

PHOSPHATE FERTILISERS.

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The use of phosphatic materials as fertilisers was practised from a very early period. As the practice is very old it is not possible to find out when and where it originated. These materials, especially bone, fish and guano, were largely used without understanding the real significance in using such materials. The increase in crop yield resulting from the use of such materials was attributed to various causes. It was only after the discovery of phosphorus and phosphoric acid that it was recognised that this effect was due to the phosphorus present in those materials. From this stage onwards the use of phosphatic materials as fertilisers progressed rapidly and new methods were discovered to apply phosphorus to the soil in a form in which it would be readily available for the plants.

Before proceeding further, it is necessary to give an idea of the function of phosphoric acid in plant nutrition. Even though the amount of phosphorus finally retained by the plant is very small compared to the amount supplied, it greatly helps the plant in various other ways. While nitrogen promotes growth and delays maturity, phosphorus promotes maturity. It is closely related to the grain formation of the crop and almost always found in large proportions in the reproductive parts of the plant. It is generally considered to promote the rapid ripening of the grain. Further, its presence tends to increase the proportion of grain to straw. It stimulates the early development of the young seedling to a very great extent. The presence of large quantities of this element also keeps the soil in a very good mechanical condition and thereby indirectly helps the root system of the plant to develop vigorously.

The sources of phosphates are (i) bones, (ii) mineral phosphate, and (iii) basic slag. Even though bone and guano were used for the manufacture of superphosphate in earlier days, now superphosphate and other phosphate materials are mostly prepared from mineral phosphates. At present bone is used either in the raw state as bone meal or as a manufactured product as steamed or degreased material. So, here it is proposed to deal mainly with the mineral phosphates.

Phosphorus is one of the constituents of the lithosphere (earth's crust) and there it occurs mainly as calcium phosphate. This calcium phosphate can be classified under two main heads according to the nature of its origin. They are (i) primary, and (ii) secondary. The primary material occurs as the well crystallised (hexagonal) mineral, apatite. This mineral is of igneous

origin. Two varieties of apatite have been recognised and they are (i) fluorapatite $\text{Ca}_5(\text{PO}_4)_2 \cdot \text{CaF}_2$, and (ii) chlorapatite $\text{Ca}_5(\text{PO}_4)_2 \cdot \text{CaCl}_2$.

The secondary material occurs as an amorphous product. As it occurs in large deposits it is generally recognised as 'rock phosphate'. The deposits of this rock phosphate can be classified roughly under three heads according to their mode of origin. They are (i) residual, (ii) replacement, and (iii) sedimentary deposits. The residual deposit is the one which is derived from a deposit of phosphatic limestone due to weathering and other denuding agencies. Replacement deposits are brought about by the gradual conversion of limestone deposits by the action of phosphate-bearing solutions. Most of the Ocean Island deposits belong to this category. They can be considered as mineralised guano deposits, because the phosphorus is principally derived from guano.

Sedimentary deposits are those which result from the gradual accumulation of phosphatic material in sea bottom. These later on get raised above sea level and occur interbedded with other sedimentary rocks. This rock is also considered to be of organic origin. This type of sedimentary deposits contributes the main bulk of the rock phosphate of commerce. Workable deposits of phosphate rock have been found to occur throughout the world. Some of the world-famous deposits occur in America and North Africa (Algeria, Morocco and Tunisia) and in some of the Ocean Islands. The following table gives the approximate yearly world production and reserve of phosphate rock. (An approximate average for the period 1930-35 is given in tons.)

TABLE I.

Countries.	Production.	Reserve.*	Grade-average % of $\text{Ca}_3(\text{PO}_4)_2$.
United States	4,000,000	7,000,000,000	65
Tunisia	3,500,000	1,000,000,000	63
North Africa { Algeria	1,000,000	1,500,000,000	63
Morocco	2,000,000	1,500,000,000	75
Egypt	350,000	200,000,000	60
Nauru and Ocean Islands	700,000	200,000,000	83
Russia (both European and Asiatic)	6,000,000,000	below 50
India { Apatite	300	500,000	85
Sedimentary rock phosphate	nil	8,500,000	57
TOTAL	11,550,300	17,409,000,000	

Many methods have been suggested, patented and used to prepare soluble phosphates from these naturally occurring insoluble phosphates. These can

* Estimated from known deposits.

be classified as follows: (1) Acid treatment, (2) volatilisation, (3) decomposition by some cheap reagents at high temperature, and (4) as a by-product of steel industry (basic slag). Of these the first one is the most important and universally employed. The acid employed for this process is sulphuric acid. Nearly 50% of the world's production of this acid is utilised for this purpose. In the resulting product of acid treatment, known as superphosphate, most of the phosphorus is present in a water-soluble state as monocalcium phosphate. If excess of sulphuric acid is added, free phosphoric acid is formed. For the preparation of a concentrated superphosphate (double super) phosphoric acid obtained by treating rock phosphate with excess of sulphuric acid is utilised to treat fresh charges of phosphate rock. Most of the superphosphate and other phosphate fertilisers consumed in India are of foreign origin and are prepared from rock phosphate. The small amount that is produced in India is from bone ash and bone char which are the by-products of other industries.

Next in importance is the volatilisation process by which the natural phosphate is heated strongly with some reducing agents and silica and the volatilised elemental phosphorus is again converted into phosphoric acid. Only a small portion of the acid prepared by this process is at present utilised for the production of concentrated fertilisers. Even though this process has not yet advanced very much, it can be safely predicted that it has very good future.

In addition to these methods a number of processes have been invented for decomposing the tricalcium phosphate in the natural phosphates by calcining them with various cheap reagents, such as silica, etc. The resulting materials are similar to basic slag in their crop-producing powers. A German product of this process, called Rhenania phosphate, is extensively produced and sold. The available phosphate in this material is not present in a water-soluble state, but, as in basic slag, they are soluble in a 2% solution of citric acid. The great advantage with this process is that it eliminates the use of sulphuric acid and helps us to utilise even very inferior grades of rock phosphate. Thus the cost of the resulting material is reduced considerably.

Basic slag is obtained as a by-product from the steel industry. The phosphorus present in this material is mainly derived from the iron ore used for producing pig iron and as such it could be considered as of mineral origin.

A general survey of foreign literature on the mineral phosphate deposits of the world reveals the complete absence of any reference to the occurrence of the phosphate deposits in India. As the primary industry of India is agriculture the very limited occurrence of phosphatic rock in India should be very much regretted. At present even this limited stock is not being utilised.

The only occurrence of phosphatic deposit on a sufficient scale is near Trichinopoly. Here the phosphorus present as tricalcium phosphate occurs in the form of nodules along with calcium carbonate and calcium fluoride. These nodules occur in the cretaceous beds of the Perambalur Taluq, Trichy

District. The quantity available is about 8,000,000 tons. A similar deposit overlying the Deoban limestone occurs near Mussoorie. Apatite in massive and crystalline form occurs at various localities in India.

While India exports annually more than 80,000 tons of bone valued at Rs.90 lakhs, she imports finished phosphate fertilisers of the value of 15 lakhs.

As the Trichy rock phosphate deposit is situated very close to the agricultural tracts of Tanjore and Trichy Districts, it is highly essential that ways and means should be found for supplying phosphorus to these tracts from this deposit.

For the present scheme of work extensive investigations were carried out to find out whether it is possible to eliminate the impurities which stand in the way of using this material for the production of superphosphate. After grinding the phosphatic rock, which occur as flint-like nodules, into fine powder (100 or 80 mesh) it was subjected to various mechanical treatments. It was first treated with an air-separator. The heavy concentrate showed an increase in its phosphorus content while in the tailings an enormous reduction in the phosphorus content and a substantial increase in the calcium carbonate content was noticed. After this, concentration by Wilfley Table was resorted to find out the conditions under which the maximum yield with a minimum loss could be obtained. Experiments with samples of different particle sizes (60, 80 and 100 mesh) were tried and it was found that the sample having a particle size between 80 and 100 mesh was the best suited for the purpose. No doubt, concentration by Wilfley Table results in some loss of material and this can be prevented only with great difficulty. By heating the material before putting it on the Wilfley Table the process also works out well. By this procedure the loss of material is considerably reduced. Further, as the organic matter is also destroyed the resulting material shows a further increase in the phosphorus content. But, one serious objection would be the large amount of fuel consumed which naturally raises the cost of concentration. This method can be adopted if the fuel is obtained cheap.

(The results of these experiments are given in Table III.) The slight increase in the phosphorus content shown by the ignited specimen is probably brought about by the loss of organic matter, combined water and CO_2 . But even though the material resulting from ignition shows a slightly enhanced phosphorus content, still it could not be used for the production of acid phosphate. Because, the calcium, which was originally present as calcium carbonate, was still present as lime and so it would readily combine with sulphuric acid to form gypsum.

In Table II a complete analysis of an average sample of phosphatic nodule powder along with the calculated mineral composition is given.

TABLE II.

Oxides and other constituents.	Composition of the phosphatic nodules per cent.	
	Chemical composition.	Mineral composition.
Moisture	1.37	
Combined water and organic matter	5.02	
SiO ₂	3.08	
P ₂ O ₅	27.08	Ca ₃ (PO ₄) ₂ 59.13
CaO	43.30	Gypsum 3.25 CaSO ₄ .2H ₂ O
Fe ₂ O ₃	2.53	
Al ₂ O ₃	2.83	
MgO	0.96	
SrO	1.75	Celestite SrSO ₄ 3.10
K ₂ O } Na ₂ O }	Trace	
SO ₃	3.26	
CO ₂	5.63	CaCO ₃ 12.80
F	2.65	CaF ₂ 5.45
TOTAL	99.46	
Arsenic was absent.		

TABLE III.

Results of concentration of the nodule powder.

Constituents.	Nodule.		Calcined at *	Concentrate †
	1a	1b	950°C. for 7 hours.	62 lb. from 100 lb.
Moisture (110°C.)	1.37	1.37	..	0.72
Combined H ₂ O and organic matter	5.02	5.02	..	0.61
SiO ₂	3.08	4.98	6.30	4.70
Ca ₃ (PO ₄) ₂	59.13	61.30	67.10	80.10
CaCO ₃	12.80	10.60	..	1.00
CaF ₂	5.45	5.30	..	6.20
Fe ₂ O ₃	2.53	2.60	..	1.90
Al ₂ O ₃	2.83	4.70	..	2.30
MgO	0.96	0.42	..	0.14
SrSO ₄	3.10	2.15	..	} 1.30
celestite. CaSO ₄ .2H ₂ O	3.25	2.02	..	

N.B.—The celestite which is recovered as a heavy concentrate can be considered as a valuable by-product.

* Calcination was done with 10 lb. samples for 7 hours at 950°C. Yield = 8.7 lb.

† Wilfley Table separation was carried out with 100 lb. of calcined material. Table tilt = 5° and number of vibrations of the table per minute = 120. Yield of concentrate = 62 lb.

The calculated cost of the concentrated nodule powder.—The cost of the phosphatic nodule has not yet been fixed, but at present it can be had for Rs.12 per ton at Trichy or Rs.10 on the spot.

Cost of grinding 1 ton of the phosphatic nodule to 80 mesh	
or 100 mesh powder	Rs. 5
Cost of concentrating 1 ton of the powdered ore by the	
Wilfley Table before heating the material	5
Do. do. after heating the material	10

So the cost of one ton of concentrated nodule powder at Trichy would be roughly Rs.50. Thus it would work out to be much cheaper than bone ash which contains almost the same amount of $\text{Ca}_3(\text{PO}_4)_2$. It would be economic to use this material for the preparation of acid phosphate only when a cheap supply of sulphuric acid is available.

Owing to the very high cost of sulphuric acid prevailing at present it does not appear to be a profitable proposition to prepare superphosphate from the phosphatic nodule powder even after it is well concentrated. It will be successful only if the cost of sulphuric acid is reduced considerably, and this is not possible under the present circumstances in which sulphuric acid is being manufactured in India. So experiments were conducted to study the various other processes by which a quick-acting phosphatic fertiliser could be produced without using sulphuric acid.

With the object of eliminating the use of sulphuric acid for the preparation of quick-acting phosphate fertilisers from rock phosphates, numerous investigators have worked on the calcination processes in which the natural phosphate is heated in a powdered condition with cheap reagents which could be obtained anywhere. The resulting material contains either the whole or part of the phosphorus present in the rock in a form which is readily available for plants. Almost all the processes discovered so far are covered by patents and most of them are not being worked at present owing to the low cost of superphosphate available in those countries in which the patent rights are being held. Further, it appears that these processes would work satisfactorily only so far as a definite type of phosphate rock is treated. Because, the proportions of cheap reagents which are to be added to the phosphate rock depends entirely on the particular grade and composition of the phosphate rock.

For the present scheme of work some of the old processes were tried but they failed to give satisfactory results. So experiments were carried out using varying proportions of some of the cheap reagents which are readily available in South India and a process has been worked out which has given satisfactory preliminary results.

For this process the phosphatic rock and the other ingredients should be finely powdered and the powdered material should completely pass through a 100 mesh sieve.

The Process.—Certain proportions of the phosphatic rock powder, silica (sand or quartz) or potash feldspar, gypsum and an iron-manganese ore were thoroughly mixed and this mixture was heated in a slow current of air (oxidising atmosphere) at a temperature range of 1,100°C. to 1,200°C. for 45 minutes while it was kept constantly agitated to expose fresh surfaces. The resulting sintered mass was cooled suddenly. It was observed that it has formed very soft clinkers which could be easily crushed into fine powder. This resulting material contained as high as 16% citrate soluble P_2O_5 (determined by Wagner's citric acid method) while before ignition it held only 1.2% citrate soluble P_2O_5 . Heating the phosphate rock with silica or potash feldspar and alumina or magnesia, while it kept the resulting material in an excellent mechanical condition, yielded a definitely lower quantity of citrate soluble P_2O_5 —i.e. 11%.

One very great advantage in using potash feldspar instead of silica is that most of the K_2O in the feldspar is converted into a citrate soluble form in which it is readily available for plants.

TABLE IV.

Chemical composition of the various ingredients used.
Per cent.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	P ₂ O ₅	MnO	K ₂ O	Na ₂ O	CO ₂	CaSO ₄
Phosphate rock ..	3.5	3.0	2.5	43.30	1	27	5.7	..
Silica (quartz) ..	97	0.7	1.1
Potash feldspar ..	66.4	18.9	0.28	12.5	2.7
Alumina (bauxite)	4.3	68.5	1.45
Magnesia (magnesite).	2.0	..	trace	1.23	45.6	46.2	..
Gypsum ..	2.73	91
Iron manganese ore (from Sandur)	3.2	..	49.7	32.5

The citrate soluble P_2O_5 and K_2O were determined by the Wagner's citric acid method. From the 2% citric acid solution holding both the phosphorus and the potash the former was determined by precipitating it both by the molybdate method and by the magnesia mixture method. The potash was determined by the cobaltinitrite method after eliminating the phosphorus by precipitating it with magnesia mixture.

Large-scale experiments.—Some large-scale experiments using 50 and 30 lb. samples were carried out in the Mysore Glass and Enamel Factory (Bangalore) with the kind permission of the Manager of the factory. The various samples were heated in the glass melting pots for a period of half an hour. These experiments proved to be very successful in spite of the fact that the proper conditions of treatment could not be kept up owing to the nature of the pot in which heating was carried out. The heated mass could not be agitated properly and a strictly oxidising atmosphere could not be maintained. The temperature was also slightly lower than what is required for the complete

conversion. While complete conversion results in the material being turned into a soft, friable clinkery mass, the samples heated in the glass melting pots remained powdery. Small portions of this material which were in contact with the hottest part of the pot for a longer period developed clinkers which in one experiment gave as high as 18.3% citrate soluble P_2O_5 and 4% citrate soluble K_2O . The rest of the mass which was in a powdery state gave only 12% citrate soluble P_2O_5 and 4% K_2O . The percentage of citrate soluble K_2O was found to remain constant even under conditions of a large variation in temperature. But at slightly higher temperatures and on continued heating part of the total K_2O present in the original sample is lost.

Thus these experiments show that if a miniature portland cement kiln is utilised for heating this material under proper conditions a better yield of available P_2O_5 could be obtained. It is highly probable that a product quite as rich in available P_2O_5 as ordinary superphosphate could be obtained. Further, the presence of about 4% of available K_2O , a very valuable plant food makes this process very attractive. The cost of this material would be also definitely less than the peace-time cost of superphosphate having 18% water soluble P_2O_5 .

Before concluding this article I would like to mention a word about the position of the phosphate fertiliser trade in India. Of course at present it is in a very unsatisfactory state. Many of this phosphate fertilisers are being sold to farmers by reputable firms without informing them as to the amount of available phosphates present in their fertilisers. Many compound and mixed fertilisers under various names are being put in the market without giving any idea as to their composition. The farmer is very much handicapped by such a procedure and he does not know which would be the most suitable for his land and whether he is recovering his money's worth. So it is highly necessary that strict Government control of this trade should be exercised as early as possible to bring about satisfactory market conditions.