



# Potentiality of Indian rock phosphate as liming material in acid soil



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## ABSTRACT

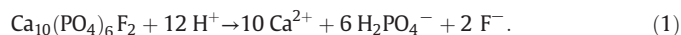
Most of the Indian rock phosphates (RPs) are not suitable for production of commercial phosphate fertilizer because of their low phosphorus (P) content (low-grade). They are suitable as source of P in acid soil, but not effective for direct use in neutral to alkaline soil. The main aim of this study was to evaluate the potentiality of these RPs as liming material and subsequently their effect on P availability in acid soil. Four Indian RPs namely, Udaipur, Mussoorie, Jhabua and Purulia were evaluated for their liming potential through theoretical calculations, laboratory titration and soil incubation studies. The incubation experiment was carried out for 90 days to quantify more accurate per cent calcium carbonate equivalence (%CCE) values of RPs as well as the changes in pH, exchangeable aluminum (Al) and P availability in an acid soil having pH 4.53. Results emanated from the theoretical calculation showed that the %CCE of Indian RPs varied from 59 to 62. While, laboratory studies on quantification of %CCE (AOAC method 955.01) of RPs by titration ranged between 39.9 and 53.7 which were lesser than the theoretical values. The %CCE values obtained in soil incubation study at lower rate of RP application followed the similar pattern as those values obtained in the theoretical calculation. Though RP was less effective in increasing soil pH as compared to CaCO<sub>3</sub>, there was an increase in soil pH due to application of RPs, which is sufficient enough to decrease the content of Al much below the toxic and safe limit for supplying available P for plant growth. Thus, application of low-grade RPs could be a potential option as liming material in acid soil in addition to a source of P for crop production.

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## 1. Introduction

Worldwide, approximately 30% of the total land area consists of acid soils and 50% of the potential arable lands are acidic (von Uexküll and Mutert, 1995). In India, acid soils occupy about 45 million hectare (Mha) which is 30% of the total cultivated area (Panda, 2007). Acid soils, in general, are deficient in nutrients, particularly phosphorus (P). It is reported that the performances of water soluble phosphate (WSP) like single superphosphate (SSP) or triple superphosphate (TSP) in acid soils are very low because of high P-fixation due to the presence of iron (Fe) and aluminum (Al) in these soils. It is estimated that about 260 million tonnes (Mt) of rock phosphate (RP) deposits are available in India (FAI, 2012), most of which are categorized as low-grade because of their low P content and unsuitable for commercial production of P-fertilizer. Application of RP for direct use in acid soils offers a potential utilization of this mineral phosphate as source of P. From economic point of view, these low-grade RP is considered as a suitable alternative to costly WSP fertilizer in acid soils (Narayanasamy et al., 1981). However, the feasibility or the agronomic effectiveness of low-grade RPs for direct use as source of P in neutral to alkaline soils is less effective than that of SSP or TSP (Narayanasamy and Biswas, 1998).

Apart from supplying P in soil for crop production, RP also imparts liming action due to its chemical reactivity in soil and could be used as amendment in acid soils. There are three types of anions (PO<sub>4</sub><sup>3-</sup>, CO<sub>3</sub><sup>2-</sup> and F<sup>-</sup>) present in the carbonate apatite structure of RPs, which may cause an increase in pH after dissolution. As the pK<sub>a</sub> value for hydrofluoric acid (HF) is so low F<sup>-</sup> has hardly any effect on increasing pH. But the pK<sub>a</sub> values for two protons on H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and H<sub>2</sub>CO<sub>3</sub> were high enough to increase the pH by releasing PO<sub>4</sub><sup>3-</sup> and CO<sub>3</sub><sup>2-</sup> into solution. The chemical reactivity of RP determines its potentiality and thereby its suitability as a direct source of P-fertilizer. The chemical reactivity can be defined as the rate at which P in apatite is released under favorable soil condition. The dissolution of RP in soil solution using fluorapatite as an example occurs according to the following hypothetical reaction (Hammond et al., 1986), resulting in the release of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and Ca<sup>2+</sup> in solution:



Thus, dissolution of RP in soil, according to law of mass action, could be favored under conditions of low (a) soil pH, (b) soil exchangeable Ca, and (c) P concentration in soil solution. The above reaction has led to the view that soil acidity or proton (H<sup>+</sup>) supply is the single most important factor influencing the dissolution of a RP in soil. Further, as a result of dissolution of RP at the expense of H<sup>+</sup> and concomitant release

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of  $\text{H}_2\text{PO}_4^-$  and  $\text{Ca}^{2+}$  in soil system, the latter being considered as the reason behind the liming effect of use of RP.

It was found in an earlier study that application of SSP over a period of 6-years decreased the soil pH by 0.16 units, while application of RP maintained the soil pH level in various soils with initial pH ranging from 5.5 to 6.0 (Sinclair et al., 1993). He et al. (1996) reported that application of North Carolina RP to a P-deficient acid loam soil resulted in significant increase in soil pH from 4.0 to 4.3, indicating its potential use as liming material. However, no information is available on the potential use of low-grade Indian RPs as liming material in acid soils. The main objectives of this study were to assess the liming ability of low-grade Indian RPs and subsequently their effect on P availability when applied to an acid soil through various laboratory methods.

## 2. Materials and methods

### 2.1. Experimental soil

To evaluate the liming potential of Indian RPs, an incubation experiment was conducted with an acid soil. For this, bulk surface soil (0–15 cm depth) was collected from the rice growing field of Kuttanad region of Kerala, India. The study area located at a latitude of  $9^{\circ}25'30''$  N and longitude of  $76^{\circ}27'50''$  E. Kuttanad is a region in the state of Kerala, India, well known for its vast rice fields and geographical peculiarities. The region has the lowest altitude in India, and is one of the few places in the world where farming is carried around 1.2 to 3.0 m below sea level.

The bulk soil was air-dried under shade, passed through a 2-mm sieve after crushing with pestle and mortar and analyzed for different parameters namely, pH (soil:water ratio 1:2), (Jackson, 1973), electrical conductivity (EC) (Richards, 1954), cation exchange capacity (CEC) (Jackson, 1973), organic carbon (OC) (Walkley and Black, 1934), available P (Mehlich, 1953) and 1 N KCl extractable Al (Jackson, 1973). The soil belongs to subgroup of Typic Sulfaquents (Soil Survey Staff, 2010). The experimental soil is clay loam in texture having sand, silt and clay content of 63.7, 10.3 and 24.9%, respectively. It had pH, 4.53; EC,  $1.39 \text{ dS m}^{-1}$ ; CEC,  $28.6 \text{ cmol (p}^+) \text{ kg}^{-1}$  soil; OC,  $3.76 \text{ g kg}^{-1}$ ; available P (Mehlich-I P)  $2.85 \text{ mg P kg}^{-1}$  soil; and KCl extractable-Al,  $126.7 \text{ mg kg}^{-1}$  soil.

### 2.2. Rock phosphates and their composition

Four Indian RPs namely, Udaipur (Udaipur RP) from Rajasthan State Mines and Minerals Ltd., Udaipur, Rajasthan; Mussoorie (Mussoorie RP) from Pyrites, Phosphate and Chemicals Ltd., Dehradun, Uttara Khand; Jhabua (Jhabua RP) from Madhya Pradesh State Mining Corporation Ltd., Meghnagar, Madhya Pradesh and Purulia (Purulia RP) from West Bengal Mineral Development and Trading Corporation Ltd., Purulia, West Bengal were collected for this study. These four RPs were used as liming materials along with standard lime ( $\text{CaCO}_3$ ) in the present laboratory and incubation experiments.

The chemical composition of the RPs (100 mesh particle size) was determined as per the standard procedure. The calcium carbonate equivalence (expressed as %CCE) of the RPs as a liming material was determined as per the method outlined by AOAC 955.01 (Kane, 1995). The %CCE represents the alkalinity of the liming material based on the alkalinity present as  $\text{CaCO}_3$  in it. It is assumed that the theoretical %CCE of chemically pure  $\text{CaCO}_3$  is 100. To determine the %CCE of RPs, sample of each RP (1.0 g) was digested with 0.5 N HCl for 5 min and cooled to room temperature. The acid digest was then titrated with 0.25 N NaOH solution to a pH value of 5.0 and 7.0 for the samples of RP and lime ( $\text{CaCO}_3$ ), respectively in order to quantify the excess amount of acid not neutralized by the liming materials.

### 2.3. Incubation experiment

An incubation experiment was carried out under laboratory conditions to see the liming effect of different Indian RPs obtained from various deposits. The treatments consisted of four RPs (i.e. Udaipur, Mussoorie, Jhabua and Purulia) and one lime ( $\text{CaCO}_3$ ) material applied at four rates of liming viz., 0.5, 1.0, 5.0 and  $10.0 \text{ g kg}^{-1}$  of soil replicated three times in a completely randomized design. An absolute control (soil alone) was also run along with the above treatments to see the changes in different parameters occurring from soil during the incubation period. The changes in different parameters in soil under control were subtracted from the values obtained in each treatment to account for the changes occurred only due to treatment application. Air-dried soil sample (100 g, 2-mm sieve) was taken on a clean polythene sheet. Required quantities of RPs and lime ( $\text{CaCO}_3$ ) were added as per the treatments details and mixed thoroughly with the soil. Soil moisture content was maintained by adding distilled water to air-dried soil at field capacity (23%, w/w). After thorough mixing, the moist soil sample was placed in 250 ml conical flask fitted with screw cap. The screw cap was tightened in such a way that it maintained an open space but minimizes the rate of water loss due to evaporation. The conical flasks were then incubated in an incubator and maintained at  $25 \pm 1^\circ \text{C}$  temperature for 90 days. During the incubation period, water content was maintained by taking the weight of the sample including conical flask and the loss of water was adjusted, if any, by adding distilled water. Assuming the weight of 1 ha of furrow soil (0–15 cm depth), application of each liming material was calculated and presented in Table 1.

After 90 days of incubation, all the conical flasks were taken out and the screw caps were removed. After mixing, the soil samples were allowed to air-dry for 3 days in the conical flasks at ambient temperature ( $25^\circ \text{C}$ ), then removed from the conical flask, crushed with a wooden pestle and mortar, passed through a 2-mm sieve and analyzed. The pH was measured using a pH meter at 1:2 ratio of soil:water. For the determination of available Al, soil sub-sample (5 g) was extracted by shaking the sample with 50 ml of 1 N KCl solution (Jackson, 1973) on a rotary shaker for 30 min at 170 rpm at an ambient temperature followed by filtration through a  $0.2 \mu\text{m}$  millipore filter. The Al content in the extract was determined by an atomic absorption spectrophotometer (AAS). Available P in the soil was analyzed after extracting a sub-sample (10 g) with Mehlich I extractant (Mehlich, 1953) and the P content in the extract was determined spectrophotometrically after developing phosphomolybdate blue color method using ascorbic acid as reductant (Watanabe and Olsen, 1965). The amount of P dissolved from a RP was measured by the method as outlined by Bolan and Hedley (1989). To determine the amount of total P dissolved except P in the RP, a sub-sample of soil (1.0 g) was extracted by shaking the sample with 100 ml of 0.5 N NaOH solution on a rotary shaker for 16 h and filtered it through a  $0.2 \mu\text{m}$  millipore filter. The amount of P released from limed soil without RP application was considered as the base level of NaOH extractable P. The amount of P dissolution from a RP was calculated from the difference between the NaOH extractable P in the RP treated soils and base level of NaOH extractable P.

**Table 1**  
Rock phosphate application rate in soil incubation study and calculation for field application.

Rock phosphate application rate (g per 100 g soil)	Rock phosphate application rate ( $\text{g kg soil}^{-1}$ )	Rock phosphate application rate in field ( $\text{t ha}^{-1}$ ) <sup>a</sup>	Phosphorus application rate ( $\text{kg ha}^{-1}$ ) <sup>b</sup>
0	0	0	0
0.05	0.5	1.1	93.4
0.10	1.0	2.2	186.9
0.25	2.5	5.5	467.0
0.50	5.0	11	934.0
1.0	10.0	22	1869.0

<sup>a</sup> Assuming 1 ha of arable soil (furrow slice) having weight of 2200 tonnes.

<sup>b</sup> On an average P content in Indian rock phosphate is 8.5%.

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