SUPERPHOSPHATE

INTRODUCTION

Superphosphate, Ca(H₂PO₄)₂, also refereed as single superphosphate (SSP), is the first chemically manufactured commercial fertilizer. John B Lawes named as superphosphate. Single superphosphate is produced as a combination of rock phosphate and concentrated sulfuric acid. Approximately equal amounts of the two ingredients are thoroughly mixed, dried and cured. Chemically, SSP contains monocalcium phosphate and calcium sulfate. The hardened mass is either ground or granulated.

The monocalcium phosphate of single superphosphate dissolves in the soil moisture and the roots absorb phosphoric acid in that form. The rest of the solution of monocalciumphosphate precipitates in the soil pores and forms different phosphate compounds which are water-insoluble and do not leach out. A compound like dicalcium phosphate dissolves in carbonic acid in water and becomes available to plants, but the insoluble tri-calcium phosphate remains fixed in the soil. Where soil is markedly acidic i.e., rich in active iron and aluminum monocalcium phosphate gets converted into insoluble phosphate compounds

\[ 2\text{Ca(H}_2\text{PO}_4\text{)}_2 + \text{Fe}_2\text{O}_3 \rightarrow 2\text{FePO}_4 + 2\text{CaHPO}_4 + 3\text{H}_2\text{O} \]

Because iron and aluminum phosphates are insoluble, phosphorus does not available to the plant. That why SSP does not use in acidic soils unless it is limed.

If single superphosphate is applied just before sowing, plants get enough supply of phosphorus at their critical growing stages. Single superphosphate is not suitable for top dressing because of its slow movement.

Sometimes, single superphosphate is mixed with lime or dolomite in order to increase its effectiveness. The production of single superphosphate is on the rise in tropical countries, like India.

SSP compared to various sulfur-containing fertilizers like DAP and TSP, significantly increases the grain yield of many agronomical important crops like wheat, chickpea and groundnut. SSP is compatible to mix with \((\text{NH}_4)_3\text{PO}_4\), \((\text{NH}_4)_2\text{SO}_4\), \(\text{NH}_4\text{Cl}\), \(\text{KCl}\) and \(\text{K}_2\text{SO}_4\). Mixtures of SSP with materials containing free lime or CAN or
urea should not be stored for long as they cause reversion of water-soluble phosphate.

In order to get the maximum benefits, single superphosphate should be applied to soils deficient in phosphorus as well as sulfur. The time, place and the quantity of application are critical.

SSP is the principal phosphate fertilizer due to

- The production process is simple, requires little skill and small investment
- It sets a standard of comparison for other phosphate fertilizers
- It supplies two secondary nutrient elements, namely, sulfur and calcium

Despite these advantages, single superphosphate has a low phosphorus content (16 to 22 % P$_2$O$_5$), and 6 to 10% moisture content which sometimes make SSP production uneconomical.

**MANUFACTURE**

**Raw Materials**

Basis: 1000kg Superphosphate (den process)

- Calcium phosphate = 625kg
- Sulfuric acid = 320kg
- Water = 90kg
- Electricity = 0.2kWH
- Labour = 0.1man-hr

**Sources of raw material**

Phosphate rock can be obtained and purified as described in Module: 4, Lecture: 20.

Sulfuric acid can be obtained by contact process as described in Module: 4, Lecture: 18.

**Reactions**

\[
\begin{align*}
\text{Ca}_{3}(\text{PO}_4)_2 + 2\text{H}_2\text{SO}_4 + 4\text{H}_2\text{O} & \longrightarrow \text{CaH}_4(\text{PO}_4)_2 + 2(\text{CaSO}_4\cdot 2\text{H}_2\text{O}) \\
\text{CaF}_2 + \text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} & \longrightarrow \text{CaSO}_4\cdot 2\text{H}_2\text{O} + 2\text{HF} \\
4\text{HF} + \text{SiO}_2 & \longrightarrow \text{SiF}_4 + 2\text{H}_2\text{O} \\
3\text{SiF}_4 + 2\text{H}_2\text{O} & \longrightarrow \text{SiO}_2 + 2\text{H}_2\text{SiF}_6
\end{align*}
\]

**Overall reaction**

\[
\text{CaF}_2\cdot 3\text{Ca}_3(\text{PO}_4)_2 + 7\text{H}_2\text{SO}_4 + 3\text{H}_2\text{O} \longrightarrow 3\text{CaH}_4(\text{PO}_4)_2\cdot \text{H}_2\text{O} + 2\text{HF} + 7\text{CaSO}_4
\]
Manufacture

Block diagram of manufacturing process

Diagram with process equipment

Animation

The manufacture of superphosphate involves following steps

a) Preparation of phosphate rock

The quality of the product is determined by the grade of phosphate rock. Fine grinding is demanded due to low reactivity of the rock. Phosphate rock is finely ground up to the size of less than 100 meshes. Grinding of phosphate rock to fine powder has following advantages

- Increase the rate of reaction
- Less sulfuric acid is needed
- A higher grade of product in better condition is obtained.

It is difficult to make SSP from igneous apatite. Up to a point, the presence of aluminum and iron compounds can be tolerated, though they reduce the solubility
of phosphorus in water. The increase in the ratio of $\text{CaO}:\text{P}_2\text{O}_5$ raises the consumption of sulfuric acid per unit of $\text{P}_2\text{O}_5$ and decreases the grade. Silica has no adverse effect and higher chloride content in the phosphate rock is acceptable.

b) Mixing with acid

A finely ground (less than 100 meshes) phosphate rock is mixed with sulfuric acid in a cone mixer. The commercial concentrated sulfuric acid (77 to 98 %) is diluted to around 68 to 75% before reacting with the rock.

c) Curing and drying of the original slurry by completion of the reactions

The fluid material from the cone mixer goes to a den where it solidifies owing to a continued reaction and crystallization of monocalcium phosphate. The superphosphate is removed from the den after 0.5 to 4 hours. It is still at temperature of about 100°C and plastic in nature.

d) Excavation, milling, and bagging of the finished product

The product from the den is sent to storage piles for final curing of 2 to 6 weeks. During curing, the free acid, moisture and the unreacted rock content decreases, whereas the available water-soluble phosphorus content increases. As the reaction approaches completion during curing, the material hardens and cools. The cured product is crushed in a hammer mill or cage mill to a size of about 6 mesh.

e) Granulation

When granular superphosphate is required, the product is granulated before or after curing. Granulation before curing is advantageous as it requires less steam or water. After granulation, the product is dried in a direct contact drier and screened.

Super phosphate is manufactured by

1. Batch process
2. Continuous process

1. Batch - den process

Rock phosphate and sulfuric acid in correct quantities are added to a pan mixer of 1 to 2 tons capacity. After mixing for 2 minutes, the fluid slurry is discharged into a box den which has 10 to 40 ton capacity. When the den is filled completely after 1 hour, it is moved slowly to a mechanical cutter which removes thin slices of product to the conveyor. Some plants have two dens, which are used alternatively. This set up gives a production rate of 40 tons per hour.

Advantages

- If only igneous rock is available, batch mixing are preferred due to precise control of mixing conditions available and den can be made tight enough to
contain the very fluid slurry.

- For a small phosphate source in a remote place, batch process can be built.

Although newer plants use continuous processes, some plants still conduct these operations stepwise. All plants first pulverize the rock with modern pulverizing and air-separation equipment, most rock is ground so that 70 to 80% of particles are passed through 200mesh screen.

2. Continuous-den process

Finely ground phosphate rock is fed by a weigh feeder into a double-conical mixer, where it is thoroughly mixed with metered quantities of sulfuric acid. The acid and water are fed into the cone mixer tangentially to provide the necessary mixing with the phosphate rock. The sulfuric acid is dilute with water in the cone to the concentration of 51°Be. The heat of dilution of the sulfuric acid serves to maintain proper reaction temperature, and excess heat is dissipated by evaporation of extra water added. The rate of water addition and acid concentration may be varied to control product moisture. The fresh superphosphate is discharged from the cone mixer into a pug mill, where additional mixing takes place and the reaction starts. From the pug mill the superphosphate drops onto the den conveyor, which has a very low travel speed to allow about 1hr 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 “currying” or completion of the chemical reaction, which takes 10-20 day to reach P₂O₅ availability acceptable for plant food. The conveyers den is enclosed so that fumes do not escape into the working area. These fumes are scrubbed with water sprays to remove acid and fluoride before being exhausted to the atmosphere. Scrubber water is neutralized by passing through the limestone bed.

Granulation

Both granulation and drying of the SSP are carried out in the same piece of equipment. The powdered superphosphate enters to rotary drum granulator, where it is mixed and granulated with recycled fines (recycle ratio: > 0.6). Granulation is controlled by adjusting the water content and temperature of the product in the 1st part of the rotary drum. Drying is achieved near the exit from the granulator and involves adding more sulfuric acid and ground limestone (about 60 kg/ton SSP). The heat produced by the reaction dries the product and the calcium sulfate formed encapsulates the product in such a way that caking is avoided during final curing and storage of the product. No P₂O₅ reversion is noticed. Product is sized using a conventional system of screens and crushers such that 90% of the product is between 1 and 4 mm in size. Final curing of the product occurs during storage for less than two weeks.
Nitric and mixed acid acidulation of phosphate rock

First use of nitric and mixed acid acidulation of phosphate rock was carried out in Europe. It is desirable, since nitrogen has an essential value as plant food and can be resold at its purchase price. Also, this saves sulfur. Simple acidulation of phosphate rock with nitric acid produces the hydroscopic superphosphate, since it contains calcium nitrate.

There are various commercial modification in the process is carried out

In one, the phosphate rock is extracted by mixed nitric and sulfuric acids, followed by ammonization, drying. In another method, mixed nitric and phosphoric acidulation followed by the conventional steps and others use nitric acid alone for acidulation. These processes, as well as conditioning against moisture absorption as practiced for ammonium nitrate, have led to an extension of this acidulation with nitric acid. Nitrophosphate is also gaining importance particularly in European countries. Phosphate rock is decomposed with nitric acid plus small amount of...
phosphoric acid. The resulting slurry is ammoniated and carbonated and, if desired, combined with potassium salts and spray-dried to yield a uniform palletized product.

**Special grades**

A technical variation among superphosphates is the Kotka superphosphate, a mixture of superphosphate and phosphate rock. It is so named because it was originally made in Kotka, Finland. It needs little curing and the free acid content is low. Its effectiveness is equal to fully acidulated superphosphate and raw phosphate rock applied separately.

Another special grade superphosphate is serpentine superphosphate, a product obtained by mixing 20% serpentine (a mineral consisting of magnesium silicate) with 80% single superphosphate. Serpentine supplies magnesium to crops and improves the physical properties of superphosphate by reaction with free acid. For serpentine superphosphate to be effective, SSP must contain at least 16% phosphorus (as P₂O₅) soluble in neutral ammonium citrate, of which at least 93 % is water-soluble.

‘Enriched superphosphate’ is essentially a mixture of single superphosphate and triple superphosphate made by acidulation of phosphate rock with a mixture of sulfuric and phosphoric acids. The grade contains 25 to 35 % phosphorus (as P₂O₅) and is useful for application in sulfur deficient areas.

**Handling and storage**

Powder SSP is not free flowing and has the tendency to cake. Granulated SSP can be easily handled and uniformly distributed in the field without any problem.

Due to the presence of free acid, single superphosphate is normally bagged in polyethylene lined HDPE woven bags. Polypropylene woven bags can also be used.

**Kinetics**

\[
\text{Ca}_3(\text{PO}_4)_2 + 2\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow \text{Ca(H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + 2\text{CaSO}_4 \quad \Delta H = -108.44 \text{kcal}
\]

The above reaction takes place in two stages. In the first stage, sulfuric acid reacts with the phosphate rock, forming phosphoric acid and calcium sulfate. In the second step, phosphoric acid reacts with more phosphate rock, forming monocalcium phosphate. The first step occurs readily, while the second stage takes several days.

Since most phosphate rock is fluorapatite, fluorides react with sulfuric acid to give hydrogen fluoride, which reacts with silica to form silicon tetra fluoride as well as fluorosilicates.
\[
\begin{align*}
4HF + SiO_2 & \rightarrow SiF_4 + 2H_2O \\
3SiF_4 + 2H_2O & \rightarrow SiO_2 + 2H_2SiF_6
\end{align*}
\]

HF acid reacts with silica to form fluosilicic acid results in to incomplete removal of fluorine. An excess of sulfuric acid is consumed by such impurities in the phosphate rock (as CaCO_3, Fe_2O_3 and CaF_2). The product increase in weight over the 70-75\(^{\circ}\)bpl (bone phosphate of line) by phosphate rock used as much as 70\%, resulting in superphosphate with 16 to 20\% available P_2O_5.

**Cost**

The costs of bagging, transportation and storage of SSP are high, because the mass of SSP required is more than twice that for TSP. Hence small plants of SSP are economically better suited to serve small local markets.

**PROPERTIES**

- Molecular formula : CaH_4(PO_4)_2
- Molecular weight : 234.05gm/mole
- Elemental analysis : 16\% P_2O_5 (7\%P), 12\% S, 21\% Ca, 4\% phosphoric acid
- Appearance : White, Gray or brown granular
- Odour : Odourless
- Boiling point : 203\(^{\circ}\)C
- Melting point : 109\(^{\circ}\)C
- Density : 2.22gm/ml
- Solubility : Solubility in water, HNO_3 and HCl
- Angle of repose : 26\(^{\circ}\)
- Critical humidity : 93.7\% at 30\(^{\circ}\)C

**USES**

- It is the principal carrier of phosphate, the form of phosphorus usable by plants, and is one of the world’s most important fertilizers.
- It is low cost source of phosphorous in a wide range of pasture and cropping situations
- Generally mixed with sulfate of ammonia and muriate of potash, but can be blended with other fertilizers