Fertilizer and Steels

Fertilizer are the substances which are added to the soil in order to make up the deficiency of essential elements like nitrogen, phosphorous, and potassium required for the growth of the plants.

Essential qualities of a good Fertilizer: Every substance containing plant nutrients can not be used as a fertilizer. However, the essential requisites of a good fertilizer are:

(i). The nutrient elements present in it must be readily available to the plants.

(ii). It must be fairly soluble in water so as to enable it to dissolve in soil.

(iii). By rain or water, the fertilizer must be converted into a form which the plant can assimilate easily.

(iv). It must be stable so that it is available for a long time to the growing plant.

(v). It should not be injurious to plant

(vi). It should be able to correct the acidity of the soil

(vii). It should be cheap.

Manufacture of Urea or Carbamide NH_2CONH_2:

Urea is in many ways the most convenient form for fixed nitrogen. It has the highest nitrogen content available 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 leaves no salt residue after use on crops. The principal raw materials required for this purpose are NH_3 & CO_2. Two reactions are involved in the manufacture of urea. First, ammonium carbamate is formed under pressure by reaction between CO_2 & NH_3.

$CO_2 + 2NH_3 \rightarrow NH_2COONH_4$ $\Delta H = -37.4$ Kcal

This highly exothermic reaction is followed by an endothermic decomposition of the ammonium carbamate to urea.

$NH_2COONH_4 \leftrightarrow NH_2CONH_2 + H_2O$ $\Delta H = +6.3$ Kcal

Various processes for the manufacture of urea are: (1) Snamprogetti ammonia stripping process (2) Stamicarbon CO_2 stripping process (3) Once through urea process (4) Mitsui Toatsu total recycle urea process.

Among them the **Snamprogetti ammonia stripping** process is considered for the manufacture of urea. In this process ammonia & CO_2 are compressed & fed to the reactor. The unconverted carbamate is stripped and recovered from the urea synthesis reactor effluent solution at reactor pressure, condensed to an aqueous solution in a steam producing high pressure condenser & recycled back to the reactor by gravity. Part of the liquid NH_3 reactor feed, vapourized in a steam heated exchanger, is used as inert gas to decompose & strip ammonium carbamate in the steam heated high pressure stripper.

Uses of Urea:

1. About 56 % of Urea manufactured is used in solid fertilizer.
2. About 31 % of Urea manufactured is used in liquid fertilizer.
3. Urea-formaldehyde resins have large use as a plywood adhesive.
4. Melamine-formaldehyde resins are used as dinnerware & for making extra hard surfaces.

Classification of Fertilizers:

Fertilizers are classified according to the nature of the element/elements like N, P or K they provide to the soil.

1. **Nitrogenous fertilizers:** These fertilizers mainly supply nitrogen to the plants or soil. $(NH_4)_2SO_4$, Calcium ammonium Nitrate (CAN), basic calcium nitrate, urea etc. are the example of nitrogenous fertilizers.
2. **Phosphatic fertilizers:** These fertilizers provide phosphorous to the soil. Superphosphate of lime, triple superphosphate and phosphate slag are the example of phosphatic fertilizers.
3. **Potash fertilizers:** These fertilizers supply potassium to the plant. These are useful to the plants especially to mendow, glass, tobacco, cotton, coffee, potatoes and corn. KCl, KNO_3, K_2SO_4 etc are the important examples.
4. **NP fertilizers:** These fertilizers contain two elements namely nitrogen and phosphorous. These are obtained by mixing together nitrogenous and phosphatic fertilizers in suitable proportions. Example of NP fertilizers are calcium superphosphate nitrate $Ca(H_2PO_4)_2 . 2Ca(NO_3)_2$ and ammoniated phosphate sulphate, $(NH_4)H_2PO_4 . (NH_4)_2SO_4$
5. **NPK or Complete fertilizers:** These fertilizers supply all the three essential elements namely nitrogen, phosphorous and potassium to the soil and are produced by mixing nitrogenous, phosphatic and potash fertilizers in suitable proportions.

Manufacture of ammonium nitrate (NH_4NO_3) fertilizer:

Synthesis: Ammonium nitrate (NH_4NO_3) is synthesized through a chemical reaction between ammonia (NH_3) and nitric acid (HNO_3). The reaction can be represented as follows:

$NH_3 + HNO_3 \rightarrow NH_4NO_3$

This reaction is exothermic, meaning it releases heat. Care must be taken to control the temperature during the reaction to prevent overheating and potential hazards.

Neutralization: The synthesis reaction typically occurs in a neutralization vessel where the ammonia gas is bubbled through a solution of nitric acid. The reaction produces an aqueous solution of ammonium nitrate.

Concentration: After the reaction, the solution of ammonium nitrate is concentrated through evaporation to remove excess water. This step increases the concentration of ammonium nitrate in the solution.

Crystallization: The concentrated solution is then cooled to induce crystallization. As the solution cools, solid crystals of ammonium nitrate precipitate out. These crystals are then separated from the remaining solution.

Drying: The separated crystals are dried to remove any remaining moisture. This step ensures that the final product is in a stable, solid form suitable for storage and transportation.

Granulation: In some cases, the dried crystals may undergo further processing to form granules of a specific size. Granulation improves the handling characteristics of the fertilizer and allows for more precise application in agricultural settings.

Manufacture of Urea or Carbamide (NH_2CONH_2):

The manufacture of urea involves the following steps:

Synthesis of Ammonia: The primary raw material for urea production is ammonia (NH_3). Ammonia is typically synthesized through the Haber-Bosch process under high pressure and temperature in the presence of a catalyst. The reaction produces anhydrous ammonia.

Reaction with Carbon Dioxide: Anhydrous ammonia is then reacted with carbon dioxide (CO_2) under high pressure and temperature in a process known as the Bosch-Meiser process or the urea synthesis process. The reaction can be represented as follows:

$2NH_3 + CO_2 \rightarrow NH_2CONH_2 + H_2O$

This reaction forms urea (NH_2CONH_2) and water.

Condensation and Concentration: The urea produced in the synthesis reaction is in the form of a solution. This solution is concentrated through evaporation to remove excess water, resulting in the formation of urea crystals.

Prilling or Granulation: The urea crystals may undergo further processing to achieve the desired physical form for application as fertilizer. Granulation involves compacting the urea crystals into larger granules of a specific size using a granulation process.

Drying: After prilling or granulation, the urea pellets or granules are dried to remove any remaining moisture.

Manufacture of Calcium ammonium nitrate fertilizer:

The manufacturing process for calcium ammonium nitrate (CAN) fertilizer:

Raw Materials Preparation: The main raw materials required for the production of CAN fertilizer are limestone ($CaCO_3$), ammonia (NH_3), and nitric acid (HNO_3).

Ammonia Production: Ammonia is produced through the Haber-Bosch process under high pressure and temperature in the presence of a catalyst.

Nitric Acid Production: Nitric acid is produced through the Ostwald process, which involves the oxidation of ammonia (NH_3) to form nitrogen dioxide (NO_2), followed by the absorption of NO_2 in water to form nitric acid (HNO_3).

Calcium Ammonium Nitrate Synthesis: Calcium ammonium nitrate is synthesized through a reaction between calcium carbonate ($CaCO_3$), ammonia (NH_3), and nitric acid (HNO_3). The reaction can be represented as follows:

$CaCO_3 + 2NH_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + (NH_4)_2CO_3 + H_2O$

This reaction forms calcium nitrate $Ca(NO_3)_2$, ammonium carbonate ($(NH_4)_2CO_3$), and water.

Crystallization and Separation: The reaction mixture undergoes crystallization, during which calcium ammonium nitrate crystals precipitate out. The crystals are separated from the remaining solution through filtration or centrifugation.

Drying: The separated crystals are dried to remove any remaining moisture.

Granulation: The dried calcium ammonium nitrate crystals may undergo further processing to form granules of a specific size. Granulation improves the handling characteristics of the fertilizer and allows for more precise application in agricultural settings.

Manufacture of Ammonium phosphate fertilizer:

The manufacture of ammonium phosphate fertilizer typically involves the reaction of ammonia (NH_3) with phosphoric acid (H_3PO_4) to produce various types of ammonium phosphate fertilizers.

Raw Materials Preparation: The main raw materials required for the production of ammonium phosphate fertilizer are ammonia (NH_3) and phosphoric acid (H_3PO_4).

Reaction: Ammonium phosphate fertilizers are produced through the reaction between ammonia and phosphoric acid. The specific type of ammonium phosphate fertilizer produced depends on the ratio of ammonia to phosphoric acid used in the reaction. The two most common types of ammonium phosphate fertilizers are monoammonium phosphate (MAP) and diammonium phosphate (DAP). The reactions for producing these fertilizers are as follows:

Monoammonium Phosphate (MAP):

$NH_3 + H_3PO_4 \rightarrow NH_4H_2PO_4$

Diammonium Phosphate (DAP):

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

These reactions result in the formation of monoammonium phosphate or diammonium phosphate, depending on the specific reaction conditions.

Crystallization: After the reaction, the solution containing the desired ammonium phosphate fertilizer is subjected to crystallization. This process involves cooling the solution to promote the formation of solid crystals of MAP or DAP.

Separation and Drying: Once crystallization is complete, the solid crystals of MAP or DAP are separated from the remaining solution through filtration or centrifugation. The separated crystals are then dried to remove any remaining moisture.

Granulation: The dried MAP or DAP crystals may undergo further processing to form granules of a specific size. Granulation improves the handling characteristics of the fertilizer and allows for more precise application in agricultural settings.

Manufacture of Polyphosphate fertilizer:

Polyphosphate fertilizers are a group of fertilizers that contain various forms of polyphosphates, which are compounds containing multiple phosphate groups. They are typically used to provide plants with a slow and steady supply of phosphorus over time.

Raw Materials Preparation: The main raw materials required for the production of polyphosphate fertilizers include phosphoric acid (H_3PO_4), which is typically derived from phosphate rock, and ammonia (NH_3).

Phosphoric Acid Production: Phosphoric acid is usually produced through the wet process or the thermal process

Reaction with Ammonia: Phosphoric acid is then reacted with ammonia to produce various forms of polyphosphate fertilizers. The specific reaction conditions and the type of polyphosphate fertilizer produced depend on factors such as the ratio of phosphoric acid to ammonia and the temperature and pressure of the reaction.

Polyphosphate Formation: The reaction between phosphoric acid and ammonia results in the formation of polyphosphate compounds. These compounds can have different chain lengths and structures, depending on the reaction conditions.

Granulation and Formulation: The polyphosphate fertilizer may undergo further processing to form granules or other physical forms suitable for application in agriculture. Additives such as fillers, binders, and coatings may also be incorporated to improve the handling and performance characteristics of the fertilizer.

Manufacture of superphosphate fertilizer:

Superphosphate fertilizer is a type of fertilizer that is produced by treating phosphate rock with sulfuric acid. Here's a general outline of the manufacturing process for superphosphate fertilizer:

Raw Materials Preparation: The main raw material for superphosphate fertilizer production is phosphate rock, which is typically mined from natural deposits. Phosphate rock contains phosphorus compounds that are insoluble in water and not readily available to plants.

Grinding and Crushing: The phosphate rock is first crushed and ground into a fine powder to increase its surface area and facilitate the subsequent chemical reactions.

Reaction with Sulfuric Acid: The ground phosphate rock is then treated with sulfuric acid (H_2SO_4) in a process known as acidulation. The reaction can be represented as follows:

$Ca_3(PO_4)_2 + 2H_2SO_4 \rightarrow 2CaSO_4 + 2H_3PO_4$

This reaction converts insoluble calcium phosphate in the phosphate rock into soluble monocalcium phosphate and gypsum (calcium sulfate).

Formation of Superphosphate: The monocalcium phosphate formed in the acidulation reaction reacts further with the remaining phosphate rock to produce superphosphate fertilizer. The reaction can be represented as follows:

$Ca(H_2PO_4)_2 + CaSO_4 \rightarrow 2Ca(H_2PO_4) + CaSO_4$

This reaction forms superphosphate fertilizer, which contains a mixture of soluble monocalcium phosphate and gypsum.

Granulation: The superphosphate fertilizer may undergo further processing to form granules of a specific size. Granulation improves the handling characteristics of the fertilizer and allows for more precise application in agricultural settings.

Drying: If necessary, the granulated superphosphate fertilizer is dried to remove any remaining moisture. This step ensures that the final product is in a stable, solid form suitable for storage and transportation.

Superphosphate fertilizer is commonly used in agriculture to provide plants with phosphorus, which is an essential nutrient for plant growth and development. The manufacturing process for superphosphate fertilizer requires careful control to ensure product quality and consistency. Additionally, environmental regulations must be followed to minimize the release of pollutants during production.

<u>Manufacture of Mixed fertilizer:</u>

Manufacturing mixed fertilizers involves blending two or more fertilizer materials to create a product that provides a balanced combination of essential nutrients for plant growth. Here's an overview of the process:

Raw Materials Selection: Various raw materials are selected based on the desired nutrient composition of the mixed fertilizer. These materials typically include nitrogen (N), phosphorus (P), potassium (K), and sometimes secondary and micronutrients like sulfur (S), magnesium (Mg), calcium (Ca), and micronutrients such as zinc (Zn), copper (Cu), and boron (B).

Grinding and Crushing: Some raw materials may need to be ground or crushed to achieve a uniform particle size and facilitate blending.

Weighing and Mixing: The selected raw materials are accurately weighed according to the desired nutrient ratio for the mixed fertilizer formulation. They are then mixed together thoroughly in a blending unit. The blending process ensures homogeneity and uniform distribution of nutrients throughout the final product.

Granulation: The mixed fertilizer blend may undergo granulation to form granules of a specific size. Granulation improves the handling characteristics of the fertilizer and allows for more precise application in agricultural settings. Granules can be made using various techniques such as agglomeration, compaction, or coating.

Drying: If the mixed fertilizer blend contains moisture or if granulation is performed, the product may need to be dried to remove excess moisture and ensure stability during storage and transportation.

Packaging: Once the mixed fertilizer is manufactured and quality control checks are completed, it is packaged into bags, bulk containers, or other suitable packaging formats for distribution to farmers and agricultural suppliers.

Manufacture of Potassium Chloride fertilizer:

Mining: Potassium chloride is primarily obtained through mining potassium-bearing minerals such as sylvite (KCl) and carnallite ($KCl.MgCl_2.6H_2O$).

Extraction: The mined ore is crushed and ground into small particles to increase its surface area for subsequent processing. The crushed ore is then dissolved in hot water to form a brine solution.

Filtration: The brine solution undergoes filtration to remove insoluble impurities such as clay, sand, and other minerals.

Evaporation: The filtered brine solution is then evaporated in large evaporation ponds or evaporators to concentrate the potassium chloride content. As water evaporates, potassium chloride crystallizes out of the solution.

Crystallization: The concentrated potassium chloride solution is cooled further to promote the formation of solid potassium chloride crystals. The crystals are then separated from the remaining solution using centrifuges or other separation methods.

Drying: The separated potassium chloride crystals are dried to remove any remaining moisture. This step ensures that the final product is in a stable, solid form suitable for storage and transportation.

Sizing and Packaging: The dried potassium chloride crystals may undergo sizing to produce granules or pellets of a specific size range. The finished product is then packaged into bags, bulk containers, or other suitable packaging formats for distribution to customers.

Potassium chloride is a widely used source of potassium in agriculture, primarily as a fertilizer. It provides essential potassium nutrients to plants, promoting overall growth, fruit development, and resistance to diseases and stress. The manufacturing process for potassium chloride involves several steps to extract, purify, and refine the mineral from natural deposits, ensuring a high-quality product for agricultural and industrial applications

Manufacture of Potassium sulphate fertilizer:

The manufacture of potassium sulfate (K_2SO_4) fertilizer involves several steps, typically starting from either potassium chloride (KCl) or potassium-bearing minerals.

Raw Materials:

Potassium Chloride (KCl): If potassium chloride is used as the starting material, it undergoes a reaction with sulfuric acid (H_2SO_4) to produce potassium sulfate and hydrochloric acid (HCl).

Potassium-bearing minerals: Alternatively, potassium sulfate can be produced from potassium-bearing minerals such as langbeinite ($K_2Mg_2(SO_4)_3$), kainite ($KMg(SO_4)Cl.H_2O$), or polyhalite ($K_2Ca_2Mg(SO_4)_4.2H_2O$).

Reaction:

Potassium Chloride Route: The reaction between potassium chloride and sulfuric acid can be represented as follows:

$KCl + H_2SO_4 \rightarrow K_2SO_4 + HCl$

Mineral Route: Potassium-bearing minerals are treated with sulfuric acid to release potassium sulfate. The specific reaction depends on the mineral used as the raw material.

Crystallization:

The resulting potassium sulfate solution is then concentrated and allowed to crystallize. Crystallization can occur through evaporation or cooling processes.

During crystallization, potassium sulfate crystals are formed and separated from the remaining solution.

Drying:

The separated potassium sulfate crystals are dried to remove excess moisture and obtain a solid, granular product.

Sizing and Packaging:

The dried potassium sulfate fertilizer may undergo sizing to produce granules of a specific size range suitable for agricultural application.

The final product is then packaged into bags, bulk containers, or other suitable packaging formats for distribution to customers.

Potassium sulfate fertilizer is valued for its high potassium content and sulfur content, making it suitable for crops that require both nutrients. The manufacturing process involves chemical reactions and crystallization steps to produce a high-quality fertilizer product suitable for agricultural use.

Manufacture of steels:

The manufacturing of steel involves several refining steps to achieve desired properties such as strength, ductility, and corrosion resistance. Here's an overview of the refining processes involved in steel production:

Removal of Silicon:

Silicon is often present in steel as an impurity from the raw materials used in steelmaking.

The removal of silicon typically occurs during the refining process in the basic oxygen furnace (BOF) or the electric arc furnace (EAF).

Lime-based fluxes are added to the molten steel to react with silicon, forming slag (calcium silicate) which floats on top of the molten metal. This slag is then removed from the surface of the steel.

Decarburization:

Decarburization is the process of reducing the carbon content in steel to achieve the desired carbon level.

This process is typically carried out in the BOF or EAF by blowing oxygen onto the surface of the molten metal. Oxygen reacts with carbon to form carbon monoxide gas, which is then removed from the steel.

The extent of decarburization is controlled to achieve the desired carbon content for the specific grade of steel being produced.

Demanganization:

Manganese is often added to steel as an alloying element to improve its strength and toughness. However, excessive manganese can lead to brittleness and other undesirable properties.

Demanganization is achieved by adding iron oxide (FeO) or other manganese scavengers to the molten steel. These scavengers react with manganese, forming slag, which is then removed from the surface of the steel. The process is carefully controlled to ensure that the desired manganese level is achieved in the final steel product.

Desulfurization:

Sulfur is another impurity that can negatively affect the properties of steel, such as its machinability and toughness. Desulfurization is typically achieved by adding lime-based fluxes containing calcium oxide (CaO) or magnesium oxide (MgO) to the molten steel. These fluxes react with sulfur to form slag, which is then removed. Alternatively, desulfurization can also be carried out by injecting gases such as oxygen or argon into the molten steel, which react with sulfur to form gaseous sulfur compounds that are then removed.

Dephosphorization:

Phosphorus can cause embrittlement and other problems in steel, especially at elevated temperatures.

Dephosphorization is typically achieved by adding lime-based fluxes containing calcium oxide (CaO) to the molten steel. These fluxes react with phosphorus to form slag, which is then removed.

Alternatively, dephosphorization can also be carried out by injecting gases such as oxygen or argon into the molten steel, which react with phosphorus to form phosphorus oxide (P_2O_5) that is then removed as slag.

Overall, these refining processes are essential for producing high-quality steel with the desired properties for various applications in construction, automotive, aerospace, and other industries. Each step must be carefully controlled to achieve the required chemical composition and mechanical properties of the final steel product.

Surface treatment:

Surface treatment is a critical aspect of steel manufacturing, as it can significantly impact the mechanical, chemical, and physical properties of the steel. Here's an overview of some common surface treatment processes used during steel manufacturing:

Argon Treatment:

Argon treatment, also known as argon purging or argon bubbling, is a process used to remove impurities and improve the cleanliness of the steel surface.

In this process, argon gas is blown onto the surface of the molten steel, creating agitation and stirring that helps to remove dissolved gases, such as oxygen, nitrogen, and hydrogen, as well as non-metallic inclusions. Argon treatment helps to refine the microstructure of the steel, resulting in improved mechanical properties and surface finish.

Heat Treatment:

Heat treatment is a process used to alter the microstructure of steel by heating and cooling it to specific temperatures under controlled conditions.

Common heat treatment processes include annealing, tempering, quenching, and normalizing, each of which serves to achieve different properties such as hardness, toughness, strength, and ductility.

Heat treatment can also relieve internal stresses, refine grain structure, and improve machinability, weldability, and dimensional stability of the steel.

Nitriding:

Nitriding is a surface hardening process used to improve the wear resistance, fatigue strength, and corrosion resistance of steel. In nitriding, the steel is heated in the presence of ammonia gas (NH_3) at elevated temperatures (500-600 °C) for an extended period (several hours to days). During nitriding, nitrogen diffuses into the surface of the steel, forming nitrides such as iron nitride (Fe_3N) and iron nitride (Fe_4N). These nitrides significantly increase the surface hardness of the steel while maintaining a tough core, making it suitable for applications where high wear resistance is required, such as gears, crankshafts, and cutting tools.

Carburizing:

Carburizing is a surface hardening process used to increase the surface hardness and wear resistance of steel by introducing carbon into its surface layer. In carburizing, the steel is heated in the presence of a carbon-rich atmosphere (such as methane, propane, or carbon monoxide) at elevated temperatures (typically 800-950 °C) for an extended period (several hours to days). Carbon atoms diffuse into the surface of the steel, forming carbides such as iron carbide (Fe_3C) and iron carbide (Fe_4C).

These carbides increase the surface hardness and wear resistance of the steel, making it suitable for applications such as gears, bearings, and shafts that require high wear resistance.

Surface treatment processes play a vital role in enhancing the properties and performance of steel, making it suitable for a wide range of applications in various industries. Each surface treatment process is carefully selected based on the desired properties and requirements of the final steel product.