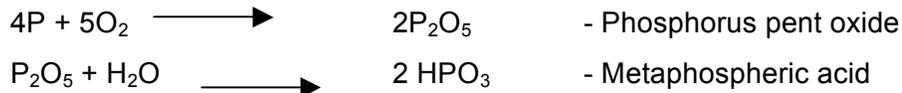


10. P fertilizers – rock phosphate – bone meal – basic slag

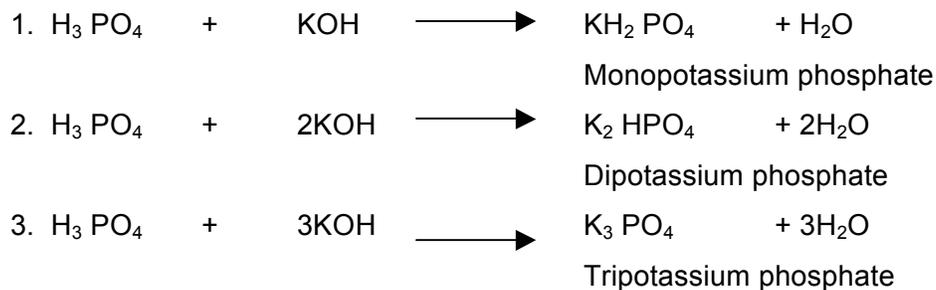
The element was discovered in 1669 and was found to be widely distributed in the lithosphere as phosphates. It is found to occur mostly as calcium phosphate (Tricalcium phosphate). The $\text{Ca}_3(\text{HPO}_4)_2$ is considered to be the basic material for the manufacture of very many phosphatic fertilizers. More than 50 countries produce phosphatic fertilizer. The top five fertilizer producing countries were United States, China, Russia, India and Brazil. Phosphorus when heated in an abundant supply of O_2 , it burns and forms P_2O_5 which, when dissolved in waters, forms metaphosphoric acid.



When this meta phosphoric acid is heated with water, it forms orthophosphoric acid which is commonly called as phosphoric acid.



This orthophosphoric acid has three replaceable H^+ atoms and hence it forms three classes of salts replacing one or two, or all the three H^+ atoms. The neutralization is said to occur in stages as follows.



The corresponding calcium salts are

1. Monocalcium phosphate - $\text{Ca}(\text{H}_2\text{PO}_4)_2$ - Water soluble
2. Dicalcium phosphate - $\text{Ca}_2(\text{HPO}_4)_2$ - or $\text{Ca}(\text{HPO}_4)$ – Soluble in citric acid
3. Tricalcium phosphate - $\text{Ca}_3(\text{PO}_4)_2$ - soluble in strong acids.

This monocalcium phosphate is an acid salt having a solubility of 100 g L^{-1} of water. The di and tricalcium phosphates are almost neutral salts having the solubility of 0.25 g and 0.005g per liter of water respectively.

Sources of phosphorus

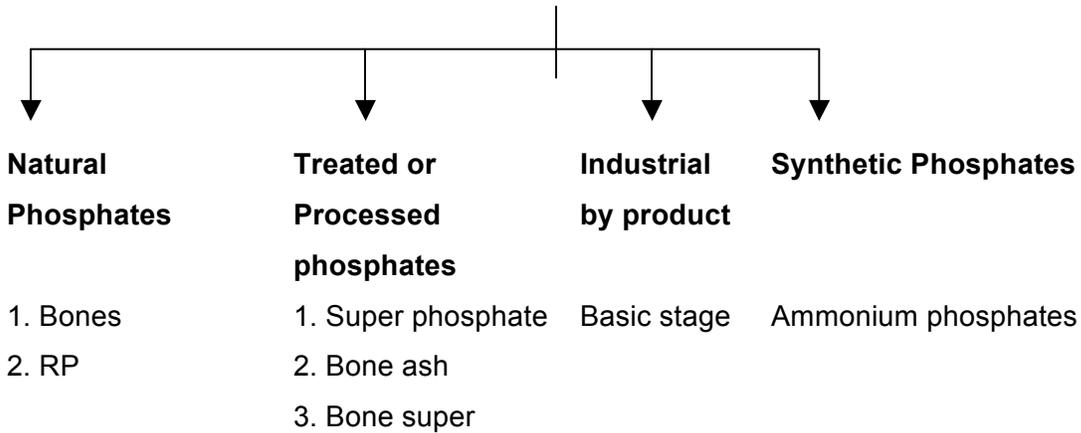
1. Mineral deposit

It occurs naturally, as mineral deposits consisting mainly of $\text{Ca}_3(\text{PO}_4)_2$ combined with either CaF_2 , CaCO_3 , $\text{Ca}(\text{OH})_2$ or CaCl_2 . The naturally occurring mineral is called "Apatite" or "Phosphorite" or "Phosphate rock" having the general formula $(\text{Ca}_3(\text{PO}_4)_2)$

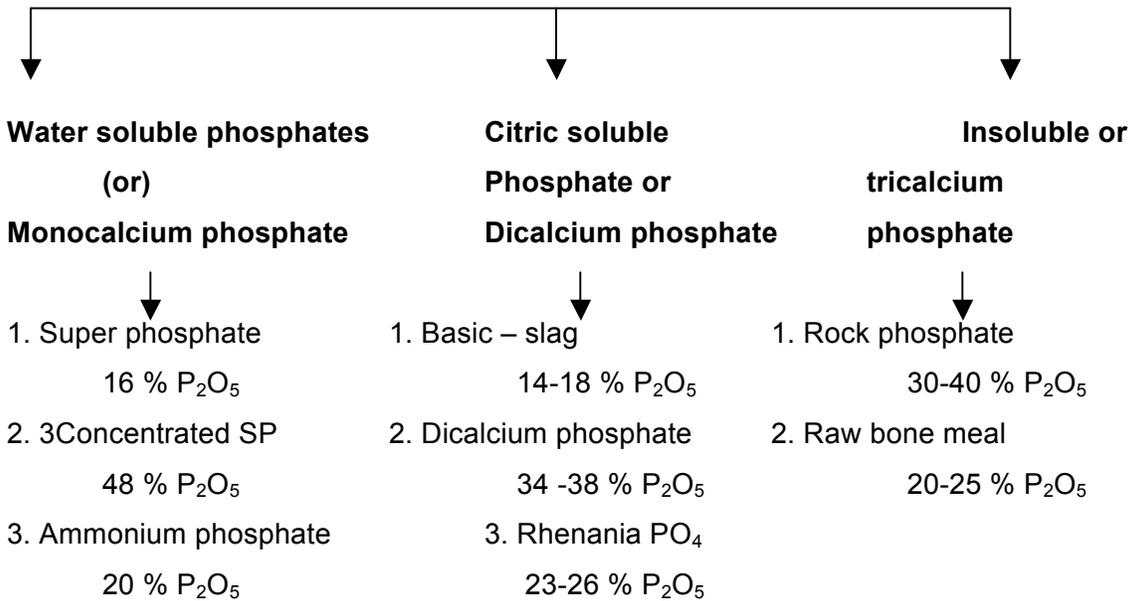
Ca X. These natural deposits serve as the basic material for the synthesis of all other phosphoric fertilizers.

Classification of phosphatic fertilizers

1. Based on nature of source or manufacture Phosphatic materials



2. Based on the solubility of the phosphate



As in the case of N, the P is incapable of being utilized in the elemental form, but only in the combined form as acid ions (anions). All plants absorb P either in the monovalent (H₂PO₄) or divalent (HPO₄) ions.

1. Water soluble phosphate

These include either monocalcium phosphate Ca(H₂PO₄) or other water soluble phosphates like ammonium phosphates. These fertilizers are readily soluble in water which can be observed quickly, as plants absorb P as monovalent phosphate ion H₂PO₄. But, when applied to the soil, the water – soluble form is converted to water insoluble

forms resulting in the reduced availability, though there may not be any total loss to the applied P. The fertilizers included in this group are found to be suitable for neutral and alkaline soils but not for acid soils.

2. Citric –soluble phosphates

The materials, having water – insoluble phosphates, but soluble in one percent citric acid, are included in this group. The availability of P is not as quick as in the case of water – soluble P, but adequate quantities are found to be released in the available form as divalent phosphates (HPO_4) for plant utilization. This group is found to be useful for acid soils, as under low pH of the soil the citrate soluble phosphates does not easily get converted into monocalcium phosphates or water soluble phosphates, and there are less chances of phosphate getting fixed up as iron and aluminum phosphates. Moreover, due to their basic reaction and high Ca content, they act particularly well on acidic soils and as such, this group is well suited for **lateritic** and acidic soils.

3. Insoluble phosphates

This group includes those materials having water and citric acid insoluble phosphates. The phosphates are being present mainly as tricalcium phosphate. The availability is very low and the phosphates will be converted to available form very slowly through various chemical reactions. Though the solubility of phosphates is low, the phosphates will be available for prolonged period of time.

These fertilizers are well suited for strongly acidic soils or organic soils which require large quantities of phosphatic materials to raise the soil P status.

The following table illustrated the phosphate (P_2O_5) content and the form of phosphate.

Sl. No.	Fertilizers	Total P_2O_5 (%)	Form of PO_4	Avail. P_2O_5
1.	Ordinary super phosphate	16	Water soluble	16.5 - 17.0
2.	Concentrate super phosphate	46 – 48	-do-	
3.	Monoammonium phosphate	48 (11 N)	-do-	
4.	Diammonium phosphate	53 (21 N)	-do-	46 (18N)
5.	Ammophos – A	48 (11 N)	-do-	
6.	Ammophos – B	20 (20 N)	-do-	
7.	Basic slag	14 – 18	Citric soluble	

8.	Dicalcium phosphate	34 – 38	-do-	34.0
9.	Fused tricalcium phosphate	28	-do-	
10.	Rhenania phosphate	23 – 26	-do-	
11.	Raw bone meal	20 – 25	Insoluble	NA
12.	Steamed bone meal	22 – 25	-do-	NA
13.	Rock phosphate	30 – 40	-do-	NA

1. Rock phosphate

The phosphate mineral in soil is found to occur as tricalcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ in combination with either CaCO_3 , CaF_2 , $\text{Ca}(\text{OH})_2$ or CaCl_2 . The primary mineral is called 'apatite' and its massive form is sometimes called as 'Phosphorite'. The apatite is of igneous origin found as a constituent of granites, gneisses and basalt. The apatite is usually found as crystals having a clear and transparent colour. There are five important forms of apatite that are found to occur and they are called according to the other components contained in the molecules.

Apatite General formula $(\text{Ca}_3(\text{PO}_4)_2)_3 \text{Ca}_x$ or $\text{Ca}_{10}(\text{PO}_4)_5 x$ where
 $x = \text{CO}_3, \text{Cl}_2, \text{F}_2, \text{SO}_4$ or $(\text{OH})_2$.

1. Carbonato apatite $[\text{Ca}_3(\text{PO}_4)_2]_3 \text{CaCO}_3$
2. Fluor apatite $[\text{Ca}_3(\text{PO}_4)_2]_3 \text{CaF}_2$
3. Chlor apatite $[\text{Ca}_3(\text{PO}_4)_2]_3 \text{CaCl}_2$
4. Hydroxy apatite $[\text{Ca}_3(\text{PO}_4)_2]_3 \text{Ca}(\text{OH})_2$
5. Sulphate apatite $[\text{Ca}_3(\text{PO}_4)_2]_3 \text{CaSO}_4$

All the above five apatite are primary minerals, of which the fluor apatite is the most commonly occurring one. In some acid soils the phosphate may be found in combination with titanium and iron in varying quantities and there when present in the soil are classified as secondary mineral. The apatite as such is found to occur in the amorphous form and it may be in the compact, concretionary or earthy form and these forms are commonly referred as rock or boulder phosphate, pebble phosphate and soft phosphate respectively. The apatite deposits are classified into residual deposit, replacement deposit and sedimentary deposit.

Deposits of apatite of economic importance have been found in every continent and in many islands of the world. In India, the phosphoric deposits are found in Trichy district of Tamil Nadu, Udaipur of Rajasthan and Singbhum of Bihar. The deposits in Trichy are found in the form of nodules in a bed of clay and hence are called Trichy phosphatic nodules. The exact locality is Uttalur about 30km from Trichy and the deposit

is found to spread over an area of 11 to 12 square miles. The Trichy phosphatic nodule analyses as follows

P_2O_5	-	24 – 27%
$CaCO_3$	-	42 – 47 %
F	-	2 – 3 %
Fe_2O_3 & Al_2O_3 -		4 – 9 %

As compared to the phosphatic deposits found in other countries, this phosphate deposit contains a high content of F (2-3%), high content of sesquioxides (4-9%) and low content of phosphate. The high contents of F and R_2O_3 made the RP unsuitable for the manufacture of other phosphatic fertilizers at a lower cost. Larger quantities of acids are required to eliminate the F and R_2O_3 which will thus increase the cost of production. Moreover, the Trichy deposit is not suitable for direct use as fertilizer because of high F and R_2O_3 contents. The deposit is mainly in the form of carbonate apatite and fluor apatite. The fertilizing value is nil unless the F and R_2O_3 are removed. The ground RP is marketed, which passes through 200 mesh sieve.

Bone meal

Bone meal contains tri calcium carbonate or hydrated tri-calcium phosphate. This also contain sodium, magnesium and carbonate. Bone meal is prepared by crushing bones and availability of phosphorus in bone meal increases as material is crushed to a finer size.

Raw bone meal

It is prepared by grinding the bones as such without any treatment. The bones are collected, dried before grinding. The protein present in the form of remaining flesh provides nitrogen ranging between 2 to 4%. This contains fat of glue which prevents the decomposition of bone when applied in the soil.

Total $P_2 O_5$ on dry weight basis (Max.)	:	20 %
Available $P_2 O_5$ soluble in 2% citric acid (Min.)	:	8 %
Total nitrogen, % by weight (Min.)	:	3 %

Steamed bone meal

Steamed bone meal is obtained by the boiling the bones under steam pressure. Under this process the fat and some other materials are removed so that decomposition can take place readily in the soil after it is applied. However this process reduces the nitrogen content but phosphate content is increased. The bones are then ground and

sold as fertilizer material in the market. The steamed bone meal should have the following standard according to fertilizer quality control order (1957) if Government of India:

Free moisture percentage by weight (Max.) : 7.0

Total phosphates as P_2O_5 percentage by weight (Min) : 22.0

Available phosphates as P_2O_5 soluble in 2 %

Citric acid solution % by weight (Min.) : 16.0

Bone meal consists of P_2O_5 in citric acid soluble form hence it should always be applied as basal. The bone meal sources are limited and hardly 30,000 to 35,000 tonnes of bone meal is produced and consumed annually in the country. Now-a-days it is also used as feed to the animals in the form of concentrate hence the materials, as fertilizers, is further reduced.

Basic slag

It is a by-product from the steel industry. During the steel manufacture, the P in the iron ore is removed to get a high quality steel as the steel containing more than 2% of P is brittle. The basic slag is obtained by the various processes of steel manufacture.

1. Thomas and Gilchrist method

The method was introduced as a modification to the old Bessemer process in 1877. In this, molten pig iron containing the various impurities like Ca, SiO_2 and P is introduced into a limed converter with air blast arrangements. At a particular temperature, lime melts and combines with the acid forming impurities and the resulting product, which are lighter, rise to the surface of the molten mass. The floating solids are poured off as slag, cooled, powdered and marketed. This is containing 17 or 20% P_2O_5 .

2. Open Hearth method (Modern Method)

Here the impurities are oxidized by means of the iron ore (Iron oxide) itself. Iron ore and lime are heated in an open heater and molten pig iron is then added. This carries not more than 15% P_2O_5 and not less than 8% P_2O_5 .

Properties

The name 'basic slag' is derived from metallurgy. Any flux that is added to remove the impurities is recovered mixed with the impurities as a slag. The flux that is added to remove basic impurities produces acid slag and the one that is added to remove acid impurities forms basic slag. The basic slag is a heavy dark powder and is alkaline to litmus. The availability of P is found to increase with the fineness of the product as well as with silica content and decrease as the F content increase. Basic

slag should not be used as an ingredient in manure mixtures. The phosphate is found to be present in a double silicate form with lime $[(CaO)_5 P_2O_5 SiO_2]$ but some consider it as tetra calcium phosphate $(Ca_4 P_2O_5)$ and still others consider it is a basic silicon oxyapatite. It is only a slow acting fertilizer. This more useful for acid soils and in addition to the phosphate it is valued for the magnesium and Mn content. Following is the average composition of basic slag.

Phosphate (P_2O_5)	-	12 - 20 %
Lime (CaO)	-	40 - 50 %
Silica (SiO_2)	-	5 - 16 %
Sesquioxides (R_2O_3)	-	12 - 16 %
Manganese oxide (MnO)	-	5 - 10 %
Magnesium Oxide (MgO)	-	2 - 3 %

Artificial Basic slag

When PR is fused with Mg containing minerals like serpentine and olivine, the resultant product is called as artificial basic slag. The fertilizing value of basic slag is influenced by the fineness of the fertilizer and material passing through a 100 mesh sieve is found to be better. It is more suitable for acid soils because of high lime content. The presence of Mg and Mn corrects the deficiency of these elements in the soil.