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A New Angle on Trichy Phosphatic Nodules

by

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Introduction : Attempts have been made since 1892, both in this Institute and elsewhere, to convert the rich phosphatic material available as nodules in the Tiruchirapalli district of the Madras State into a readily available phosphatic fertilizer. The high content of lime (calcium carbonate) present in the raw material mitigated against its conversion into superphosphate by the usual sulphuric acid treatment. Consequently, the material, inspite of its high total P_2O_5 content (25 to 30%), remained unexploited for use as a fertilizer.

With the advancement of chemistry and technology, newer methods have been developed in recent years to convert rock phosphates into readily available phosphatic fertilizers without the use of sulphuric acid. The outcome of such developments have led in other countries to the production of phosphatic fertilizers by the following process:

(a) defluorinated phosphatic rock produced both by calcination and fusion (b) fertilizers produced by calcination of phosphatic rock with alkali salts (c) "phosphate rock-magnesium silicate glass" fertilizer produced by fusion with magnesia and silica and (d) fertilizers obtained by treatment of phosphate rock with nitric acid (Jacob, 1953).

Of the above products, the "Phosphate-rock-magnesium silicate glass' is prepared by fusing phosphate rock with olivine or serpentine rocks, which are inexpensive natural sources of magnesium and silica. This product has the following advantages over the other products:

i. No defluorination furnace or rotary kiln with its attendant refractory problems and fuel consumption is required;

ii. Olivine and serpentine rocks are readily available and cheap;

iii. Besides phosphorus, magnesium which is also a plant food, is present in this fertilizer and

iv. The product is similar to the silico-phosphate which does not undergo reversion in acid soils as is the case with superphosphate (Crowther and Lea, 1946; Mariakulandai, Venkatachalam and Rajagopal Iyengar, 1955)

Hence it was felt that the technique used in the preparation of "phosphate-rock-magnesium silicate glass" might serve the purpose of rendering the phosphorus in the Trichy phosphatic nodules available to plants.

Object: Accordingly, the process was studied under the following heads to arrive at the best technique and ingredient for rendering the P_2O_5 in the Trichy nodules available to plants:

(1) To study the effect of pure compounds of magnesium and silica in the fusion mixture.

(2) To study the possibility of using naturally occurring olivine and serpentine rocks of Salem, as cheap sources of magnesia and silica.

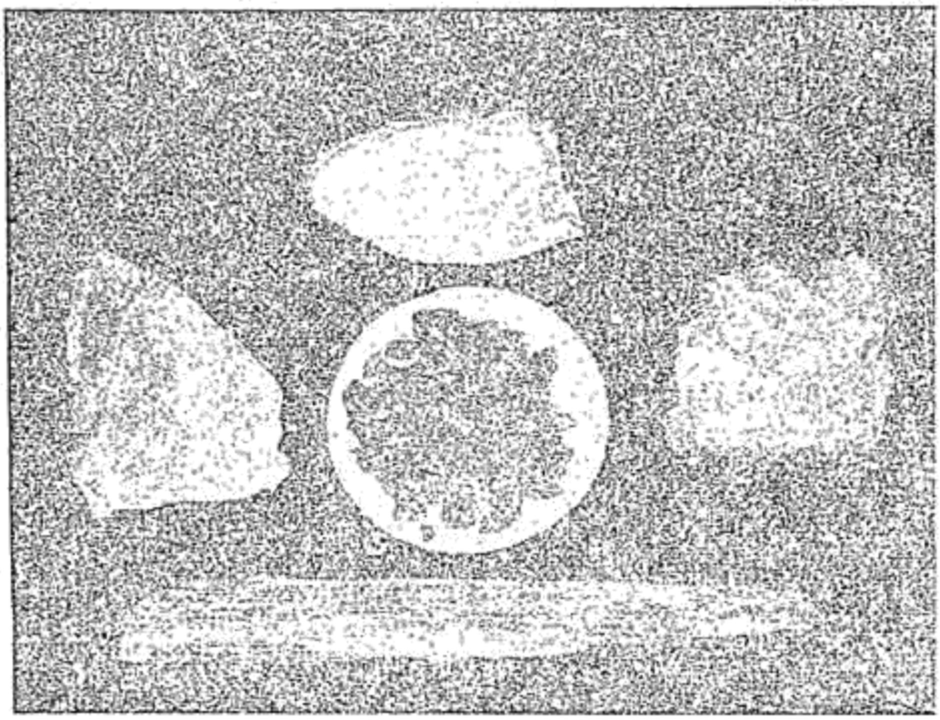
(3) To study the use of sulphates in improving the availability.

(4) To note the effect of quenching the fused mass in cold water.

A preliminary report of this work was published by the authors in Current Science (Mariakulandai *et al* 1955.)

Materials and Methods: Trichy phosphatic nodules giving a total P_2O_5 content of 28% were powdered to pass through a 50 mesh sieve and used. This material was mixed with a number of other chemicals like silicate, sulphates and carbonates of sodium, magnesium or calcium and also with materials like olivine and serpentine rocks obtained as by-products in the magnesite quarries of Salem, Madras State and bagasse ash obtained as waste in sugar factories. Bagasse ash used in this study was from the sugar factory at Pugalur in Trichy District. Plate 1 shows the raw materials used in this study with the fused product obtained from them.

About 100 grams of mixtures of the above materials were mixed in different proportions in a mortar using a little quantity of water and formed into small pellets of the size of a playing marble. These pellets were first air-dried and then dried in an oven at 150°C. The dried pellets had to be fused next. The fusion is usually done at a temperature of 1550°C in a three-phase electric arc furnace in other countries (Moulton, 1949). As this facility was not available locally, oxy-acetylene flame was used (excepting for mixture No. 34 which was fused using graphite arc) for fusing the pellets prepared as above, one by one on a firebrick. The hot fused mass was then immediately quenched in cold water. All the mixtures presented in Tables 1 to 3 were quenched immediately after fusion.



1. Trichy nodule 2. Bagasse ash
3. Olivine 4. Serpentine
5. Fused Product

The fused product thus obtained was powdered to pass through a 90 mesh sieve and analysed for "total P_2O_5" and "available P_2O_5". "Total P_2O_5" was estimated volumetrically after precipitation as ammonium-phospho-molybdate, after extraction with 1:1 HCl to which a few ccs of HNO_3 was added while "available P_2O_5", which represents the form in which phosphorus is available to plants was estimated in the 2% citric acid extract of the material.

Raw materials used in the mixture, like olivine, serpentine and bagasse-ash, were analysed for their $Mg0$ and $Si0_2$ contents (Tables 5 & 6).

The results of analysis of the mixtures tried out are presented in Tables 1 to 4. From the data obtained, the following points emerge as answers to the problem under study.

(i) Presence of a silicate along with magnesia is better than either of them alone in the fusion mixture, in rendering the phosphate available in Trichy nodules (Table 1).

TABLE 1.

Showing the effect of fusing Trichy phosphate with pure compounds of magnesium and silica

S. No.	Mixture No.	Composition of mixture		Total P_2O_5%	Available P_2O_5%	% rendered soluble in 2% citric acid
1.	4	10:3	T. P: $MgCO_3$	29·33	2·83	9·65
2.	7	10:6	T. P: $MgSO_4$	29·57	4·83	16·33
3.	12	10:6	T. P: Na_2SiO_3	19·15	7·70	40·22
4.	5	10:3:3	T. P: Na_2SiO3: $MgCO_3$	23·56	9·13	38·76
5.	6	10:3:3	T. P: Na_2SiO3: $MgSO_4$	23·42	12·75	54·44

T. P:— Stands for Trichy phosphate

(ii) The naturally occurring olivine and serpentine rocks of Salem could be used as a source of silica and magnesia in the fusion mixture for rendering the P_2O_5 in the Trichy nodules available to plants. The bagasse-ash supplying mainly silica to the mixture was better than either of the two raw materials mentioned above when the latter are used alone in the mixture, without addition of other materials such as sodium sulphate (Table 2). In the presence of sodium sulphate, olivine and bagasse-ash mixtures are equal, while serpentine mixture is the best. (Table 3).

TABLE 2.

Showing the effect of fusion with raw materials containing magnesia and silica

S. No.	Mixture No.	Composition of mixture		Total P_2O_5%	Available P_2O_5%	% rendered soluble
1.	16	10:6	T. P: Olivine	19·68	5·66	28·76
2.	17	10:3	,, ,,	23·00	5·10	22·18
3.	18	10:3	,, Serpentine	24·68	6·55	26·55
4.	19	10:6	,, ,,	19·74	5·73	29·02
5.	20	10:3	,, Bagasse ash	19·80	9·74	49·19

(iii) Of the sulphates tried along with olivine and serpentine in the mixture, sodium sulphate was found to be the best, and sodium sulphate was necessary to get a 95% availability (Table 3).

TABLE 3.

Showing the effect of sulphates in improving the availability of phosphate in Trichy phosphate

S. No.	Mixture No.	Composition of mixture	Total P_2O_5%	Available P_2O_5%	% rendered soluble
1.	16	10 : 3 T. P : Olivine	23·00	5·10	22·18
2.	22	10 : 3 : 3 ,, Olivine : $CaSO_4$	22·15	5·60	25·28
3.	26	10 : 3 : 3 ,, ,, : $MgSO_4$	22·35	10·15	45·19
4.	27	10 : 3 : 3 ,, ,, : Na_2SO_4	19·70	14·10	71·57
5.	18	10 : 3 ,, Serpentine	24·68	5·10	22·18
6.	23	10 : 3 : 3 ,, ,, : $CaSO_4$	22·15	5·60	25·28
7.	34*	10 : 3 : 3 ,, ,, : Na_2SO_4	21·65	20·65	95·33
8.	20	10 : 3 T. P : Bagasse ash	19·80	9·74	49·19
9.	39	10 : 3 : 3 ,, ,, : Na_2SO_4	19·03	13·60	71·47

* Fusion done using the graphite arc at the Electrochemical Research Institute, Karaikudi.

(iv) As already observed by other workers, (Jacob 1953), fused product has to be quenched as it granulates the material for easier grinding and also prevents the reversion of the P_2O_5 to the unavailable form (Table 4).

TABLE 4.

Showing the effect of quenching the fused mass on the availability of phosphorus in Trichy phosphate

S. No.	Mixture No.	Composition of mixture	Total P_2O_5%	Available P_2O_5%	% rendered soluble
1.	2	10 : 3 : 3 T. P : $MgCO_3$: Na_2SiO_3 (Not quenched)	22·78	6·13	26·92
2.	5	10 : 3 : 3 T. P : ,, Quenched	23·56	9·13	38·76

Discussion and Conclusions: Rendering phosphate rock available to plants through fusion has been tried by a number of workers. Waggaman and Esterwood (1927) have reviewed the conditions under which phosphate rock could be rendered citrate-soluble through calcination. The temperature range is a very important factor and is considered to be narrow for each type of salt and proportions tried (Guernsey and Yee, 1924). In the United States of America, mixtures of rock phosphate and olivine or serpentine are fused at

1550°C in a triple arc furnace and is estimated that with 850 kw. hr. of electricity and 15 to 20 pounds of graphite for the arc furnace, a ton of the product could be prepared on a commercial scale. In the present study, the objective was to render the phosphate in the Trichy nodules, citrate-soluble, so that the phosphorus in the nodules will be available to the plants. As a three-phase electric arc furnace was not available at this laboratory, the fusion was done with oxy-acetylene flame, the temperature of which was round about 1500°C in all cases reported in this study, barring mixture No. 34 which was fused in graphite arc at the Karaikudi Electro-chemical Research Institute at about 1500°C. The main objective of the experiment was directed towards finding out the best ingredients to be used, keeping the temperature factor as nearly constant as possible.

The use of silica and alkali salts such as KCl or K_2SO_4 has been found to be beneficial by Day (1895), in cases of phosphate rocks containing calcium carbonate. Wolter (1903) found alkaline earths and silicates to be good for the purpose, while Walthall and Bridger (1943) showed that fusion of phosphate rock with magnesia and silica gave a product with a high availability of phosphate. With Makatea phosphate of Japan, Ando and Kataoka (1952) report best results when mixed with Na_2SO_4, carbon and SiO_2.

This study has clearly brought out that of the pure chemicals tried in the mixture, magnesia or silica individually did not bestow as much benefit as would be obtained by a judicious mixture of both. Under the conditions of this experiment the best combination to render the phosphorus in Trichy nodules available to plants was 10 : 3 : 3 of Trichy nodules with $MgSO_4$ and sodium silicate respectively. But in any commercial venture of exploiting the process, the addition of pure chemicals would not be economical and in the search for such natural products to go into the mixture, a reference to literature indicated that Boylan (1953) found "langebeinite" containing K_2SO_4 and $MgSO_4$ to give 96% availability. Walthall and Bridger (1943) used olivine rock in the mixture with good results, Nagai *et al* (1951) in Japan found fusion of rock phosphate with serpentine and potassiun liparite in the ratio of 60 : 35 : 5, good. Huang (1953) has used both olivine and serpentine successfully in the fusion mixture. In the present study, olivine and serpentine rock samples obtained from Salem were used. These rock samples contained MgO and SiO_2 in good amounts (Table 5). But, it was found that the rocks by themselves could not give a high availability of P_2O_5 without addition of sodium sulphate in the mixture (Table 3).

TABLE 5.

Showing the analysis of the olivine and serpentine rocks used in the study

		Olivine rock	Serpentine rock
SiO_2%	..	36·20	42·50
MgO%	..	47·61	42·72

Bagasse ash thrown out as a waste product from sugar factories and consisting mainly of silica (Table 6) with 2% P_2O_5 and a little lime was also useful in rendering the phosphorus in Trichy nodules available to the extent of 50%, when used alone with the Trichy nodules and to about 70% when used with sodium sulphate.

TABLE 6.

Showing the analysis of Bagasse ash used in the study

1.	Insolubles (mainly silica)	..	94·19
2.	Iron and alumina	..	2·31
3.	Lime	..	1·91
4.	Magnesia	..	trace
5.	Potash	..	,,
6.	Soda	..	,,
7.	Sulphate	..	Nil
8.	Phosphoric acid	..	2·23

Whatever be the mixture, quenching of the molten mass immediately in cold water gave a higher solubility and this is in keeping with the observation made by Jacob (1953).

From the above, it is evident therefore, that fusion at about 1500°C of the Trichy phosphatic nodules with the proper mixture followed by quenching in cold water would be a solution to the age-old problem of rendering the P_2O_5 in the Trichy nodules available to plants.

With the availability of cheap fuel and power at the lignite mines at Neiveli and the growing fertilizer consciousness in the country, the need for exploiting the natural phosphate resources has been keenly felt of late. The conversion of the phosphorus in the Trichy nodules to a useful form of fertiliser such as ammonium phosphate etc., is being studied. In this connection, it is felt by the authors that the conversion of the nodules to the silico-phosphate form is likely to be cheaper than the conversion to ammonium phosphate. The latter involves multiple processing of the nodules viz., conversion of the phosphate in the nodules to elemental phosphorus, oxidation of the phosphorus so obtained to the oxide through thermal processing, hydration of the oxide to produce phosphoric acid and then again treating the acid with ammonia to be obtained through lignite, whereas the conversion to silico-phosphate involves only one step, of fusing the phosphate mixture at about 1500°C. Moreover, silico-phosphate is found to be the remedy for the problem of phosphate fixation in laterite soils of the Nilgiris and hence will be highly useful to the potato growers of the Nilgiris.

Summary: Work done as early as 1925 by Sivan *et al* had indicated that approximately 8 million tons phosphatic nodules containing nearly 25·6% of total P_2O_5 occur in Utatur village of Ariyalur Taluk in Trichy District. The phosphate in the nodules is in a form unavailable to plants due to its very low citrate solubility. The conversion to the commonly known useful form of fertilizer such as superphosphate was found to be uneconomical due to its high content of calcium carbonate.

Of the various techniques now available, the conversion to "phosphate rock-magnesium silicate glass" was adjudged as the best suited to avoid the use of acids for processing the material into an easily available plant food. The main objective of the study was towards finding out the most suitable mixture with magnesia and silica to obtain a highly citric-soluble fertilizer from the Trichy phosphatic nodule. To start with, pure salts of magnesia and silica were tried and it was found that 10 : 3 : 3 Trichy phosphate, magnesium sulphate and sodium silicate was the best. The next step was to attempt to substitute the pure salts with cheaply available raw material. Olivine and serpentine (from Salem) were used as sources of magnesia and silica. Though it has been reported by other workers that fusion of phosphate rock with olivine or serpentine gives the maximum solubility, yet in the case of Trichy phosphatic nodules it is seen that olivine or serpentine alone was not sufficient and that sodium sulphate is also necessary to bring about the maximum citric acid solubility. Quenching of the hot fusion product was also necessary to get the maximum solubility. Bagasse ash, a waste product from furnaces of sugar factories, which consists mainly of silica was also tried as a cheap source of silica and was

found to give a citric solubility of 50% only by itself and 71% availability when Na_2SO_4 was added to the mixture. 95% availability of the P_2O_5 was achieved in the case of mixture No. 34 consisting of 10 : 3 : 3 of Trichy Phosphatic nodules with serpentine and sodium sulphate fused in the graphite arc furnace.

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