP:**

- 1) MOP in pure form is white crystalline salt. However, colour ranges from white to red based on the impurities present in K minerals and methods of refinement.
- 2) It has a solubility of 37 grams per 100 grams of water at 30 °C.
- 3) The crystalline MOP is not very hygroscopic ,flows freely and does not cake
- 4) Has specific gravity is 1.98.

**Chemical properties of MOP:**

- 1) MOP contains 58% by weight of  $K_2O$  and about 47 % chloride
- 2) MOP is neutral in reaction and does not produce acidity and alkalinity on soil application.

**II. POTASSIUM SULPHATE(  $K_2SO_4$ ) [SOP] :**

The entire potassium sulphate fertilizer used in India is imported and it is more expensive than MOP.

**Raw materials: 1) Langbeinite**

The manufacturing process is of two types viz.,

1. Langbeinite process
2. Mannheim furnace process

**1. Langbeinite process:**

The ore Langbeinite is a double sulphate of potassium and magnesium ( $K_2SO_4 \cdot 2MgSO_4$ ).

In this process Langbeinite is ground and dissolved in water and concentrated solution of KCl (brine) is added, when the potassium sulphate precipitates and is separated by centrifuging. The wet material is dried, screened and sent to storage. The chemical reaction involved is

**2. Mannheim furnace process:**

In this process, potassium chloride (KCl) is reacted with sulphuric acid in a special furnace provided with rotary plough to form potassium bisulphate ( $KHSO_4$ ) in exothermic reaction and to form potassium sulphate in endothermic reaction. HCl gas is evolved as a by product which is cooled and absorbed in water. Reactions that occur are

**Physical properties of SOP**

1. Potassium sulphate [SOP] is a white crystalline salt, less hygroscopic as compared to MOP and free flowing.
2. It has specific gravity of 2.66 and has a solubility of 13 g/100 grams of water at 30 °C.

**Chemical properties of SOP:**

1. SOP contains 48 %  $K_2O$  and 18 % S by weight.
2. Like MOP, it is also neutral salt providing neither acidity nor alkalinity on soil application.
3. The SOP is widely desirable. The chloride content of KCl affects the burning quality of tobacco. Never use KCl (MOP) on tobacco crop.

**Mode of action of N, P and K fertilizers in soils or reactions of fertilizers in soils**

- I. Nitrogenous fertilizers
- II. Phosphorus fertilizers
- III. Potassic fertilizers

### I. Nitrogenous fertilizers:

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

2. Nitrate ( $\text{NO}_3^-$ ) N fertilizers when applied to soil

i. Nitrate fertilizers raise the pH of the soil .These are superior in highly acid soil

ii. Nitrate fertilizers are immediately effective and as such are specially suited for top dressing

iii. These are also suitable for moderately to slightly acidic soils

iv. Loss through leaching of Nitrate from soil are unavoidable but can be limited by precise N-fertilization

3. Ammoniacal N fertilizers [ $\text{NH}_4^+$ ]

i) It is soil acidifier .It superior to neutral to very slightly alkaline soil.

ii) Application of  $\text{NH}_4^+$  Fertilizers to alkaline soils (pH =7.5) resulting in losses of gaseous ammonia .For this reason there are generally inferior in alkaline soils.

iii) These are moderately quick in action. It becomes more mobile in the soil only after conversion to  $\text{NO}_3^-$

iv) 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 trace elements are better mobilized through acidification .

v)  $\text{NH}_3$  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.

### II. Phosphatic fertilizers:

i) Water soluble P-fertilizers lead to better P-absorption in the neutral soils, whereas water insoluble P fertilizers are often superior in acid soils

ii) Fertilizers like SSP improves the soil structure because of its gypsum component .It also have a slight soil acidifying action.

### III. Potassic fertilizers :

i) Water soluble and as such act rapidly

ii) In the soil K-fertilizers first enters the soil solution, but most of it directly absorbed on the complex and stored as loosely bound K and easily available to plants.

**Lecture: 13** Complex fertilizers-preparation and properties of ammonium phosphates - urea ammonium phosphates, ammonium Phosphate sulphates, ammonium polyphosphates

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The major plant nutrients supplied by fertilizer are nitrogen, phosphorus and potassium. The fertilizers that contain these three plant nutrient elements N P K is designated as complete fertilizers according to fertilizer technology .However, scientifically, such fertilizers are called as multi nutrient fertilizers. They are guaranteed by the fertilizer industry, to contain more than one major nutrient .However; they may or may not contain secondary nutrients such as calcium and sulphur.

Multi nutrient fertilizers can be classified into two categories

**I. COMPLEX FERTILIZERS**

**II. MIXED FERTILIZERS**

**I. COMPLEX FERTILIZERS**

The fertilizers containing two or more major plant nutrients, which are in chemical combination are called as complex fertilizers .They are solids and homogeneous in nature that each fertilizer granule is guaranteed to contain two or more major plant nutrients in a specified ratio .Their production involve homogeneous mixing of two or more nutrient carriers in a slurry followed by granulation.

**II. MIXED FERTILIZERS :**

These are simply physical mixtures of solid fertilizer, material containing two or more major plant nutrients .They are also called as bulk blended fertilizers .Each individual fertilizer particle of this blend represented only one of the ingredients of the mixture

The principle techniques involved in the manufacture of complex fertilizers

1. Acidulation

2. Ammoniation

3. Granulation

1. Acidulation: Is the process of treating the material with an acid .Eg.Treatment of rock phosphate with sulphuric acid.

2. Ammoniation : Is the process of introducing ammonia into super phosphate to obtain ammoniated super phosphate

3. Granulation : Is the process of making small size particles into large granules or pellets of about 2.3 to 4.3 mm .This technique is primarily intended to improve handling and storage properties of fertilizers.



## I. COMPLEX FERTILIZERS

### Chief characteristics of complex fertilizers:

1. They generally have a high content of plant nutrients .More than 40 kg per 100 kg of fertilizer .As such they are also called “high analysis” fertilizers.
2. They usually have a uniform grain size and have good physical condition.
3. They supply N and P in an available form to the soil in one operation .Nitrogen is present as nitrate and ammoniacal form and phosphorus is present in water soluble form up to 50 to 90 per cent of total  $P_2O_5$
4. Though their manufacture is costlier to straight fertilizers, they are cheaper to the cultivators when the cost is worked out on the basis of per kg of plant nutrient.
5. Since complex fertilizers are high analysis fertilizers, transport and distribution costs to the cultivators are less when worked out on the basis of per kg plant nutrient
6. They are non-caking and non hygroscopic, thus safe for storage

### The value of complex fertilizers is dependent on the following considerations

- a) The content of individual nutrients N,  $P_2O_5$  ,  $K_2O$
- b) Their ratio of N to  $P_2O_5$  or  $K_2O$
- c) The form in which the individual nutrients are present
- d) The resultant acid or basic residual effect
- e) The contents of trace elements

### Classification of complex fertilizers:

The complex fertilizers being produced in India can be classified into

#### A) Incomplete complex fertilizes

#### B) Complete complex fertilizers

**A) Incomplete complex fertilizes:** Contain only two major nutrients such as N and  $P_2O_5$  in chemical combination. They are of two types

- I. Ammonium phosphates: May be present in the combination of mono or diammonium salt or mixture of two .Most of these formulations are in granular form

MAP 11:46,DAP18:46, AP 16:20 and UAP28:28:0

- II. eg . Nitrophosphates eg. 20:20:0, 24:24:0

**B) Complete complex fertilizers:** Contains all the three major nutrients in chemical combination .E.g. 17:17:17 and 19:19: 19

## 1.AMMONIUM PHOSPHATES

**Manufacturing process and physical and chemical properties of Ammonium phosphates:**

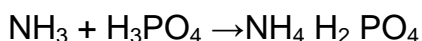
1. MONOAMMONIUM PHOSPHATE [MAP]
2. DIAMMONIUM PHOSPHATE [DAP]
3. AMMONIUM PHOSPHATE SULPHATE [APS]
4. AMMONIUM POLY PHOSPHATES [APP]
5. UREA AMMONIUM PHOSPHATE [UAP]

### 1. MONOAMMONIUM PHOSPHATE [MAP]

Raw material: 1.Ammonia 2) phosphoric acid

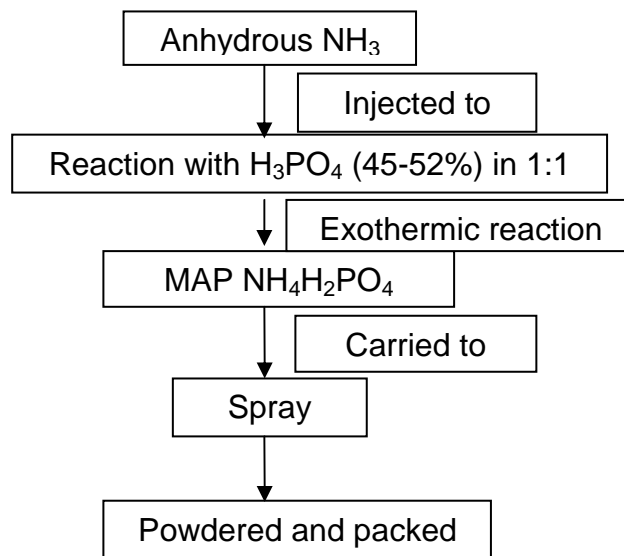
#### Manufacturing process:

Anhydrous ammonia is injected in to a large reactor containing liquid phosphoric acid [45-52% concentration] in the 1:1 ratio ( $\text{NH}_3 : \text{H}_3\text{PO}_4$ ), when thick viscous slurry of mono ammonium phosphate [MAP ] is formed .The reaction is exothermic



The slurry is carried to a spray drier, where it becomes a powdered material for packing

Flow diagram



#### Physical properties:

1. Free flowing , non hygroscopic and white to dark grey granular material with excellent storage without caking
2. Has specific gravity of 1.8

#### Chemical properties:

1. MAP contains 11%N and 52% P<sub>2</sub>O<sub>5</sub> out of which 44% P<sub>2</sub>O<sub>5</sub> is in water soluble form.
2. 10 per cent solution of MAP has a pH of 3.5 to 4.0 .Thus it is acid forming fertilizer requires 86 kg of CaCO<sub>3</sub> to neutralize acidity developed due to 100 kg of MAP on soil application

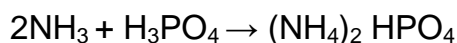
## 2. DIAMMONIUM PHOSPHATE [DAP]

DAP is a popular fertilizer in India

**Raw material :** a) Ammonia b) Phosphoric acid

### Manufacture process:

DAP is manufactured by reacting anhydrous ammonia and liquid phosphoric acid in 2:1 molar ratio .The chemical reaction is



The preliminary neutralization of  $\text{H}_3\text{PO}_4$  with anhydrous  $\text{NH}_3$  is affected in preneutralize.The resultant slurry containing MAP is sent to a granulator where it is further ammoniated to obtain 2:1 molar ratio of product [ $\text{NH}_3$  or  $\text{H}_3\text{PO}_4$ ]. It is dried and screened and stored in bags.

### Physical and chemical properties:

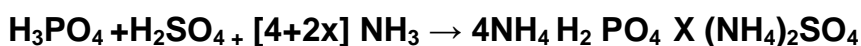
1. Free flowing and non –caking fertilizer
2. It contains 18% Nitrogen and 46%  $\text{P}_2\text{O}_5$  out of which 41 per cent  $\text{P}_2\text{O}_5$  is in water soluble form.
3. 10% of DAP solution has a pH of 7.8

## 3. AMMONIUM PHOSPHATE SULPHATE [APS]

**Raw material:** 1.Ammonia 2) Phosphoric acid 3) sulphuric acid

### Manufacture process:

APS is made by neutralizing the mixture of phosphoric acid and sulphuric acids with anhydrous ammonia.



The mixture of phosphoric acid and sulphuric acid can be introduced in varying proportion to obtain different grades of the fertilizer .The slurry is granulated ,dried and stored for use .

### Physical and chemical properties:

1. APS is granular, non hygroscopic and free flowing with excellent storage capacity.
2. It contains 16% N and 20%  $\text{P}_2\text{O}_5$  [Grade -16:20-0] with almost entire  $\text{P}_2\text{O}_5$  is water soluble
3. Acid forming fertilizer

## 4. AMMONIUM POLY PHOSPHATE [APP] LIQUID FERTILIZER

A relatively new to the field of ammonium phosphates is APP

**Raw material:** 1. Ammonia 2) Super phosphoric acid

### Manufacturing process:

It is made by ammoniating super phosphoric acid [70%] .

The acid is kept hot prior to ammoniation as the concentrated acid solidifies at ambient temperatures.

**Physical properties:**

1. Ammonium poly phosphate is stored in a mild steel containers at 17 °C, such a low temperature is essential to prevent salting out effect . Prolonged storage in hot summer renders partial hydrolysis of polyphosphates.
2. APP is more soluble than other P fertilizers
3. It has a viscosity of 80 centipoises at 24°C.

**Chemical properties**

1. Green coloured near neutral solution [pH 6.0]
2. It has total  $P_2O_5$  of 65% in polyphosphate form
3. Polyphosphates are primarily pyrophosphates with the formula  $(NH_4)_3 H P_2O_7$
4. It has the ability to form complex ions with some metal ions like Zn
5. It is used for production of complete liquid fertilizers and for direct application.

**5. UREA AMMONIUM PHOSPHATE [UAP]**

- Urea ammonium phosphate (UAP) is essentially made in order to enrich the nitrogen content of ammonium phosphates. This is popularly called as *URAMPHOS*
- It was first manufactured in India that in Andhra Pradesh at Viskhapatnam in fertilizer Coramandal Ltd.,

**Raw Material:** 1) Phosphoric acid 2) Ammonia 3) Urea

**Manufacturing process:**

The process involves the reaction of phosphoric acid with the effluent of urea in a rotary ammoniator .Two steps are involved.

**1<sup>st</sup> step :** The reaction between ammonia and carbon dioxide being partial ,results in the production of effluent consisting of mixture of urea ,  $NH_3$  ,water and  $CO_2$ .

**2<sup>nd</sup> step:** Phosphoric acid reacts with ammonia of the mixture to form urea ammonium phosphate .The product is granulated, dried, screened, cooled, coated with a coated agent and stored in a polyethylene lined gunny bags.

**Physical properties:**

1. Granular, free flowing, good handling and storage properties. Longer exposure to high humidity results in caking.

**Chemical properties:**

1. UAP is manufactured in India consists of two grades viz., 28:28: 0 and 24:24: 0 containing N and  $P_2O_5$ , respectively.
2. UAP of grade 28:28: 0 contains 28% N of which is 9% is ammonical N for and the remaining N is amide form [ $NH_2$ ].It also contain 28 %  $P_2O_5$  of which 25.2 % is in water soluble form .For grade 24:24: 0 ,7.5% Nitrogen in ammonical form and 16.5% N in amide form and .Of the 24%  $P_2O_5$  , 20.4% is water soluble form.

**Lecture: 14** Preparation and properties of nitro phosphates and NPK Complex Fertilizers

## II. NITRO PHOSPHATES

Nitro phosphates are also called as nitric phosphates .They are the fertilizers derived from the digestion of rock phosphate with nitric acid by ammoniation of the resultant slurry.

**Raw materials: 1.HNO<sub>3</sub>, 2. Phosphate rock and 3.Ammonia**

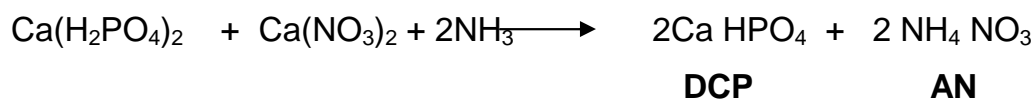
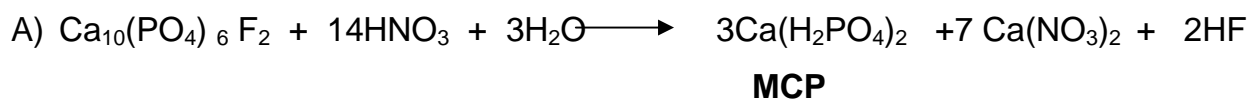
Two methods are widely followed:

### I. ODDA PROCESS

### II. PEC PROCESS

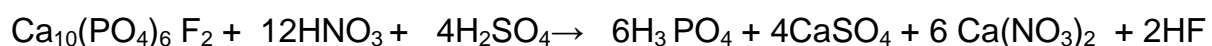
#### I. ODDA PROCESS :

The phosphate rock is treated with HNO<sub>3</sub> and the acidulate is cooled until there is partial crystallization of calcium nitrate [Ca (NO<sub>3</sub>)<sub>2</sub>], which is removed by centrifugation or filtration .The remaining solution is ammoniated and the slurry in granulated to produce fertilizer containing ammonium nitrate and dicalcium phosphate .

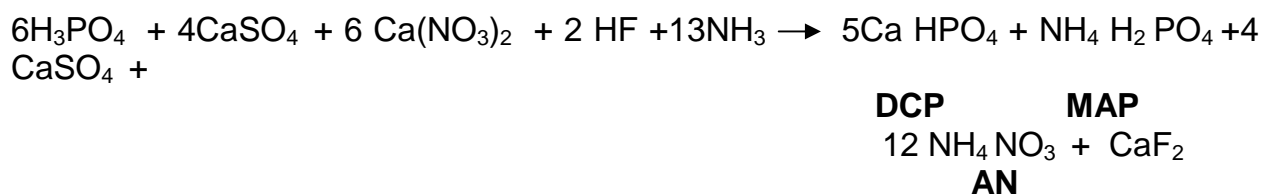


#### II. PEC PROCESS [Potasse etal engrais Chimiques]:

It is also called as multi-acid process in which rock phosphate is treated with a mixture of HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub> .In order to make the fertilizer as a source of sulphur as well.



On ammoniation of the products obtained from the above reaction



#### Physical properties:

1. Nitrophosphates are granular ,free flowing fertilizers with good storage quality ,provided it is packed in multi wall paper bags
2. Dicalcium phosphate present in nitro phosphates is soluble in normal ammonium citrate solution, but not in water, by using more sulphuric acid in the process, greater portion of water soluble phosphate such as mono ammonium phosphates is obtained.

**Chemical properties:**

1. Nitro phosphates of grade 20:20 contains 20%N out of which 10.6% is in  $\text{NH}_4^+$  form while 9.4 %  $\text{NO}_3^-$  form .As for phosphate it has 20%  $\text{P}_2\text{O}_5$  in ammonia citrate soluble form out which 5.4 % is water soluble form.

**N P K COMPLEXES [Complete complex fertilizers]**

N P K complexes are the fertilizers which are granular containing three major plant nutrients .Different grades of these fertilizers are being manufactures in India viz., 17-17 -17; 14-35-14; 14-28-14; 10-26 -26; 12-32-16 etc.,

**Manufacturing process:**

**Raw material: 1) Ammonia 2) Phosphoric acid 3) Potassium chloride and 4) urea**

Ammonia and phosphoric acid are mixed in a specified proportion in the pre neutralizer and the resultant slurry is pumped to a granulator [Rotating drum] where nitrogen content of the product is enriched by adding more ammonia and feeding in urea. Potassium chloride is also added to make up the required formulation .Filler like sand or dolomite is also added to improve the handling property of the fertilizer product.

**Physical properties:**

1. NPK complexes are grey or cream coloured granules .They are free flowing with good storage properly
2. Exposure to high humidity however can cake hence to be packed in polyethylene lined gunny bags

**Chemical properties:****1.N P K complex grade 17 :17 :17**

- It contains 5% ammonical and 12 % amide N
- 15% water soluble and 2 %citrate soluble  $\text{P}_2\text{O}_5$
- 17% water soluble  $\text{K}_2\text{O}$

**3. Grade 14:35:14**

- All N in ammonical form 14%
- 29% water soluble and 6% citrate soluble  $\text{P}_2\text{O}_5$
- 14 % water soluble  $\text{K}_2\text{O}$

**Salient feature of complex fertilizer:** If we analyze any granule from particular grade, it should contain the same ratio with respect to N, P and K

### **MIXED OR BULK BLENDED FERTILIZERS**

**Mixed fertilizer:** Mixed fertilizers are simply physical mixture of solid fertilizers materials containing 2 or more major plant nutrients .Each individual particle of this blend represents only one of the ingredients of the mixture.

- Bulk blending was started in 1947 .It has considerable potential in developing countries that cannot afford plant (factory) facility to manufacture complex fertilizers
- Blending provides a convenient and economical means of mixing dry fertilizer materials to produce specified ratios and grades of varying nutrient percentage depending on the needs of the crops .

#### **Production of mixed fertilizers**

##### **Raw materials:**

1. Single or Triple super phosphate
2. Diammonium phosphate [DAP]
3. Ammonium nitrate
4. Urea and
5. Potassium chloride

Mixed fertilizers or fertilizer mixtures or bulk blended fertilizers (BBF) .Among these names BBF is widely used

Based on the method of preparation of the BBF is studied as

#### **I. FARM MIXTURES**

#### **II. MECHANICAL MIXTURES**

#### **I. FARM MIXTURES**

The manually blended fertilizers are called “farm mixtures ” .Implying that they can be prepared by the farmers themselves based on the crop requirements .

##### **Equipment Required for Farm Mixing:**

- 1) Coarse screen
- 2) Grinder
- 3) Hard floor
- 4) Weighing balance
- and 5) Shovels and spade

**Method:** The weighed quantities of fertilizer materials are spread in layers placing bulky materials at the bottom of the floor ,followed by materials which are less bulky .The materials are turn over number of times with spade to ensure through mixing .The high grade or concentrated mixtures need to be diluted by mixing the materials like sand ,soil ,saw dust or dolomite .In order to prevent salt damage on their application to crops and to improve the physical condition to the farm mixture. .The material used for this cause is called fillers .It is also desirable to mix the fertilizers on the day of application or a day of application or a day before to avoid caking .

## II. MECHANICAL MIXTURES:

These are prepared by mixing different fertilizer materials to obtain the required grades of the product. Based on the preparation, these are studied in 2 ways

### 1) Dry process

### 2) Wet process

**1) Dry process:** Dry mixtures are prepared by mechanically mixing different fertilizer materials to obtain the required grades of the product. Dry mixing does not involve chemical reaction. The product can be obtained in pulverized form (Fine powder)

**Manufacture:** (Pulverized mixtures)

In case of pulverized mixtures, the ingredients are weighed and put in the rotary mixer, where the contents are thoroughly mixed for a specified time and the product obtained is bagged and used immediately.

**Disadvantages of pulverized mixtures:**

The ingredients with different bulk density and particle size of the pulverized mixtures are very likely to segregate, thereby cause uneven distribution when applied to soil. So, if the mixtures are pulverized state they don't flow properly.

### 2. Wet process :

By using this method Granular mixtures are prepared

**GRANULAR OR GRANULATED MIXTURES:**

**Manufacture:** Granulated mixtures are prepared by moistening the ingredients with small quantity of water or steam. In this process, the ingredients are stored in the process bin from which proportionate quantities of the materials are fed to the weighing hopper. These are later ground, mixed in a rotary mixer and sent to granulator, where the material is exposed to water vapour (steam) to obtain granulated product, which is dried, screened and packed into multi-wall paper bags

When compared to pulverized mixtures, granulated mixtures have a less caking tendency and are less dusty and easy to apply to the fields.

**Advantages of granulation**

1. Every granule is complete in plant food containing major nutrients in balance quantities
2. This ensures easy and uniform absorption by crops resulting in vigorous and healthy growth.
3. The granular fertilizers are dry and free flowing and easy to apply. Thus they can be applied through seed drill.
4. These are less dusting and less caking
5. There is no loss due to dusting while transport and handling due to wind.
6. Being high analysis fertilizers, they are considerably more economical in application and transport.
7. There is no possibility of adulteration.



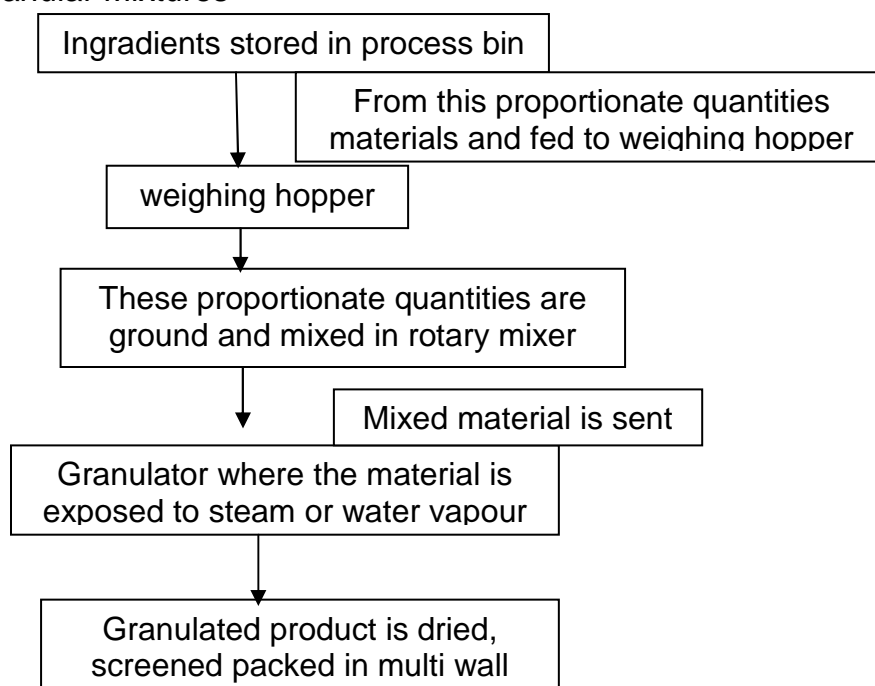
## Types of fertilizer mixtures

**I. Open formula fertilizers mixtures :** The formula of such fertilizers in terms of kind and quantity of ingredients mixed are disclosed by the manufacturer . Knowing the formula ,the farmer or extension worker is able to judge the type and quantity of the ingredients and suitability for specific soils and crops and is able to determine roughly the quantity of filler or other nutrient material contained in any fertilizer .

## II. Closed formula fertilizer mixtures :

The ingredients or straight fertilizers used in such mixtures are not disclosed .So these mixtures have the disadvantage that the farmer cannot know the type and quantity of the nutrient in them .

Flow diagram for Granular Mixtures



## Advantages of mixed fertilizers over straight fertilizers

1. Less labour is required to apply mixtures than to apply its various components separately .This is an important factor in areas where farm labour is scarce and expensive
2. If proper mixture used to suit particular soil type and crop ,the use of fertilizer mixture leads to balanced manuring
3. The residual acidity of fertilizers can be effectively controlled by the usage of proper quantity of liming material in the mixtures.
4. Micronutrients, which are applied in small amounts to soil, can be incorporated in fertilizer mixtures .This facilitates uniform soil application of plant nutrients required in small amounts.
5. Mixtures have better physical condition and are more easily applied than many straight fertilizers .This advantage is most marked when mixtures are prepared in granular form.

**Disadvantages of fertilizer mixtures:**

1. Their use does not permit application of individual nutrients which may well suit the needs of the crop at specific times.
2. The unit cost of plant nutrients in the mixtures is usually high than these straight fertilizers, because labour is required to prepare mixtures
3. Farmers often use mixtures without careful study of their needs leads to economical loss.

**Physical problems and chemical problems associated with bulk blended fertilizers**

In bulk blending of fertilizers certain physical and chemical problems have to be considered. Since, the fertilizer material varies differently in physical characteristics care has to be taken while preparing mixtures. Some times mixing of materials of diverse nature and properties involves chemical reactions due to which the products very different from the

initial material in composition and character, thereby seriously affecting the fertilizer value of the product.

**I. Physical problems:**

1. Physical condition of BBF is important, for sustaining their storage value
2. Hygroscopic character of the ingredients make them unsuitable for use is not suitable for use
3. Drillability of fertilizer mixture is necessary for the distribution by equipment because of ease and uniform distribution of fertilizer in the field which is an important aspect of fertilizer.
4. Particle size and moisture content of fertilizer mixture influence drillability.
5. Fertilizers like urea, ammonium nitrate being hygroscopic in nature affect drillability.
6. All fertilizer mixtures containing 2-6 % moisture may dissolve soluble component of mixtures forming saturated salt solutions.

The volume of this liquid phase varies with the nature of the moisture content and temperature of blended fertilizers.

7. Raise in temperature and moisture, increases the proportion of the liquid phase and subsequent fall in temperature and moisture, salts crystallize out during storage and results in Bagset or caking of fertilizers.
8. Finely divided material may cake due to cohesion and adhesion between particles under pressure in storage.

**II. Chemical problems:**

The chemical problems that occur on account of mixing incompatible fertilizer material during the preparation of mixed fertilizers are classified in to the following categories.



**A) Make weight materials or fillers**

In mixed fertilizers often there is difference between the weight of the fertilizer material ingredients that produce major nutrients (NPK) and desired quantity of mixed fertilizers. To make up the desired quantity of the mixture some fillers like Sand, Coal, Dolomite, Ash, Lime stone are added.

**B) Conditioners :**

Conditioners are those materials added to non-granular or granular mixtures to improve their physical condition and to decrease their caking. The actual purpose of adding conditioner is to reduce crystal knitting.

**a) Conditioners for non –granulated fertilizers :** In this case the conditioners serve as a separator between the fertilizer particles eg : well ground corn cobs or cocoa shells serve as conditioners which are usually applied at 50kg per tonne of mixed fertilizer.

**b) Conditioners for granulated fertilizers :** In this case, conditioners serve as a coating agents. Materials like diatomaceous earth, hydrated silica which have low bulk densities are efficiently suited for this purpose.

[ Diatomaceous means a powdery siliceous material (deposit) of diatoms of fistules (small flowers) Diatoms = one class of microscopic algae unicellular

**Guide lines for mixing solid fertilizers.**

Many fertilizers can be mixed without detriment and can be distributed. However, there are three reasons due to which indiscriminate mixing of fertilizers should be avoided for the following reasons:

1. Loss of nitrogen by chemical reactions
2. Immobilization of water soluble phosphate
3. Deterioration in drillability owing to the absorption of moisture

**COMBINED USE OF FERTILIZERS AND AGRICULTURAL CHEMICALS [PESTICIDES]**

Keeping the factors, labour, time and energy in view, the agricultural chemicals viz., fungicides, insecticides and herbicides are combined with the fertilizers and applied to the crops. This practice however convenient from agronomic point is being set with problems of technical chemistry, application and legal requirements

**A) Insecticides –fertilizer mixtures :**

- 1) The use of chlorinated hydrocarbons mixed with fertilizers was a quite popular practice, until these insecticides were found to raise insect resistance and persist in the soil.
- 2) The stability of insecticides mixed fertilizer is a serious problem since the quantity of fertilizer and insecticide required for crops widely vary and stability is affected.

- 3) The use of BHC (Benzene Hexa Chloride) was found to impart musty odour to groundnut kernels.

**B) Herbicide –fertilizer mixture:**

1. They are commonly called as weed and feed mixture
2. More herbicides are physically compatible in suspension fertilizer than in clear liquids
3. Dry herbicide- fertilizer mixtures can be used as basal dose

**Formulation of fertilizer mixtures**

Fertilizer mixtures or farm mixtures can be prepared by the farmers based on soil test data and crop needs. For this it is essential to know nutrient content of different fertilizers.

1. **Fertilizer grade:** It refers to the minimum guaranteed quantity of plant nutrient content in terms of N, available  $P_2O_5$  and available  $K_2O$  present in a given multinutrient fertilizer.
2. **Fertilizer ratio:** It indicates the relative proportion of N,  $P_2O_5$  and  $K_2O$  of a given multinutrient fertilizer. For example 6-24-24 grades have a 1-4-4 ratio. The prefixes open formula and closed formulas are affixed to the fertilizer mixtures depending on whether or not the kinds and quantities of fertilizer ingredients are disclosed by the manufacturer respectively.

**PROBLEMS ON FORMULATION OF FERTILIZER MIXTURES:**

- I. How do you prepare one tonne of the fertilizer mixtures of the fertilizer grade 10:6:4 [N,  $P_2O_5$ ,  $K_2O$ ] by using the following fertilizers and the percent nutrient content against each.
  - a) Ammonium sulphate 20.5 N
  - b) Single Super Phosphate 16  $P_2O_5$
  - c) Muriate of potash 60  $K_2O$

Ans : The following are the quantities of individual fertilizers required for the mixture 10:6:4

$$\text{Quantity of fertilizer required} = \frac{\% \text{nutrient desired}}{\% \text{ nutrient content of the fertilizer}} \times 1000$$

Thus

$$N = \frac{10 \times 1000}{20.5} = 487.80 \text{ kg Ammonium sulphate}$$

$$P_2O_5 = \frac{6 \times 1000}{16} = 375.00 \text{ kg super phosphate}$$

$$K_2O = \frac{4 \times 1000}{60} = 66.70 \text{ kg Muriate of potash}$$

Sum of the quantities of fertilizers } = 929.50 kg  
 [487.80+375+66.70]

Balance to be made good by addition of } = 70.50 kg  
 The filler to obtain one tonne of the mixture }  
 [1000-929.50= 70.50] -----  
 1000.00 kg  
 -----

II. Calculate the quantities of different fertilizers required to prepare one tonne of the bulk blended fertilizers of the grade 6-4-3 .The fertilizers available, and their nutrient content are given below.

S.No.	Fertilizer	Nutrient content (%)
1	Neem cake	5.0 %
2	Urea	46.0%
3.	Basic slag	18.0 %
4	TSP	45.0%
5	Sulphate of potash	50%

The fertilizer mixed should have the following specified ratios

- a) Neem cake to urea : 1:2
- b) Basic slag : 1:3

ANSWERS:

Total N required for the mixtures : 6 N  
 So neem cake : 6 x 1  
 ----- = 2 N  
 3  
 Urea : 6 x 2  
 ----- = 4 N  
 3

Quantity of neem cake required = 2 x 1000/5 = 400 kg

Quantity of urea required = 4 x 1000/46 = 87 kg

Total P<sub>2</sub>O<sub>5</sub> required for the mixture = 4 P<sub>2</sub>O<sub>5</sub>

So through basic slag: 4 x 1 /4 = 1

Through TSP = 4 x 3 /4 = 3 P<sub>2</sub>O<sub>5</sub>

Quantity of basic slag required: 1 x 1000/18 = 55.5 kg

Quantity of TSP required : 3 x1000/45 = 66.70 kg

Quantity of SOP required: 3 x 1000/50 = 60 kg

Sum of the quantities [400+87 +55.5 + +66.67 +60 ] = 669.20  
 [1000-669.20] = 330.80  
 -----

1000.00

Note the sum of three parts of the mixture calculated exceeds 1000 kg of mixture of the composition can not be prepared from the fertilizers in question.

### UNIT VALUE OF FERTILIZERS: [PROBLEMS]

The term unit value which refers to the cost per unit of the plant nutrient contain in a given fertilizer. The calculation of unit value of different fertilizers that would supply same

kind of plant nutrient will enable the farmer to choose the cheapest fertilizer in terms of cost .This concept was first adopted in ENGLAND,

**PROBLEM:** Nitrogen fertilizer available in the market are mentioned below along with their nutrient content and cost per tonne .Calculate the unit cost of nitrogen in each case to find out the cheapest N-fertilizer

S.No.	Fertilizer	N (%)	Cost per tonne (rupees )
1	Ammonium sulphate	20.50	1720
2	Ammonium chloride	25.00	1700
3	Calcium ammonium nitrate	25.00	1720
4	Urea	46.00	2274

Cost of one tonne of fertilizer

Unit value= -----

Concentration of plant nutrients per tonne of fertilizers

Ammonium sulphate  $1720/205 = 8.39$

Ammonium chloride  $1700/250 = 6.80$

CAN  $1720/250 = 6.88$

Urea  $2274/460 = 4.94$

- ❖ Among the above nitrogen sources urea will be the cheapest fertilizer based on unit value .

In case of multi-nutrient fertilizers ,difficulty in the unit value calculations arises as all the plant nutrients contained in the complex fertilizer should be assessed in such cases ,there is a convenient method where in the unit values are calculated from the prices of standard fertilizers viz., 1)Ammonium sulphate 2) Single super phosphate 3) Muriate of potash

**PROBLEM:**

Find out which among the complex fertilizers and mixed fertilizer if prepared is economical when a complex fertilizer of graded 20:20:20 is purchased at a cost of Rs.5500 /- per tonne.

Given unit value of mixed fertilizer

a) ammonium sulphate : 11.00 per kg per kg of N

b) SSP : 11.50 per kg of P<sub>2</sub>O<sub>5</sub>

c) S.O.P : RS3.50 kg

20 N @of Rs a unit =11 x 20 = RS.220.00

20 kg P<sub>2</sub>O<sub>5</sub> @ RS.11.50/kg = 11.50 x 20 =RS.230.00

20 kg K<sub>2</sub>O @ RS.3.50/kg = 3.50 x20 =RS. 70.00

Cost of 100 kg of mixed fertilizer

Rs.520

Cost of one tonne of mixed fertilizer =Rs 5,200.00

Cost of complex fertilizer per tonne = Rs.5500.00

So at normal rates the cost of mixed (prepared) fertilizer should be Rs.5,200/- per tonne where as the cost of complex fertilizer price offered at market per tonne is Rs.5500/- so an amount of Rs.300/- higher price than mixed fertilizer (prepared).

**PROBLEM:**

A rice crop requires 100 kg N, 50kg P<sub>2</sub>O<sub>5</sub> and 50 kg K<sub>2</sub>O per hectare. Calculate the amount of urea, SSP, MOP required for application to one hectare .The contents given [46 % N in urea, 16 % P<sub>2</sub>O<sub>5</sub> SSP and 60 % K<sub>2</sub>O].

Nutrient desired

$$\text{Amount of fertilizer required} = \frac{\text{Nutrient desired}}{\% \text{ nutrient content in fertilizer}} \times 100$$

Urea required =  $100/46 \times 100 = 217.40$  kg} these are the quantities required  
 SSP required =  $50/16 \times 100 = 312.50$  kg} to supply 100 kg N, %50 kg P<sub>2</sub>O<sub>5</sub>  
 MOP =  $50/60 \times 100 = 83.40$  kg } and 50 kg K<sub>2</sub>O for one tonne



**PROBLEM**

Calculate the amount of DAP, Urea and MOP required to a ground nut crop of one hectare to supply 40 kg N, 40 kg  $P_2O_5$  and 50 kg  $K_2O$

Contents: {DAP- 18 % N and 46 %  $P_2O_5$ , Urea – 46 % N and MOP-60 %  $K_2O$ }

Quantity of DAP required to supply 40 kg  $P_2O_5$  =  $40/46 \times 100 = 87$  kg of  $P_2O_5$

Note: incidentally it also supplies nitrogen also from 87kg of DAP

Therefore 87 kg DAP supplies =  $18/100 \times 87 = 15.70$  kg of N

The amount of N to be supplied through urea is  $40 - 15.70 = 24.30$  kg N

So urea required to supply 24.30 kg N is =  $24.3/46 \times 100 = 53$  kg urea

MOP required to supply 50 kg  $K_2O$  =  $50/60 \times 100 = 83$  kg of MOP

So total quantity individual fertilizers required to supply 40 kg N, 40 kg  $P_2O_5$  and 50 kg  $K_2O$  are: DAP- 87 kg, Urea -53 kg and MOP is 83 kg

**AMENDMENTS**

Soil amendments are substances that influence the plant growth favorably by producing in the soil one or more of the following beneficial effects.

1. Changing the reaction, that is making the soil less acidic or less alkaline;
2. Changing the plant nutrients in the soil from unavailable to available forms;
3. Improving the physical conditions of the soil and
4. Counteracting the effects of injurious substances

Soil amendments usually contain plant nutrients also. Agricultural liming materials, for example, supply calcium and, sometimes magnesium as nutrient element.

**Types of soil amendments**

Mainly there are three types of soil amendments

1. materials for correcting acidic soil
2. Materials for correcting alkaline soils; and
3. Soil aggregating agents or soil conditioners to stabilize soil aggregates and to form granular structure

**Lecture: 16** Secondary and micronutrient fertilizers –Different sources of these nutrients and their contents .Conditions leading to their deficiency

## SECONDARY NUTRIENT FERTILIZERS [Ca, Mg and S]

### I. CALCIUM FERTILIZATION :

Nearly all multi nutrient liquid fertilizer formulations and more than 50 per cent multi nutrient solid fertilizers are almost devoid of calcium .Multi nutrient fertilizers use, warrants the use of calcium. The source of calcium with basic chemical formula, its content and solubility are mentioned in the following table.

**Table: Basic chemical data of various calcium sources:**

S.No.	Source	Formula	Ca (%)	Water solubility g /100 g at 25 °C
1	Burnt lime	CaO	70	0.12
2	Hydrated lime	Ca(OH) <sub>2</sub>	50	0.16
3	Calcite lime	CaCO <sub>3</sub>	36	0.01
4	Dolamitic lime	CaCO <sub>3</sub> Mg CO <sub>3</sub>	17	>0.1
5	Basic slag	[CaO] <sub>5</sub> P <sub>2</sub> O <sub>5</sub> SiO <sub>2</sub>	29	>0.1
6	Gypsum	CaSO <sub>4</sub> 2H <sub>2</sub> O	22	0.24
7	Calcium nitrate	Ca(NO <sub>3</sub> ) <sub>2</sub> 2H <sub>2</sub> O	20	100
8	Single Super phosphate	Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> CaSO <sub>4</sub>	20	1.0
9	Triple super phosphate	Ca(H <sub>3</sub> PO <sub>4</sub> ) <sub>2</sub>	13	1.80
10	Rock phosphate	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F	33	0.002
11	Calcium chloride	CaCl <sub>2</sub>	36	100.00

Of the different sources, the Gypsum has been gaining importance for crops such as legumes.

Global reserves of Ca are considerably large since whole mountain ranges consist of lime stone. Calcium nick named as root developer ,which is slightly mobile in plants .Calcium deficiency in plants is rarely caused by shortage of available reserves in the soil , except in acidic soils.

### II. MAGNESIUM FERTILIZERS :

In multi nutrient fertilizers, finely ground dolamitic limestone is used as filler and it is a incidental supplier of Mg.

S.No.	Source	Formula	Mg (%)	Water solubility g /100 grams at 25 °C
1	Magnesium oxide	MgO	45	6.2 x10 <sup>-5</sup>
2	Dolomite	CaCO <sub>3</sub> MgCO <sub>3</sub>	12	0.032
3	Kiserite	MgSO <sub>4</sub> H <sub>2</sub> O	18.2	68.40
4	Langbeinite	K <sub>2</sub> SO <sub>4</sub> 2MgSO <sub>4</sub>	11.2	100.0
5	Magnesium sulphate	MgSO <sub>4</sub> 7H <sub>2</sub> O	10.5	91.10

**CAUSES FOR DEFICIENCY:**

1. Soils subjected to intensive NPK fertilization, reveal Mg deficiency
2. Due to increased crop removal
3. Due to leaching losses especially in acid soils
4. Reduced supply of Mg through multi nutrient fertilizer
5. Antagonistic decrease in Mg uptake due to large K supply

The above are the conditions in which Mg fertilization becomes necessary.

**III.SULPHUR FERTILIZERS:**

1. Plants take sulphur in the form of sulphate [ $\text{SO}_4^{2-}$ ] ion. Sulphur fertilizers predominantly contain sulphate, some of which are easily soluble and some are slightly soluble
2. Gypsum [ $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ] is a calcium sulphate because its slight solubility in water which is slow acting
3. Elemental sulphur is also an important sulphur fertilizer with strong acidifying action. It can be used either directly or as an additive to other solid fertilizers eg sulphur coated urea. The following table gives the basic chemical data of sulphur sources

S.No.	Source	Formula	S (%)
1	Ammonium sulphate	$(\text{NH}_4)_2 \text{SO}_4$	23
2	Potassium sulphate	$\text{K}_2\text{SO}_4$	18
3	Magnesium sulphate	$\text{MgSO}_4$	13
4	Super phosphate	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{CaSO}_4$	12
5	Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	18
6	Aluminium sulphate	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	14

The sulphur requirements of plants are approximately 2/3 of their phosphorus requirements and are provided from various sources such as air, rain water, soil and fertilizer. Fields near industrial zones are supplied with 10-30 kg ha<sup>-1</sup> per year from SO<sub>2</sub> waste gases.

**MICRONUTRIENT FERTILIZERS**

Higher green plants are known to require seven micronutrients viz., Fe, Mn, Cu, B, Mo, Cl etc.,. But this number may have to be increased in future

**Sources of micronutrients:**

S.No.	Micronutrients	Formula	Content (%)
<b>A</b>	<b>IRON</b>		
	1.Ferrous sulphate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	20
	2.Fe-chelate	Fe-EDTA	5
	3.Fe-Chelate	FeEDHA	6
<b>B</b>	<b>MANGANESE</b>		
	1. Manganous sulphate	$\text{Mn SO}_4 \cdot 4 \text{H}_2 \text{O}$	24
	2.Manganous sulphate (Monohydrate)	$\text{Mn SO}_4 \cdot \text{H}_2 \text{O}$	32
	3. Mn -chelate	Mn-EDTA	13
<b>C</b>	<b>ZINC</b>		
	1.Zinc sulphate	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	23
	2.Zinc sulphate (Monohydrate)	$\text{ZnSO}_4 \cdot \text{H}_2\text{O}$	36
	3.Zn-chelate	Zn-EDTA	14
<b>D</b>	<b>COPPER</b>		
	1.Copper sulphate	$\text{Cu SO}_4 \cdot 5\text{H}_2\text{O}$	25
	2.Copper sulphate (Monohydrate )	$\text{Cu SO}_4 \cdot \text{H}_2\text{O}$	36
<b>E</b>	<b>BORON</b>		
	1. Borax (Na-tetra borate )	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	11
	2.Borax anhdrous	$\text{Na}_2 \text{B}_4\text{O}_7$	22
	3.Boric acid	$\text{H}_3\text{BO}_3$	18
<b>F</b>	<b>MOLYBDENUM</b>		
	1 Sodium molybdate	$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	40
	2.Ammonium molybdate	$(\text{NH}_4)_6\text{MoO}_{24}$	54
	3Molybdenum trioxide	$\text{MoO}_3$	66
	4.Calcium molybdate	$\text{CaMoO}_4$	48

**The need for the micronutrient fertilization has been increasing due to the following causes :**

- 1. Change in the plants :** Change in the plant varieties from traditional to high yielding varieties (HYV). HYV have a capacity to remove more nutrients both major and minor. HYV have low mobilizing capacity of micro nutrients from the soils hence they are to be applied through external application.
- 2. Changes in soil :** Change in soil condition from acid to alkaline(Increased soil reaction) and aeration cause greater immobilization of most micronutrients except molybdenum (Fe, Zn, Cu and Mn). High acidic nature of the soil induces both calcium and magnesium deficiency.
- 3. Changes in fertilization:** Using high doses of NPK in the form of complex fertilizers, induces deficiencies of secondary and micro nutrients.

Antagonistic action due in part to excessive fertilization with NPK

Eg. Higher K content in soils effects the uptake of Fe, Mn, and B.

Excess P leads to deficiencies of Zn, Fe, Cu and increases Mo availability.

More the sulphate present in the soils, lesser the availability of Mo.

Lesser or least micronutrient constituents in multinutrient fertilizers.

#### 4. Changes in overall growth conditions.

1. Intensive cultivation: Intensive cultivation leads to micro nutrient deficiencies
2. Non availability and application of organic manure.
3. Under/ over limed condition.
4. Parent material: Most of the micronutrients originates from parent material and influences the availability or deficiency of micronutrients to plants
5. Land levelling and shaping: Most of the micronutrients are concentrated on the surface soil except Molybdenum. Levelling of land and deep tillage operations leads to deficiencies.
- 6 Low Si/Mg ratio: Leads to fixation of Zn in soil.
7. Calcium carbonate: More the  $\text{CaCO}_3$  in soils lesser the availability of Fe, Cu, Mn, Zn.
8. Soil texture: Boron availability is more in coarse textured soils and in finer textured soils it gets fixed, unavailable to plants.
9. Secondary clay minerals: Montmorillonite clay adsorb more of Zn, Cu and leads to deficiency or unavailability to plants.
10. Soil moisture: Dry conditions of soil fix more of Boran and is released under wet conditions. Presence of more moisture reduces the availability of Mn.
11. Interaction with macronutrients: Heavy nitrogen interferes with availability of Cu, Mn, Zn and leads to deficiencies in plant.
12. Liming reduces the availability of Mn, Zn, Fe, Cu.
13. Seasonal variation: Nutrient deficiencies are more during cold season.
  - Out break of B deficiency is common in dry seasons
  - Summer drought aggravate Fe chlorosis.
  - High and low soil temperatures induces Zn deficiency in soils having low Zn.

### PRINCIPLES INVOLVED IN MICRONUTRIENT FERTILIZATION

#### I. IRON FERTILIZATION :

Majority of Fe-fertilizers are water soluble .Salts or organic complexes (chelates). They are predominantly applied as foliar sprays, however this requires repeated application. In addition to supplying iron to deficit soils, it is necessary to mobilize iron in the soil itself through acid –N –fertilization .Fe removal amounts to a few kg/ha /year

#### II. MANGANESE FERTILIZATION :

Manganese sulphate is the best known water soluble fertilizer and is suitable for leaf fertilization .It can also be used as a soil dressing, but is easily fixed in deficit soils when the pH is more

Soil Mn supplies can be improved by

- i) Using acid forming fertilizers
- ii) Compacting loose soils
- iii) Preventing excessive drying
- iv) Supply of easily decomposed organic matter, which on conversion creates reducing conditions and thus Mn released. It is a practical means of Mn supply than to add Mn fertilizer. About  $\frac{1}{2}$  to 1.0 kg of Mn /ha/year is removed by crops in general

### III. COPPER FERTILIZATION :

- i) Copper sulphate [Blue Vitriol] is the oldest water soluble Cu-fertilizer. It can be applied as soil dressing or foliar nutrient. However; its acidic side effects are likely to cause leaf scorch on foliar application.
- ii) Hence less caustic agents like green copper  $\text{Cu}_2\text{Cl}(\text{OH})_3$  or Cu-chelates are safe to use
- iii) Copper removal by crops in general varies 30-100 g/ha /year
- iv) Copper is highly immobile in soil and as such needs thorough mixing with top soil

### IV. ZINC FERTILIZATION :

- i) Zinc sulphate is the simplest form of water soluble fertilizer
- ii) It is acidic in reaction and causes leaf scorch on foliar application unless free acidity is neutralized with lime
- iii) Improvement of natural zinc sulphate ( Soil zinc) can be done by the application of acid forming N -fertilizers to combat Zn-deficiency. Crop removal of Zn varies from 100-400 g /ha /year

### V. BORON FERTILIZATION :

- i) Borax (Na –tetra borate) is historically famous water soluble boron fertilizer.
- ii) The effectiveness of chile –salt peter was attributed to the presence of borax as natural admixture.
- iii) It can be applied to soil or foliage
- iv) Boron removal by crops is about 50 g / ha /year

### VI. MOLYBDENUM FERTILIZATION

- i) Sodium molybdate and ammonium molybdate are the important Mo fertilizers suitable for soil or foliar application and also for seed treatment
- ii) Molybdenum removal by crops varies from 5 to 20 g/ha /year

## Classification of micronutrient fertilizers

Micronutrient fertilizers are classified into two broad categories :

- I. Inorganic salts**
- II. Chelates**
  - I. Inorganic salts:** Supplying micronutrients are salts like  $\text{Zn SO}_4$  ,  $\text{Cu SO}_4$  , $\text{Mn SO}_4$   $\text{Fe SO}_4$  etc., All these are readily soluble in water and can be used both for soil application and foliar spray.
  - II. Chelates :** This is next important category of micronutrient fertilizers .Chelates are metallic molecules of varying sizes and shapes in which the organic part binds the nutrient in a ring like structure . For the chelation of nutrient cation the common chelating agents used in chelating micronutrients as follows.
    1. EDTA :Ethylene Diamine Tetra Acetic Acid
    2. HEDTA Hydroxy Ethylene Diamine Tetra Acetic Acid
    3. EDDHA Ethylene Diamine Dihydroxy Acetic Acid
    4. NTA : Nitrilo Tri Acetic Acid
    5. DTPA : Diethylene Triamine Penta Acetic Acid

**Lecture: 17** Fertilizer Control Order (FCO) – its importance and regulations  
 .Specifications and fertilizer storage standards of important fertilizers

## **QUALITY CONTROL OF FERTILIZERS**

**Objectives:** Laws and regulations governing the manufacture and sale of fertilizers are imperative in order to check

1. Spurious standards and adulterated fertilizers entering in to the market.
2. To ensure quantity of nutrients and quality of carriers present in the fertilizer
3. To ensure quantity of nutrients and quality of carriers present in the fertilizer
4. To eliminate black marketers off the market
5. The total N, P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O must be guaranteed in terms of percentage of each of these nutrients in a given fertilizer .The oxide expression for P and K are actually in accurate and confusing as they are based on early practices with which chemists determined the elements by ignition and weighing the oxides .The current practice is to express the elemental concentration of these nutrients

By considering the above said objectives, the government of India passed The FERTILIZER CONTROL ORDER [FCO] on 28<sup>th</sup> of April, 1957 in exercise of the power conferred by the section III of the essential commodities act of 1955 .This order is intended to regulate the manufacture, distribution and supply of the fertilizers in India at a control cost .This has been effective from May 18<sup>th</sup> 1957 .It is revised in 1985 with effect from 25-9-1985. The Government of India has delegated to powers to state Governments to implement the order

The Government of India (G O I) also passed the Fertilizer Movement Order (FMO) on 31<sup>st</sup> December, 1960 in order to regulate the inter state movement of fertilizers and the export of fertilizers which came into force with effect from 1-1-1961

### **FERTILIZER CONTROL ORDER [FCO] REGULATIONS:**

1. All the fertilizer manufacturer should obtain licence from the Commissioner of Agriculture ,state Government concerned for the manufacture of fertilizer and mixed fertilizers
2. The fertilizer dealers should on renewable basis, register their dealership with the Assistant Director of the Agriculture (ADA) Regular of the division concerned in a state.
3. The terms and conditions of manufacture ,distribution and sales imposed by the government should be followed
4. Duties of inspecting officers and the dealers are specified
5. Fertilizer specifications and kind of package are stated
6. Method of drawing fertilizer samples for analysis in the fertilizer testing laboratories is stated
7. Powers are vested with the FCO enforcing officials to book the cases against the fraudulent manufacturers, distributors and dealers of fertilizers.



**Specifications and standards for important fertilizers [As per FCO,1957]**

- 1 Urea** Moisture per cent by weight 1.0 Maximum  
Total nitrogen per cent by weight 44.0 minimum  
Biuret per cent by weight 1.50 maximum  
Particle size :In the form of granule the material shall pass through 2.8mm and not less than 80% by weight shall be retained on 1mm
- 2 SSP**
  1. Moisture per cent by weight, maximum 12
  2. Free phosphates as ( $P_2O_5$ ) percent by weight 4.0
  3. Water soluble phosphates ( as  $P_2O_5$ ) by weight maximum 16.0
- 3 MOP** Moisture per cent by weight maximum 12.00  
Water soluble potassium per cent by weight minimum 60
- 4 DAP** Moisture per cent by weight 1.0  
Total nitrogen per cent by weight minimum 18  
Total phosphates (as  $P_2O_5$ ) per cent by weight minimum 46.0  
Water soluble phosphates (as  $P_2O_5$ ) per cent by weight 41.6

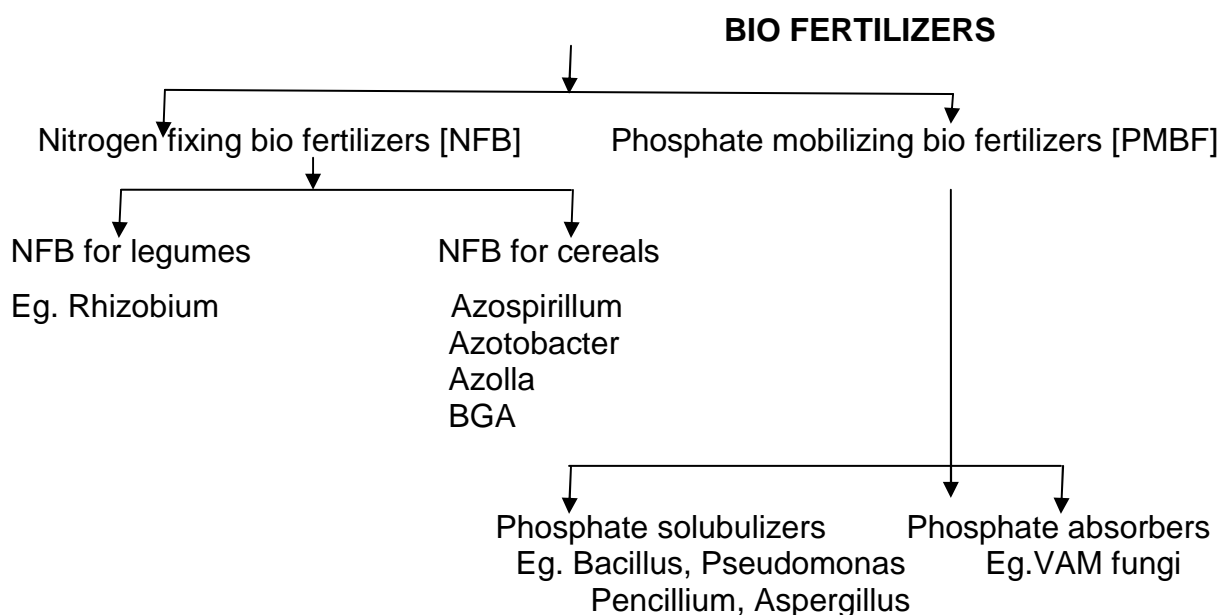
## Lecture: 18 BIOFERTILIZER – Use of biofertilizers in agriculture and their advantage

**Bio-fertilizers** or **bio-inoculants** are productions containing living organisms such as nitrogen fixers or phosphorus solubulizers which are useful for agricultural production.

Biofertilizers play a significant role in improving soil fertility and plant growth.

- by fixing atmospheric nitrogen both in association with plants and without plants
- solubulize insoluble soil phosphates into soluble phosphates there by increasing the availability of phosphorus
- Secrete growth promoting substances and supplies to the inoculated plants.

**VERMA & BHATTACHARYYA (1994)** classified the bio fertilizers based on the nutrient provided, which is as follows.



### I. *Rhizobium* inoculant :

Belongs to the family Rhizobiaceae and symbiotic in nature. *Rhizobium* establishes symbiotic relations with pulses and other legumes and can fix 50 to 100 kg N ha<sup>-1</sup> by which application of chemical nitrogen fertilizers could be reduced and supplemented nearly 80-90 per cent of nitrogen requirement of crop is met by nitrogen fixation in root nodules of legume crops .It is used for pulse legume crops like chick pea ,red gram , chickpea, lentil , black gram etc., and oil seed legumes like soybean and groundnut and forage legumes like besrseem , lucerne and pillipesara .On average yield increase was 15-30 % due to rhizobium inoculation .

The rhizobia show host specificity to some extent. In other words rhizobia isolated from ground nut can not be used for red gram. Particular rhizobium species has the ability to form nodules only on roots of limited and related plant species. Again effective strains are to be selected for effective nodulation.

The response of inoculation is governed by

1. Host plant
2. Strains effectiveness
3. Soil type
4. Rain fall

**Method of preparation:**

This biofertilizer is available commercially as carrier based (lignite or peat ) biofertilizers .Direct application of rhizobium to seed is the most common form of legume inoculation (seed coat ) .However , for groundnut ,slurry of peat based inoculam in the seed furrows is recommended as the seeds are fragile . The recommended quantity of rhizobium fertilizer is 2-3 packets / ha (packet: 200 grams). The rhizobium culture is available in the market by names of

JAWAHAR CULTURE

RHIZOBIUM COMPOSITE

Nitrogen R-H

**II. *Azotobacter* inoculant:**

*Azotobacter* belongs to the family Azotobacteriaceae, which is a chemoautotrophic in nature ,free living , non-symbiotic in nature and is recommended for application to non-legume crops .It thrives well in many types of soils ,with a minimal dose of phosphorus and carbon compounds. It grows best in neutral to alkaline soils .By the application of *Azotobacter* to various crops ,the amount of recommended doses of nitrogenous fertilizers can be reduced by 10-20% . It produces plant growth promoting substances like vitamins of B group , Indole acetic acid ,Gibberellic acid by which plants grow quickly and healthy. Yield increase of 10-15 % was noticed in some millets .This biofertilizer is recommended for rice , wheat , millets and other cereals ,vegetables ,sunflower ,mustard ,tobacco sugarcane ,cotton etc., and also fruit crops .

**Method of usage:** It is carrier based biofertilizer (lignite / peat) . *Azotobacter* can be applied by seed inoculation, seedling inoculation, or by broad casting in the field after mixing with FYM or with well decomposed compost.

Seed inoculation: Seed is treated with Jaggery to make it sticky and then treated with biofertilizer and shade dried.Seedling inoculation: Make slurry of biofertilizer and dip the roots in it. The recommended dose of *Azotobacter* is 2-3 packets /ha .

**III. *Azospirillum* Inoculant :**

It belongs to the family spirillaceae, chemoautotrophic and associative in nature. It is an associative nitrogen fixing organism was found to be beneficial for sorghum, wheat, maize, barley, fodder grasses and minor millets. Yield increase was 15-30 % .By the application of this fertilizer nitrogen saving is 20-30 kg /ha .It also produces growth regulating substances.

**Application of this biofertilizer results in:**

1. Increased mineral uptake
2. Increased water up take
3. Root development
4. Vegetative growth
5. Make the plant drought resistant

**NOTE:** Principle and mode of application is that of *Azotobacter*

#### IV. AZOLLA [Botanical name is *Azolla pinnata*]:

1. It belongs to the family Azollaceae. Azolla is a water fern .It is considered as aquatic weed commonly found in floating in idle ponds, tanks shallow ditches and canals. Azolla is associated with rice field. A blue green algae (BGA) *Anabaena azollae* living in the epidermal cavity of lower side of the leaf of Azolla. The symbiotic association of *Azolla pinnata* and *Anabaena azollae* is termed as Azolla Anabaena complex .This algae fixes atmospheric nitrogen for Azolla and in exchange ,the plant provides shelter and food to the algae . As this complex fixes atmospheric nitrogen, it has great potentiality for use, in agricultural field as biofertilizer and can be used as an alternative to nitrogen fertilizers. It is recommended as green manure because of its large biomass and high N content( 4-6%N) for sub merged rice fields, with in maximum temperature of 38<sup>0</sup>C. The yield increase is 15-20%

Fresh Azolla contains 90-95 water . Decomposed Azolla contains the following plant foods

S.No.	Nutrient	Per cent (%)
1	Nitrogen	4 to 6
2	Phosphorus	0.5 to 0.9
3	Potassium	2 to 6
4	Calcium	0.4 to 1
5	Magnesium	0.5
6	Manganese	0.11 to 0.16
7	Iron	0.06 to 0.16
8	Total ash	9 to 10

#### Ideal conditions for growth and multiplication of Azolla

2. Depth of water should be maintained at 8-10 cm in the field
3. Temperature in between 14 to 35 <sup>0</sup>C .Optimum for quick growth and multiplication is 20 to 28 <sup>0</sup>C.
4. Suitable soil pH is 6.0 to 8.0
5. Single Super Phosphate should be applied at the rate of 20-25 kg ha<sup>-1</sup> , should be applied
6. Furadon granules @2-3 kg /week should be applied to control leaf eating insects and snails.

#### Methods of growing Azolla:

1. Green manuring
2. Dual cropping
3. Composting
4. Just growing

1. **Green manuring:** When there is standing water in the field, Azolla is grown by spreading 200-500 kg /ha fresh Azolla .After 25 days of the whole field will be covered by Azolla, if condition is ideal. Green Azolla is incorporated by ploughing after dewatering in the field. This will add 30- 40 kg of N fertilizer /ha .
2. **Dual cropping :**
  - A) Azolla nursery is prepared simultaneously with the paddy nursery
  - B) The area of Azolla nursery should be half that of paddy nursery (seed bed ) .
  - C) The Azolla nursery should be kept free from other aquatic weeds and there should be 8-10 cm standing water in the Azolla nursery.
  - D) Where the paddy seeds are sown in the paddy nursery fresh Azolla is spread in the Azolla nursery @40-80 grams per square meter.
  - E) After 25 days the Azolla will increase an extent of 60 times and super phosphate is applied @25 grams/Sq.Meter/week.
  - F) With in 25 days the paddy seedlings will be ready for transplanting . Before transplantation of paddy seedlings ,there will be standing water in the main field .Azolla is taken out from the Azolla nursery and spread in the transplanted field @ 200- 500 kg /ha .
  - G) Single super phosphate @25-50 kg /ha /week is applied for 3 weeks and water level is maintained 5-10 cm.
  - H) After another 25 days, the whole field may be covered by Azolla .Azolla is incorporated after dewatering the field .This will add 30-40 kg N /ha besides another nutrients.
3. **Composting:** Azolla is grown in permanent Azolla nursery. The Azolla is collected every week from the nursery and kept in layers on the side of nursery .Within 10 days, the Azolla will decompose and can be used in any crop.

#### 4. **Just growing :**

Azolla can be grown along with paddy .nitrogen will be added where it is not incorporated .Azolla when grown in one hectare of land through out the year and ideal conditions are maintained it can fix 800 kg of nitrogen per hectare .

Azolla is suitable for only flooded rice and fixes up to 40-80 kg N/ha. Symbiotically with *Anabaena azollae* .The yield increase is 15-20 %.

#### **Advantages of azolla:**

1. It contains higher Nitrogen content
2. Release of nitrogen is easy
3. There is no leaching loss
4. Releases nutrient slowly
5. Weed interference is less where grown as dual crop

#### **V. Blue green algae or Cyanobacteria:**

BGA is phototrophic in nature .These are photosynthetic ,prokaryotic microorganisms and capable of fixing molecular nitrogen .B G A are found to grown in a paddy filed and marshland .It is used as biofertilizer for irrigated rice crop.

The rice field ecosystem provides an environment favorable for the growth of BGA with respect to their requirements viz., light, water and temperature.

Nitrogen fixation by BGA have been estimated to be 25-30 kg N/ha. Yield increases by 10-15 % .BGA has some species viz., Nostoc, Anabaena ,Olocia , Calothrix ,Tolipothix etc., They fix nitrogen in the presence of sunlight .They also contain growth promoting substances like auxin ,Indole acetic acid and Gibberellic acid . Recommendation : application of 10 kg /ha flakes of BGA .It is applied 10 days after the transplanting of rice crop .

### **Algal production technology:**

**Mainly three methods are followed.**

#### **1) Trough method**

#### **2) Pit method**

#### **3) Field scale**

#### **1. Trough method:**

- ❖ Take 3 m x 2 m x 20 cm size (L x B x h) galvanized iron sheet trough or to the convenient size. Add about 8 to 10 kg of soil and well mixed with 200 grams of SSP .The soil pH should be about neutral .If acidic correct by lime .Add water to the trough 5-15 cm (height) to protect from insects, and add Carbofuran 3.0 G at the rate of 25 grams / tray .
- ❖ Sprinkle the algal culture on the surface of the standing water and keeping it in air (open) and exposed to sunlight.
- ❖ In hot summer months ,the growth of algae will be rapid in about 7 to 10 days and form a thick mat, where algal growth becomes sufficiently thick stop watering and allow the water to evaporate completely ,the dry algae cracks in to flakes
- ❖ Collect the dry algal flakes from the trough and store in bags for the use in the field .One trough gives 1.5 to kg mats.

#### **2. Pit- method :**

- Adopted by number of farmers in south India
- Demark the area in the field for algal production
- Flood the area with to a depth of about 12.5 cm
- Apply SSP @12.0 kg /40 m<sup>2</sup> area
- Apply the algal culture
- In clayey soils good growth of algae takes place in about two weeks in clear sunny weather while in loamy soils it takes about 3-4 weeks
- Once algal growing mats are formed, they are allowed to dry up in the field and deed algal flakes are thin collected and stored in bags.
- BGA benefit the rice crop up to 25-30 kg N /ha
- Dose :Apply BGA @10-15 kg /ha after transplanting .

### **VI . MYCORRHIZAE:**

Mycorrhizae means root fungi or VAM .These are obligate symbiotic .They are ubiquitous in nature and with very few exceptions found on a wide range of plant

species .They form vesicular –arbuscular –mycorrhizal (VAM) symbiosis .VAM fungi infects and spreads inside the root by providing an aseptate mycelium .Vesicles which are sac like structure provided by these fungi are known to store phosphorus as phospholipids .Arbuscules formed inside the cortical cells are attributed to help in the exchange of nutrients.Common genera that form VAM associations are **Glomus, Gigaspora , Enterospora etc.,**

#### **Advantages:**

1. VAM fungi enhancing the nutrient uptake of P, Zn and S
2. Enhances the water uptake under drought conditions
3. Enhances resistance to root damage
4. Increases the yield

It is recommended for forest trees, forage grasses, maize, millets, sorghum and barely and also leguminous crops.

Mycorrhizae can substitute up to 560 kg phosphorous fertilizer per hectare for citrus .Only enriched soil in the presence of suitable plant has to multiplication are not yet known .

#### **Phosphate solubilizing microorganisms**

Phosphorus is present in soils in both organic and inorganic forms and most of which is insoluble and unavailable to plants. Several soil bacteria particularly those belonging to the genera **Pseudomonas** and **Bacillus** and fungi belonging to the genera **Penicillium** and **Aspergillus** possess the activity to bring insoluble phosphates in the soil to the soluble forms by secreting organic acids such as acetic acid ,propeonic acid etc., These acids lowers the pH and bring about the dissolution of the bound phosphate forms .

#### **Mode of applications: As that of VAM fungi**

#### **Constraints in usage of biofertilizers**

1. Farmers acceptance has been for from satisfaction
2. Difficult to demonstrate striking increase in yield due to biofertilizers unlike chemical fertilizers
3. Strains fail to establish if the soil moisture in the surface in the surface zone
4. Fungicide treatment is a problem in crops like groundnut
5. Inoculants manufacturing is for below the requirement
6. Availability of quality of inoculants is another problem
7. Seed inoculation is no more suitable when seeds are sown on dry soil under
8. When seeds are coated with toxic chemicals and pesticides
9. Soil containing higher number of ineffective native rhizobia
10. Seeds have fragile seed coat
11. When seed coat is toxic to rhizobia .In such situation soil inoculation with granulated inoculant is followed in USA ,New Zealand ,France etc.,Granulated inoculation is prepared using grains of sand ,gypsum ,peat etc.,
12. Problem like transport form the manufacturing centre.

**Lecture: 19** Out lines of organic chemistry –Theory of vitalism –Classification of organic compounds based on their chemical nature/structure with examples .

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### AGRICULTURAL CHEMICALS

Agricultural chemicals are the chemical substances that are used in the field of agriculture, particularly in crop production practices. Fertilizers, pesticides, growth regulators, amendments *etc.*, belong to this class.

Consumption of agricultural chemicals increasing steadily. In India, consumption of pesticides was 15,000 tonnes in 1965. By 1997 it reached 2,05,000 tonnes.

Zone wise - south zone accounts for more than 40 per cent of India's total consumption due to cash crops like cotton, tobacco, sugarcane , chillies *etc.* ,

Among the agrochemicals, insecticides find widest use (80%), others are fungicides(10 %) , herbicides (7%) , rodenticides (1.6 %) , others (1.4 %).

In A.P Guntur district ranks first in consumption of agricultural chemicals .In A.P. pesticides use is more on cash crops.

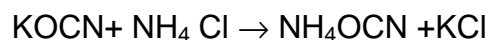
There are two main classes of chemical compounds i.e., organic and inorganic .The compounds, which are of mineral origin, are known as inorganic and those of plant and animal origin are called organic.

### ORGANIC CHEMISTRY

It was assumed that the organic compounds could be produced only living matter, for living matter was thought to possess "Vital force". This theory is known as theory of vitalism or Vital force, which is proposed by the scientist namely **Berzelius**. As long as this concept prevailed no effort was made to produce organic compounds in the laboratory and the vital force or vitalism theory long went unchallenged.

In 1828, the German chemist, **Friedrich Wohler** heated ammonium cyanate derived from inorganic substances and obtained the organic compound urea. Hence, the theory of vitalism was disproved by **Friedrich Wohler**.

The urea formed in this way proved to be identical in all respects with urea isolated from urine.



It had become evident that most of the compounds formed by living cells (plants and animals) contained carbon. Hence, the emphasis was shifted from origin to composition and organic compounds came to be considered as those containing carbon.

Organic chemistry is the study of the compounds of carbon. Since, all organic compounds could be considered as derived from hydrocarbons, a more exact definition would be organic chemistry is the study of hydrocarbons and their derivatives.



**Lecture:20** Differences between organic and inorganic compounds .Functional groups  
 .Isomerism and stereoisomerism

### Differences between organic and inorganic compounds

S. No.	Organic compounds	Inorganic compounds
1	These are formed from few elements like C, H, O, N, P, S and halogens.	Formed from any of more than 100 elements known
2	These are of living origin	These are of mineral origin
3	Exhibit covalent bonding	Exhibit ionic bonding
4	Exhibit isomerism	Isomerism is not possible
5	Have low melting and boiling points	Have high melting and boiling points.
6	Highly combustible	Non- combustible
7	Highly volatile	Non-volatile
8	Low solubility in water, Highly soluble in organic solvents	Highly soluble in water but less soluble in organic solvents.
9	These are non conductors of electricity	Solutions are good conductors of electricity
10	Reactions are slow require catalysts	Reactions are rapid, in general donot require catalysts.

### Functional groups:

An atom or a group of atoms that determines the properties and reactivity of an organic compound is called functional groups .

Some common functional groups are as follows

1	Alcoholic	-OH
2	Aldehyde	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{H} \end{array}$
3	Carbonyl (Ketone)	$-\overset{\text{O}}{\underset{ }{\text{C}}}=\text{O}$
4	Ester	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O} \end{array}$
5	Ether	- O -
6	Carboxyl	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH} \end{array}$
7	Thioether	=S
8	Amine	-NH <sub>2</sub>
9	Amide	-CONH <sub>2</sub>
10	Imine	=N- H
11	Oxime	=C=N-O
12	Nitriles	- C $\equiv$ N
13	Thiol or mercapton	- SH
14	Nitro	=N-

**Homologous series** (*Homos* = the same ; *legein* = to speak i.e, to have similar properties ): If a number of organic compounds with the same functional groups are arranged in an ascending order of their molecular weights and in a systematic way , the

resulting series (of the compounds) is called a Homologous series, in which the adjacent members differ by a  $\text{CH}_2$  group. The individual members are called homologs.

Example :

$\text{CH}_3\text{OH}$	Each member differs from adjacent
$\text{C}_2\text{H}_5\text{OH}$	member by $\text{CH}_2$ group
$\text{C}_3\text{H}_7\text{OH}$	
$\text{C}_4\text{H}_9\text{OH}$	

**General characteristics:**

1. All the compounds in the series contain the same elements and the functional groups
2. All the compounds can be represented by general formula
3. The molecular formula of each homolog differs one above and one below by  $\text{CH}_2$  unit
4. All the compounds in the series can be prepared by similar methods
5. All the compounds in the series have similar chemical properties
6. There is a gradual variation in physical properties in increasing molecular weight, decrease in reactions.

### CHEMICAL BONDS

Atoms of an element try to attain a stable configuration similar to that of the nearest zero group element. This tendency is responsible for the formation of chemical bond. A bond is kind of force or attraction that tends to keep two atoms or ions or radicals or molecules together.

The principal bonds that join atoms or ions or ion radicals are

1. **Ionic bond:** Formed by the loss or gains of electrons between two participating atoms. It is a very strong bond. So, melting and boiling points are very high. Because of charged ions, they are water-soluble and solutions conduct electricity i.e., electrolyzed.
2. **Covalent bond:** Formed by the sharing of electrons between two atoms, so that the electron pair is used by each in full comparatively weaker bond.
3. **Hydrogen bond:** Is formed between molecules in which hydrogen atom is attached to an atom of an element with large electro- negativity and very small size. Because of hydrogen bond the molecules associate themselves and hence possess higher boiling and melting point.

The hydrogen bond formed between two molecules is called intermolecular hydrogen bond. Hydrogen bond is formed between different groups of the same molecule is called intra molecular hydrogen bond.

4. **Coordinate covalent bond:** This is a special type of covalent bond in which shared pair of electrons is contributed by one of the two bonded atoms. This was proposed by **Sidgwick**.

In ammonia molecule, nitrogen atom has a lone pair of electrons in its valence shell. Hydrogen ion ( $\text{H}^+$ ) can take two electrons to get stability. A coordinate bond is formed

between  $\text{NH}_3$  and  $\text{H}^+$  to form  $\text{NH}_4^+$  (ammonium ion) in which the lone pair of electrons of N is shared by both N and  $\text{H}^+$ .

The atom that contributes the lone pair for bonding is called donor and the one which shares is called acceptor. In the above example, N is the donor and  $\text{H}^+$  is the acceptor. The coordinate bond is represented by putting an arrow ( $\rightarrow$ ) between the symbols of the two atoms directing from the donor towards acceptor.

## ISOMERISM

Two (or) more compounds consist of equal number of like atoms. These compounds have the same molecular formula but differ from each other in physical or chemical properties and are called isomers and the phenomenon is called isomerism (Greek **Iso** = equal; **meros** = parts). This is due to different modes of combination or arrangement of atoms within the molecule.

There are two main types of isomerism

### I. Structural isomerism and

### II. Space or stereoisomerism

#### I. Structural isomerism is divided into 5 types. They are

1. Chain isomerism
2. Position isomerism
3. Functional isomerism
4. Metamerism
5. Tautomerism

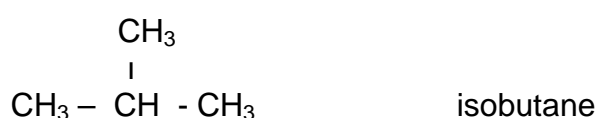
#### II. Space or stereoisomerism is of two types viz.,

1. Geometrical isomerism or Cis-trans isomerism
2. Optical isomerism

**I. Structural isomerism:** This is due to difference in the arrangement of atoms within the molecules without any reference to space. They are compounds that have the same molecular formula but different structural formulae.

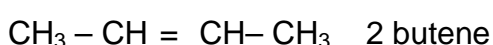
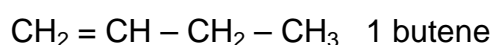
1. **Chain isomerism:** Compounds have the same molecular formula but differ in the order in which the carbon atoms are bonded to each other.

Eg.  $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$  n-butane



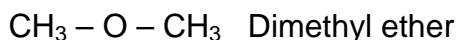
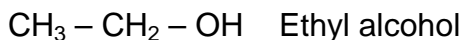
2. **Position isomerism:** Compounds have same molecular formula but differ in the position of a functional group on the carbon.

Eg.



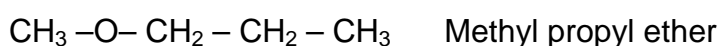
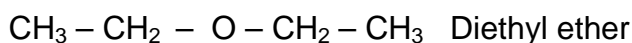
3. **Functional isomerism:** Have the same molecular formula but different functional groups .

Eg.

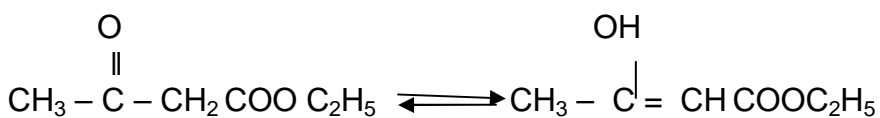


4. **Metamerism:** Is due to the unequal distribution of carbon atoms on either side of the functional group.

Eg.



5. **Tautomerism:** It is a special type of functional isomerism in which the isomers are in dynamic equilibrium with each other .For example ethyl acetoacetate is an equilibrium mixture of 93 per cent of keto form and 6 per cent of enol form.



Ketoform

Enol form

II. **Stereoisomerism:** When isomerism is caused by the different arrangement of atoms or groups in space, the phenomenon is called stereoisomerism. Compounds have the same structural formula but differ in configuration.

1. **Geometrical isomerism:** It results from a restriction in rotation about double bonds or about single bonds in cyclic compounds.

**Cis-** isomer: is one in which two similar groups on the same side of the double bond .This is less stable

**Trans-** isomer: Is one in which two similar groups are on the opposite side of the double bond. This is more stable

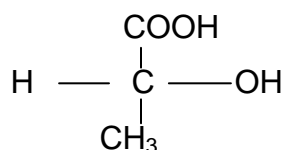
2. **Optical isomerism:** The compounds have the ability to rotate plane polarized light in opposite directions i.e., the optically active compound can exist in two isomeric form .Optical isomers have at least one asymmetric carbon atom .The isomer which rotates the light towards right is called dextro-rotatory and towards left is called leavo- rotatory .

Example: 1. .D- Glucose ,

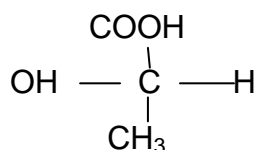
L -Glucose

Example: 2.

D(-) Lactic acid



L(+)-Lactic acid



\* is the asymmetric carbon atom (Chiral centre)

The two are mirror image isomers of each other. i.e., enantiomers.

### CLASSIFICATION OF ORGANIC COMPOUNDS

Organic compounds are divided into two groups.

#### 1) Aliphatic compounds

#### 2) Aromatic compounds

**1) Aliphatic compounds:** These are open chained structures. The term is used to denote compounds that don't have the special stability of aromatic compounds. All non-cyclic organic compounds are aliphatic.

Cyclic aliphatic compounds are said to be alicyclic.

Eg. A) Alkanes (Paraffins ) saturated hydrocarbons

B) Alkenes (Olefines ,Olefins ) unsaturated double bonds

C) Alkynes unsaturated having one or more triple bonds

Alkanes, alkenes that have one double bond and alkynes that have one triple bond can form homologous series

**2) Aromatic compounds:** These are closed chain structures. Compounds that contain a benzene ring in their molecule or that have chemical properties similar to benzene.

These are divided into two groups.

A) Homocyclic

B) Heterocyclic

**A) Homocyclic:** All the atoms in the ring are the same type.

Eg. Benzene ( $C_6H_6$ ); Cyclohexane ( $C_6H_{12}$ )

In the above compounds in the ring, all are carbon atoms only.

**B) Heterocyclic:** If different atoms are present in the ring .

In the ring C and N atoms are present

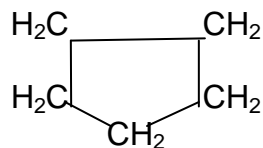
The aromatic rings are again divided into

I. Five (5) membered ring structure

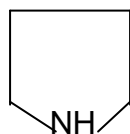
II. Six(6) membered ring structure

#### I. Five (5) membered ring structure

##### 1. Saturated

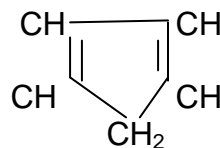


Cyclopentane  
**Saturated N containing**

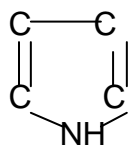


Pyrrolidine

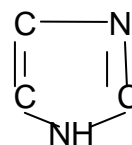
##### 2. Unsaturated



Cyclopentadiene  
**unsaturated N containing**

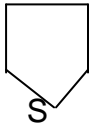


Pyrrole

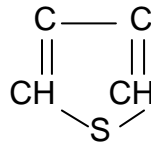


Imidazole

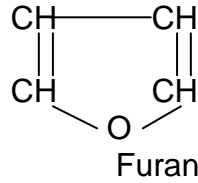
Pyrazole

**Saturated S containing**

Thiophane

**Unsaturated S containing**

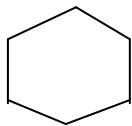
Thiophene

**Unsaturated O containing**

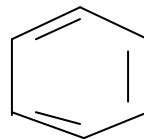
Furan

Furan is present in insecticides like carbofuran

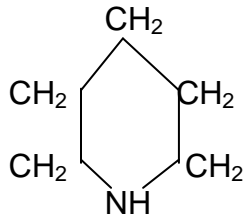
Pyrrole is present in chlorophyll, alkaloids, riboflavin etc.,

**II. Six(6) membered ring structure****1. Saturated**

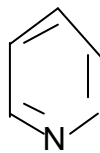
Cyclohexane

**2. Unsaturated**

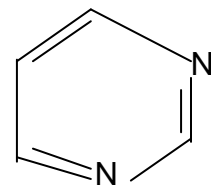
Benzene

**Saturated N containing**

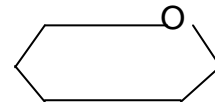
Piperidine

**Unsaturated N containing**

Pyridine

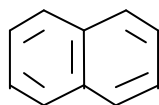


Pyrimidine

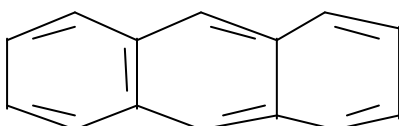
**Unsaturated O containing**

Pyran

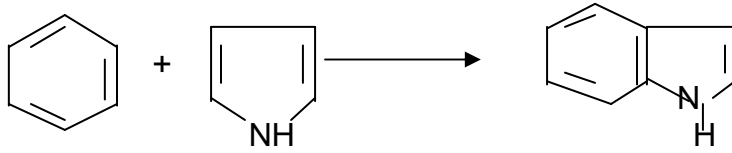
1) When two benzene rings fused to form Naphthalene



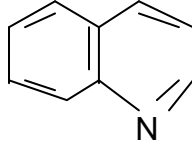
2) When three benzene rings are fused to form Anthracene



- 1) When benzene ring is fused with pyrrole, then it is called indole .It is present in IAA , Jasmine flowers etc



- 2) When benzene is fused with pyridine, it gives quinoline



**Lecture : 21** Diverse types of agrochemicals –Classification based on their use with examples. Classification of insecticides based on their chemical nature with examples. Botanical insecticides –Brief mention about vegetable oils (Fixed oils) and essential oils.

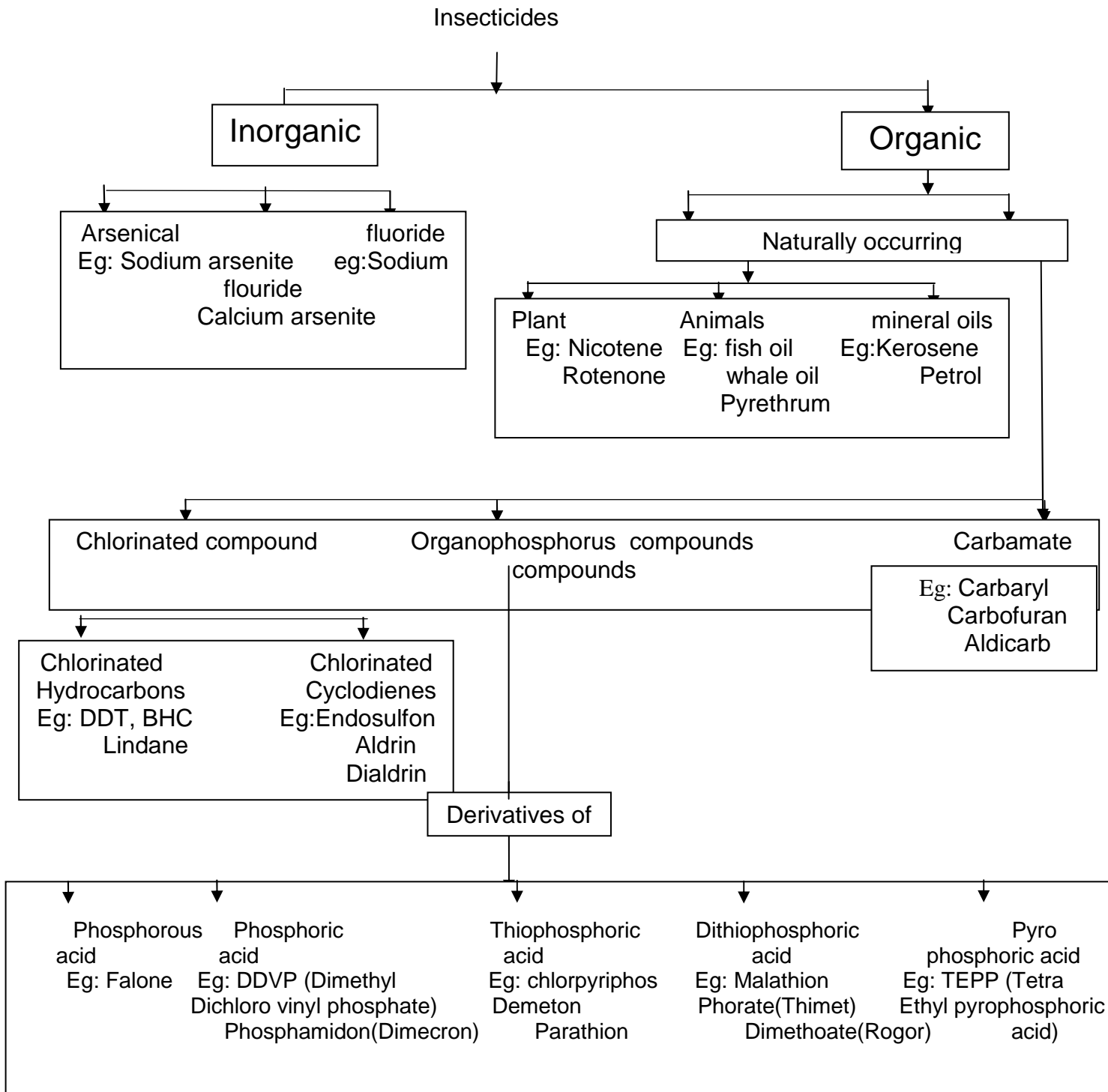
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**Classification of agricultural chemicals based on the purpose:**

1. Insecticides : Eg. Malathion , phorate
2. Fungicides : Eg. Zineb, captan
3. Herbicides : Eg. Paraquat, Butachlor
4. Acaricides : To kill mites and ticks , Eg. Dicofol and sulphur
5. Nematicides : Eg. Nemegon, carbofuran, Aldicarb
6. Zococides : To kill the rodents and other small creatures.  
Eg. Aluminum phosphide, warfarin, zinc phosphide, Celphos tablets
7. Bactericides : To control bacteria Eg. Oxime , Streptomycin
8. Algicides : To destruct algae and other aquatic vegetation  
Eg. Phygon, Dicolose
9. Molluscicides : To control molluscs including gastropods or slugs  
Eg. Metaldehyde
10. Antibiotics : Eg. Cycloheximide, Phycoactin and Aphomide
11. Antiseptics : Eg. Zinc oxide
12. Sex attractants : Eg. Gyplure, Helilure
13. Chemosterilant : Eg. TEPA, Aphomide, Azaridine
14. Insect attractants : Methyl Eugenol
15. Insect repellants : Citronella oil , Naphthalene
16. Fumigants : Methyl Bromide
17. Plant growth regulators : IAA, Kinetin , Gibberellic acid
18. Fertilizers : Urea , SSP,  $K_2SO_4$
19. Amendments : Lime , Sulphur, Gypsum
20. Soil sterilants : Borax
21. Nitrification inhibitors : Eg. N-Serve and A M
22. Chitin inhibitors : Eg. Diflubenzuron
23. Defoliants : To remove leaves from plants Eg. Gramoxone
24. Desiccants : : To remove moisture from plants  
Eg. Penta Chloro Phenol



**Classification of insecticides based on chemical nature:**



## **BOTANICAL INSECTICIDES**

Plant materials are important sources of insecticides. The toxicant may be present in any part of the plant and these toxic materials are collected and dried and powdered and that powder is used as insecticide. The toxicant also extracted from the powder using some solvent and chemical compound thus obtained used as insecticide.

Plant products which are used as insecticides may be classified as

1. **Primary toxicants** such as nicotine, rotenone
2. **Essential oils** (structure resembles to menthane) such as Pine oil, citronella oil
3. **Fixed oils** like Cotton seed oil and Neem oil
4. **Miscellaneous oils** such as walnut shell flour, plant gurr

### **Advantages of botanical insecticides**

1. Relatively cheaper
2. Don't pollute the environment
3. Don't leave any residue
4. Availability is relatively easier
5. Don't harm the beneficial organisms.

### **Disadvantages or difficulties involved in the use of botanical insecticides:**

1. It takes fairly long time (**2-5 years**) to establish a plant in a new environment. Some times the plant can't be introduced at all.
2. Availability of botanical insecticides is confined to a particular season, making import compulsory in off season.
3. Botanical insecticides decompose very fast and don't have long self life.
4. Testing of biological materials as botanical insecticides is very difficult and time consuming process and so far, a fraction of flora and fauna has been tested.

**Lecture: 22 & 23** Natural pyrethrum –Discovery –Sources –Chemistry-Extraction and properties .Neem and its products –Extraction –Mode of action of neem based products .Advantages and Disadvantages of natural botanical insecticides .Brief note on synthetic pyrethroids

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### PYRETHRUM

The original home of pyrethrum is said to be East or Middle East. In the 19<sup>th</sup> century it was introduced to U.S.A., Japan, U.K., Africa and South America. At the beginning of 20<sup>th</sup> century, Dalmatia and adjoining countries became leading producers. In 1941, Japan became the leading producer. However, at present, the principal producer of pyrethrum is KENYA. Other countries producing pyrethrum are Congo, Uganda, Tanzania, Ethiopia, Equador and Brazil .

In INDIA also pyrethrum is grown to a small extent in the

1. Hilly belts of Assam
2. Himalyan mountain range of J & K
3. Nilgiri areas of Tamil Nadu

Pyrethrum has been used for the control of harmful insects for many countries.

#### **SOURCE:**

Pyrethrum is found to occur in the flowers of some plants belonging to family compositae / Asteraceae. Important sources are

1. *Chrysanthemum cinerariifolium*
2. *C. coccineum*
3. *C.roseum*
4. *C.marshalli*
5. *C.tamrutene*

#### **Extraction of Pyrethrum:**

Pyrethrum is present in the Achenes of flower heads. The content is maximum when the flowers are in full bloom stage. At this stage, the flowers are harvested by hand picking .They are then dried at 54.4 °C and compressed. In the industries the dried and compressed flowers are ground to a fine powder. The powder / dust can be used as an insecticide.

The toxicant can be extracted by extracting with an organic solvent like Isopropanol, acetone or odor less kerosene. The solvent is repeatedly percolated through the powder and the weak extract is evaporated in a vacuum still to get concentrated extract .The concentrated extract together with an emulsifier is sold in the market for the use.

Also, the concentrated extract can be mixed uniformly with an inert carrier like benonite clay, charcoal powder, diatomaceous earth and the mixture can be used as a ready to use low power dust.

The extracted powder containing traces of pyrethrum is some times used as carrier in the dust preparation .To increase the pyrethrum activity compounds like DDT and Rotenone etc., are added.

### CHEMISTRY AND STRUCTURE OF PYRETHRUM

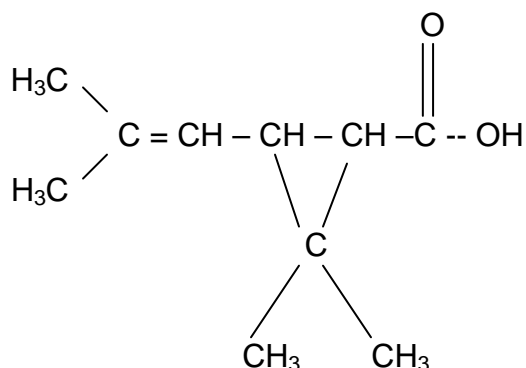
Elucidation of the chemical nature and structure of natural pyrethrum was by no means an easy task. Three groups of scientists worked together for decade for unfolding mystery of chemistry of pyrethrum .They are

1. Staudinger and Ruzicka
2. La Forge and Barthel
3. Godin , Beevor and Snarey

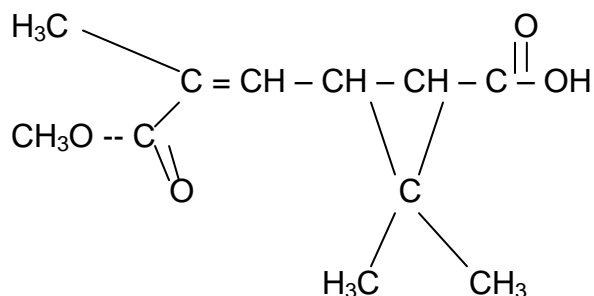
**Natural pyrethrum** is composed of **six (6) esters**. An ester product formed by reaction of an acid with an alcohol. The six esters are formed by reacting to two carboxylic acids and three alcohols in different combinations.

#### The two carboxylic acids are

1. **Chrysanthemum Monocarboxylic Acid (CMA)** or Cyclopropane monocarboxylic acid or Chrysanthemic acid

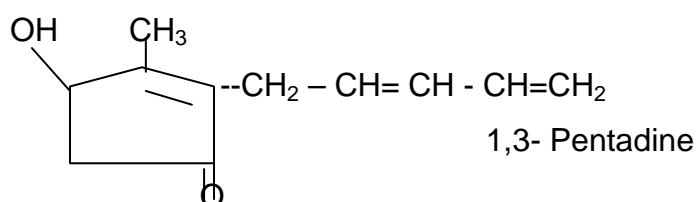


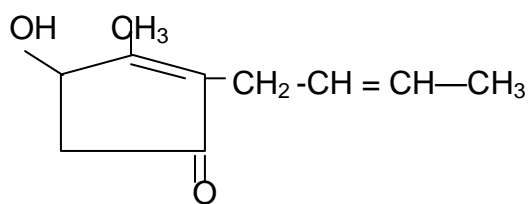
2. **Chrysanthemum Dicarboxylic Acid (CDA)** or Cyclopropane dicarboxylic acid or Pyrethric acid



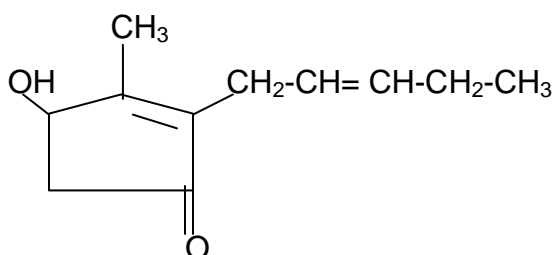
#### The alcohols are

1. **Pyrethrolone :**



**2. Cinerolone:**

2- Butene

**3. Jasmalone:**

3-Pentene

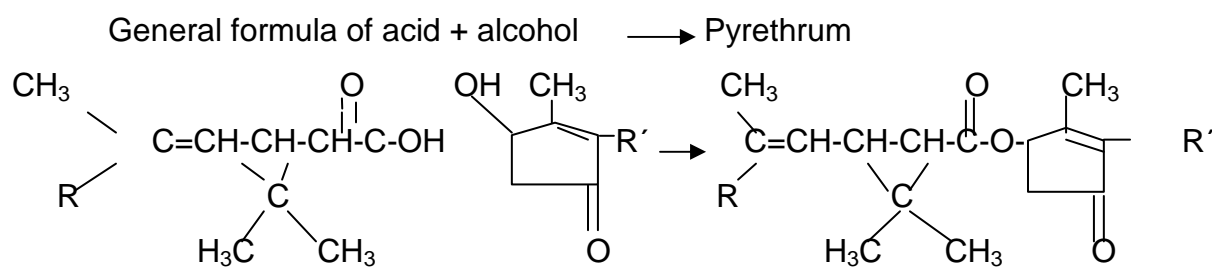
**Alcohols contains**

2. Cyclopentane ring
3. A keto group
4. A methyl group
5. A hydroxyl group
6. An aliphatic side chain

An ester is formed by the reaction between an organic acid and an alcohol

**General structure of pyrethrum esters:**

S.No.	Ester	R	R1
1	Pyrethrin -I	CH <sub>3</sub>	-CH <sub>2</sub> .CH=CH .CH= CH <sub>2</sub> (1,3 pentadiene)
2	Pyrethrin-II	COOCH <sub>3</sub>	-----do-----
3	Cinerin -I	CH <sub>3</sub>	-CH <sub>2</sub> .CH=CH .CH <sub>3</sub> ( 2 butene)
4	Cinerin -II	COOCH <sub>3</sub>	-CH <sub>2</sub> .CH=CH .CH <sub>3</sub> ( 2 butene)
5	Jasmolin -I	CH <sub>3</sub>	-CH <sub>2</sub> .CH=CH. CH <sub>2</sub> .CH <sub>3</sub> ( 3 pentene)
6	Jasmolin-II	COOCH <sub>3</sub>	----- do-----

**Another way of representing esters of pyrethrum is**

S.No.	Ester	Acid	Alcohol
1	Pyrethrin -I	Chrysanthemic acid	Pyrethrolone
2	Pyrethrin -II	Pyrethric acid	---do-----
3	Cinerin -I	Chrysanthemic acid	Cinerolone
4	Cinerin-II	Pyrethric acid	Cinerolone
5	Jasmolin -I	Chrysanthemic acid	Jasmolone
6	Jasmolin-II	Pyrethric acid	Jasmolone

### Properties of pyrethrum:

1. It is an amber coloured viscous liquid
2. Insoluble in water but soluble in organic solvents
3. It is non-volatile, hence non-fumigant action.
4. Being an ester, it is easily decomposed by acid, alkali or even by moisture on long standing to produce primary constituents.
5. On prolonged storage, pyrethrum loses its insecticidal action due to degradation by oxidation .Hence; antioxidants like hydroquinolene are added to increase the life.
6. An exposure to sunlight, it is degraded to nontoxic products in no time i.e., highly photodegradable. This is what restricts the use of natural pyrethrum in out door agriculture.

### Insecticidal action:

- Pyrethrins are more toxic than cinerins and Jasmolins .Cinerins are however, better knock down agents.
- The toxicity of pyrethrum can be increased by the addition of non –toxic substances called synergistics such as piperonyl butoxide, sesamin , sesamex etc.,
- Pyrethrum affects the Central Nervous System of insects.
- It is relatively safe for mammals .LD50 value for rats is **570** mg/Kg body weight (oral) and 1880 mg /Kg body weight(dermal)

### NEEM

Neem, ***Azadirachta inidaca* A.Juss** is grown throughout India, since time immemorial , it is a very useful plant and utilized in diverse ways .

The interest of entomologists towards the use of neem in pest management arose with the discovery of **Pradhan et al (1963) who reported** the extraordinary **anti feeding** property of neem seed kernel against desert locust. Now there is a global attention for the use of neem for pest control.

Although, all parts of the neem tree are biologically active but the highest activity could be seen in seed kernel. Havie et al (1967) were first to report the isolation of **teriterpenoid alcohol** (Meliantriol ) from the fruits of Dharek (*Melia azedarach*) and neem which inhibits the feeding of desert locusts.

Butterworth and Morgan (1968) isolated **tetranotriterpinoid, azadirachtin** from neem seed kernel, which is stronger inhibitor than Meliantriol.This is also present in the leaves of neem and also in fruits of neem

Henderson et al (1964) isolated **salanin** from neem and was found poor feeding deterrent

Kraus et al (1980) isolated

- |                          |   |                |
|--------------------------|---|----------------|
| a) Diacetyl vilasinin    | } |                |
| b) 3 – desacetyl salanin | } | From Neem Seed |
| c) Nimbandiol            | } |                |
| d) Salannin              | } |                |

Thus , Neem owes its toxic attributes due to the presence of **azadirachtin , Melantriol, Salannin , Nimbandiol , Diacetyl vilasinin etc.**, Among which azadirachtin is more potent .

Neem seed contains 0.2 to 0.3 % azadirachtin .Neem has diverse affect on insects such as

1. Feeding deterrent
2. Growth disruptor
3. Repellant
4. ovispositional deterrent
5. Insecticidal etc.,

In few insects hatchability and reproduction are impaired .Pest resurgence has not been in neem treated plots. Insects cannot develop resistance to neem compounds as they contain a number of bioactive principles.

Azadirachtin, causes disorders in metmorphosis. In some insects when neem seed extract mixed with food caused growth inhibition, mal formation, mortality and reduced fecundity . Neem seed extraction at 12 percent concentration has been found as potential anti feedant for brown plant hopper.

Neem has systemic activity , non phytotoxic remain active in plants up to 25 days .Neem products are highly degradable (photo) residual action of neem can be increased by the addition of adsorbents . It has no adverse effect on the environment and have no toxic residue in the harvested agro - commodities.

**Neem products** : Nimbecidine , Neemgaurd, Neemplus , Neemrich, Cropgaurd, Neemostar, Azadit-20, Radon, Jawan, ,Neem mark, Navagaurd, ,Margosol, nemidin

### **SYNTHETIC PYRETHROIDS**

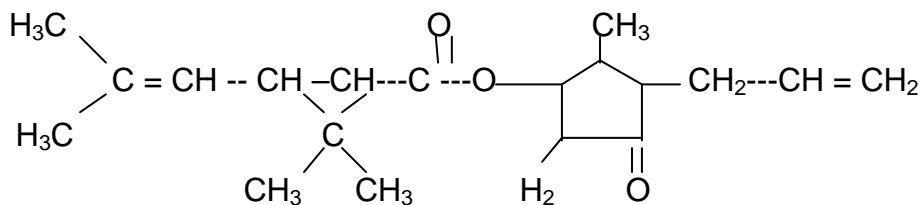
These are 4<sup>th</sup> generation insecticides .The unstable nature of pyrethrum, coupled with the establishment of structure of pyrethrum. Many workers stimulated their research on synthetic pyrethroids. Synthetic pyrethroids are more stable than many of the organic phosphorus compounds and carbamate insecticides .These are insecticidally more active than others.

1. Synthetic pyrethroids are viscous, lypophilic liquids, insoluble in water,
2. Biodegradable,
3. Have low mammalian toxicity,
4. Don't leave any residues in biological systems and cause less contamination to the environment.
5. Cause less contamination to the environment.

## 1. ALLETHRIN / DIVINYL PYRETHRIN -I (DVP-I)

It was introduced with trade name **pynamin**. It is also called as divinyl pyrethrum -I. This was the first synthetic pyrethroid. This was first reported by **LAFORGE&SCHECHTER**. It is a pale yellow oil sparingly soluble in water, soluble in organic solvents. It has a more stable side chain than pyrethrins. It is more persistent and contact insecticide effective against houseflies, mosquitoes, but less effective against household pests.

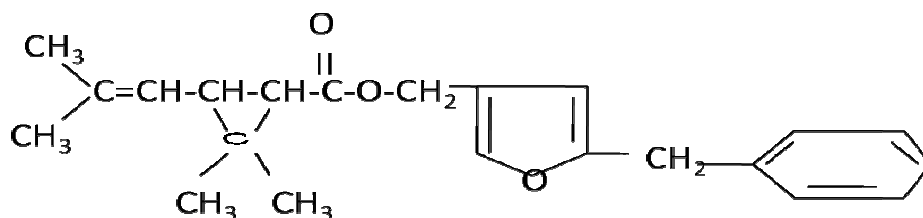
It is an allyl analog of pyrethrin -I.



2-methyl-4-oxo-3(2-propenyl)-2 cyclopentane-1-cis trans -3(2,2-dimethyl vinyl-2,2-dimethyl cyclopropane-1-carboxylate.

## 2. BIORESMETHRIN

- First synthesized at Rothemsted Experimental station (1966)
- CMA+5 Benzyl furyl 3 methanol



More toxic(50 times) than to natural pyrethrum(house flies)

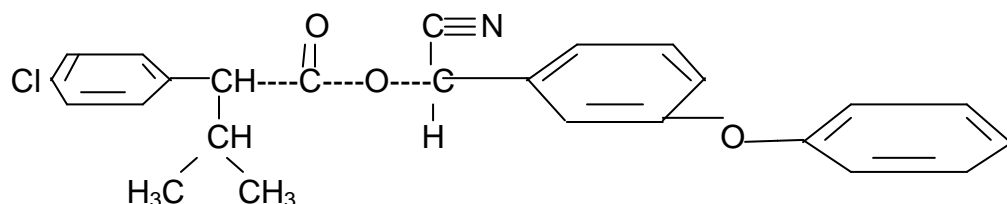
LD<sub>50</sub> = 7070 mg - 8000mg / kg body weight

## 4. FENVALERATE /SUMICIDIN/ FEN FEN/ FENVOL

Synthesized by Sumitomo chemical company of Japan

### Properties:

1. It is a viscous yellow liquid, less soluble in water. More soluble in organic solvents
2. It is thermally stable, more stable in acid medium than in alkaline medium.
3. It is a contact and stomach poison.
4. It is effective against cotton boll worm, lepidopteron larvae and used in public health management and animal husbandry.
5. It is a cyanide containing synthetic pyrethroids



α-cyano-3-phenylbenzyl-s-isopropyl-p-chlorophenyl acetate



## 5. PERMETHRIN

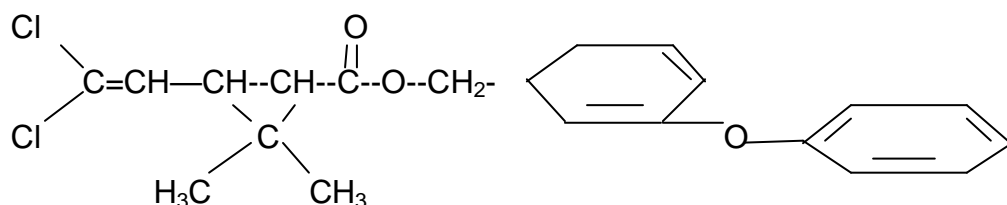
Trade names AMBUSH, TALCORD, KALFIL

This was first reported by MICHEAL ELLIOTT.

### Properties:

It is a yellowish brown liquid, highly viscous, insoluble in water, highly soluble in organic solvents.

- Stable to heat , more stable in acid than in alkaline medium .
- It is a contact insecticide
- It has good residual activity
- It has low mammalian toxicity
- It is very effective against lepidopterous larvae and used in live-stock management .



$\alpha$ -3 phenoxy benzyl ( $\pm$ ) cis trans -3(2,2-dichlorovinyl-2,2-dimethyl-cyclopropane-1-carboxylate)

Synthetic pyrethroid containing two chlorine atoms is Permethrin, one chlorine atom is Fenvalarate.

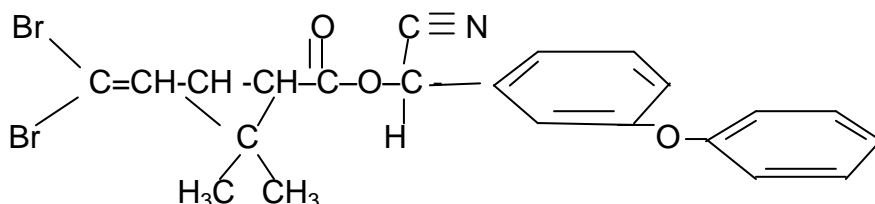
## 4. DECAMETHRIN/DELTA METHRIN / DECIS

This was first introduced by " ROUSSEL UCLAF " and reported by MICHAEL ELLIOTT.

This is bromine and cyanide containing synthetic pyrethroid.

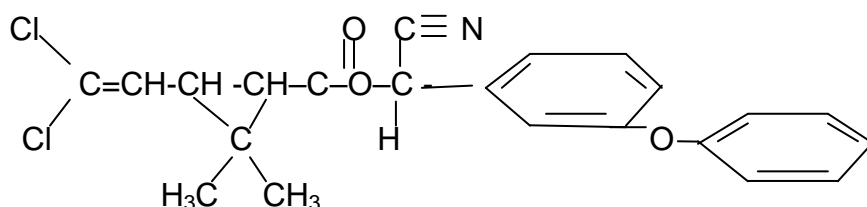
### Properties:

1. It is a colourless crystalline powder.
2. It is stable having no degradation even after 6 months.
3. It is insoluble in water. Soluble in organic solvents .Non-phytotoxic, proved effective against insects which are resistant to conventional pesticides.
4. It is not effective against mites.



## 5. CYPERMETHRIN/CYMBUSH/ RIPCORDER/BARRICAD

Dichloro CMA + Cyano-3- Phenoxy benzyl alcohol



**Lecture: 24** Synthetic organic insecticides – Cyclodiene –Diels- Alder reaction – structure , properties

### ORGANO CHLORINE INSECTICIDES

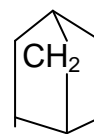
The organo chlorine insecticides are classified into two categories

1. **Chlorinated Hydrocarbons** Eg. DDT, BHC, Methoxy chloar, Lindane
2. **Cyclodiene compounds** Eg. Aldrin , Dieldrin, Endrin, Endosulfan

### CYCLODIENE INSECTICIDES

#### Major characteristics:

1. These are polychlorinated compounds
2. Must contain at least one bicyclic ring
3. Must contain at least one Endomethylene bridge
4. prepared by Diels Alder Additive Reaction
5. HCCP (Hexa Chloro Cyclo Pentadiene) is the basic raw material required for their synthesis.
6. Highly persistent
7. Very effective contact insecticide



#### Disadvantages:

1. Highly toxic to mammals
2. Long persistence in the environment

DIENE: An alkene that has two double bonds in its molecules.

CONJUGATED DIENE: The compound in which the two double bonds are separated by one single bond.

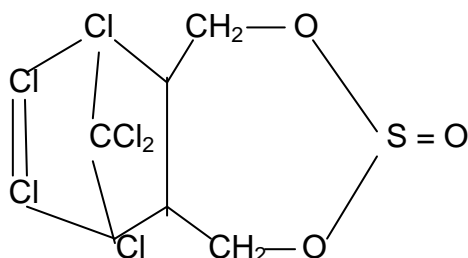
Eg. 1,3 Butadiene ,  $\text{CH}_2=\text{CH} - \text{CH}=\text{CH}_2$

#### DIELS –ALDER REACTION:

A type of chemical reaction in which a conjugated diene adds to a suitable compound containing one double bond (dienophile) to give a ring compound .It is named after the German chemist **OTTO DIELS & KURT ALDER** who discovered it 1928.

#### ENDOSULFAN /THIODAN

An important cyclodiene insecticide used very extensively.

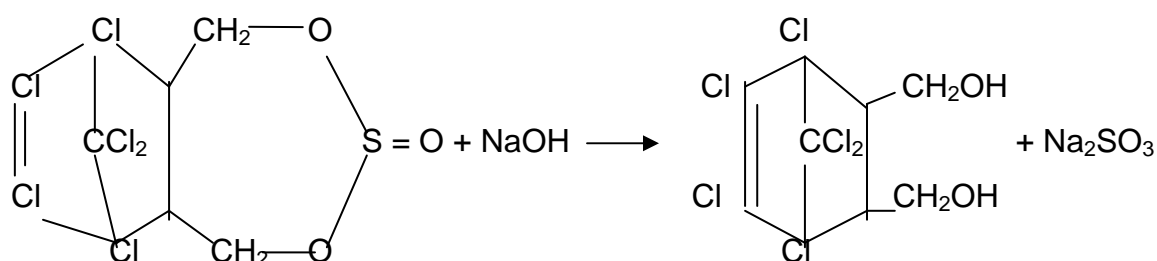


6,7,8,9,10,10- hexa chloro –1,5,5a,9,9a- hexa hydro 6,9 methano-2,4,3,-benzo dioxo thiepin -3- oxide.

**Properties:**

1. It is a mixture of two isomers  $\alpha$  and  $\beta$  in 4:1 ratio.
2. Technical grade is an amorphous powder.
3. It is insoluble in water but soluble in most of non-polar organic solvents.
4. Readily decomposed by alkali to form endosulphan alcohol and inorganic sulphite .

Reaction:



5. It is a stomach and contact poison
6. It is highly toxic to mammals with an LD<sub>50</sub> value 40-110 mg/kg body weight.
7. Formulated as dust , granules etc.,
8. It is metabolized to sulphate in the metabolism of insects, plants and animals.

**Mode of Action of cyclodiene compounds:**

They inhibit the activity of Respiratory enzymes. This leads to disruption of oxidative phosphorylation. The symptoms of poisoning in insects are:

1. Hyper sensitivity,
2. Hyper activity
3. Violent burns and
- 4 .Collapse of insects finally.

**Lecture: 25** Organo phosphorus insecticides – Discovery – Advantages – Classification – Mode of action .Structure , properties and uses of Dichlorvos (DDVP)

### **ORGANO PHOSPHORUS INSECTICIDES**

Organo phosphorus compounds constitute a variety of Agrochemicals and as a group they rank first in consumption .They were discovered as toxic nerve gases by the defence labs of Germany during II World war. Insecticidal properties of organo phosphorus compounds were identified by GERHARD SCHRADER (1937) .These also act as Acaricides, Nematicides, Defoliant and Desiccants .These are good substitute for Nicotine.

#### **Advantages of organo phosphorus compounds:**

1. These are required in very small quantity.
2. These are quickly decomposed leaving no toxic residues
3. These are very quickly metabolized in vertebrates and tendency to be excreted.
4. These have wide insecticidal spectrum.
5. Some of these are systemic in nature
6. Some do have Nematicidal action in addition

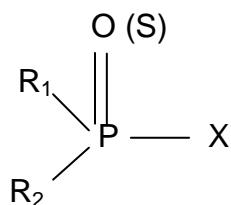
#### **Classification of organo phosphorus compounds:**

1. Derivatives of phosphoric acid ( $H_3PO_4$ ) :  
Eg. DDVP(Dimethyl dichloro vinyl phosphate) or Dichlorvos or Nuvan  
Phosphomidan (Dimecron)
2. Derivatives of thiophosphoric acid ( $H_2PO_3S$ ):  
Eg. Methyl parathion, Parathion, Diazinon, Dursaban
3. Derivatives of dithiophosphoric acid ( $H_2PO_2S_2$ ):  
Eg. Malathion, Phasolone(zolone), Phorate (Thimmet)
4. Derivatives of pyrophosphoric acid Eg.  
Eg. TEPP (Tetra Ethyl Pyrophosphate), Pestox –III, Sacradan
5. Derivatives of phosphorous acid  
Eg. Falone

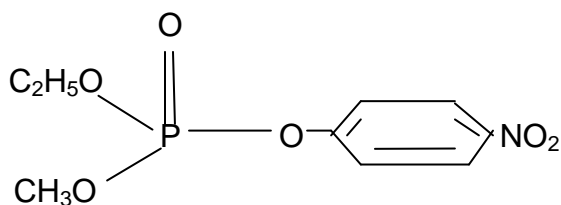
#### **Mode of action of organo phosphorus (O.P.) insecticides:**

Acetyl choline esterase is a key enzyme of nervous system and is responsible for hydrolyzing acetyl choline to acetic acid and choline .By doing so, the enzyme helps in carrying nerve impulses to brain. When O.P. insecticides are applied ,the central phosphorus atom of O.P. insecticides phosphorylates the active site of acetyl choline esterase enzyme and inhibits the enzyme activity .As a result acetyl choline cannot be hydrolyzed to acetic acid and choline to carry nerve impulses to brain .Thus O.P. insecticides disrupt the nervous system in susceptible animals and insects.

General structure of O.P. insecticides:



Where  $\text{R}_1$  and  $\text{R}_2$  are short chain alkyl groups ( $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ) or alkoxy ( $\text{CH}_3\text{O}$ ,  $\text{C}_2\text{H}_5\text{O}$ ) or alkyl thio ( $\text{CH}_3\text{OS}$ ,  $\text{C}_2\text{H}_5\text{OS}$ ) groups and X is any labile group which will be metabolized *in vivo*

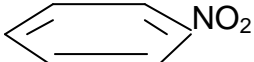


Ethyl Methyl Parathion

Where ,

$\text{R}_1$  is  $\text{C}_2\text{H}_5\text{O}$  (Ethoxy)

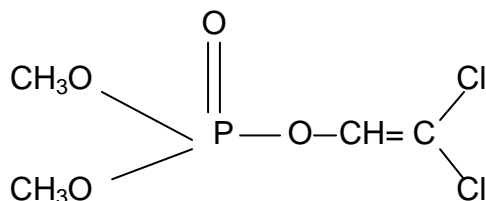
$\text{R}_2$  is  $\text{CH}_3\text{O}$  (Methoxy)

X is 

## 1. DERIVATIVES OF PHOSPHORIC ACID:

Most of the derivatives of phosphoric acid insecticides are vinyl esters of the acid

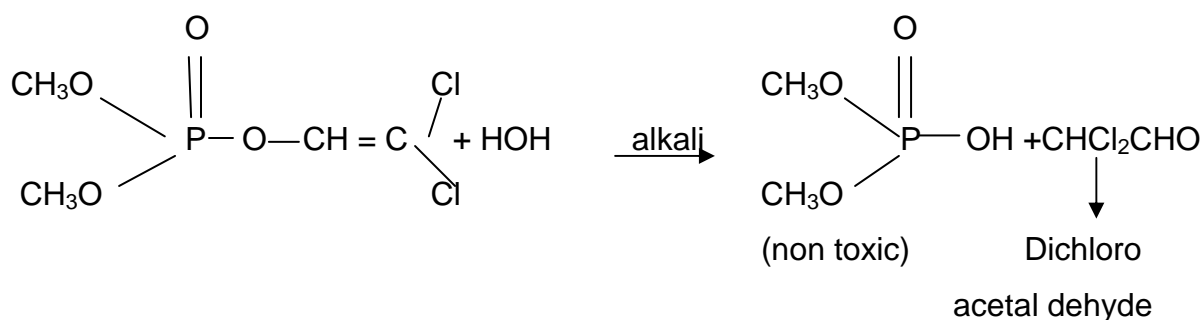
### A) DDVP/ Dichlorovos / Nuvan



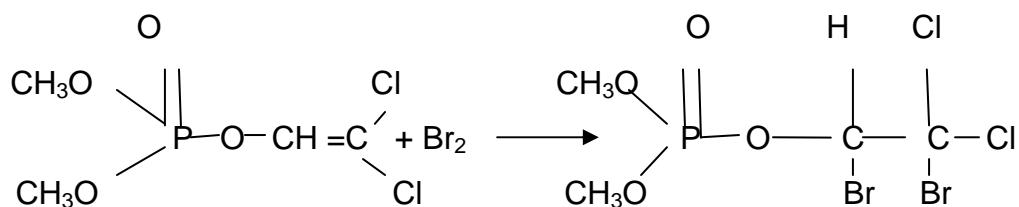
O, O, di methyl O-2,2-dichloro vinyl phosphate .This was introduced in 1955.

### Properties:

1. It is a colourless liquid
2. It is moderately volatile and does have considerable fumigant action
3. It is water soluble to the extent of 1 % but highly soluble in organic solvents.
4. It is stable to light and heat .However in the presence of water it gets hydrolyzed to form Dimethyl phosphoric acid (DMPA). This acid acts as a catalyst for further degradation of DDVP .That is why DDVP is formulated with 2 to 4 % epichlorohydrin.



- The degradation products of DDVP are quickly lost by further decomposition. Thus, use of DDVP poses no residue hazard.
- DDVP has a vinylic double bond and responds to addition reaction with halogens or hydrogen particularly with bromine. With bromine it reacts as follows.



(O,O- dimethyl-O-1,2 dibromo-2,2-dichloro ethyl phosphate)

Incidentally, this compound is also an effective insecticide and sold as Naled or Dibrom

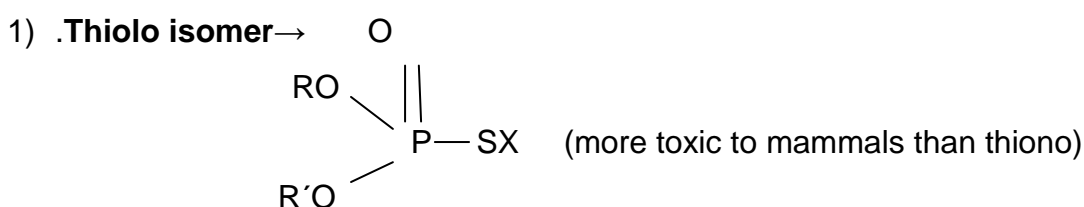
- It is a contact and stomach poison - Suitable for the control of sucking insects, flies and mosquitoes etc.,
- It is moderately toxic to mammals with a L.D.<sub>50</sub> value of 80 mg/kg body weights of rats.

**Lecture: 26** Thiophosphoric acid derivatives –Thiolo and thiono isomers . Structure and activity relationships of thiophosphoric acid derivatives, structure, properties and used of Methyl parathion.

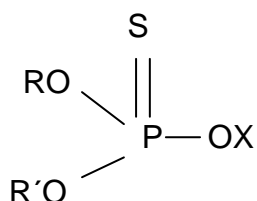
### DERIVATIVES OF THIO PHOSPHORIC ACID AND INSECTICIDES

Replacement of one 'O'(oxygen) atom by 'S' , in the phosphoric acid derivatives produces thiophosphoric acid insecticides with such replacement, the mammalian toxicity is decreased markedly but the insecticidal toxicity remains unaltered more or less.

As insecticides, thiophosphoric acid derivatives are of two types



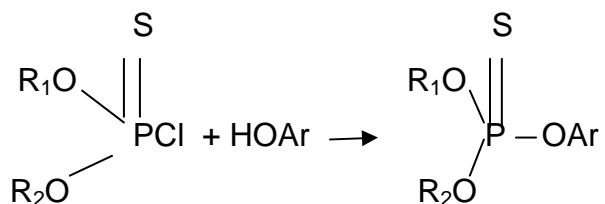
2) **.Thiono isomer**→



- Thiolo isomers are more toxic than Thiono isomers.
- Thiono isomers can be converted to Thiolo isomers (Isomerisation) by heat and by chemical reagents or by oxidase enzymes.
- Conversion is called as "PISCHEMEUKA" rearrangement.

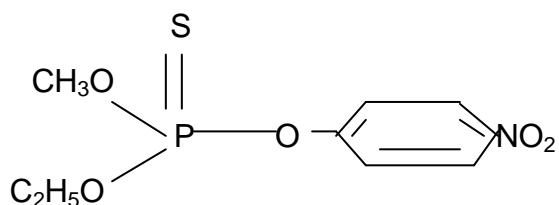
Structure, Activity Inter Relationship Of Thiophosphoric Acid Derivatives

Most of the insecticides of thiophosphoric acid derivatives are mixed esters of formula



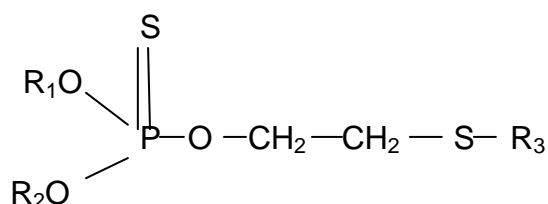
Where  $\mathbf{R}_1$  and  $\mathbf{R}_2$  are short chain alkyl groups and  $\mathbf{Ar}$  is aromatic nucleus.

Eg.

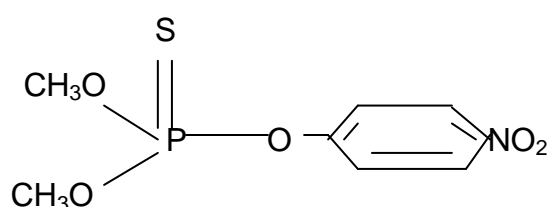


**Methyl Ethyl Parathion**

1. Most effective insecticides are those in which both  $R_1$  and  $R_2$  are aliphatic radicals and the total number of C atoms in  $R_1$  and  $R_2$  put together does not exceed 4
2. If both  $R_1$  and  $R_2$  are methyl groups  $\rightarrow$  minimum insecticidal activity  
If  $R_1$  is methyl and  $R_2$  is Ethyl  $\rightarrow$  medium insecticidal activity  
If  $R_1$  and  $R_2$  are Ethyl groups  $\rightarrow$  maximum insecticidal activity
3. Both insecticidal activity and mammalian toxicity are increased remarkably, if a nitro ( $-\text{NO}_2$ ) group is introduced in 4<sup>th</sup> or para position of the aromatic ring.
4. Introduction of same nitro ( $-\text{NO}_2$ ) group in second and third position of the aromatic ring decreases the insecticidal activity markedly.
5. Introduction of another group (besides  $-\text{NO}_2$  group at 4<sup>th</sup> position) into the aromatic ring decreases insecticidal activity, while mammalian toxicity decreases considerably.
6. Introduction of three or more groups, into the aromatic ring decreases both insecticidal activity and mammalian toxicity.
7. If at all, a second group is to be introduced it should be introduced only in third position of the aromatic ring .
8. Introduction of other groups like cyano ( $-\text{C}\equiv\text{N}$ ) or sulfoxide ( $\text{S}=\text{O}$ ) or Sulfone ( $\text{O}=\text{S}=\text{O}$ ) in fourth position also exhibits increased insecticidal activity but the mammalian toxicity is also increased dangerously, often prohibiting their use.
9. Some times, the replacement of aromatic ring by heterocyclic ring also produces very effective insecticides like dursaban and diazinon.
10. Most of the compounds with the following formula are systematic insecticides.



### Methyl Parathion /Metacid /Folidol-80



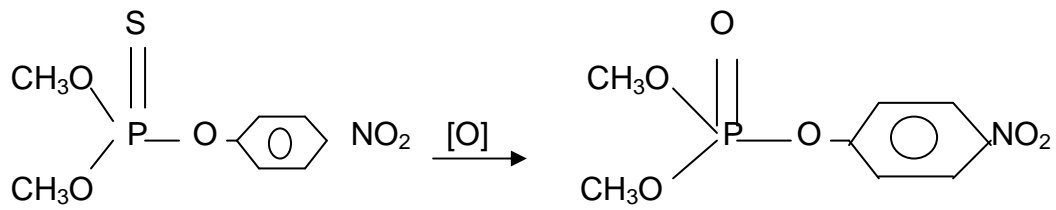
Chemical name: O,O – dimethyl O-4-nitrophenyl thiophosphate

#### Properties:

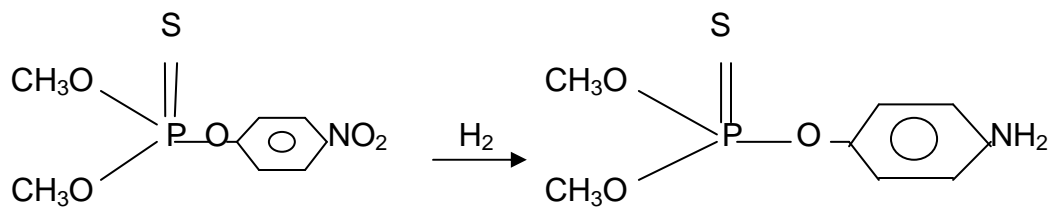
1. It is a white crystalline substance.
2. Its water solubility is only 55 mg / l, highly soluble in organic solvents.
3. It is quickly hydrolyzed in alkaline medium to produce 4- nitrophenol (yellow coloured) as an important product to determine the purity of methyl parathion.



4. Oxidizing agents and oxidase enzymes oxidise the P=S groups to P=O forming methyl paraoxone which is more toxic than methyl parathion.



5. Reducing agents reduce the nitro group [NO<sub>2</sub>] to [NH<sub>2</sub>] group making the compound non-toxic.



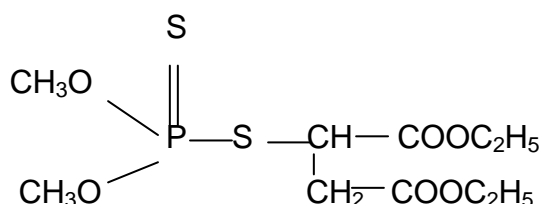
6. Methyl parathion is an effective alkylating agent and alkylates a number of biochemical substances such as amines and thiourea. Most of the compound is lost by methylation before it reaches the enzyme acetyl choline esterase. This explains the low mammalian toxicity of methyl parathion.
7. It is relatively safe compound for mammals
8. Formulated as EC and dusts

**Lecture:27** Dithiophosphoric acid derivatives – structure, properties and uses of Phorate and Malathion

### DITHIOPHOSPHORIC ACID INSECTICIDES

In the change from Thiophosphoric to dithiophosphoric acid derivative insecticides, the toxicity of the compounds decreases, but chemical stability of the compounds increases.

#### 1. Malathion / Carbophos

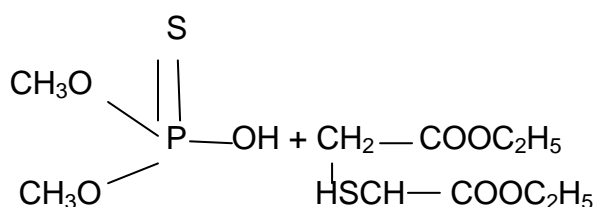


Chemical name: O, O dimethyl –S-1, 2 dicarboethoxy ethyl dithiophosphate

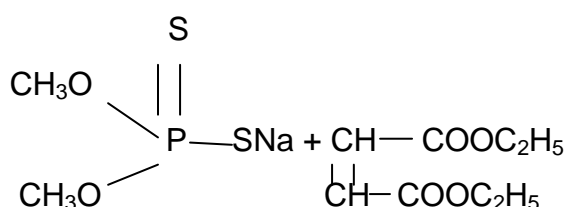
#### Properties:

1. Colourless liquid
2. Almost water soluble, but soluble in most of organic solvents.
3. It is moderately volatile and does have fumigant action.
4. It is hydrolyzed in both acidic and alkaline medium but in different direction.
5. In insects, it is oxidized by oxidases to form the more toxic malaoxon

In acid medium, the products are dimethyl thiophosphoric acid and diethyl mercapto succinic acid.



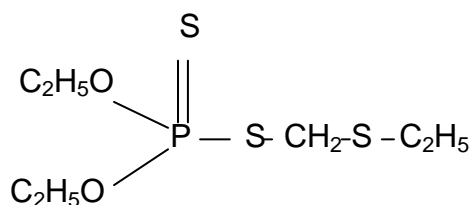
In alkaline medium, the products are dimethyl dithio –phosphoric acid and diethyl furmerate.



But in vertebrates, it is detoxified by loss of ethyl groups to form malathion acid which is non toxic, that's why it is safe for mammals.

6. Malathion is moderately persistent i.e., 20 days
7. It is a general purpose contact insecticide
8. It is one of the safest insecticides .L.D.50 value is 500-1500 mg /kg body weight .Its use thus permitted in live-stock management, public health, house hold and storage.

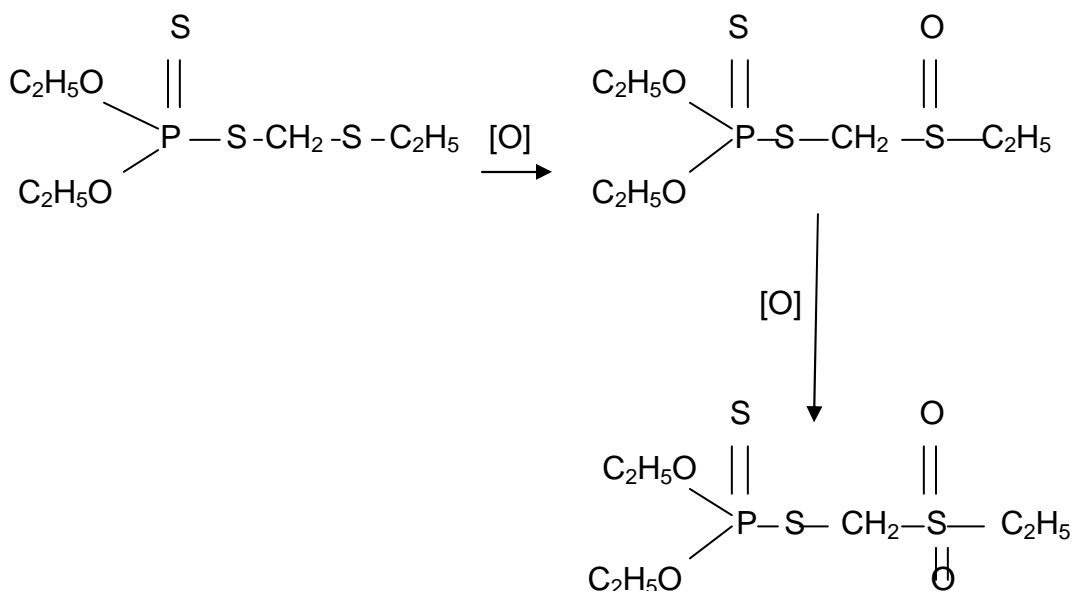
## 2. Phorate (Thimet)



Chemical Name: O, O- diethyl -S- (ethyl thio methyl) dithiophosphate.

### Properties:

1. It is transparent oil.
2. Almost water insoluble but soluble in organic solvents.
3. It is slightly volatile and does have an unpleasant odour
4. In alkaline medium, it is rapidly hydrolyzed to form the respective acid and alcohol.
5. Phorate is oxidized to its sulphoxide and sulphone. Both are more toxic and more persistent than phorate. The reaction takes in dry soils and explains the relatively long life of phorate in soils.



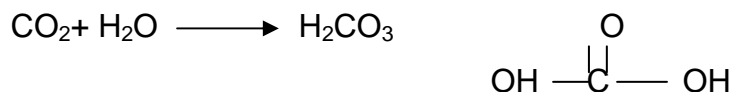
6. Phorate is a very effective systemic insecticide. Very suitable for the control of chewing and sucking insect pests. It is used also as a nematicide.
7. It is extremely toxic for mammals. L.D. 50 is 1.1 to 2.3 mg/kg.
8. Phorate is formulated mainly as granules (10 G)

**Lecture: 28** Carbamate insecticides –Chemistry, discovery and mode of action, structure, properties and uses of Carbofuran

### CARBAMATE INSECTICIDES

In production and consumption, this rank - II, apart from the insecticides, this act as fungicides, herbicides and acaricides .Eg. Carbaryl, Carbofuran, Aldicarb etc.,

Carbamates are the derivatives of carbamic acid, may be considered as molecule of urea in which an amine (NH<sub>2</sub>) group is replaced by a OH group (or) a molecule of carbonic acid in which OH group is replaced by a NH<sub>2</sub> group.

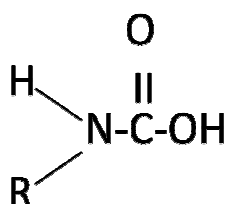


Carbamates are in fact esters of carbamic acid. Carbamic acid can be esterified by either aliphatic or aromatic alcohol forming alkyl or aryl carbamates.

Further, one or two H atoms of the NH<sub>2</sub> group may be replaced by aliphatic or aromatic radicals i.e., N-alkyl or N- aryl carbamates.

In general, N-alkyl aryl carbamates are good insecticides

General structure of Carbamate:



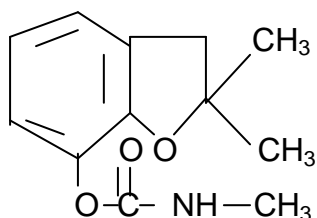
Where R is alky radical like CH<sub>3</sub>,  
C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub> etc.,

Ar- is aromatic radical like phenyl,  
Naphthyl etc.,

N-alkyl aryl carbamate

### Carbofuran /Furadon

It is very effective systemic insecticide and very suitable as a soil insecticide .It is also used as nematicde.

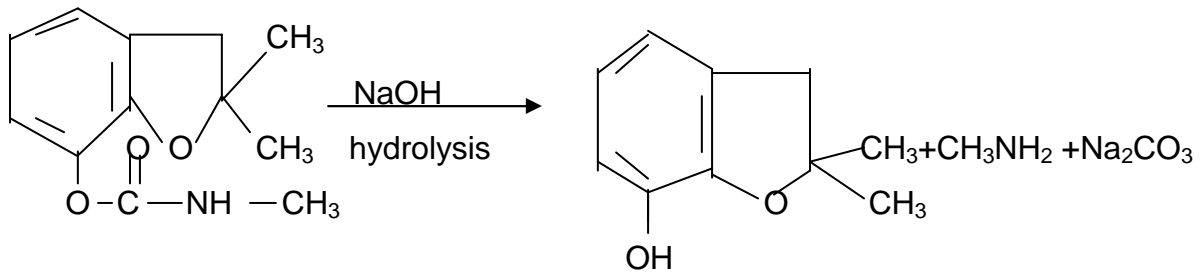


Chemical name: (2,2-dimethyl 2,3-dihydro benzofuranyl- 7-N-methyl carbamate)

### Properties:

1. It is a white crystalline substance.
2. Poorly water soluble, but soluble in organic solvents.

3. Somewhat stable in neutral and slightly acidic medium, but readily decomposed in alkaline pH, when the ester bond is readily degraded to produce the alcohol (2,2-dimethyl-2,3-dihydrobenzofuranol) and methylamine



It is thus not compatible with alkaline agricultural materials like, lime or Bordeaux mixture. Hence, it should not be mixed with agricultural chemicals of alkaline nature

4. Carbofuran is highly toxic for mammals. L.D.50 value for Rats is 5 mg /kg body weight.
5. It is formulated as granules (3G).
-

**Lecture: 29** Fungicides –Definition –Systemic and non –systemic –Classification of fungicides based on chemical nature with examples –structure and properties and uses of copper oxy chloride and Zineb

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## FUNGICIDES

Fungicide is a chemical substance that has the ability to kill fungi and is thus an antifungal substance. Some fungicides act on the “surface” near the site of application and these fungicides are called non-systemic fungicides.

A systemic fungicide is a fungi toxic compound which when applied to any part of the plant is absorbed by plant tissues and is translocated either upward or downward or both and exert toxicity in the fungi directly or indirectly through its metabolite at a site away from its application .

### Classification of fungicides

#### I. Based on the chemical nature

##### 1. Sulphur containing fungicides :

A). Inorganic: Eg .Lime sulphur; powdered sulphur

B). Organic: Eg. Zineb, Maneb, Thiram and Vapam

##### 2. Copper containing fungicides:

Eg. Bordeaux mixture [ $\text{Ca}(\text{OH})_2 + \text{CuSO}_4$ ]

Eg. Burgundy mixture [ $\text{CuSO}_4 + \text{Na}_2\text{CO}_3$ ]

Eg. Cheshnut compound [ $(\text{NH}_4)_2\text{CO}_3 + \text{CuSO}_4$ ]

##### 3. Mercury containing fungicides:

A). Inorganic: Eg. Hg Cl (Mercurous chloride or Calomel)

Hg Cl<sub>2</sub>( Mercuric chloride)

B) .Organic: PMA (Phenyl Mercuric Acetate)

EMC (Ethyl Mercuric Chloride)

##### 4. Quinones : Chloranil ; Dichlone

##### 5. Heterocyclic nitrogenous compounds : Captan , Captafol, Folpet

##### 6. Benzimidazoles: Eg. Carbendazim, Thiobendazole, Benomyl

##### 7. Oxanthins: Eg. Carboxin ; Oxycarboxin

##### 8. Morpholines: Tridemorph ; Dodemorph



##### 9. Thiophanates:

These are derivatives of thio aliphatic acid [ $\text{H}_2\text{N}-\text{C}-\text{NH}-\text{COOH}$ ]

Eg. Topsin and Topsin -M

##### 10. Organophosphorus fungicides: Kitazin; Hinosan

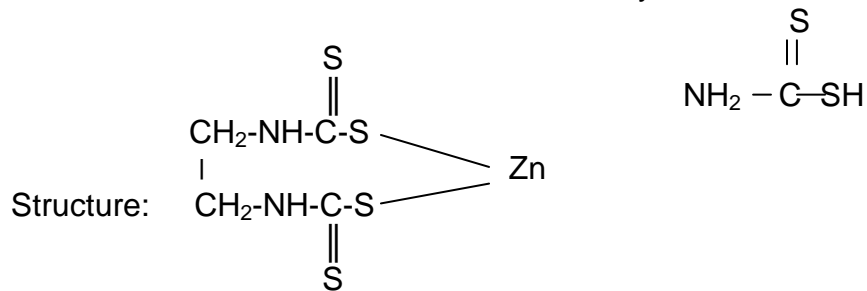
##### 11. Pyrimidines : Ethrimol, Dimethrimol; Triarimol

##### 12. Miscellaneous : PCNB(Penta Chloro Nitrobenzene)

##### 13. Antibiotics: Streptomycin, Cycloheximide, Chloroneb, Triphenyl acetate

## 1. ZINEB

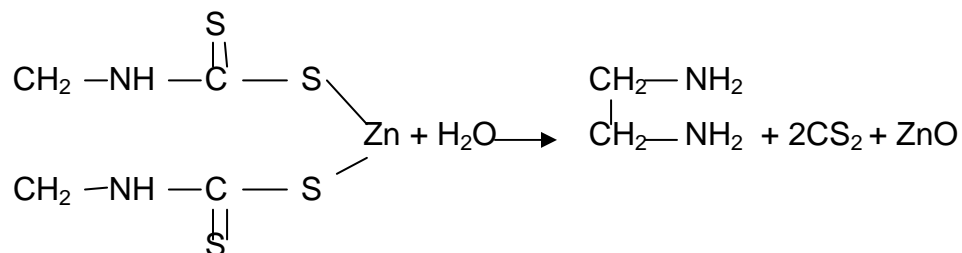
Chemical Name: Zinc ethylene bis dithiocarbamate



This is a widely used 'S' containing fungicide

### Properties:

- It is a white crystalline substance, decomposes before melting point which is usually between 140 and 160 °C
- It is insoluble in water as well as organic solvents, but highly soluble in pyridine.
- Zineb containing 74 % moisture, under unfavourable conditions, may decompose with the evolution of explosive CS<sub>2</sub>. So it should be stored in well ventilated place at low temperature.



- Zineb breaks down in the plants, within 10-15 days of its application, resulting in the formation of volatile products like ZnSO<sub>4</sub>, which is used as a source of micronutrient zinc.
- Its L.D.<sub>50</sub> value is 2000 to 5000 mg /kg or 2-5 grams per kg body weight.

## 2. COPPER OXY CHLORIDE/ BLITOX/FYTOLAN

{It is the most widely used copper based fungicide}

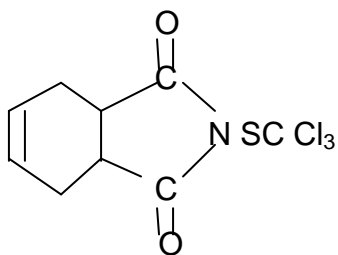
Copper oxy chloride: Cu (OH)<sub>2</sub>. Cu Cl<sub>2</sub>

### Properties:

1. It is a green coloured powder, insoluble in water
2. It is mixture of cupric hydroxide and cupric chloride
3. It is marketed in the form of Wettable Powder containing 88 % COC which is equivalent to 50 % copper.

**Lecture: 30** Structure, properties and uses of Carbendazim, Captan, Carboxin and tridemorph .

### 3. CAPTAN



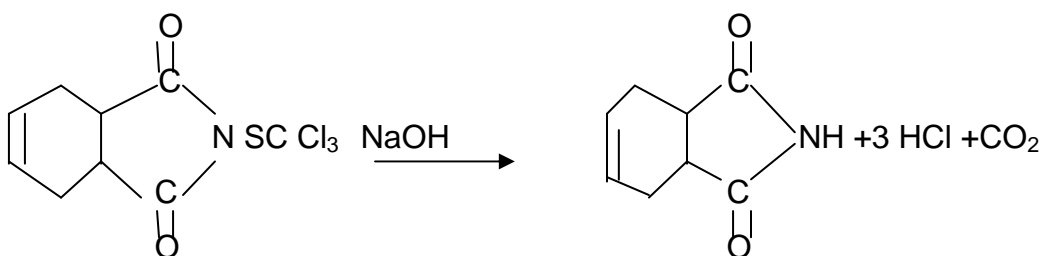
N-Tri chloro methyl thio tetra hydro phthalamide

$\text{SCCl}_3 \rightarrow$ thio phosogene group responsible for fungicidal action of the compound.

This is a widely used, broad spectrum protective fungicide and used as seed dresser and also for seed disinfection. It is a heterocyclic nitrogenous compound

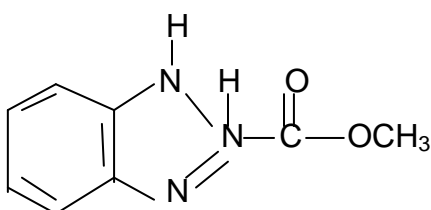
#### Properties:

1. It is a white crystalline substance, almost odourless.
2. It is insoluble in water (slightly) and most soluble in organic solvents .
3. Capton is hydrolyzed particularly in alkaline medium. That's why it should not be mixed with agricultural chemicals of alkaline nature



4. L.D.<sub>50</sub> value is 9000 mg /kg or 9 grams per kg body weight .

### 4. CARBENDAZIM / MBC



Chemical name: 2 methyl benzimidazole Carbamate

It is a potent broad spectrum, systemic fungicide against powdery mildew and soil borne fungi, but ineffective against phycomycetes.

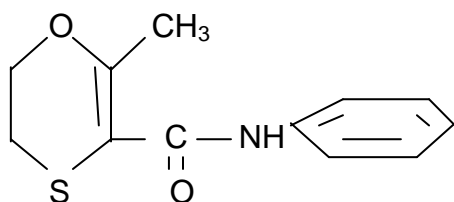
#### Properties:

- It is a whitish grey powder with a faint acid odour
- It is insoluble in water, slightly soluble in organic solvents but highly soluble in acetic acid.
- Carbendazim is stable even at 50 °C for a period of two years. But in alkaline medium it decomposes rapidly.



- The fungi toxicity of Carbendazim is clearly due to benzimidazole nucleus. It exerts its toxicity by inhibiting fungal DNA synthesis or Cell division or nuclear division. The interference with DNA synthesis is probably due to structural similarity with purine bases namely Guanine and Adenine.
- Its L.D.50 Value is 6400 mg /kg body weight.

### 5. CARBOXIN /VITAVAX

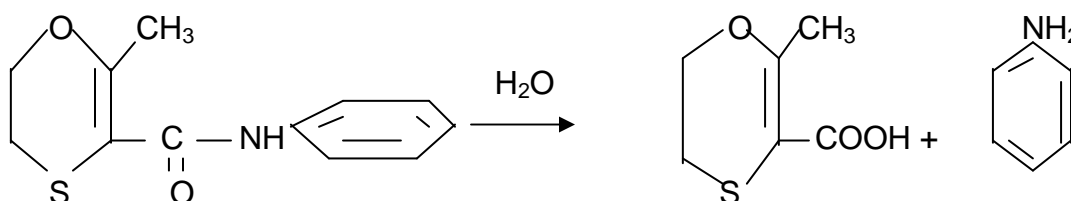


Chemical name: 2,3,dihydro 6 methyl 5 phenyl carbonmyl 1,4,oxathin

It is a very effective systemic fungicide against basidiomycetes which include rust, smut and bunts of cereals. It is also used as seed dresser. It is the most widely used member of oxathin group. The other important member of the group is its sulphon analog i.e., that is oxycarboxin (Plantavax).

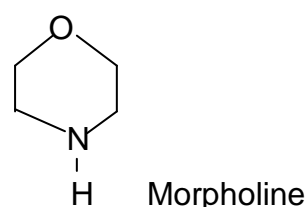
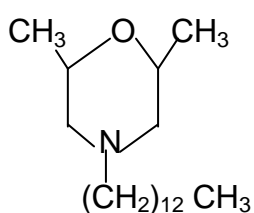
#### Properties:

- It is a white crystalline substance with two crystalline forms. One form is melted between 91.50 to 92.50 °C and another is melted between 98 and 100 °C.
- It is insoluble in water and highly soluble in inorganic solvents.
- It is oxidized in soils plants and water to the corresponding sulphoxide
- On long standing in water Carboxin is converted to corresponding carboxylic acid



- In most susceptible fungi it inhibits the activity of succinate dehydrogenase
- Its L.D.50 value is 3,200 mg/kg body weight

### 6. TRIDEMORPH/ CALIXIN



Chemical name: 2, 6 dimethyl 4 tridecyl 1,4 morphaline

It is an effective systemic, eradicant fungicide mainly against mildews and ensures long lasting protection. Replacement of tri decyl group at 4<sup>th</sup> position by a cyclic dodecyl group results in the formation of dodemorph, the other important member of this group

**Properties:**

1. It is faint yellowish liquid
2. It is immiscible with water, but miscible with organic solvents.
3. It is fairly stable compound because of the absence of very reactive functional groups in its structures .It does not degrade even for two years under normal storage
4. It has considerable fish toxicity also
5. It effects the permeability of fungal cell membranes resulting in the leakage of cellular material
6. Its L.D.50 value is 1250 mg /kg body weight.

**Lecture: 31** Herbicides –Classification of herbicides based on chemical nature with examples .Selectivity of herbicides brief nt on mode of action of herbicides (Respiration ,mitochondrial activity ,photosynthesis , protein and nucleic acid metabolism

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## HERBICIDES

### I. Classification of herbicides based on chemical nature

1. Aliphatics : Dalapon , Acrolein , TCA (Tri Chloro Acetic Acid ),  
Allyl alcohol
2. Amides and acetamides : Alachlor, Butachlor , Propanil , Diphenamid
3. Arsenicals : MAA( Methane Arsenic Acid ),  
DSMA ( Disodium Methyl Arsenate )
4. Phenyl acetates and Benzoics : Dicamba, 2,3,6 trichlorobenzoic acid
5. Carbamates : Propham , Swep, Barbam
6. Phenols : Penta chloro phenol (PCP) , Dinoseb
7. Bipyridilliums: Paraquat , Diquat
8. Triazines : Atrazine ,Simazine and Propazine
9. Triazoles : Amitrole, Amitrole – T
10. Diphenyl ethers : Nitrofen , Oxyfluorfen
11. Thiocarbamates : Benthicarb , Triallate
12. Substituted urea: Manuron ,Diuron , Metaxuron
13. Dinitroanilines : Trifluralin, fluchloralin
14. Nitriles : Bromoxynil , Dichlobenil
15. Pyridazinones: Pyrazon, Oxypyrazon
16. Uracils : Bromacil, Terbacil
17. Phenoxy acids : 2,4-D, 2,4,5-T
18. Miscellaneous : Picloram, Glyphosate
19. Inorganic herbicides: Borax, Sodium chlorate,  
Ammonium sulfamate.  
Mercurous chloride, Ferrus sulphate .

### Selectivity of herbicides

Selectivity refers to the ability of a herbicide to kill a target plant in a mixed plant population.

Activity refers to the ability of a herbicide to control a weed. Selectivity of a herbicide play an important role in developing the chemical weed control.

Selectivity is achieved physically, chemically, mechanically, environmentally and metabolically.

Each herbicide has its own physical and chemical properties like water solubility, absorptive force, vapour pressure and polarity which contribute to the selectivity of the herbicide.

Before exerting toxicity to a target plant the chemical should be absorbed and translocated .For example, hydrophilic herbicides because of high surface tension of water molecules, tend to form large spherical droplets which don't readily wet the waxy cuticle of the leaf surface .This results in poor and improper wetting of the foliage and as a consequence, the herbicide activity reduced. In case of lipophilic herbicides they enter the waxy cuticle better than the hydrophilic ones but translocation within the plants is very slow in the water continuum. This in turn plays a crucial role in conferring selectivity and activity. A very important factor of the selectivity of the herbicide is the plant morphology and anatomy. Thus, thin cuticle permits greater absorption of herbicide compared to thick cuticle. Similarly plants with larger size and greater number stomata absorb higher amount of herbicides and make the plants more susceptible.

The most important factor governing the selectivity of herbicides is differential metabolism of a chemical in plants. In tolerant plants , the chemical is inactivated in one or more pathways .In certain plant species , detoxification of the herbicide takes place at a rate slower than that of accumulation resulting in the plant mortality , while in others it is much faster , enabling the plants to be tolerant. Several species of leguminous plants are resistant to the phenoxy butyric acid herbicides because they lack  $\beta$ -oxidases to convert *in vivo* to the active phenoxy acid derivatives. Therefore 2,4, DB is a selective post emergence herbicide in legumes .

### Mode of action of herbicides

Most of the herbicides act by inhibition of one or more of the following biochemical processes

- I. Respiration and Mitochondrial Activities
- II. Photosynthesis
- III. Protein and Nucleic acid metabolism
- IV. Synthesis of hydrolytic enzymes

**I. Respiration and mitochondrial activities:** Mitochondria are cellular organelles responsible for the oxidation of respiratory fuels and conservation of energy emanating thereof in the form of ATP. The process thus involves the synthesis of ATP from ADP and transport of electrons from the substrate to the molecular oxygen.

Herbicides inhibit these processes by uncoupling the reaction of ATP formation or interference with electron transport and energy transfer. Uncouplers usually act on the membranes of mitochondria where phosphorylation takes place.

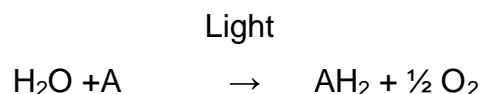
Dalapon and Propanil are important herbicides of this category. Dalapon is reported to impair glucose metabolism by interfering glycolysis and Kerb's cycle in susceptible plants. Propanil interferes with the oxidation of malate and succinate in Kerbs cycle and also with electron transport and ATP generation in mitochondria.

**li.photosynthesis:** The events of photosynthesis can be divided into two phases

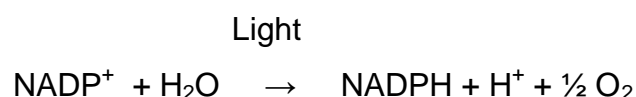
**A. Light phase:**

The phase in which light energy is conserved resulting in the formation of NADPH and ATP. Light phase involves the Hill reaction, the usual photosynthetic electron transport system and two photosystem like P.S.I and P.S.II which differ in the distinctive optimum wavelength and the ratio of Chlorophyll a to Chlorophyll b. The photosynthetic electron transport chain has three segments, a short segment from H<sub>2</sub>O to PS-II , a central chain from P.S-II to P.S.I and the a segment from PS-I to NADP+ .

The reaction involving the evolution of oxygen form H<sub>2</sub>O and simultaneous reduction of the electron acceptor as depicted in the following equation is called the Hill reaction



Where A is the Hill reagent . In photosynthetic systems , the eventual Hill reagent is NADP+ . Thus



The transfer of electrons from H<sub>2</sub>O to NADP<sup>+</sup> is however not direct and involves a number of intermediaries and both P.S.I and P.S.II.

**B. Dark phase:**

The phase in which CO<sub>2</sub> is reduced by NADPH and ATP.

A large number of herbicides inhibit photosynthesis principally by inhibiting or blocking or enacting

- a) The Hill reaction and the production of oxygen from H<sub>2</sub>O in P.S.II Ex Ureas, Uracils, Nitriles and Dphenyl ethers.
- b) The transfer or transport of electron in P.S-II Eg. Niriles and Ureas
- c) Removal of electrons from the electron transport chain from Ferredoxin in P.S.II eg.Bypyridiliniums.
- d) The non-cyclic photopohprylation or ATP synthesis Eg. Ureas , Triazines , Uracils, Nitriles

**lii. Protein and nucleic acid metabolism:** The various steps of protein synthesis are i) amino acid activation ii) chain initiation iii) chain elongation iv) termination.

Herbicides like barbam, a carbamate, inhibits protein synthesis, the degree of inhibition is related to the susceptibility of the species to the herbicide C.D.A.A. (N,N-diallyl -2-chlo acetamide) inhibits the incorporation of exogene aminoacids in protein chain elongation.

Nucleic acids inhibition (both DNA and RNA) is considered to be the primary mechanism of dinitroaniline herbicides like trifluralin and fluchloralin, while diphanamid inhibits RNA synthesis.

**iv. Inhibition of the syntheis of hydrolytic enzymes:**

During seed germination, enzymes are activated, synthesized and stored insoluble foods degraded, soluble foods translocated, nutrients mobilized and synthetic reaction related to growth take place at a faster pace. One of the major metabolic processes that needs take place during this time at a faster rate is the production of hydrolytic enzymes such as amylases, proteases, lipases, phosphatases, esterases etc., some of these hydrolases are under the control of the gibberellins. Aleurone layers of the cereal grain are the seats of production of these enzymes. During imbibition of the seeds, embryo supplies the hormone gibberillic acids to the aleurone which then induces the synthesis of polyribosomes, and nucleic acids. An effect of the herbicides on any one or more of these events would lead to the other events as well, consequently effecting the eventual germination of the seed.

A number of pre-emergence herbicides particularly amides and thiocarbamates exert action by inhibition of one or more these events.

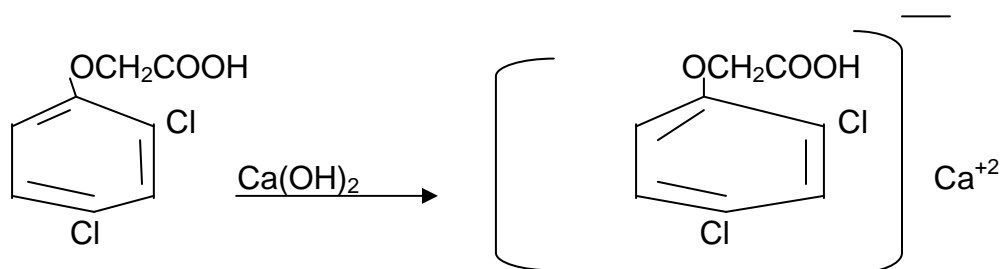
**LECTURE-32** Structure, properties and uses of 2,4 D, Atrazine ,Butachlor Glyphosate and Benthocarb

**(1) 2, 4-D ( 2, 4 – Dichlorophenoxy acetic acid )**

It is a most important member of the phenoxy acid family and is used for the control of broad leaved dicotyledonous weeds.

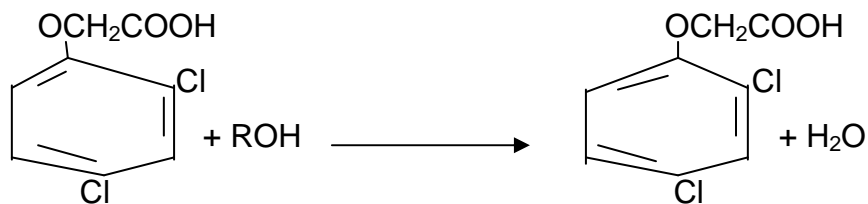
It is a white crystalline substance, insoluble in water but soluble in organic solvents like ethanol and acetone. Technical product emits a characteristic smell of 2,4 dichlorophenol present as an impurity .

With organic and inorganic bases 2, 4 –D forms stable salts .In fact 2,4-D formulated in the form of metal or amine salts .



2,4-D Calcium salt

2,4-D reacts with the alcohols to form esters which are more effective than its salts .



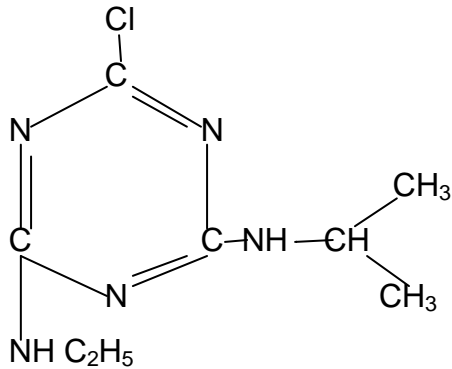
2,4-D ester

2, 4-D is formulated in the form of its esters also. Practical use is now being made of ethyl, isopropyl, butyl, heptyl and octyl and isocrotyl esters of 2, 4-D for its commercial use.

L.D.<sub>50</sub> value of 2,4-D for experimental animals is in the range of 375 to 1000 mg /kg body weight (oral ) .It is thus a compound of medium toxicity to mammals .

## 2. ATRAZINE

It is selective pre-emergence herbicide for the control of grass and broad leaved weeds in maize, sorghum, sugarcane, pine apple and orchards and also as a non-selective herbicide along the railway tracks.

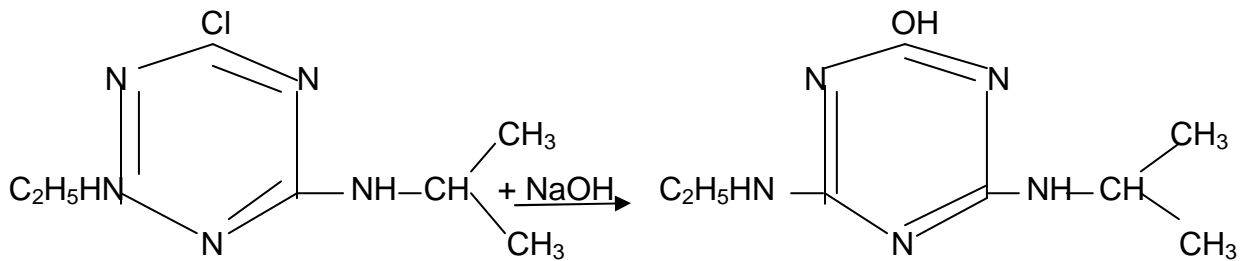


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Chemical name:

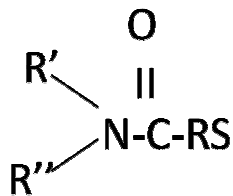
Atrazine is 2-chloro-4-(ethylamino)-6-(isopropylamino)-S-triazine.

1. It is a white crystalline substance. It is almost insoluble in water.
2. when boiled with NaOH, the chlorine at 2<sup>nd</sup> position is split off resulting in the formation of 2-hydroxyl-4-(ethyl amino)-6-(isopropyl amino)-S triazine which does not have any herbicidal properties.

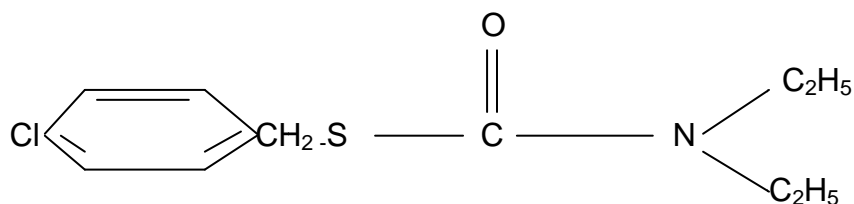


3. It is a highly persistent herbicide
4. It is very safe compound for mammals and L.D.50 value for rats is 3000 mg/kg body weight.

## 4. BENTHIOCARB/BENDIOCARB/THIOBENCARB



it belongs to thiocarbamate groups and derivatives of thiocarbamic acid.

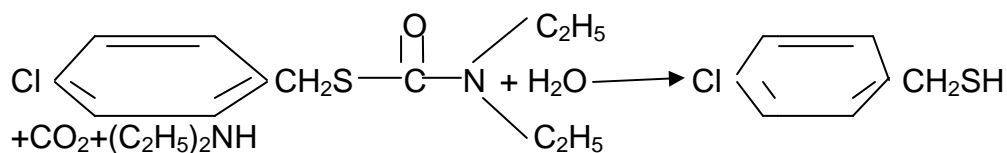


Chemical name: S-(4-chlorobenzyl) N, N- diethyl thiocarbamate.



Benthiocarb is very popular for the control of broad leaf and aquatic weeds in rice .

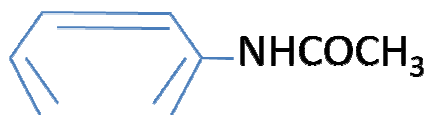
It is a white crystalline substance . The low water solubility compels its use either in suspension or emulsions. It is moderately persistent in soil. In true solution it is rapidly hydrolysed under alkaline medium to produce 4- chlorobenzyl mercaptan and diethyl amine among others.



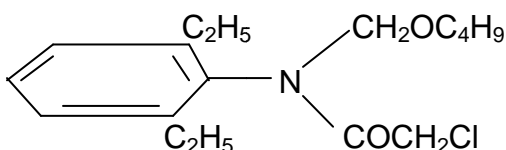
It is moderately volatile and its entry to the underground shoot tissues of the plant mainly through vapour phase .Its L.D.50 value for experimental animals is between 2200 to 3100 mg /kg body weight.

### BUTACHLOR

Belongs to amides/ acetamides/ anilides



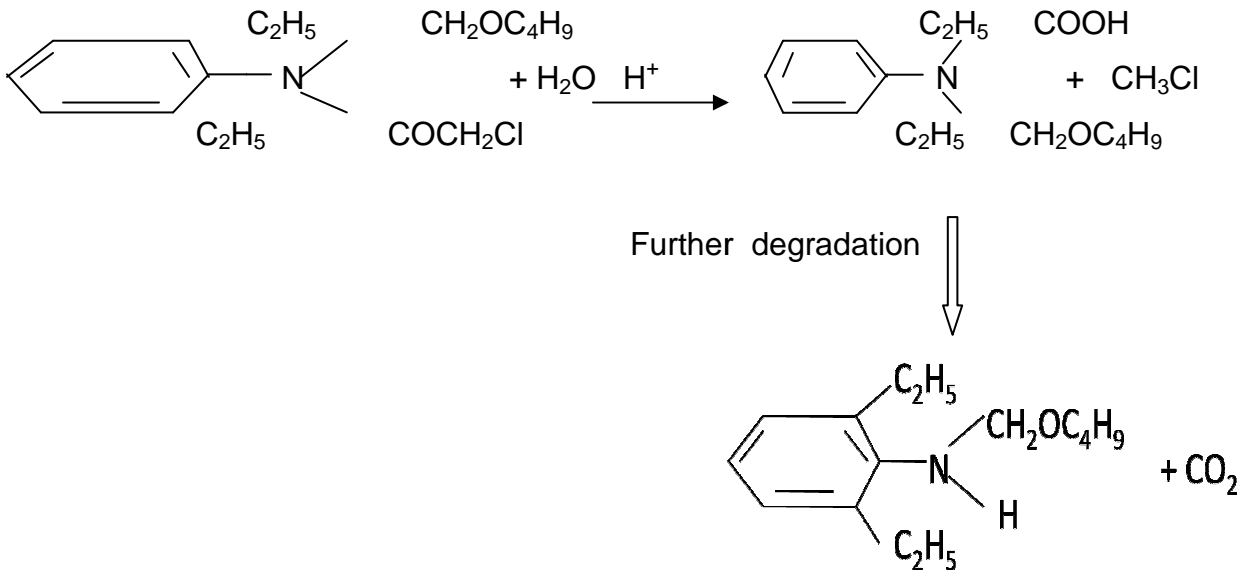
### acetanilide



Chemical name: N-(butoxy methyl ) -2-chloro- 2 , 6 - diethyl acetanilide .

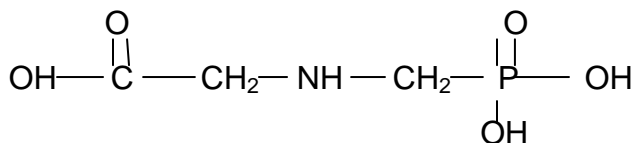
1. Butachlor is used extensively in India in the form of granules in rice as a post emergence herbicide.
2. Butachlor resembles alachlor another promising herbicide of this group, which has  $-\text{CH}_2\text{OCH}_3$  instead of  $-\text{CH}_2\text{OC}_4\text{H}_9$
3. It is a white crystalline substance, it is insoluble in water but soluble in aromatic solvents .

4. Amide linkage is very prone to cleavage and in acidic medium, it is broken to produce the corresponding carboxylic acid and the aliphatic chloride.



5. Crop species resistant to Butachlor, the compound is presumably detoxified by this pathway. Other detoxification pathways too operate simultaneously.
6. Butachlor is practically non-toxic for mammals. L.D.50 Value for experimental animals is more than 5,500 mg/kg body weight

### GLYPHOSATE



N-Phosphomethyl glycine

#### Properties :

- The herbicidal activity of glyphosate was discovered in 1971 and introduced as an isopropyl ammonium salt by Monsanto.
- Glyphosate is a broad spectrum selective post emergence herbicide used for effective control of rhizomatous and deep rooted perennial weeds.
- The susceptible plants show growth inhibition within 4-7 days of application followed by general foliar chlorosis and necrosis.
- Extensively used in plantation crop such as tea, coffee, rubber, oil palm etc., orchard crops, vine yards, pine apple, sugarcane and in non-cropped areas such as banks of irrigation channels, drainage ditches, road sides and industrial and recreation.

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