11. Single and triple super phosphates – thermophosphates – method of manufacturing Super phosphate

The term super phosphate is generally applied to phosphates which are present in a readily available form to plants. After the resolution passed in the meeting of the first world International congress on chemical fertilizers, 1938, the term super phosphate is restricted to refer those phosphates having less than 25% of P_2O_5 and the term concentrated SSP for all those phosphates containing more than 25% P_2O_5 .

The super phosphates are generally manufactured from phosphate rock, but bones and phosphatic guanoes are also extensively used for the manufacture. The super phosphates prepared from organic sources (bones & guano) are said to be having good physical condition, but with a lower P_2O_5 content. In recent times only the phosphate rock is being utilized for the manufacture of various super phosphate.

Phosphate rock containing less than 50% of tricalcium phosphate are not suitable for manufacture of phosphatic fertilizers and are not used in the industry. Phosphate rocks containing > 4% total R_2O_3 are considered unsuitable and the phosphate rock should not contain > 2% iron oxide.

The following method are commonly followed to convert the insoluble phosphate found in RP into more soluble forms.

- 1. Acid treatment method.
- 2. Phosphorus volatilization method
- 3. Decomposition with an alkali or silicate, and
- 4. Method followed in steel industry.

a. Ordinary super phosphate

This is also called as Den super phosphate. Often the term 'super' is used to refer only to this product. This is the most extensively used fertilizers among the farmers.

Manufacture

The principle involved in the process is the treatment of RP with acids, mainly H_2SO_4 to convert the insoluble and unavailable tricalcium phosphate to available dicalcium and monocalcium phosphates. Concentrated HNO₃, HCl, H_3PO_4 and H_2SO_4 can be used, but sulphuric acid is found to be more suitable because of the fact that when it reacts with the RP, CaSO₄ is formed, which is a dehydrating agent and improves the physical condition of the final product to a better condition.

The method consisted of mixing equal quantities of RP with H_2SO_4 in open tanks and then powdering the resultant product after the reactions are over. The calculated

quantity of H_2SO_4 and ground phosphate rock (material passing through a four-mesh sieve only has to be used) are introduced and mixed very thoroughly and then dropped in a pit or den. The process is also called Den method. Sufficient time of 24 to 36 hrs is allowed for the completion of the reaction. Temperature rises to 100°C and there is a loss of volume by 10% due to evaporation of water, CO_2 and F. The CaSO₄ act as a dehydrating agent and artificial drying is also done wherever necessary. Then the product is ground to a very fine powder and stored for sufficient time for the curing of the material.

1. $(Ca_{3}(PO_{4})_{2})_{2}$ CaF_{2} + 7 H_{2} SO₄ ($H_{3}PO_{4})_{2}$ + 7 $CaSO_{4}$ + 2HF (mcp) 2. $(Ca_{3}(PO_{4})_{2})_{2}$ Ca X + 7 H_{2} SO₄ 3 Ga ($H_{3}PO_{4})_{2}$ + 7 $CaSO_{4}$ + H_{2} X

Precautions

- 1. An excess quantity of H_2SO_4 should not be used.
- 2. The quality of the RP must be pre decided.

Properties

The commercial super phosphate is grey in colour and it is only partly soluble in water. It has an acid odour and acid reactions due to the presence of some free acids and the acid salt monocalcium phosphate. It addition to the presence of phosphate, it contains gypsum, silica and aluminum sulphate, CaF etc. It contains about 20% Ca and 12% Sulphur which are the secondary nutrient elements required for the plants.

b. Concentrated super phosphate

The main principle involved in the preparation is to first manufacture, phosphoric acid ($H_3 PO_4$) by treating the RP with excess quantity of HCl or HNO₃ or H_2SO_4 and secondly the H_3PO_4 so obtained is used for the treatment of another quantity of phosphate rock to get this fertilizer. Hence, there are two acid treatments involved and so the product in called double super phosphate (double insulation). Following are the main steps in the manufacturer of concentrated super phosphate.

- 1. Preparation of H_3PO_4 using RP and one of the mineral acids.
- 2. Preparation of the concentrated super phosphate by treating fresh quantity of RP with the prepared H₃PO₄.

1. $(Ca_3(PO_4)_2)_3$ Ca X + 10H₂ SO 4^{-1} 6 H₃PO₄ + 10 CaSO₄ + H₂ X 2. $(Ca_3(PO_4)_2)_3$ Ca X + 20 HNO₃ 4 H₃PO₄ + 10 Ca(NO₃)₂ + H₂ X 3. $(Ca_3(PO_4)_2)_3$ Ca X + 20 HCl --- 6 H₃PO₄ + 10 CaCl₂ + H₂ X

PR is ground and allowed to pass through a constant weight feeder to which a measured flow of H_3PO_4 under pressure enters. All the mixing is done in the funnel like mixer and the mixture is allowed to stand for sufficient time for the reaction to take place. The slurry is conveyed to a troughed belt conveyor where the product sets in a few seconds to plastic mass. To get a dried material, sufficient retention time is allowed and at the end of the belt- conveyor, a rotary disintegrator reduces the lumps to less than 2" size. The disintegrated super phosphate a stored for curing at least for a period of 15 weeks.

Properties

This fertilizer resembles in all respects the ordinary super phosphate. It is grey in color, a major portion being soluble in water. It contains 45 to 48% water soluble P_2O_5 . It contains lesser quantity of other ingredients.

Thermophosphates

These are manufactured by heating phosphate rock in varying temperatures.

The main drawbacks in thermal phosphates are

They are generally more expensive than acid derived phosphates. It contains no water soluble P. They do not have any value in the manufacture of NPK fertilizers

Polyphosphates

Differ slightly from the more common orthophosphate fertilizers. Nearly all of the liquid fertilizers containing P are of the polyphosphate type. Polyphosphates are composed of a series of orthophosphate molecules connected by the process of dehydration (removal of water). Commercial ammonium polyphosphates are usually a mixture of ortho- and polyphosphate. With prolonged storage, polyphosphates will hydrolyze to orthophosphates. Solutions of ammonium polyphosphate most commonly made are 10-34-0 and 11-37-0. The most common dry polyphosphate is 13-52-0.