

SOURCE OF FERTILIZERS

Fertilizers can be obtained from natural and artificial sources:

NATURAL ORGANIC FERTILIZERS

(a) **Plant matter**- Oil cakes from cotton seed meal, linseed meal and castor cake belong to this class and contain 7%, 5.5% and 6% of nitrogen respectively.

(b) **Farmyard manures**- A typical farmyard manure consists of cow dung, sheep dung and human excretions.

(c) **Animal matter**- Powdered dry fish and red dry blood from the slaughter house are important nitrogenous fertilizers.

(d) **Guano**- Guano is a classic example of complete fertilizer and it is a mixture of bird's excrement, fish refuse and fish bones.

GRANULATION

In the early years of the fertilizer industry (prior to 1920) no attempt was made to alter the particle size of the fertilizer during the manufacturing process. As a result, the product was generally finely divided, with some lumps often present because of the relatively high moisture contents of the product. With the introduction of materials such as ammonium nitrate, urea and ammonium phosphates, it became more and more difficult to produce fertilizers of acceptable physical properties. So various methods were developed to increase the particle size of such fertilizers, in order to reduce moisture absorption by reducing surface area and to minimize caking by reducing the number of contact points between the particles. Nitrophoska (1935) first prepared a multinutrient fertilizer in granular form containing a granulated mixture of ammonium nitrate, diammonium phosphate and potassium chloride. Granulation of other fertilizers soon started to the extent that in 1950 about 75% of the total fertilizer production was granulated in United States.

There is wide variation in range of particle size and sphericity of granules. Products range from semigranular mixed fertilizers to granular and to urea and ammonium nitrate prills that have a small size range and are quite spherical.

An ideal granular fertilizer is that which is free of lumps, made up of homogeneous, spherical particles in the size range of 10-14 mesh and capable of maintaining the initial drilling rate of 1hr, when exposed to 88% relative humidity at 70°F.

Modern granular fertilizers are satisfactory products which also reduce fertilizer cost by the use of high analysis, hygroscopic materials. Farmers now also demand granular fertilizer because of its attractive appearance, freedom from dust and ease of handling.

BULK BLENDING

In the early 1950's most of the emphasis was on the granulation of mixed fertilizers of ammoniated superphosphate types. Some granulation of fertilizers based on ammonium phosphate was also carried out, often with ammonium sulphate and potassium chloride. In 1955, another method known as bulk blending

was introduced for making granular mixed fertilizers. This is the simple mechanical mixing of high analysis, granular materials giving a product of high analysis and good physical properties. Materials used in this technique are granular ammonium sulphate or ammonium nitrate, triple superphosphate or ammonium phosphate and potassium chloride.

NATURAL INORGANIC FERTILIZERS

(a) **Chile saltpetre**- The recent export figures of chile saltpetre (NaNO_3) have shown a fairly sharp decline and about 250,000,000 kg are exported every year. It has been estimated that chilean deposits would not last for more than 250 years. Even at present about 83% of the world's requirements of NaNO_3 come from artificial sources.

(b) **Rock phosphates**- Finely divided rock phosphate, although insoluble in water, weathers rapidly and may be used directly. Bone meal is another source which supplies phosphorus. It should, however, be noted that phosphorus is exclusively supplied by the artificial sources.

(c) **Potassium salts** - Natural potassium sources are wood ash (containing 5-6% potash) and waste materials of sugar beet crops.

These natural organic and inorganic fertilizers are not sufficient to make the soil productive, as they can no wholly meet the demand. Hence fertilizers are made artificially.

ARTIFICIAL FERTILIZERS

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

NITROGENOUS FERTILIZERS

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

These fertilizers are added to the soil in order to remove the deficiency of nitrogen in the soil and hence their fertilizing value is expressed as available quantity of nitrogen in them.

Most nitrogenous fertilizers are synthetic products obtained by the neutralization of acids with alkalis. The initial materials used in the manufacture of nitrogenous fertilizers are H_2SO_4 , HNO_3 , CO_2 , liquid or gaseous NH_3 , $\text{Ca}(\text{OH})_2$ etc. The nitrogen is contained in the fertilizers either as NH_4^+ cation, as NH_2 (amide) or as NO_3^- anion form. On the basis of the form of nitrogen, nitrogenous fertilizers are divided into **ammonia** (containing nitrogen as NH_4^+ ion), **nitrate** (containing nitrogen as NO_3^-) **ammonia-nitrate** (containing both NH_4^+ and NO_3^- ions), and **amide** (containing nitrogen in the form of NH_2) fertilizers. All nitrogenous fertilizers are soluble in water and well assimilated by plants, but they are easily carried away into the deeper layers of the soil during abundant rainfall or irrigation.

AMMONIUM NITRATE

Ammonium nitrate is most important nitrogenous fertilizer. Ammonium nitrate plants are found in most of the fertilizer producing countries of the world. Over 80% of the worldwide ammonium nitrate production goes into fertilizers and minor amounts to other uses, mainly to industrial explosives.

Properties - Ammonium nitrate contains 32-35% nitrogen, half in ammonium form and half in nitrate form and the former is fairly resistant to leaching. It is white crystalline salt, very soluble in water and highly hygroscopic in nature. It has marked tendency to absorb moisture from air and it forms cake. It is acidic in reaction and its acid equivalent is 60, that is, 60 lb of CaCO_3 is required to neutralise the acidity developed by application of 100 lb of ammonium nitrate.

The most important properties of ammonium nitrate (which are of great value in the fertilizer field) are given in the table 1.

Raw materials- All Ammonium nitrate plants are operated in conjugation with an ammonia plant and nitric acid plant. Thus the raw materials for ammonium nitrate are ammonia and nitric acid and

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both of these are usually produced at the same installation.

Practically all nitric acid is made by oxidising ammonia and absorbing the resulting nitrogen oxides in water. Modern plants make acid of 60-70% concentration. Older plants are still using a concentration of about 45%.

Method of production - There are three important methods of producing ammonium nitrate. These are:

(a) Crystallisation. (b) Flaking. (c) Prilling.

	State	Temp. °C	System
1. Percent of nitrogen		170 to 125	cubic
2. Solubility, g/100 g. water 32°F		155 to 84	tetragonal
212°F		84 to 32	rhombic
3. Melting Point, °C		32 to -18	rhombic
4. Particle size		below -18	tetragonal
5. Hygroscopic point			
6. Sp. gravity, 20/4° C			
7. Bulk density, lb/ft ³			
8. Crystal state			

The latest and the most important method is prilling. This method was developed in 1940. A modern ammonium nitrate prilling plant consists of the following operations:

(a) Neutralisation - Heated ammonia vapour (obtained by Haber's process) and 60-80% nitric acid (prepared by the oxidation of ammonia) are introduced at the base of a neutralizer tower operating under a pressure of 3-5 atmospheres and through which neutralized solution is recycled. The neutralisation reaction is exothermic indicating a high yield to be subjected to (a) use of HNO₃ of nearly 60% strength (b) Preheating the reactants before mixing and (c) Efficient utilisation of heat of reaction for concentration purpose.

$\text{HNO}_3 + \text{NH}_3 \rightarrow \text{NH}_4\text{NO}_3$; $\Delta H = -20.6 \text{ k. cal}$
In some plants, in which low cost steam from other sources is available, atmospheric neutralisation is used.

(b) Evaporation - Solution obtained from the neutralizer contains about 83% NH₄NO₃. This solution is allowed to pass through a heater supplied with steam for the neutralizer. Means are provided to recover ammonia flashed off the neutralizer with the steam. The heated solution from the heater is then passed to a vacuum evaporator when its concentration is increased to about 95%, 83% solution (if left) is drawn off at this point and used in making solution.

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

(d) Drying and finishing - It is very difficult to dry the prills of ammonium nitrate because it is deliquescent in nature. The drying temperature must be low to avoid melting.

Various methods of drying are available. In one method, the material is cooled to below 90°F and the remaining moisture is removed in a second dryer.

In another method, known as short tower prilling, ammonium nitrate solution concentrated to about 99.5% rather than the usual 95% is prilled in a short tower, making use of the fact that strong solution solidifies faster. The last trace of water may be removed by the process of evaporation than removing it in dryers. However, the quality of ammonium nitrate obtained by this method is not as good as it should be.

In Stengel process, super heated ammonia vapour (145°C) and concentrated nitric acid preheated to 170°C are allowed to react in a packed tower and the reaction mixture is then passed into a cyclone designed to separate steam and solution quickly. Air is blown through the melt as a result of which water is removed from the melt to a greater extent and a melt containing only about 0.25% moisture is produced directly. The melt can be used directly, prilled in a short tower or passed into a cooled steel belt to give a thin layer of solid nitrate. The latter is subsequently broken up to give granular crystals.

In Bamag process, nitric acid and ammonia gas are pumped into a melt of ammonium nitrate at about 150°C, which is then cooled and converted into solid NH₄NO₃.

In crystallisation method, 83% solution is crystallised and the crystals are removed by centrifuging and then dried. This method has two major disadvantages.

- (a) Difficulty in growing crystals of adequate size at a satisfactory rate
- (b) Poor physical conditions.

Production economics - Production cost of ammonium nitrate depends mainly on the cost of raw materials ammonia and nitric acid.

Handling - The latest practice is to store in bulk in buildings equipped with dehumidification equipment.

Explosive nature - A major drawback of ammonium nitrate is its explosive nature. It is very sensitive to heat and shock. The principal method used for reducing the explosive nature or hazard of ammonium nitrate is to mix some thing with it. The risk of explosion may, therefore, be avoided by mixing it with chalk (CaCO₃), obtained as a byproduct in the manufacture of ammonium sulphate). A mixture of NH₄NO₃ and CaCO₃, called nitrochalk contains 16% nitrogen and does not explode. The ammonium sulphate and ammonium phosphate have also been used for the same purpose. The amounts of calcium carbonate and ammonium sulphate used with ammonium nitrate reduce detonation sensitivity of NH₄NO₃ to a large extent. In actual practice, nitrochalk can be prepared by mixing ammonium nitrate solution with dry calcium carbonate and sprayed from the top of a tower. A semisolid mixture is first obtained which on cooling sets to hard mass. It is dried, crushed and passed over screen to yield nitrochalk. The use of NH₄NO₃ or nitrochalk avoids overdependence on sulphur or sulphur bearing ores which are less available in India. The mixing of CaCO₃ with NH₄NO₃ prevents the ammonium salt from making the soil acidic.

Ammonium nitrate can, therefore, be used safely by avoiding contact with oxidisable materials, keeping fire and open flames away and prompt disposal bags. Sensitivity to thermal decomposition of ammonium nitrate may be avoided by mixing it with small amount of urea.

Physical condition - Ammonium nitrate is hygroscopic in nature. So the bags in which it is packed should be made entirely of plastic. Ammonium nitrate must be dried to a very low moisture content in order to store it properly. A coating of inert materials, such as clay holds the granules apart. Such coating agents are called parting agents.

Ammonium nitrate sulphate - A mixture of ammonium nitrate and ammonium sulphate contains about 27% nitrogen and used in order to reduce the explosive nature of ammonium nitrate as seen above.

IMPORTANT POINTS

(a) Ammonium nitrate is a ballast free nitrogenous fertilizer containing 32-35% nitrogen in ammonium and nitrate forms and it can therefore be used with advantage on soils of all types and for all kinds of

Crops.

Ammonium nitrate fertilizer has poor physical properties. The crystals of NH_4NO_3 are highly hygroscopic and, therefore, deliquesce in the air. When exposed to air they also cake into large aggregates because of hygroscopicity, high solubility in water and large temperature coefficient of solution of the material. Moreover, temperature changes during storage can result in a changeover from one crystalline form into another (i.e. recrystallization) and this also leads to caking. Such cakes are very difficult to be incorporated into the soil. To reduce the caking of NH_4NO_3 , it is granulated with non-hygroscopic substances such as calcium or magnesium nitrates, calcium phosphates etc. The granules so produced are powdered with finely ground gypsum, kaolin, bone meal or phosphorite.

(b) The danger of fire and explosions complicates the manufacture of ammonium nitrate and its use as fertilizers.

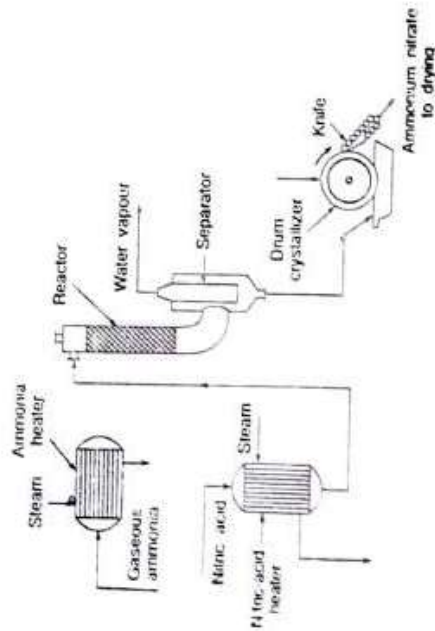
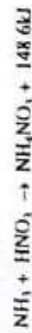


Fig. 1. Flow diagram of ammonium nitrate no- evaporation manufacturing process.

(c. Ammonium nitrate is generally produced at plants where synthetic ammonia and nitric acid are manufactured. The process of producing NH_4NO_3 consists of neutralisation of weak nitric acid with gaseous ammonia, evaporation of the solution, and granulation of the ammonium nitrate.

(d. The reaction between gaseous ammonia and dilute nitric acid is a typical chemisorption reaction, in which the absorption of NH_3 gas by the liquid HNO_3 is accompanied by a rapid chemical reaction. It is diffusion controlled and highly exothermic.



The heat of neutralisation is utilized in evaporating water from the NH_4NO_3 solution. If the process is carried out with the use of the reaction heat to evaporate the water, then by using 58-60% HNO_3 , it is possible to obtain directly a melt of ammonium nitrate (with a concentration of 95-97% NH_4NO_3) without the evaporation stage.

(e. In recent years, the most extensively used scheme is that in which the solution is partially concentrated by evaporation at the expense of the heat of neutralisation. The main part of water is evaporated in a neutraliser, which consists of a cylindrical vessel made of stainless steel with a second cylinder inside it. Gaseous NH_3 and nitric acid are continuously fed into the inner cylinder, where nitric acid is

introduced through a sprayer nozzle. The inner space of the cylinder is the neutralizing part of the unit, while the annular space between the outer and inner cylinders is the evaporating part. The reactants move through the neutralizer in a counter current flow. Heat is removed from the reaction zone through the wall of the internal cylinder. The removal of heat in neutralisation is required not only for evaporation of water, but also to prevent the thermal decomposition of the ammonium nitrate formed. The steam liberated when the water evapo-rates (secondary steam) is used further as a heat carrying agent. The solution of ammonium nitrate formed (contains about 70% NH_4NO_3) flows over the upper rim of the cylinder into the evaporator part, where water is evaporated as a result of heat transfer from the secondary steam. In the evaporator part, containing a system of multiple-body vacuum evaporators. In the after neutralizer, the weakly acidic solution is additionally neutralized with NH_3 . In the multiple body vacuum evaporator where the heat carrying agent (steam) is economized by using the secondary steam of the neutralizer, the concentration of the solution is brought upto 98-99% of NH_4NO_3 . A melt of ammonium nitrate is formed which is transferred first to the separator and then to a prilling or granulating tower. The nitrate is granulated by spraying the melt with the aid of a rotating disc in a hollow reinforced concrete tower 30-35 m. high. The falling drops of the melt solidify in the form of granules in the stream of cold air blown through tuyeres into the lower part of the tower, the granules drop on to a conveyor belt, which transports product to the drying and packing sections.

(f) Some plants produce NH_4NO_3 in the form of crystalline aggregates or flakes instead of granules, by crystallising the melt on the surface of a rotary drum cooled from the inside with water.

(g) The no- evaporation, single stage method of manufacturing NH_4NO_3 is based on a rapid reaction between ammonia and 60% HNO_3 under a pressure of 4 atm, preheated in interchangers. The vapour-liquid emulsion leaving the reactor is separated into its composite parts in a separator and the 97-98% NH_4NO_3 melt is transferred to a granulator.

(h) Because of a number of negative features of NH_4NO_3 , it is advisable to use it as the basis for making complex and mixed fertilizers. Calcium ammonium nitrate, ammonium sulphate nitrate etc are made by mixing ammonium nitrate with limestone and with ammonium sulphate.

(i) Nitrogenous-potash-phosphatic fertilizers can be made by melting NH_4NO_3 with salts of potassium and phosphorus. Ammonium nitrate is also used for making liquid fertilizers, by dissolving it in liquid ammonia or ammonia liquor.

✓AMMONIUM SULPHATE

Ammonium sulphate containing 21% nitrogen is another important nitrogenous fertilizer. It can be obtained as a byproduct or may be manufactured synthetically.

Ammonium sulphate is obtained as a byproduct in the steel industry in which ammonia (another byproduct) from coke ovens is absorbed in sulphuric acid.

Ammonium sulphate is also manufactured by reacting synthetic ammonia with sulphuric acid.

Waste streams from various chemical and metallurgical industries are another source of ammonium sulphate. For example, ammonia leaching of ores, production of pigments and synthetic fibres, manufacture of caprolactam etc. produce byproduct solutions containing ammonium sulphate.

Flue gases are another source of the ammonium sulphate. The metallurgical smelters and coal burning power plants liberate large quantities of SO_2 that pollute the atmosphere. The sulphur dioxide is collected and converted into sulphuric acid. Ammonium sulphate is then produced by passing ammonia gas through 60% sulphuric acid (obtained above) placed in lead lined vats at about 60°C. The crystals of ammonium sulphate separate out on cooling.



Properties - Properties of fertilizer grade ammonium sulphate are given in the following table 2.

Manufacture (byproduct)- Manufacture of byproduct ammonium sulphate may be carried out by passing cleaned coke oven gases into an absorption column, counter current to a recirculating stream of

under saturated solution of ammonium sulphate. A 90-98% sulphuric acid is now introduced into the stream at another point. The neutralisation takes place and the effluent solution containing ammonium sulphate is passed to a crystalliser, where crystals of ammonium sulphate separate out on cooling. The crystals are separated either by filtering or by centrifuging and then dried. The mother liquor overflowing from the crystalliser is acidified and recycled to the absorber.

In an old saturation process, ammonium sulphate is produced by passing coke oven gas and sulphuric acid into a vat containing a saturated solution of ammonium sulphate and then setting out the crystals.

Synthetic manufacture - Ammonium sulphate made with manufactured ammonia (as in Haber's process) is called synthetic ammonium sulphate. Both saturators and crystallizers are also employed in the synthetic manufacture of ammonium sulphate. The heat of reaction of anhydrous ammonia and concentrated sulphuric 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.

Sulphuric acid may also be obtained as a byproduct from alcohol manufacture, nitrating process, alkylation in petroleum refining and benzene production. The acid obtained by such processes is called spent acid and contains a large number of impurities.

Ammonium sulphate is dried thoroughly to prevent caking. Free sulphuric acid is removed either by washing on a centrifuge or filter or by neutralising with weak ammonia solution.

AMMONIUM SULPHATE FROM GYPSUM OR ANHYDRITE ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)

A new method, which is used at Sindri in India consists in passing a concentrated aqueous solution of ammonia down a tower, packed with aluminium rings against a current of CO_2 so as to form ammonium carbonate



Ammonia is manufactured by Haber process and CO_2 is manufactured by heating limestone.



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.



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

Factors promoting high yield of ammonium sulphate are :

- High concentration of NH_3 , which shifts the equilibrium to the side of the products.
- Control of CO_2 partial pressure, which keeps the bicarbonate formation to the minimum.

- Fine crushing of gypsum to expose a large surface area to the action of gases.
- Boiling of the mother liquor only after the settlement of the precipitated matter.

ACTION OF $(\text{NH}_4)_2\text{SO}_4$ AS FERTILIZER

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

Sindri fertilizer factory is probably the largest ammonium sulphate factory in Asia. Ammonium sulphate is also being manufactured in India by Fertilizers and Chemicals, Travancore.

AMMONIUM SULPHATE NITRATE

Ammonium sulphate nitrate [$(\text{NH}_4)_2\text{SO}_4 + \text{NH}_4\text{NO}_3$] is double salt of ammonium sulphate and ammonium nitrate. It is available in white crystalline form or granules of a dirty white colour. It contains 26% nitrogen, 19.5% of which is in ammonical form and the rest 6.5% is in nitrate form. It is readily soluble in water and readily available to crops. It is acidic in nature and its acid equivalent is 93.

Ammonium sulphate nitrate can be manufactured by mixing solution or moist salts of ammonium sulphate (62.5%) and ammonium nitrate (37.5%) and then drying the mixture. This fertilizer can be used for all crops and is suitable for application to all types of soil. It may be applied prior to sowing, at sowing time or as top dressing. It should, however, not be applied with the seed.

UREA

Urea occupies the third place among the world's solid nitrogenous fertilizers, but it is the highest in nutrient concentration because, if pure, it contains nearly 45-47% nitrogen. The most important properties of fertilizer grade urea are given in the following table.

1. Nitrogen percentage	45%
2. Solubility, g/100 ml. H_2O at 25 °C	119
3. Melting point	132.7°C
4. Particle size	95% - 8 mesh, + 16 mesh
5. Hygroscopic point, %	72
6. Sp. gravity 20/4°C	1.335
7. Bulk density, lb/ft ³	42 - 45

Urea came into prominence as a fertilizer in 1950. There are some practical difficulties encountered with urea. The biuret ($\text{NH}_2\text{CONHCONH}_2$) content is regarded as an important property of urea, because under certain conditions a small percentage can cause plant toxicity. This is true when urea is used in citrus crops.

Another property adverse to urea is its tendency to hydrolyse and lose ammonia, a reaction promoted by high temperature, low pH and certain catalysts. In some respects, it is desirable, because it must occur before plants can use the nitrogen efficiently, but if the urea is applied to the surface of the soil, ammonia produced by hydrolysis can be lost to the atmosphere before it has time to combine with soil constituents. High temperature aggravates hydrolysis. Another adverse property of urea is its slower conversion to nitrate in the soil (called nitrification) as compared with ammonia, ammonium nitrate or ammonium sulphate. The urea must hydrolyse and release ammonia, whereas the other materials are already in the ammonical form or in the case of ammonium nitrate, already partially in the nitrate form. In very cold places, urea may not produce nitrate nitrogen as rapidly as desired.

RAW MATERIALS

Like ammonium nitrate, urea is always made in an ammonia plant. The reason for associating urea ammonia production is that most ammonia plants produce carbon dioxide as a byproduct which can be

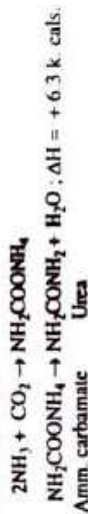
used directly for urea manufacture without further treatment. This availability of a major raw material at practically no cost is one of the main reasons for the relatively low cost of producing urea.

The CO_2 available from a modern ammonia plant comes from synthesis gas used for producing hydrogen. Most of the CO in the synthesis gas is converted into CO_2 by reaction with water, to produce as much hydrogen as possible. Thus the initial carbon, the principal raw material in the synthesis of ammonia, is converted by steps to the lower energy levels represented by CO and CO_2 . Production of urea then realises most of the remaining chemical potential of the carbon by using the relatively weak reactivity of CO_2 to form urea.

Ammonia plants that use a source of hydrogen other than synthesis gas, such as byproduct refinery gas or coke oven gas, have the disadvantage of not being able to produce urea. The main alternative source of CO_2 is flue gas. In some places, blast furnace gas from a steel plant has been used to supply carbon dioxide for urea production.

MANUFACTURE

Urea can be manufactured by passing liquid CO_2 and liquid NH_3 in a silver lined special autoclave when ammonium carbamate is formed. The latter is heated at 130-135° under about 35 atmospheric pressure to get urea. The conversion is about 40%. Urea remains in the aqueous solution. The resultant charge is passed into another vessel and steam is introduced.



Since the rate determining step is endothermic, the overall reaction should be favoured by a rise in temperature. But conversion of $\text{NH}_2\text{COONH}_4$ to NH_2CONH_2 actually records increasing yield upto about 170°C and above it, it falls. Temperature above 200°C in a 180-200 atm. unit is not conducive, because it promotes corrosion, and favours biuret formation (a side reaction) at the cost of urea.



Because the vapour pressure of ammonium carbamate is high, its dehydration is attended with a decrease in the number of moles. Hence increase of pressure favours the yield of urea. The operating pressure should be above the dissociation pressure of the carbamate at a given temperature.

An excess of NH_3 shifts the equilibrium towards the formation of urea, by combining with water formed thus using slightly higher ratio of NH_3 ; CO_2 is beneficial.

There are several variations of urea production process. All of them, however, include the basic step of treating ammonia with carbon dioxide in a reactor at elevated temperatures and pressures usually in the range of 350-400°F and 2500-3500 psig. An excess of ammonia over the stoichiometric amount is used to drive the reaction to completion, but conversion of CO_2 to urea does not exceed 60%. The reaction takes place in the liquid phase, producing a solution of urea, ammonium carbamate and free ammonia in water. Release of pressure and heating decomposes the carbamate and evaporates NH_3 and CO_2 , leaving a solution containing 75-90% urea.

The main difference among the various processes lies in the method for recycling the unreacted ammonia. Some of the methods of doing this are given below.

(1) Carbon dioxide and ammonia are absorbed in water and then recycled as a solution of ammonium carbamate. (2) Ammonia and carbon dioxide are separated by a selective absorbent and then recycled separately in the form of liquid NH_3 and liquid CO_2 . (3) Ammonia and carbon dioxide are absorbed in a light oil, and then recycled as a slurry of ammonium carbamate.

The processes (2) and (3) were developed to avoid introduction of water into the reactor and other advantages to the carbamate method.

Another major difference in urea plant is the proportion of unreacted ammonia recycled. There are three recycle processes; total recycle, partial recycle and once through cycle. The choice between the three depends upon various factors, but the majority choice in new plants is total recycle.

In once through operation, excess ammonia fed to the reactor normally is held as low as feasible to reduce the amount of unreacted ammonia, which is used in making the ammonium nitrate portion of the solution or may go also to solid ammonium nitrate made in the same plant. Unreacted ammonia is also used in the manufacture of HNO_3 and $(\text{NH}_4)_2\text{SO}_4$. This process therefore involves no recycle of residual gas mixture back to the reactor, but utilizes these gases in the production of other nitrogenous fertilizers.

The partial recycle is accomplished by omitting the second stage absorber (please see below); ammonia and carbon dioxide from second stage decomposer are allowed to pass to some other process and that form the first stage decomposer is recycled. Partial recycle is used when other available processes can not take all the unreacted ammonia from once through operation.

In carbamate solution recycle process the off gas mixture from the carbamate stripper is dissolved under pressure in water and solution sent back to the reactor.

Following is the description of a typical urea plant based on carbamate solution recycle, (total recycle type).

1. **Ammonia pumping.** Piston type pumps are used to introduce NH_3 into the reactor, which is a vertical vessel lined with stainless steel, protected from corrosion by a film of oxide. The film is maintained by continuously passing a small amount of air into the reactor along with the reactant materials. The temperature of the reactor is maintained below 380°F.

2. **Carbon dioxide compression.** CO_2 is taken directly from the desorbers in the ammonia plant without any purification.

3. **Carbamate decomposition.** Solution from the reactor is allowed to pass through a valve that reduces the pressure from about 2500-3000 psig to 200 psig and then to a high pressure decomposer which is heated by making use of steam. Excess of ammonia and some ammonia and carbon dioxide (evolved as a result of partial decomposition of carbamate) escape from the solution. The evolved gases are introduced into a high pressure absorber, where they are scrubbed with carbamate solution from a latter stage. The resulting enriched carbamate solution now contains all the unreacted CO_2 as carbamate. This enriched carbamate solution is recycled back into the reactor. Excess of ammonia liberating from the absorber (as gas) is condensed and pumped back as liquid ammonia.

Solution from the first stage decomposer passes to the low pressure (near atmospheric) decomposer, where remaining carbamate is decomposed as a result of heat and boiled out of the solution. The carbamate solution formed in this manner acts as the scrubbing agent in the first absorber.

Concentration. Urea solution, free from carbamate is passed through a vacuum evaporator, whereby it is concentrated to 99+%. A falling film type of evaporator is used with two stages of concentration.

Prilling. The concentrated solution is crystallised into globules by spraying from the top of a prilling tower and heated by hot air (similar to the production of NH_4NO_3). Drying of the prills is not required.

CONDITIONS FOR A GOOD YIELD

(a) Carbon dioxide be free from oxygen and hydrogen to avoid hazard of corrosion or explosion. (b) NH_3/CO_2 ratio varies widely, ranging from about 10% excess NH_3 over the stoichiometric amount to 100% or more. The larger excess gives better results. (c) Preheating of ammonia is essential for better results. (d) Reaction temperature should be as high as possible, but must be limited because of corrosion. The maximum temperature that can be attained in stainless steel lined reactors (used in the majority of plants) is about 380°F. (e) The average pressure is about 2700 psig, but pressure as low as 2400 and as high as 6000 psig have been reported.

Production economics. The cost of producing urea depends on the proportion of unreacted ammonia recycled. Production per tonne of urea by the above method is as follows

Ammonia 0.58 tonnes, Power, kWh 173, Water 15000 gal., Steam (1000lb) 2.5, Operating labour, hr 1.1.

Sindri method - Urea is also manufactured at Sindri in India, by introducing pure liquid ammonia and liquid carbon dioxide in an autoclave in which the temperature remains at about 182°C and pressure 180 kg/cm². In this manner 37-40 urea is formed. Unreacted ammonia and carbon dioxide are converted into ammonium carbonate.



Ammonium carbonate is then allowed to react with dilute nitric acid (prepared in the factory) to form ammonium nitrate and carbon dioxide.



Carbon dioxide thus formed is recycled. Urea solution is then concentrated to 78% and then to 97% solution. The concentrated solution is then crystallised into globules as described above.

Handling - Urea is less hygroscopic than ammonium nitrate and therefore presents fewer problems in storing and handling.

Some variations in working procedures and reactor designs, depending upon local conditions have also been made in different procedures. For example,

In **Solvay process**, one part by weight of CO₂ is allowed to react with two or more parts by weight of CO₂ at 160 - 180 °C and 150 - 200 atmospheres.

In **DuPont process**, purified CO₂ reacts with 3.5 moles of NH₃ at 200 - 210°C and 400 atmospheric pressure. The conversion is about 75%.

In **Pechiney process**, a slurry of solid carbonate in a mineral oil is charged into the lead lined reactor at 180°C and 200 atmospheres.

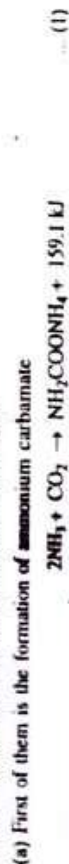
In **Krase process**, liquid NH₃ and liquid CO₂ are used to be converted into urea. Excess of NH₃ is neutralised with H₃PO₄. The product obtained is a mixed fertilizer.

IMPORTANT POINTS

(a) Urea or carbamide is a high quality and most valuable nitrogen fertilizers with a 46% nitrogen content. It is easily assimilated by plants and can also be used directly like a nitrogen addition in live stock feeds or animal food.

(b) Carbamide is used not in agriculture, but also in industry. It is used in making urea resins which in turn are used to produce valuable plastics, wood-particle boards, synthetic glues, compositions for impregnating cloth etc. Urea is also used widely in preparing the synthetic fibres.

Urea is synthesised from NH₃ and CO₂ in two stages



The overall production of urea is a gas liquid heterogeneous process occurring in kinetically controlled region. In general, the manufacture involves the following stages : chemical reaction between NH₃ and CO₂ (synthesis), distillation of the synthesis products, and processing the urea solutions obtained in the distillation operation into the end product. The rate of the overall reaction is determined by dehydration of ammonium carbamate in the melt, the slowest stage

(c) The equilibrium ratios and rate of urea synthesis depend on the temperature, pressure and chemical composition of the system. Since the vapour pressure of ammonium carbamate is very high, and the overall result of the synthesis reaction is a decrease in the gas volume, the equilibrium yield of urea increases as the pressure is increased. The rate of reaction and actual urea yield also grow rapidly with the pressure

because of increased driving forces of the process, that is, concentration of the gas-phase reactants. The rate of the process and particularly that of reaction (2) increases sharply with the temperature as a result of which actual urea yield increases. If the residence time of the reaction mixture in the heated zone is increased further (above 180°C) the yield of urea decreases as a result of the speed up of side reactions. The product yield can also be increased by using an excess of ammonia in the initial mixture over the stoichiometric ratio. An excess of NH₃ impedes formation of side products of carbamate hydrolysis and shifts the equilibrium of reaction (2) towards the formation of urea, because excess combines with water formed by dehydration of the ammonium carbamate. The excess of NH₃ in the reaction mixture also decreases the apparatus corrosion.

(e) The formation of ammonium carbamate in optimum conditions proceeds almost to the end and at a high rate, but carbamate dehydrates slowly, not completely, and is accelerated only in the liquid phase. The duration of carbamate dehydration sharply decreases with increase in temperature and yield of urea increases. In addition to raising the temperature, the yield of urea can be increased by using pressure and an excess of NH₃ above the stoichiometric amount, (as seen above) which prevents by-product formation.

(f) In industry, urea synthesis is carried out without using a catalyst, at 180-200 atm and 180-200°C temperatures. Higher temperatures can not be employed because they increase corrosion of the apparatus. 100% excess NH₃ is used.

(g) The raw materials are the expansion gas obtained in the process of manufacturing NH₃ (contains upto 90% CO₂) and liquid NH₃, used in 100-125% excess over the stoichiometric amount. When using 100% CO₂ and absolutely pure ammonia, the urea yield (relative to CO₂) under optimum conditions is 60-70% and the molten mass obtained by dehydration of carbamate contains about 35% urea. Good economics of the process and low cost of urea can only be achieved by using the parts of the reactants, NH₃ and CO₂ which do not take part in the reaction. Thus unreacted NH₃ and CO₂ are generally used either for manufacturing other products (open systems) or are recycled to the process (closed system).

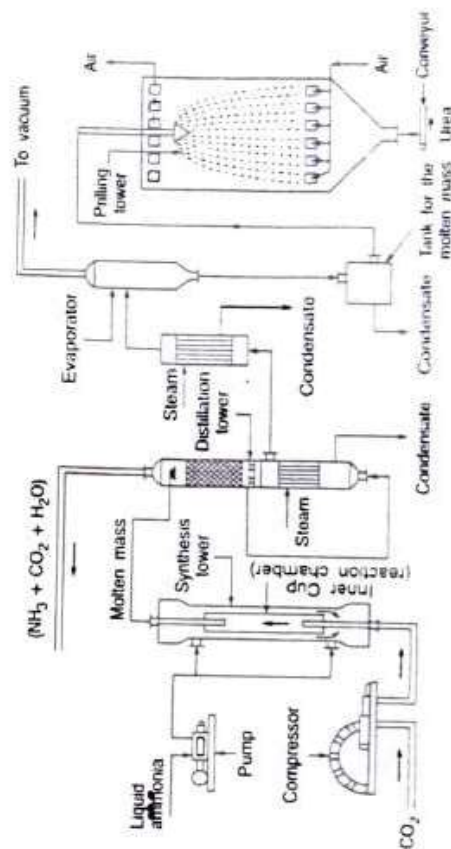


Fig 2 Flow diagram of urea production process

(h) Figure 2 shows an open system for producing urea. Synthesis takes place in a lower made of alloy steel. The inner cylinder of the tower acts to protect the walls of the high pressure vessel against corrosion by the reaction mixture. Liquid NH₃ is fed to the annular space between the lower wall and the inner cylinder by a pump. It flows along the walls, protecting them from corrosion. NH₃ reacts with

clay minerals etc.

For example, **Mussorie rock** contains phosphate (P_2O_5), carbonate (CO_3), calcium (CaO), magnesium (MgO), potash (K_2O), alumina (Al_2O_3), silica (SiO_2), iron pyrite (FeS_2), copper (Cu), zinc (Zn), molybdenum (Mo) and boron (B).

The most important advantages of using **Mussorie phos** are:

- It is an important source of phosphorus.
- It increases the fertility of acid soils.
- It releases gradually plant assimilable forms of phosphorus reserves, concurrently with the growth of plant. Thus split application of phosphorus is not required. In phosphatic fertilizers containing water soluble forms of phosphorus, instant ingestion of soluble forms of phosphates leads to quick and continuous reversion in soils from soluble to insoluble forms.
- In addition to macronutrients such as phosphorus, magnesium and sulphur, it also contains micronutrients such as Cu, Zn, Mo and B.
- It makes available the phosphorus that has become fixed in acid soil to the plants.
- It can be an effective substitute for superphosphate in acid soils in India for a number of crops.
- Use of Mussorie phos would help us to utilise our national resources most profitably. It would save foreign exchange required for the import of raw materials for the manufacture of soluble phosphatic fertilizers.
- It is easily soluble in both organic and inorganic acids present in the soil.

Rock phosphate is suitable for wide range of soils and crops. Legumes respond well to rock phosphate because of their high calcium requirements. It is not suitable for application in acid soils.

The primary object in the phosphate fertilizer industry is to convert the fluorapatite in phosphate rock to a form available to plants. In order to make it available to plants it is treated with a mineral acid, such as sulphuric acid or phosphoric acid.

Sulphuric acid converts the fluorapatite into ordinary superphosphate and also used in the manufacture of phosphoric acid (fig. 5).

Phosphoric acid thus produced is allowed to react with phosphate rock for production of triple super phosphate. It is also used to make ammonium phosphate by reacting it with ammonia. The growing demands of triple super phosphate and ammonium phosphate make phosphoric acid a very important intermediate in fertilizer industry.

Phosphoric acid, called **furnace acid** can be prepared either by treating phosphate rock with sulphuric acid or burning phosphorus and absorbing the resulting oxide in water. Phosphoric acid obtained by the wet process acid or green acid and is used mainly in fertilizers.

Phosphoric acid by wet process is manufactured through the following steps.

- Phosphate rock is dissolved in $66^\circ Be$ (93-98% H_2SO_4). The phosphate rock fed to the process

is as high in grade as economically feasible, usually ranging from 30-35% P_2O_5 .

- The acidulate slurry is held until the calcium sulphate crystals grow to adequate size.
- Calcium sulphate crystals are separated from the acid by filtration.
- The acid is concentrated to the desired level.

The reaction is



The wet process acid thus obtained contains 30-32% P_2O_5 . The concentrations of phosphoric acid required for the manufacture of ammonium phosphate and triple superphosphate are 31-32% and 52-54% respectively. So the 30-32% acid is concentrated to the level needed for the particular use.

The wet acid contains a wide variety of impurities introduced mainly by phosphate rock and consists of organic matter and compounds of Fe, Al, Ca and F.

(Singh) - NORMAL SUPERPHOSPHATE

Phosphate manure can be taken up by the plants in soluble form. When tricalcium phosphate in the form of bone meal or rock phosphate powder (main source of P_2O_5) is applied to the soil, $Ca_3(PO_4)_2$ is slowly converted into $Ca(H_2PO_4)_2$ in the soil through the agency of acids present in the soil and then the soluble phosphate is taken up by the plants. In order to avoid the slow transformation, rock phosphate is transformed quickly into soluble phosphate, which is then applied to the soil. This artificially prepared mono calcium phosphate, $Ca(H_2PO_4)_2$ is known as superphosphate. Commercial superphosphate is a mixture of mono calcium phosphate and crystalline calcium phosphate $Ca(H_2PO_4)_2 + CaSO_4 \cdot 2H_2O$. It contains about 16% P_2O_5 . The soluble calcium phosphate prepared by treating rock phosphate with sulphuric acid is called superphosphate.



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

As the reaction proceeds, the mixture stiffens and ultimately sets to a solid mass. Successive charges from the mixer are introduced to the pits A_1 or A_2 until it is full and then it is allowed to stand for some days. When it has become perfectly dry, it is dug out of the pit and meanwhile the second pit is filled. The gases from the mixture and pits are washed by spraying water in two successive towers. The resulting hydrofluoric acid solution is then neutralised either by sodium carbonate or sodium fluoride and finally treated with washed sand to form hydrofluosilicic acid. The latter is further neutralised with sodium carbonate to form sodium silico fluoride (Na_2SiF_6) or with magnesium to form magnesium silico fluoride ($MgSiF_6$). The product is used without further treatment other than breaking it upto the desired size. The main reaction is,



Na_2SiF_6 or $MgSiF_6$ are useful byproducts.

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

IMPORTANT POINTS

- In the manufacture of normal superphosphate, the ground phosphate rock is fed by a weigh feeder

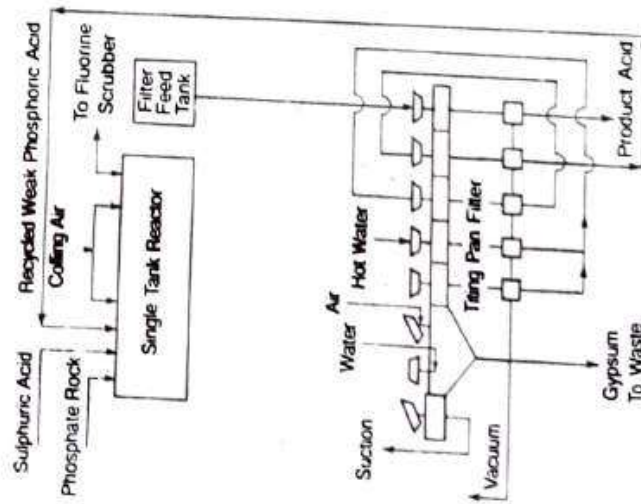


Fig. 5. Manufacture of sulphuric acid on phosphate rock is also called wet process acid or green acid and is used mainly in fertilizers.

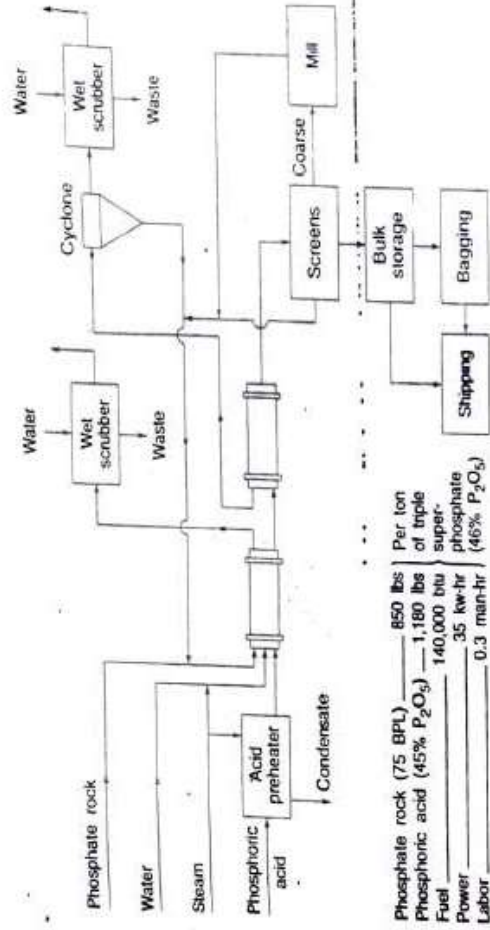


Fig. 7. Flow diagram for superphosphate by the continuous den process

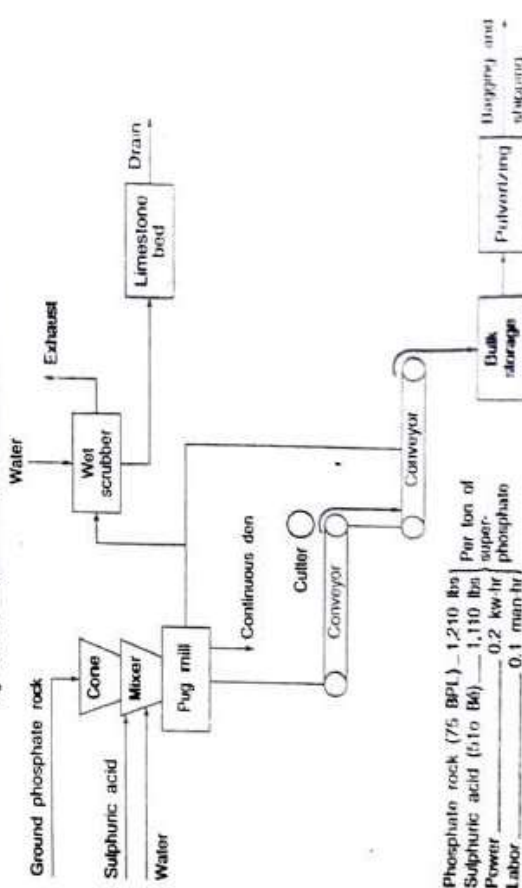


Fig. 8. Flow diagram for triple superphosphate process

into a double conical mixer, where it is thoroughly mixed with calculated amount of sulphuric acid. The latter is diluted with water in the cone to a concentration of 51Be'. The heat of dilution is utilized in heating the sulphuric acid to proper reaction temperature and excess heat is dissipated by evaporation of extra water added. In order to control the product moisture, the rate of water addition and acid concentration may be varied.

(b) The acid and water are fed into the cone mixer tangentially in order to provide complete mixing with the phosphate rock. The fresh superphosphate discharges from the cone mixer to a pugmill, where additional mixing takes place and reaction starts.

(c) From pug mill the superphosphate drops onto the den conveyor for solidifying before reaching the cutter. The cutter slices the solid mass of crude product so that it may be conveyed to pile storage for cooling or completion of the chemical reaction, which takes 10-20 days to reach an acceptable P_2O_5 availability as plant food. The fumes from the continuous den are scrubbed with water sprays to remove acid and fluoride before being exhausted to the atmosphere.

(d) The Scrubber water is discharged to a limestone bed to neutralise the acid.

(e) Nitric and mixed acid acidulation of phosphate rock has also been performed. Nitric substitution for sulphuric acid is desirable because nitrogen has an essential value as plant food. This also saves sulphur. Simple acidulation of phosphate rock with nitric acid produces a hygroscopic superphosphate because it contains calcium nitrate. The phosphate rock is extracted by mixed nitric and sulphuric acid, followed by ammoniation, drying and addition of KCl. In another method, mixed nitric and phosphoric acidulation, followed by the conventional steps, has been used. In some cases, only nitric acid has been used for acidulation. These processes, as well as the conditioning against moisture absorption as practiced for NH_4NO_3 , have led to the extension of this acidulation with nitric acid.

(f) Nitrophosphate has also been prepared in some plants. Here the phosphate rock is decomposed with nitric acid and a small amount of phosphoric salts and spray dried to get a uniform pelletized product.

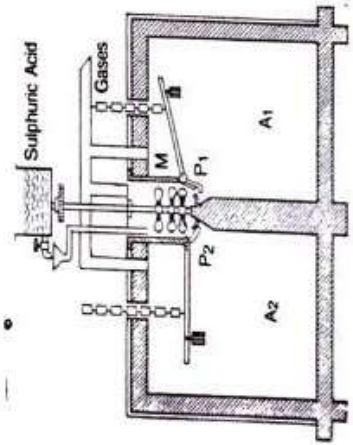


Fig. 6. Manufacture of super phosphate.

MODIFICATION IN MANUFACTURING EQUIPMENT

- (1) Mixers in early practice were quite crude and often involved hand labour. Modern plants contain continuous weighing and mixing equipments. Batch mixers are still in use. The most common batch mixer is a vertical shaft, pan type equipped with an assembly of plows. Continuous mixers are of three types:
 - (1) Horizontal trough-type mixers fitted with a shaft that carries heavy paddles.
 - (2) Cone type mixers having no moving parts. In it, mixing is done by the swirling action of acid and rock streams passed simultaneously into the cone.
 - (3) Small volume mixers fitted with a high speed stirrer.

The container which holds the mixture until it becomes solid enough to handle is called den. The den must be tight enough to receive and retain a slurry, must hold it during setting so that it can be removed easily after setting is complete. It should also be provided with the means for removing gases

evolved during the day in the den.

Stationary box **crucible dens** were used in the early days and are still in operation. **Batch mechanical den**, which is a box type den mounted on wheels that travel on a short track has also been used in United States. In the beginning of the operating cycle, the den is kept under a mixture—either batch or continuous, and is filled with rock acid slurry. The slurry set up rapidly so that a few minutes after the den is filled excavation can start. The den is provided with a sliding door at one end. The sliding door is raised and the den is moved along the track into a revolving cutter. As a result of the movement of the den in the forward direction, the cutter shaves thin silica from the face of the block and pushes them off into a conveyor at the side.

The thin slicing and fanning action has been found to aerate the superphosphate, to promote the removal of fluorine and moisture and to give a product with good properties.

Some other types of dens, which have also been developed are :

- Continuous Dens**—All involve receiving the rock and slurry at one end, carrying the mix for some distance during which time the slurry sets up and discharging the product to a conveyor.
- Sackett Den, Kuhlmann Den, Saint Gobian and Montecatini rotary drum type dens**—All employing linear horizontal travel.
- The **Den** employing circular horizontal travel is a cylindrical vessel that rotates on a vertical axis and contains an inner cylinder to give an annular space.

PROPERTIES

- Superphosphate normally contains 5–8% moisture after curing.** Low moisture contents help in reaching the general objective of 20% available P_2O_5 contents.
- Hygroscopicity is quite low, the critical relative humidity at 86°F is 94%.**
- Bulk density for non granular and granular material ranges from about 50 to 70 lb/ft³ respectively.**

TRIPLE SUPERPHOSPHATE

Triple superphosphate or concentrated superphosphate contains about 44–47% P_2O_5 content, which is nearly three times as high as in normal superphosphate. It can be manufactured by the action of 78% phosphoric acid (containing 52–54% P_2O_5) on finely powdered calcium phosphate or phosphate rock containing about 32.5–38% P_2O_5 content. The manufacturing procedure is quite similar to that of normal superphosphate. The reaction mixture is allowed to stand for about 3 months to make the reaction complete. The grey solid mass thus obtained is crushed to powder.



Triple superphosphates are essentially an impure mono-calcium phosphate, made by the following reaction.



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

- In wet and dry method, granulation is carried out by treating the crude product with water and steam in a rotary drum, followed by drying and screening.**

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

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

IMPORTANT POINTS

- The chemical industry produces simple superphosphate and triple superphosphates. The simple superphosphate is one of the most widely used inorganic fertilizers. It is a powder or in the form of granules, grey in colour, which mainly contains monocalcium phosphate, $Ca(H_2PO_4)_2$ and calcium sulphate (gypsum), $CaSO_4 \cdot 0.5H_2O$. Triple superphosphate is hydrated calcium monophosphate, $Ca(H_2PO_4)_2 \cdot H_2O$. Triple superphosphate, in contrast to simple superphosphate, consists mainly of monocalcium phosphate and is a concentrated fertilizer, containing 40–50% P_2O_5 , that is 2 to 3 times more than simple superphosphate.
- Superphosphates also contain a number of impurities, such as phosphates of iron and aluminium, silica and phosphoric acid. The manufacture of superphosphates consists mainly in decomposition of naturally occurring phosphates with sulphuric acid.
- The production of simple superphosphate consists in decomposition of calcium fluor-apatite with sulphuric acid. This is a complicated, multiphase, heterogeneous process which is usually diffusion limited. The overall reaction is,



The decomposition, however, takes place in two stages. The first is the reaction of exchange decomposition proceeding on the surface of solid phosphate particles with an excess of sulphuric acid, as a result of which free phosphoric acid is formed. In other words, the first stage is the diffusion of H_2SO_4 to the apatite particles accompanied by a chemical reaction on the surface of particles which continues until H_2SO_4 is consumed, and $CaSO_4$ crystallises.

This reaction begins immediately after the phosphate is mixed with sulphuric acid and stops within 20–40 minutes. The temperature in this period increases to 10–120°C. The second stage is diffusion of phosphoric acid formed into the pores of the undecomposed apatite particles.

The monocalcium phosphate so formed remains first in solution and then begins to crystallise out when the solution becomes supersaturated.

As seen above, reaction (1) ends in superphosphate reaction chamber in 20–40 minutes, during the period of setting and hardening of the superphosphate pulp, which is caused by relatively rapid crystallisation of low solubility calcium sulphate and recrystallization of the hemihydrate to the anhydrite by the reaction,



The next stage of the process, ageing of the superphosphate, that is, formation and crystallization of monocalcium phosphate, is a slow process and it ends only at the storage site (final ageing), where superphosphate is kept for 6–25 days. The low rate of this stage is because of low rate of diffusion of the phosphoric acid through the crust of monocalcium phosphate formed on the surface of the apatite grains and also due to extremely low rate of crystallisation of the new solid phase, $Ca(H_2PO_4)_2 \cdot H_2O$. The second stage of the process is also known as ripening of the superphosphate and proceeds very slowly. Ripening is accelerated by lowering the temperature and removing the moisture. The result is more rapid

crystallisation of the monocalcium phosphate and a higher concentration of H_3PO_4 reacting with the unreacted $Ca_4F(PO_4)_3$ by the reaction (3). In order to accelerate the ripening of superphosphate at the storehouse, it is periodically mixed with the help of a bucket crane.

(d) The most important stage in the production of superphosphate in the chamber, which is a complicated heterogeneous process, that in addition to chemical reactions includes the slow diffusion of phosphoric acid in to the undecomposed phosphate and crystallisation of monocalcium phosphate.

(e) The main factors affecting the rate of ripening and also the structure and physical properties of the superphosphate are the temperature in the chamber and the concentration of H_2SO_4 . The range of optimum sulphuric acid concentrations for the industrial process lies within 62-69%. In the continuous process for making superphosphate the initial H_2SO_4 concentration is 68-69.5%. At this concentration of the acid, the temperature in the reaction den is about 110-115°C. The increase in temperature is due to the heat liberated in the exothermic reactions (2) and (3). Under these conditions a friable, porous layer of calcium sulphate is formed on the phosphatic particles, and diffusion of H_3PO_4 into the apatite particles takes place at a fairly high rate.

(f) The ageing or curing (which is the slowest stage of the process) can be increased by cooling the superphosphate and by evaporating water from it, because it promotes crystallisation of monocalcium phosphate and increases the rate of reaction (3) by increasing the H_3PO_4 concentration of the solution. To accomplish this the superphosphate is agitated and scattered during storage.

(g) The P_2O_5 content of the end product is about 50% that of the raw material and amounts to 19-20% P_2O_5 for superphosphate made from apatite and 14% for superphosphate made from phosphate rock.

The end product still contains some uncombined phosphoric acid, which makes the fertilizer hygroscopic. In order to remove free acid of the superphosphate, neutralisation admixtures are used or the superphosphate is treated with gaseous ammonia. As a result, the physical properties of the superphosphate improve and moisture content decreases. The hygroscopicity and the tendency to cake also decrease. When ammonia treatment is used, an additional nutrient, nitrogen is also introduced in the fertilizer.

(h) The flow sheet for the production of superphosphate consists of four basic operations.

(a) The batching of sulphuric acid and fluorapatite concentration. (b) Mixing of the reactants in mixer to prepare a pulp. (c) Setting and solidification of the superphosphate mass in the reaction chamber. (d) Ripening of the superphosphate at the storehouse.

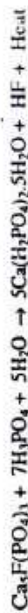
(i) Batch, semicontinuous and continuous processes have been used for the manufacture of superphosphate. In recent years, batch operation dens are not in much use because they have all typical faults of batchwise operations. They are of low production capacity, costs are high, the composition and properties of the product are not constant, the air in the plant is contaminated with the gases and dust from the process etc. In recent years, all new plants are designed to employ a continuous operation method. In this method ground apatite concentrate (or phosphate rock powder) is transported from the storage site to automatic weigh feeder, which feeds it to a continuous action mixer, by a system of belt and screw conveyors. The H_2SO_4 (75% tower acid) is continuously diluted with water in a batch feeder mixer to 68% concentration, and is then fed to the mixer, where the raw material and H_2SO_4 are mechanically agitated. The pulp formed is then transferred to the continuous action reaction den, where formation of the superphosphate (setting and hardening of the pulp in the first stage of ageing of superphosphate) takes place. The powdered superphosphate from the den is transferred for ageing by a conveyor belt to the superphosphate storage site, where it is uniformly distributed by a scattering device. The ageing can be accelerated by agitating the superphosphate during storage by means of a grab bucket crane.

(j) Superphosphate is granulated in revolving drum granulator in order to improve its physical properties. In the granulator, the powdered superphosphate is wetted with water fed into the drum through nozzles, and rolled into granules of different sizes which are then dried, separated into size fraction and weighed into paper bags.

(k) During decomposition of the phosphates with H_2SO_4 in the den, HF is evolved, which reacts with

silica contained in the phosphates and forms gaseous silicon tetra-fluoride. SiF_4 and hydrofluoric fluorosilicic acid, H_2SiF_6 . The fluoros gases containing H_2SiF_6 vapours are withdrawn through an opening in the den roof and ventilation pipe to an absorption unit and are utilized for making sodium fluosilicate. The most common type of continuous action superphosphate dens is a cylindrical revolving chamber, which is a reinforced concrete cylinder, covered with sheet metal and with an inner lining of acid resistant dibase blocks. The cylinder, together with the reinforced concrete bottom revolves slowly on roller supports about a stationary, hollow cast iron tube, which passes up through a seal in the den bottom and acts for removing the superphosphate from the den. The production capacity of a den 7.1 m in diameter and 2.5 m high is about 30-50 tonnes of superphosphate per hour and its operation intensity lies between 550 and 650 kg per cu.m.

(l) The principal shortcoming, of simple superphosphate is the relatively low content of P_2O_5 in the fertilizer. To produce a more concentrated phosphate fertilizer, natural phosphates are decomposed with 70% H_3PO_4 .



The product so formed is called triple superphosphate, which contains 40-50 percent P_2O_5 (that is, two or three times more P_2O_5 than the simple superphosphate). The triple superphosphate is more valuable ballast free fertilizer and its manufacture is rapidly growing now a days.

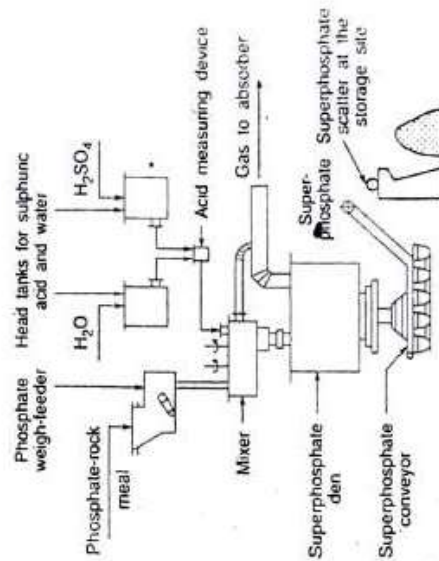
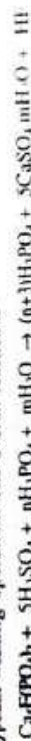


Fig. 10. Continuous superphosphate manufacturing process.

(m) Phosphoric acid is an intermediate product used in the manufacture of triple superphosphate mixed concentrated fertilizers and other phosphatic compounds. Phosphoric acid can be prepared both by electrothermal methods and by extraction methods, that is, by winning H_3PO_4 from naturally occurring phosphates with acids. The sulphuric acid process is one of the most commonly used methods for manufacturing technical grade, wet process phosphoric acid. This method consists in treating naturally occurring crushed phosphates with an excess of H_2SO_4 to produce phosphoric acid and solid phosphogypsum (calcium sulphate which contains a remainder of undecomposed phosphate). Sulphuric acid is mixed with the phosphate to form a slurry with liquid solid ratio between 2.5 : 1 and 3.5 : 1. The required ratio is maintained by diluting H_2SO_4 with a mixture of phosphoric acid product and wash water from phosphogypsum washing operation. The overall reaction is



The solution of phosphoric acid obtained by filtering off the phosphogypsum contains impurities with phosphate-silica sulphates and phosphates of Fe and Al etc. Phosphoric acid obtained by wet method does not usually contain more than 36% H₃PO₄. So the acid must be evaporated to a concentration of 50-80% H₃PO₄ for use in manufacturing triple super phosphate and other fertilizers. For concentration, drum concentrators, in which heating takes place by direct contact of the gaseous combustion products with acid, in the same fashion as in H₂SO₄ concentration, have been used.

(r) The electrothermal method of making H₃PO₄ is based on reduction of phosphorus in calcium phosphate at 1400-1500°C in electric furnace. The phosphorus vapour in the furnace effluent is oxidised to form P₂O₅, which is hydrated to produce phosphoric acid, called thermal phosphoric acid. The most important advantages of the electrothermal process in comparison to the extraction process are the possibility of making H₃PO₄ of any desired concentration upto even 100% H₃PO₄ and the high degree of purity of the product. Moreover, any phosphates, including low quality ones not subjected to beneficiation, can be used as raw materials. However, electrical consumptions are higher than that for manufacture of H₃PO₄ by extraction method.

(s) The equipment used for manufacture of triple superphosphate is similar to that used in making simple superphosphate, that is, various types of mixers for reaction of phosphoric acid with the phosphate raw material and continuous action dens.

(t) Sulphuric acid decomposition of phosphates produces a simple fertilizer as the end product. Nitric acid decomposition of phosphates gives an extract containing calcium, nitrogen and phosphorus, which can be converted into concentrated and complex fertilizers. For example, if potassium salts are added, a nitrogen-potash-phosphatic fertilizer is formed.

AMMONIUM PHOSPHATE ✓ (DAP)

(a) Monoammonium phosphate - Monoammonium phosphate is prepared by the action of sulphuric acid on a mixture of calcium phosphate and ammonium sulphate. As a result, monoammonium phosphate is formed, along with a slurry of CaSO₄. The phosphate is separated from the slurry and crystallised to get fine crystals of monoammonium phosphate containing about 12% nitrogen and 50% P₂O₅.



Monoammonium phosphate can also be prepared by treating anhydrous ammonia with phosphoric acid with a P₂O₅ content of 40-42%, at a controlled pH of 5.6 in a tank. 90% neutralisation takes place through the exothermic reaction.



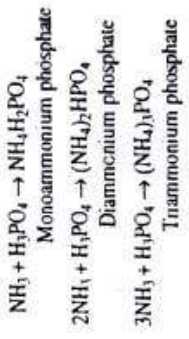
The slurry from the neutraliser is spread over a revolving drum fitted with water absorption device. The cakes of monoammonium phosphate thus formed are dried, disintegrated, cooled, screened and packed. Ammonium phosphate is best suited for all crops and soils. It is readily soluble in water and so becomes available to crops readily. It is slightly acidic in nature. The acidity developed by application of 100 lbs of ammonium phosphate requires 86 lbs of CaCO₃ to neutralise the acidity. Ammonium phosphate is well suited for use in calcareous and alkaline soils.

(b) Diammonium phosphate - It is prepared by a continuous process in which anhydrous ammonia gas and almost pure phosphoric acid are passed into a saturated mother liquor containing monoammonium phosphate. The temperature is kept at about 60-70°C and pH about 6.0. The heat of reaction vapourises water from the liquor and crystals of pure diammonium phosphate are formed. These are centrifuged, washed and dried.

Diammonium phosphate can also be prepared by taking the slurry from the neutralisation tank for the preparation of monoammonium phosphate into a second water cooled neutraliser. Here it is allowed to react with anhydrous NH₃. The unreacted NH₃ is taken out for neutralisation of a second lot of monoammonium phosphate. Rest of the process is similar to the preparation of monoammonium phosphate.



This fertilizer is better in nitrogen but poor in phosphorus. Similarly, triammonium phosphate can also be prepared



OTHER PHOSPHATES

(1) Calcium metaphosphate - Phosphorus is burnt to form P₂O₅ and then reacted with phosphate rock to give a glassy product, calcium metaphosphate containing about 65% P₂O₅.

(2) Thermal phosphates - Thermal phosphates, such as sintered phosphates are prepared by heating rock with soda ash and lime. They have also been prepared by fusing rock with magnesium silicate. The P₂O₅ content varies from 19%-24%.

(3) Thomas-Gilchrist basic slag - During the manufacture of steel, the Bessemer converters are lined with a basic material like dolomite and receive a charge of lime before the pig iron is added to it. This process is used to remove phosphorus from iron. The slag, therefore, contains phosphorus in plenty. The slag is cooled and crushed to powder and is made use of as a fertilizer. It contains about 18-20% P₂O₅.

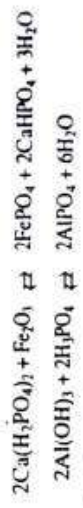
Depending on the phosphorus content of iron ore, the basic slag may contain 6 to 20% phosphoric acid. Basic slag produced from Indian steel mills is poor in phosphoric acid (3-8%). So it is not used largely as fertilizer. Basic slag is alkaline in nature and so it is especially suitable for acidic soils. It should be pulverized before application for its effective use.

(4) Bonemeal - Bonemeal is phosphatic manure as well as fertilizer. It is cheap source of phosphoric acid, but it is slowly available to crop. It is obtained as raw bonemeal (untreated bonemeal) or steamed bonemeal (treated bonemeal). Raw bonemeal is the bones collected from city slaughter houses and from countryside. These are dried and crushed without treatment and used as manures. The raw bonemeal contains 2-4% organic nitrogen and 20-25% phosphoric acid. Nitrogen in it is present in the organic form which becomes slowly available to crops on decomposition in the soil. The bones may be steamed under pressure in order to remove fats, greases, nitrogen and glue making substances. As a result, steamed bonemeal is formed and in it availability of phosphoric acid increases. Steamed bones are more brittle and can be readily ground. Bonemeals having particles not larger than 3/32 inch in size have been regarded suitable for use as fertilizer. Steamed bonemeal contains 1-2% nitrogen and 25-30% phosphoric acid. Bonemeal is however slowly available in the soil.

Bonemeal is well suited for acidic soils and for long duration crops like sugarcane and fruit crops. Excessive use of bonemeal produces no harmful effects on the crop growth.

PHOSPHATE FIXATION

The availability of phosphorus mainly depends on soil pH. In acid soil, the dissolved monocalcium phosphate combines with iron and aluminium, which are more soluble in acid soil and form iron and aluminium phosphate.



In alkaline soil, the phosphoric acid or super phosphate is converted slowly into di-calcium phosphate and tricalcium phosphate.

FERTILIZERS

when large amounts of potash are to be applied to tobacco, the sulphate form (K_2SO_4) is generally preferred. It can be applied at the time of sowing or before sowing. In recent years, application of this fertilizer as a top dressing has been regarded good as nitrogenous fertilizer.

Potassium sulphate (K_2SO_4) is also a potassium fertilizer and marketed as sulphate of potash. Pure potassium sulphate contains 54% of potash (K_2O), but the commercial fertilizer contains 48-52% of potash (K_2O). It is readily soluble in water and becomes available to the crops almost immediately.

Potassium sulphate is prepared by any of the following methods.

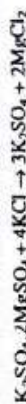
(1) By the action of sulphuric acid on potassium chloride.



(2) By the reaction of potassium chloride and sulphur.

(3) From burkette $Na_2CO_3 \cdot 2Na_2SO_4$ by reaction with KCl.

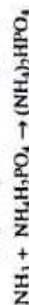
(4) From langbenite, $K_2SO_4 \cdot 2MgSO_4$, by ion exchange to remove magnesia. It is manufactured by dissolving langbenite in water and adding concentrated solution of KCl. The solubility of K_2SO_4 is more than that of $MgCl_2$. The K_2SO_4 is separated by fractional crystallisation.



The product contains about 54% K_2O . Potassium sulphate can be used for all crops and for all types of soils. But it is better than Muriate of potash for crops like potato, tobacco and fruit trees. It can be applied at any time upto sowing. When applied to the soil, the fertilizer gives K^+ ions and SO_4^{2-} ions. K^+ ions are absorbed in the soil as well as by the growing plants. Hence the fertilizer, though soluble in water, is not easily lost by leaching. The modern trend is towards the production of mixed fertilizers containing nitrogen, phosphorus and potash. Such a fertilizer is called NPK fertilizer.

NPK FERTILIZERS

Example of NPK fertilizers are ammonium sulphate, phosphate and potash (KCl) combination. This mixed NPK fertilizer can be prepared by taking anhydrous liquid ammonia, phosphoric acid (25-30% P_2O_5), sulphuric acid (93-98%) and potash (KCl) as raw materials. The manufacture involves three neutralisation tanks. The acid mixture and anhydrous ammonia are allowed to react, as a result of which 80% neutralisation takes place. The exothermic reaction boils the liquid producing a slurry that is taken into second neutraliser for further ammoniation and finally to the third neutraliser for final treatment furnishing a diammonium salt. The slurry from the third neutraliser is mixed with calculated amount of potash (KCl) to get NPK fertilizer of proper grade. It is passed through a granular, dried in hot air at about 140-150°C, screened and packed.



MIXED FERTILIZERS

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

The homemade fertilizer mixture is prepared by cultivators manually. It is desirable to mix the fertilizer ingredients on the day of application or a day before, in order to prevent caking. If the fertilizer mixture is to be used immediately after preparation, there is no need of adding filler. Otherwise, filler may be added to check the mixture from caking into hard mass.

Factory made fertilizer mixture is prepared in fertilizer mixing plants, where machine mixing is generally used. The fertilizer mixing plant has started to manufacture the fertilizer mixture in granulated form.

Dicalcium phosphate is slowly dissolved in soil water containing carbonic acid and becomes available to growing plant. The tricalcium phosphate, being insoluble, remains in the soil as fixed phosphate.



POTASSIUM FERTILIZERS

Potassium containing fertilizers are KNO_3 , KCl and K_2SO_4 . Potassium is most conveniently expressed as K_2O . KNO_3 or Chile saltpetre has already been discussed. KCl is obtained by the evaporation of dead sea brine by solar energy. During the process of evaporation, the concentration increases from 1.2 in the brine to 23% in liquor which crystallizes in the pan. After refining, about 97% pure KCl can be obtained. KCl contains about 63.17% K_2O and K content of about 52.44%.

Potassium chloride is most common potassium fertilizer having potash (K_2O) in chloride form. It is sold in the market as **Muriate of potash**. It is cheaper than all other potassium fertilizers and so it is extensively used by the farmers and cultivators throughout the world. It can also be prepared by ores such as carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$, and kainite, $KCl \cdot MgSO_4 \cdot 3H_2O$ by crystallisation and floatation method.

Potassium chloride is commonly marketed as commercial fertilizer in granules or powder form. It contains 50-60% potash, the whole of which is readily available to the plants. It is readily soluble in water and hence it is rated as readily available. It undergoes ionisation into K^+ ions and Cl^- ions in the soil and like NH_4^+ ions, K^+ ions are absorbed by the soil. As such it is not lost from the soil although it is highly soluble in water. It has little or no effect on soil pH.

Table (4) Major fertilizer compounds

Compound	Formula	% Nutrient content	
		Element	Oxide
Nitrogen	NH_3	82.3	
Ammonia	NH_4NO_3	34.8	
Ammonium Nitrate	$(NH_4)_2SO_4$	21.2	
Ammonium Sulphate	NH_4CONH_2	46.7	
Urea	$NaNO_3$	16.5	
Sodium Nitrate	$Ca(NO_3)_2$	17.1	
Calcium Nitrate	NH_4Cl	26.2	
Ammonium Chloride	$CaH_4(PO_3)_2 \cdot H_2O$	24.6	56.2
Phosphate	$CaHPO_4$	22.8	52.2
Monocalcium Phosphate	KCl	52.3	63.2
Dicalcium Phosphate	K_2SO_4	44.7	54.0
Potash	$(NH_4)_2HPO_4$	12.2 (N), 26.9 (P)	61.8
Potassium Chloride	$(NH_4)_2HPO_4$	21.2 (N), 23.5 (P)	53.8
Potassium Sulphate			
Multi Nutrients			

Potassium chloride has been applied as fertilizer to a wide range of soils and crops. But in case of potato and tobacco large doses of KCl have been considered to lower the quality of the product. Hence

Some common granulated fertilizer mixtures available in the market now a days are IFFCO - 10 - 26 : 26, Gramon 14-35-14 and suphala 15-15-15

The mixed fertilizer is available in the market in the particular grade. The fertilizer grade refers to the minimum guarantee of plant nutrients in terms of total nitrogen, available P_2O_5 and water soluble potassium. As seen above, home made fertilizer mixtures are prepared just before their application, because they are not suitable for storing.

The mixed fertilizers are of two types:

- Open formula fertilizer mixture, and
- Closed formula fertilizer mixture.

The ingredients mixed in open formula mixtures in terms of kind and quality are disclosed by the manufacturer. This is helpful to the cultivators for knowing the ingredients of fertilizers for the application of the mixture in particular crop in suitable amounts.

The ingredients used in closed formula mixture are not disclosed. It is called as a trade secret of the industry. So it is not possible for farmers or cultivators to know the quantity and types of ingredients used in this fertilizer mixture. Hence it is difficult for the farmers to choose the correct mixture for use in production of crops.

The major ingredients of fertilizer mixture, namely nitrogen, phosphorus and potassium are supplied by nitrogenous fertilizer (e.g., urea, ammonium sulphate, ammonium sulphate nitrate, ammonium nitrate etc), phosphate fertilizer (e.g. superphosphate single or triple) and potash fertilizer (e.g. potassium chloride, potassium sulphate etc). Complex fertilizers have also been used in the preparation of fertilizer mixture.

Low grade organic materials are added at the rate of about 75 kg per ton of fertilizer mixture in order to reduce caking and also keeping them in good drilling condition. These organic materials are known as conditioners.

The basic substances such as dolomite, limestone etc are added to the fertilizer mixture in order to counteract the acidity of the nitrogenous fertilizers which are acidic in nature. For example, ammonium sulphate and urea are acidic in nature. These basic substances are known as neutralisers of residual acidity. Filler is the make weight material added to a fertilizer mixture of mixed fertilizer. It is generally added to make up the difference between the weight of the added ingredients required to supply the nutrient per kg of given analysis. Soil, sand, coal ash, wood ash etc. are the common fillers used in fertilizer mixture.

There are various types of fertilizer mixtures:

(a) **Grade - 1 fertilizer mixture (6-12-0)** - It contains 6% of nitrogen and 12% of phosphoric acid. 30 kg of ammonium sulphate and 75 kg of superphosphate are required for preparing 100 kg of grade-1 fertilizer mixture. This fertilizer mixture has been found to be suitable for grains crops and used in silty loam soils.

(b) **Grade - 2 fertilizer mixture (10-6-6)** - This fertilizer mixture contains 10% of nitrogen, 6% of phosphoric acid and 6% of potassium. 50 kg of ammonium sulphate, 38 kg of single superphosphate and 12 kg of Muriate of potash are required for preparing 100 kg of grade - 2 fertilizer. This fertilizer is suitable for potato, cotton, jute, banana, papaya and vegetable crops.

(c) **Grade - 3 fertilizer mixture (6.6-6.5-6)** - This fertilizer mixture contains 6.6% of nitrogen, 6.5% of phosphoric acid and 6% of potassium. 33 kg of ammonium sulphate, 41 kg of single superphosphate and 12 kg of muriate of potash are required for preparing 100 kg of this fertilizer. This fertilizer mixture is suitable for application in sugarcane and grain crops.

(d) **Grade - 4 fertilizer mixture (8-8-8)** - It contains 8% of nitrogen, 8% of phosphoric acid and 8% of potassium. 100 kg of this mixture can be prepared by mixing 30 kg of ammonium sulphate, 4.5 kg of urea, 50 kg of single superphosphate and 16 kg of muriate of potash. It is generally used for potato, cereals and oilseed crops. It should be noted that one fertilizer can not be mixed with any other fertilizers. This is because of the fact that uneven mixing of incompatible fertilizer leads to.

(a) Loss of some of the fertilizer nutrients in the form of gas. (b) Conversion of soluble nutrients into insoluble form, and (c) Caking.

Following points should be taken into consideration while preparing a fertilizer mixture.

(a) Ammonium sulphate, ammonium chloride and other ammonical fertilizers and nitrogenous organic manure should not be mixed with lime. (b) Urea should not be mixed with superphosphate. (c) Calcium cyanamide, basic slag, quick lime, slaked lime etc. should not be mixed with fertilizers containing nitrogen in ammonical form. (d) Superphosphate should not be mixed with lime or limestone or wood ashes. (e) $NaNO_3$ or KNO_3 should not be mixed with superphosphate. (f) Ammonium sulphate nitrate should not be mixed with lime. (g) Nitrochalk should not be mixed with lime or superphosphate.

The most common mixture which can easily be stored can be prepared from superphosphate, sulphate of ammonia and sulphate of potash. Bone meal, sulphate of potash and muriate of potash can be mixed with fertilizers.

The most important advantages of fertilizer mixtures are:

(a) These mixtures usually meet nutrient deficiencies in a more balanced way. (b) Less labour is required to apply mixture than straight fertilizer used separately. This is very important factor where farm labour is scarce and expensive. (c) Mixed fertilizer added to a crop gives higher yields and more profit to the farmer, and it can be applied without any hesitation. (d) When fertilizer mixture is used, there is no need of using any straight fertilizer separately to the soil. (e) Micronutrients which are applied in minor amounts to the soil, can uniformly be applied by mixing them with the fertilizer mixture. (f) Granular fertilizer mixtures are more easily applied than many straight fertilizers. (g) Fertilizer mixture containing suitable filler improves the physical conditions of the soil.

The most important disadvantages of fertilizer mixtures are:

(a) Fertilizer mixture of a particular grade is suitable only for particular crops. It can not be applied profusely to all types of crops. (b) Use of fertilizer mixture does not allow application of individual nutrients which may best suit the requirements of a crop at specific time. (c) Because labour is required to prepare fertilizer mixture, the cost of the latter is usually higher than the straight fertilizer.

COMPOUND OR COMPLEX FERTILIZERS

The commercial fertilizer containing atleast two or more of primary plant nutrients (that is, N, P_2O_5 and K_2O) is called compound or complex fertilizer. Such type of fertilizers are of two types.

(a) **Incomplete complex fertilizers** - Those fertilizers which contain only two of the three primary plant nutrients are called incomplete complex fertilizers.

(b) **Complete complex fertilizers** - Those fertilizers which contain all the three primary plant nutrients (N, P_2O_5 and K_2O) are called complex fertilizers.

The commercial complex fertilizers being manufactured in India are classified into the following two groups.

(a) **Nitrophosphate.** (b) **Ammonium phosphate.**

(a) **Nitrophosphate** - This fertilizer can be prepared by combining ammonium phosphate monoammonium phosphate and diammonium phosphate and potassium salt, if need be. This fertilizer is known as **suphala**. Examples are : Suphala - 20:20:0 and suphala - 15:15:15. Nitrophosphate contains nitrogen and phosphoric acid in different proportions, depending on the type of process of manufacture (in the absence of potash). Nitrophosphate is granulated fertilizer. It maintains excellent physical condition during storage and handling.

Suphala - 20:20:0 contains nitrogen as ammonium nitrate and ammonium phosphate. It contains 54% nitrogen as ammonium nitrogen and 46% nitrogen as nitrate nitrogen and citrate soluble phosphate.

Suphala - 15:15:15 contains 15% nitrogen, 15% phosphoric acid and 15% potash. Out of 15% nitrogen, 8.2% nitrogen is present as ammonium nitrogen and 6.8 as nitrate nitrogen. Out of 15% phosphoric acid,