Lecture 8: Classification, Composition, Synthesis and Properties of Straight Phosphatic Fertilizers

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

Classification of phosphatic fertilizers:

1. based on relative solubility of phosphate :

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

a. Water soluble phosphorus fertilizers

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. Examples:

Single super phosphate (16-18% P_2O_5)

Double super phosphate (32 % P_2O_5)

Triple super phosphate (46-48% P_2O_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.

b. Water insoluble but citrate soluble phosphorus fertilizers

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 soil.

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.

c. Water and citrate insoluble phosphorus fertilizers

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

Rock phosphate (20 to 40 % P_2O_5)

Raw bone meal (20 to 25% P_2O_5)

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.

2. 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

Manufacturing process and properties of phosphatic fertilizers

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 industryas 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 ($OH)_2$ ($CO_3)_2$]**

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.

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.

Waste pond phosphates contain 7-9 % P out of which 1 to 2 % phosphate rock is soluble in 1 N neutral ammonium acetate.

Ground rock phosphate should be applied in large quantities of 500 to 1000 kg per hectare once in three years, but should not be applied in small quantities every year. It should be thoroughly mixed in the top soil with country Plough or disc harrow.Strongly acidic soils are most suitable for direct application of rock phosphates .Such areas are found in whole Kerala , Shimoga ,Mysore , parts of Assam , Bihar ,Mussorie rock phosphate and Purulia rock phosphate have been recognized by ICAR for direct application .

Single super phosphate

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

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

i. Den process

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

ii. Continuous rock acidulation process:

This is a popular and latest process in which acidulation of rock phosphate with sulphuric acid is done continuously in mixer provided with indigenous metering (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

$Ca_{10}[PO_4]_6 F_2 + 7 H_2SO_4 + 3H O \longrightarrow 3 CaH_4(PO_4)_2 H_2O + 7CaSO_4 + 2HF$ [Super phosphate i.e.,Monocalcium phosphate]

Three points are suggestive of the above equation viz.,

Phosphate originally present as apatite is converted into water soluble Monocalcium phosphate

The by-product reaction is gypsum which is initially mixed with the monocalcium phosphate

The reaction releases toxic hydro fluoric acid gas

Physical properties of SSP:

- SSP is in granular form has bilk density 961.10 kg m^{-3} and is easy to handle
- 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.
- Free acid in the SSP, will usually rot the jute fiber bags and hence the fertilizer has to be stored in polythene lined gunny bags or polyethylene bags.

Chemical properties of SSP:

- SSP has 2/5 Mono calcium phosphate and 3/5 Gypsum by weight
- 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 .

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

TRIPLE SUPER PHOSPHATE (TSP-contains 46 % P_2O_5)

Factors for its popularity**:**

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:

- 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.
- It has bulk density 800-881 kg m^{-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

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

BASIC SLAG [$(CaO)_5 P_2O_5 SiO_2$]

Basic slag is a byproduct 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:

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

Chemical properties of phosphatic fertilizers:

- The basic slag is a double silicate of phosphate and lime
- 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.
- 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
- It is alkaline in reaction and has neutralizing effect equal to 70% $CaCO_3$ equivalent.