Chapter - 9

Phosphatic fertilizers –Manufacturing process and properties of SSP, TSP and Basic slag

Phosphatic Fertilizers

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

Origin and reserves:

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

Magma: Weathering and decomposition of primary minerals

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

Large deposits of rock phosphates occurs in

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

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

Production of phosphate fertilizers

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

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

Classification of phosphatic fertilizers

Phosphatic fertilizers were classified by two ways. They are-

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

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

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

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

1. Water soluble phosphorus fertilizers
2. Water insoluble but citrate soluble phosphorus fertilizers
3. Water and citrate insoluble phosphorus fertilizers

1. Water soluble phosphorus fertilizers:

Phosphorus in these fertilizers is present in water soluble form. P is present in the form of monocalcium phosphate Ca $(H_2PO_4)_2$. This form of P is generally regarded as the most readily available to plants.

1. Single super phosphate (16-18% P_2O_5)
2. Double super phosphate (32 % P_2O_5)
3. Triple super phosphate (46-48% P_2O_5)
4. Higher content or concentrated super phosphate
5. Ammonium phosphate (20% N and 20% P_2O_5)

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

2. Water insoluble but citrate soluble phosphorus fertilizers:

Phosphorus present in these fertilizers is soluble in 2% citric acid or neutral normal ammonium acetate solution. P is present as dicalcium phosphate $Ca_2H_2(PO_4)_2$ / $CaHPO_4$.

1. Basic slag (14 to 18% P_2O_5)
2. Dicalcium phosphate (34-39 % P_2O_5)

3. Raw and steamed bone meal (part of the P_2O_5 soluble in citric acid) – suitable for acid soils and lateritic soils.

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

3. Water and citrate insoluble phosphorus fertilizers:

Phosphorus present in the fertilizer is not soluble both in water and citrate solution containing insoluble phosphoric acid or tri calcium Phosphate ($Ca_3(PO_4)_2$.

1. Rock phosphate (20 to 40 % P_2O_5)
2. Raw bone meal (20 to 25% P_2O_5)
3. Steamed bone meal (22% P_2O_5)

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

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

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

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

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

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

Manufacturing processes:

1. Ground rock phosphate
2. Single super phosphate
3. Triple super phosphate
4. Basic slag.

I. Ground Rock Phosphate:

The World phosphate industry is based essentially on deposits of rock phosphate – a fluoride bearing complex of calcium phosphates. The content of rock is usually expressed in terms of its tricalcium phosphate [$Ca_3(PO_4)_2$] equivalent.

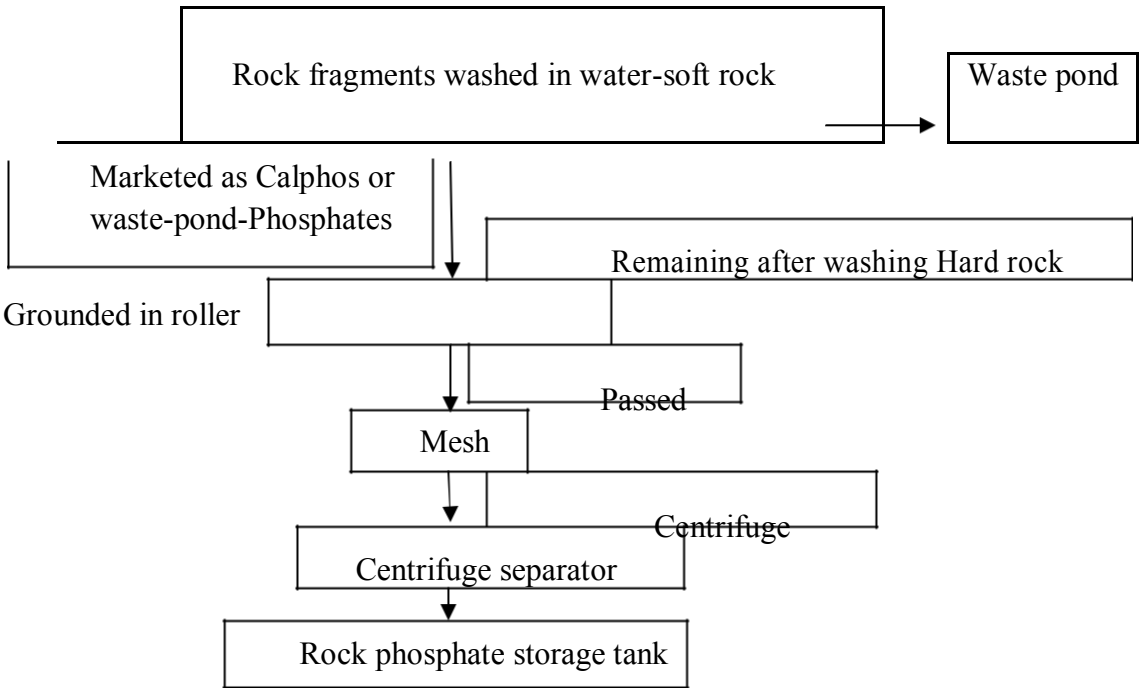
Four kinds of rock phosphate are recognized viz., 1) soft rock phosphate. 2) Hard rock phosphate (Hard earth). 3) Land pebble phosphate. 4) River pebble phosphate.

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

Physical and chemical properties:

1. The fine powder of phosphate rock is known as float to mean un acidulated ground rock phosphate
2. The mineral in phosphate rock is apatite which has the general formula **[Ca_{10} (PO_4) $_6$ (F, Cl ($OH)_2$ ($CO_3)_2$]**
3. Contain about 10-16 % P and varying amounts of lime (7-10% Ca CO_3) and, silica fluoride [3-4% F] iron and aluminum as impurities.
4. It has no practically water soluble phosphates (10^{-7} molar P), but less than 30% of P is soluble in 2.0% citric acid solution.
5. Waste pond phosphates contain 7-9 % P out of which 1 to 2 % phosphate rock is soluble in 1 N neutral ammonium acetate.

FLOW DIAGRAM



Action of rock phosphate on acid soils:

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

$$[Ca_3(PO_4)_2]_3 + 6\,H_2CO_3 \rightarrow 3\,Ca(H_2PO_4)_2 + 7CaCO_3$$

[Rock Phosphate [Carbonic acid] → [Mono calcium phosphate]

Containing no fluoride] [Available]

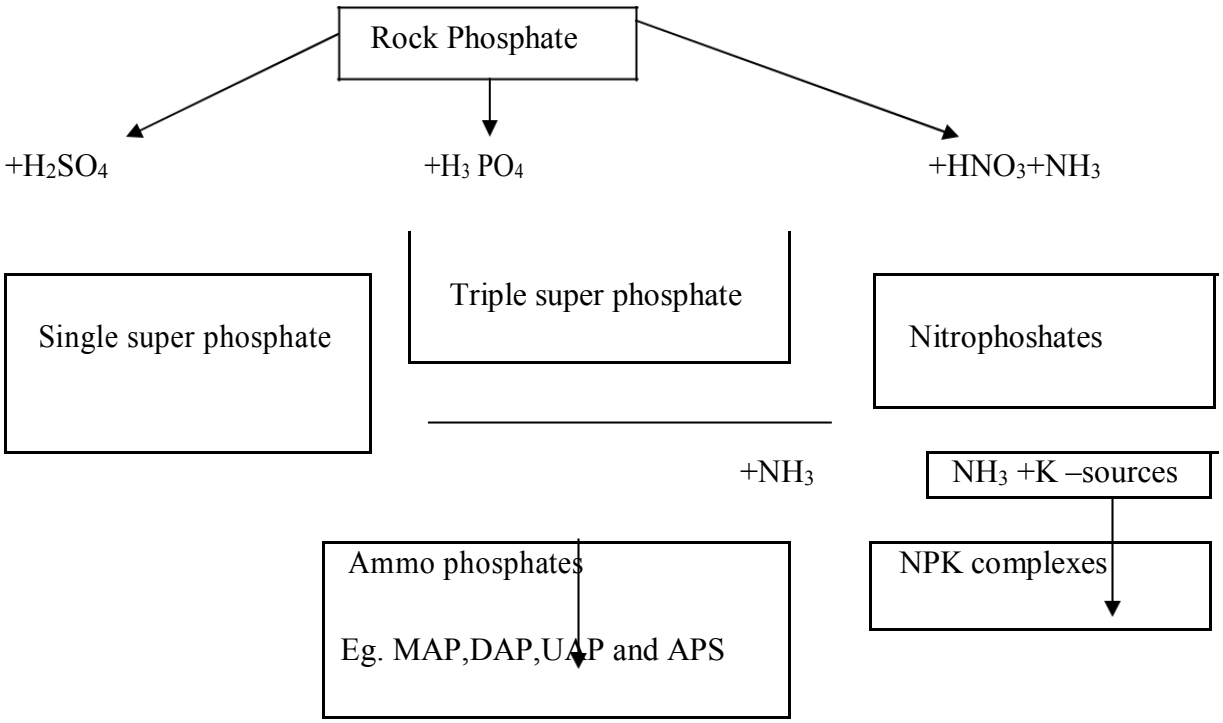
$$Ca_3(PO_4)_3\,CaCO_3 + 14\,HNO_3 \rightarrow 3\,Ca(H_2PO_4)_2 + 7Ca(NO_3)_2 + H_2CO_3$$

In general ground rock phosphate should be applied in large quantities of 500 to1000 kg per hectare once in three years, but should not be applied in small quantities every year. It should be thoroughly mixed in the top soil with country plough or disc harrow.

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

Direct uses of rock phosphate [R.P.]

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



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

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

1. **Soil reaction**: Not applied in neutral and alkaline soils
2. **Dose and time of application:** It should be applied in large quantities once in 5-6 years, it should be finely ground
3. **Plant Species:** R.P. is useful for calcium loving plants like legumes .It should be applied for long duration commercial crops.
4. **Soil organic matter:** Can be applied in soils containing higher amounts of organic matter because acids are produced during decomposition, then the tricalcium phosphate (TCP) is converted to mono calcium phosphate (MCP).
5. **Organic manures:** R.P. can be applied along with undecomposed organic materials like green manures because during decomposition acids are secreted.

6. **Phosphocompost:** Applying rock phosphates along with phosphorus solubulizing bacteria with or without sulphur and sulphur oxidizing bacteria. During the decomposition process of plant and animal sources (residues) is called phosphor compost. Acids produced during composting convert TCP to MCP.
7. **Phosphate solubulizing bacteria:** When RP is applied to neutral soils, it is applied with phosphorus solubulizing bacteria.
8. **Fertilizers:** It can be applied along with acid producing fertilizers. It is also applied along with the SSP, because MCP produces H_3PO_4 which in turn converts TCP in R.P. to MCP.
9. **Biosuper:** Super phosphate produced by biological organisms. Application of R.P. along with sulphur or without sulphur oxidizing bacteria.

$$S+2O_2 \longrightarrow SO_4^{-2}$$

$$SO_4^{-2}+H_2O \longrightarrow H_2SO_4$$

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

II. SINGLE SUPER PHOSPHATE [16% P]:

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

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

Manufacture process of single super phosphate

Raw materials:

1) Phosphate rock.
2) Sulphuric acid.

Single super phosphate is (SSP) is manufactured by mixing gravimetrically equal parts of sulphuric acid (75%) and rock phosphate of 0.14 mm [100 mesh seive] There are two methods of preparation of SSP viz**.,**

1. Den process

2. Continuous rock phosphate acidulation process

1. Den process:

Weighed quantities of Rock phosphate (0.14mm) and sulphuric acid (75%) are mixed in a mixer**,** capable of handling40-50 tonnes per hour, are allowed to react for about a minute and the resultant slurry is dumped in to a compartment known as DEN [100-300 tonnes capacity]. In a few hours the reaction goes to completion. Water, carbon dioxide, fluorine, volatilize away resulting in the reduction in the bulk of the material by retaining the material in the Den becomes a hard block and removal is accomplished by means of mechanical excavators equipped with revolving knifes which cut into the block and the disintegrated SSP is stored for 2 to 6 weeks to cure and attain the desired physical condition.

2. Continuous rock acidulation process:

This is a popular and latest process in which acidulation of rock phosphate with sulphuric acid is done continuously in mixer provided with indigenous metering (H_2SO_4) and weighing (RP) devices. The mixer is agitated for 2-3 minutes and is then discharged into an endless conveyer belt on which it solidifies. The belt conveyer moves the blocks of hardened super phosphate towards a revolving cutter which disintegrate the material. It is then transferred to a storage bin and stored for 2-6 weeks to cure and attain the desired physical condition.

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

$$Ca_{10}[PO_4]_6F_2 + 7H_2SO_4 + 3H\,O \longrightarrow 3\,CaH_4(PO_4)_2\,H_2O + 7CaSO_4 + 2HF$$

[Super phosphate i.e.,Monocalcium phosphate]

Three points are suggestive of the above equation viz.,

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

Physical properties of SSP:

1. SSP is in granular form has bilk density 961.10 kg m^{-3} and is easy to handle.
2. SSP is also available in powder form, it is not free flowing and being slightly hygroscopic has a tendency to cake. Hydration of monocalcium phosphate may be the cause for hardening SSP. It has grey colour and an acidic odour.

3. Free acid in the SSP, will usually rot the jute fibre bags and hence the fertilizer has to be stored in polythene lined gunny bags or polyethylene bags.

Chemical properties of SSP:

1. SSP has 2/5 Mono calcium phosphate and 3/5 Gypsum by weight.
2. SSP manufactured in India consists of two grades viz., Garde I: 16% P_2O_5 % or (7%P) by weight of water soluble P_2O_5 and Grade II: 14% P_2O_5 or (6%P) by weight of water soluble P_2O_5 .
3. SSP also contains 21.0% calcium, 12% sulphur and traces of micronutrients .Obviously it contains more sulphur (12%) than phosphorus (6 to 7%).
4. SSP has a pH of about 3.0.

3. TRIPLE SUPER PHOSPHATE (46 % P_2 O_5):

Its high plant nutrient content and its capacity to react with NH_3 in the production of multinutrient fertilizers. The 'prefix' 'TRIPLE' was first used when SSP contained 16 % P_2O_5 and TSP contained three times as much as 48% P_2O_5 .

Manufacturing process:

Raw materials:

1. Rock phosphate.
2. Phosphoric acid.

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

$$Ca_{10}[PO_4]_6F_2 + 14H_3PO_4 + 10H_2O \rightarrow 10CaH_4(PO_4)_2H_2O + 2HF$$

The method of manufacture is called CONE MIXER PROCESS**.**

The phosphate rock (100 mesh) is mixed with phosphoric acid (75%) in a cone mixer in the acid –rock ratio (expressed as eh mole ratio of total P_2O_5 to CaO in the acidulate) of 0.91 to 0.95.The resultant slurry is then fed to a belt conveyer [as already described in case of SSP. An extended curing period of about 30 days is required for the reaction to complete, for attaining described physical condition].

Physical properties of TSP:

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

Chemical properties of TSP:

1. The main phosphate compound present in TSP is monocalcium sulphate.
2. It contains 46% total P_2O_5 by weight and 36.8% minimum by weight of water soluble P_2O_5.
3. It has 3% free phosphoric acid.
4. TSP also contains 12 to 16% of calcium and 1.0 to 2.0 % of sulphur**.**

4. BASIC SLAG [$(CaO)_5 P_2O_5 SiO_2$]:

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

Manufacturing process:

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

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

Physical properties of slag:

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

Chemical properties of phosphatic fertilizers:

1. The basic slag is a double silicate of phosphate and lime
2. The slag obtained from Indian steel industry contain only 3-8 % P_2O_5. Being low in P_2O_5 having highest viscosity, it is not popularly used in Indian agriculture.
3. Being low in P_2O_5 it is currently enriched with rock phosphate and marketed as pelophos which on analysis contains 11.0 % citrate soluble and 5.0% water soluble P_2O_5
4. It is alkaline in reaction and has neutralizing effect equal to 70% $CaCO_3$ equivalent.

Mode of action of P fertilizers in soils or reactions of fertilizers in soils

1. Water soluble P-fertilizers lead to better P-absorption in the neutral soils, whereas water insoluble P fertilizers are often superior in acid soils.
2. Fertilizers like SSP improves the soil structure because of its gypsum component. It also have a slight soil acidifying action.