

Enhancing solubility of low grade phosphorus minerals

for their utilization as plant nutrients

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Phosphorous (P) is one of the essential, least available and least mobile mineral nutrients to the plants where its concentration ranges from 0.1 to 0.5%. Orthophosphates, $H_2PO_4^-$ and HPO_4^{2-} are the primary forms of phosphorus taken up by plants. When the soil pH is less than 7.0 $H_2PO_4^-$ is the predominate form in the soil while above pH 7, HPO_4^{2-} form available. But due to low phosphorus use efficiency, P-deficiency is a significant challenge for agricultural productivity on acidic and calcareous soils in many regions of the world.

Key words: Minerals, Nutrients, Phosphorus, Plant, Utilization

PHOSPHORUS is known to play an important physiological and biochemical role in crop plants, animals and micro-organisms as a component of nucleic acid, phospholipids that compose cellular membranes, ATP and ADP molecules and intermediate compounds of respiration and photosynthesis.

Rock phosphate is the major raw material required for the manufacture of a number of phosphatic fertilizers. The phosphate rock means any rock containing large proportion of phosphate minerals that can be used for such commercial purposes as manufacture of fertilizers. About 150 minerals containing more than 1% P_2O_5 occur in nature, but minerals belonging to two groups namely 'apatites' and 'aluminous phosphates' are of commercial importance.

In India the total resources of rock phosphate as per United Nations Framework Classification for Fossil Energy and Mineral Reserves and Resources system is placed at 296.3 million tonne, as on 1 April 2010.

Out of these, the reserves constitute only 34.8 million tonne whereas 261.5 million tonne are under remaining resources category. Of the total resources, 36% are in Jharkhand, 30% in Rajasthan, 17% in Madhya Pradesh, 9% in Uttar Pradesh, and 8% in Uttarakhand.

Scope of rock phosphate

Cost of applying conventional water soluble P fertilizer is high in India because their manufacture requires importing high-grade rock phosphate and sulphur. So use of indigenously available low-grade rock phosphate is gaining importance in India. There are four types of rock phosphate (RP) available in Jhabua (Madhya Pradesh), Mussorie (Uttarakhand), Purulina (West Bengal) and Udaipur (Rajasthan). Out of it Udaipur rock phosphate has highest percentage of total phosphorus content (8.62%).

Choice of fertilizer

P-fertilizers are divided into three groups on the basis of solubility; the

water soluble group, citrate soluble, and acid soluble (Fig. 1). The rock phosphate and bonemeal are applied directly in large amounts to acid soil, where the sparingly soluble phosphates are converted into a form usable by plants.

Mixing low-grade rock phosphate with water soluble phosphorus- dry granulation compaction process: Under certain conditions, such as low rock phosphate reactivity, high soil pH, or short-term crop growth, the agronomic use of rock phosphate may not be as feasible as water soluble phosphorus. Mixing rock phosphate with water soluble phosphorus by compaction process can sometimes be an agronomically and economically effective P-source under these conditions. The explanation is that water soluble phosphorus can provide initially available P to plants (starter effect) that results in better plant root development that in turn may utilize rock phosphate more effectively later then, if rock phosphate is applied alone.

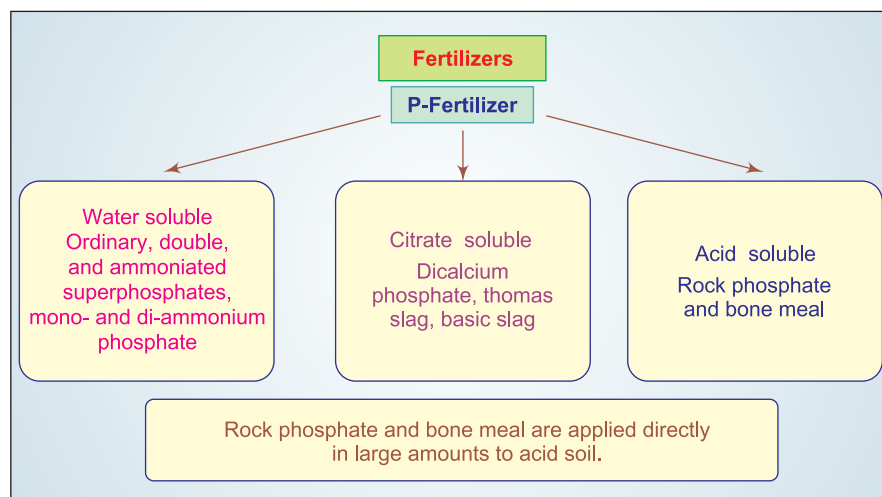


Fig. 1. Classification of P-fertilizer on the basis of solubility.

Mobilization of P through earthworm

Earthworm enhances nutrient availability through casting mainly in tropical soils. The positive effects of earthworms on the availability of N and P to plants is due to increased microbial population and hence enzyme activity in the casts. Extractable P and S also showed significant increase in casts during incubation. In red soil casts, Bray's P (an estimate of available P in acid soils) increased 2-fold compared to non-ingested soil (Table 1).

Table 1. Effect of soil ingestion by earthworms on extractable phosphorus (mg kg⁻¹)

Treatments	Days of incubation				
	0	7	14	21	28
<i>Red soil</i>					
With worm	6.3	9.8	9.1	11.7	12.2
Without worm	6.8	6.8	7.5	6.8	6.4
<i>Black soil</i>					
With worm	4.2	9.7	11.4	14.8	15.3
Without worm	4.21	4.6	5.1	5.6	5.5

In black soil casts the Olsen's P (an estimate of available P in neutral and calcareous soils) increased by more than 3-fold and α 2- to 12-fold increase in alkaline phosphatase. It is hence possible that some of the ester-bound P and S are hydrolyzed to inorganic P and S, thereby, contributing to their availability.

Application of lime in acid soil

Fertilizer application time: In acid soil the contact time had a highly significant impact on the phosphate uptake on crops. Phosphate fertilizer,

given 6 months before seeding, yielded a significantly lower recovery than phosphate fertilizer applied just before seeding. In the calcareous soil the fertilizer/soil contact time had no influence on the P-uptake as there is no major formation of unavailable calcium phosphates.

Liming: Phosphate adsorption is a peculiar problem in highly weathered soils of the tropics (oxisols and ultisols) because of their high phosphate adsorption potential. Most of these soils are acidic and require liming which does not improve phosphate availability in all cases. Liming may induce polymerization of aluminium cation species which because of their high positive charge are strong phosphate adsorbers. It was found that there is a decrease of phosphate availability due to liming of oxisols which is associated with their very low pH (3.7 to 4.4) whereas at a soil pH of 5.5 liming had a beneficial effect on phosphate availability. To save fertilizer phosphate on these strongly phosphate-fixing soils, band placement of fertilizers is recommended.

Fertigation: It is the application of fertilizers, soil amendments, or other water-soluble products through an irrigation system, it was observed that fertigated single super phosphate enhanced the grain yield of wheat significantly compare to fertigated diammonium phosphate over broadcast method. The yield potential was lower in (4,882 kg/ha) in fertigated diammonium phosphate

than fertigated single super phosphate (5,249 kg/ha). This showed that fertigation with diammonium phosphate is less effective than fertigation with single super phosphate.

Phosphorus solubilizing microorganisms

Phosphorus solubilizing bacteria *Bacillus* and *Pseudomonas*; PSB fungi such as *Penicillium* spp. *Aspergillus* spp., *Actinomyces* spp. and inoculation with *A. awamori* into the composting mass increased the content of total P as well as water soluble phosphorus and citrate soluble phosphorus. Introduction of *A. awamori* increased the CSP possibly due to release of organic acids in greater extent through microbial mediated processes during composting. Also, significant increase in organic P was observed due to inoculation with *A. awamori* as compared to the control. Fungus transformed the P in rock phosphate from insoluble to soluble form. Microbial biomass, carbon and acid phosphatase activity increased significantly when rock phosphate-compost was inoculated with *A. awamori*. The result was reverse of alkaline phosphatase activity. This might be attributed to the fact that *A. awamori* releases various acids during the process of composting, which in turn, increased acid phosphatase activity and decreased alkaline phosphatase activity.

Root foraging strategies

These strategies improve acquisition of soil P, support higher yields in low P soil and thus lower the critical P requirement for plant growth. This enables fertilized agriculture to be operated at lower plant available P-concentrations and this, can slow the rate at which P-accumulates in moderate to high P-sorbing soils.

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.

- Modification of rhizosphere to increase P availability through release of bio-molecules.
- Increased production of phosphatases.
- Enhanced rate of P uptake.

Recent advancements in the production of slow release phosphatic fertilizers

Regarding developments in phosphatic fertilizers, it is interesting to mention that most of the widely used soluble P-fertilizers were developed in early-or mid-nineties. Some of the recent findings are polymer coated water soluble P-fertilizers, rhizosphere-controlled fertilizer, organic complexed superphosphate, slow-release phosphate fertilizer with super absorbent property, nano-clay polymer composite containing phosphorus and double-coated slow-release phosphatic fertilizer.

Polymer-coated water-soluble phosphorus fertilizers: Recently, some fertilizer companies have developed thin coating of water soluble phosphorus fertilizers (DAP, MAP, TSP) with water-insoluble polymers, with or without S, as a slow-release P-fertilizer. Another type is coated with water-soluble polymers to reduce the rate of water soluble phosphorus conversion to water insoluble P by soil-fixation. Thin polymer coating of mono-ammonium phosphate (MAP) improved plant recovery of fertilizer P and provided a modest barley grain yield advantage relative to uncoated MAP.

Rhizosphere-controlled fertilizer

The 'rhizosphere-controlled fertilizer' are specific fertilizers having nutrient release patterns that are dependent on plant activity in the rhizosphere. This fertilizer is based on the introduction of an organo-mineral matrix composed of metal and humic phosphates. Some researchers compared the cumulative water solubility of P in NPK-RCF (19:9:11) with that in the standard fertilizer of same chemical composition (19:9:11). The P in the

standard fertilizer was introduced as simple superphosphate. The NPK-RCF fertilizer presented a slow release rate of nutrient P, whereas the equivalent NPK fertilizer presented a rapid release of the P fraction soluble in water.

Utilization technology of non-conventional or non-apatite rock phosphate

There are limited rock phosphate deposits in the world that contain Ca-Al-P minerals in crandallite ($\text{CaO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$). Due to its high Al content, the non-apatite rock phosphate is not suitable for the conventional chemical acidulation process. The natural crandallite rock phosphate sources are very low in reactivity and therefore, not suitable for direct application. The reactivity, however, can be significantly increased upon calcination at temperatures ranging from 450° to 700°C. Recently, in a study it was observed that the solubility of two calcined crandallite rock phosphate sources in neutral ammonium citrate increased and reached a maximum at 500°C upon calcinations. After calcination, total P content of all crandallite samples moderately increased due to the loss of hydrated water from the crandallite structure. As expected, the neutral ammonium citrate solubility of all crandallite samples significantly increased after calcination compared with the uncalcined sample.

Nano-composite super absorbent containing fertilizer nutrients

Recently, the preparation and combined application of super absorbent polymer and fertilizers, *i.e.*, incorporating fertilizers and super absorbent polymer in a single formulation named as water-absorbent slow release fertilizer, is a new trend in international fertilizer research to regulate water and nutrients all in one formulation. Nano-clay-polymer composite super-absorbent was prepared by aqueous solution co-polymerization of partially neutralized acrylic acid and acrylamide in the presence of different types of nano-clays, and it was loaded with di-ammonium

phosphate (DAP) and urea solution. The effectiveness of soil application of NCPC in relation to P-uptake by pearl millet was also evaluated in a pot experiment and it was observed that the uptake was highest with the application of NCPC @ 60-40 (60% N-40% P_2O_5).

FUTURE ASPECTS

- There is little information on the soil chemistry of polymer-coated phosphorus fertilizers.
- Long-term field trials must be conducted to ensure the effectiveness of newly developed fertilizers to conform improved P-use efficiency in the field.
- Economic analysis is needed to assess the feasibility of using non-conventional P sources compared to conventional water soluble phosphatic fertilizers.
- Commercialization of newly developed products.
- Identifying new strain of Phosphorus solubilizing microorganism for better availability of phosphorus to plants.

SUMMARY

Rock phosphate is one of the important sources for phosphatic fertilizer, but solubility of rock phosphate is low. In general it was observed that due to phosphorus-fixation availability of phosphorus to crop plants is always low, causes phosphorus deficiency to crop plants. Solubility of rock phosphate can be increased by following several measures like using biological organism (VAM, vermicompost) with soil, nano-technological approaches and several coated fertilizers like polymer-coated water-soluble phosphorus fertilizers. Nano-clay polymer composite containing nutrients (N- P_2O_5) was found to be more effective than urea-DAP mixture in relation to P.

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