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SCHOOL OF BIO AND CHEMICAL

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – I – FERTILIZER TECHNOLOGY – SCH1604

Introduction to Plant nutrients, Fertilizer specifications, Terminology and Definitions

1.1 Introduction

A fertilizer is a material that furnishes one or more of the chemical elements necessary for the proper development and growth of plants. The most important fertilizers are fertilizer products (also called chemical or mineral fertilizers), manures, and plant residues. A fertilizer product is a material produced by industrial processes with the specific purpose of being used as a fertilizer. Fertilizers are essential in today's agricultural system to replace the elements extracted from the soil in the form of food and other agricultural products.

1.2 Plant Nutrients

Chemical elements that are essential for the proper development and growth of plants are typically referred to as plant nutrients. The list of plant nutrients recognized as being necessary for plant growth has increased over the years and now totals sixteen,

1.2.1 **Expression**

Many countries express quantities or percentages of the primary nutrients in terms of elemental nitrogen (N), phosphorus pen oxide (P_2O_5), and potassium oxide (K_2O_2). Secondary nutrients and micronutrients usually are expressed on an elemental basis although calcium and magnesium sometimes are expressed in the oxide form. However, several countries express all plant nutrients on an elemental basis.

Classification of Elements Essential for Plant Growth

Major elements (Macronutrients)	(Available from air or water)	Carbon Hydrogen Oxygen
	Primary nutrients	Nitrogen Phosphorus Potassium
	Secondary nutrients	Calcium Magnesium Sulfur
Minor elements (Micronutrients)		Boron Chlorine Copper Iron Manganese Molybdenum Zinc

1.2.2 **Fertilizer Grade**

All fertilizer labels have three bold numbers. The first number is the amount of nitrogen (N), the second number is the amount of phosphate (P_2O_5) and the third number is the amount of potash (K_2O). These three numbers represent the primary nutrients (nitrogen(N) - phosphorus(P) - potassium(K)).

This label, known as the fertilizer grade, is a national standard. A bag of 10-10-10 fertilizer contains 10 percent nitrogen, 10 percent phosphate and 10 percent potash.

Fertilizer grades are made by mixing two or more nutrient sources together to form a blend that is why they are called "mixed fertilizers." Blends contain particles of more than one color. Manufacturers produce different grades for the many types of plants.

You can also get fertilizers that contain only one of each of the primary nutrients. Nitrogen sources include ammonium nitrate (33.5-0-0), urea nitrogen (46-0-0), sodium nitrate (16-0-0) and liquid nitrogen (30-0-0). Phosphorus is provided as 0-46-0 and potash as 0-0-60 or 0-0-50.

1.2.3 Fertilizer Specifications

Specifications are the requirements with which a fertilizer should conform, as agreed upon between buyer and seller. Fertilizer specifications meet differing requirements depending on the use or intent of the specification information.

Specifications are normally used in the contract between the buyer and seller of a fertilizer to ensure agreement on product characteristics or more often to define the product in sufficient detail to effect the satisfaction of both buyer and seller.

1.3 Terminology and Definitions

The below specified definitions are those given by International Association for Standardization (ISO) and Association of American Plant Food Control Officials (AAPFCO)

Fertilizer Material- A fertilizer that meets any of the following conditions (AAPFCO):

1. Contains important quantities of no more than one of the primary plant nutrients (nitrogen, phosphorus, or potassium).
2. Has 85% or more of its plant nutrient content present in the form of a single chemical compound.

3. Is derived from a plant or animal residue or by product or natural material deposit which has been processed in such a way that its content of plant nutrients has not been materially changed except by purification and concentration.

Fertilizer- In the simplest terminology, a material, the main function of which is to provide plant nutrients.

Soil Conditioner – Material added to soils, the main function of which is to improve their physical and/ or chemical properties and/ or their biological activity.

Liming Material – An inorganic soil conditioner containing one or both of the elements calcium and magnesium, generally in the form of an oxide, hydroxide, or carbonate, principally intended to maintain or raise the pH of soil.

Straight Fertilizer: A qualification generally given to a nitrogenous, phosphatic, or potassic fertilizer having a declarable content of only one of the primary plant nutrients, i.e. nitrogen, phosphorus, or potassium.

Compound Fertilizer: A fertilizer that has a declarable content of at least two of the plant nutrients nitrogen, phosphorus and potassium, obtained chemically or by blending or both.

Granular Fertilizer:– Solid material that is formed into particles of a predetermined mean size.

Coated Fertilizer – Granular fertilizer that is covered with a thin of a different material in order to improve the behavior and/ or modify the characteristics of the fertilizer.

Other related terms are:

Coated Slow-Release Fertilizer (AAPFCO)- A product containing sources of water-soluble nutrients, release of which in the soil is controlled by a coating applied to the fertilizer.

Polymer-Coated Fertilizer (AAPFCO)-A coated slow-release fertilizer consisting of fertilizer particles coated with a polymer (plastic) resin. It is a source of slowly available plant nutrients.

Controlled-Release Fertilizers- Fertilizers in which one or more of the nutrients have limited solubility in the soil solution, so that they become available to thea growing plant over a controlled period.

Nitrogen Stabilizer (AAPFCO) - A substance added to a fertilizer to extend the time that the nitrogen component of the fertilizer remains in the soil in the ammonia cal form.

Liquid Fertilizer – A term used for fertilizers in suspension or solution and for liquefied ammonia (ISO).

Solution Fertilizers (ISO) – Liquid fertilizer free of solid particles.

Suspension Fertilizer (ISO) – A two-phase fertilizer in which solid particles are maintained in suspension in the aqueous phase.

Suspension Fertilizer (AAPFCO) – A fluid containing dissolved and UN dissolved plant nutrients. The suspension of the undissolved plant nutrients may be inherent with the materials or produced with the aid of a suspending agent of nonfertilizer properties. Mechanical agitation may be necessary in some cases to facilitate uniform suspension of undissolved plant nutrients.

Suspension Fertilizer – A liquid (fluid) fertilizer containing solids held in suspension, for example, by the addition of a small amount of clay. The solids may be water-soluble in a saturated solution, or they may be insoluble, or both.

Slurry Fertilizer (AAPFCO)–A fluid mixture that contains dissolved and undissolved plant nutrient materials and requires continuous mechanical agitation to assure homogeneity.

Powder – A solid substance in the form of very fine particles. Powder is also referred to as "no granular fertilizer" and is sometimes defined as a fertilizer containing fine particles, usually with some upper limit such as 3 mm nut no lower limit.

Formula – A term used in some countries to express, by numbers, in the order N-P-K (nitrogen- phosphorus- potassium), the respective content of these nutrients in a compound fertilizer.

Bulk – Qualification given to a fertilizer or soil conditioner not packed in a container (ISO).

Guarantee (of Composition) – Quantitative and/ or qualitative characteristic with which a market product must comply for contractual or legal requirements.

Declarable – Content – That content of an element (or an oxide) which, according to national legislation, may be given on a label or document associated with a fertilizer or soil conditioner.

Fertilizer unit – The unit mass of a fertilizer nutrient (in the form of the element or an oxide) generally I kg.

Plant Food Ratio – The ratio of the numbers of fertilizer units in a given mass of fertilizer expressed in the order N – P – K.

Nitric acid – Part 1

Nitric acid (HNO_3), also known as aqua fortis and spirit of niter, is a highly corrosive and toxic strong mineral acid which is normally colorless but tends to acquire a yellow cast due to the accumulation of oxides of nitrogen if long-stored. Ordinary nitric acid has a concentration of 68%. When the solution contains more than 86% HNO_3, it is referred to as fuming nitric acid. Depending on the amount of nitrogen dioxide present, fuming nitric acid is further characterized as white fuming nitric acid or red fuming nitric acid, at concentrations above 95%. Nitric acid is also commonly used as a strong oxidizing agent.

Pure anhydrous nitric acid (100%) is a colorless mobile liquid with a density of 1.512 g/cm^3 which solidifies at −42 °C to form white crystals and boils at 83 °C. Anhydrous nitric acid should be stored below 0 °C to avoid decomposition. The nitrogen dioxide (NO_2) remains dissolved in the nitric acid coloring it yellow, or red at higher temperatures. While the pure acid tends to give off white fumes when exposed to air, acid with dissolved nitrogen dioxide gives off reddish-brown vapors, leading to the common name "red fuming acid" or "fuming nitric acid". Fuming nitric acid is also referred to as 16 molar nitric acid. It is the most concentrated form of nitric acid at Standard Temperature and Pressure (STP).

Nitric acid forms an azeotrope with water at a concentration of 68% HNO_3, which is the ordinary concentrated nitric acid of commerce. This solution has a boiling temperature of 120.5 °C at 1 atm. Two solid hydrates are known; the monohydrate ($HNO_3 \cdot H_2O$) and the trihydrate ($HNO_3 \cdot 3H_2O$). Nitrogen oxides (NO_x) are soluble in nitric acid and this property influences more or less all the physical characteristics depending on the concentration of the oxides. These mainly include the vapor pressure above the liquid and the boiling temperature, as well as the color mentioned above.

Nitric acid is subject to thermal or light decomposition: $4\ HNO_3 \rightarrow 2\ H_2O + 4\ NO_2 + O_2$. This reaction may give rise to some non-negligible variations in the vapor pressure above the liquid because the nitrogen oxides produced dissolve partly or completely in the acid.

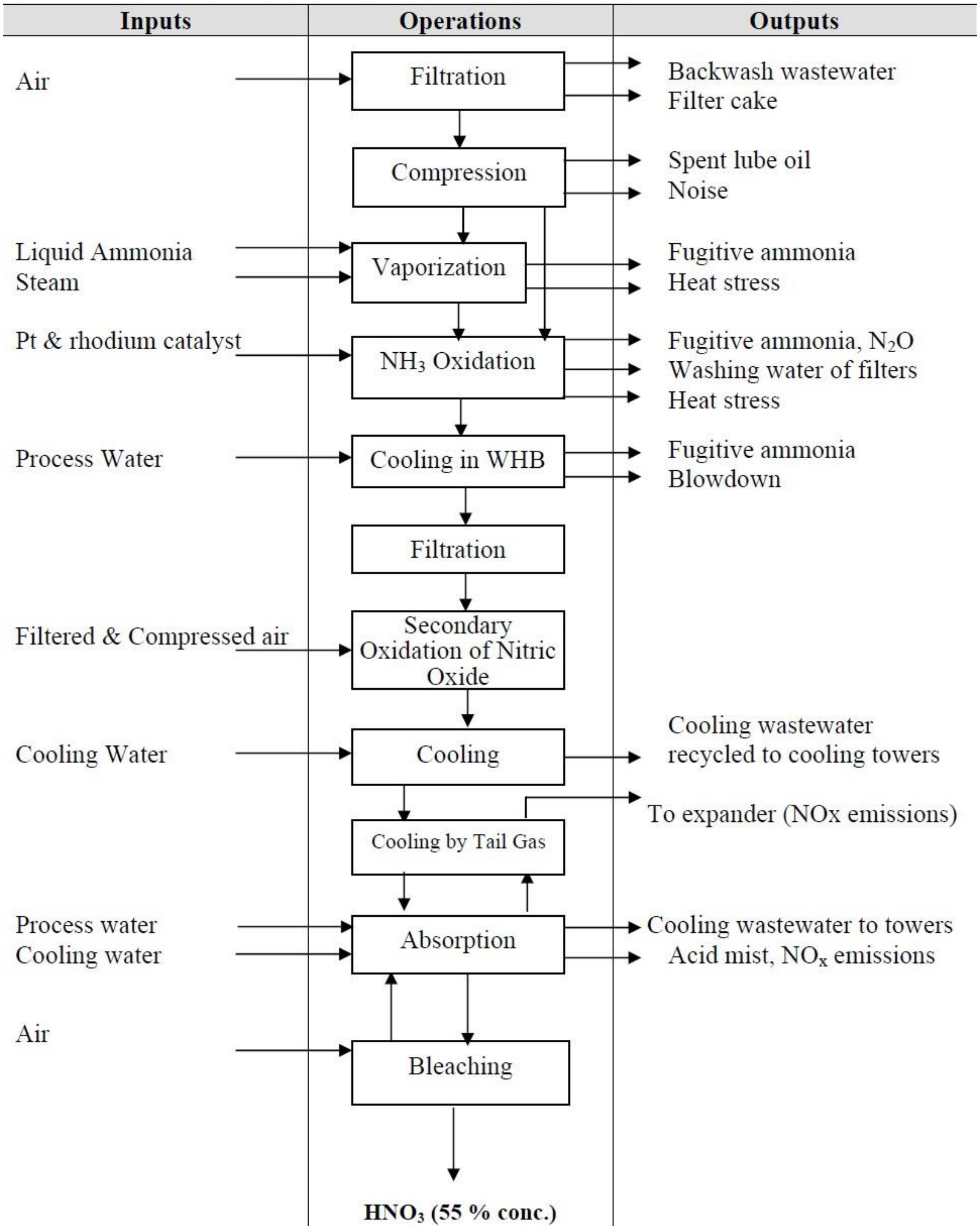
1. Preparation of Nitric Acid

All plants for the production of nitric acid are currently based on the same basic chemical operations: Oxidation of ammonia with air to give nitric oxide and oxidation of the nitric oxide to nitrogen dioxide and absorption in water to give a solution of nitric acid. The efficiency of the first step is favoured by low pressure whereas that of the second is favoured by high pressure. These considerations, combined with economic reasons give rise to two types of nitric acid plant, single pressure plants and dual pressure plants. In the single pressure plant, the oxidation and absorption steps take place at essentially the same pressure. In dual pressure plants absorption takes place at a higher pressure than the oxidation stage.

The oxidation and absorption steps can be classified as: low pressure (pressure below 1,7 bar), medium pressure (1,7 - 6,5 bar) and high pressure (6,5 - 13 bar). Except for some very old plants, single pressure plants operate at medium or high pressure and dual pressure plants operate at medium pressure for the oxidation stage and high pressure for the absorption.

The main unit operation involved in the nitric acid process are the same for all types of plant and in sequential order these are: air filtration, air compression, air/ammonia mixing, air/ammonia oxidation over catalytic gauzes, energy recovery by steam generation and/or gas re-heating, gas cooling, gas compression, energy recovery and cooling (dual pressure plants only), absorption with the production of nitric acid, waste gas (tail gas) heating and energy recovery by expansion of the waste gas to atmosphere in a gas turbine.

Fig 1. Process Flow Diagram for Nitric Acid Manufacturing



Although there are three main processes in the nitric acid production (mono, dual and atmospheric pressure) but the routes are more or less the same as follows:

1. *Primary air filtration*

Feed air contains, beside nitrogen and oxygen, some inert gases, carbon monoxide and some dust and impurities. Dust and impurities harmfully affect the platinum catalyst efficiency, therefore air must be filtered through a series of filters. Air is sucked (by Nox turbo- compressor set in case of atmospheric or by an air compressor in case of mono or dual pressure processes) through a filter (usually candle felt filter elements in case of atmospheric or special paper filter elements) and then heated.

2. *Air Preheating:*

In this step filtered air is introduced through a series of steel pipes, in which fledges are provided on its outer surface to increase the heating surface area. Steam, at 3 kgm/cm^2, 140ºC is passed through the pipes and air outside. The steam condensate is collected by steam traps and recycled to the boilers.

3. *Ammonia evaporation and filtration*

Anhydrous liquid ammonia is evaporated, superheated and its pressure is maintained according to the process (whether atmospheric or pressure). The ammonia is filtered (usually across ceramic candle filters that are cleaned every now and then).

Ammonium Sulphate

Ammonium sulfate was once the leading form of nitrogen fertilizer, but it now supplies a relatively small percentage of the world total nitrogen fertilizer because of the rapiud growth in use of urea, ammonium nitrate. The main advantages of ammonium sulfate are its low hygroscopicity, good physical properties (when properly prepared), chemical stability and good agronomic effectiveness. It reaction in the soil is strongly acid forming, which is an advantage on alkaline soils and for some crops such as tea; in some other situations its acid forming character is a disadvantages. Its main disadvantages is its lower analysis (21%N), which increases packaging, storage and transportation costs. As a result, the delivered cost at the farm level is usually higher per unit of nitrogen than that of urea or ammonium nitrate. However, in some cases, ammonium sulfate may be the most economic source of nitrogen when the transportation at low cost, or when a credit can be taken for its content.

Ammonium sulfate is available as a byproduct from the steel industry (recovered from coke oven gas) and from some metallurgical and from chemical processes.

Commercial form, storage and transportation:

Fertilizer grade ammonium sulfate specifications normally indicate a minimal nitrogen content, which is usually not less than 20.5%. limitations on free acidity and free moisture are also generally demanded; typical figures are 0.2% for free H_2SO_4 and 0.2% for free H_2O. occasionally, maximal values for certain organic or inorganic impurities may also be specified for byproduct material.

Properties of Pure Ammonium sulfate:

Formula	$(NH_4)_2 SO_4$
Molecular weight	132.14
Nitrogen content	21.2%
Color	White
Density of soild, 20^0	1.769

Specific gravity of saturated solutions	1.2414 at 20^{0}C
	1.2502 at 93^{0}C
Specific heat of solid	0.345 cal/g-^{0}C at 91^{0}C
Specific heat of saturated solutions	0.67 cal/g-^{0}C at 20^{0}C
	0.63 cal/g-^{0}C at 100^{0}C
Heat of crystallization	11.6 kcal/kg from 42% solution
Heat of dilution	6.35 kcal/kg from 42% to1.8% solutions
Melting point	512.2^{0}C
Thermal stability	Decomposes above 280^{0}C
pH	5.0
Loose-bulk density	962kg/m^3
Angle of repose	28^0
Critical relative humidity	
At 20^{0}C	81.1%
At 30^{0}C	81%
Solubility, g/100g of water	
At 0^{0}C	70.6
At 100^{0}C	103.8

Several factors contribute to trouble free storage of ammonium sulfate and other fertilizers. First, the product should be of uniform crystal size and should contain a low percentage of lines. It should be dry and preferably have below 0.1% free moisture. No free acidity should be cooled with dry air under controlled condition after drying, particularly when the ambient temperature and humidity are sufficient high to cause subsequent moisture condensation after cooling in a bulk storage pile or in sealed bags. Ammonium sulfate is commonly shipped in polyethylene or paper bags.

The majority of its production is coming from coking of coal as a byproduct. Ammonium sulphate is produced by the direct reaction of concentrated sulphuric acid and gaseous ammonia and proceeds according to the following steps.

1. *Reaction of Ammonia and Sulphuric Acid:*

Liquid ammonia is evaporated in an evaporator using 16 bar steam and preheated using low pressure steam.

The stiochiometric quantities of preheated gaseous ammonia and concentrated sulphuric acid (98.5% wt/wt) are introduced to the evaporator – crystalliser (operating under vacuum). These quantities are maintained by a flow recorder controller and properly mixed by a circulating pump (from upper part of the crystalliser to the evaporator)

2. *Crystallization*

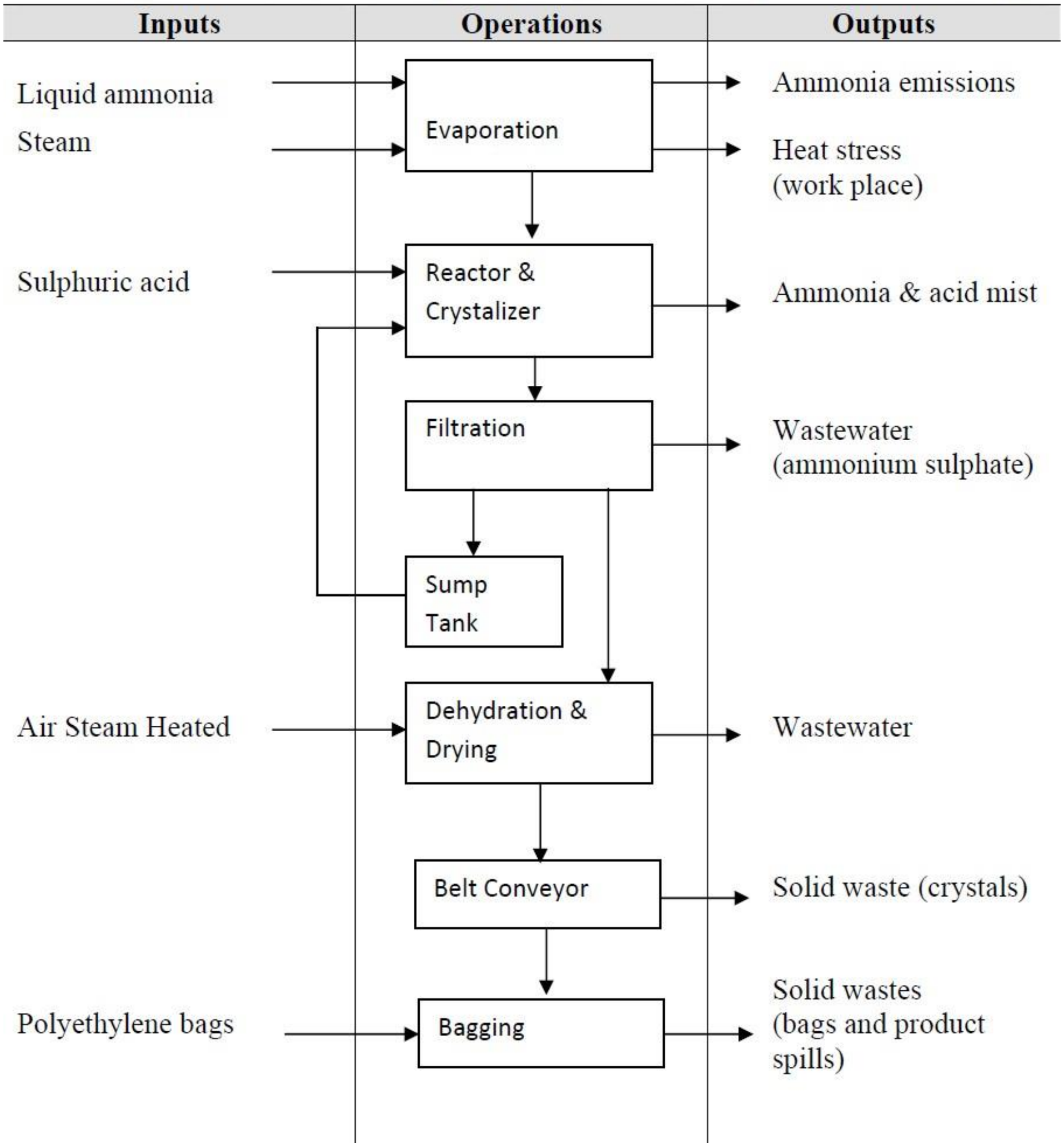
The reaction takes place in the crystallizer where the generated heat of reaction causes evaporation of water making the solution supersaturated. The supersaturated solution settles down to the bottom of crystalliser where it is pumped to vacuum metallic filter where the A. S crystals are separated, while the mother liquor is recycled to the crystalliser.

3. *Drying of the wet Ammonium Sulphate Crystals*

The wet A.S crystals are conveyed (by belt conveyors) to the rotary dryer to be dried against hot air (steam heated) and then conveyed to the storage area where it naturally cooled and bagged.

The following presents the process block diagram for ammonium sulphate production.

Fig 10.1 Process Flow Diagram for Ammonium Sulphate Manufacturing



Ammonium Nitrate

Ammonium Nitrate is in the first place a nitrogenous fertilizer representing more than 10% of the total nitrogen consumption worldwide. It is more readily available to crops than urea. In the second place, due to its powerful oxidizing properties is used with proper additives as commercial explosive.

8.1 Introduction

It is applied as a straight material or in combination with calcium carbonate, limestone, or dolomite. The combination is called calcium ammonium nitrate (CAN) or ammonium nitrate-limestone (ANL) or various trade names and in compound fertilizers including nitrophosphates. It is also a principal ingredient of most liquid nitrogen fertilizers. The nitrogen in ammonium nitrate is more rapidly available to some crops than urea or ammonium sulfate; most crops take up nitrogen mainly in nitrate form; thus, ammoniacal nitrogen must be converted to nitrate in the soil before it becomes effective. Many crops respond well to a mixture of ammonium and nitrate nitrogen. Even though the nitrification process is rapid in warm soil, it is slower in cool soil (10°C and below). Urea may cause seedling damage due to volatilization of ammonia, and ammonium sulfate is strongly acid forming. For these and reasons ammonium nitrate and CAN are effective fertilizers in zones with medium and low temperatures during the cropping period, especially in those with a short vegetation period.

The main advantages of ammonium nitrate are as follows:

- It is quite hygroscopic;
- There is some risk of fire or even explosions unless suitable precautions are taken;
- It is less effective for flooded rice than urea or ammoniacal nitrozen fertilizers;
- It is more prone to leaching immediately after application than ammoniacal products.

8.2. Ammonium Nitrate Properties

Ammonium nitrate is a white crystalline substance with a nitrogen content of 35% and a density of about 1.725 kg/m₃. The melting points depend on the content of the water, and it is practically impossible to obtain dry product in the industrial conditions.

In production and storage of ammonium nitrate, transformations of the crystal states that may affect the quality of the product occur.

Some additives such as $Mg(NO_3)_2$, $(NH_4)\ _2SO_4$, and some others can slightly change the critical relative humidities.

8.3 Ammonium Nitrate Production

The production process comprises three main unit operations: neutralization, evaporation, solidification (prilling and granulation). Individual plants vary widely in process detail.

Neutralization:

Anhydrous liquid ammonia is evaporated in an evaporator using cooling water. The stoichiometic quantities of nitric acid (55% concentration wt/ wt) and gaseous ammonia are introduced by an automatic ratio controller to a neutralizer. The reaction between Ammonia and nitric acid produces ammonium nitrate solution according to the following exothermic reaction.

$$NH_3 + HNO_3 \longrightarrow NH_4\,NO_3$$

Neutralization can be performed in a single stage or in two stages. The neutralizer can be carried out at atmospheric (either normal or low emission neutralizers where the temperature does not exceed 105°C and pH will be 6 and 3 respectively) or at elevated pressure of almost 4 atmospheres. The normal neutralizers are usually followed by flash evaporation in order to in crease the out let A.N concentration to 70%. In case of pressure neutralizers the temperature will be in the range of 178°C and the steam generated from the heat of reaction will be utilized in the subsequent step namely concentration of A.N solution.

During evaporation some ammonia is lost from the solution. The steam which is boiled off is contaminated. The control of the neutralizer is important. The pH and the temperature must both be strictly controlled to limit the losses from the neutralizer. All installations must include pH and temperature controls. At the operating temperature of the neutralizer, impurity control is of great importance because a safety incident will also be a significant environmental incident. The ammonium nitrate solution from neutralizer may be fed to storage without further processing but, if it is used in the manufacture of solid ammonium nitrate, it is concentrated by evaporation.

1. *Evaporation to Concentrate the A.N*

The outlet from the neutralizer is received in an intermediate tank. The solution should be made alkaline before being pumped (no need for pumps in case of pressure neutralizers since the pressure will maintain the flow) to the evaporation section (multi-effect) running under vacuum. The solution will be steam heated in the multi effect evaporation section. The solution will be concentrated up to 97.5-99.5% (normally over 99 %) depending on whether ammonium nitrate will be granulated or prilled.

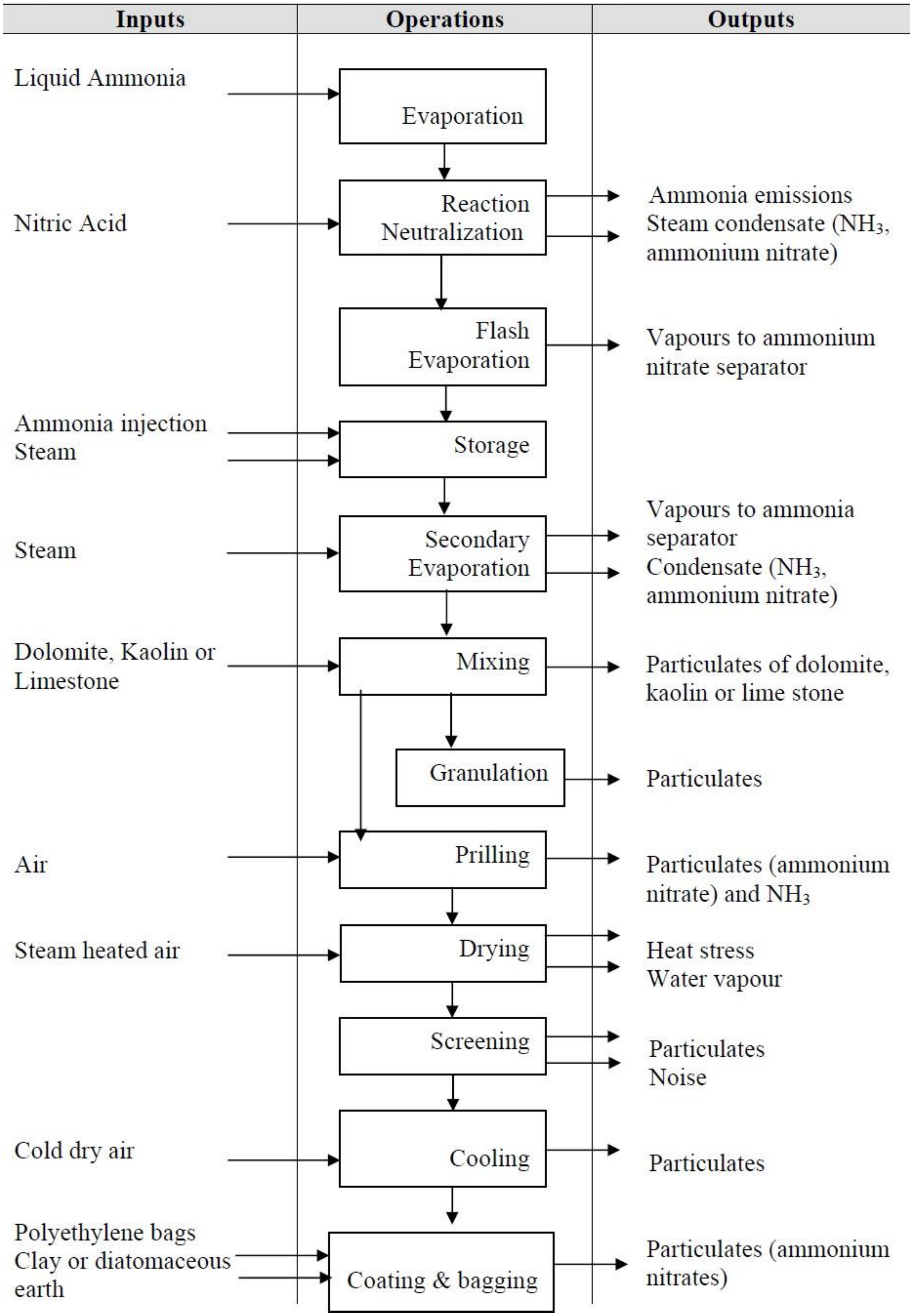
2. *Mixing the Filling Material:*

In order to reduce the nitrogen content of A.N from 35% to 33.5%, the proper filling material is added (about 4% by weight of powdered limestone or dolomite or even kaolin)

3. *Prilling or Granulation*

The hot concentrated melt is either granulated (fluidize bed granulation, drum granulation … etc) or prilled. Ammonium nitrate is formed into droplets which then fall down a fall tower (prill tower) where they cool and solidify. Granulation requires more complicated plant than prilling and variety of equipment. The main advantage of granulation with respect of environment is that the quantity of air to be treated is much smaller and abatement equipment is cheaper.

Fig 8.1 Process Flow Diagram for Ammonium Nitrate Manufacturing



4. ***Drying, Screening***

   The ammonium nitrate (prills or granules) is dried (usually in drums) using hot air (steam heated), then screened to separate the correct product size. The oversize and undersize will be recycled either in the mixing tank (in case of prilling) or to the granulator.

5 ***Final Cooling***

   The hot proper size granules, are then cooled (against cooled and humid free air) down to 40°C and treated with anti-caking (usually amines) and then coated with an inert material (usually, kaolin, limestone or dolomite) and then conveyed to the storage.

Fig 8.1 illustrates the block flow diagram for ammonium nitrate production process.

Major Hazards

Ammonia, nitric acid and ammonium nitrate are the hazardous chemicals present in ammonium nitrate plants. A.N is an oxidizing agent and precautions must be taken in manufacturing, transport and storage.

The main chemical hazards associated with ammonium nitrate are fire, decomposition and explosion. Burns caused by hot AN solution should also be considered from a safety point of view.

Ammonium nitrate itself does not burn. Being an oxidizing agent, it can facilitate the initiation of a fire and intensify fires in combustible materials. Hot AN solution can initiate a fire in rags, wooden articles ets., on coming into contact with them. Similarly, fertilizer products or dust contaminated with oil or other combustible materials can also start fires when left on hot surfaces.

Pure solid A.N melts at 169° C. On further heating it decomposes by way of a complex series of reactions. Up to about 250° C it decomposes primarily into N_2O and H_2O. Above 300° C reactions producing N2, NO, NO_2 etc., become significant. These reactions are exothermic and irreversible. They are accompanied by the vapour pressure dependent endothermic dissociation into HNO_3 and NH_3 vapours which can provide a temperature limiting mechanism, provided the gases can escape freely. If they cannot, the endothermic dissociation is suppressed and a run-away decomposition can develop, leading to explosive behavior.

A number of materials have a strong catalytic effect on the thermal decomposition of A.N. These include acids, chlorides, organic materials, chromates, dichromate, salts of manganese, copper and nickel and certain metals such as zinc, copper and lead. The decomposition of AN is suppressed or prevented by an alkaline condition. Thus the addition of ammonia offers a major safeguard against the decomposition hazard. The release of toxic fumes is one of the main hazards associated with the decomposition of AN.

Strongly acidic conditions and the presence of contaminants should be avoided to counter the explosion hazard in AN solutions. Explosions can occur when ammonium nitrate is heated under confinement in pumps. Reasons for pump explosions include:

1) No (or insufficient) flow through the pump.
2) incorrect design (design may incorporate low flow and/or high temperature trips).
3) poor maintenance practices.
4) contamination.

8.4. Product Handling

Ammonium nitrate may be stored in bulk although in most climates this requires air-conditioned facilities. Storage facilities should have adequate ventilation to allow quick dispersion of heat and toxic gases in the event of fire The storage area must be equipped with a high efficiency sprinkler system. Ammonium nitrate has its own oxygen for burning, and only large amounts of water can extinguish a fire. In most countries the commercial product is bagged in bags that should be "moisture proof "; at least one ply should be impermeable to moisture. If they are properly designed, plastic-film bags or bags with plastic liners are suitable. Bulk shipment is common in some countries using covered, hopper-bottom cars. Before loading, the inside of the vehicle should be thoroughly cleaned. It is important to prevent contamination of ammonium nitrate with organic materials such as grease or other hydrocarbons, chlorates, nitrates, and metal salts (Zn, Cu), which when ignited may support fire.

CALCIUM AMMONIUM NITRATE

INTRODUCTION

Calcium ammonium nitrate (CAN) is a nitrogenous fertilizer produced by treating ammonium nitrate solution with powdered limestone. It is a white to grey chalky powder, with the colour depending on the limestone used in the manufacturing process. Made with dolomitic limestone, the fertilizer contains 20% nitrogen, 6 % calcium and 4 % magnesium. If the quantity of limestone is smaller than that of used ammonium nitrate, the nitrogen content can go up to 28 %. CAN is preferred to ammonium nitrate in acid soils. The most common grade of CAN contains about 21% nitrogen, corresponding to 60% ammonium nitrate.

Calcium nitrate contains 15.5% nitrogen and its manufacturing process involves reaction of lump limestone with concentrated nitric acid, addition of ammonia to neutralize excess of acid, evaporation of the resulting solution, and prilling or flaking the melt. The resulting product is a double salt, $Ca(NO_3)_2NH_4NO_3$ called calcium ammonium nitrate and is more useful than the single salt calcium nitrate.

Ammonium nitrate is first prepared by the reaction of ammonia and nitric acid. Ammonium nitrate so obtained contains some un-reacted nitric acid which is neutralized by adding calcium carbonate (obtained as a by-product, in the manufacturing of ammonium sulfate) on cooling grains of calcium ammonium nitrate separates out.

The granules of calcium ammonium nitrate are finally coated with thin layer of soap stone powder, which; acts as a protective coating and prevents the absorption of moisture during storage and transportation CO_2 is obtained as a byproduct.

Reaction

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

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

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

Manufacture

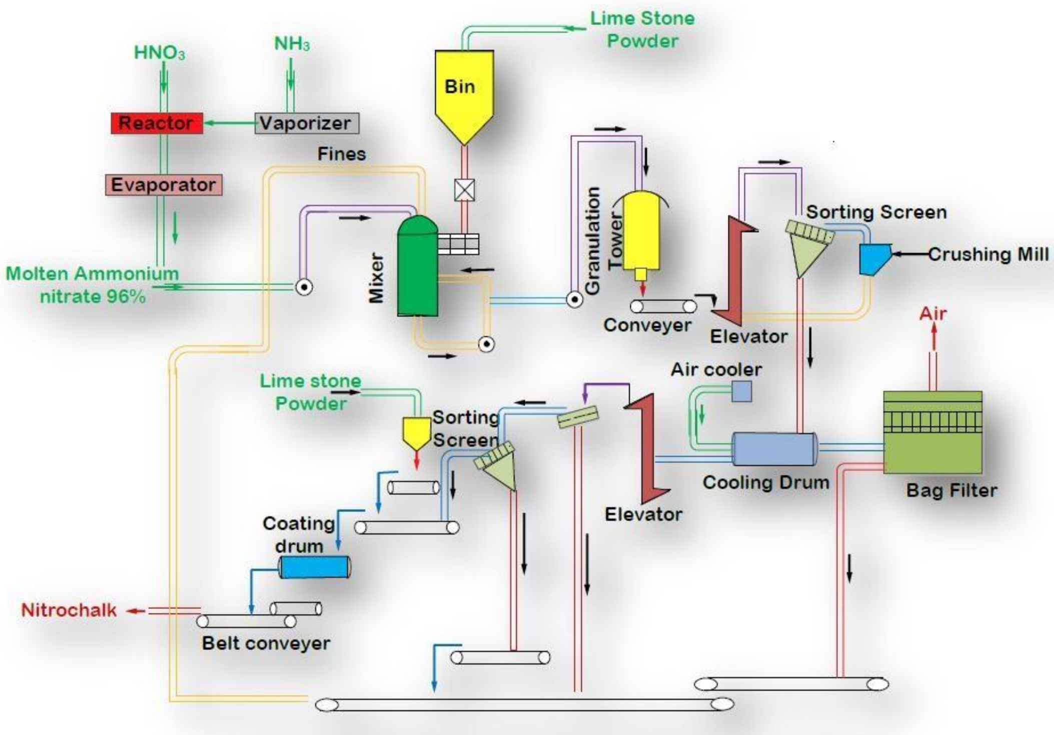


Figure: Manufacturing of Calcium Ammonium Nitrate

CAN is produced by mixing quickly concentrated ammonium nitrate solution with ground or powdered calcitic or dolomitic limestone. Both prilling and granulation technologies are used to produce CAN.

Prilling process

Ammonium nitrate solution is premixed with ground limestone just before prilling. Prill towers of 30 to 50m height are employed. 1 to 3 % China clay, kieselghur or calcined fuller's earth is used to condition the prilled CAN. The mean particle size of CAN formed is 2 to 2.5 mm.

Granulation process

The various methods used for granulation are

- Pug mill process
- Drum process
- Cold spherodizer process
- Fluid bed process

Calcium ammonium nitrate is produced by granulating concentrated ammonium nitrate solution with pulverized limestone or dolomite in a granulator. Ammonium nitrate solution is prepared by reacting preheated ammonia with nitric acid in a neutralizer. Ammonia is preheated to 85^{0}C by vapours from the neutralizer which also preheats nitric acid to about 65^{0}C. Ammonium nitrate liquor of 82-83% concentration which is produced in the neutralizer is concentrated to 92-94% in a vacuum concentrator heated with steam and stored in a tank.

Concentrated ammonium nitrate is pumped and sprayed into the granulator which is fed with weighed quantity of limestone powder and recycle fines from the screens. The hot granules are dried in a rotary drier by hot air.

Dried hot granules are screened and fines and oversize recycled. Granules of proper size are cooled in a rotary cooler by air and coated with soapstone dust in a coating drum. The final product is sent to storage.

Handling and storage

CAN is better to store in air conditioned silos below 30°C. CAN is normally bagged in polyethylene-lined jute or HDPE bags

PROPERTIES

- Molecular formula : $5Ca(NO_3)2.NH_4NO_3.10H_2O$
- Molecular weight : 1080.71gm/mole
- Appearance : White granular
- Odour : Odourless
- Melting point :169^0C (approximately)
- Density : 1.725gm/ml (20^0C)
- Solubility : Solubility in water

CAN is a granulated nitrogenous fertilizer that supplies nitrogen to plants in a balanced and secure manner. The combination of ammonium nitrogen and nitrate nitrogen makes CAN a special product with neutral pH. The excellent granulation and specific surface coating has very good spreading properties

USES

- CAN is a valuable source of nitrogen. As a fertilizer it can be applied for all types of soil and all plants.
- It is a nitrogen fertilizer supplying nutritive elements (N as NH_4^+ and NO_3^-, Mg and Ca as carbonates). It is suitable for blending with other granulated fertilizers
- Commonly used on fruit, process and vegetable crops

UREA

INTRODUCTION

Urea (NH_2CONH_2) or carbamide is an organic compound has two —NH_2 groups joined by a carbonyl (C=O) functional group. Urea serves an important role in the metabolism of nitrogen containing compounds by animals and is the main nitrogen containing substance in the urine of mammals.

Urea has the highest nitrogen content ava*ilable in a solid fertilizer (46%). It is easy to produce as prills or granules and easily transported in bulk or bags with no explosive hazard. It dissolves readily in water. It leaves no salt residue after use on crops and can often be used for foliar feeding.

Urea is an acceptable fertilizer for rice and preferable to nitrates for flooded rice because of the reduction of nitrates to N_2O and/or nitrogen (in anaerobic conditions) which is lost to the atmosphere. Also, rice can utilize the ammonium form of nitrogen efficiently. Hydrolysis and nitrification (in aerobic conditions) are rapid in tropical, sub-tropical and warm climates

Urea can be sprayed on leaves and can also be mixed with insecticides or herbicides for soil application. A urea ammonium nitrate mixture with herbicide is also used for weed control.

Disadvantages

- When applied to a bare soil surface, urea hydrolyzes rapidly result into loss of significant quantity of ammonia by volatilization. Such losses vary from soil to soil and are greater for urea in a pellet form rather than in solution form.

- It is phytotoxic due to rapid hydrolysis of urea in soils can cause injury to the seedlings by ammonia,
- The fertilizer grade urea may contain toxic biuret which is formed during urea manufacture by an excessive temperature rise. Above 2% concentration of biuret in urea is harmful to plants.

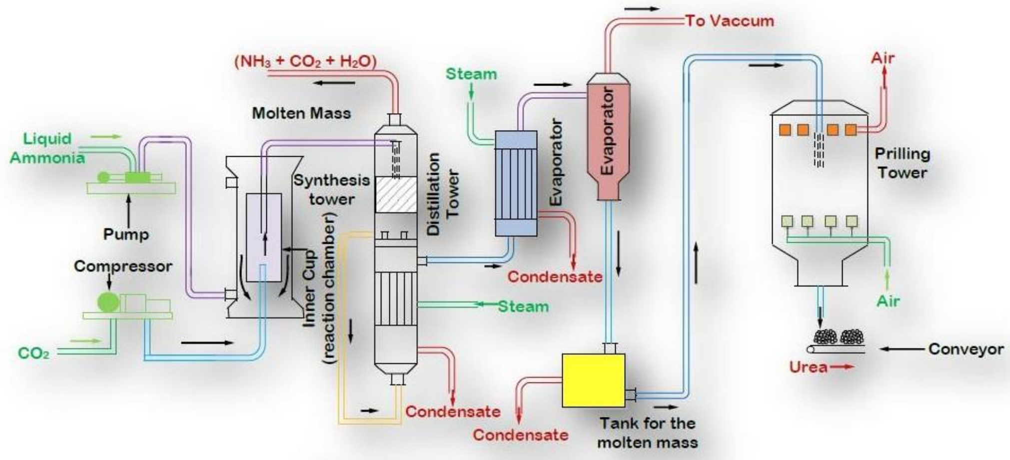


Figure: Manufacturing of Urea

Reaction

$$CO_2 + 2NH_3 \rightleftharpoons NH_2COONH_4 \quad \Delta H = -\ 37{,}021\ \text{Kcal}$$

$$NH_2COONH_4 \rightleftharpoons NH_2CONH_2 + H_2O \quad \Delta H = +\ 6.3\ \text{kcals}$$

Urea is always made in an ammonia plant because it produces CO_2 as by product, which can be used directly without further treatment.

Two reactions are involved in the manufacture of urea. First ammonium carbonate is formed under pressure by highly exothermic reaction between carbon dioxide and ammonia followed by the endothermic decomposition reaction. While the former reaction under pressure, reaches to almost completion and the decomposition reaction incomplete. Unconverted carbon dioxide and ammonia, along with un decomposed carbamate, must be recovered and reused. The synthesis is further complicated by the formation of a dimer called biuret, $NH_2CONHCONH_2.H_2O$ which must be kept low because it adversely affects the growth of some plants.

Liquid ammonia, gaseous carbon dioxide and recycle materials charged in the heat exchanger-reactor at the pressure of 14MPs at 170 - 190^{0}C to form carbamate, with most of the heat of reaction carried away as useful process steam. The carbamate decomposition reaction is both slow and endothermic. The mixture of unreacted reactants and carbamate flows to the decomposer. The stoichiometric ratio of CO_2/NH_3 conversion to urea is essentially about 55%, but by using an excess of CO_2 (or NH_3) the equilibrium can be driven as high as 85%. The reactor must be heated to force the reaction to proceed. CO_2 is introduced at process pressure followed by stripper. All the unreacted gases and undecomposed carbamate to be removed from the product, the urea must be heated at lower pressure (400kPa). The reagents are reacted and pumped back into the system. Evaporation and prilling or granulating produces the final product. Overall, over 99% of both CO_2 and NH_3 are converted to urea, making environmental problems to minimum. Carbamate is highly corrosive to both ordinary and stainless steel, but with oxygen present, 300 series stainless steel resist it very well, so some air is introduced along with CO_2 reagent to reduce system corrosion.

AMMONIUM CHLORIDE

INTRODUCTION

Ammonium chloride (NH_4Cl) is white crystalline salt highly soluble in water. Solutions of ammonium chloride are mildly acidic. Sal ammoniac is a name of the natural, mineralogical form of ammonium chloride. The mineral is commonly formed on burning coal dumps, due to condensation of coal derived gases. It is also found around some types of volcanic vent. It is used as a flavouring agent in some types of liquor ice. It is the product from the reaction of hydrochloric acid and ammonia.

Several methods are used to produce ammonium chloride. The most important is the dual salt process (modified Solvay process) wherein ammonium chloride and sodium carbonate are produced simultaneously using common salt and anhydrous ammonia as the principal starting materials. When ammonium chloride is mixed with phosphorous and potassium fertilizers, a large amount of soil calcium is lost as its conversion into soluble calcium chloride causes it to leach out easily.

Ammonium chloride is used as fertilizer. A coarse form of it is preferred to the powdered form for direct application. Its crystals are used in compound fertilizers. As a fertilizer, ammonium chloride has an advantage in that it contains 26% nitrogen, which is higher than that found in ammonium sulfate (20.5%). In terms of per unit cost of nitrogen, ammonium chloride is relatively cheaper than ammonium sulfate and has some agronomic advantages for rice. Nitrification of ammonium chloride is less rapid than that of urea or ammonium sulfate. Therefore, nitrogen losses are lower and yields, higher.

However, ammonium chloride is a highly acid forming fertilizer and the amount of calcium carbonate required to neutralize the acidity is more than the fertilizer itself, Further, it has lower nitrogen content and higher chloride content compared to urea and ammonium nitrate, making it harmful to some plants.

Like ammonium sulfate, ammonium chloride can be applied to wet land crops. In terms of the agronomic suitability, it is generally rated as equal to other straight nitrogenous fertilizers.

Ammonium chloride is used as a fertilizer for rice and some other crops in a limited way since, it may increase the residual chloride content of some soils. It is not ideal for chilies, potatoes and tobacco as the added chlorine affects the quality and storability of these crops.

MANUFACTURE

Ammonium chloride is manufactured by two processes

1. Direct reaction
2. Duel salt process

1. Direct reaction

The direct reaction process for manufacture of ammonium chloride is not widely used.

2. Duel salt process

Raw materials

Basis: 1000kg of ammonium chloride
Ammonia (30%) = 1000kg
CO_2 = 840kg
NaCl = 1115kg
Water = 350kg

Reaction

$$NH_3 + H_2O + CO_2 \longrightarrow NH_4HCO_3$$

$$NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 + NH_4Cl$$

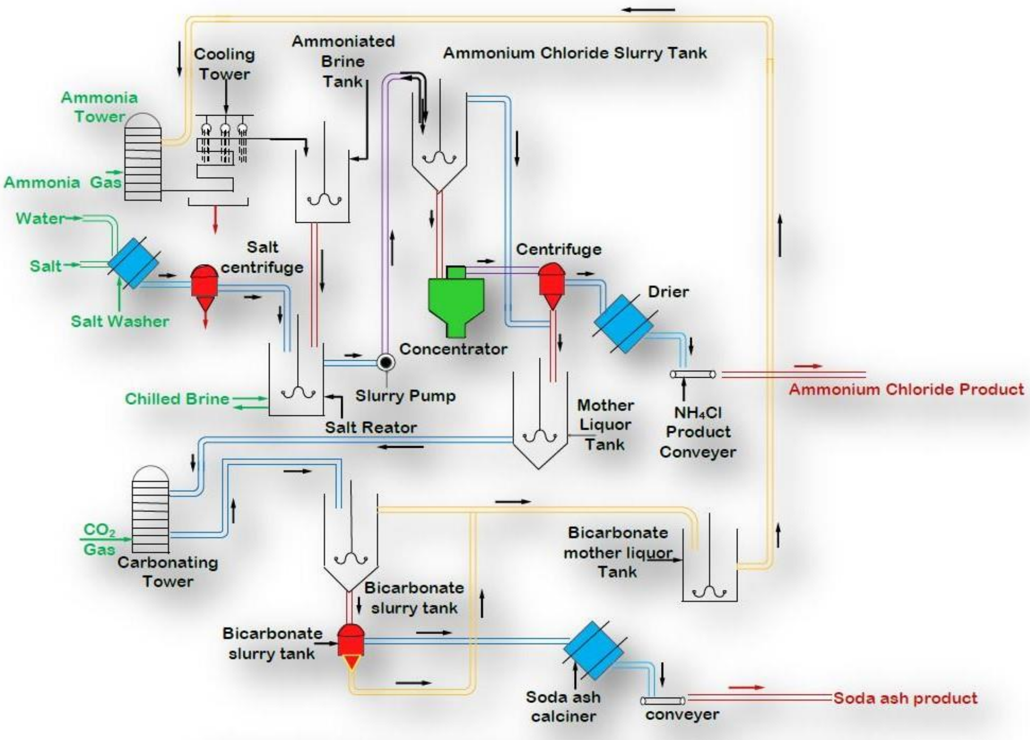


Figure: Manufacturing of Ammonium Chloride by dual salt process

Manufacture

The most widely used process for producing ammonium chloride is the salting out process for soda ash manufacture or modified Solvay's process.

In the process, 30% solution of ammonia is treated with carbon dioxide in a carbonating tower to form ammonium carbonate. The ammonium bicarbonate as it is formed, reacts with sodium chloride to give sodium bicarbonate and ammonium chloride. The bicarbonate is separated by filtration, washed and calcined to produce sodium carbonate.

In the modified Solvay's process, ammonium chloride in the solution, after separation of the sodium bicarbonate, is salted out by ammoniating the solution, cooling below 15^{0}C and adding washed sodium chloride.

The precipitated ammonium chloride is centrifuged, washed and dried. The fine crystals can be granulated by roll compaction. Large ammonium chloride crystals of 2 to 3 mm size have been developed by cooling, nucleation and crystallization, under closely controlled conditions in specially designed vessels.

The slurry from the crystallizer is centrifuged, washed and dried to about 0.25% free moisture in a rotary drier at 105^{0}C. After the removal of ammonium chloride, the liquor is reammoniated to start a new cycle of operations.

As the demand for soda ash is comparatively lower than that for nitrogen fertilizers, ammonium chloride from this source is not likely to meet the nitrogen fertilizer needs.

NH_4Cl as fertilizer

Advantages

- Its low cost, as it is often directly available as a by-product from important industries such as the Solvay soda industry and potassium sulfate industry
- The fact that it combats certain plant diseases and prevents others

Disadvantages

- Incompatibility of Cl^- ions with the physiology of many plants
- The corrosive action which it exhibits owing to the high degree of hydrolysis that it undergoes
- Difficult to store as it has tendency to cake.

The pronounced acidic behaviour of ammonium chloride can be countered by mixing it with $Ca(OH)_2$ and calcium cyanamide.

PROPERTIES

- Molecular formula : NH_4Cl
- Molecular weight : 53.491gm/mole
- Appearance : White solid, hygroscopic
- Odour : Odourless
- Melting point : $338^{0}C$ (decomposes)
- Density : 1.527gm/ml
- Solubility : Solubility in water, alcohol

USES

- Used as fertilizer.
- Used to produce low temperatures in cooling baths. Ammonium chloride solutions with ammonia are used as buffer solution.
- It is an ingredient in fireworks, safety matches and contact explosives.
- Used in a ~5% aqueous solution to work on oil wells with clay swelling problems.
- It is also used as electrolyte in zinc carbon batteries.
- Uses in hair shampoo, in the glue that bonds plywood, and in cleaning products. In hair shampoo, it is used as a thickening agent in ammonium based surfactant systems, such as ammonium lauryl sulfate.
- Used in the textile and leather industry in dyeing, tanning, textile printing and to luster cotton

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SCHOOL OF BIO AND CHEMICAL

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – II– FERTILIZER TECHNOLOGY – SCH1604

POTASSIUM CHLORIDE

INTRODUCTION

Potassium chloride (KCl) is a metal halide salt composed of potassium and chlorine. It is odorless and has a white or colorless vitreous crystal appearance, with a crystal structure that cleaves easily in three directions. Potassium chloride crystals are face centered cubic. "Muriate of potash" is name which is occasionally association with its use as a fertilizer containing 60% plant food as K_2O.

Potash varies in colour from pink or red to white depending on the mining and recovery process used. White potash or soluble potash is usually higher in analysis and is used primarily for making liquid starter fertilizers. It occurs naturally as the mineral sylvite and in combination with sodium chloride as sylvinite.

Potash mineral or brine

Potash mineral or sylvinite contain potassium chloride and sodium chloride

Manufacture

Potassium chloride is obtained by following methods

1. Leaching process
2. Flotation process

Leaching process

The solubility of potassium chloride and sodium chloride increases as the temperature increases. Individually both are much more soluble in hot water than in cold water. But in solutions saturated with both sodium and potassium chloride, the concentration of NaCl diminishes as temperature rises, while the concentration of potassium chloride increases. These solubility characteristics are used to extract potassium chloride from sylvinite. Crushed ore is mixed with sufficient quantity of recycle brine which is already saturated with NaCl and heated almost to hilling to dissolve KCl. The KCl rich brine on clarification and then cooling by vacuum evaporation produces KCl crystals which are centrifuged, washed, dried and packed. The filtrate (brine) is recycled for leaching more ore.

Flotation process

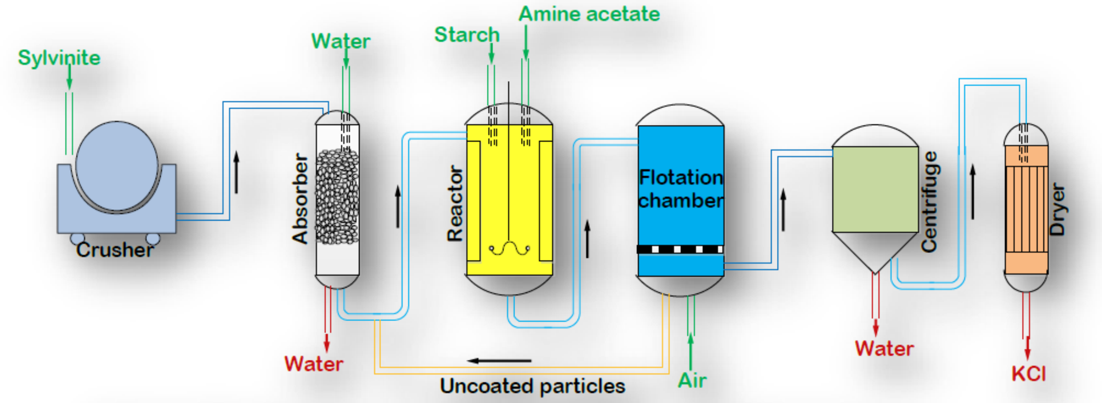

Figure: Manufacturing of Pottasium Chloride by Flotation Process

Floatation process for extraction of potassium chloride is much cheaper than leaching process and hence is used more extensively in the industry. In the process the ore is crushed to +10 mesh size then washed to remove clay slimes. To render it inert to amines, washed crushed ore is treated first with starch or mannogalactan gums and then with an amine acetate which selectively coats KCl particles. Air is then bubbled through the slurry. The air bubbles attach themselves to the coated particles and float them to the surface while the uncoated particles sink. The floated KCl is centrifuged, dried and packed.

Handling and storage

The crystalline potassium chloride is free flowing and does not normally pose any problem in handling and storage. Potassium chloride is imported as bulk cargo and transported to NPK fertilizer and mixing plants in open trucks or in bags.

It is stored in bulk in closed storage yards. Caking occurs in presence of impurities when humidity is high and the mass tends to become like rock. Retrieval from such storage may pose problems and sometimes explosives may have to be used.

PROPERTIES

- Molecular formula : KCl
- Molecular weight : 74.55gm/mole
- Appearance : white crystalline solid
- Odour : Odourless
- Boiling point : 1420^{0}C
- Melting point : 770^{0}C
- Density : 1.984gm/ml
- Solubility : Soluble in glycerol and water, slightly soluble in alcohol, insoluble in ether
- Moisture : 0.5% by wt. (Max.)

USES

- As a fertilizer
- Used as thickeners, stabilizer, mineral salts, gelling agents and acidity regulator in food
- Used as a salt replacer in foods, for recovery of potassium in the human body,
- It's used in brewing, as a salt substitute (as salt free, sodium free, and low sodium products), gelling agent, and in reduced sodium breads.
- Used in various pharmaceutical preparations to correct potassium deficiency.
- It used as a substitute for table salt in the diet of people with cardiovascular disorders, in administration of the potassium ion, and as a constituent of Ringer's solution.

Functions of Potassium in Plants

Potassium is vital to many plant processes. A review of its role involves understanding the basic biochemical and physiological systems of plants. While K does not become a part of the chemical structure of plants, it plays many important regulatory roles in development.

Enzyme Activation

Enzymes serve as catalysts for chemical reactions, being utilized but not consumed in the process. They bring together other molecules in such a way that the chemical reaction can take place. Potassium "activates" at least 60 different enzymes involved in plant growth. The K changes the physical shape of the enzyme molecule, exposing the appropriate chemically active sites for reaction. Potassium also neutralizes various organic anions and other compounds within the plant, helping to stabilize pH between 7 and 8...optimum for most enzyme reactions.

Potassium (K) increases crop yield and improves quality. It is required for numerous plant growth processes.

The amount of K present in the cell determines how many of the enzymes can be activated and the rates at which chemical reactions can proceed. Thus, the rate of a given reaction is controlled by the rate at which K enters the cell.

Stomatal Activity (Water Use)

Plants depend upon K to regulate the opening and closing of stomates...the pores through which leaves exchange carbon dioxide (CO_2), water vapor, and oxygen (O_2) with the atmosphere. Proper functioning of stomates is essential for photosynthesis, water and nutrient transport, and plant cooling.

When K moves into the guard cells around the stomates, the cells accumulate water and swell, causing the pores to open and allowing gases to move freely in and out. When water supply is short, K is pumped out of the guard cells. The pores close tightly to prevent loss of water and minimize drought stress to the plant.

If K supply is inadequate, the stomates become sluggish – slow to respond – and water vapor is lost. Closure may take hours rather than minutes and is incomplete. As a result, plants with an insufficient supply of K are much more susceptible to water stress.

Accumulation of K in plant roots produces a gradient of osmotic pressure that draws water into the roots. Plants deficient in K are thus less able to absorb water and are more subject to stress when water is in short supply.

Photosynthesis

The role of K in photosynthesis is complex. The activation of enzymes by K and its involvement in adenosine triphosphate (ATP) production is probably more important in regulating the rate of photosynthesis than is the role of K in stomatal activity.

When the sun's energy is used to combine CO_2 and water to form sugars, the initial high-energy product is ATP. The ATP is then used as the energy source for many other chemical reactions. The electrical charge balance at the site of ATP production is maintained with K ions. When plants are K deficient, the rate of photosynthesis and the rate of ATP production are reduced, and all of the processes dependent on ATP are slowed down. Conversely, plant respiration increases which also contributes to slower growth and development.

In some plants, leaf blades re-orient toward light sources to increase light interception or away to avoid damage by excess light, in effect assisting to regulate the rate of photosynthesis. These movements of leaves are brought about by reversible changes in turgor pressure through movement of K into and out of specialized tissues similar to that described above for stomata.

How potassium works to increase crop yields:

- Increases root growth and improves drought resistance
- Activates many enzyme systems
- Maintains turgor; reduces water loss and wilting
- Aids in photosynthesis and food formation
- Reduces respiration, preventing energy losses
- Enhances translocation of sugars and starch
- Produces grain rich in starch
- Increases protein content of plants
- Builds cellulose and reduces lodging
- Helps retard crop diseases

Transport of Sugars

Sugars produced in photosynthesis must be transported through the phloem to other parts of the plant for utilization and storage. The plant's transport system uses energy in the form of ATP. If K is inadequate, less ATP is available, and the transport system breaks down. This causes photosynthates to build up in the leaves, and the rate of photosynthesis is reduced. Normal development of energy storage organs, such as grain, is retarded as a result. An adequate supply of K helps to keep all of these processes and transportation systems functioning normally.

Water and Nutrient Transport

Potassium also plays a major role in the transport of water and nutrients throughout the plant in the xylem. When K supply is reduced, translocation of nitrates, phosphates, calcium (Ca), magnesium (Mg), and amino acids is depressed. As with phloem transport systems, the role of K in xylem transport is often in conjunction with specific enzymes and plant growth hormones. An ample supply of K is essential to efficient operation of these systems.

Protein Synthesis

Potassium is required for every major step of protein synthesis. The "reading" of the genetic code in plant cells to produce proteins and enzymes that regulate all growth processes would be impossible without adequate K. When plants are deficient in K, proteins are not synthesized despite an abundance of available nitrogen (N). Instead, protein "raw materials" (precursors) such as amino acids, amides and nitrate accumulate. The enzyme nitrate reductase catalyzes the formation of proteins, and K is likely responsible for its activation and synthesis.

Starch Synthesis

The enzyme responsible for synthesis of starch (starch synthetase) is activated by K. Thus, with inadequate K, the level of starch declines while soluble carbohydrates and N compounds accumulate. Photosynthetic activity also affects the rate of sugar formation for ultimate starch production. Under high K levels, starch is efficiently moved from sites of production to storage organs.

Crop Quality

Potassium plays significant roles in enhancing crop quality. High levels of available K improve the physical quality, disease resistance, and shelf life of fruits and vegetables used for human consumption and the feeding value of grain and forage crops. Fiber quality of cotton is improved. Quality can also be affected in the field before harvesting such as when K reduces lodging of grains or enhances winterhardiness of many crops.

The effects of K deficiency can cause reduced yield potential and quality long before visible symptoms appear. This "hidden hunger" robs profits from the farmer who fails to keep soil K levels in the range high enough to supply adequate K at all times during the growing season. Even short periods of deficiency, especially during critical developmental stages, can cause serious losses.

Quality factors are addressed in more detail on pages 28 and 29.

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UNIT – III– FERTILIZER TECHNOLOGY – SCH1604

Unit-III

3.1 Raw Materials-Phosphoric acid, Sulphuric acid, Phosphate rock, Sulfur pyrite

3.2 Method of Production-Specification, Storage and handling of Phosphatic Fertilizers

3.3 Ground Rock Phosphate

3.4 Bone Meal

3.5 Single super phosphate

3.6 Triple super phosphate

3.7 Thermal Phosphate

3.1 Phosphate rock (PR) is the raw material used in the manufacture of most commercial phosphate fertilizers on the market. With access to large, high-quality reserves of phosphate rock, Morocco, China and US are the most important players in phosphate industry.

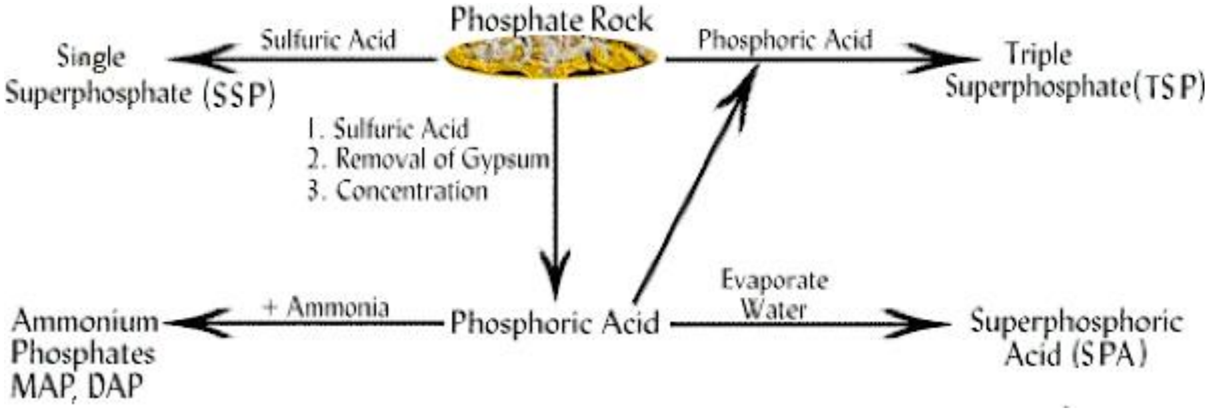
Ground phosphate rock from the mines is first sent to recovery units to separate sand and clay and to remove impurities. Most of the processes are wet to facilitate material transport and to reduce dust.

A weak phosphoric acid (40-55%) is produced from the reaction of PR with sulfuric acid, using a wet- process. The obtained phosphoric acid is then used in the production of a series of liquid or solid fertilizers. The most important ones are single and triple superphosphates (SSP, TSP) and ammonium phosphates (MAP, DAP). Usually the plants are using flexible process technologies, allowing the manufacture of at least two products with interchangeable lines (e.g. TSP and DAP combination).

SSP is simple to produce but is nowadays less popular. TSP results from the reaction of PR with phosphoric acid, using the common Dorr-Oliver slurry granulation process. GTSP (granulated TSP) is obtained in this way, with very good storage and handling properties.

Economical and with high nutrient content, ammoniated phosphates such as mono- and di-ammonium phosphate (MAP, DAP) are another popular choice of fertilizers. They are obtained when ammonia (liquid or gaseous) is added to the weak phosphoric acid.

Phosphate fertilizers production flow-cart can be illustrated in the following figure :



3.2 Phosphatic fertilizers

As the name suggests, insoluble phosphatic fertilizers are completely insoluble in water. They are very slightly soluble in weak acids like citric acid but are readily soluble in strong acids. Their use is, therefore, always recommended for strongly acidic soils. These fertilizers also contain phosphorus in the available form PO_4 but this form is very slowly available in comparison to pervious two forms, i.e. H_2PO_4 and HPO_4. These fertilizers are applied in large quantities and also ploughed under with green manuring crops or other organic materials. This group of phosphatic fertilizers is available in two main forms:

a. Rock phosphate -	20-40% P_20_5
b. Bonemeal -a. Raw bonemeal	2- 25% P_20_5
c. Steamed bonemeal	22% P_20_5

a. Rock phosphates: In India, rock phosphate is mainly utilized for the manufacturing of various other phosphatic fertilizers. It is also used directly to the field, as a phosphatic fertilizer in strongly acidic soils. After mining, it is processed and finally ground and sold in the polythene bags for field use. Rock phosphate is suitable for permanent, long duration crops like fruit and plantation crops (orange, apple, tea, coffee, etc.). Rock phosphate responds very well in soils rich in organic matter, because acids released by decomposing organic matter help in solubilizing the rock phosphate. Legumes which have a high Ca and P requirement, give greater response to rock phosphate than non-legumes.

Areas having strongly acid soils are the most suitable ones for application of rock phosphate. Such areas are found in the whole of Kerala. Shimogha, Coorg and Mysore districts of Karnataka, Chotanagpur region of Bihar, parts of Assam, Meghalaya, West Bengal and rice cropped laterite soils of Orissa.

b. Bonemeal: Bonemeal is the oldest phosphatic fertilizer used by Indian farmers. Presently. it is marketed: in two forms.

i. Raw bonemeal -The bones collected from city slaughter houses and from the countryside, are dried and crushed without any treatment. Besides 20-25% P205' raw bonemeal also contains 2-4% nitrogen.

ii. Steamed bonemeal -The bones collected are given a steam treatment in a sterilization chamber. They are then dried in warm, rotating ovens. Bones become brittle and easy for grinding.

3.3 Apatite is the most abundant crystalline phosphate mineral found as an accessory mineral in practically all kinds of igneous rocks. Sometimes, it is concentrated in pegmatite’s, metallic veins and magmatic deposits. It also occurs in metamorphic rocks and as a secondary mineral in phosphatic rocks of sedimentary origin.

Fluor-apatite Ca (PO4)3F is the most common variety of apatite and also a secondary source of fluorine. Collophane is apparently a cryptocrystalline or amorphous calcium phosphate complex. Rock phosphates or phosphorites are sedimentary phosphatic deposits comprising fine- grained mixture of various calcium phosphates, most important being hydroxyl-apatite, carbonate- apatite, fluor-apatite and their solid solutions. About 80% phosphate production in the world is derived from phosphate rocks (phosphorite) containing one or more phosphatic minerals, usually calcium phosphate of sufficient purity and quantity to permit its use directly or after concentration in manufacturing commercial products.

Phosphate rock is also the source of by-product fluorine. Apatite & rock phosphate containing 3 to 4% CaF2 are useful for recovery of fluorite. Hydrofluoro-silicic acid is recovered as by-product from phosphoric acid plants during processing of rock phosphate.

10. P fertilizers – rock phosphate – bone meal – basic slag

The element was discovered in 1669 and was found to be widely distributed in the lithosphere as phosphates. It is found to occur mostly as calcium phosphate (Tricalcium phosphate). The $Ca_3(HPO_4)_2$ is considered to be the basic material for the manufacture of very many phosphatic fertilizers. More than 50 countries produce phosphatic fertilizer. The top five fertilizer producing countries were United States, China, Russia , India and Brazil. Phosphorus when heated in an abundant supply of O_2, it burns and forms P_2O_5 which, when dissolved in waters, forms metaphospheric acid.

$4P + 5O_2 \longrightarrow 2P_2O_5$ - Phosphorus pent oxide
$P_2O_5 + H_2O \longrightarrow 2\,HPO_3$ - Metaphospheric acid

When this meta phosphoric acid is heated with water, it forms orthophosphoric acid which is commonly called as phosphoric acid.

$HPO_3 + H_2O \longrightarrow H_3\,PO_4$ - orthophosphoric acid.

This orthophosphoric acid has three replaceable H^+ atoms and hence it forms three classes of salts replacing one or two, or all the three H^+ atoms. The neutralization is said to occur in stages as follows.

1. $H_3\,PO_4 + KOH \longrightarrow KH_2\,PO_4 + H_2O$
   Monopotassium phosphate
2. $H_3\,PO_4 + 2KOH \longrightarrow K_2\,HPO_4 + 2H_2O$
   Dipotassium phosphate
3. $H_3\,PO_4 + 3KOH \longrightarrow K_3\,PO_4 + 3H_2O$
   Tripotassium phosphate

The corresponding calcium salts are

1. Monocalcium phosphate - $Ca\,(H_2PO_4)_2$ - Water soluble
2. Dicalcium phosphate - $Ca_2\,(HPO_4)_2$ - or $Ca\,(HPO_4)$ – Soluble in citric acid
3. Tricalcium phosphate - $Ca_3\,(PO_4)_2$ - soluble in strong acids.

This monocalcium phosphate is an acid salt having a solubility of 100 g L^{-1} of water. The di and tricalcium phosphates are almost neutral salts having the solubility of 0.25 g and 0.005g per liter of water respectively.

Sources of phosphorus

1. Mineral deposit

It occurs naturally, as mineral deposits consisting mainly of $Ca_3\,(PO_4)_2$ combined with either CaF_2, $CaCO_3$, $Ca\,(OH)_2$ or $CaCl_2$. The naturally occurring mineral is called "Apatite" or "Phosphorite" or "Phosphate rock" having the general formula ($Ca_3\,(PO_4)_2$)

Ca X. These natural deposits serve as the basic material for the synthesis of all other phosphoric fertilizers.

Classification of phosphatic fertilizers

1. **Based on nature of source or manufacture Phosphatic materials**

Natural Phosphates	**Treated or Processed phosphates**	**Industrial by product**	**Synthetic Phosphates**
1. Bones	1. Super phosphate	Basic stage	Ammonium phosphates
2. RP	2. Bone ash		
	3. Bone super		

2.Based on the solubility of the phosphate

Water soluble phosphates (or) Monocalcium phosphate	**Citric soluble Phosphate or Dicalcium phosphate**	**Insoluble or tricalcium phosphate**
1. Super phosphate 16 % P_2O_5	1. Basic – slag 14-18 % P_2O_5	1. Rock phosphate 30-40 % P_2O_5
2. 3Concentrated SP 48 % P_2O_5	2. Dicalcium phosphate 34 -38 % P_2O_5	2. Raw bone meal 20-25 % P_2O_5
3. Ammonium phosphate 20 % P_2O_5	3. Rhenania PO_4 23-26 % P_2O_5	

As in the case of N, the P is incapable of being utilized in the elemental form, but only in the combined form as acid ions (anions). All plants absorbs P either in the monovalent (H_2PO_4) or divalent (HPO_4) ions.

1.Water soluble phosphate

These include either monocalcium phosphate $Ca(H_2PO_4)$ or other water soluble phosphates like ammonium phosphates. These fertilizers are readily soluble in water which can be observed quickly, as plants absorb P as monovalent phosphate ion H_2PO_4. But, when applied to the soil, the water – soluble form is converted to water insoluble forms resulting in the reduced availability, though there may not be any total less to the applied P. The fertilizers included in this group are found to be suitable for neutral and alkaline soils but not for acid soils.

2.Citric –soluble phosphates

The materials, having water – insoluble phosphates, but soluble in one percent citric acid, are included in this group. The availability of P is not as quick as in the case of water – soluble P, but adequate quantities are found to be released in the available form as divalent phosphates (HPO_4) for plant utilization. This group is found to be useful for acid soils, as under low pH of the soil the citrate soluble phosphates does not easily get converted into monocalcium phosphates or water soluble phosphates, and there are less chances of phosphate getting fixed up as iron and aluminum phosphates. Moreover, due to their basic reaction and high Ca content, they act particularly well on acidic soils and as such, this group is well suited for l**ateritic** and acidic soils.

3.Insoluble phosphates

This group includes those materials having water and citric acid insoluble phsophates. The phosphates are being present mainly as tricalcium phosphate. The availability is very low and the phosphates will be converted to available form very slowly through various chemical reactions. Though the solubility of phosphates is low, the phosphates will be available for prolonged period of time.

These fertilizers are well suited for strongly acidic soils or organic soils which require large quantities of phosphatic materials to raise the soil P status.

The following table illustrated the phosphate (P_2O_5) content and the form of phosphate.

Sl. No.	**Fertilizers**	**Total P_2O_5 (%)**	**Form of PO_4**	**Avail.P_2O_5**
1.	Ordinary super phosphate	16	Water soluble	16.5 - 17.0
2.	Concentrate super phosphate	46 – 48	-do-	
3.	Monoammonium phosphate	48 (11 N)	-do-	
4.	Diammonium phosphate	53 (21 N)	-do-	46 (18N)
5.	Ammophos – A	48 (11 N)	-do-	
6.	Ammophos – B	20 (20 N)	-do-	
7.	Basic slag	14 – 18	Citric soluble	

8.	Dicalcium phosphate	34 – 38	-do-	34.0
9.	Fused tricalcium phosphate	28	-do-	
10.	Rhenania phosphate	23 – 26	-do-	
11.	Raw bone meal	20 – 25	Insoluble	NA
12.	Steamed bone meal	22 – 25	-do-	NA
13.	Rock phosphate	30 – 40	-do-	NA

1.Rock phosphate

The phosphate mineral in soil is found to occur as tricalcium phosphate $Ca_3 (PO_4)_2$ in combination with either $CaCO_3$, $Ca F_2$, $Ca(OH)_2$ or $CaCl_2$. The primary mineral is called 'apatite' and its massive form is sometimes called as 'Phosphorite'. The apatite is of igneous origin found as a constituent of granites, gneisses and basalt. The apatite is usually found as crystals having a clear and transparent colour. There are five important forms of apatite that are found to occur and they are called according to the other components contained in the molecules.

Apatite General formula $(Ca_3(PO_4)_2)_3\ Ca\ \ x$ or $Ca_{10}\ (PO_4)_5\ \ x$ where

$x = CO_3,\ Cl_2,\ F_2,\ SO_4$ or $(OH)_2$.

1. Carbonato apatite	$[Ca_3\ (PO_4)_2]_3$	$CaCO_3$
2. Fluor apatite	$[\ Ca_3(PO_4)_2]_3$	$CaFa_2$
3. Chlor apatite	$[Ca_3(PO_4)_2]_3$	$CaCl_2$
4. Hydroxy apatite	$[Ca_3(PO_4)_2]_3$	$Ca(OH)_2$
5. Sulphate apatite	$[Ca_3(PO_4)_2]_3$	$CaSO_4$

All the above five apatite are primary minerals, of which the fluor apatite is the most commonly occurring one. In some acid soils the phosphate may be founding combination with titanium and iron in varying quantities and there when present in the soil are classified as secondary mineral. The apatite as such is found to occur in the amorphous form and it may be in the compact, concretionary or earthy form and these forms are commonly referred as rock or boulder phosphate, pebble phosphate and soft phosphate respectively. The apatite deposits are classified into residual deposit, replacement deposit and sedimentary deposit.

Bone meal

Bone meal contains tri calcium carbonate or hydrated tri-calcium phosphate. This also contain sodium, magnesium and carbonate. Bone meal is prepared by crushing bones and availability of phosphorus in bone meal increases as material is crushed to a finer size.

Raw bone meal

It is prepared by grinding the bones as such without any treatment. The bones are collected, dried before grinding. The protein present in the form of remaining flesh provides nitrogen ranging between 2 to 4%. This contains fat of glue which prevents the decomposition of bone when applied in the soil.

Total P_2O_5 on dry weight basis (Max.) : 20 %
Available P_2O_5 soluble in 2% citric acid (Min.) : 8 %
Total nitrogen, % by weight (Min.) : 3 %

Steamed bone meal

Steamed bone meal is obtained by the boiling the bones under steam pressure. Under this process the fat and some other materials are removed so that decomposition can take place readily in the soil after it is applied. However this process reduces the nitrogen content but phosphate content is increased. The bones are then ground and sold as fertilizer material in the market. The steamed bone meal should have the following standard according to fertilizer quality control order (1957) if Government of India:

Free moisture percentage by weight (Max.) : 7.0
Total phosphates as P_2O_5 percentage by weight (Min) : 22.0
Available phosphates as P_2O_5 soluble in 2 %
Citric acid solution % by weight (Min.) : 16.0

Bone meal consists of P_2O_5 in citric acid soluble form hence it should always be applied as basal. The bone meal sources are limited and hardly 30,000 to 35,000 tonnes of bone meal is produced and consumed annually in the country. Now-a-days it is also used as feed to the animals in the form of concentrate hence the materials, as fertilizers, is further reduced.

Basic slag

It is a by-product from the steel industry. During the steel manufacture, the P in the iron ore is removed to get a high quality steel as the steel containing more than 2% of P is brittle. The basic slag is obtained by the various processes of steel manufacture.

3.5

SUPERPHOSPHATE

INTRODUCTION

Superphosphate, $Ca(H_2PO_4)_2$, also refereed as single superphosphate (SSP), is the first chemically manufactured commercial fertilizer. John B Lawes named as superphosphate. Single superphosphate is produced as a combination of rock phosphate and concentrated sulfuric acid. Approximately equal amounts of the two ingredients are thoroughly mixed, dried and cured. Chemically, SSP contains monocalcium phosphate and calcium sulfate. The hardened mass is either ground or granulated.

The monocalcium phosphate of single superphosphate dissolves in the soil moisture and the roots absorb phosphoric acid in that form. The rest of the solution of monocalciumphosphate precipitates in the soil pores and forms different phosphate compounds which are water-insoluble and do not leach out. A compound like dicalcium phosphate dissolves in carbonic acid in water and becomes available to plants, but the insoluble tri-calcium phosphate remains fixed in the soil. Where soil is markedly acidic i.e., rich in active iron and aluminum monocalcium phosphate gets converted into insoluble phosphate compounds

$$2Ca(H_2PO_4)_2 + Fe_2O_3 \longrightarrow 2FePO_4 + 2CaHPO_4 + 3H_2O$$

Because iron and aluminum phosphates are insoluble, phosphorus does not available to the plant. That why SSP does not use in acidic soils unless it is limed.

SSP is the principal phosphate fertilizer due to

- The production process is simple, requires little skill and small investment
- It sets a standard of comparison for other phosphate fertilizers
- It supplies two secondary nutrient elements, namely, sulfur and calcium

Despite these advantages, single superphosphate has a low phosphorus content (16 to 22 % P_2O_5), and 6 to 10% moisture content which sometimes make SSP production uneconomical.

MANUFACTURE

Reactions

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O \longrightarrow CaH_4(PO_4)_2 + 2(CaSO_4.2H_2O)$$

$$CaF_2 + H_2SO_4 + 2H_2O \longrightarrow CaSO_4.2H_2O + 2HF$$

$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O$$

$$3SiF_4 + 2H_2O \longrightarrow SiO_2 + 2H_2SiF_6$$

Overall reaction

$$CaF_2.3Ca_3(PO_4)_2 + 7H_2SO_4 + 3H_2O \longrightarrow 3CaH_4(PO_4)_2.H_2O + 2HF + 7CaSO_4$$

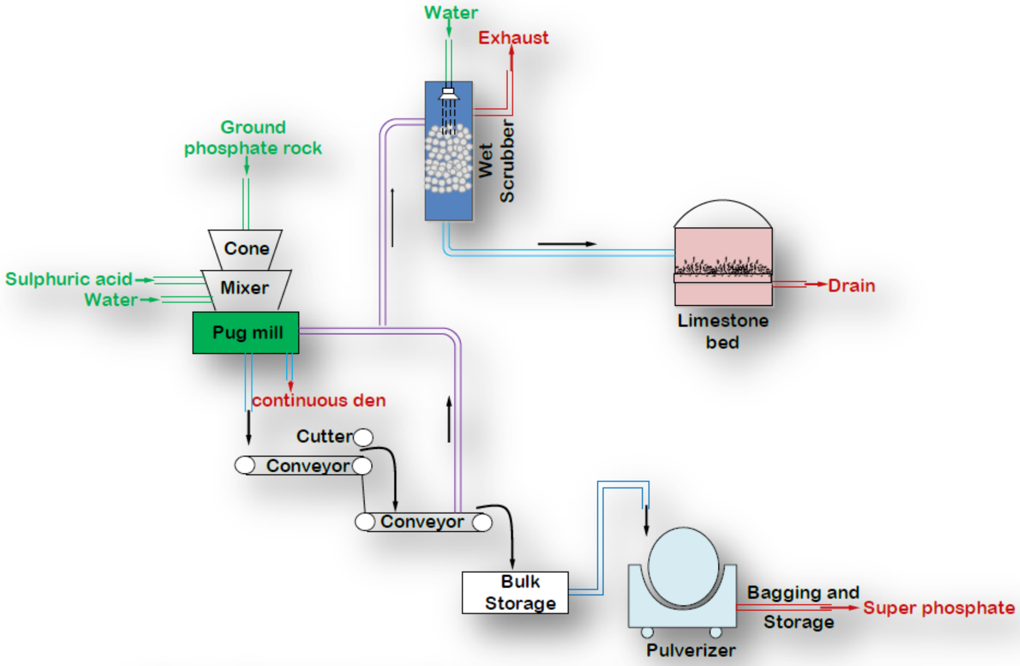


Figure: Manufacturing of Superphosphate by Continuous-den process of phosphorus in water. The increase in the ratio of $CaO:P_2O_5$ raises the consumption of sulfuric acid per unit of P_2O_5 and decreases the grade. Silica has no adverse effect and higher chloride content in the phosphate rock is acceptable.

b) Mixing with acid

A finely ground (less than 100 meshes) phosphate rock is mixed with sulfuric acid in a cone mixer. The commercial concentrated sulfuric acid (77 to 98 %) is diluted to around 68 to 75% before reacting with the rock.

c) Curing and drying of the original slurry by completion of the reactions

The fluid material from the cone mixer goes to a den where it solidifies owing to a continued reaction and crystallization of monocalcium phosphate. The superphosphate is removed from the den after 0.5 to 4 hours. It is still at temperature of about 100°C and plastic in nature.

d) Excavation, milling, and bagging of the finished product

The product from the den is sent to storage piles for final curing of 2 to 6 weeks. During curing, the free acid, moisture and the unreacted rock content decreases, whereas the available water-soluble phosphorus content increases. As the reaction approaches completion during curing, the material hardens and cools. The cured product is crushed in a hammer mill or cage mill to a size of about 6 mesh.

e) Granulation

When granular superphosphate is required, the product is granulated before or after curing. Granulation before curing is advantageous as it requires less steam or water. After granulation, the product is dried in a direct contact drier and screened.

Super phosphate is manufactured by

1. Batch process
2. Continuous process

1. Batch - den process

Rock phosphate and sulfuric acid in correct quantities are added to a pan mixer of 1 to 2 tons capacity. After mixing for 2 minutes, the fluid slurry is discharged into a box den which has 10 to 40 ton capacity. When the den is filled completely after 1 hour, it is moved slowly to a mechanical cutter which removes thin slices of product to the conveyor. Some plants have two dens, which are used alternatively. This set up gives a production rate of 40 tons per hour.

Advantages

- If only igneous rock is available, batch mixing are preferred due to precise control of mixing conditions available and den can be made tight enough to

contain the very fluid slurry.
- For a small phosphate source in a remote place, batch process can be built.

Although newer plants use continuous processes, some plants still conduct these operations stepwise. All plants first pulverize the rock with modern pulverizing and air-separation equipment, most rock is ground so that 70 to 80% of particles are passed through 200mesh screen.

Handling and storage

Powder SSP is not free flowing and has the tendency to cake. Granulated SSP can be easily handled and uniformly distributed in the field without any problem.

Due to the presence of free acid, single superphosphate is normally bagged in polyethylene lined HDPE woven bags. Polypropylene woven bags can also be used.

PROPERTIES

- Molecular formula : $CaH_4(PO_4)_2$
- Molecular weight : 234.05gm/mole
- Elemental analysis : 16% P_2O_5 (7%P), 12% S, 21% Ca, 4% phosphoric acid
- Appearance : White, Gray or brown granular
- Odour : Odourless
- Boiling point : 203^{0}C
- Melting point :109^{0}C
- Density : 2.22gm/ml
- Solubility : Solubility in water, HNO_3 and HCl
- Angle of repose : 26^{0}
- Critical humidity : 93.7% at 30^{0}C

USES

- It is the principal carrier of phosphate, the form of phosphorus usable by plants, and is one of the world's most important fertilizers.
- it is low cost source of phosphorous in a wide range of pasture and cropping situations
- Generally mixed with sulfate of ammonia and muriate of potash, but can be blended with other fertilizers

3.6

TRIPLE SUPERPHOSPHATE

INTRODUCTION

Triple superphosphate (TSP) is the more concentrated fertilizer than ordinary superphosphate, containing from 44 to 51% of available P_2O_5 or nearly three times the amount in the regular superphosphate. Owing to the high concentration of phosphorus, TSP is used widely in the production of high analysis compound fertilizers.

Triple superphosphate, also known as concentrated superphosphate, contains 45 to 50% monocalcium or water-soluble phosphate and 17 to 20% lime. Its concentrated form is cheaper to transport, store and apply when compared with the dilute form.

TSP is manufactured by adding phosphoric acid to rock phosphate, producing mainly water-soluble monocalcium phosphate with no calcium sulfate. In most processes, a large percentage of fluorine remains in the product, probably as fluorosilicate or calcium fluoride. When triple superphosphate is used as a fertilizer, the yield from short season crops like cereals, potato and some vegetables is markedly higher. This fertilizer lets a weak root system establish itself firmly and supports the crop to stand during the growing period.

Advantages

- It is a highly concentrated straight phosphate fertilizer.
- It has a low-cost source.
- Its manufacture requires small capital investment and low-skilled manpower.

Disadvantages

- Its total nutrient content is lower than that of ammonium phosphate.
- Its acidic character deteriorates storage bags.
- It is not suitable for blending with urea as it causes the latter to deteriorate

The manufacture of triple super phosphate involves following steps

a) Reaction
b) Denning or Den process step
c) Storage and curing

d) Granulation

a) Reaction

The reaction is carried out in a cone-mixer. A similar process known as Kuhlman process uses a mixer that has a high-speed stirrer in a cylindrical vessel. 95 to 98% of the ground rock phosphate, passed through 100 mesh sieve, is mixed with phosphoric acid (1kg rock phosphate of 34% P_2O_5 is mixed with 2.6kg acid). The acid is of commercial grade with P_2O_5 content of 52%.

b) Den step

The den step, of TSP is faster (10-30min) than that for SSP (30-120min). The mixture from the reaction vessel goes to the den where it solidifies owing to continued reaction and crystallization of monocalcium phosphate.

c) Storage and curing step

Product from den step is stored in piles for curing. Curing requires 3 to 6 weeks, depending on the quality of raw materials. During curing, the free acid, moisture and unreacted rock contents decrease and the available phosphorus and the water soluble P_2O_5 increase. Fluorine compounds evolved in minor quantities which are scrubbed to prevent atmospheric pollution.

After storage and curing, TSP is ground to a 6 mesh screen (3.3 mm). This material is called run off pile TSP or ROP-TSP and is used for making compound fertilizers by agglomeration granulation.

d) Granulation process

Granulation is preferred due to powder form have dusty nature and caking quality when moist. The milled and screened TSP is conveyed to a drum granulator where water is sprayed and steam is spurge underneath the bed to wet the material. The wet granules are dried in the rotary drier. The dried granules are screened, and the oversized and the fines are returned to the granulator. The dust and fumes from the drier are scrubbed or removed by the dust filter.

MANUFACTURE

Reaction

$$CaF_2 + 3Ca_3(PO_4)_2 + 14H_3PO_4 \longrightarrow 10Ca(H_2PO_4)_2 + 2HF$$

Manufacture

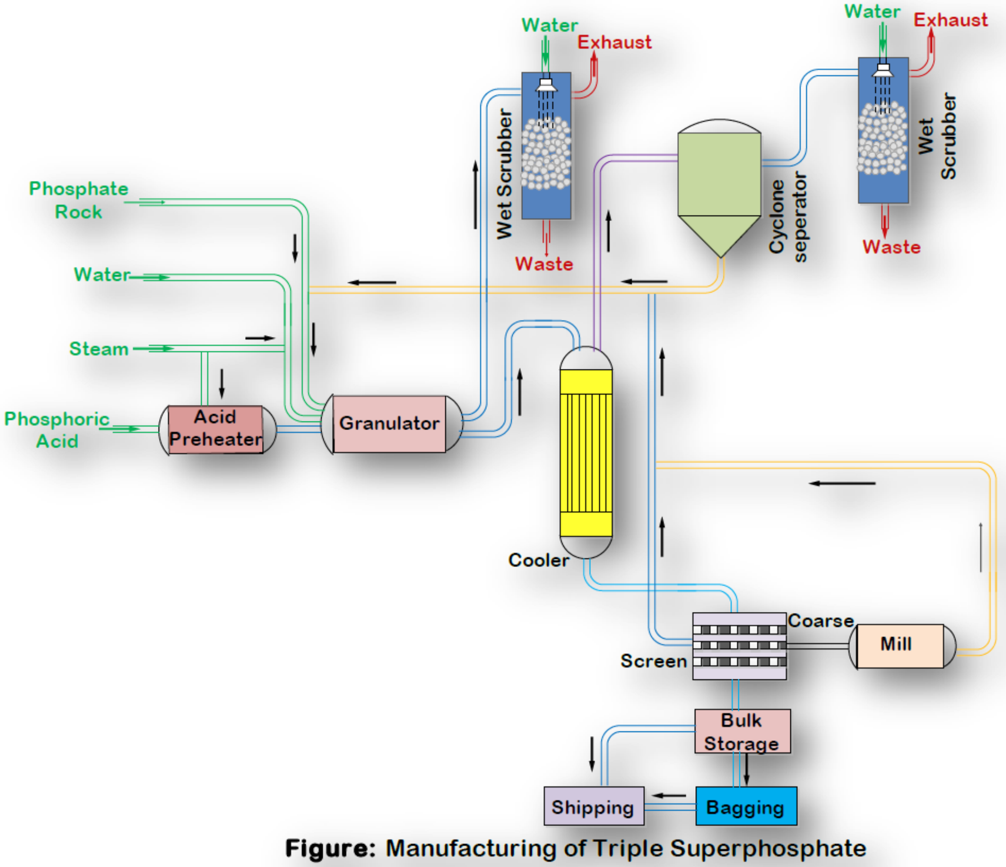


Figure: Manufacturing of Triple Superphosphate

Finely ground phosphate rock and 62% H_3PO_4 are charged continuously to the granulator, where reaction and granulation take place. Fines from the product screen are recycled to the granulator, and the moisture and temperature required for proper granulation are maintained by addition of water and/or steam. The granulator is a cylindrical vessel rotating about a horizontal axis and has in overflow dam at the discharge end.

The phosphoric acid is fed uniformly under the bed of material through a perforated pipe. When wet-process phosphoric acid is used, it is also necessary to provide an acid pre-heater. The granules overflow the dam into the rotary cooler, where they are cooled and dried slightly by counter current flow of air. The exhaust gases from the cooler pass through the cyclone, where dust is collected and returned to the granulator as recycle, the cooled product is screened, the coarse material being milled and returned, along with the fines, to the granulator.

The product is then conveyed to bulk storage, where the material is cured for 1 to 2 weeks, during which a further reaction of acid and rock occurs, which, increases the availability of P_2O_5 as plant food, the exhaust gases from the granulator and cooler are scrubbed with water to remove silicofluorides.

The cost per unit of P_2O_5 is higher as compared to ordinary superphosphate, because of more capital investment and additional labour and processing. However, this is balance to the great extent by the ability to use the lower-grade, cheaper phosphate rock to make the phosphoric acid. There are also substantial savings on handling, bagging, shipping, and distributing.

Granulation

The Den process or direct slurry granulation process may prepare triple superphosphate either in a granular or non-granular form. The granular form of TSP is preferred for direct application or blending and the non-granular form for making compound fertilizers.

Advantages of the direct slurry granulation process

- Product is available at a lower cost
- Generate denser and stronger granules
- Use of conventional granulation equipment

Disadvantages

- Uses phosphate rocks which have a short reaction time, resulting in a greater loss of soluble phosphorus (as P_2O_5) due to an incomplete reaction or higher ratio of phosphoric acid

Granular triple superphosphate is produced directly rather than from the powder fertilizer.

Handling and storage

TSP in powder form is not free flowing and has a tendency to cake on storage. The granulated product has excellent handling and storage characteristics, and is free flowing. The material is packed in polyethylene film lined HDPE bags.

3.7

PROPERTIES

- Molecular formula : Triple superphosphate
- Molecular weight : 252.07gm/mole
- Appearance : White or gray granules
- Solubility : water soluble
- Density : 1.089gm/ml
- pH : 2.5-3.0 (aqueous solution)
- P_2O_5 (water soluble) : 42.5% minimum
- Free phosphoric acid : 3% by wt. (Max.)
- Angle of repose : 45^0
- Bulk density : 800-881kg/m^3
- Moisture : 12.0% by wt. (Max.)

USES

- TSP can be used in wastewater treatment to reduce lead levels
- As a low cost source of phosphorus, TSP is the main substitute for single superphosphate in cropping blends.
- It is used mainly in blends with DAP and MAP
- Source of phosphorus in situations where no nitrogen is required e.g. good fallow after clover dominant pasture.
- In horticultural blends where the phosphorus content needs boosting

3.7 THERMAL PHOSPHATE

Rhenania Phosphate

Rhenania Phosphate is another thermally produced phosphate fertilizer. It is made by calcining a mixture of phosphate rock, sodium carbonate, and silica in a rotary kiln at 1250^0C [15]. Enough sodium carbonate is used to form the compound $CaNaPO_4$ and enough silica to form Ca_2SiO_4 with the excess calcium. Typical charge proportions are one part of sodium carbonate to three parts of phosphate rock and enough silica to raise the SiO_2 content of the product to about 10%. The product contains 28% - 30% P_2O_5 , which is nearly all soluble in neutral or alkaline ammonium citrate solution even though much of the flurine remains in the product. It is applied to the soil in pulverized form or granulated in small granules with potash salts. Some grades are produced containing magnesium or boron, which are added during granulation as kieserite or borax, respectively.

A somewhat similar product, Roechling phosphate, uses a soda slag that is a byproduct from the steel industry. Also, the naturally occuring minerals, trona (sodium sesquicarbonate) or natron (sodium carbonate), may be used. Experimants have shown that a similar product can be made by sintering potassium carbonate with phosphate rock and silica to produce a product grade of 0-25-25. The phosphate compound in this product is presumed to be $CaKPO_4$.

The overall reaction in producing Rhenania phosphate is assumed to be:

$$Ca_{10}\,F_2\,(PO_4)_6 + 4Na_2\,CO_3 + 2SiO_2 \rightarrow 6CaNaPO_4 + 2Ca_2\,SiO_4 + 2NaF + 4CO_2$$

Any grade of phosphate rock can be used, but since the grade of the product is determined by the grade of the rock, a high grade is preferred.

Dicalcium Phosphate

Dicalcium Phosphate is a common constituent of nitrophosphate fertilizers and of compound fertilizers formed by ammoniation of superphosphates. The process of production consists of dissolving phosphate rock in hydrochloric acid and then precipitating dicalcium phosphate by stepwise addition of limestone and slaked lime. The product is recovered by filtration and washing, and the remaining solution of calcium chloride may be used or discarded.

Magnesium Phosphates

Monomagnesium, dimagnesium, and trimagnesium phosphates are known to be effective fertilizers, but there is no known commercial production of these materials for fertilizer use. No doubt small percentages of these compounds are formed in processing phosphate rock containing magnesium.

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SCHOOL OF BIO AND CHEMICAL

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – IV– FERTILIZER TECHNOLOGY – SCH1604

Unit-IV

4.1 Types of Complex Fertilizers-composition

4.2 Production of Ammonium phosphate fertilizer

4.3 Ammonium sulphate

4.4 Diammonium phosphate

4.5 Nitro phosphate

4.1 Complex fertilizers

Complex fertilisers contain varying ratios of two or three macronutrients (nitrogen, phosphorous and potassium) required by plants. Their application simplifies the task of balancing soil nutrients and boosts yields. Complex fertilisers supply crops with essential nutrients in a form favourable for plant nutrition, assuring peak efficiency in a variety of climatic conditions.
The Group manufactures NPK, blends, and NP complex fertilisers.

NPK

NPK is a multipurpose nitrogen-phosphate-potassium mineral fertiliser. In its highly digestible form, it includes all basic nutrients ensuring balanced plant nutrition.

Nitrogen content

At least 50% in ammonium form, no more than 50% in nitrate form.

Characteristics and advantages

- NPK activates the plant growth process and increases the seed germination rate
- Strengthens plant immunity by activating protective properties; reduces damage caused by root rot, powdery mildew, and rust
- Increases the durability of plant stems and grain resistance to lodging
- Ensures a significant increase in yield (from 20% to 50%)
- Can be applied using different rates and methods to customize for crop and soil type
- NPK is well retained in soils; it has almost zero scavenging rate by precipitation and is less fixed by the soil-absorbing complex than single-component fertilisers
- Reduces time and money due to the high concentration of active elements, as well as storage and application characteristics
- Anti-caking agents ensure long-term preservation of all fertiliser properties, with increased flowability and slower dissolution, which significantly reduces nitrogen loss during irrigation

Application

NPK is effective on soils of various grain-size distribution in the Central Black Earth Region. It is suitable for unstable and insufficient watering conditions with regular droughts and intensive erosion processes. NPK is recommended for use in autumn during the main application for sugar beet, sunflower, and buckwheat. Sowing application is effective for spring wheat, barley, millet, maize for silage and grain, and various vegetable crops.

The fertilizer shows increased efficiency when topping winter grain crops using a localised band placement method to a depth of 8-10 cm. It is indispensable for overgrown plants that require additional nutrition. NPK positively influences product quality and increases nutritional value and oil content in grains and fruits, which is beneficial for the duration of storage of the crop, as well as the ability of plants to resist bad weather conditions.

Complex fertilizers (also known as compound fertlizers) are made from mixing two or more of macro-nutrient type fertlizers. They may also be further blended with elements that provide some of the less-common plant nutrients (known as secondary or trace nutrients, such as sulfur, calcium and magnesium). Compound fertilizer can be packaged and distributed in liquid or granular form.

A numbering system is used to define the percentages of the three essential plant nutrients. For example, a 20-20-10 fertilizer would contain 20 percent nitrogen, 20 percent phosphorus and 10 percent potassium. Secondary nutrients and trace elements are typically listed.

Diammonium Phosphate (18-46-0)

DAP Improves plant resistance to stress such as drought or frost and certain diseases. Increases the sugar content in fruit and root crops. Especially efficient as the main fertilizer for cereals, fodder-crops and vegetables and as a supplementary dressing for fruits. Suitable for greenhouse application.

Mono Ammonium Phosphate (MAP 11-52-0)

Monoammonium phosphate is an ideal source of Phosphorus and Nitrogen at all stages of plant growth. It can be used as a foliar spray on crops early during cell division and also during times of stress. Suitable for use on a wide range of indoor and outdoor crops

NPK 23-23-0

Highly efficient complex mineral fertilizer. Suitable for all soil and crop types. Especially efficient on podzolic soils with low reserves of phosphorous and potassium. Efficient as either the main fertilizer or extra-nutrition for vegetables, legumes, wheat, barley and maize .

4.2 AMMONIUM PHOSPHATE

There are two major types of ammonium phosphates, namely: mono-ammonium phosphate and di-ammonium phosphate. Mono-ammonium phosphate is made by reacting ammonia with phosphoric acid, centrifuging and drying in a rotary dryer. Di-ammonium phosphate requires a two-stage reactor system in order to prevent loss of ammonia. A granulation process follows with completion of the reaction in a rotary dryer which is heated by a furnace using fuel.

Ammonium dihydrogen phosphate (ADP), or monoammonium phosphate, $NH_4H_2PO_4$, is formed when a solution of phosphoric acid is added to ammonia until the solution is distinctly acidic. It crystallizes in tetragonal prisms. Monoammonium phosphate is often used in the blending of dry agricultural fertilizers. It supplies soil with the elements nitrogen and phosphorus in a form which is usable by plants. The compound is also a component of the ABC powder in some dry chemical fire extinguishers. This substance is also supplied in an emerald green or aquamarine crystal growing box kit for children.

Solid mono ammonium phosphate show a dissociation pressure of ammonia of 0.05 mmHg at 125°C based on the decomposition reaction as follows:

$$NH_4H_2PO_4(s) \rightleftharpoons NH_3(g) + H_3PO_4(l)$$

ADP is a widely used crystal in the field of optics due to its birefringence properties. As a result of its tetragonal crystal structure, this material has negative uniaxial optical symmetry with typical refractive indices n_o=1.522 an n_e=1.478 at optical wavelengths.

ADP crystals are piezoelectric which is a property required in some active sonar transducers (the alternative being transducers that use magnetostriction.

Diammonium phosphate (DAP) (chemical formula $(NH_4)_2HPO_4$, IUPAC name diammonium hydrogen phosphate) is one of a series of water-soluble ammonium phosphate salts which can be produced when ammonia reacts with phosphoric acid. Solid diammonium phosphate shows a dissociation pressure of ammonia as given by the following expression and equation:

$(NH_4)_2HPO_4(s) \rightleftharpoons NH_3(g) + NH_4H_2PO_4(s)$ $\log P_{mmHg} = -3063 / T + 175 \log T + 3.3$

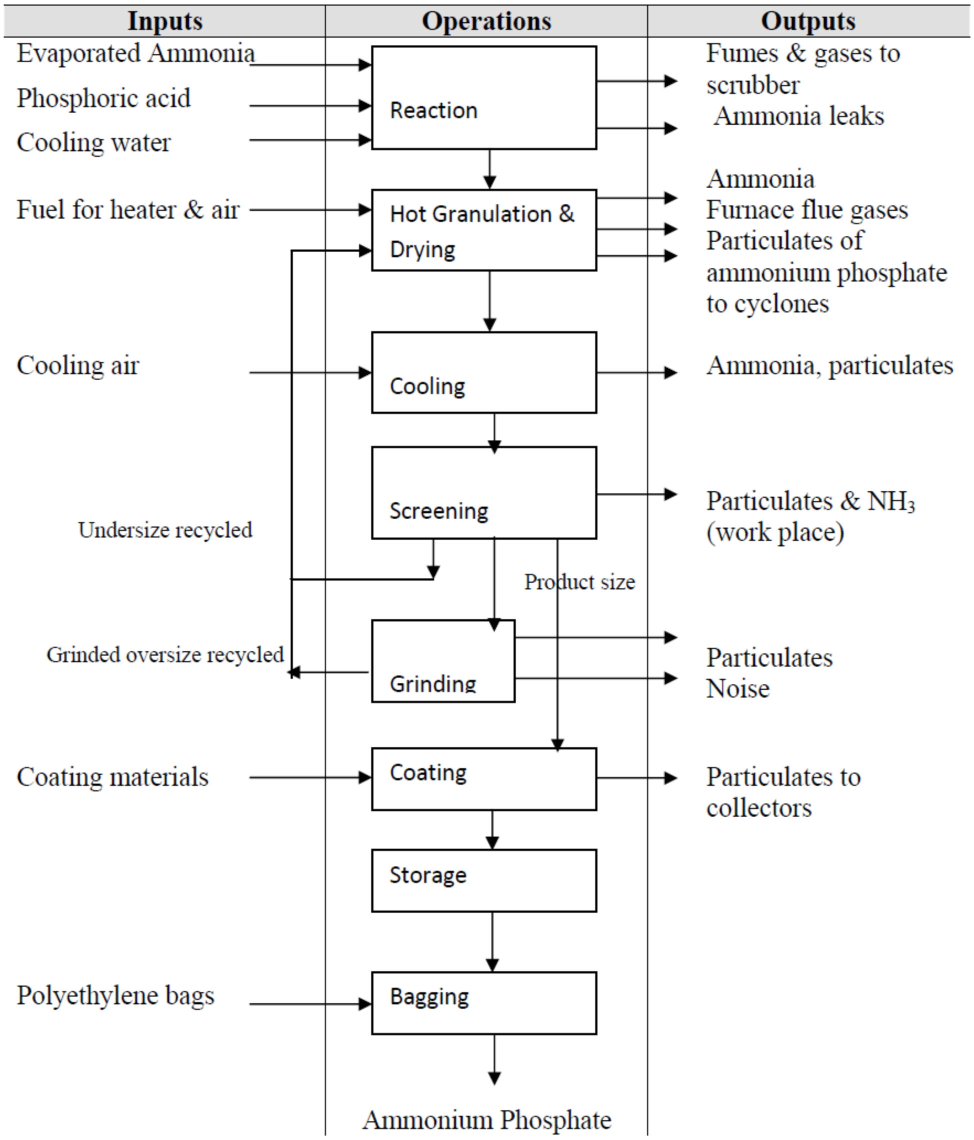
where:

P = the resultant dissociation pressure of ammonia

T = absolute temperature (K)

At 100ºC, the dissociation pressure of diammonium phosphate is approximately 5 mmHg

DAP is widely used as a fertilizer. When applied as plant food, it temporarily increases the soil pH, but over a long term the treated ground becomes more acidic than before upon nitrification of the ammonium. It is incompatible with alkaline chemicals because its ammonium ion is more likely to convert to ammonia in a high-pH environment.



PROCESS FLOW DIAGRAM FOR AMMONIUM PHOSPHATE

Ammonium polyphosphate is an inorganic salt of polyphosphoric acid and ammonia containing both chains and possibly branching. Its chemical formula is $[NH_4\ PO_3]_n$ showing that each monomer consists of an orthophosphate radical of a phosphorus atom with three oxygens and one negative charge neutralized by an ammonium cation leaving two bonds free to polymerize. In the branched cases some monomers are missing the ammonium anion and instead link to three other monomers.

The properties of ammonium polyphosphate depend on the number of monomers in each molecule and to a degree on how often it branches. Shorter chains ($n<100$) are more water sensitive and less thermally stable than longer chains ($n>1000$), but short polymer chains (*e.g.* pyro-, tripoly-, and tetrapoly-) are more soluble and show increasing solubility with increasing chain length.

Ammonium polyphosphate can be prepared by reacting concentrated phosphoric acid with ammonia. However, iron and aluminum impurities, soluble in concentrated phosphoric acid, form gelatinous precipitates or "sludges" in ammonium polyphosphate at pH between 5 and 7. Other metal impurities such as copper, chromium, magnesium, and zinc form granular precipitates. However, depending on the degree of polymerization, ammonium polyphosphate can act as a chelating agent to keep certain metal ions dissolved in solution.

Ammonium polyphosphate is used as a food additive and emulsifier, (E number: E545). It is also used as a flame retardant for polyolefins and polyurethanes and as a fertilizer.

As a fire retardant, ammonium polyphosphates decompose to form ammonia and phosphoric acid. The phosphoric acid acts as an acid catalyst in the dehydration of carbon-based poly-alcohols, such as cellulose in wood. The phosphoric acid reacts with alcohol groups to form heat-unstable phosphate esters. The esters decompose to release carbon dioxide and regenerate the phosphoric acid catalyst. The release of non-flammable carbon dioxide helps to dilute the air of oxygen and flammable decomposition products of the material that is burning. The resultant carbonaceous char is less-flammable than before. Use as an intumescent is achieved when combined with starch-based materials

4.3

AMMONIUM SULFATE

INTRODUCTION

Ammonium sulfate containing 21% nitrogen is another important nitrogenous fertilizer.

It occurs naturally as the mineral mascagnite and offers many advantages as a fertilizer, such as low hygroscopicity, good physical properties, excellent chemical stability, good agronomic effectiveness and long shelf life.

Ammonical nitrogen is fixed in the soil in an exchangeable form until nitrated by nitrifying bacteria. The ammonical nitrogen of ammonium sulfate does not leach out easily. Ammonium sulfate is an acid forming fertilizer, and hence used in neutral or alkaline soils. In its free flowing form, it is directly applied to the soil or blended with other granular materials. Ammonium sulfate also supplies sulfur, which is an essential nutrient for plants. It is a quick-acting fertilizer. It is resistant to leaching as it gets adsorbed on the soil colloids, clay and humus, and replaces calcium. This adsorbed ammonium salt is converted to nitrate by nitrifying bacteria for use by growing plants.

It can be obtained as a by-product or may be manufactured synthetically. Ammonium sulfate is obtained as a byproduct; in the steel industry in which NH_3 (another by-product) from coke ovens is absorbed in sulfuric acid. $(NH_4)_2SO_4$ is also manufactured by reacting synthetic ammonia with sulfuric acid.

$(NH_4)_2SO_4$ is obtained from waste streams of chemical and metallurgical industries e.g. ammonia leaching of ores, production of pigments and synthetic fibers, manufacture of caprolactam produce by product; solutions containing ammonium sulfate.

Flue gases are another source of the ammonium sulfate. The metallurgical smelters and coal burning power plants liberate large quantities of SO_2 that pollute the atmosphere. SO_2 is collected and converted into sulfuric acid, $(NH_4)_2SO_4$ is then produced by passing ammonia gas through 60% sulfuric acid placed in lead lines vats at about 60°C the crystals of ammonium sulfate separate out on cooling.

$$2NH_4OH + H_2SO_4 \longrightarrow (NH_4)_2SO_4 + 2H_2O$$

MANUFACTURE

a) As by-product from caprolactam
b) Recovery from cock oven
c) Direct neutralization
d) Gypsum process

a) As By-product from caprolactam

$(NH_4)_2SO_4$ solution is formed during the manufacture of caprolactam. The waste liquor containing 35% solution of ammonium sulfate is concentrated, and ammonium sulfate, is recovered by crystallization, centrifuging and drying.

b) Recovery from coke oven gas

Cleaned coke even gases passed into an absorption column, counter current to the recirculating stream of saturated solution of $(NH_4)_2SO_4$. 96-98% sulfuric acid is introduced into the stream at another point. The neutralization takes place and the effluent solution containing $(NH_4)_2SO_4$ is passed to the crystallizer, where, crystals of $(NH_4)_2SO_4$ are separated out on cooling. The crystals are dried after separation by filtration or by centrifuge. The mother liquor overflowing from the crystallizer is acidified and recycled to the absorber.

In an old saturation process ammonium sulfate is produced by passing coke oven gas and sulfuric acid into a vat containing a saturated solution of $(NH_4)_2SO_4$ and then setting out the crystal.

c) Direct neutralization or Synthetic Manufacture

Reaction

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

Ammonium sulfate made with manufactured ammonia is called synthetic ammonium sulfate. Both saturator's and crystallizers are employed in the synthetic manufacture of ammonium sulfate. The heat of reaction of anhydrous ammonia and concentrated sulfuric acid obtained by contact process is very high. Hence water evaporated from the crystallizer must be returned either by means of a condenser or by addition of water.

Ammonia and sulfuric acid are introduced via the slurry recycle line, wherein they react and superheat the recycling slurry. The slurry is subsequently flashed in the upper chamber at a reduced pressure (550 – 580mm of Hg). The exothermic heat of reaction is removed by evaporating water either present in the feed acid or added to the system for temperature control of the process. The loss of water in this zone supersaturates the slurry which recirculates to the lower suspension vessel via an internal pipe and comes into contact with small crystals and nuclei. This induces further crystal growth in terms of size rather than in number. The slurry is recycled by a thermal syphon and/ or by an external pump. This type of crystallizer is generally known as 'Krystal' or 'Oslo unit'.

During operation the pH control is required to be maintained within close limits (3.0 to 3.5), otherwise, thin crystals result. The excessive acidity promotes an overgrowth of crystals in the pipelines. A higher pH or a lower acidity leads to inferior crystals which are difficult to wash and store and may cause ammonia losses as well.

d) Gypsum process

Raw materials

Ammonia
CO_2
Gypsum

Reaction

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

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

$CaCO_3 \longrightarrow CaO + CO_2$

Manufacture

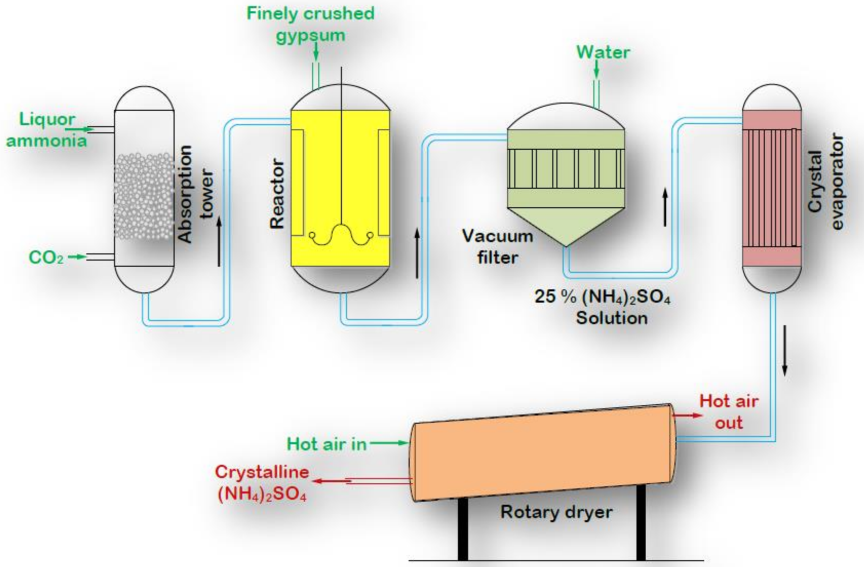


Figure: Manufacturing of Ammonium Sulphate

Ammonia is manufactured by Haber process and CO_2 is manufactured by heating limestone. Ammonia is absorbed in water and carbonated at the pressure of about 2.1kg/cm^2 in towers packed with aluminum rings. The prepared liquor strength corresponds to approximately 170gms of ammonia and 225gms of CO_2 per liter. In another method jet absorbers are used for preparing ammonia solution and ammonium carbonate liquor in conjunction with a carbonating tower.

Natural gypsum or anhydrite, when used, is ground so that about 90% of the material passes through 120 mesh sieve. When the byproduct gypsum of phosphoric acid plant is used, the impurities are removed by repulping the filter cake prior to washing and dewatering on a drum or disc filter.

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

Reactions of ammonium carbonate and gypsum solutions are carried out in a series of wooden vessels or mild steel vessels having steam coils and agitators to give a total retention time of 4 to 6 hours. CO_2 and NH_3 are passed until all the gypsum is converted into $CaCO_3$. The slurry produced is filtered and the calcium carbonate cake washed and dewatered. The solution is evaporated and the crystals are centrifuged and dried in a rotary drier at 120^{0}C. $CaCO_3$ obtained as by product is used as a raw material for the manufacture of cement.

Action of $(NH_4)_2SO_4$ as fertilizer

It reacts with lime present in the soil to for ammonium hydroxide which is oxidized by air with the help of nitrifying bacteria into nitrous acid. Later is then converted into nitrites. The nitrous acid and nitrites also undergo oxidation by means of air in presence of nitrifying bacteria and form nitric acid and nitrate.

Handling and storage

Crystalline ammonium sulfate is free flowing and does not normally pose any problem in handling and storage. However, it generally contains some powdered material which causes caking, especially under high humidity.

Due to its susceptibility to caking and slight acidity, ammonium sulfate is normally bagged in polyethylene lined gunny bags or high density polyethylene (HDPE) woven sacks.

PROPERTIES

- Molecular formula : $(NH_4)_2SO_4$
- Molecular weight : 132.14gm/mole
- Appearance : Fine white hygroscopic granules or crystals
- % of nitrogen : 20-21%
- Bulk density : 720-1040kg/m^3
- Melting point : $>280^0C$
- Specific gravity : 1.769
- Angle of repose : 32^0
- Solubility : Solubility in water and insoluble in alcohol, ether, acetone
- Moisture : 1% wt. (Max.)

USES

- Most commonly used in fertilizers. It is often used in combination with other materials, such as urea, to make dry fertilizers.
- It is a good source of nitrogen for cotton, rice, wheat, barley, maize, sorghum, sugar cane and fiber crops.
- It is also used as a general purpose food additive, dough conditioner and food for yeast.
- In medicine, ammonium sulfate plays an important role in the development of vaccines. The DTaP vaccine, for example, which protects children from diphtheria, tetanus and whooping cough, uses ammonium sulfate in the purification process
- Used in rice and jute cultivation

4.4 Diammonium Phosphate

Chemical Name
Diammonium phosphate
Crop Segments
All
Features
High analysis nitrogen and phosphorus contained in every granule.
Quality & Handling
Nominal 2-4mm size granule, free flowing product.
Bulk density 0.9 tonnes per cubic metre.
Blending
Can be blended with most products and trace elements.

Features

- High analysis source of phosphorus.
- N:P ratio of 1:1 makes it an effective source of nitrogen.
- DAP releases free ammonium. Nitrogen in the ammonium form resists leaching and is a slower release form of nitrogen.
- The free ammonium gives a higher pH reaction immediately around the granule.

- The low cost of nitrogen in DAP makes it a cost effective source of nitrogen if Phosphorus is also required.

Manufacture

Ammonia gas is combined with phosphoric acid in a ratio of 1:1, granulated, dried and screened.

Uses

One of the major cropping fertilisers used in Australia as a source of both phosphorus and nitrogen. The high phosphorus content makes it a true high analysis fertiliser. DAP and DAP blends are used on a range of crops in broad-acre farming, cereals, sugar cane, sowing pastures, dairy pastures, fodder crops and also in horticultural crops; for example, vegetables and tree crops.

Storage and handling

- Does tend to take up moisture, both in storage and in the field.
- Storage in a bulk shed is the preferred storage method. Covering with a tarp may reduce any moist air uptake.
- The use of augers may damage the fertiliser and increase any handling problems.
- Do not leave exposed to moist air.
- Either fill or empty (completely), the drill or air-seeder fertiliser box overnight.
- Cover seeding equipment with a tarp.
- Raise the equipment tynes from the soil to stop moisture moving up the tubes.

Restrictions

- For sowing there is little risk of affecting germination, even at high rates. The general rule of a maximum of 20kg/ha of nitrogen at seeding of cereals should be used.
- When applying DAP, the fertiliser should be banded 5cm away from the seed, either below or to the side. DAP is low in sulphur – 1.5%. It is not recommended for high sulphur requiring crops such as canola, unless blended with sulphate of ammonia.
- Do not store in silos.

4.5 Nitro Phosphate

Introduction

"Nitrophosphate" is the generally accepted term for any fertilizer that is produced by a process involving treatment of phosphate rock with nitric acid.

Fundamentals of Nitrophosphates

The basic (and simplified) acidulation reaction can be represented by the following reaction equations:

$Ca_3(PO_4)_2 + 4\,HNO_3 \rightarrow 2\,Ca(NO_3)_2 + Ca(H_2PO_4)_2 + 20.2$ kcal

$Ca(H_2PO_4)_2 + 2\,HNO_3 \rightarrow Ca(NO_3)_2 + 2\,H_3PO_4 + 2.05$ kcal

Overall

$Ca_3(PO_4)_2 + 6\,HNO_3 \rightarrow 3\,Ca(NO_3)_2 + 2\,H_3PO_4 + 22.25$ kcal

After separation of the insoluble material, phosphoric acid is neutralized with ammonia to produce a fertilizer. If the calcium nitrate is left in the solution, it reverts to dicalcium phosphate ammonium following the reaction:

$2H_3PO_4 + Ca(NO_3)_2 + 4NH_3 \rightarrow CaHPO_4 + (NH_4)_2HPO_4 + 2NH_4NO_3 + 66.67$ kcal

Calcium is non-nutrient in terms of N, P, and K and is therefore seen as a diluent. For these reasons alone, it is desirable to remove calcium from the solution. But there is another, more important reason. If the calcium nitrate is left in the solution, when it is neutralized the N:P ratio will be fixed. To produce grades with lower N:P ratios, it is necessary to remove calcium nitrate, whereas if higher nitrogen grades are required, the removed calcium nitrate can be converted to ammonium nitrate and returned to the solution. Therefore, most nitrophosphate processes include some means of removing calcium nitrate from the solution.

Nitrophosphate Processes

Selection of Phosphate Rock

In general, reactivity of the phosphate rock is no problem; even igneous apatites dissolve readily in nitric acid. The rock need not be finely ground; rock finer than 1 mm is satisfactory, and some operators even accept particles up to 4 mm. In general, the rock need only be fine enough to prevent rapid settling in stirred reaction vessels. High-silica rock can be used if the equipment is designed for that purpose. Most nitrophosphate plants include a silica removal step. Coarse silica particles can be very abrasive to pumps and piping, and this fact should be considered in plant design.

It is desirable that the $CaO:P_2O_5$ ratio in the rock should be as low as economically feasible to minimize the amount of calcium that must be removed or offset(in mixed-acid processes). While additional calcium requires more nitric acid, it does not necessarily involve a direct economic penalty because the nitrate is subsequently converted to ammonium nitrate either in the nitrophosphate product or in a coproduct.

Carbonates is phosphate rock cause foaming, which is usually dealt with by using mechanical foam breakers. However, foaming can be a difficult problem with some rocks.

Organic matter is undesirable in nitric phosphate processes; it reacts with nitric acid with emission of nitrogen as NO_2 or other nitrogen oxides.

Iron and aluminum oxides present no special problem within the range of occurrence in commercial phosphate rocks; these oxides usually are dissolved in nitric acid and reprecipitated during ammoniation as citrate-soluble phosphates. TVA tested “leached-zone” Florida phosphate containing a high percentage of aluminum phosphate minerals in a special nitrophosphate process.

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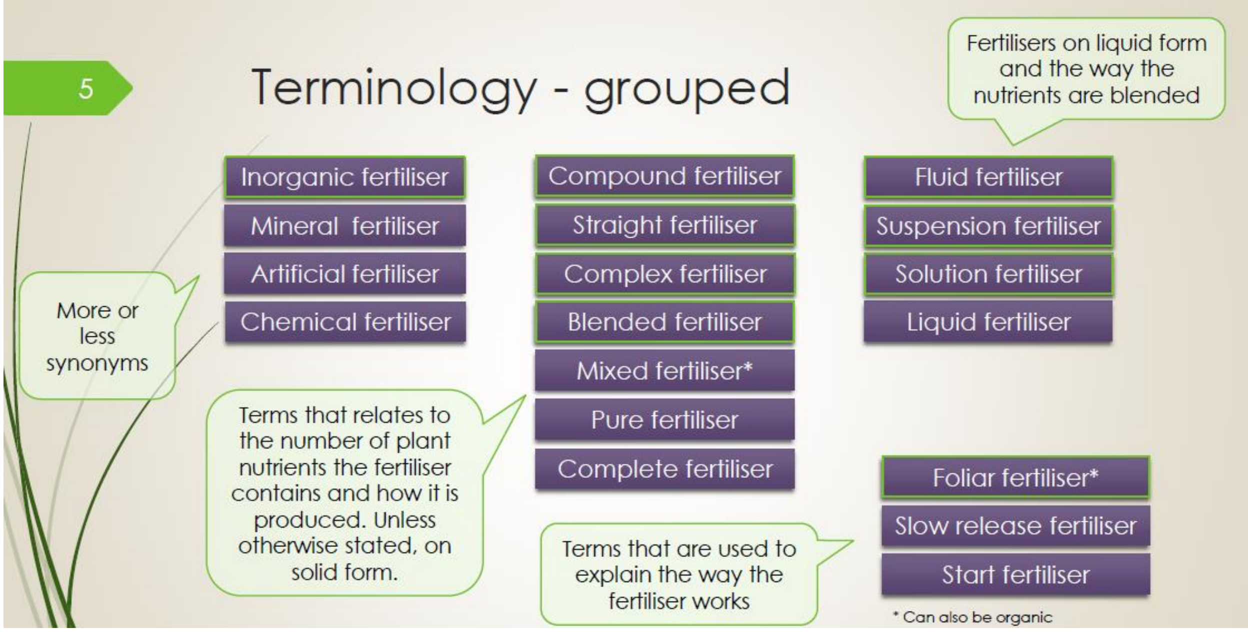
SCHOOL OF BIO AND CHEMICAL

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – V– FERTILIZER TECHNOLOGY – SCH1604

Mixed or granulated fertilizer



Terminology - grouped

Fertilisers on liquid form and the way the nutrients are blended

More or less synonyms

- Inorganic fertiliser
- Mineral fertiliser
- Artificial fertiliser
- Chemical fertiliser

Terms that relates to the number of plant nutrients the fertiliser contains and how it is produced. Unless otherwise stated, on solid form.

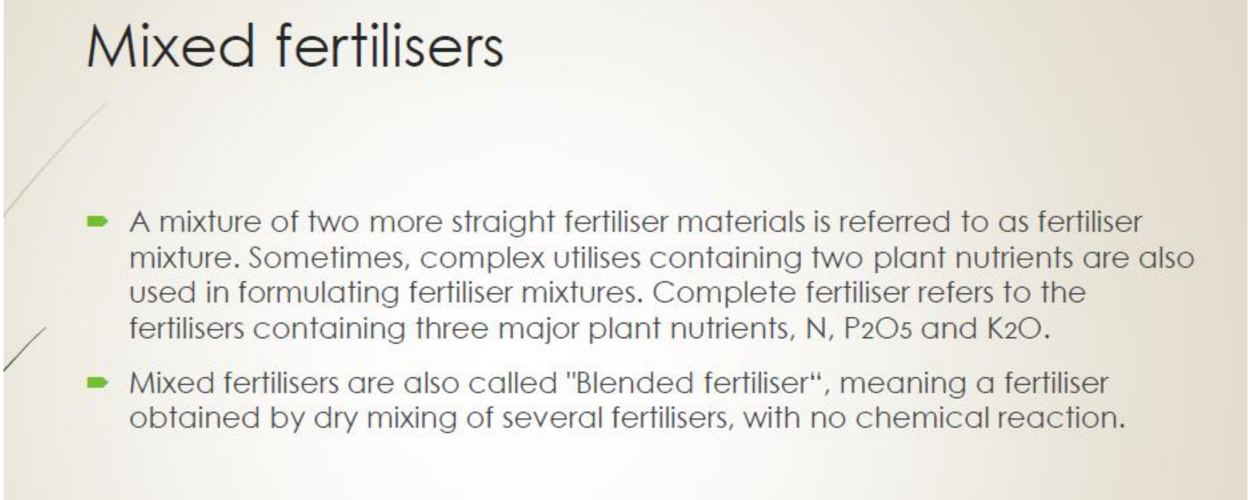
- Compound fertiliser
- Straight fertiliser
- Complex fertiliser
- Blended fertiliser
- Mixed fertiliser*
- Pure fertiliser
- Complete fertiliser

- Fluid fertiliser
- Suspension fertiliser
- Solution fertiliser
- Liquid fertiliser

Terms that are used to explain the way the fertiliser works

- Foliar fertiliser*
- Slow release fertiliser
- Start fertiliser

* Can also be organic

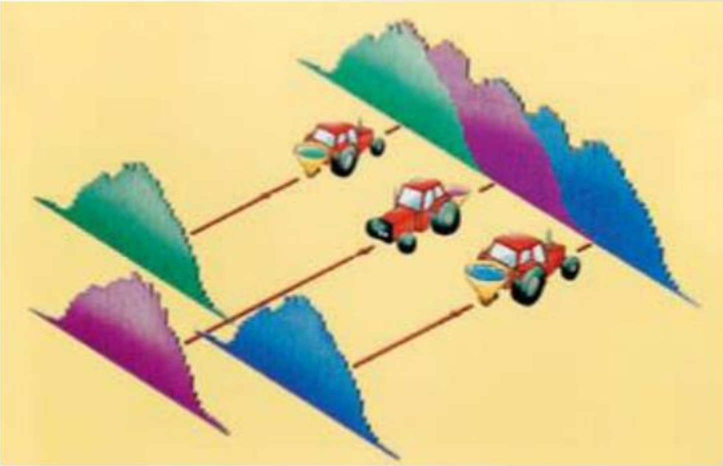


Mixed fertilisers

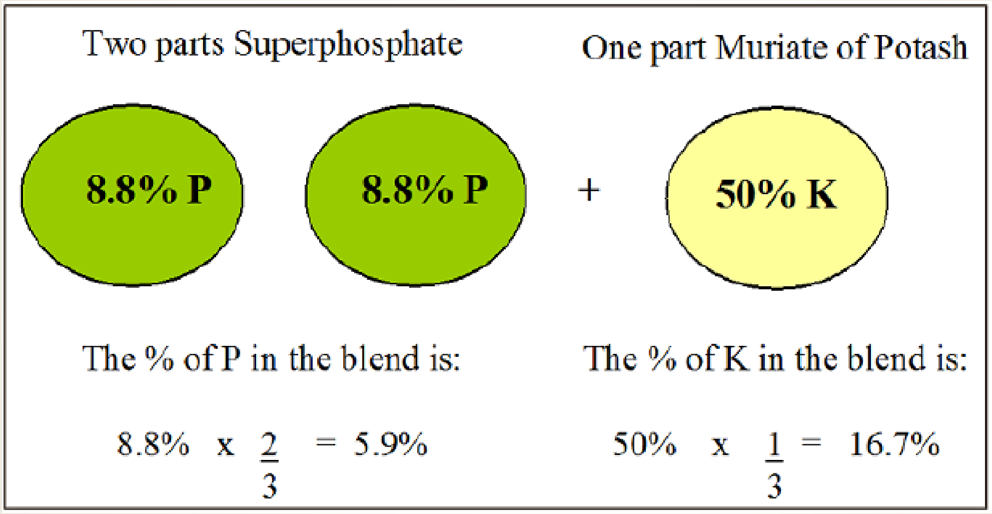
- A mixture of two more straight fertiliser materials is referred to as fertiliser mixture. Sometimes, complex utilises containing two plant nutrients are also used in formulating fertiliser mixtures. Complete fertiliser refers to the fertilisers containing three major plant nutrients, N, P_2O_5 and K_2O.
- Mixed fertilisers are also called "Blended fertiliser", meaning a fertiliser obtained by dry mixing of several fertilisers, with no chemical reaction.

Mixed fertilisers

- If the mixed fertilisers are of different granule size or density, the risk is that the nutrients by spreading are unevenly distributed on the field, because the largest and heaviest granules tends to fly longest, while dust and small granules dumps down shortly behind the spreader and is taken by the wind.



Mixing fertilisers



Two parts Superphosphate

One part Muriate of Potash

8.8% P **8.8% P** + **50% K**

The % of P in the blend is:

$8.8\% \times \frac{2}{3} = 5.9\%$

The % of K in the blend is:

$50\% \times \frac{1}{3} = 16.7\%$

Mixed or complex – the difference is visible

Mixed fertiliser

Complex fertiliser

Mixed fertilisers - advantages

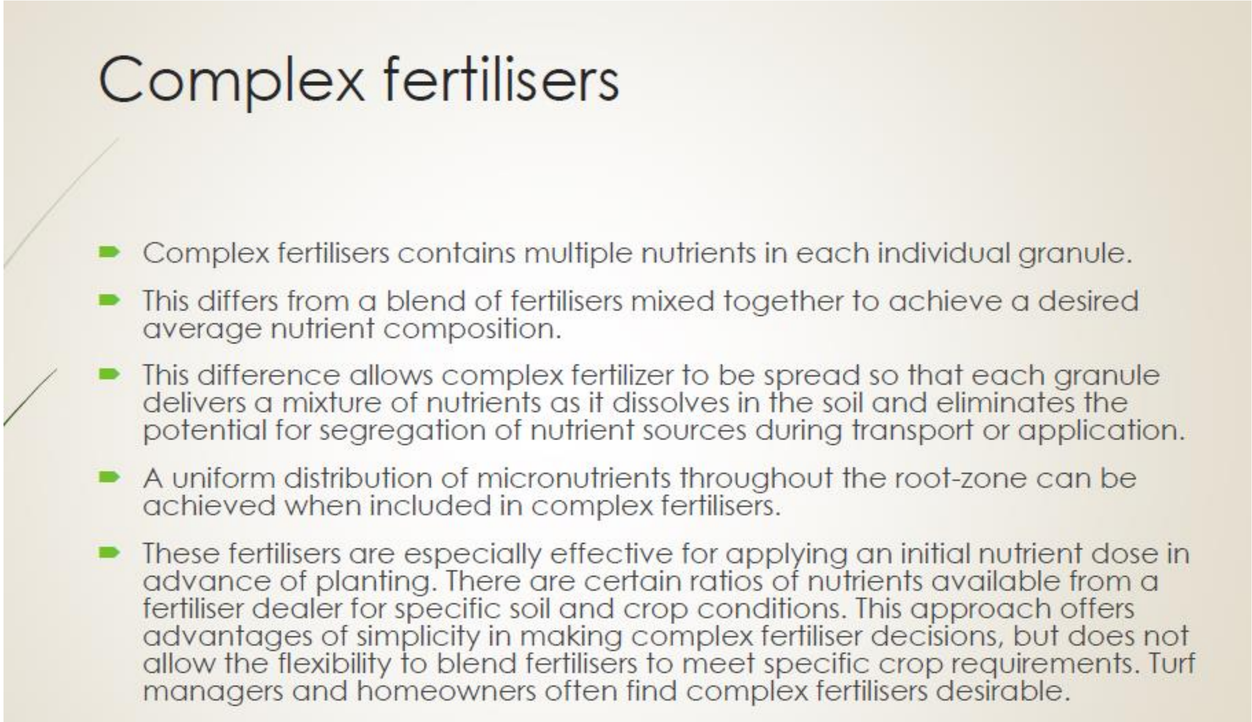
- Mixed fertilisers allow to design the fertiliser exactly to the need of each crop/field, so that
  - Each nutrient is in balance with the norm (but it does seldom happen in practice)
  - One field application is enough – saves time and money

Complex fertilisers

- Complex fertilizers - are fertilizers during the production of which a chemical reaction occurs among the components which react reciprocally, whereby a homogenous product of uniform composition is created, representing certain chemical compounds.
- They may also be produced with elements that provide some of the less-common plant nutrients (known as secondary or trace nutrients, such as sulphur, calcium and magnesium).
- Compound fertiliser can be packaged and distributed in liquid or granular form.
- A numbering system is used to define the percentages of the three essential plant nutrients. For example, a 20-20-10 fertilizer would contain 20 percent nitrogen, 20 percent phosphorus and 10 percent potassium. Secondary nutrients and trace elements are typically listed.

Complex fertilisers

- Complex fertilisers are made using basic fertiliser materials, such as NH_3, ammonium phosphate, urea, S, and K salts. There are many methods used for making these fertilisers, with the specific manufacturing processes determined by the available basic components and the desired nutrient content of the finished product. Here are three brief examples.
  - Compaction methods (agglomeration) involve binding small fertiliser particles together using compaction, a cementing agent, or a chemical bond. Various nutrient ratios can be combined using undersized particles that may not be suitable for other applications.
  - Accretion-based fertilisers are made by repeatedly adding a thin film of nutrient slurry which is continually dried, building up multiple layers until the desired granule size is reached.
  - Pipe-cross reactors are used to chemically melt NH_3, acids containing S or P, and other nutrients—such as K sources and micronutrients—into a solid fertiliser with the desired nutrient content.



Complex fertilisers

- Complex fertilisers contains multiple nutrients in each individual granule.
- This differs from a blend of fertilisers mixed together to achieve a desired average nutrient composition.
- This difference allows complex fertilizer to be spread so that each granule delivers a mixture of nutrients as it dissolves in the soil and eliminates the potential for segregation of nutrient sources during transport or application.
- A uniform distribution of micronutrients throughout the root-zone can be achieved when included in complex fertilisers.
- These fertilisers are especially effective for applying an initial nutrient dose in advance of planting. There are certain ratios of nutrients available from a fertiliser dealer for specific soil and crop conditions. This approach offers advantages of simplicity in making complex fertiliser decisions, but does not allow the flexibility to blend fertilisers to meet specific crop requirements. Turf managers and homeowners often find complex fertilisers desirable.

BIOFERTILIZERS

Biofertilizers

Biofertilizers are defined as preparations containing living cells or latent cells of efficient strains of microorganisms that help crop plants’ uptake of nutrients by their interactions in the rhizosphere when applied through seed or soil. They accelerate certain microbial processes in the soil which augment the extent of availability of nutrients in a form easily assimilated by plants.

Very often microorganisms are not as efficient in natural surroundings as one would expect them to be and therefore artificially multiplied cultures of efficient selected microorganisms play a vital role in accelerating the microbial processes in soil.

Use of biofertilizers is one of the important components of integrated nutrient management, as they are cost effective and renewable source of plant nutrients to supplement the chemical fertilizers for sustainable agriculture. Several microorganisms and their association with crop plants are being exploited in the production of biofertilizers. They can be grouped in different ways based on their nature and function.

S. No.	Groups	Examples
N2 fixing Biofertilizers		
1.	Free-living	*Azotobacter, Beijerinkia, Clostridium, Klebsiella, Anabaena, Nostoc,*
2.	Symbiotic	*Rhizobium, Frankia, Anabaena azollae*
3.	Associative Symbiotic	*Azospirillum*
P Solubilizing Biofertilizers		
1.	Bacteria	*Bacillus megaterium* var. *phosphaticum, Bacillus subtilis Bacillus circulans, Pseudomonas striata*
2.	Fungi	*Penicillium sp, Aspergillus awamori*
P Mobilizing Biofertilizers		
1.	Arbuscular mycorrhiza	*Glomus sp.,Gigaspora sp.,Acaulospora sp.,* *Scutellospora sp.* & *Sclerocystis sp.*
2.	Ectomycorrhiza	*Laccaria sp., Pisolithus sp., Boletus sp., Amanita sp.*
3.	Ericoid mycorrhizae	*Pezizella ericae*
4.	Orchid mycorrhiza	*Rhizoctonia solani*
Biofertilizers for Micro nutrients		
1.	Silicate and Zinc solubilizers	*Bacillus* sp.
Plant Growth Promoting Rhizobacteria		
1.	Pseudomonas	*Pseudomonas fluorescens*

2. Different types of biofertilizers

Rhizobium

Rhizobium is a soil habitat bacterium, which can able to colonize the legume roots and fixes the atmospheric nitrogen symbiotically. The morphology and physiology of Rhizobium will vary from free-living condition to the bacteroid of nodules. They are the most efficient biofertilizer as per the quantity of nitrogen fixed concerned. They have seven genera and highly specific to form nodule in legumes, referred as cross inoculation group. *Rhizobium* inoculant was first made in USA and commercialized by private enterprise in 1930s and the strange situation at that time has been chronicled by Fred (1932).

Initially, due to absence of efficient bradyrhizobial strains in soil, soybean inoculation at that time resulted in bumper crops but incessant inoculation during the last four decades by US farmers has resulted in the build up of a plethora of inefficient strains in soil whose replacement by efficient strains of bradyrhizobia has become an insurmountable problem.

Azotobacter

Of the several species of *Azotobacter*, *A. chroococcum* happens to be the dominant inhabitant in arable soils capable of fixing N2 (2-15 mg N2 fixed /g of carbon source) in culture media.

The bacterium produces abundant slime which helps in soil aggregation. The numbers of *A. chroococcum* in Indian soils rarely exceeds 105/g soil due to lack of organic matter and the presence of antagonistic microorganisms in soil.

Azospirillum

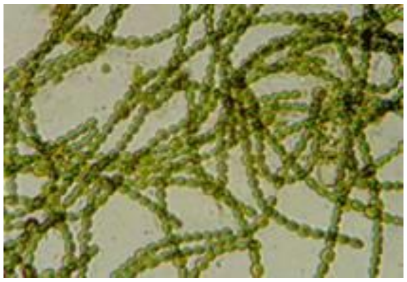
Azospirillum lipoferum and *A. brasilense* (*Spirillum lipoferum* in earlier literature) are primary inhabitants of soil, the rhizosphere and intercellular spaces of root cortex of graminaceous plants. They perform the associative symbiotic relation with the graminaceous plants.

The bacteria of Genus *Azospirillum* are N2 fixing organisms isolated from the root and above ground parts of a variety of crop plants. They are Gram negative, *Vibrio* or *Spirillum* having abundant accumulation of polybetahydroxybutyrate (70 %) in cytoplasm.

Five species of *Azospirillum* have been described to date *A. brasilense*, *A.lipoferum*, *A.amazonense*, *A.halopraeferens* and *A.irakense*. The organism proliferates under both anaerobic and aerobic conditions but it is preferentially micro-aerophilic in the presence or absence of combined nitrogen in the medium.

Apart from nitrogen fixation, growth promoting substance production (IAA), disease resistance and drought tolerance are some of the additional benefits due to *Azospirillum* inoculation.

Cyanobacteria

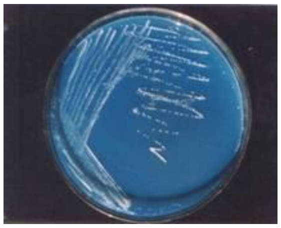


Both free-living as well as symbiotic cyanobacteria (blue green algae) have been harnessed in rice cultivation in India. A composite culture of BGA having heterocystous *Nostoc*, *Anabaena*, *Aulosira etc*. is given as primary inoculum in trays, polythene lined pots and later mass multiplied in the field for application as soil based flakes to the rice growing field at the rate of 10 kg/ha. The final product is not free from extraneous contaminants and not very often monitored for checking the presence of desiredalgal flora.

Once so much publicized as a biofertilizer for the rice crop, it has not presently attracted the attention of rice growers all over India except pockets in the Southern States, notably Tamil Nadu. The benefits due to algalization could be to the extent of 20-30 kg N/ha under ideal conditions but the labour oriented methodology for the preparation of BGA biofertilizer is in itself a limitation. Quality control measures are not usually followed except perhaps for random checking for the presence of desired species qualitatively.

Azolla

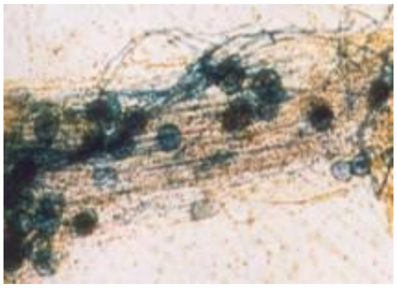
Azolla is a free-floating water fern that floats in water and fixes atmospheric nitrogen in association with nitrogen fixing blue green alga *Anabaena azollae*. *Azolla* fronds consist of sporophyte with a floating rhizome and small overlapping bi-lobed leaves and roots. Rice growing areas in South East Asia and other third World countries have recently been evincing increased interest in the use of the symbiotic N2 fixing water fern *Azolla* either as an alternate nitrogen sources or as a supplement to commercial nitrogen fertilizers. *Azolla* is used as biofertilizer for wetland rice and it is known to contribute 40-60 kg N/ha per rice crop.



Phosphate solubilizing microorganisms(PSM)

Several soil bacteria and fungi, notably species of *Pseudomonas, Bacillus, Penicillium, Aspergillus etc.* secrete organic acids and lower the pH in their vicinity to bring about dissolution of bound phosphates in soil. Increased yields of wheat and potato were demonstrated due to inoculation of peat based cultures of *Bacillus polymyxa* and *Pseudomonas striata*. Currently, phosphate solubilizers are manufactured by agricultural universities and some private enterprises and sold to farmers through governmental agencies. These appear to be no check on either the quality of the inoculants marketed in India or the establishment of the desired organisms in the rhizosphere.

AM fungi



The transfer of nutrients mainly phosphorus and also zinc and sulphur from the soil *milleu* to the cells of the root cortex is mediated by intracellular obligate fungal endosymbionts of the genera *Glomus, Gigaspora, Acaulospora, Sclerocysts* and *Endogone* which possess vesicles for storage of nutrients and arbuscles for funneling these nutrients into the root system. By far, the commonest genus appears to be *Glomus*, which has several species distributed in soil.

Availability for pure cultures of AM (Arbuscular Mycorrhiza) fungi is an impediment in large scale production despite the fact that beneficial effects of AM fungal inoculation to plants have been repeatedly shown under experimental conditions in the laboratory especially in conjunction with other nitrogen fixers.

Silicate solubilizing bacteria (SSB)

Microorganisms are capable of degrading silicates and aluminum silicates. During the metabolism of microbes several organic acids are produced and these have a dual role in silicate weathering. They supply H+ ions to the medium and promote hydrolysis and the organic acids like citric, oxalic acid, Keto acids and hydroxy carbolic acids which from complexes with cations, promote their removal and retention in the medium in a dissolved state.

The studies conducted with a Bacillus sp. isolated from the soil of granite crusher yard showed that the bacterium is capable of dissolving several silicate minerals under *in vitro* condition. The examination of anthrpogenic materials like cement, agro inputs like super phosphate and rock phosphate exhibited silicate solubilizing bacteria to a varying degree. The bacterial isolates made from different locations had varying degree of silicate solubilizing potential. Soil inoculation studies with selected isolate with red soil, clay soil, sand and hilly soil showed that the organisms multiplied in all types of soil and released more of silica and the available silica increased in soil and water. Rice responded well to application of organic sliceous residue like rice straw, rice husk and black ash @ 5 t/ha. Combining SSB with these residues further resulted in increased plant growth and grain yield. This enhancement is due to increased dissolution of silica and nutrients from the soil.

Plant Growth Promoting Rhizobacteria (PGPR)

The group of bacteria that colonize roots or rhizosphere soil and beneficial to crops are referred to as plant growth promoting rhizobacteria (PGPR).

The PGPR inoculants currently commercialized that seem to promote growth through at least one mechanism; suppression of plant disease (termed Bioprotectants), improved nutrient acquisition (termed Biofertilizers), or phytohormone production (termed Biostimulants). Species of *Pseudomonas* and *Bacillus* can produce as yet not well characterized phytohormones or growth regulators that cause crops to have greater amounts of fine roots which have the effect of increasing the absorptive surface of plant roots for uptake of water and nutrients. These PGPR are referred to as Biostimulants and the phytohormones they produce include indole-acetic acid, cytokinins, gibberellins and inhibitors of ethylene production.

Recent advances in molecular techniques also are encouraging in that tools are becoming available to determine the mechanism by which crop performance is improved using PGPR and track survival and activity of PGPR organisms in soil and roots. The science of PGPR is at the stage where genetically modified PGPR can be produced. PGPR with antibiotic, phytohormone and siderophore production can be made.

Despite of promising results, biofertilizers has not got widespread application in agriculture mainly because of the variable response of plant species or genotypes to inoculation depending on the bacterial strain used. Differential rhizosphere effect of crops in harbouring a target strain or even the modulation of the bacterial nitrogen fixing and phosphate solubilizing capacity by specific root exudates may account for the observed differences. On the other hand, good competitive ability and high saprophytic competence are the major factors determining the success of a bacterial strain as an inoculant.

Studies to know the synergistic activities and persistence of specific microbial populations in complex environments, such as the rhizosphere, should be addressed in order to obtain efficient inoculants. In this regards, research efforts are made at Agricultural College and Research Institute, Madurai to obtain appropriate formulations of microbial inoculants incorporating nitrogen fixing, phosphate- and silicate- solubilizing bacteria and plant growth promoting rhizobacteria which will help in promoting the use of such beneficial bacteria in sustainable agriculture.

Liquid Biofertilizers

Biofertilizers are such as *Rhizobium, Azospirillum* and Phosphobacteria provide nitrogen and phosphorous nutrients to crop plants through nitrogen fixation and phosphorous solubilization processes. These Biofertilizers could be effectively utilized for rice, pulses, millets, cotton, sugarcane, vegetable and other horticulture crops.

Biofertilizers is one of the prime input in organic farming not only enhances the crop growth and yield but also improves the soil health and sustain soil fertility.

At present, Biofertilizers are supplied to the farmers as carrier based inoculants. As an alternative, liquid formulation technology has been developed in the Department of Agricultural Microbiology, TNAU, Coimbatore which has more advantages than the carrier inoculants.

Benefits

The advantages of Liquid Bio-fertilizer over conventional carrier based Bio-fertilizers are listed below:

- Longer shelf life -12-24 months.
- No contamination.
- No loss of properties due to storage upto 45º c.
- Greater potentials to fight with native population.
- High populations can be maintained more than 109 cells/ml upto 12 months to 24 months.
- Easy identification by typical fermented smell.
- Cost saving on carrier material, pulverization, neutralization, sterilization, packing and transport.
- Quality control protocols are easy and quick.
- Better survival on seeds and soil.
- No need of running Bio-fertilizer production units through out the year.
- Very much easy to use by the farmer.
- Dosages is 10 time less than carrier based powder Bio-fertilizers.

- High commercial revenues.
- High export potential.

Liquid Bio-fertlizer application methodology

There are three ways of using Liquid Bio-fertilizers

1. Seed treatment
2. Root dipping
3. Soil application

Seed Treatment

Seed Treatment is a most common method adopted for all types of inoculants. The seed treatment is effective and economic. For small quantity of seeds (up to 5 kgs quantity) the coating can done in a plastic bag. For this purpose, a plastic bag having size (21" x 10") or big size can be used. The bag should be filled with 2 kg or more of seeds. The bag should be closed in such a way to trap the airs as much as possible. The bag should be squeezed for 2 minutes or more until all the seed are uniformly wetted. Then bag is opened, inflated again and shaked gently. Stop shaking after each seeds gets a uniform layer of culture coating. The bag is opened and the seed is dried under the shade for 20-30 minutes. For large amount of seeds coating can be done in a bucket and inoculant can be mixed directly with hand. Seed Treatment with *Rhizobium, Azotobacter, Azospirillum,* along with PSM can be done.

The seed treatment can be done with any of two or more bacteria. There is no side (antagonistic) effect. The important things that has to be kept in mind are that the seeds must be coated first with *Rhizobium, Azotobacter* or *Azospirillum*. When each seed get a layer of above bacteria then PSM inoculant has to be coated as outer layer. This method will provide maximum number of each bacteria required for better results. Treatments of seed with any two bacteria will not provide maximum number of bacteria on individual seed.

Root dipping

For application of *Azospirillum*/ /PSM on paddy transplating/ vegetable crops this method is used. The required quantity of *Azospirillum/* /PSM has to be mixed with 5-10 litres of water at one corner of the field and the roots of seedlings has to be dipped for a minimum of half-an-hour before transplantation.

Soil application

Use 200ml of PSM per acre. Mix PSM with 400 to 600 kgs of Cow dung FYM along with ½ bag of rock phosphate if available. The mixture of PSM, cow dung and rock phosphate have to be kept under any tree or under shade for over night and maintain 50% moisture. Use the mixture as soil application in rows or during leveling of soil.

Mass production of Bacterial Biofertilizer


Azospirillum


Rhizobium


Phosphobacteria


Azotobacter

Biofertilizers are carrier based preparations containing efficient strain of nitrogen fixing or phosphate solubilizing microorganisms. Biofertilizers are formulated usually as carrier based inoculants. The organic carrier materials are more effective for the preparation of bacterial inoculants. The solid inoculants carry more number of bacterial cells and support the survival of cells for longer periods of time.

- The mass production of carrier based bacterial biofertilizers involves three stages.
- Culturing of microorganisms
- Processing of carrier material
- Mixing the carrier and the broth culture and packing

Culturing of Microorganisms

Although many bacteria can be used beneficially as a biofertilizer the technique of mass production is standardizedfor *Rhizobium*, *Azospirillum*, *Azotobacter* and phosphobacteria.
The media used for mass culturing are as follows:

Rhizobium : Yeast extract mannitol broth.

Growth on Congo red yeast extract mannitol agar medium

Mannitol - 10.0 g

$K_2 HPO_4$	-	0.5 g
$Mg So_4 7H_2 O$	-	0.2 g
NaCl	-	0.1 g
Yeast extract	-	0.5 g
Agar		20.0 g
Distilled water		1000.0 ml

Add 10 ml of Congo red stock solution (dissolve 250 mg of Congo red in 100ml water) to 1 liter after adjusting the PH to 6.8 and before adding agar.

Rhizobium forms white, translucent, glistening, elevated and comparatively small colonies on this medium. Moreover, *Rhizobium* colonies do not take up the colour of congo red dye added in the medium. Those colonies which readily take up the congo red stain are not rhizobia but presumably *Agrobacterium*, a soil bacterium closely related to *Rhizobium.*

Azospirillum : Dobereiner's malic acid broth with NH_4Cl (1g per liter)

Composition of the N-free semisolid malic acid medium

Malic acid	-	5.0g
Potassium hydroxide	-	4.0g
Dipotassium hydrogen orthophosphate	-	0.5g
Magnesium sulphate	-	0.2g
Sodium chloride	-	0.1g
Calcium chloride	-	0.2g
Fe-EDTA (1.64% w/v aqueous)	-	4.0 ml
Trace element solution	-	2.0 ml
BTB (0.5% alcoholic solution)	-	2.0 ml
Agar	-	1.75 g
Distilled water	-	1000 ml
pH	-	6.8
Trace element solution		
Sodium molybdate	-	200 mg
Manganous sulphate	-	235 mg
Boric acid	-	280 mg
Copper sulphate	-	8 mg
Zinc sulphate	-	24 mg
Distilled water	-	200 ml

Waksman medium No.77 (N-free Mannitol Agar Medium for *Azotobacter*)

Mannitol	:	10.0 g
Ca CO3	:	5.0 g
K2HPO4	:	0.5 g
Mg SO4.7H2O	:	0.2 g
NaCl	:	0.2 g
Ferric chloride	:	Trace
MnSO4.4H2O	:	Trace
N-free washed Agar	:	15.0 g
pH	:	7.0
Distilled Water	:	1000 ml

Phosphobacteria : Pikovskaya's Broth

Glucose	:	10.0 g
Ca3(PO4)2	:	5.0 g
(NH4)2SO4	:	0.5 g
KCl	:	0.2 g
MgSO4. 7H2O	:	0.1 g
MnSO4	:	Trace
FeSO4	:	Trace
Yeast Extract	:	0.5 g
Distilled Water	:	1000 ml

The broth is prepared in flasks and inoculum from mother culture is transferred to flasks. The culture is grown under shaking conditions at 30±2°C as submerged culture. The culture is incubated until maximum cell population of 1010 to 1011 cfu/ml is produced. Under optimum conditions this population level could be attained with in 4 to 5 days for *Rhizobium*; 5 to 7 days for *Azospirillum*; 2 to 3 days for phosphobacteria and 6-7 days for *Azotobacter*. The culture obtained in the flask is called **starter culture**. For large scale production of inoculant, inoculum from starter culture is transferred to large flasks/seed tank fermentor and grown until required level of cell count is reached.

Inoculum preparation

- Prepare appropriate media for specific to the bacterial inoculant in 250 ml, 500 ml, 3 litre and 5 litre conical flasks and sterilize.

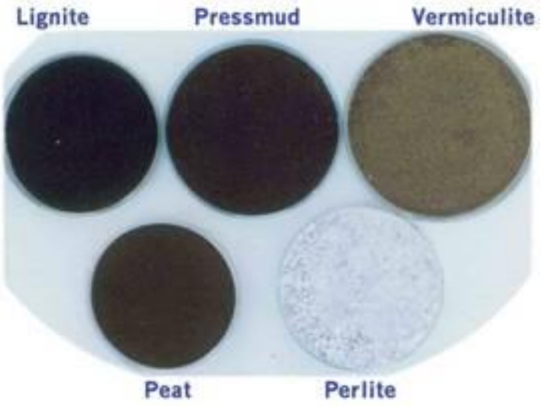
- The media in 250 ml flask is inoculated with efficient bacterial strain under aseptic condition
- Keep the flask under room temperature in rotary shaker (200 rpm) for 5- 7 days.
- Observe the flask for growth of the culture and estimate the population, which serves as the starter culture.
- Using the starter culture (at log phase) inoculate the larger flasks (500 ml, 3 litre and 5 litre) containing the media, after obtaining growth in each flask.
- The above media is prepared in large quantities in fermentor, sterilized well, cooled and kept it ready.
- The media in the fermentor is inoculated with the log phase culture grown in 5 litre flask. Usually 1 -2 % inoculum is sufficient, however inoculation is done up to 5% depending on the growth of the culture in the larger flasks.
- The cells are grown in fermentor by providing aeration (passing sterile air through compressor and sterilizing agents like glass wool, cotton wool, acid etc.) and given continuous stirring.
- The broth is checked for the population of inoculated organism and contamination if any at the growth period.
- The cells are harvested with the population load of 109 cells ml-1 after incubation period.
- There should not be any fungal or any other bacterial contamination at 10-6 dilution level
- It is not advisable to store the broth after fermentation for periods longer than 24 hours. Even at 4o C number of viable cells begins to decrease.

Processing of carrier material

The use of ideal carrier material is necessary in the production of good quality biofertilizer. Peat soil, lignite, vermiculite, charcoal, press mud, farmyard manure and soil mixture can be used as carrier materials. The neutralized peat soil/lignite are found to be better carrier materials for biofertilizer production The following points are to be considered in the selection of ideal carrier material.

- Cheaper in cost
- Should be locally available
- High organic matter content
- No toxic chemicals
- Water holding capacity of more than 50%
- Easy to process, friability and vulnerability.

Preparation of carrier material



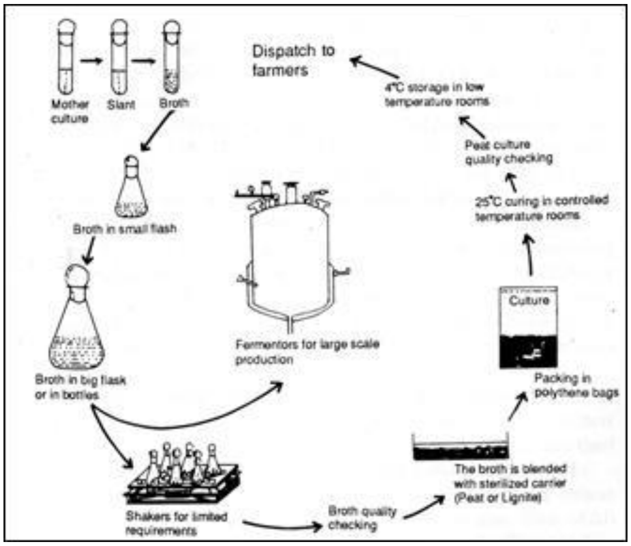
- The carrier material (peat or lignite) is powdered to a fine powder so as to pass through 212 micron IS sieve.
- The pH of the carrier material is neutralized with the help of calcium carbonate (1:10 ratio) , since the peat soil / lignite are acidic in nature (pH of 4 - 5)
- The neutralized carrier material is sterilized in an autoclave to eliminate the contaminants.

Mixing the carrier and the broth culture and packing

Inoculant packets are prepared by mixing the broth culture obtained from fermentor with sterile carrier material as described below:

Preparation of Inoculants packet

- The neutralized, sterilized carrier material is spread in a clean, dry, sterile metallic or plastic tray.
- The bacterial culture drawn from the fermentor is added to the sterilized carrier and mixed well by manual (by wearing sterile gloves) or by mechanical mixer. The culture suspension is to be added to a level of 40 – 50% water holding capacity depending upon the population.
- The inoculant packet of 200 g quantities in polythene bags, sealed with electric sealer and allowed for curing for 2 -3 days at room temperature (curing can be done by spreading the inoculant on a clean floor/polythene sheet/ by keeping in open shallow tubs/ trays with polythene covering for 2 -3 days at room temperature before packaging).



Schematic representation of mass production of bacterial biofertilizers

4.7.1 Secondary and micronutrients

Secondary nutrients are nutrients that slightly limit crop growth and are moderately required by plants. These nutrients are calcium (Ca), magnesium (Mg), and sulfur (S). Secondary nutrients are as significant as primary nutrients in plants, but they are needed in smaller quantities. They are necessary for the augmentation levels of roots and cells.

The secondary nutrients include:

1. Calcium (Ca)

Calcium is an essential nutrient that plays a significant role in plant growth. Calcium helps to neutralize the organic acids that form during metabolism. Calcium also assists plants in the following ways:

- Absorption and translocation of other nutrients by roots
- Facilitates disease resistance
- Assists in conversion of nitrate-nitrogen to other essential forms required for protein formation
- Required for cell division and cell wall formation
- Activation of growth-regulating enzyme systems

2. Magnesium (Mg)

Magnesium is an essential nutrient for plants because it is a fundamental element making up enzymes that support plant development, leaf chlorophyll, and for crop quality. The nutrient also assists in the formation of oils, sugars, and fats, and the nutrient serves as a phosphorous hauler. A magnesium deficiency causes a decrease in photosynthesis, which limits crop production.

3. Sulfur (S)

Sulfur is an essential element of chlorophyll. It is involved in nitrogen fixation in leguminous plants and also helps in seed production. Sulfur adds color, a different smell, and flavor to various plants like garlic, brassica crops, and onions. The nutrient also forms a significant part of proteins and amino acids. Sulfur is crucial for ensuring the protein content of leguminous plants.

Plant Requirements and Soil Availability

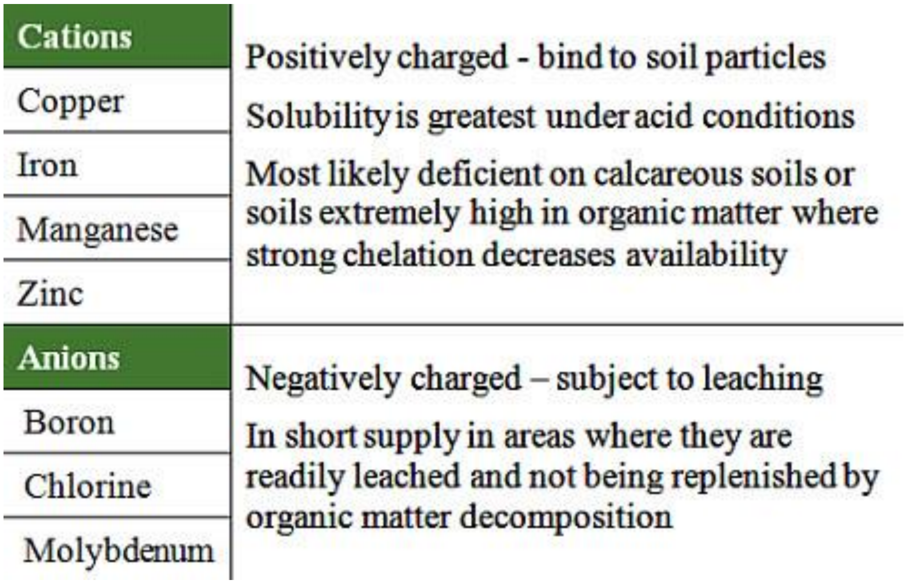
There are 16 elements essential to growth of crop plants:

Supplied by air and water: carbon, hydrogen, oxygen

Macronutrients: nitrogen, phosphorous, potassium

Secondary Nutrients: calcium, magnesium, sulfur

Micronutrients: boron (B), chlorine (Cl), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), and zinc (Zn).



Cations	Positively charged - bind to soil particles Solubility is greatest under acid conditions Most likely deficient on calcareous soils or soils extremely high in organic matter where strong chelation decreases availability
Copper	
Iron	
Manganese	
Zinc	
Anions	Negatively charged – subject to leaching In short supply in areas where they are readily leached and not being replenished by organic matter decomposition
Boron	
Chlorine	
Molybdenum	