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Optimizing the solubility of low-grade rock phosphate to enable its use as a fertilizer in agriculture

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Abstract

Phosphorus (P) is the second most limiting nutrient for crop production, with 43% of global arable soils deficient in P, significantly restricting crop growth. In India, the rising demand for P-fertilizers is challenged by reliance on imported high-grade rock phosphate (RP) and sulphur. Low-grade RP, suitable for acid soils, offers potential for alternative applications through methods such as mixing with elemental sulphur, partial acidulation and dry compaction with soluble P-fertilizers. RP has been a fundamental raw material for producing phosphatic fertilizers like single super phosphate, diammonium phosphate and nitro phosphates. Despite large reserves of total P in soils, only a small fraction is available to plants, necessitating the continuous application of phosphatic fertilizers to enhance crop yield. The efficiency of water-soluble P fertilizers is low (15–20%) under acidic and neutral to alkaline conditions. Various factors influence the effectiveness of RP as a direct P-fertilizer, including soil properties, plant species and fertilizer management. Efforts to enhance RP's immediate availability include partial acidulation, dry granulation, phospho-composts, microbial solubilization, earthworm casts, calcination and transgenic approaches, offering promising pathways to improve P availability for sustainable agriculture.

Keywords: Phosphorus (P), limiting nutrient, crop production, global soil deficiency, India

Introduction

Phosphorus (P) is the second most limiting nutrient for crop production, with 43% of the world's arable soils being P-deficient, restricting crop growth (Liu *et al.*, 2012) ^[20]. India faces a rising shortage of affordable P-fertilizers due to reliance on imported high-grade rock phosphate (RP) and sulphur for manufacturing. India's RP reserves are estimated at 260 Mt, but only 142 Mt are recoverable, sufficient for 94 years at the current extraction rate of 1.5 Mt/year (FAI, 2002) ^[13]. Low-grade RP, suitable for acid soils, holds potential for alternative use through methods like mixing with elemental sulphur (Basak *et al.*, 1987) ^[5], partial acidulation (Hammond *et al.*, 1986) ^[15], and dry compaction with soluble P fertilizers (Menon and Chien, 1996) ^[22].

Rock phosphate is one of the basic raw materials needed in the manufacture of phosphatic fertilizers like single super phosphate, diammonium phosphate, nitro phosphates *etc.* Liebig in 1840 pointed out that sulphuric acid added to ground bones gave a form of phosphate which was more quickly available to plants than raw bones. The discovery of low-grade mineral phosphates (Apatite) in France and England in 1840 led to the production of first 'artificial' fertilizer superphosphate in England in 1843 from apatite and sulphuric acid by J. B. Lawes. The development of the phosphate industry was secured by the discovery of large sedimentary phosphate deposits in South Carolina (USA). Mining began in 1867 and by 1889 the USA was supplying 90 per cent of the apatite used worldwide for phosphate fertilizer production. Use of phosphoric acid instead of sulphuric acid for apatite dissolution resulted in TSP being commercialized in 1890. In 1917, a new phosphorus fertilizer was developed in the USA by reacting phosphoric acid with ammonia gas to form mono- and diammonium phosphate. $\text{H}_3\text{PO}_4 + \text{NH}_3 \rightarrow \text{NH}_4\text{H}_2\text{PO}_4$ (MAP), $\text{H}_3\text{PO}_4 + 2\text{NH}_3 \rightarrow (\text{NH}_4)_2\text{HPO}_4$ (DAP).

In the late 1920s, the nitro-phosphate process was developed by Erling Johnson in Norway, who named it as the ODDA process after the town of ODDA where it was developed.

$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 + 20\text{HNO}_3 \rightarrow 10\text{Ca}(\text{NO}_3)_2 + 6\text{H}_3\text{PO}_4 + 2\text{HF}$,
 $\text{H}_3\text{PO}_4 + \text{NH}_3 \rightarrow \text{NH}_4\text{H}_2\text{PO}_4$. Rock phosphate, has been the main source for phosphorus fertilizer production since the first commercial development (mining) started in 1867 in South (USA). Commercial rock phosphate occurs in nature as deposits of apatites (P bearing minerals) along with other accessory minerals such as quartz, silicates, carbonates, sulphates, sesquioxides *etc.*, Four types of rock phosphate minerals are: Carbonate apatite $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCO}_3$, Fluoro

apatite $[\text{3Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2]$, Hydroxy apatite $[\text{3Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2]$, Sulpho apatite $[\text{3Ca}_3(\text{PO}_4)_2 \cdot \text{CaSO}_4]$. The apatites of igneous and metamorphic origin are generally regarded as less reactive because of their well-developed crystalline form. However, the apatites of sedimentary rock deposits are soft minerals possessing micro-crystalline structure and are of major commercial importance for direct application in the soil (Narayanasamy and Biswas, 1998) [25].

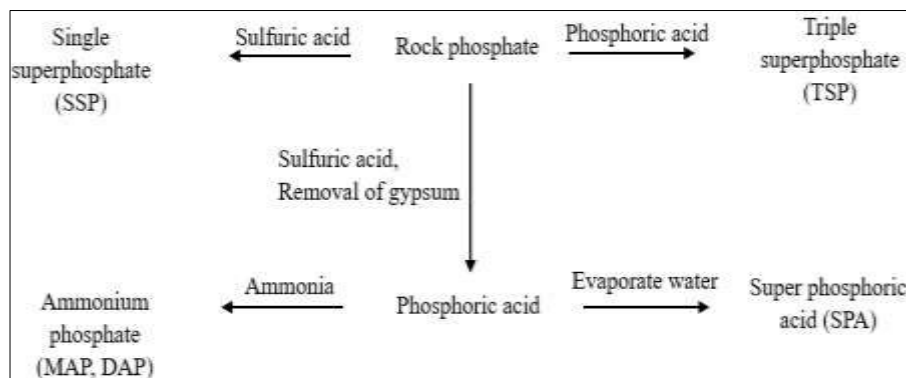


Fig 1: Rock phosphate -A key component for phosphate fertilizers

Availability of rock phosphate

The known global resources of rock phosphate are of the order of 163,000 million tons of all grades and types even though globally adequate rock phosphate is inequitably distributed geographically. Africa contains RP of about 41 per cent, USA has 21 per cent, erstwhile USSR 13 per cent, the Middle East 10 per cent, Asia 8 per cent, South America 3 per cent, while Australia, New-Zeland and Oceania together accounts for only 2 per cent and entire Europe less than 1 per cent. The rock phosphate scenario in India is, however, not very comfortable as it possesses a resource of only 260 million tones (0.19% of the world) of rock phosphate of all types and grades. Out of the total rock

phosphate resource, the country has a predominance of low-grade rock phosphate having only 15.27 million tones reserve of high-grade rock phosphate (Table 1), and the remaining low grade rock phosphate is unacceptable to P-fertilizer industry due to its very low P_2O_5 and high CaCO_3 content (McLean and Ssali, 1977) [21].

Grades of rock phosphate

The classification of reserves of indigenous rock phosphate as done by Indian Bureau of Mines and the purpose for which each grade can be used is given in Table 1 and percent solubility in Table 2.

Table 1: Classification of known reserves of indigenous rock phosphate in India

Grade	P_2O_5 (%)	Reserve (Mt)	Generalized remarks
High	+30	15.27	Could be considered for wet process production of fertilizers.
Medium	25-30	18.95	Could be considered mainly for partially acidulated rock phosphate and for processed phosphates after less beneficiation.
Low	11-25	55.22	About 20% P_2O_5 grade and relatively more reactive material may be considered for partially acidulated rock phosphate production and others for direct application.
Unclassified	--	170.04	
Total	--	259.48	

(Adopted from: Biswas *et al.*, 2006) [40]

Table 2: Phosphorus content in Indian rock phosphate

Rock phosphate	Total P (%)	Water soluble P (%)	Citrate soluble P (%)
Jhabua, M.P	7.25	0.003	1.1
Mussorie, U.K	8.25	0.001	1.19
Purulina, W.B	9.87	0.004	1.25
Udaipur, Rajasthan	8.62	0.002	1.26

(Adopted from: Biswas *et al.*, 2006) [40]

P-fertilizer industry largely depends on sulphur, phosphoric acid, ammonia besides rock phosphate. India imports around 1.7 million tonnes of sulphur, 2-4 million tonnes of phosphoric acid, 1.5 million tonnes of NH_3 and 4.9 million tonnes of rock phosphate for phosphate industry which constitutes a substantial part of our international trade in

fertilizer raw material. Thus, the rapidly increasing price of soluble phosphatic fertilizer has raised interest in cheaper alternatives. Under such conditions, we must explore new methodologies for the utilization of indigenous low grade rock phosphate by converting it into a potential resource of P for direct application to the soil. The direct utilization of indigenous rock phosphate deposits could only alleviate the dependence of the country on foreign supplies.

Factors affecting solubility of rock phosphate

Most of the soils have a large reserve of total P but the amount of P which is actually available to the plants to support optimum plant growth is very small. Therefore, continuous application of phosphatic fertilizers is essential for increasing crop yield. The efficiency of water-soluble

phosphatic fertilizer is generally low (15 to 20%) under both acidic and neutral to alkaline conditions. Several factors influence the direct application of rock phosphate as P-fertilizer. The availability of rock phosphate-P to plant largely depends on the properties of rock phosphate affecting its rate of dissolution, soil characteristics, plant species and fertilizer management practices.

Rock phosphate properties affecting its solubility

Rate of dissolution of rock phosphate in a given soil is determined by its chemical composition which includes apatite lattice composition, the type of accessory minerals and particle size. It has been well established that increasing substitution of CO_3 for PO_4 in the lattice structure increases the solubility of carbonate apatites. This occurs due to decreased a-dimension of the unit cell, and crystal instability on increased incorporation of planar CO_3 and F-1 for PO_4 -tetrahedral (Lehr and McClellan, 1972) [19]. Calcium carbonate is the most abundant accessory mineral in rock phosphates. As CaCO_3 is more soluble than the most chemically reactive apatites and its dissolution increases the concentration of Ca^{2+} and pH at the surface of apatite (Silverman *et al.*, 1952) [34]. Thus, it is not surprising that accessory CaCO_3 reduces the rate of rock phosphate dissolution in some soils (Anderson *et al.*, 1985; Robinson *et al.*, 1992) [2, 32]. However, under field conditions where Calcium may be removed by plant uptake and due to leaching, this effect may be minimized. As the rock phosphates are relatively insoluble materials, their geometric surface area has an important bearing on their rate of dissolution in soil. Bagavathi Ammal *et al.* (2000) [3] reported that the finer particles of rock phosphate (100 mesh) resulted in higher values of dissolution than relatively coarser particles (60 mesh). This might be due to the fact that finer the particle size, the greater the degree of contact between rock phosphate and soil, and therefore, greater the rate of dissolution.

Soil properties affecting rock phosphate solubility

In addition to the properties of rock phosphate, the efficiency of rock phosphate also depends on its reaction and retention in the soil, and on the chemical properties and type of soil to which it is applied (Chien and Hammond, 1978) [9], however, Anderson *et al.* (1985) [2] reported that no single soil characteristic has a consistent and predominant effect on P release. However, pH buffering capacity was nearly twice as important as any other soil parameter. Studies (Rajan 1991) [29] indicated that the amount of rock phosphate-P dissolved, decrease either exponentially or linearly with the increasing soil pH. Following the law of mass action, the dissolution of rock phosphates is favored as long as Ca concentration in the soil solution is maintained at a lower level. A sensitivity analysis using the Kirk and Nye model (Kirk and Nye, 1986) [18] showed that the rate of dissolution of rock phosphate is highly sensitive to Ca^{2+} activity in the soil solution. A linear relationship between the log of Ca^{2+} activity and log of P in soil solution has been reported by Robinson and Syers (1991) [32].

Capacity of the soil to retain P and soil moisture are also important soil parameters affecting rock phosphate dissolution. Dissolution of rock phosphate is considerably enhanced by the soil if it remains sufficiently wet to allow the dissolution products to be transported away from the

surface of the rock phosphate particles. The water retained at field capacity is sufficient to support near potential maximum dissolution. The positive influence of organic matter on rock phosphate dissolution has also been recognized which is due to its high cation exchange capacity (CEC) and organic acids produced as a result of microbial and chemical transformation of organic debris. The CEC of organic matter which exceeds even 200 cmol kg^{-1} soil enhance rock phosphates dissolution by increasing the Ca buffering capacity of the soil. Numerous organic acids (*e.g.*, oxalic, citric, tartaric, gluconic *etc.*) have been reported to be produced in the soil as a result of microbial and chemical transformation of organic debris.

Influence of plant species on rock phosphate solubility

There are marked differences in the ability of plant species to extract P from rock phosphates which has been recognized as early as 1898 (Flach *et al.*, 1987) [14]. Plants can influence the rate of rock phosphates dissolution by the secretion of acid or alkali, uptake of large quantity of Ca, production of chelating organic acids (citric, malic and 2-ketogluconic acid) which complex Ca and deplete P in the soil solution. A huge amount of literature is available on the root induced pH changes in the rhizosphere. The causes of the pH change are attributed to the imbalance in the proportion of anionic (usually NO_3^- , H_2PO_4^- , SO_4^{2-} and Cl^-) and cationic nutrient (K^+ , Ca^{2+} , Mg^{2+} and Na^+) uptake by the plants. This imbalance in the rhizosphere is corrected by the release of either H^+ or $\text{OH}^- / \text{HCO}_3^-$ as the case may be, thus altering the pH of the rhizosphere. Increased soil acidity in the rhizosphere can enhance rock phosphate dissolution. Since rock phosphates are essentially calcium phosphate compounds, removal of Ca from rock phosphate will release P into solution. Thus, effective utilization of rock phosphate by some plant species (*e.g.*, buckwheat and rapeseed) has been attributed to their high Ca uptake. Flach *et al.*, (1987) [14] determined the ability of maize, pearl millet and finger-millet to utilize P from rock phosphates in a pot experiment. They concluded that finger-millet utilized maximum P from rock phosphates followed by pearl-millet and maize. This was attributed to a greater Ca uptake by finger-millet. Thus, plant species influence P dissolution through secretion of acids, uptake of Ca, increased acidity of the soil etc. The choice of the crop is, therefore, very important for maximizing the solubility of rock phosphate.

Methods to improve solubility of low-grade rock phosphate

There are only a limited number of climatic and soil situations in which rock phosphate is sufficiently reactive for use as direct P-fertilizer. Keeping in view, numerous studies have been conducted to amend rock phosphate, in order to increase its immediate P availability and enhance its rate of dissolution after application to the soil. The various amendments include: partial acidulation of phosphate rock, dry granulation compaction process, phospho-composts, earthworm casts, use of phosphorus solubilizing microorganisms, VAM, calcination of non-apatite phosphate rock and transgenic approach.

Partial acidulation of rock phosphate

Partially acidulated rock phosphates (PARP) are rock phosphates which have been acidulated, usually with sulphuric or phosphoric acid with less than the quantity of

acid needed for making SSP or TSP. In the field, PARP has been found to enhance the dissolution of rock phosphate when compared with that of directly applied rock phosphate (Rajan and Watkinson, 1992) [28]. The PARPs are consistently inferior to any commercial fertilizer but markedly superior to rock phosphate, in terms of P uptake by plant, but the benefits of PARP were only for short term as in the long run the unacidulated part of PARP is unable to solubilize in alkaline conditions. $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 + 7y \text{H}_2\text{SO}_4 + 3y \text{H}_2\text{O} \rightarrow 3y \text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + 7y \text{CaSO}_4 + 2y \text{HF} + (1-y) \text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$

Kato *et al.* (1995) [16] reported that P recovery in the soil was 0.25 per cent for the North Carolina rock phosphate, whereas, it ranged between 1.2-1.6 per cent for the corresponding 50 per cent PARP. Various scientists have tried acidulation of rock phosphate with different acids,

singly or in combination, in different ratios. Rajan *et al.* (1994) [30] compared the relative effectiveness of PARP prepared from 30 per cent acidulation of North Carolina rock phosphate with H_2SO_4 and H_3PO_4 . H_2SO_4 - PARP was found inferior to H_3PO_4 - PARP containing similar amounts of water-soluble P. This was attributed to the presence of CaSO_4 coatings. The performance of PARP prepared from the mixture of $\text{HNO}_3 + \text{H}_2\text{SO}_4$, $\text{HNO}_3 + \text{HCl}$, $\text{HNO}_3 + \text{H}_3\text{PO}_4$ at 10 and 20 per cent acidulation was tried by Basak and De (1997) [4]. Research on the agronomic effectiveness of PAPR has been reviewed (Bolan *et al.*, 1990) [7] and the general conclusion is that PAPR of 40-50 percent acidulation with H_2SO_4 or 20-30 percent acidulation with H_3PO_4 are as effective as fully acidulated SSP. In soils of a high pH (pH 6.5-8.0), PAPRs may be as effective as superphosphate (Hammond *et al.*, 1986) [15].

Table 3: Total, water soluble and citrate soluble phosphates of PAPR

RP source	Sulfuric acid acidulation level (%)			Phosphoric acid acidulation level (%)		
	Total phosphate (% P)					
	25	50	75	25	50	75
Mussoorie	8.96	8.20	7.40	10.80	11.98	14.40
Udaipur	7.20	6.20	6.00	8.97	9.60	11.20
Purulia	7.20	6.80	6.20	10.00	11.20	12.00
North Carolina	11.20	9.60	9.00	14.40	15.20	16.40
Water soluble phosphate (% P)						
Mussoorie	0.37	0.71	1.17	0.56	0.59	1.08
Udaipur	0.54	1.06	1.53	0.69	1.26	2.90
Purulia	0.73	1.77	2.49	1.16	2.71	3.90
North Carolina	1.25	3.69	4.07	1.24	4.69	7.77
Citrate soluble phosphate (% P)						
Mussoorie	0.73	0.92	1.15	1.36	2.31	4.41
Udaipur	0.48	0.50	0.41	1.47	1.44	1.83
Purulia	0.36	0.58	1.24	0.77	1.39	1.71
North Carolina	1.87	1.40	1.45	3.33	2.18	1.30

(Source: Biswas *et al.*, 1998) [25]

Dry granulation compaction process

Under certain conditions, such as low RP reactivity, high soil pH, or short-term crop growth, the agronomic use of rock phosphate may not be optimum. Mixing rock phosphate with water soluble phosphorus (WSP) by

compaction process (Fig. 2) can sometimes be an agronomically and economically effective. This is called as starter effect that results in better plant root development that may utilize rock phosphate more effectively than if rock phosphate is applied alone (Chien and Hammond 1978) [9].

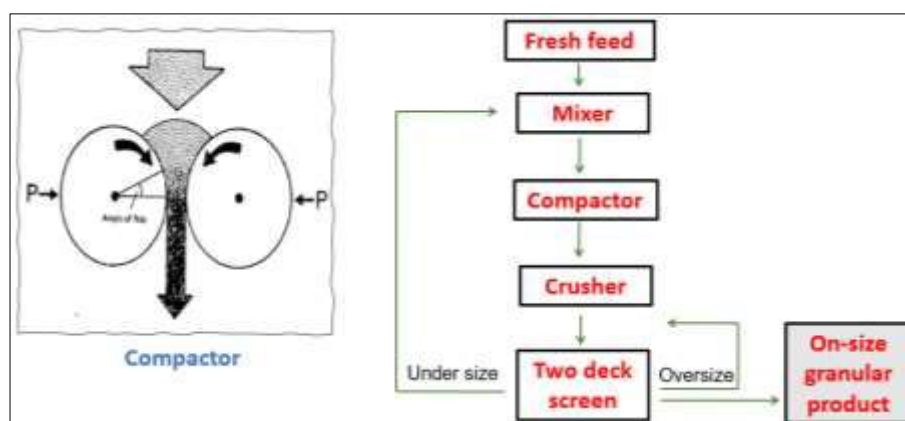


Fig 2: Dry granulation compaction process

Research on effectiveness of panda hills phosphate rock compacted with triple superphosphate as source of phosphorus for wheat and maize was conducted by Mnkeni *et al.*, (2000) [23] in international fertilizer development center, Alice, South Africa.

The performance of the modified Panda PR products as reflected by yield and grain P uptake of wheat (Table 4) followed the order $\text{TSP} > (\text{RPR} + \text{TSP}) > (\text{RPR}) + (\text{TSP})$. The mixture of Panda PR and TSP resulted in significantly lower yields and P uptake than the compacted product even though they both had the same amount of water-soluble P. This

could be attributed to the fact that the water-soluble P in the (RPR)+(TSP) mixture being in powder form was more

susceptible to fixation due to greater contact with soil minerals than in the compacted and granulated product.

Table 4: Wheat grain yield, relative agronomic effectiveness (RAE), and P uptake as influenced by modified products of Panda-Hills phosphate rock. (Mnkeni *et al.*, 2000) ^[23]

P-sources	P rate (mg P kg ⁻¹)	Grain yield (g pot ⁻¹)	RAE (%)	Grain P uptake (mg P kg ⁻¹)	Relative efficiency in P uptake (%)
Control	0	0d	--	0d	--
PPR	100	0d	0	0d	0
(PPR)+(TSP)	100	10.7c	51	13.6c	36
(PPR+TSP)	100	15.0b	72	23.1b	61
TSP	50	14.6b	70	21.0b	55
TSP	100	20.9a	100	38.0a	100

Note: PPR = Panda PR; (PPR+TSP) = Physical mixture of PPR and TSP; (PPR+TSP) = compacted mixture of PPR and TSP.

Phospho-Composts

The loss of soil organic matter due to intensive agriculture is responsible for a decrease in soil fertility. The most common practice to preserve and restore soil fertility is to add organic matter to these soils regularly. The feasibility of commercial production for P-fertilizers by partial acidulation and compaction are low due to the cost involved in those methods. Considering all these factors, there is a need to develop a cost effective, eco-friendly and sustainable system where the supply of P to plants can be ensured. Preparation of rock phosphate enriched compost (RP-compost) using crop residue holds a lot of promise in developing countries like India. To explore the possibility of increasing the availability of P from low-grade RP incorporated during decomposition of rice straw where potential biochemical transformations of P could be expected.

Moharana *et al.* (2015) ^[25] conducted an experiment to evaluate mineralization of phosphorus in soil as influenced by rock phosphate enriched compost and chemical fertilizers. Changes in Olsen-P during the course of incubation period revealed that at the start of incubation, Olsen-P ranged from 6.1 to 20.4 mg kg⁻¹ in different treatments. At 7 days of incubation, values of Olsen-P ranged from 6.1 mg kg⁻¹ in control to 18.7 mg kg⁻¹ in treatment receiving 100 per cent NPK. The Olsen-P in soil treated with 100 per cent NPK decreased rapidly up to 30 days of incubation, followed by a slower decrease during the remaining period of 120 days. The soil treated with RP enriched compost showed a declining trend in Olsen-P during the initial stages up to 30 days, but improved significantly with the progress of incubation period, indicating that RP enriched compost released P for a longer period. At the end of incubation of 120 days, the Olsen-P ranged from 5.7 mg kg⁻¹ in control to 20.6 mg kg⁻¹ in treatment receiving RP enriched compost + 50 per cent NPK. While, Olsen-P was 15.1 mg kg⁻¹ in soil treated with only RP enriched compost. It is also observed that the Olsen-P in soil treated with any of the P sources declined up to 30 days of incubation which may be due to fixation of available P into unavailable forms.

Mobilization of Phosphorous by earthworm casts

Earthworm casts are the indurated soil material surrounding channels left in the soil by earthworms. Casts are initially quite unstable, since they are essentially puddled soil emitted from the earthworm's gut. Earthworm enhance nutrient availability through casting mainly in tropical soils. The positive effects of earthworms on the availability of Phosphorous to plants is due to increased microbial population and hence enzyme activity in the casts (Tiwari *et*

al., 1989) ^[37]. Microorganisms in earthworm gut obtain their nourishment from the ingested organic material while earthworms promote soil microbial activity through their microorganism-rich casts. The abundance of fulvic acids, humic acids and enzymes in earthworm cast enhances the solubility of the RP.

Phosphorus solubilizing microorganisms

Microorganisms have evolved several mechanisms to mobilize and mineralize occluded and insoluble phosphorus (P), thereby promoting plant growth in terrestrial ecosystems. To access P of various forms, plants are aided by the growth and activity of soil microorganisms, which possess metabolic mechanisms to mineralize and mobilize plant inaccessible P into orthophosphate by enhanced dissolution of P containing minerals through soil acidification or release of metal chelating ligands *e.g.*, organic acids, siderophores, *etc.*, (Khan *et al.*, 2014) ^[17]; secretion of extracellular enzymes to mineralize organic P and reductive dissolution of Fe(Al)-complexed organic P (Chen *et al.*, 2018) ^[8]. Although, a number of organisms *e.g.*, *Pseudomonas*, *Burkholderia*, and *Bacillus* spp. have been identified as phosphate-solubilizing bacteria (PSB), *Penicillium* spp. and *Aspergillus* spp. as phosphorus solubilizing fungi and some phosphorus solubilizing actinomycetes.

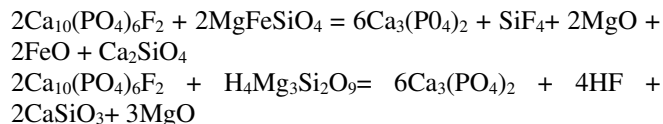
Vesicular-Arbuscular Micorriza (VAM)

VAM improves P uptake by plants because of presence of special structures known as vesicles and arbuscules. The highly branched arbuscules help in the transfer of nutrients from the fungus to the plant-root cells. *E.g.*, *Glomus fasciculatum*, *G. mosseae*, *G. etunicatum*, *G. tenue* and *Giaspora margarita*. Enhanced P uptake in VAM-infected plants seems to be facilitated by; fungal hyphae exploring a greater volume of soil for P, fungi dissolving sparingly soluble P minerals (*e.g.*, RP), infected roots increasing the rate of P uptake, by increasing the diffusion gradient by depleting P to lower P concentrations than can non-mycorrhizal roots. The P inflow rates of mycorrhizal roots are calculated to be 2-6 times those of non-mycorrhizal roots. Compared with non-mycorrhizal plants, Pairunan *et al.* (1980) ^[27] have reported that mycorrhizal plants enhance the effectiveness of fertilizers by about 30 per cent.

Preparation of fused calcium magnesium phosphate (FCMP) – A thermal fertilizer

Fused Calcium Magnesium Phosphate (FCMP) is manufactured either by fusing phosphate rock with lime stone and quartzite at 1400-1450 °C in an open hearth or

shaft furnace. Phosphate rock can also be fused at lower temperature of 1250-1350 °C in presence of magnesium minerals like serpentine *i.e.*, hydrated magnesium silicate ($\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9$) or olivine (Mg, Fe^{2+}) $_2\text{SiO}_4$. These additives form eutectics, which assists in reducing the fusion temperature. The melt leaving the furnace is quenched with water so as to disintegrate into fine granules and also assists in preserving high percentage of citrate soluble P_2O_5 in the product. Fused phosphates contain about 80-90 percent P_2O_5 in citric acid soluble form. (Dwivedi and Gupta, 2006) ^[10] FCMP is widely used in China, South Korea, Japan, Vietnam, Russia, Brazil and USA. The chemical reactions are as follows.



Advantages of thermal phosphate includes; a) Utilizes secondary phosphate ores which are not suitable for beneficiation, b) Low cost as well as long lasting fertilizer, c) No adverse effect on soil fertility, d) Viable alternative to either SSP or DAP, e) Calcination removes impurities and increases P concentration, f) Do not fixed or revert to soil, not readily leached, h) Free running and will not cake,

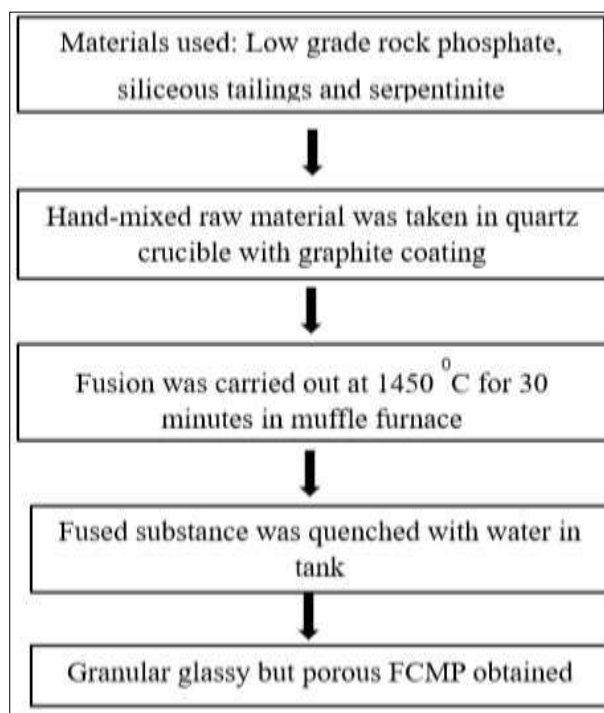


Fig 3: Flow chart representing preparation of fused calcium magnesium phosphate

Calcination of non-apatite phosphate rock containing crandallite mineral ($\text{CaO} \cdot 2\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$)

Calcination is a matured and technically sound technology. The product obtained after calcining phosphate ore at a temperature of 1250-1350 °C, is called calcined phosphate. Calcination of phosphate ore removes most of the organic, carbonate, fluoride and other impurities. Calcination is usually carried out by heating phosphate rock along with silica in the presence of soda ash at 1250-1350 °C, in rotary kiln. It has been found that the presence of silica promotes the disintegration of apatite lattice, which speeds up removal of fluorine. Calcined phosphate have a significant portion of phosphate in citrate soluble form.

It is effective in acidic soils and is extensively used in Australia, Germany, Russia, USA, Malaysia, Indonesia, Vietnam, England, Belgium *etc.*, various types of calcined phosphate available in the international market are shown in the Table 6 and 7. In India, calcined phosphate could be preferably used in acidic soils of high rainfall area of Kerala, Orissa, West Bengal, North Eastern States, Tamil Nadu *etc.* Such area occurs to an extent of about 149 million hectares. In India, calcined phosphate could be preferably used in acidic soils of high rainfall area of Kerala, Orissa, West Bengal, North Eastern States, Tamil Nadu *etc.* Such area occurs to an extent of about 149 million hectares.

Table 5: Various calcined phosphate available in international market

S.L. No.	Trade name of calcined product	Country	Available phosphate (%)	Citric acid solubility (%)
1	Rhenania	Germany	33	100
2	Base Phosphate	Belgium	N.A	N.A
3	Supra Phosphate Belgium N.A N.A	Belgium	N.A	N.A
4	Thermo Phosphate	Senegal 20-40	80-90	
5	Phospal	Senegal	34	80
6	Christmas Island calcined phosphate	Christmas Island	N.A	26

Table 6: Comparison of solubility of phosphorous between Calcined and uncalcined non-apatite phosphate rock containing crandallite mineral ($\text{CaO} \cdot 2\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$)

P source	Total P	NAC	2% CA
	g kg ⁻¹		
Uncalcined Sapucaia PR (Ca–Al–P)	112	1.30	0.50
Calcined Sapucaia PR (Ca–Al–P)	128	114	24.9
Uncalcined Juquia PR (Ca–Al–P)	64.6	0.90	0.00
Calcined Juquia (Ca–Al–P)	77.3	39.3	1.30
Gafsa PR (Ca – P)	127	26.0	46.1

Plants strategies

Phosphorus acquisition

Plants are known to adapt several mechanisms to increase their P acquisition, uptake, absorption efficiency such as; modification of soil exploration by roots through increasing absorptive area. Better symbiosis with soil microbes such as arbuscular mycorrhizal fungi (Sukarno *et al.*, 1993) [36]. Modification of rhizosphere to increase P availability through release of bio-molecules increased production of phosphatases enhanced rate of P uptake.

Phosphorus translocation

The P transporters actually are proton/phosphate ($\text{H}^+/\text{H}_2\text{PO}_4$) symporters, moving P ions against large gradients of charge and P concentration (From 2 mM to 10 mM) through proton-coupled co-transporter proteins. In active proteoid-root cells, H^+ and organic anions are exported separately by the modification of plasma membrane (Yan *et al.*, 2002) [39]. When external-P level drops low to micro-molar concentration, the high affinity transporter mRNA transcripts in roots increase, leading to enhanced capacity of roots for P uptake.

Preparation of metallic-humic-phosphate (MHP): a rhizosphere-controlled fertilizer (RCF)

The preparation of fertilizers containing MHP complexes with a large proportion of water-insoluble complexed P that can be solubilized by the organic anions released by plant roots as an expression of P metabolic need, these fertilizers are called as “rhizosphere-controlled fertilizers” (RCF). These types of fertilizers are produced through the simultaneous reaction of rock phosphate with phosphoric acid in the presence of at least, two metals, and a specific proportion of an HA (Erro *et al.*, 2007) [12]. This reaction leads to the formation of complexes between HA and P through metal bridges involving one or two metals. The formation of MHP involving two metals leads to the formation of water-insoluble MHP complexes, while the presence of only one metal in the complex is associated with a fraction of MHP complexes that are partially soluble in water. For instance, the reaction involving Mg and Zn oxides or carbonates favored the formation of a significant concentration of water-insoluble MHP complexes containing both Mg and Zn (around 70%), while the water-soluble fraction involving MPH complexes containing either Mg or Zn was minor (Fig. 7). The concentration of humic acid also influenced the water solubility of MHP complexes (Erro *et al.*, 20011) [11].

Citric acid loaded nano clay polymer composite (CA-NCPC) for solubilization of Indian rock phosphates was studied by Roy *et al.* (2018) [33]. The surface morphology of synthesized NCPC with and without citric acid loading was observed under SEM. The NCPC formed by polymerization

of acrylic acid and acrylamide in the N environment had a rough and irregular surface morphology with visible pore spaces on the surface. The crystal of citric acid was deposited on the surface as spindle and fine needle shaped objects when citric acid was loaded.

The periodic data of available soil P as influenced by variable P sources indicate that CA-NCPC + indigenous RP (Udaipur and Purulia) maintained available mean P status of 17.4 mg P kg⁻¹ and 17.6 mg P kg⁻¹, respectively which was statistically at par with DAP (18.4 mg kg⁻¹). The Purulia and Udaipur RP brought about 60.6 and 62.5 per cent increase in available P, respectively over unfertilized control; while DAP brought about 96.7 per cent increase in available P over control. Among the three levels of CA-NCPC employed for P solubilization from indigenous RP the maximum available P status was observed at 40 mg citric acid kg⁻¹ (82.2% increase in mean P over control). The mean available P status was 13.8 mg kg⁻¹ when no CA-NCPC was applied, while 18.9 and 19.8 mg P kg⁻¹ were observed with application of CA-NCPC at the level of 20 and 40 mg kg⁻¹ soil, respectively.

Formulation of phosphorous rich organic manure (PROM) from rock phosphate and its dose optimization for the improvement of maize (*Zea mays* L.) was evaluated by Noor *et al.* (2020) [26]. Results revealed that gradually plant height increased under all five treatments ranging from 108.8 to 152 cm. Highest plant height was observed under the treatment T₅ (Combination of recommended dose of N, P, K from DAP, and full dose of P from PROM) and the lowest height was from the treatment T₂ (Recommended N and K but zero P) combination of recommended dose of N, P, K from DAP, and full dose of P from PROM. Plants with appropriate amount of nutrients ensure healthy plant roots resulting in good plant health. When PROM was applied, the root length significantly increased. T₅ (Recommended N, K, P from DAP and PROM) with full dose of N, K, P from both organic and inorganic source, which showed the highest root length (9 cm). The lowest length of roots was observed in T₂ (Recommended N, K, P₀) where phosphorus application was zero and only nitrogen and potassium source of fertilizers were used. This is because, growth of roots in soil is depend upon the availability of nutrients and water, more the nutrients longer will be the plants root. Root of the plants treated with phosphorus enriched compost was longer than the control. Weight of freshly harvested roots was recorded, and it was observed that as the amount of PROM increased, the weight of the plant roots also increased. Treatment T₅ (Recommended P, K, N from DAP and PROM) resulted in the highest weight of plant roots (3.88 g). As the amount of organic manure decreased the weight of the freshly harvested roots also decreased. From the study it is concluded that there was a significant increase in yield and various yield components with integrated use of organic manures and inorganic phosphorus source that is RP as compared to sole organic fertilizer or inorganic rock phosphorus.

Roy *et al.* (2018) [33] studied about citric acid loaded nano clay polymer composite (CA-NCPC) for solubilization of Indian rock phosphates and concluded that the combined action of CA-NCPC and indigenous RPs acted as a slow release fertilizer material which would help to synchronize the P supply with crop demand, reduce the chances of P-fixation and enhance the P use efficiency Tapping this green technology at field scale would allow to harness the benefits

of indigenous RPs and help in replacing the costly phosphatic fertilizers, if not fully but partially.

Mineralization of phosphorus in soil as influenced by rock phosphate enriched compost and chemical fertilizers was evaluated by Moharana *et al.* (2015) [25]. Results revealed that soils treated with different RP enriched compost along with chemical fertilizers mineralized greater amount of P. Soil treated with RP enriched compost showed a declining trend in Olsen-P during the initial stages up to 30 days, but improved significantly with the progress of time, indicating that RP enriched compost releases P for longer period which, in turn, supply P to crops for a longer growth period. Field experiment on effectiveness of panda hills phosphate rock compacted with triple superphosphate as a source of phosphorus for wheat and maize was conducted by Mnkeni *et al.* (2000) [23]. The mixture of PPR and TSP as well as the compacted product increased wheat and maize yields and phosphorous uptake significantly. Increase in the yield were, however, largely attributed to the TSP component of the (PPR)+ (TSP) mixture with little contribution from PPR.

Mineralization of soluble P fertilizers and insoluble rock phosphate in response to phosphate-solubilizing bacteria and poultry manure was studied by Abbasi *et al.* (2015) [1] and results of incubation experiment indicated that chemical P fertilizers used in the study, *i.e.*, SSP and DAP, released the highest P at the start of the experiment, but this mineral P significantly decreased with subsequent incubation periods. However, the use of PSB and PM with RP in the combined treatment (1/2 RP+1/2 PM+PSB) released a substantial amount of P (25 mg kg⁻¹) that remained at high levels (Without any loss) until the end of incubation (Day 60), showing that the combination of PSB and PM with RP may be a feasible option for releasing P from insoluble RP for a longer period.

Release of phosphorous by using phosphate rich organic manure (PROM) from RP and to determine the amount of released phosphorus uptake by maize plants was evaluated by Noor *et al.* (2020) [26]. It was revealed by results that by using combination of PROM and DAP sufficiently increased various yield components like height and biomass yield. PROM also indicated changes to other soil associated properties like EC (dSm⁻¹) and pH. Treatment receiving PROM and Recommended NKP) showed maximum plant growth, yield, and concentration of nutrients among all the treatments.

Conclusion

Partially acidulated low-reactive RP (PARP) proved to be an agronomically effective P source. Phosphorus uptake from low-grade RP (LGRP) in presence of water-soluble phosphate (compacted RP) was higher than that from RP alone, indicating the starter effect of water-soluble P on improving the effectiveness of LGRP. The reactivity of low-reactive non-apatite RP can be significantly increased through calcination and the calcined RP can indeed be used for upland and flooded rice. RCF was more efficient P source than SSP or dicalcium phosphate (DCP) in relation to P extraction in acid soil. Even low-grade rock phosphate can be efficiently used in alkaline and neutral soil conditions if it is amended with organic matter, composted with organic/farm waste, incorporated with green manure, partially acidulated with commercial acids, use of PSB or used in conjunction with certain chemicals.

Partially acidulated low-reactive RP (PARP) proved to be an agronomically effective P source. The reactivity of low-reactive non-apatite RP can be significantly increased through calcination. Thus, we can reduce a lot of financial burden from our economy by reducing the import of rock phosphate and other byproducts required in the manufacture of commercial P- fertilizer.

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