

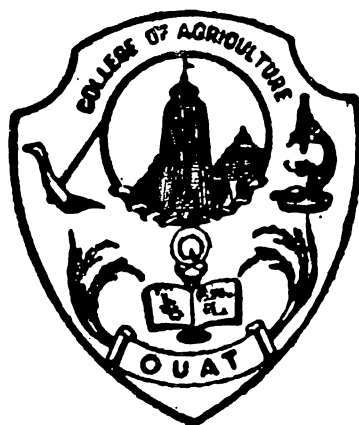
DISSOLUTION OF ROCK PHOSPHATE IN AN ACID SOIL AND THE FERTILISER QUALITY OF THE MIXTURE OF ROCK PHOSPHATE AND SUPER PHOSPHATE AS AFFECTED BY STORAGE TEMPERATURE AND HUMIDITY

A THESIS SUBMITTED TO
THE ORISSA UNIVERSITY OF AGRICULTURE AND TECHNOLOGY, BHUBANESWAR
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

MASTER OF SCIENCE IN AGRICULTURE
(AGRICULTURAL CHEMISTRY, SOIL SCIENCE AND BIOCHEMISTRY)

BY

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DEPARTMENT OF AGRICULTURAL CHEMISTRY, SOIL SCIENCE AND BIOCHEMISTRY
COLLEGE OF AGRICULTURE
Orissa University of Agriculture and Technology
BHUBANESWAR

1990

THESIS ADVISOR

Dr. U K MISHRA

Dedicated

to

My Beloved Parents

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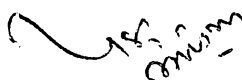
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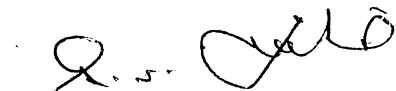
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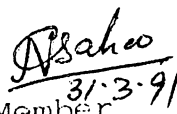
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C E R T I F I C A T E

Certified that the Thesis entitled "DISSOLUTION OF ROCK PHOSPHATE IN AN ACID SOIL AND THE FERTILISER QUALITY OF THE MIXTURE OF ROCK PHOSPHATE AND SUPER PHOSPHATE AS AFFECTED BY STORAGE TEMPERATURE AND HUMIDITY" submitted in partial fulfilment of the requirements for the award of the degree of Master of Science in Agriculture (Agricultural Chemistry, Soil Science and Biochemistry) to Orissa University of Agriculture and Technology, Bhubaneswar is a faithful record of bonafide research work carried out by Sri Bijaya Ketan Sahoo under my guidance and supervision during the academic year, 1990. No part of this thesis has been submitted for the award of any other degree or diploma. It is further certified that all possible help and sources of information availed during the course of this investigation, have been duly acknowledged by him.

Bhubaneswar

Date:


Dr. U.K. Mishra

A C K N O W L E D G E M E N T

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Bhubaneswar

Date: 4-3-1991

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DISSOLUTION OF ROCK PHOSPHATE IN AN ACID SOIL AND
THE FERTILISER QUALITY OF THE MIXTURE OF ROCK
PHOSPHATE AND SUPER PHOSPHATE AS AFFECTED BY STORAGE
TEMPERATURE AND HUMIDITY

A B S T R A C T

Four grades of URP (6.35 to 14.75 % P) were characterised for their apatite structure using the cumulative P content by successive extraction (five times) with ammonium citrate and a chemical statistical model to compute the unit cell dimension, a_0 . The chemical formula of apatite was calculated from a_0 . From the total P content and Mg content of the rock and the theoretical P percentage (17.8 %) of apatite in the rock, the amount of apatite and dolomite in the rock was calculated. The chemical composition and unit cell dimension of apatite in all grades of URP was found to be same having the formula $\text{Ca}_{9.91}, \text{Na}_{0.07}, \text{Mg}_{0.02}(\text{PO}_4)_{5.72}(\text{CO}_3)_{0.28}\text{F}_{2.11}$ and a_0 of 9.366 Å. The apatite content of the rock phosphate varied between 35.67 to 82.86 per cent and dolomite content varied between 14.58 to 54.6 per cent. The high grade contained the highest amount of apatite and lowest amount of dolomite.

The application of all the grades of rock phosphates increased the available P content of the soil but the dissolution of the rock and availability of P was dependent on their dolomite content. Increase in dolomite content decreased the availability of P. Application of mixtures of SSP and URP in 1:1 proportions increased the P availability as compared to rock phosphate application at equal level of P. Further, addition of phosphobacterin (containing 10^9 viable cells per gram) to soil at the rate of 2 to 6 kg/ha increased the availability of P from rock phosphate and its

mixture applied to soil. Addition of a carbon source like glucose along with the bacterial culture increased the bacterial activity and solubilised more P from URP and its mixture with SSP.

Studies on effect of storage temperature (room temperature and 40°C) and relative humidity (50 %, 70 % and 90 %) on different forms of P in SSP and its 1:1 and 1:3 mixtures with low grade URP showed that the water soluble P decreased and citrate soluble P increased with increasing storage time for SSP. The water soluble P content of the mixture decreased initially and then increased whereas the citrate soluble P content increased at 15 days of incubation as compared to the citrate soluble P at 0 days. However, the available P content of the mixture did not change significantly even after one year of storing the material in polythene bottles at room temperature. Therefore, the mixtures of SSP and URP can be safely stored for a reasonable time before use without decreasing the available P present in the mixture after preparing the mixture.

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CHAPTER I

INTRODUCTION

CHAPTER - I

I N T R O D U C T I O N

Phosphorus is one of the essential elements for plant growth which plays an important role in plant metabolism without which life cannot exist on the earth. This element was found to be a principal constituent of some igneous and sedimentary rocks. Phosphatic rock and apatite are referred to microcrystalline calcium fluorapatite of sedimentary origin and macrocrystalline fluorapatite of igneous origin respectively. The work on phosphate nutrition of plant carried out in India and abroad suggest that about 15-25% of the added phosphate is only utilized by the crop. The applied water soluble phosphatic fertilisers are likely to undergo transformation in the soil in accordance with the physical, chemical and biological properties of the soil. Plants derive phosphate from the relatively less soluble transformed products after they undergo a process of dissolution or solubilization.

In India nearly one third of the cultivated land is under acid soils. A large part of Orissa is also covered with acidic red and lateritic soils having low available phosphorus content and very high phosphorus fixing capacities. Therefore, the quantity of phosphorus required to develop a satisfactory potential are so great that it is not economical to satisfy

the absorptive capacity of these soil by using water soluble phosphate carriers. So less expensive insoluble and citrate soluble sources of phosphorus like rock phosphate and its mixture with water soluble phosphatic fertiliser like single super phosphate (SSP) needs to be tested as a source of P fertiliser.

The rock phosphate deposits of India is estimated to be about 180 million tonnes (Choudhary and Subramanian, 1988) and the bulk of the known reserves are boradly clustered in four geographical locations viz, Udipur^a area in Rajasthan Jhabua in M.P, Hirapur area of Sagar district, Lalitpur district and Mussoorie areas of U.P. About 50% of the known national phosphate resource is clustered around Udaipur. The Indian rock phosphates are of low grade and poorer quality as compared to the imported rock phosphates such as Moroco, Jordan or North Carolina. Bulk of the phosphate reserve is having P_2O_5 content ranging between 15-22%. The industrial use of the rock phosphate are limited since benification is difficult and prove to be expensive. It is in the backdrop of this scenario that the direct application of Indian rock phosphate assume significance. The relevance of direct application also assumes importance in view of the fact that India's phosphate requirement is fairly large and the country is likely to remain critically dependant on the import of rock phosphate and sulphur required for production of phosphatic

fertilisers currently marketed in the country. Therefore, number of studies have been made to explore the possibility of direct use of indigenous rock phosphates as phosphatic fertiliser. Many such studies have shown that rock phosphate can be directly used in strongly acid soils and mixtures of soluble phosphatic fertiliser like SSP and rock phosphate in slightly acidic soils for crop production.

However, such mixtures are neither available in market nor the change in available P content of the mixture on prolonged storage is known. The present investigation was carried out with the following objectives.

- 1) To study the dissolution of Udaipur rock phosphates of different grades and its mixture with super phosphate in an acid soil and to study the effect of associated minerals on the solubility of P in the rock.
- 2) To investigate the effect of application of phosphate solubilising bacteria on availability of P in soil treated with rock phosphate.
- 3) To study the effect of storage temperature and humidity on the transformation of available P in SSP and its mixtures with rock phosphate.

CHAPTER II

REVIEW OF LITERATURE

CHAPTER - II

REVIEW OF LITERATURE

Phosphorus being one of the most important essential elements for growth of plants has drawn the attention of soil Scientists and agronomists for a long time. More soil fertility investigations have been conducted on phosphorus than on any other element. Yet characterisation and assessment of its availability has not been fully possible. Rock phosphate is the main source of P for manufacture of all the phosphatic fertilisers. A large part of the rock phosphate deposits of India are of low grade phosphates and cannot be economically used for production of phosphatic fertilisers. It is for the soil scientists and fertiliser technologists to work out the ways and means through which we will be able to make best use of the raw materials that we have in the country.

COMPOSITION OF ROCK PHOSPHATE STRUCTURE AND ITS AVAILABILITY

The primary source of phosphorus in rock phosphate is the mineral apatite which is present in the form of finely divided fluorapatite, hydroxy apatite and Chloroapatite. The composition of rock phosphate varies widely not only from source to source but also within the same deposits. Its composition may vary depending upon its depth and location. In rock phosphate, all most all phosphorus exists as water insoluble tricalcium phosphate in the apatite

constituent of the rock. Lack of adequate, rapid and precise simple laboratory procedure and mineralogical guidelines for predicting the suitability of rock phosphate for direct application, is probably another problem coming in the way of spread of rock phosphate as a fertiliser.

Rao and Rao (1971) conducted textural, mineralogical and petrographic studies on some of the Indian rock phosphate obtained from Udaipur, Mussoorie, Kanpur and Biramania in Rajasthan. These studies revealed that mussoorie phosphorites contain phosphatic mineral in the form of collophane which is pelletal, interstitial, massive and isotropic and is rarely crypto crystalline or micro-cryptocrystalline. Infrared spectra along with chemical analysis shows that the sample of phosphorites from mussoorie and Biramania can be called carbonate hydroxyl fluorapatite, while those from Kanpur and Maton fall in the category of fluorapatite. It also shows the possibility of substitution of C for P in the phosphorites of Mussoorie and Biramania. Collophane from Maton and Kanpur areas occur in precambrian rock and approach fluorapatite in composition.

The citrate soluble P in the rock was correlated with its efficiency (Khasawneh and Doll, 1978) Dash et al. (1988) have reported that the Indian phosphate rocks contained much lower amounts of citrate soluble P compared to many exotic phosphate rocks. The reasons for this was investigated

in a series of studies on the crystal chemical structure of apatite of the phosphate rocks. The pure fluorapatite may be represented by formula $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$. Sedimentary phosphate rocks contain fluorapatites which are affected by isomorphous replacements of their constituent ions Ca^{2+} , PO_4^{3-} and F^- by $(\text{Na}^+, \text{K}^+, \text{Mg}^{2+})$, $(\text{CO}_3^{2-} + \text{F}^-)$ and $(\text{OH}^-, \text{Cl}^-)$ respectively. The electrostatic imbalance resulting from the substitution of planar CO_3^{2-} for tetrahedral PO_4^{3-} is only partially corrected by substitution of F^- in vacate oxygen sites so that a coupled monovalent cation substitution for Ca^{2+} is necessary to maintain electrostatic neutrality in sedimentary apatites, the cations most likely to replace Ca^{2+} are Na^+ , Mg^{2+} and K^+ . Chien (1977), from a consideration of change in free energy showed that the degree of $\text{CO}_3^{2-} + \text{F}$ substitution appear to affect the solubility of P from the apatite in neutral ammonium citrate. This isomorphous replacement also affects the unit cell dimensions (a_0 and c_0) of the hexagonal apatite crystal. The unit cell dimensions are determined by the X-ray diffraction analysis and a related computer programme (Mc Clellan and Lehr, 1969). The a_0 value ranges from 9.322 \AA^0 for such highly substituted apatite to 9.376 \AA^0 for zero substitution (fluorapatite). These variations are systematic and are directly proportional to the degree of CO_3 substitution in the apatite crystal. From informations on a_0 obtained from X-ray diffraction, the apatite of sedimentary phosphate rocks could be calculated (Mc Clellan and Gremillion, 1980).

Several authors (Lehr and Mc Clellan, 1972, Olsen 1975, Chien and Black 1976, Chien 1977) opined that the

reactivity of phosphate rock utilized for direct application varies with mineral composition and the solubility of P in a phosphate rock source can be used as an index of its reactivity. Chien and Hammond (1978) studied the reactivity of phosphate rocks and suggested that factors such as (i) presence of calcite depress the apatite solubility in neutral ammonium citrate, (ii) the grade of the phosphate rock affect the apparent solubility and (iii) the textural effect of apatite and silica intermixing, need to be considered when the correlation of chemical reactivity of the various phosphate rocks and their agronomic effectiveness are compared.

Caro and Hill (1956) have observed that physical compactness or surface area rather than the particle size is associated with reactivity of rock because there is no definite relationship between particle size and surface area. They also proved that the presence of phosphate bound carbonates in apatite increased the solubility of phosphorus from rock phosphate where as fluorine decreased it. Howeller and Woodruff (1968) reported that CaCO_3 incorporated within the apatite structure by replacing phosphate group by $\text{CO}_3^{--}\text{OH}$ group decreased the crystallinity of rock. But the free CaCO_3 particles intermixed with apatite particle were indifferent with available phosphorus of rock phosphate. Further they observed that absence of carbonate from the apatite crystals in case of rocks of igneous origin resulted in a strong crystalline structure and very low availability of P. Chow (1966) showed that the availability of phosphorus in natural phosphates increases with the increase of carbonate content in fluorapatite.

He also revealed that compactness and regularity of the crystal lattice were of primary importance whereas the graininess of rock were of secondary importance. Armiger and Fried (1957) emphasised the significance of chemical and physical properties of different rock phosphates for determining the agronomic value of these materials and explained that carbonate content of rock phosphate was responsible for availability of phosphorus except in low fluorine curacao rock.

Benette et al. (1957) studied the availability of phosphorus from various sources of rock phosphates in the green house and did not find any correlation between fluorine content and phosphorus availability to plants. According to them chemical solubility was a better measure of availability than fluorine content or specific surface.

Lehr and McClellan (1972) examined the important World deposits and observed that with few exception the apatites are not fluorapatite, but belonged to series of carbonate apatite in which PO_4^{3-} was partially replaced by CO_3 and F, and Ca by Na and Mg in the apatite structure. They also found that citrate soluble P of the apatite increased as the degree of CO_3 substitution for PO_4^{3-} in the apatite structure increased. Chien and Black (1976) and Chien (1977) found that the substitution of CO_3 for PO_4 in apatite structure decrease the free energy of neutralisation in the acid solution, resulting in an increase in the chemical reactivity of phosphate rock and the more the degree of

substitution the greater is the chemical reactivity of phosphate rock.

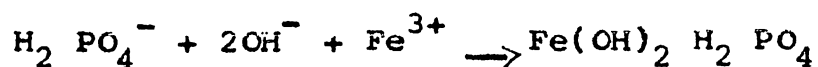
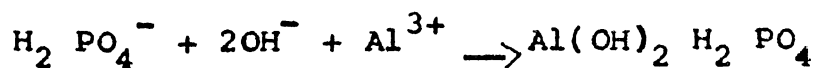
The reactivity of sedimentary phosphate rocks as measured by extraction with ammonium citrate is considerably influenced by the amounts of accessory minerals like calcite, dolomite gypsum etc. present in the phosphate rock sample. Pattnaik (1988) reported that higher content of these minerals consume a part of the added citrate, as a result of which the release of P into the extractant is reduced in the first extraction. Successive extractions of phosphate rocks with ammonium citrate showed that the citrate soluble P in general decreased with each successive extraction. This was more marked for the first 3-5 extractions after which the values remained more or less unchanged. The increase in cumulative P both as percent of rock and as percent of P in the rock, in the successive citrate extractions was less marked in the rocks containing lower amounts of citrate soluble P like Indian phosphate rocks as compared to those of foreign origin. The petrological examination of different phosphate rocks showed that the apatite in most sedimentary ores was homogeneous. Most of the P forms in a given deposit consisted of a single type of apatite whose physical and chemical characteristics are relatively uniform. However, the content of apatite in the ore varied considerably from one location of the deposit to another. Therefore, the reactivity of the phosphate rock for a given deposit cannot be related to the grade of the ore, but can be better expressed in terms of

the grade of the apatite which is relatively uniform in a given deposit.

ROCK PHOSPHATE TRANSFORMATION AND AVAILABILITY OF P
IN ACID SOILS

The fate of applied phosphorus in soil is mainly regulated by adsorption, isomorphous replacement and double decomposition reaction in soil. The insoluble P in rock phosphate is solubilised by action of soil acidity. The hydrogen ions are furnished principally by the hydrolysis of Al^{3+} , the amount of Fe and Al - phosphates formed would be expected to depend on the relative quantities of active Al and Fe present in the soil. In all the experiments a definite relationship exists between soil acidity and iron content in one hand and parent rock decomposed and Fe-phosphate Al-phosphate ratio on the other. Another factor is the increase in the Fe-phosphate/Al-phosphate ratio with time. This would be expected from relative solubilities of Fe and Al-phosphates.

Hsu and Jackson (1960) have stressed the importance of pH in the formation of Fe and Al-phosphates in acid soils. In acid soils, one would expect the reactions to be either of the following two as given below.



The above reactions may occur with Al^{3+} and Fe^{3+} in solution. They also may occur with adsorbed oxides or hydroxides of Al and Fe. In the first instance the H_2PO_4^- ions are precipitated while in the second they may be regarded as adsorbed. Both types of reactions apparently occur in acid soils, but in more weathered soils the amounts of a adsorbed Al and Fe compounds are vastly higher than the quantities of Al^{3+} and Fe^{3+} in solution. Thus most phosphate is adsorbed in such soils. Jackson (1962) has suggested that the final product formed has about the same properties whether precipitated or adsorbed.

Ellis et al. (1955) suggested that soil acidity has a marked influence on the availability of P from rock phosphate, the availability increases as the pH is lowered. Rock phosphate is decomposed by acid to form monocalcium phosphate and other soluble compounds. Once H_2PO_4^- ions are formed, their fate depend upon soil environment.



Bhujabal and Mistry (1981) experimenting with Indian phosphate rocks observed that citrate solubility of the phosphate rock increased as the mole ratios of $\text{CO}_3:\text{PO}_4$ in each apatite increased. The solubility of phosphate rock incubated in an acid soil under flooded condition increased upto 3rd week and decreased thereafter. Pot experiments conducted by Atanasiu (1977) on acid soils from different

humid tropic regions demonstrate a superiority of citrate soluble phosphate over water soluble phosphate with respect to yields and phosphorus uptake of crop plants. Incubation experiments show a higher fixation of water soluble phosphate in these soils. Field experiment confirms these results.

Juo and Kang (1978) studied the availability and transformation of two rock phosphate samples from Morocco and North Carolina and compared it with concentrated super phosphate. They found that the relative effectiveness of the three phosphorus sources followed the order CSP > North Carolina > Morocco. A larger portion of rock phosphate (Ca-P) applied to soils was transformed into Al-P and Fe-P from North Carolina sources than from Morocco source after 90 days of incubation. In an incubation experiment the dissolution pattern of six Indian rock phosphate in acid soils was studied by Kumar and Mishra (1986). The rate of dissolution of each rock phosphate was rapid in the 1st week and decreased thereafter. Most of the dissolution occurred within six weeks of application. Increase in pH and Ca-concentration in the solution due to dissolution of rock phosphate seem to have depressed the rate of dissolution during the later stages. The amount of impurities present in rock phosphate such as Calcite, dolomite and iron oxides appear to have had considerable effects on the rate of dissolution in soils. Low rate of dissolution of mussoorie rock phosphate might be due to the presence of high amount of Calcite and dolomite, which would lower the acidity and thereby decrease the rate of dissolution of apatite mineral.

Saranganath, Shinde and Patnaik (1977). Studied the ³²P tracer on the methods of increasing the efficiency of citrate soluble and insoluble phosphates for rice and acid soils. They found that a considerable proportion of the applied phosphates even from DCP and TCP were converted to Al-P and/or Fe-P due to gradual dissolution by the H⁺ ions of the system resulting in increased Olsen and Bray P. Dry matter production of rice and utilization of applied P was found to be higher when the P-carriers were applied to moist acid soils 2 weeks before flooding than when these were applied at flooding.

Sawarkar and Dikhit (1990) studied the effect of oxalic acid industry waste as a source of sulphur and its effect on the availability of P from rock phosphate. This factory waste which contained 16% S and 5% free acidity as H₂SO₄ when applied with rock phosphate increase the uptake of S, P, K, Ca and Mg by Maize and Soyabean significantly.

Chien (1978) studied the interpretation of Bray-1 extractable phosphorus from acid soil treated with phosphate rocks. Incubation increased the amount of P extracted with Bray-1 from the soil treated with phosphate rock at the rate of 800 ppm P added, the amount of Bray-1 extractable P derived from the unreacted phosphate rocks varied with the source of the phosphate rocks ranging from 9.6 to 93.7 ppm. The amounts of Bray-1 extractable P in the soil treated with

phosphate rocks before and after incubation correlated very well with the citrate soluble P of the phosphate rocks, the amount of phosphorus extracted from the unreacted phosphate rocks decreased as the application rate increased conversely the contribution from the unreacted phosphate rock to the total Bray-1 extractable P in the samples incubated for 3 weeks increased as the application rate increased.

Narwal et al. (1990) studied the efficiency of TSP and mussoorie rock phosphate mixture incubated with sulphitation process press mud. A green house experiment was conducted to study the efficiency of TSP vis-a-vis mixture of TSP and MRP in ratio of 1:1 at 3 levels (0,25,50 ppm P) with and without incubation with press mud of sulphitation process at 4 levels for wheat on a sandy soil. Application of press mud at the rate of 0.3% increased the dry matter yield of wheat by about 2.8 times over absolute control. Organic-carbon and phosphorus content of the soil after harvest of wheat increased with increasing level of applied P incubated with press mud irrespective of the source of P.

Syers and Mackay (1986) studied reaction of Sechuraphosphate rock and SSP in soil for 90 days. The rate and extent of dissolution of SPR measured by a single extraction with 0.5 M NaOH increased as the PO_4 -P adsorption capacity of the soil in contrast the initial dissolution of SSP was independent of soil type. Whereas the amount of

water and Olsen extractable P in soil to which SSP was added declined from the time of application, the amounts of Olsen and Bray extractable P in soils to which SPR was added initially increased.

Chien et al. (1987) studied the combination of finely ground rock phosphate and TSP represents a method that can improve the agronomic value of PR at a lower cost that would be required to manufacture the conventional fully acidulated fertiliser from that same rock. Phosphorus availability from PR appeared to increase with increase in the proportions of TSP to PR in the TSP and PR mixtures. Although PR alone was less effective than TSP, PR was just as effective as TSP when mixed with TSP when mixed with TSP at a P ratio of at least 1:1.

Terman, Bouldin and Lehr (1958) reported that monocalcium phosphate is slightly more available than dicalcium phosphate in alkaline soils but was less available in acid soils. Availability of octacalcium phosphate was less than dicalcium phosphate and decreased with increasing soil pH above 4.8.

Chu et al. (1962) showed that transformation of rock phosphate into both Al and Fe phosphate fractions in soil decreased with increasing pH. The relationship between the pH and Al-phosphate was essentially, the same for all soils studies, whereas the amount of Fe-phosphate formed varied both with pH and free iron content in soil. From these relationship it appears that soils which respond well

to rock phosphate applications are those with low pH and relatively low free iron content.

Chaudhury and Mishra (1980) found that the transformation of rock phosphate in soil was mainly related to soil acidity and phosphate potential as these two soil parameters accounted for 94% variation in the degree of transformation of rock phosphate.

Khaswnah and Doll (1978) found that Ca is one of the product in phosphate rock dissolutions in acid soils, which is released in amount proportional to the rate of P released. The dissolved P undergo transformation while Ca remain as an exchangeable cation in soil solution, affecting the rate of dissolution of phosphate rocks. They reported that phosphate rock dissolution was greater when soil Ca level were low.

EFFECT OF TYPE AND AMOUNT OF CLAY ON AVAILABILITY OF PHOSPHORUS

It has been clearly established that soluble phosphorus is liable to immobilization when it reacts with silicate clays either by replacing hydroxyl groups attached to the alumina sheets or by forming a clay -Ca-phosphate linkage. The hydroxy groups attached to the broken edge of Kaolinite may also be responsible for fixation of phosphorus.

Studies on the reaction of monocalcium phosphate with Kaolinite (Tahoun 1976) indicated gradual decomposition of Kaolinite when it was treated with monocalcium phosphate and the reaction was allowed to proceed at 50°C for a period of 10 weeks. The decomposition was explained by the formation of coordinate bond between octahedral Al of kaolinite and phosphate ions where by metaveriscite, an amorphous silicate are produced. De Datta et al. (1966) showed that within 4 days of equilibrium the concentration of added phosphorus in soil solution was lowest in acid lato-solic soil containing kaolinite type of clay mineral, moderately high in soils containing montmorillonite and essentially unaltered in calcareous soils. They also predicted that the soil containing kaolinite as the only clay mineral fixed more of phosphorus than soil containing both kaolinite and vermiculite. It was proved that the iron present in the interlayers of vermiculite did not account for phosphorus fixation although they were extractable with dithionite. Olsen and Watanabe (1963) reported that there exists a negative relationship between clay content and solubility of phosphorus in soil solution. Gokhale et al. (1954) working on acid soils reported that the acid soils having low silica sesquioxide ratio of their clays fixed up the soluble phosphate irreversibly hence they preferred the use of rock phosphate and bone meal over others in acid soils. Chatterjee and Dutta (1951) found kaolinite to have the greater phosphorus fixing capacity

than Montmorillonite. Lateritic soils having a halloysitic type of clay colloid and high content of aluminium and iron, together with corresponding lack of bases caused relatively high fixation of phosphorus .

PHOSPHORUS AVAILABILITY AS AFFECTED BY FINENESS
OF PHOSPHATE ROCK

The degree of fineness to which the phosphate rock is ground is likely to influence its availability to plants. The more fine the material is ground the greater is the surface of the material exposed to the soil.

Nair and Aiyer (1983) conducted an incubation study of Mussoorie rock phosphate (MRP) by taking 80,100,200 mesh sizes applied at rates of 30,45 and 60 kg P_2O_5 /ha was compared with superphosphate at 30 kg/ha. In general, there was no significant difference in the pattern of dissolution of P indicating that 80-100 mesh MRP was sufficiently fine for an effective crop response on these acid soils. Fe-P in the soil increased with increasing period of incubation and rate of MRP application. Hill et al. (1954) reported that the surface area of some varieties of phosphate rock was very little increased with finer grinding (from 100 mesh to 325 mesh) whereas that of others increased markedly. The former group of rock was of loose structure but latter of extremely compact structure. The compactness of rock according to them depends on the pore

space that lies between elementary grains which constitute a particle or aggregate. The pore distribution is more important than total pore volume of the rock phosphate in determining the chemical reactivity. Baranov (1964) suggested that the phosphorite meal having the particle size less than 0.1 mm was more effective in pot experiments with millets on moderately acid soils even though the chemical composition of coarser fraction was almost same as that of finer fractions. He further stated that finer grinding in poor phosphorites did not increase the effectiveness of the materials much.

Panda and Panda (1968) working with lateritic soils and UAR rock phosphate reported that finely powdered rock phosphate passing through 180 mesh sieve was not significantly superior to 100 mesh sieve in respect of economic return. Panda and Mishra (1970) presented that raw rock phosphate ground to pass through 100 or 60 mesh sieve can directly be applied to acid lateritic soils growing rice. They have also reported that Udaipur rock phosphate can be best utilized for direct application to acid soils for increased availability of phosphorus as it has got amending effect on acid soils containing high percentage of calcium. Das et al. (1990) while studying the effect of fineness of Udaipur rock phosphate on availability of P to maize grown in a laterite soil taken in a pot observed that grinding the rock beyond 100 mesh size did not increase the availability of P.

ROLE OF ORGANIC MATTER ON PHOSPHORUS AVAILABILITY

Carbon dioxide evolved out of organic matter decomposition combines with water and produces carbonic acid which helps in increasing the soil available phosphorus in calcareous and neutral soils. The organic matter forms phosphoric complexes by replacing phosphate ions from the clay lattice. In acid soils organic acids such as tartaric, citric, Malonic and Malic acids released by organic matter decomposition are also expected to chelate iron and aluminium and decrease the fixation reactions of phosphorus mostly in acid soils.

When rock phosphate from Mussoorie, UP and tripple super phosphate were added to fresh cattle dung at rates of 0.5, 1.0 and 2.0% P (dry wt. basis) and were incubated at $30 \pm 4^{\circ}\text{C}$ and 80% moisture saturation for 105 days initially higher recoveries of organic P were obtained with TSP than with MRP. But subsequently a reverse trend was observed (Khana et al. 1984). Immobilization of P was more in TSP treated samples largely in the form of lipid P and humic acid P, while a reverse trend was noted in case of MRP treatment. Singh et al. (1982) observed that indigenous low grade rock phosphate was solubilised by composting with pearl millet boobla (Pmb) in the presence of nitrogen, molasses and pyrites. The solubilisation of rock phosphate was rapid upto 15 days in Pmb + N + RP and reached a maximum of 60% in 120 days of composting. Tomar et al. (1987) studied the effect

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of fresh cattle dung on rock phosphate and TSP solubilization by incubating the phosphate carrier with cattle dung at room temperature. The pH of the rock phosphate treated manure samples was higher than that treated with TSP. P solubilisation of rock phosphate increased when it treated with manure and cattle dung.

USE OF PARTIAL ACIDULATED ROCK PHOSPHATE OR MIXTURES OF
ROCK PHOSPHATE AND SUPER PHOSPHATE AS A POSSIBLE MEANS OF
MINIMISING P FIXATION IN ACID SOILS

Partially acidulated phosphate rock and mixture of rock phosphate and super phosphate have been used with success in increasing the availability of P from phosphate rock. Several workers have observed that performance of either 1:1 or 1:3 mixture of SSP and RP is as good as that of SSP applied at same dose for crop production.

Murdock and Seay (1955) have found that application of a small amount of super phosphate with large amount of rock phosphate increase the uptake of phosphorus from rock phosphate. But when equal amount of rock and super were applied the uptake of phosphorus from rock phosphate was decreased. Smier (1962) observed that lower dose of super phosphate as a starter dose combined with base fertilisation of rock phosphate was more effective than an initial application at high rate.

Lehr and Brown (1958) studying the efficiency of some Calcium phosphates summarised that dicalcium phosphate dihydrate gave the best response in acid soils and monocalcium phosphate in alkaline soils. In all the soils hydroxyapatite and tricalcium phosphate were the poorest sources and practically produced no response on basic soils.

The relative efficiency of Mussoorie rock phosphate and single super phosphate with lime on yield and phosphorus availability in maize-wheat and soyabean-wheat rotation was studied by Dwivedi et al. (1989). Performance of MRP was always superior to SSP regarding increased crop yield and phosphate availability irrespective of lime application. Panda and Panda (1968) investigating the effect of raw rock phosphate on acid lateritic soils of Orissa observed that ground UAR rock phosphate of proper fineness can effectively be used for growing rice. The UAR rock phosphate was more efficient than Mussoorie and was much superior to Singhbhum rock phosphate in effecting higher yields of dry matter and uptake of phosphorus by plants. Mishra and Panda (1969) and Panda and Mishra (1970) evaluating partially acidulated rock phosphate (acidulated with either H_3PO_4 or HNO_3) as a source of P for maize and rice grown in a lateritic soil observed that in acid soils of pH-4, 10 and 20% acidulated materials were as efficient as 100% acidulated material when soils were limed to pH 5.6 and 6.5. 50 and 100% acidulated materials performed better than lower acidulated materials. They also suggested the use of acidulated material with H_3PO_4 for short duration crop and HNO_3

acidulation for long duration crop. Evaluation of rock phosphate acidulated with H_3PO_4 and HNO_3 as a source of P for wheat-blackgram cropping sequence grown in an acid soil of pH 5.6 by Marwaha (1983) revealed that 50% acidulated product with either of the acids was as effective as super phosphate. However, the effect of raw rock phosphate was not much different from control.

According to Mclean and Wheeler (1964) when partially acidulated rock phosphate is applied to soil a part of the acidity produced by the dissolution of monocalcium phosphate in partially acidulated phosphate rock would be neutralised by the unacidulated rock. This not only protect the water soluble P of partially acidulated phosphate rock from reacting with substantial quantities of Al and Fe, but additional P could be released into the water soluble pool from the reaction of acid with unacidulated phosphate rock. Partially acidulated phosphate rock produce relatively small concentration of P in soil solution thereby reducing the fixation of P by metal oxide polymer or immobilizations through displacement on structural sillicate.

EVALUATION OF PHOSPHORUS AVAILABILITY BY CHEMICAL EXTRACTION

Various extractants have been recommended to measure the available P status of soil. Many workers have investigated

to find a suitable method for the purpose and have suggested different extractants to be used in different conditions but an extractant is suitable when the soil test value well correlate with the yield and uptake of nutrient by the crop.

In most of the soil testing laboratories Bray's-I method is recommended for acid soils and Olsen's method for neutral and alkaline soils. It is true that none of the chemical methods is suitable for all types of soils. But Panda and Mishra (1970) working on utilization of rock phosphate in acid laterite soils of Orissa reported that Bray's P was correlated with uptake of P by maize. The soils varying in pH 4.9-7.4, P extracted by the Bray's-I and Olsen's methods were equally suitable for estimation of available P. (Sharma and Bhumbra 1980).

Widely used chemical method for estimation of available phosphorus today are Olsen's method and Bray and Kurtz (1945) method in which fluorine is used to extract from soils at two concentration of HCl. Bray's strong solutions contained 0.1 N HCl and 0.03 N NH_4F . Fluorine is a very active anion in replacing phosphorus from soil compounds. The reagent has the following advantages. (a) it extracts adsorbed P. (b) it represses the solubility of rock phosphate in the presence of acid extractants (c) it reduces the fixation of phosphorus by hydrous oxides in acid suspension.

Sharma and Tripathi (1984) in a study on the indices of P availability in some Himalayan acid soils found that Olsen's extractant removed most of its P from Al-P fraction followed by Ca-P fraction. Bray's procedure derived mainly from Al-P followed by Fe-P and Ca-P . in almost equal proportion. The better predictive ability of the Bray's test with soil receiving phosphate rock appear to result from the ability of the procedure to extract both unreacted phosphate rock which is likely dissolve in the short term and absorbed P as suggested by Mackay and Syer's (1984). They found the poor initial performance of Olsen's procedure. So in situations where unreacted phosphate rock contributed significantly to plant available P in the soil e.g. where phosphate rock applied annually the Bray's procedure appears to be the most effective soil testing procedure.

Salmon and Smith (1956) tried with various methods to extract available phosphorus from acid soils treated with super phosphate, rock phosphate, thomas slag and ground bone. The amount of phosphorus extracted by the method using solutions 0.1 N HCl, 0.03 N NH_4F and 0.002 N H_2SO_4 buffered to pH 3.0 gave the most consistent positive correlation.

Ghosh (1966) measured the available phosphorus in acid laterite soils of Bhubaneswar by different extractants and reported that Bray's and Olsen's method extract almost equal amounts of phosphorus. Regarding correlation of the soil test values Olsen's methods and Bray's I method were also reported superior.

SOLUBILITY OF ROCK PHOSPHATE IN SOIL AS AFFECTED
BY MICRO-ORGANISM

Some phosphorus solubilising micro-organisms viz. bacteria and fungi play important role in availability of applied phosphorus from different sources. Thiobacillus ferrooxidans was found to be efficient in solubilising phosphate from a sterilised pyrite mixed low grade rock phosphate (Mahapatra et al. 1985). Efficient solubilisation from high grade rock phosphate is also reported by the authors. Lipman and Mclean (1918) reported that appreciable amount of phosphorus in pulverised rock phosphate were made soluble by composting soil and sulphur with the rock over a period of 44 weeks. Thiobacillus organisms were found to be responsible for oxidising sulphurs to H_2SO_4 which reacted with the apatite to form super phosphate. Muchovej et al. (1989) studied the role of Thiobacillus thiooxidans in rock phosphate solubilisation in anoxisol treated with low grade rock phosphate, elemental S and organic matter. The addition of Thiobacillus thiooxidans and sulphur caused a rapid decrease in pH of soil to levels below 4.0 and a concurrent increase in P levels in the soil. After incubation, the soil was limed and sorghum was grown successfully on the solubilised P. Past studies have demonstrated the ability of soil micro-organisms to solubilise phosphate rock (gaur et al 1973) Thiobacillus are chemolithotrophic bacteria which occurs naturally in many soils. A common species is Thiobacillus thiooxidans. The presence of an oxidisable sulphur source in

the soil is required for the growth of these organisms. The resultant acidification can cause solubilisation of phosphate rock.

Four species of P dissolving bacilli i.e. Bacillus magaterium, Bacillus cereus, Bacillus mycoides, Bacillus circulans were identified which showed considerable but variable capacity of phosphate solubilisation in soil treated with rock phosphate and incubated after inoculation with the cultures of these bacteria (Gupta et al. 1986).

Tiwari et al. (1988) studied the effect of inoculation with Azotobacter and phosphate solubilising micro-organisms and of addition of Mussoorie rock phosphate during composting of rice straw. Composting with rock phosphate increased both citrate and water soluble P content of the compost and this was further increased by inoculation with Aspergillus awamori optimum response were recorded with the treatment receiving microbial culture and rock phosphate. Rasal et al. (1988) have also reported that phosphate solubilising fungi Aspergillus awamori increased the availability of phosphorus from rock phosphate and enhanced the rate of decomposition which affected significantly the growth parameter of chick pea plants.

EFFECT OF STORAGE CONDITIONS ON THE QUALITY OF FERTILISER

The literature on the effect of storage condition on the quality of phosphatic fertiliser is sparse and no information on the storage quality of mixtures of rock phosphate and

super phosphate is not available.

Choudhary et al. (1988) studied about reversion of phosphorus in different fertiliser during storage. They have taken six samples of commonly used phosphatic material and found that in all the phosphatic materials, the water soluble P content increased with increased storage temperature, from 10 to 40°C which was accompanied with the decrease in relative humidity. The low relative humidity at high temperature reduced the moisture adsorption and consequently reduced the reaction between chemical compounds present in the fertiliser granules. In all the phosphatic materials, the citrate soluble P content declined with increased storage temperature from 10 to 40°C. The citrate soluble P consistently increased in all phosphatic materials with higher storage period. It is evident from investigation that storage of phosphatic materials especially NPK mixtures should be avoided during the month of high relative humidity to prevent the reversion of water soluble P to other insoluble form.

Malonosov et al. (1984) suggested that chemical composition, hygroscopicity, anticaking qualities, strength of granules, friability and storage behaviours of dihydrated calcium phosphates obtained by decomposing rock phosphate with phosphoric acid or a mixture of P and H_2SO_4 and subsequent granulation and dehydration at 280-300°C are described. So for long storage, bitumen impregnated paper bags are recommended.

CHAPTER III

MATERIALS AND METHODS

CHAPTER - III

M A T E R I A L S A N D M E T H O D S

SOIL USED IN THE INVESTIGATION

A typic Haplustult was collected from the upland of Central Research Station, Bhubaneswar. The soil was air dried and ground to pass through a 2mm sieve and stored for further studies.

PHOSPHATE CARRIERS USED IN THE INVESTIGATION

The rock phosphate samples of different grades of Udaipur rock phosphate (URP) such as low grade URP-I, low grade URP-II, medium grade URP and high grade URP used in the investigation were supplied by Rajasthan state mines and minerals limited, Udaipur. The rock phosphate samples of medium and high grade were ground to pass through a 100 mesh sieve. The other two samples were supplied by the farm in powdered form (passed through a 100 mesh sieve). The single super phosphate (SSP) sample used in the study was purchased from local market.

PHOSPHOBACTERIN

The phosphate solubilising bacteria marketed as phosphobacterin was supplied by microbac India Ltd., Calcutta was used in the investigation.

LABORATORY INCUBATION STUDIES

(a) Dissolution of rock phosphate and its mixture with SSP in soil

Soil samples of 150g each were taken in beakers of 250 ml capacity and to each calculated amounts of different phosphate rocks and their 1:1 mixture with SSP and SSP only were added at the rate of 100 ppm P and were mixed thoroughly. The treatments were as follows.

TABLE 1. DETAILS OF TREATMENTS OF INCUBATION STUDY

Sl No.	Sources of fertilisers
1.	Control
2.	Low grade URP-I
3.	Low grade URP-II
4.	Medium grade URP
5.	High grade URP
6.	SSP
7.	1:1 mixture of low grade URP-I and SSP
8.	1:1 mixture of low grade URP-II and SSP
9.	1:1 mixture of medium grade URP and SSP
10.	1:1 mixture of high grade URP and SSP

The 1:1 mixture of rock phosphate and SSP were prepared on the basis of P applied. Water was added to bring the moisture contents of the sample to field capacity and the sample were incubated for sixty days at room temperature which varied between 15°C to 32°C during the period of

incubation (started on 15th Nov. 1989). Each treatment was replicated twice. Alternate wetting and drying was done through out the period of incubation. Water was added to bring the moisture content to field capacity as and when needed. The samples from the beakers were drawn out at an interval of 15 days for measuring pH and available phosphorus. Each time after drawing a sample, the content of each beaker was mixed thoroughly.

Available phosphorus was determined by extracting the soil with olsen's reagent and determining the P in the extract by following the method suggested by murphy and Rieley (1962).

(b) Determination of bacterial count in phosphobacterin culture

For this purpose, the culture of phosphate solubilising microorganism was diluted 10^5 times serially and from the last dilution, 1ml of suspension was inoculated in three petridishes containing molten pikovskaya's medium suggested by Subba Rao (1986) and incubated for 3 days after which the number of bacterial colonies were counted.

(c) Effect of phosphobacterin on solubilising P from rock phosphate

Two hundred grams of soil was taken in each of 24 beakers of 250 ml capacity. Phosphorus was added at the rate of 100 ppm P either as low grade URP 1 or as 1:1 mixture of low grade URP-I and SSP. Then phosphobacterin suspension at

the rate of 0ml, 1ml, 1.5ml, 2ml, 2.5ml and 3ml which contain 0mg, 0.1mg, 0.15mg, 0.2mg, 0.25mg and 0.3mg of carrier based culture were added to each treatment. The treatments were replicated twice. After 7 days of incubation at field capacity analysis of available P showed no effect of phosphobacterin on P solubilisation. The soil was allowed to dry and then one replication was treated with 4g of glucose and the other replication was not treated with glucose. Then the samples were treated again with phosphobacterin at the rates of 0 mg, 100mg, 150mg, 200mg, 250mg and 300mg per 100g soil and incubated at room temperature maintaining the soil moisture at field capacity. Samples were drawn at 7, 15, 22 and 30 days after incubation and analysed for pH and available P (Olsen's method).

(d) Incubation of fertiliser mixture

The 1:1 and 1:3 mixtures of SSP and low grade URP-I were prepared by thoroughly mixing of the required quantity of each material to provide the P in desired ratios as indicated. About 50g sample of each mixture and SSP taken in 50ml beakers were incubated at three moisture level i.e. 50% RH, 70% RH, 90% RH and two temperature conditions i.e. room temperature and at 40°C. The desired relative humidity was maintained by taking calculated amount of H_2SO_4 (Hodgman et al. 1959) inside the desiccator in which samples were kept. One set of three desiccators containing fertiliser samples maintained at 50%, 70% and 90% relative humidities were kept

at room temperature for 90 day and another set was kept inside a B.O.D incubator maintained at 40°C for 60 days. Samples were drawn at regular intervals of 15 days and analysed for total, water soluble and citrate soluble P. The 1:1 and 1:3 mixture of SSP and low grade URP-I prepared during 1989 and stored for one year in polythene bottles were also analysed for caking by sieving and calculating the percentage of granules greater than 2mm size formed. Fertiliser granules which were > 2mm size and that passed through a 2mm sieve were analysed for water soluble, citrate soluble and total P.

SOIL ANALYSIS

The water holding capacity of soil, pH of 1:1 soil water suspension, the cation exchange capacity of soil and mechanical analysis of soil using Bouyoucus hydrometer were determined following the standard procedure. The organic carbon was estimated using walkley and Black's rapid titration method (1934). The available P content of soil was determined by olsen's method (Jackson, 1962). Phosphorus in the Olsen's extract of the soil was determined by the ascorbic acid reduction method as suggested by Murphy and Rieley (1962).

ANALYSIS OF FERTILISER MATERIAL

Total, water soluble and ammonium citrate soluble phosphorus content of the rock phosphates including the 1:1 and 1:3 mixture of super phosphate and rock phosphate were colorimetrically determined following AOAC (1960) methods

using vanadomolybdo-phosphoric acid. The ammonium citrate soluble P was estimated on the same sample which was used for extraction of water soluble P. For determination of calcium content of the rock phosphate the sample was digested with HCl. Calcium in the HCl extract was determined by modified oxalate precipitation method as described by Chopra and Kanwar (1986). Calcium and magnesium in the extract was determined by EDTA titration method described by Hoffman and Shapiro (1954). Magnesium content of the rock phosphates was estimated by subtracting the value of Ca from Ca + Mg.

CHAPTER IV

RESULTS AND DISCUSSION

CHAPTER - IV

R E S U L T S A N D D I S C U S S I O N

The rock phosphates of four different grades (Low grade URP-I, Low grade URP-II, medium grade URP and high grade URP) obtained from Rajasthan State Mines and minerals Ltd., Udaipur were analysed for their P, Ca and Mg content and reported in Table-2. The apatite present in these rock phosphate deposits is dominantly associated with dolomite (Chaudhury and Subramanian, 1988).

REACTIVITY OF THE ROCK PHOSPHATE AS RELATED TO ITS COMPOSITION

To measure the reactivity of the rock phosphate, the samples were extracted five times successively with neutral normal ammonium citrate and the concentration of P in each extract was determined and reported in Table-3 and Fig-1.(a). The reactivity of the rock as measured by extraction with ammonium citrate is likely to be considerably influenced by the amount of accessory minerals like dolomite present in the sample. Higher content of dolomite in the rock consume a part of the added citrate as a result of which the release of P into solution is reduced. In general, the citrate soluble P content decreased with each successive extraction Fig-1(a) which was more marked for first three extraction after which it remained more or less unchanged. The cumulative citrate soluble P content after five extractions varied between 0.93%

TABLE 2. TOTAL CHEMICAL ANALYSIS OF THE PHOSPHATE ROCKS

Grades of URP	Total P (%)	Ca (%)	Mg (%)
Low grade URP-I	6.35	25.8	7.17
Low grade URP-II	8.00	28.7	6.52
Medium grade URP	10.65	31.41	4.56
High grade URP	14.75	36.25	1.95

TABLE 3. CITRATE SOLUBLE P IN SUCCESSIVE AMMONIUM CITRATE EXTRACTION OF THE ROCK PHOSPHATES

Grades of URP	Ammonium citrate extract					
	1st	2nd	3rd	4th	5th	Cumulative P in successive extraction
Low grade URP-I	0.43	0.30	0.07	0.07	0.06	0.93
Low grade URP-II	0.43	0.36	0.07	0.07	0.06	0.99
Medium grade URP	0.50	0.36	0.14	0.10	0.09	1.19
High grade URP	0.50	0.43	0.14	0.10	0.11	1.28

TABLE 4. APATITE AND DOLOMITE CONTENT OF THE ROCK PHOSPHATE SAMPLES

Grades of URP	Apatite (%)	Dolomite (%)
Low grade URP-I	35.67	54.60
Low grade URP-II	44.94	47.54
Medium grade URP	59.83	34.59
High grade URP	82.86	14.58

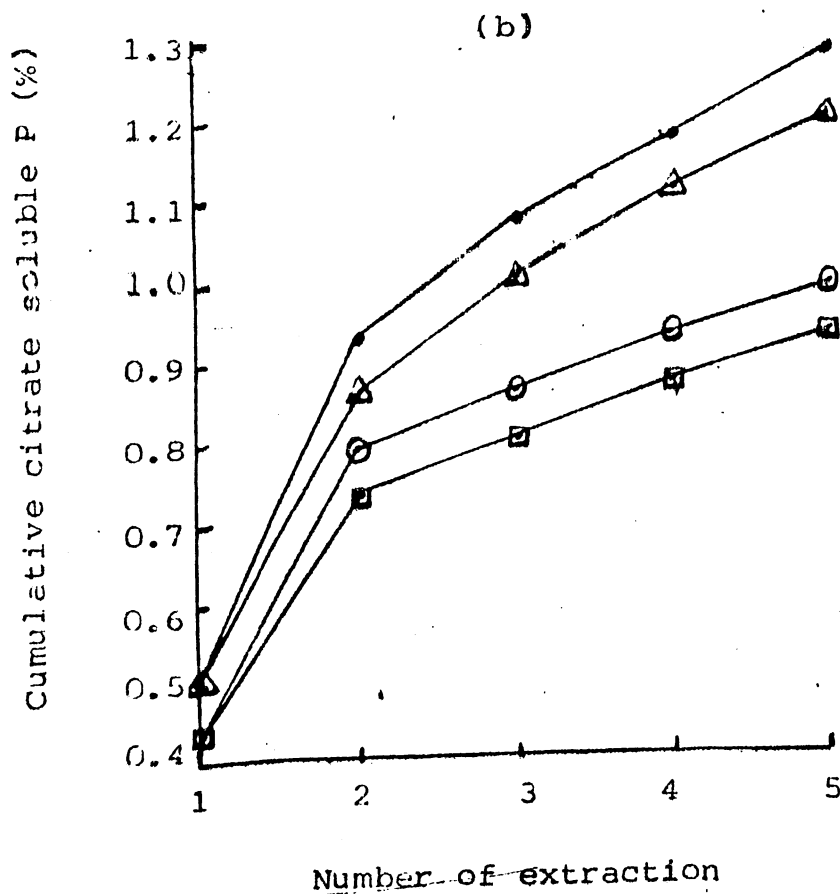
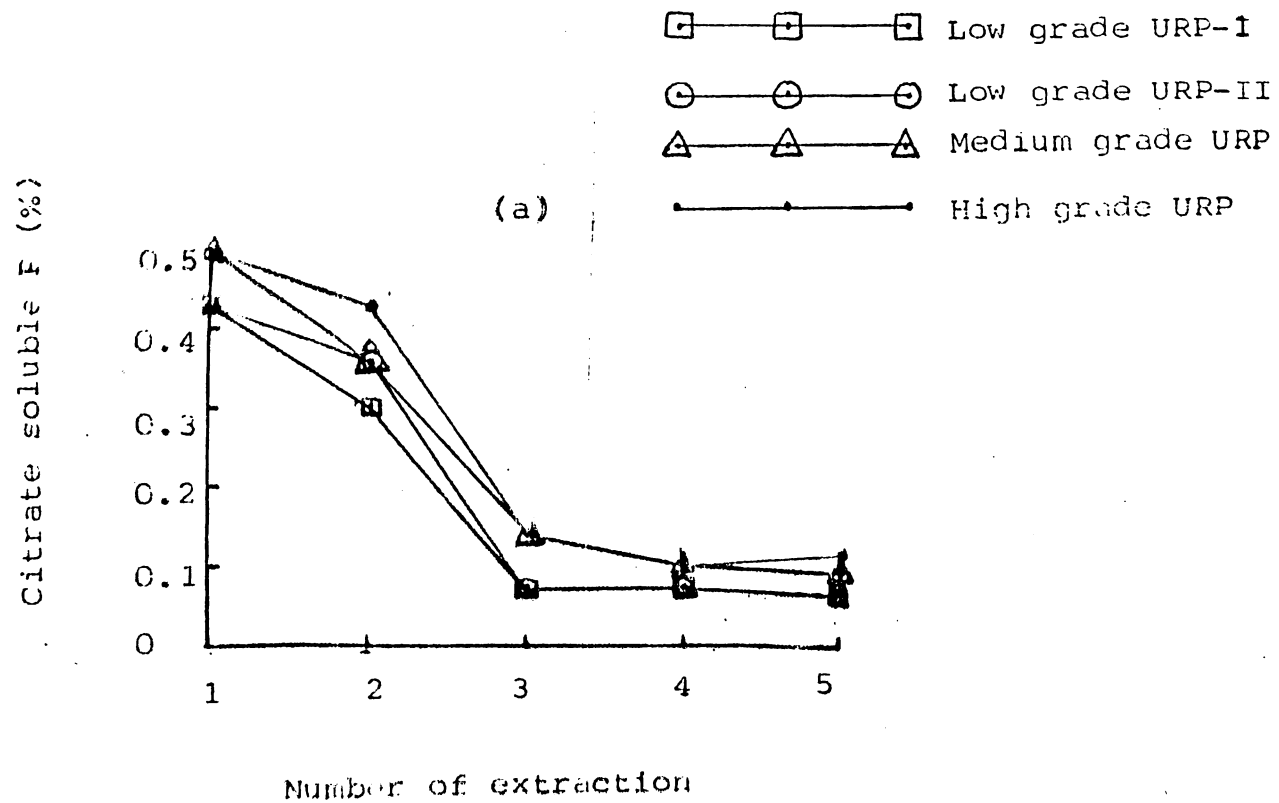
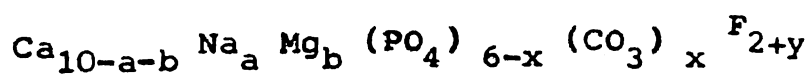


FIG: 1 EFFECT OF SUCCESSIVE EXTRACTION OF PHOSPHATE ROCK WITH AMMONIUM CITRATE ON THE RELEASE OF P (a) CONCENTRATION OF P IN EACH EXTRACT (b) CUMULATIVE CONCENTRATION

to 1.28% only. Such a small variation observed between the four samples may not be due to the difference in their crystal structure but due to variation in the apatite and dolomite content of the rock.

The citrate soluble P in the rock has been correlated with its efficiency (Khasawneh and Doll, 1978) and as reported in the literature the citrate solubility appears to be affected by $\text{CO}_3 + \text{F}$ substitution in the apatite structure. Such substitution affect the unit cell dimensions (a_0 and c_0) of the hexagonal apatite crystal. From the a_0 value chemical formula for the apatite of sedimentary phosphate rock like that of Udaipur rock phosphate can be calculated using the general formula as suggested by Mc Clellan and Gremilian, (1980)



$$\text{where } a_0 = 9.374 - 0.204 \frac{x}{6-x}$$

$$a (\text{Na}) = 1.327 \frac{x}{6-x}$$

$$b (\text{Mg}) = 0.515 \frac{x}{6-x}$$

$$y(\text{average value}) = 0.4 x$$

The a_0 values for the apatite in the rock phosphate samples used in the present study were calculated from the citrate solubility of the rock using chemical statistical model as suggested by Patnaik (1988). The a_0 was calculated

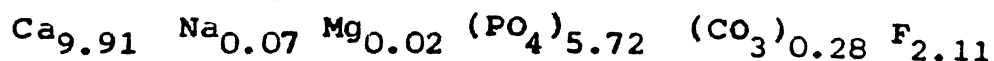
using the following regression equation.

$$a_0 = 9.367 - 0.00049 x$$

Where x = cumulative P in five successive ammonium citrate extract of the rock expressed as percentage of the rock.

The a_0 value for each of the four samples of rock phosphate calculated from the cumulative P content of the five successive extraction with ammonium citrate (Table-3) was found to be 9.366 A^0 suggested that the crystal chemical structure of apatite in all the rock phosphate samples was same.

The empirical formula of the apatite calculated from a_0 value was as follows.



The theoretical P percentage of the apatite present was calculated to be 17.8%. Assuming that all the P in the rock is apatite bound and barring the Mg in apatite the remaining Mg is dolomite bound, the percentage of apatite and dolomite present in the rock have been calculated and presented in Table-4. The apatite content of the rock increases and dolomite content decrease with increasing P percentage of the rock. Apatite and dolomite accounts for about 98.28% of constituent minerals of the high grade rock (14.75% P) and 90.84% of the low grade rock (6.35% P) the rest being other likely accessory minerals viz. SiO_2 , Al_2O_3 , Fe_2O_3 etc. Based

on the percentage of apatite and dolomite in the rock phosphate % of Ca in the rock was calculated and compared with the amount of Ca determined experimentally (Table-4). The theoretical values of Ca calculated agreed well with the experimental value.

The reactivity of the phosphate rock can not be related to the grade of the ore of a particular deposit but can be related to the grade of the apatite which is relatively uniform in the deposits around Udaipur. An availability index, absolute citrate solubility (ACS) was suggested in preference to conventional citrate soluble P (Khasawneh and Doll, 1978). The water soluble and citrate soluble P content of the rock and the absolute citrate solubility is reported in Table-6. The ACS is defined as the (citrate soluble P % / theoretical P % of apatite) x 100. The absolute citrate solubility of all the four rock phosphate samples were more or less same. The two low grade URP sample had ACS of 2.42 and the medium grade and high grade samples had ACS value of 2.80. All these results suggest that irrespective of the grades of the rock phosphate their performance is likely to be similar when applied for the soil at equal dose of P.

DISSOLUTION OF ROCK PHOSPHATE AND ITS MIXTURE WITH SSP IN SOIL

The solubility of rock phosphate and its mixture with SSP in typic haplustult collected from Central Research Station of Bhubaneswar was investigated. Results of the mechanical and chemical analysis of soil used in the investigations are presented in Table-7. Soil is of sandy loam

TABLE 5. COMPARISON OF CALCIUM CONTENT OF THE ROCK
PHOSPHATES AS DETERMINED AND AS THEORITICAL
CALCULATED

Grades of URP	Calcium determined	Calcium theoritical
Low grade URP-I	25.80	26.15
Low grade URP-II	28.70	28.30
Medium grade URP	31.40	31.42
High grade URP	36.25	36.24

TABLE 6. WATER SOLUBLE, CITRATE SOLUBLE AND TOTAL P
CONTENT OF THE ROCK PHOSPHATES USED IN THE
INVESTIGATION

Sample	P content(%)			Absolute citrate* solubility
	Water soluble	Citrate soluble	Total	
Low grade URP-I	0.03	0.43	6.35	2.42
Low grade URP-II	0.03	0.43	8.00	2.42
Medium grade URP	0.03	0.50	10.65	2.80
High grade URP	0.04	0.50	14.75	2.80

$$* \text{ Absolute citrate solubility } = \frac{\% \text{ citrate soluble P in rock}}{\text{Theoritical P \% in apatite}} \times 100$$

TABLE 7. RESULTS OF THE CHEMICAL AND MECHANICAL
ANALYSIS OF SOILS

Particulars of Analysis	Results
Water holding capacity (%)	40
Mechanical analysis	
a) Sand (%)	70.40
b) Silt (%)	11.84
c) Clay (%)	17.76
Textural class	Sandy loam
Cation exchange capacity	
C mole (p ⁺) kg ⁻¹	2.9
pH	4.6
Available phosphorus (Olsen's method)	4.5 ppm
Organic carbon (%)	0.65

texture having pH 4.6 and cation exchange capacity 2.9 meq/100 g. The available P content of the soil as determined by Olsen's method was 4.5 ppm.

(a) Dissolution of rock phosphate and availability of P.

Dissolution of rock phosphate in soil is the first step in its transformation followed by utilisation by plants. A knowledge of the dissolutions pattern of rock phosphate in soil would, therefore, provide an insight into its solubility behaviour which may be related to its agronomic effectiveness.

The change in pH and available P content of the soil incubated with 100 ppm P either as different grades of URP or their mixture with SSP are recorded in Table-8. It may be seen that after 7 days of incubation pH of the soil treated with all grades of rock phosphate, super phosphate and 1:1 mixture of low grade URP-I have increased by 0.3 to 0.9 unit as compared to a control pH of 4.7 (Table-8, Fig-2). However in case of 1:1 mixtures where medium and high grade rock phosphates have been used, the pH either slightly decreased or increased as compared to control. With progress of incubation time, the pH of the control treatment remain more or less unchanged. The pH of the rock phosphate treated soil increased with time, attaining a value of 6.8 for low grade I, 6.5 for low grade II, 6.2 for medium grade and 5.5 for high grade at 30 days. The change in pH after 30 days and upto 60 days was not significant (Fig-2). However incase of super phosphate treatment the pH at 7 days was 4.6 which

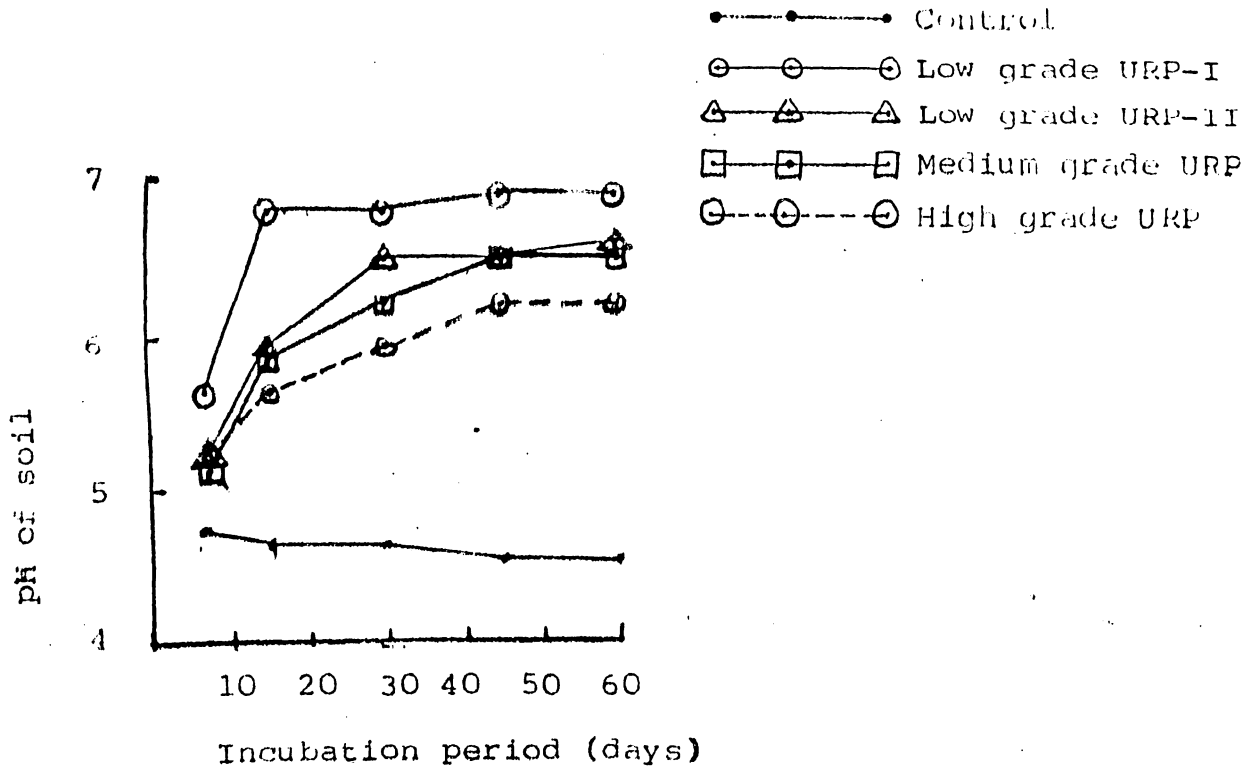


FIG:2 SOIL pH AS AFFECTED BY DISSOLUTION OF ROCK PHOSPHATE

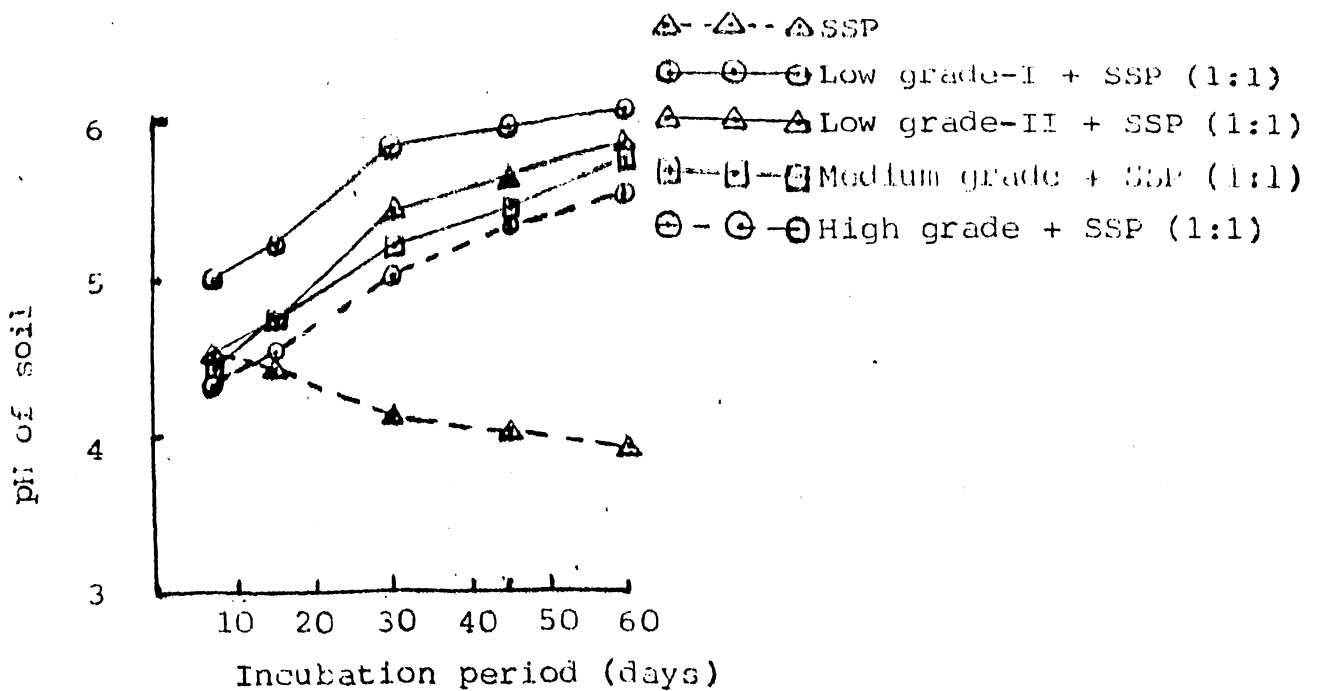


FIG:3 SOIL pH AS AFFECTED BY DISSOLUTION OF SSP OR ITS 1:1 MIXTURE WITH URP.

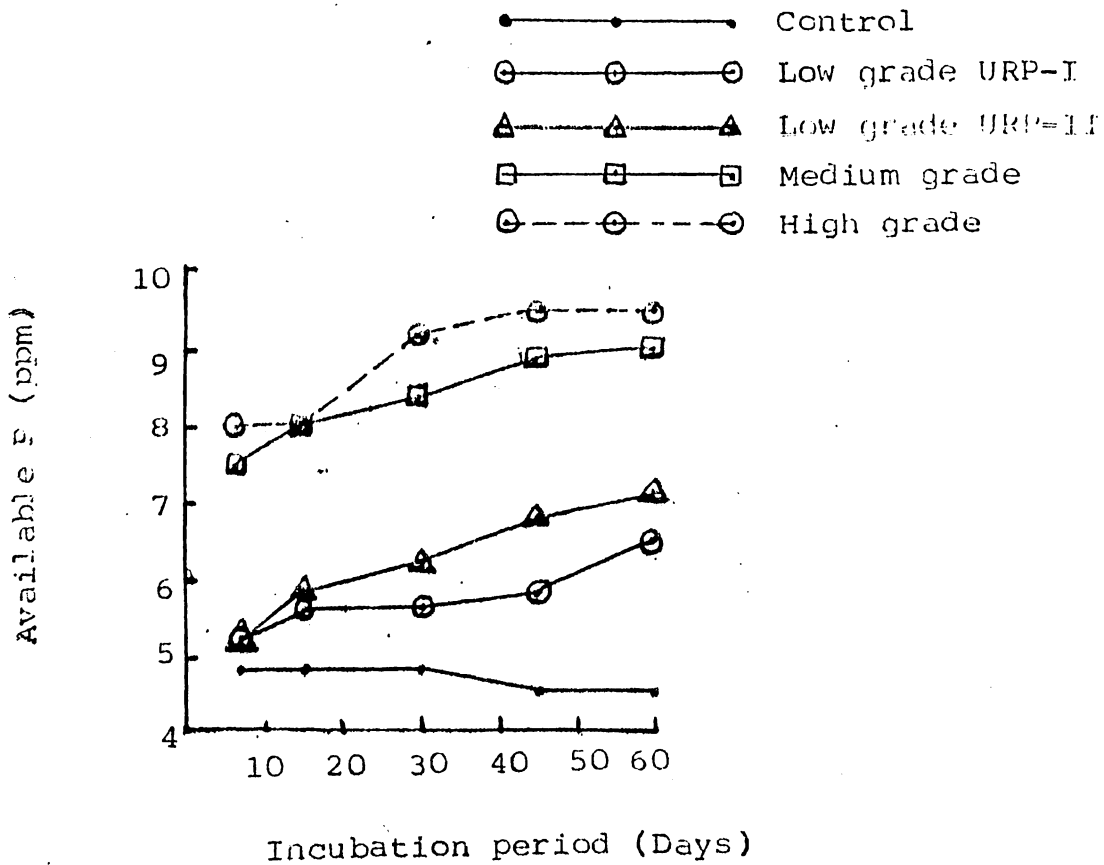


FIG: 4 DISSOLUTION OF ROCK PHOSPHATE IN ACID SOILS OF ORISSA

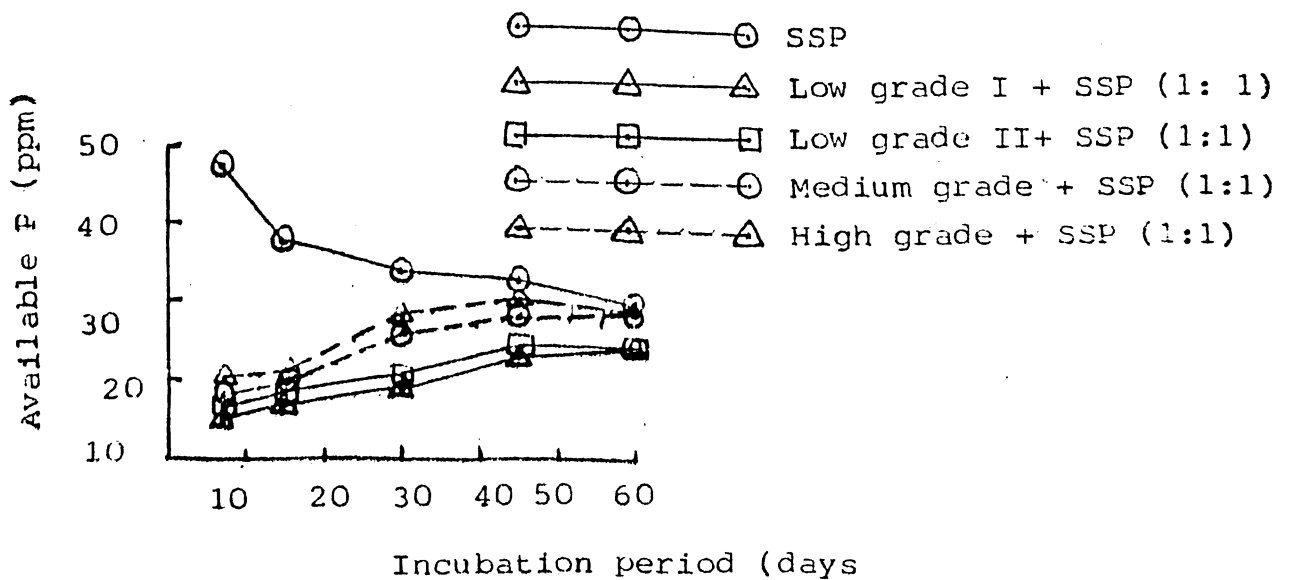


FIG: 5 DISSOLUTION OF 1:1 MIXTURE OF ROCK PHOSPHATE AND SSP IN SOIL.

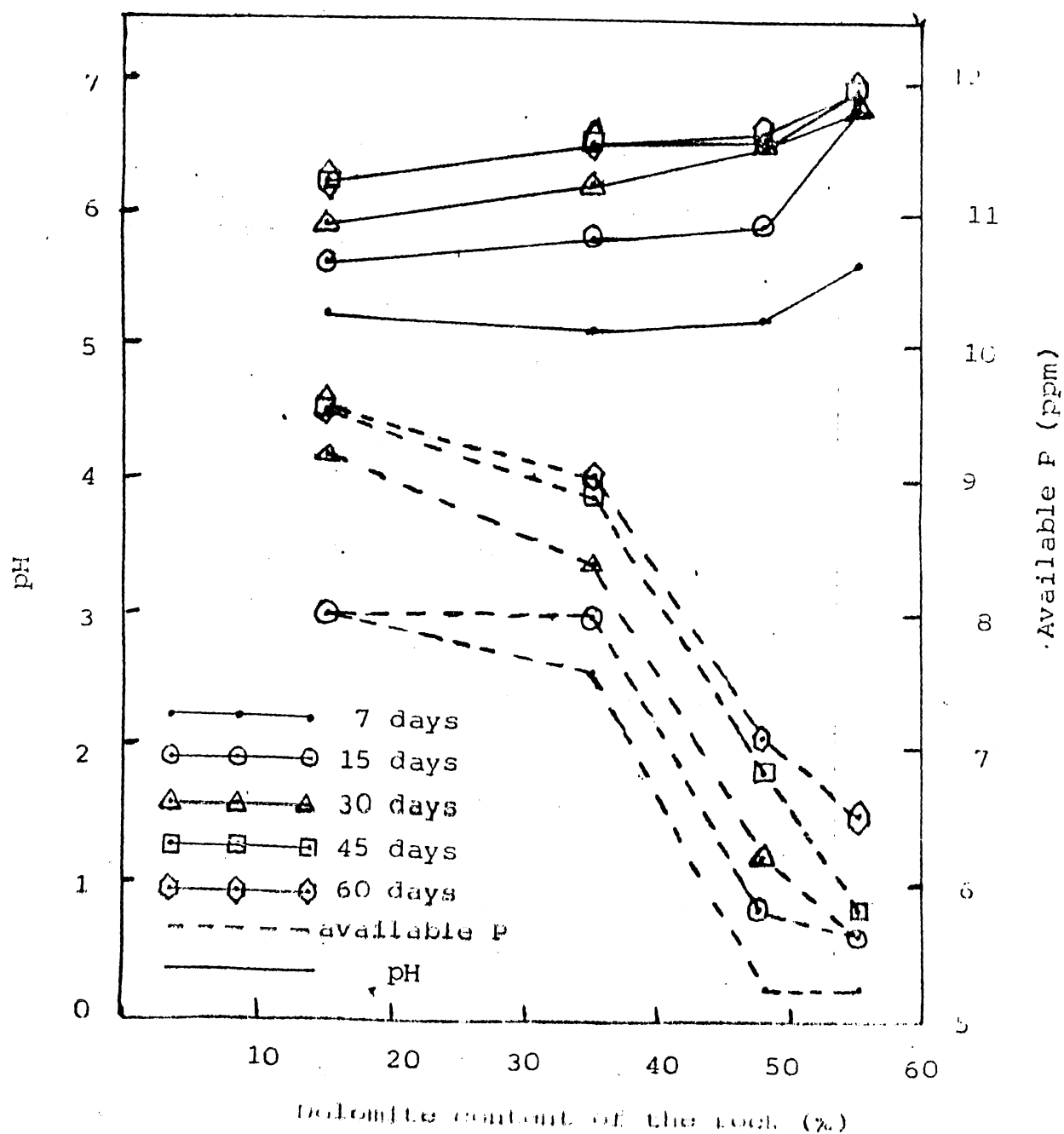


FIG. 6 DISSOLUTION OF ROCK PHOSPHATE IN SOIL AS AFFECTED BY THE DOLOMITE CONTENT OF THE ROCK.

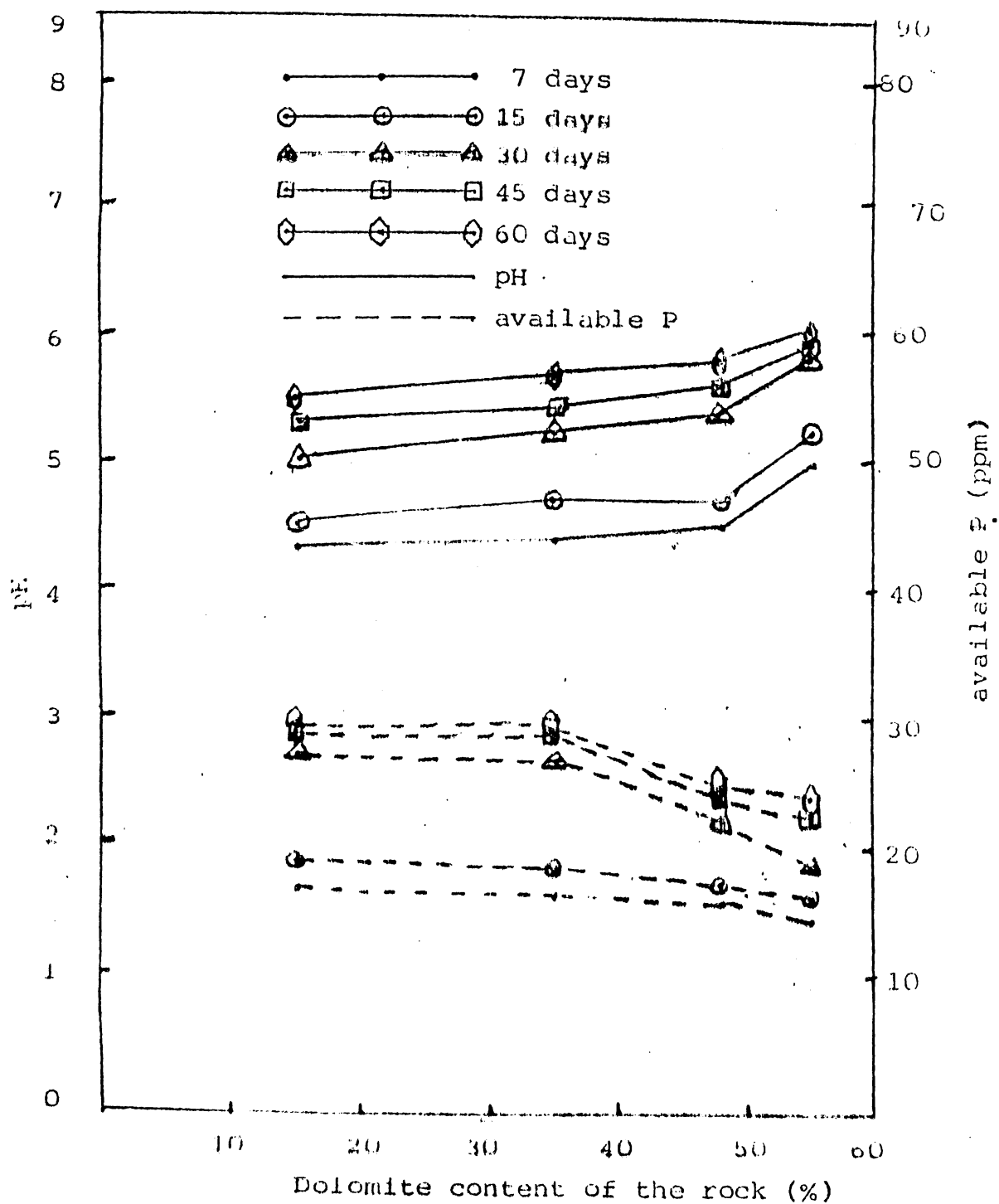


FIG: 7 DISSOLUTION OF SSP AND ITS 1:1 MIXTURE WITH ROCK PHOSPHATES IN SOIL AS AFFECTED BY THE DOLOMITE CONTENT OF THE ROCK.

TABLE 8. pH AND AVAILABLE P CONTENT OF THE SOIL TREATED WITH ROCK PHOSPHATE
OR ITS 1:1 MIXTURE WITH SSP

Treatments	pH					Available P (ppm)				
	Incubation time					Incubation time				
	7days	15 days	30 days	45 days	60 days	7 days	15 days	30 days	45 days	60 days
Control	4.7	4.6	4.6	4.5	4.5	4.8	4.8	4.8	4.5	4.5
Low grade URP-I	5.6	6.8	6.8	6.9	6.9	5.2	5.6	5.6	5.8	6.5
Low grade URP-II	5.2	5.9	6.5	6.5	6.6	5.2	5.8	6.2	6.8	7.1
Medium grade URP	5.1	5.8	6.2	6.5	6.5	7.57	8.0	8.4	8.9	9.0
High grade URP	5.2	5.6	5.9	6.2	6.2	8.0	8.0	9.2	9.5	9.5
SSP	4.5	4.4	4.1	4.0	3.9	48.0	38.0	34.0	32.4	29.4
Low grade URP-I + SSP (1:1)	5.0	5.2	5.8	5.9	6.0	14.5	16.5	19.2	22.5	24.0
Low grade URP-II + SSP (1:1)	4.5	4.7	5.4	5.6	5.8	16.0	17.8	20.2	24.0	24.2
Medium grade URP + SSP (1:1)	4.4	4.7	5.2	5.4	5.7	16.8	18.8	26.4	28.4	28.8
High grade URP + SSP (1:1)	4.3	4.5	5.0	5.3	5.5	17.0	19.2	27.2	28.4	28.8

decreased to 4.1 at 30 days (Fig-3) after which it remained more or less unchanged till 60 days. In case of the mixtures the pH values increased with time attaining a value of 5.8 at 30 days where low grade URP-I was used, 4.9 where low grade URP-II or medium grade URP was used. The variation of pH with time in different treatment have shown in Fig-3.

As a result of addition of rock phosphate and of any grade the available P content of the soil increased upto 45 days (Fig-4) after which the concentration of P decreased in cases of medium and high grade rock phosphate and the increase persisted in both of the low grade rock phosphate treatments.

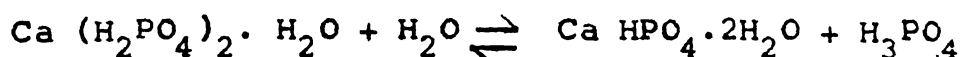
The change in pH and available phosphate content of the soil as related to the dolomite percentage in the phosphate rock has been shown in (Fig-6). As the dolomite content increases the pH also increases and available P content of the soil decreases. In most cases it appears that the equilibrium is attained around 30 days. The low grade rock phosphate which contain high amount of dolomite shows high pH and low available P. Whereas the high grade rock phosphate showed the low pH and higher amount of available P. In case of high grade rock phosphate the available P content increased from 4.5 ppm is control to 9 ppm at 60 days whereas for low grade URP-I the increase was only upto 5.8 ppm. The low increase in available P content of soil due to treatment with low grade rock phosphate as compared to high grade was due to high

dolomite content of the low grade rock which increased the pH to a high value. But incase of high grade rock phosphate treatment the pH was low which help to solubilise more of rock phosphate. The presence of high amount of dolomite in the rock considerably influenced the rate of dissolution of apatite in the rock. Such observation was also made by Mishra et al. (1985) . The decreased dissolution of rock phosphate containing high amount calcite and dolomite have also been reported by Narayansamy et al. (1981). The dissolution of rock phosphate can not be explained only on the basis of pH but might be the result of a combined effect of pH, exchange acidity and exchangeable Ca. As a portion of the phosphate released from the rock might get fixed in the soil and may escape extraction with NaHCO_3 solution and hence the phosphate fixation capacity of the soil might also influence the dissolution of rock phosphate in soil (Kumar and Mishra 1986).

(b) Dissolution of the 1:1 mixture of SSP and URP in soil and availability of P.

When the soil was treated with single super phosphate and incubated for 7 days the pH of the soil decreased from 4.7 to 4.5. The decrease in pH continued till 60 days attains a value of 3.9 (Fig-3). The available P content of the soil at 7 days of incubation was 48 ppm which continuously decreased upto 60 days attaining a value of 29.4 ppm (Table-8 and Fig-5). When single super phosphate which contains

monocalcium phosphate (MCP) is added to the soil the immediate reaction product is dicalcium phosphate dihydrate (DCPI) and phosphoric acid as per the following reaction.



Such a reaction lowers the pH of the soil. A part of the added soluble phosphate is converted to insoluble veriscite and strengite in acid soil due to high Fe and Al activity in soil. Further, the H_3PO_4 produced by incongruent dissolution of MCP help to further solubilise Fe and Al thereby leading to greater fixation. This explains the decrease in available P content of the soil treated with SSP.

The pH of the soil treated with 1:1 mixture of SSP and URP increased with time as compared to a gradual decrease in case of SSP treatment (Fig-3). Where low grade URP-I was used in the mixture a pH value of 6 was recorded at 60 days of incubation where as pH values of 5.8, 5.7 and 5.5 were recorded when low grade URP-II, medium and high grade URP respectively were used in the mixture. As expected the increase in pH values recorded for different treatments corresponds to the dolomite content of the rock phosphates used in the mixture.

The increase in soil pH is likely to reduce the solubility of apatite in the rock. But, the data presented in Fig-5 shows that the available P status of the soil treated with SSP : URP mixture increased upto 30 days (where medium and high grade URP were used) attaining a value of 26.4 to 27.2 ppm

P. Between 30 and 60 days of incubation the increase in pH was very small. However, for mixtures containing low grade URP the available P increased upto 45 days attaining a value of 22.5 to 24 ppm. This is probably due to higher dolomite content of the low grade rock phosphate which retarded the rate of dissolution of apatite. It may be seen that the available P status of the soil after 60 days varied between 24 and 29.4 ppm P for treatments receiving either SSP or 1:1 mixtures of SSP and URP. These result suggest that P availability from SSP or the mixture of SSP and URP are likely to be same after 60 days of application.

When an intimate mixture of rock phosphate and super phosphate is applied ~~is applied~~ to the soil, in addition to inherent soil acidity which help to solubilise the insoluble P in rock phosphate, a part of the acid produced by the dissolution of MCP solubilise the rock phosphate in the surrounding instead of solubilising more soil Fe and Al, there by decreasing P fixation. In addition to Ca produced by solubilisation of rock phosphate, dissolution of dolomite also produce Ca and Mg ion and the presence of more Ca in the soil solution supresses the dissolution of the rock. Therefore, mixture containing low grade rock phosphate with high dolomite content when applied to soil show relatively less available soil P than the mixture containing high grade rock phosphate.

EFFECT OF PHOSPHATE SOLUBILISING BACTERIA ON SOLUBILITY OF P
FROM ROCK PHOSPHATE OR ITS MIXTURE WITH SSP

Phosphobacterin, a carrier based culture of phosphate solubilising microorganisms prepared by microbac India limited was grown on Pikovskaya's culture medium and counted. It contained 39×10^5 number of viable organisms per gram of culture. Effect of the culture on solubility of P from rock phosphate was observed when it was applied at the rate of 0.1, 0.15, 0.2, 0.25 and 0.3 mg per 100 g of soil previously treated with 100 ppm P as low grade URP-1 or its mixture with SSP.

The available P content of the soil after 15 days of incubation was found to be 5.2 ppm for all the treatments. Probably no solubilising effect was observed at the rate of application of the culture as the number of organisms per gram was only 39×10^5 /gram instead of 10^9 /g required for getting the solubilising effect or the low organic matter content of the soil did not favour the growth of the organism.

Therefore, the experiment was repeated using a higher dose of the culture i.e. 0 mg, 100 mg, 150 mg, 200 mg, 250 mg and 300 mg per 100 g soil with 100 ppm P as rock phosphate or mixture of rock phosphate and SSP to which either glucose was not added or added at the rate of 2 g per 100 g soil. The pH and available P content of the soil recorded at 7 days interval up to 30 days of incubation are presented in Table - 9 and 10.

TABLE 9. EFFECT OF PHOSPHOBACTERIN TREATMENT ON P₂O₅ UPTAKE

ROCK PHOSPHATE OR ITS MIXTURE WITH SSP

Treatments	Without glucose				With glucose			
	-----				-----			
	7 days	15 days	22 days	30 days	7 days	15 days	22 days	30 days
100 ppm P applied as low grade URP-I								
Control	5.25	5.4	5.8	6.1	5.5	4.0	4.0	4.0
100 mg/100 g soil	5.25	5.5	5.9	6.0	5.5	4.2	3.8	3.6
150 mg/100 g soil	5.00	5.5	5.9	6.1	5.45	4.2	3.6	3.6
200 mg/100 g soil	5.00	5.6	6.0	6.1	5.6	4.3	3.9	3.6
250 mg/100 g soil	5.25	5.7	6.0	6.2	5.5	4.3	3.9	3.8
300 mg/100 g soil	5.30	5.7	6.2	6.3	5.6	4.5	3.9	3.8
100 ppm P applied as low grade URP-I + SSP (1:1)								
Control	4.8	4.9	4.9	5.1	4.8	3.3	3.8	3.6
100 mg/100 g soil	5.0	4.4	4.9	5.3	5.1	3.5	3.5	3.7
150 mg/100 g soil	4.9	4.5	5.0	5.2	5.0	4.5	3.5	3.8
200 mg/100 g soil	4.2	4.9	4.9	5.3	5.4	3.9	3.9	4.0
250 mg/100 g soil	4.5	4.8	5.0	5.1	5.7	3.9	3.9	3.9
300 mg/100 g soil	4.6	4.7	4.8	5.4	5.7	3.7	3.9	3.9

TABLE 10. EFFECT OF PHOSPHOBACTERIN TREATMENT ON AVAILABILITY OF P IN SOIL
TREATED WITH ROCK PHOSPHATE OR ITS 1:1 MIXTURE WITH SSP

Treatments	Without glucose					With glucose			
	7 days	15 days	22 days	30 days		7 days	15 days	22 days	30 days
100 ppm P applied as low grade URP-I									
Control	5.2	5.2	5.8	6.0		5.1	5.2	5.2	6.2
100 mg/100 g soil	5.4	5.6	5.8	6.8		5.6	5.6	6.25	7.25
150 mg/100 g soil	5.5	5.6	6.0	7.2		5.6	6.25	6.4	8.2
200 mg/100 g soil	5.9	6.25	6.25	7.3		6.25	6.4	6.4	9.0
250 mg/100 g soil	6.0	6.25	6.5	7.5		5.6	6.25	6.75	9.0
300 mg/100 g soil	6.2	6.4	7.0	8.2		7.75	7.75	8.25	9.25
100 ppm P applied as low grade URP-I + SSP (1:1)									
Control	13.5	14.2	14.0	14.0		13.5	13.5	14.0	14.5
100 mg/100 g soil	22.5	22.75	23.25	24.5		23.75	23.75	24.75	24.75
150 mg/100 g soil	22.5	24.0	25.5	26.5		24.5	25.0	25.5	26.75
200 mg/100 g soil	23.5	25.8	26.5	28.0		26.25	26.8	27.0	29.75
250 mg/100 g soil	24.5	26.2	27.0	28.5		27.0	27.0	28.8	29.75
300 mg/100 g soil	24.75	26.2	28.0	29.0		27.75	28.8	28.8	29.75

It may be seen from Table-9 that where rock phosphate was applied without glucose addition the pH gradually increased from 5 to 5.3 at 7 days to 6 to 6.3 at 30 days irrespective of the dose of bacterial culture applied. The pH recorded from treatments receiving the mixture as compared to treatment receiving rock phosphate was always less at similar level of bacterial culture application. For all treatments receiving glucose there is substantial reduction in soil pH as compared to treatments not receiving glucose. This is due to decomposition of glucose resulting in production of some organic acid in soil. The organic acid produced is likely to solubilise more P from the rock and may also form complexes with some of the Al and Fe in soil thereby preventing it to participate in P fixation reaction.

Data presented in Table-10 shows that the available P content of the soil was higher in treatments where glucose was added than the treatments to which glucose was not added. The comparative increase in available P status of the soil due to glucose treatment and the increased solubilisation of P by increasing dose of bacterial culture at 15 and 22 days of incubation may be seen from Fig-8. In case of rock phosphate treated soil the available P increased with increased dose of bacterial culture attaining a value of 6.2 ppm at 7 days after treating the soil with 300 mg culture/100 g as compared to 5.2 ppm in control. Addition of glucose further increased the available P content to 7.75 ppm level. Presence of glucose in soil provides a substrate for

increased microbial activity thereby increasing the solubilisation of P.

The rate of increase in available P with increasing dose of bacterial culture applied to soil treated with URP and SSP mixture (Fig-8) was highest at 100 mg culture/100 g soil, beyond which the rate slowed down. Application of the culture at 100 mg/100 g soil level increased the available P from 13.5 ppm in control to 22.5 ppm after 7 days of incubation. Correspondingly glucose addition further increased the available P level of 24.5 ppm. The available P in soil almost doubled due to addition of bacterial culture to soil treated with URP and SSP (at the rate of 100 mg/ 100 g) whereas the increase was only 2-3 ppm in case of the soil receiving rock phosphate and bacterial culture (Fig-9).

Phosphate solubilising bacteria are known to bring about solubilisation of insoluble phosphates by producing organic acids (Gaur et al 1979, Venkateswaralu et al, 1984) and high carbon content of the soil is likely to favour the growth of the bacteria and the dissolution of phosphate is directly linked with the growth of the bacteria (Ahmed and Jha, 1968). In the present study the data presented shows that the treatment with bacterial culture (without glucose) has increased the solubilisation of P from URP or its mixture with SSP without decreasing the pH of the soil. In some cases the pH increased slightly. This is because of release of Ca from dissolution of apatite and Ca + Mg from dolomite dissolution. However, where bacterial culture was added along with glucose, the pH of the soil decreased due to increased microbial activity producing

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⊙ --- ⊙ --- ⊙ With glucose
 ⊙ ——— ⊙ ——— ⊙ without glucose

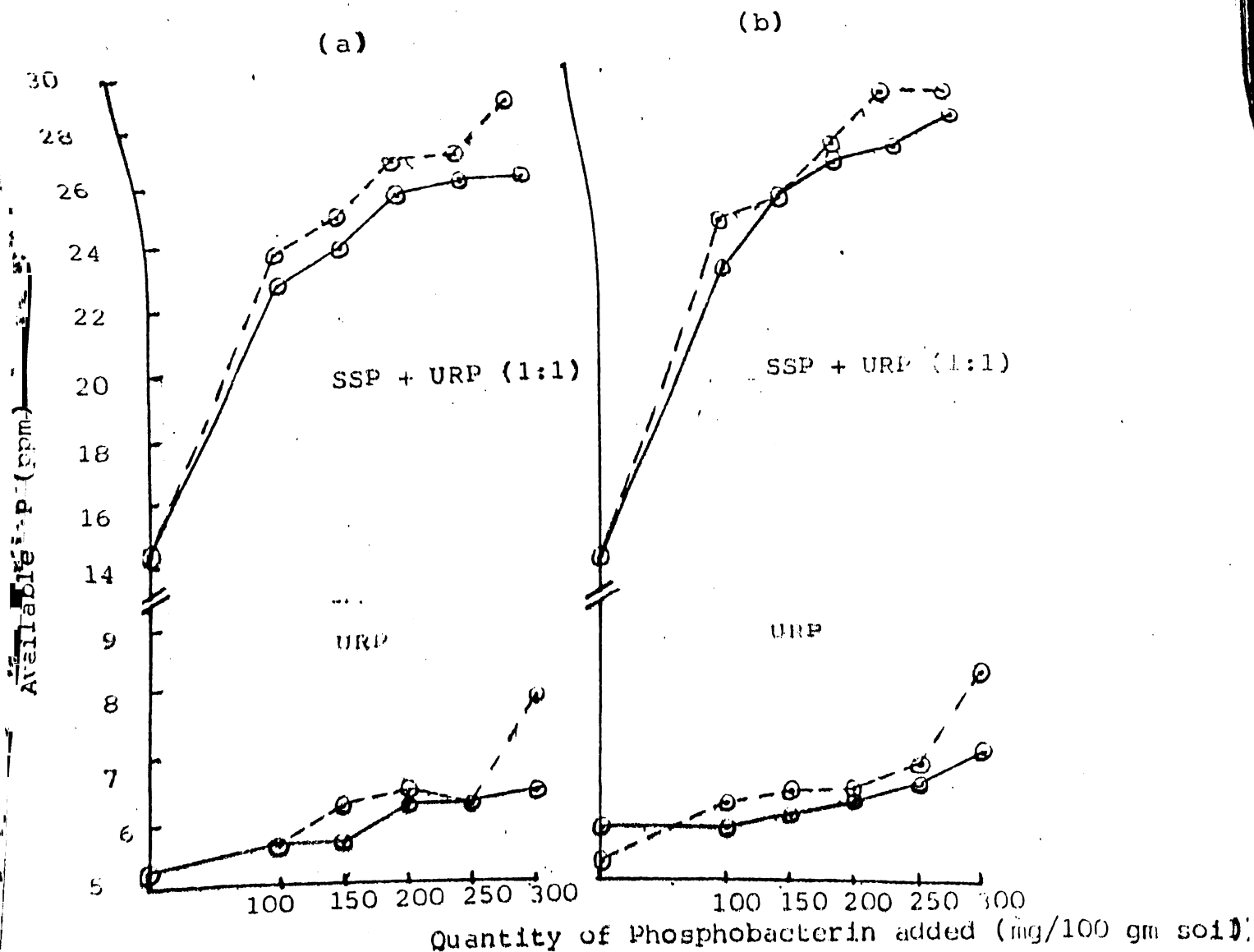


FIG:8 EFFECT OF PHOSPHOBACTERIN ON THE AVAILABLE P CONTENT OF SOIL TREATED WITH 100 ppm P EITHER AS URP OR ITS 1:1 MIXTURE WITH SSP AND INCUBATED FOR (a) 15 DAYS AND (b) 22 DAYS

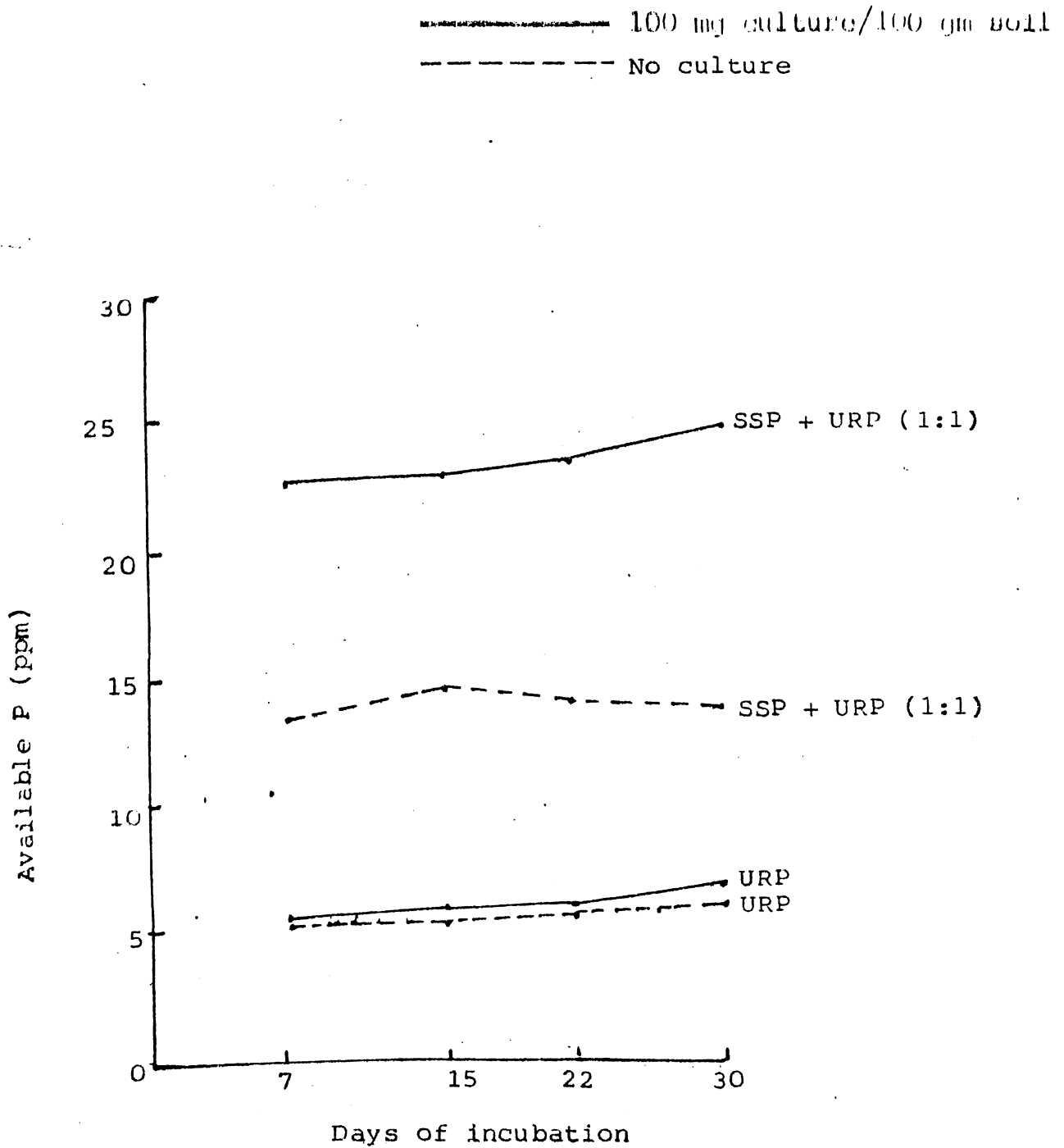


FIG: 9 VARIATION IN AVAILABLE SOIL P WITH TIME IN TREATMENTS RECEIVING EITHER ROCK PHOSPHATE OR 1:1 MIXTURE OF URP AND SSP AND TREATED EITHER WITH 100 mg CULTURE /100 gm SOIL OR NO CULTURE ADDED.

more organic acid which helped to solubilise more of insoluble P. The increased solubilisation of insoluble P in the mixture as compared to rock phosphate applied alone may be due to the availability of P needed for the growth of the microorganism.

The findings of the experiment suggest that carrier based phosphobacterin culture containing 39×10^5 number of viable cells/g can be applied to soil at the rate of 100 to 300 mg/ 100 g soil or in other words a culture containing 10^9 cells/g may be applied at the rate of 0.1 to 0.3 mg/100 g of soil (2 to 6 kg/ha) for increasing the availability of P from rock phosphate or its mixture with SSP.

EFFECT OF STORAGE TEMPERATURE AND HUMIDITY CONDITIONS ON STORAGE QUALITY OF SSP AND ITS MIXTURE WITH LOW GRADE URP

The water soluble and citrate soluble P content of SSP and its 1:1 and 1:3 mixture of low grade URP-I stored at 40°C and at room temperature and relative humidities of 50, 70 and 90 per cent are reported in Tables-11 and 12. The change in water soluble and citrate soluble P content of SSP or its mixtures with rock phosphate with time of storage is shown in Figs-10, 11 and 12. The P content at 0 days corresponds to the temperature and humidity conditions prevailing at the time of mixing. Therefore, the points corresponding to P concentrations at 0 and 15 days have been joined by dotted line.

Fig-10 shows that water soluble P in SSP decreased with time whereas citrate soluble P increased with time. Such increases or decreases are more at relative humidity of 90% than at 50%. The water soluble P content of SSP at 40°C is slightly

TABLE 11. EFFECT OF STORAGE TEMPERATURE AND HUMIDITY CONDITIONS ON WATER SOLUBLE P CONTENT (%) OF SSP AND ITS MIXTURE WITH LOW GRADE URP-I

Fertiliser	Humidity (%)	Storage time in days					

		0	15	30	60	75	90
Storage at room temperature							
SSP	50		6.74	6.74	6.68	6.60	6.54
	70	6.9*	6.72	6.68	6.62	6.54	6.50
	90		6.65	6.63	6.62	6.54	6.50
SSP + URP(1:1)	50		3.37	3.39	3.42	3.36	3.33
	70	3.4*	3.24	3.32	3.39	3.33	3.30
	90		3.20	3.29	3.31	3.30	3.30
SSP + URP(1:3)	50		1.70	1.70	1.74	1.72	1.71
	70	1.71*	1.66	1.69	1.73	1.70	1.70
	90		1.65	1.69	1.70	1.67	1.66
Storage temperature 40°C							
SSP	50		6.78	6.76	6.71		
	70	6.9	6.73	6.70	6.66		
	90		6.72	6.68	6.65		
SSP + URP(1:1)	50		3.39	3.41	3.47		
	70	3.4	3.31	3.40	3.42		
	90		3.25	3.36	3.38		
SSP + URP(1:3)	50		1.66	1.71	1.75		
	70	1.71	1.65	1.65	1.74		
	90		1.60	1.64	1.73		

* P content of SSP or the mixture corresponds to prevailing room temperature and humidity at the time of mixing.

TABLE 12. EFFECT OF STORAGE TEMPERATURE AND HUMIDITY CONDITIONS ON CITRATE SOLUBLE P CONTENT (%) OF SSP AND ITS MIXTURE WITH LOW GRADE URP-I.

Fertiliser	Humidity (%)	Storage time in days					
		0	15	30	60	75	90
SSP	50		0.18	0.20	0.22	0.23	0.24
	70	0.12*	0.22	0.23	0.27	0.29	0.30
	90		0.27	0.24	0.30	0.26	0.30
SSP + URP (1:1)	50		0.24	0.27	0.27	0.29	0.31
	70	0.24*	0.36	0.34	0.20	0.24	0.31
	90		0.35	0.16	0.13	0.23	0.28
SSP + URP(1:3)	50		0.31	0.33	0.34	0.35	0.36
	70	0.30*	0.31	0.39	0.36	0.38	0.39
	90		0.32	0.39	0.38	0.39	0.39
Storage temperature 40°C							
SSP	50		0.14	0.16	0.13		
	70	0.12	0.19	0.22	0.26		
	90		0.20	0.23	0.29		
SSP+ URP(1:1)	50		0.25	0.27	0.23		
	70	0.24	0.30	0.26	0.28		
	90		0.35	0.18	0.18		
SSP + URP (1:3)	50		0.37	0.33	0.26		
	70	0.30	0.38	0.33	0.27		
	90		0.39	0.39	0.28		

* P content of SSP or the mixture corresponds to prevailing room temperature and humidity at the time of mixing.

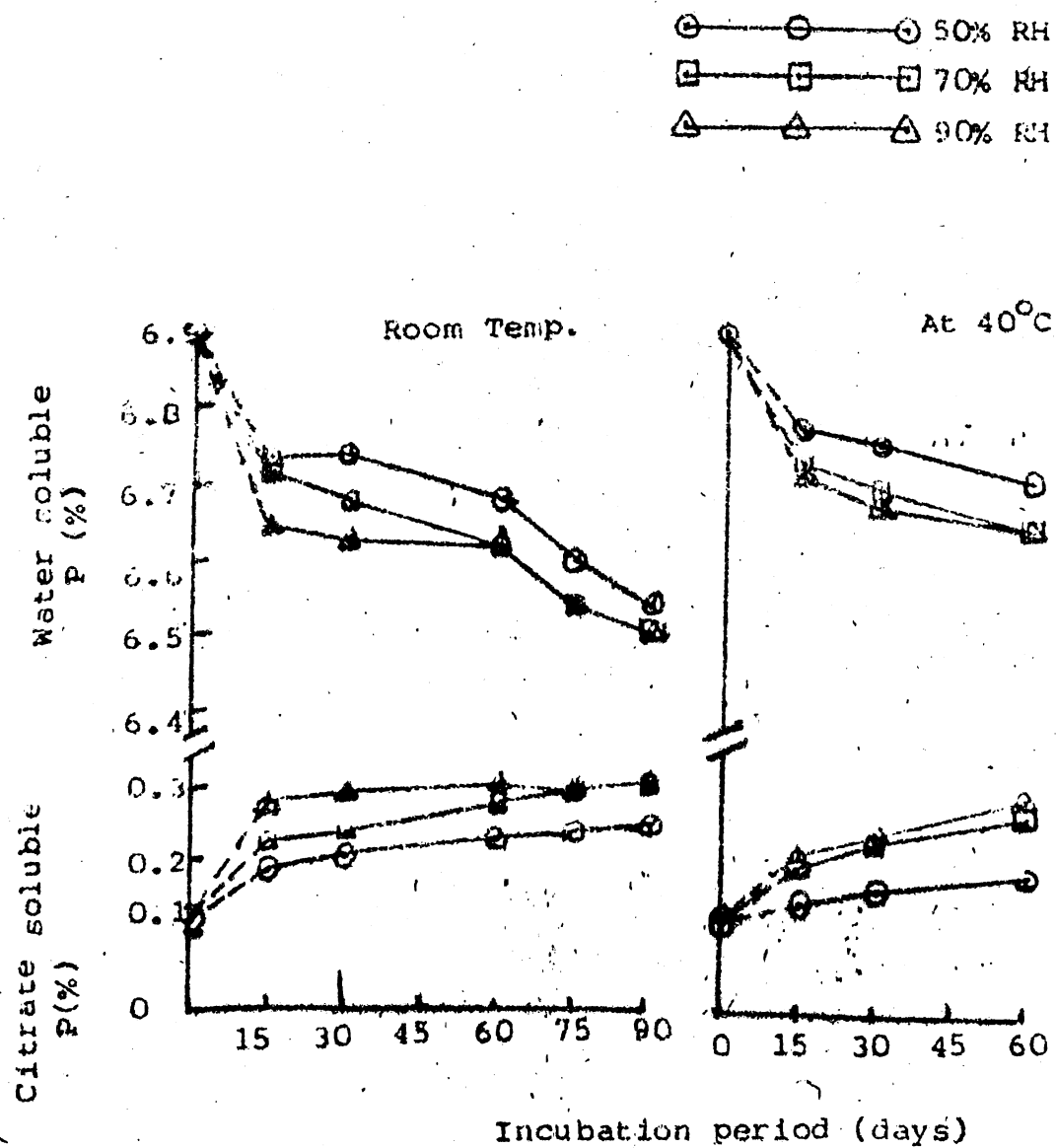


FIG: 10 EFFECT OF STORAGE TEMPERATURE AND HUMIDITY ON CITRATE AND WATER SOLUBLE P CONENT OF SSP

○—○—○ 50% RH
 □—□—□ 70% RH
 △—△—△ 90% RH

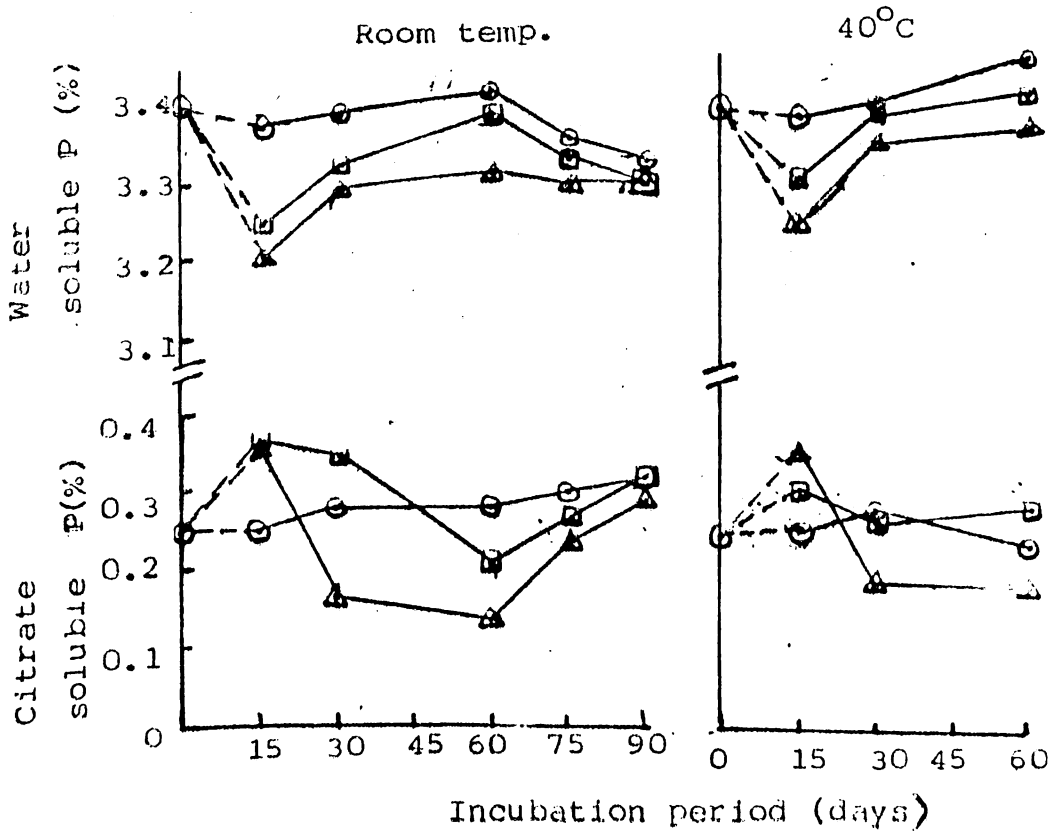


FIG:11 EFFECT OF STORAGE TEMPERATURE AND HUMIDITY ON WATER AND CITRATE SOLUBLE P CONTENT OF 1:1 MIXTURE OF SSP AND LOW GRADE URP-I

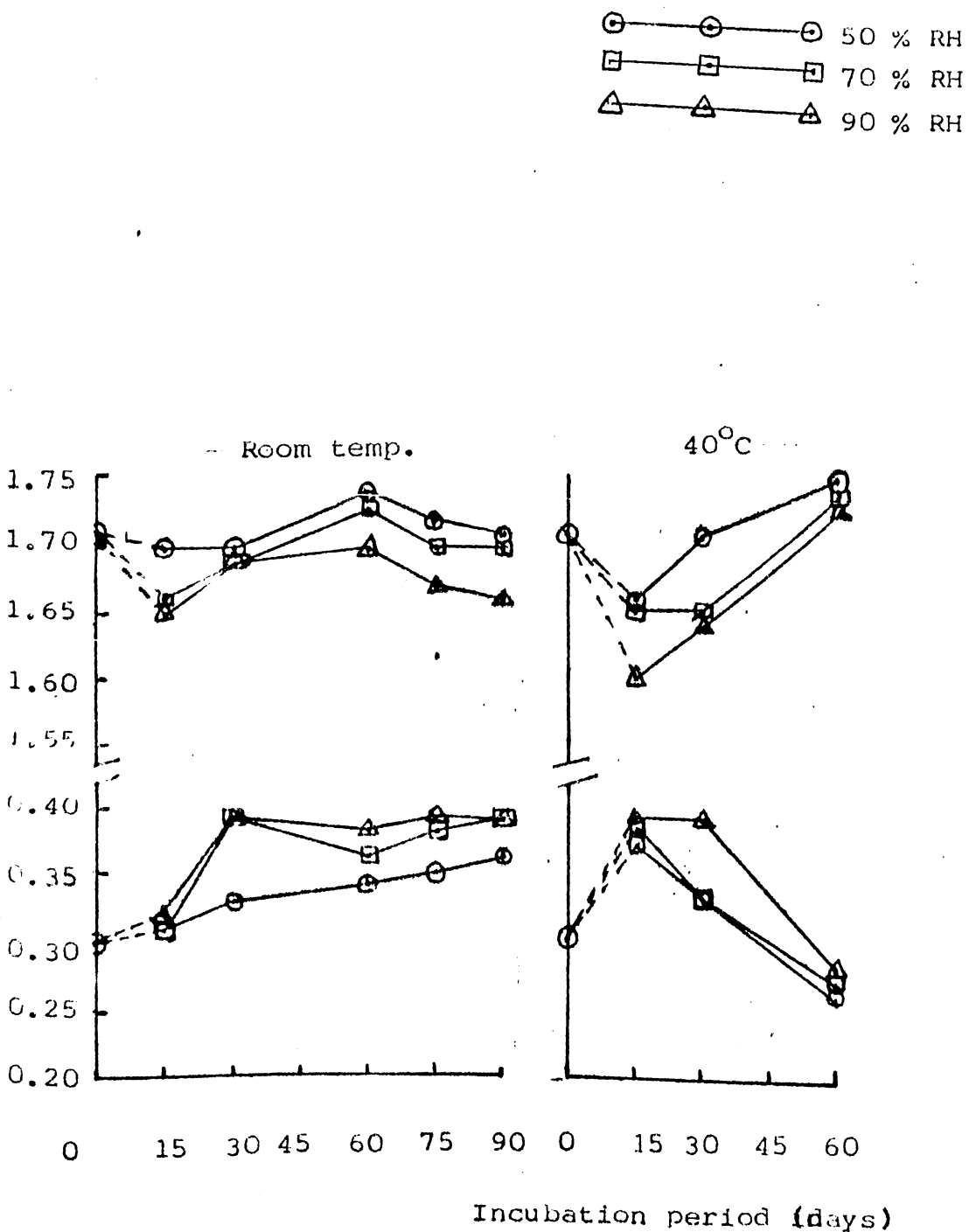


FIG:12 EFFECT OF STORAGE TEMPERATURE AND HUMIDITY ON WATER AND CITRATE SOLUBLE P CONTENT OF 1:3 MIXTURE OF SSP AND LOW GRADE URP -I

higher than at room temperature. The decrease in water soluble P and increase in citrate soluble P was maximum during the first 15 days of storage. The water soluble P in SSP varied between 6.74% and 6.5% and the citrate soluble P varied between 6.78% and 6.65% for all temperature and humidity conditions. The decrease in water soluble P and increase in citrate soluble P content of SSP can be explained based on the dissolution of monocalcium phosphate (MCP) by absorbing water produces DCP and phosphoric acid. Choudhury et al (1988) while study reversion of different soluble phosphatic fertiliser like SSP, DAP and various DAP based N:P:K complex fertilisers have also observed decline in water soluble P and an increase in citrate soluble P content with increased temperature from 10°C to 40°C which was accompanied by decreased relative humidity. The decrease in water soluble P content of SSP after 60 days of incubation at 40°C was reported to be about 7% (Choudhury et al, 1988) as compared to a decrease of 3.6% at 40°C observed in the present study. Data presented in Table-13 shows that the available P content from fresh sample of SSP was 7.02% which on incubation at room temperature decreased to 6.64% at 50% R.H. and to 6.63% at R.H. of 70% and 90% suggesting that a small fraction of P is also converted to insoluble phosphate like apatite. But the reversion of citrate soluble to insoluble P form is less at 40°C than at room temperature. Such conversion of P to apatite during storage has been observed by X-ray diffraction analysis of stored P fertilisers (Choudhury et al, 1988).

TABLE 13. EFFECT OF STORAGE TEMPERATURE AND HUMIDITY CONDITIONS OF AVAILABLE P CONTENT (%) OF SSP AND ITS MIXTURE WITH LOW GRADE URP-I

Fertilisers	Humidity (%)	Storage time in days					
		0	15	30	60	75	90
Storage at room temperature							
SSP	50		6.92	6.93	6.93	6.92	6.64
	70	7.02*	6.93	6.96	6.95	6.59	6.30
	90		6.92	6.94	6.97	6.66	6.30
SSP + URP (1:1)	50		3.61	3.66	3.69	3.54	3.62
	70	3.64*	3.60	3.66	3.69	3.69	3.61
	90		3.55	3.64	3.74	3.75	3.65
SSP + URP (1:1)	50		2.01	2.03	2.08	1.92	1.90
	70	2.01*	1.97	1.99	2.08	2.0	1.95
	90		1.95	2.04	2.09	2.07	2.10
Storage temperature 40°C							
SSP	50		6.92	6.92	6.88		
	70	7.02	6.92	6.92	6.91		
	90		6.92	6.91	6.94		
SSP + URP (1:1)	50		3.64	3.68	3.71		
	70	3.64	3.61	3.66	3.77		
	90		3.60	3.61	3.92		
SSP + URP (1:3)	50		2.03	2.04	2.08		
	70	2.01	2.03	1.98	2.08		
	90		2.04	2.04	2.12		

* P content of SSP or the mixture corresponds to prevailing room temperature and humidity at the time of mixing.

The 1:1 mixture contained 6.37% total, 3.4% water soluble and 0.24% citrate soluble P. The corresponding P percentages for 1:3 mixture were 6.37%, 1.71% and 0.3%. At 15 days of incubation the water soluble P content decreased and then increased up to 60 days where as citrate soluble P content increased at 15 days and then decreased upto 60 days. However, no such decrease of citrate soluble P after 15 days was observed for 1:3 mixture. These changes were more at 90% relative humidity than at 50% relative humidity. After 60 days of incubation the citrate soluble P content either slightly increased or remain more or less same.

In general the available P content of the mixtures increased with all storage conditions. But, the variation of available P content of the mixtures for all storage conditions was between 3.55% and 3.92% for 1:1 mixture and between 1.97 and 2.09% only for 1:3 mixtures. These results suggest that the available P content of the mixture is not reduced on storing the product at relative humidities varying between 50 and 90% and temperature varying between room temperature and 40°C, but increased slightly. The increase may be explained on the basis of acidulating effect of phosphoric acid produced by dissolution of MCP on the insoluble P in the rock. Since the moisture absorbed by the mixture during storage is small, not much MCP has been dissolved to produce sufficient H_3PO_4 . Presence of large amount of Ca and Mg through dolomite in the mixture is likely to participate in reactions leading to reversion of water soluble P compounds to citrate soluble and citrate insoluble forms on prolonged storage (Sauchelli, 1963).

Although, the present study showed some increase in citrate soluble P, there is no evidence of increase in insoluble form of P compound.

Fertiliser must be stored from the time of its production until its final use in soil. In our country the actual period of storage may vary from a few days to a year or even more in certain cases. It is important that during storage the caking should be minimum and the fertiliser should remain free flowing. It has been observed that the mixture of rock phosphate and super phosphate hardens on storing but can be easily broken. In the present investigation caking quality of the mixture has not been scientifically studied using needle penetrometer. However, the mixtures stored at room temperature for one year in polythene bottles have been analysed for formation of fertiliser granule of more than 2 mm size as an indicator of caking quality.

The 1:1 mixture contained 45% granules of > 2 mm size as compared to 34% in the 1:3 mixture. However, the granules formed can be easily broken. Increasing the proportion of super phosphate in the mixture has greater tendency to cake. The analysis of the granules formed during prolonged storage as compared to powder form of the fertiliser mixture is reported in Table-14. It may be seen from the table that the granules in the mixture contained about 0.1 and 0.16 per cent more citrate soluble P than the powdered form in 1:1 and 1:3 mixtures, respectively. In general the available P content of the granule in the mixture was higher than the powdered form. As compared

TABLE 14. COMPARISON OF AVAILABLE P PERCENTAGE IN THE MIXTURE PREPARED IMMEDIATELY AND AFTER ONE YEAR OF STORAGE

Fertiliser and storage time	% P		
	Water soluble	Citrate soluble	Available
A. Freshly prepared			
SSP + URP mixture(1:1)	3.40	0.25	3.65
SSP + URP mixture(1:3)	1.71	0.30	2.01
B. Stored for one year			
(i) SSP + URP mixture (1:1)	3.37	0.32	3.69
Fertiliser granule of > 2mm size	3.41	0.38	3.79
Powder form	3.35	0.28	3.63
(ii) SSP + URP mixture (1:3)	1.65	0.42	2.07
Fertiliser granule of > 2mm size	1.63	0.52	2.15
Powder form	1.67	0.36	2.03

to available P contents (3.65% in 1:1 mixture and 2.01% in 1:3 mixture) of the freshly prepared mixtures, the mixtures stored for one year had slightly higher available P (3.69 and 2.15% in 1:1 and 1:3 mixtures, respectively). These results suggest that the mixture of super phosphate and rock phosphate can be safely stored for a long period of time without reversion of available P to insoluble P in the mixture.

CHAPTER V

SUMMARY AND CONCLUSION

CHAPTER - V

S U M M A R Y A N D C O N C L U S I O N S

In the present investigation, the dissolution of four grades of Udaipur rock phosphates such as low grade URP-I (6.35% P), low grade URP-II (8.0% P), medium grade URP (10.65% P) and high grade URP (14.75% P) and their 1:1 mixtures with SSP in a typic Haplustult release of P was studied. Further, the effect of storage temperature and humidity conditions on the fertiliser quality of the rock phosphate and super phosphates were also carried out.

The rock phosphate samples were analysed for their water soluble, ammonium citrate soluble and total P, Ca and Mg content. From cumulative amount of ammonium citrate soluble P released from the rock by five successive extractions with ammonium citrate (which varied between 0.93% to 1.28% for all grades of rock phosphates) the a_0 value (unit cell dimension) on the apatite in the rock was calculated using a chemical statistical model. The a_0 value calculated was 9.366\AA for all the four grades of rock phosphates suggesting the uniformity of apatite. The formula of the apatite present in the rock as calculated from a_0 is $\text{Ca}_{9.91} \text{Na}_{0.07} \text{Mg}_{0.02} (\text{PO}_4)_{5.72} (\text{CO}_3)_{0.28} \text{F}_{2.11}$. The theoretical P percentage in apatite was 17.8%. Udaipur rock phosphate is known to contain dolomite as dominant associated mineral with apatite. The percentage of dolomite in the rock was computed assuming that all the P is apatite bound and barring the Mg in apatite, the rest is

associated with dolomite. The percentage of dolomite decreased with increasing grade of the rock (low grade URP-I 54.6%; low grade URP-II 47.54%, Medium grade URP 34.59%, high grade URP 14.58%). Although the citrate soluble P in the rock increased slightly with increasing grade (0.43% P in the low grade URP to 0.5% P in high grade URP) the absolute citrate soluble P of both the low grade URP was 2.42% and for the medium and high grade URP was 2.8%.

DISSOLUTION OF URP IN SOIL AND AVAILABILITY OF P

Four grades of rock phosphates and their mixtures with SSP in 1:1 proportions and SSP alone were added to the soil at the rate of 100 ppm P and incubated at room temperature maintaining the moisture content of the soil at field capacity. Periodically available P (Olson's method) and pH were measured. The soil used in the study was a typic haplustult having a pH 4.6 sandy loam texture, CEC of 2.9 C mole (p+) kg^{-1} , low in organic carbon (0.65%) and available P (4.5 ppm).

The pH of the soil increased with time due to addition of rock phosphate, the increase being more in treatments receiving URP containing more dolomite. The equilibrium was reached between 30 and 45 days. The increase in soil pH was related to the dolomite content of the URP. The soil pH recorded after 60 days of incubation were 6.9 for low grade URP-I, 6.6 for low grade URP-II, 6.5 for medium grade URP and 6.2 for high grade URP. The available P content of the soil increased from 4.5 ppm in control of 6.5 ppm, 7.1 ppm, 9.0 ppm and 9.5 ppm at 60 days for low grade-I, low grade II, medium grade and high grade

URP, respectively. The increased P availability is related to the low dolomite content of the rock but not to the grade of the rock phosphate. High dolomite content of a rock increases the soil pH and reduces the dissolution of the rock phosphate thereby releasing less P. Treatment receiving SSP showed a gradual decrease in soil pH and available P content of the soil attaining pH value of 3.9 and available P of 29.4 ppm at 60 days. The decrease in available P was due to fixation of the soluble P as veriscite and strengite. In case of the treatments receiving 1:1 mixture of SSP and URP the available P content of soil increased with time attaining values of 24.0 ppm for low grade-I, 24.2 ppm for low grade II, 28.8 for medium grade and 28.8 for high grade URP. The increase in soil pH was related to the dolomite content of the URP used in the mixture.

The observed variations of pH and available P content of soil have been explained based on the reaction of monocalcium phosphate in SSP which when added to soil is converted to dicalcium phosphate and phosphoric acid. The soluble P is converted to insoluble Fe and Al phosphates by reacting with active Fe and Al in soil. But, when an intimate mixtures of SSP and URP are used, the acid produced by the reaction of MCP act upon the apatite present in the immediate vicinity and solubilises P instead of solubilising more Al and Fe in soil. Hence application of the mixture helps in minimising P fixation and increasing the availability of P from insoluble apatite.

EFFECT OF PHOSPHOBACTERIN ON SOLUBILISATION OF INSOLUBLE P

To study the effect of phosphobacterin, a carrier based culture of phosphate solubilising bacteria on increasing

the availability of P in soil treated with 100 ppm P as low grade URP-I or its 1:1 mixture with SSP, the soil was treated with 0, 0.1, 0.15, 0.2 and 0.25 mg of culture per 100 g/100 g soil along with or without addition of glucose at the rate of 2 g/100 g soil and incubated at room temperature maintaining the moisture level at field capacity. Samples were analysed for available P and pH at 7, 15, 22 and 30 days. The phosphobacterin culture contained 39×10^5 viable cell per gram.

The available P content of the rock phosphate treated soil increased with increasing dose of bacterial culture treatment. The increase was from 5.2 ppm in control to 6.2 ppm with 300 mg culture/100 g soil after 7 days of treatment which further increased to 7 ppm after 22 days of incubation. There was further increase of 2.25 ppm at 22 days of incubation when glucose was used. In case of soil treated with 1:1 mixture of SSP : URP, the available P content of 13.5 ppm recorded for no culture treatment increased to 22.5 ppm at 7 days and to 27.75 at 22 days. Glucose treatment raised the value to 29.75 ppm. There was a greater effect of phosphobacterin treatment in increasing the availability of P from the mixture than the rock phosphate. The pH of the soils of all the treatments receiving glucose increased slightly, but decreased when glucose was added to supply energy for the growth of the bacteria. Increased bacterial activity produced more acid thereby solubilising more insoluble P. The rate of solubilisation of P was highest at 7 days of incubation which decreased thereafter.

The results of this investigation suggest that phosphobacterin culture containing about 10^9 viable cell per gram of culture may be applied at the rate of 100-300 mg/100 g soil (2 to 6 kg/ha) to increase the solubilisation of insoluble P. The effect is likely to be better in soil containing high amount of organic matter providing a source of carbon for the growth of bacteria.

EFFECT OF STORAGE TEMPERATURE AND HUMIDITY ON FERTILISER QUALITY OF SSP AND ITS MIXTURE WITH URP

Single super phosphate and its 1:1 and 1:3 mixtures with low grade URP-I were incubated at room temperature and at 40°C in an B.O.D incubator. The relative humidity was maintained at 50%, 70% and 90%. Fertiliser samples were drawn at 15 days interval and analysed for water soluble (W.S), citrate soluble (c.s) and total P.

The water soluble P content of SSP decreased and citrate soluble P increased with time of storage due to reversion of a part of monocalcium phosphate to dicalcium phosphate. On prolonged storage upto 60 days about 3.6% of total available P (6.9%) in SSP reverted to insoluble form like apatite. The water solubility was slightly more at 40°C than at room temperature. The decrease of water soluble P was more when the relative humidity was high.

In case of mixtures at 15 days the water soluble P content decreased and citrate soluble P content increase for

all storage conditions. The decrease in water soluble P was more for high humidity conditions due to conversion of a part of monocalcium phosphate into DCP. Increased moisture content in the atmosphere favoured the reaction. After 15 days the water soluble P increased again and citrate soluble P decreased at 30 days and then varied slightly increased for 1:1 mixture but only increase in citrate soluble P was observed for 1:3 mixture. In general, the available P content of the mixture increased in all the treatments irrespective of storage condition. In the mixture absorption of moisture and dissolution of MCP produces DCP and H_3PO_4 . The acid produced is used to solubilise more of insoluble P and hence the availability increases with time of storage. The available P content of the 1:1 mixture increased from about 3.6% at 15 days (for all humidity condition) to 3.7% at 60 days which again decreased to about 3.6% at 90 days at room temperature probably due to reconversion of a part of soluble P again to insoluble form. Similar effect is also observed for 1: 3 mixture. Therefore, it may be concluded that the available P do not significantly change the fertiliser value of the mixture on prolonged storage.

The fertiliser mixtures (1:1 and 1:3) stored for one year at room temperature and humidity conditions have shown the available P content of the 1:1 mixture and 1:3 mixture to be 3.69% and 2.15% respectively. But the caking quality of the fertiliser studies by calculation, the % of granules of $> 2mm$.

size formed after one year of storage show 45% granules in 1:1 mixture and 34% in 1:3 mixture. But these granules can be easily broken.

From the results presented and discussed above the following conclusions may be drawn.

CONCLUSIONS

1. The four grades of rock phosphates from Udaipur deposits have apatite with same crystal chemical structure. The chemical formula of the apatite is $\text{Ca}_{9.9} \text{Na}_{0.07} \text{Mg}_{0.02} (\text{PO}_4)_{5.72} (\text{CO}_3)_{0.28} \text{F}_{2.11}$ and its a_0 spacing is 9.366 \AA . The theoretical P percentage of the rock phosphates is 17.8%. The dolomite content of the rock phosphates increased with decreasing P content of the rock and varied between 14.58 and 54.6 percent.
2. The solubility of the apatite in the rock phosphate is not affected by the grade of the rock but by their dolomite content. Increased dolomite content reduces the available P content of the soil treated with rock phosphate.
3. Application of mixture of SSP and rock phosphate to soil helps to minimise fixation of P in soil and increase the availability of P. Use of mixture

increase the available P content of soil with time where as application of water soluble source like SSP increases the available P status of the soil immediately after application and then decreases.

4. Use of phosphobacterin a carrier based culture containing 10^9 viable cells/g at the rate of 2 to 6 kg/ha along with rock phosphate or its mixture with SSP increases the availability of P. Addition of a carbon source like glucose further increases the availability of P.
5. On prolonged storage of SSP water soluble P decreases and citrate soluble P increases. Water soluble P content is more at high temperature (40°C) than at low temperature (room temperature).
6. Available P content of the mixture of SSP and rock phosphate do not show any significant change in their available P content on storage.

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* Original not seen.