

The Influence of Pyrite on the Solubility of Minjingu and Panda Phosphate Rocks

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Abstract

A laboratory study was conducted to investigate the effect of pyrite rock on the solubility of Minjingu and Panda phosphate rocks. The rocks were ground to 100 mesh (0.045 mm) after which each phosphate rock was mixed with pyrite at P:S ratios of 1:4, 1:3, 1:2, 1:1, 2:1, and 3:1. The mixtures were moistened and incubated at 25°C. A sample was taken weekly from the mixtures and tested for pH, soluble P, Al and Mn. Results showed that mixing phosphate rocks with pyrite lower the pH and increases water soluble P of the incubation mixture. This effect was higher with Panda than with Minjingu phosphate rock. Mixing Panda phosphate rock with pyrite also resulted into high amounts of Al and Mn being released in solution. The rate of P release increased with the period of incubation up to the constant value. In mixtures with low P:S ratios this point was attained earlier than those with high P:S ratios.

Keywords: Pyrite rocks, minjingu rocks, panda phosphate rocks, incubation mixture

Introduction

Phosphorus (P) is the second nutrient needed in high quantity by plants. In Tanzania most soils are low or deficient in P hence making the application of fertilizer P necessary. Commonly used P fertilizers in Tanzania are water soluble forms, most of which are very expensive for peasant farmers.

Phosphate rocks (PRs) can be possible alternative sources of P. In Tanzania phosphate rocks are found in several forms and in several places but the large quantity are of sedimentary and igneous carbonatite form found at Minjingu in Arusha and Panda hills in Mbeya respectively.

Minjingu deposit contains between 10 to 25 million tons of PR and Panda deposit contains over 300 million tons of PR (Mwambete, 1991). So far Minjingu is the only deposit being exploited.

Studies on the usefulness of phosphate rocks as P fertilizers has been giving quite variable results, depending on the type of phosphate rock, the soils where it is applied, size of the PR, method of application and the crop (Kamasho, *et al.*, 1992; Van Straaten, *et al.*, 1992). Work done by Patel (1975) in Mwanza, Ngatunga and Deckers (1984) in Mtwara and Mnkeni *et al.* (1991) in Morogoro indicated Minjingu phosphate rock to be inferior to TSP in terms of agronomic effectiveness

particularly to soils with pH higher than 6.2. However, Minjingu phosphate rock has been reported to have higher residual effect than water soluble P fertilizers (Patel, 1975; Bromfield *et al.*, 1981; Chien *et al.* 1987a).

According to Khasawneh and Doll (1978) sedimentary rocks are less effective in neutral and alkaline soils and phosphate rocks of igneous origin are less effective even in acidic soils. Studies conducted in Tanzania on a phosphate rock of sedimentary origin from Minjingu have shown highest responses on relatively low pH light textured soils (Kimambo *et al.*, 1989; Mnkeni *et al.*, 1993), whereas phosphate rock of igneous origin from Panda hill have shown low responses even in acidic soils (Semoka *et al.*, 1993).

The common property of phosphate rocks is their low solubility. Panda phosphate rock has a relatively lower solubility than Minjingu phosphate rock (Van Straaten, *et al.*, 1992). The low reactivity and solubility of these phosphate rocks reduce their suitability of being used as direct source of P to crops. The agronomic effectiveness of phosphate rocks can be increased by raising the solubility of these rocks.

The dissolution of phosphate rocks can be improved by raising the level of H^+ supply or increasing the size of Ca^{2+} sink in the soil (Robinson *et al.*, 1992). Methods of improving the solubility of Minjingu and other phosphate rocks include compaction of the PRs with TSP or urea, partial acidification of PRs and combining PRs with elemental S, FYM or compost (Chien *et al.*, 1987b; Chien *et al.*, 1987c; Rajan, 1987; Menon *et al.*, 1991; Ikerra *et al.* 1994). In Tanzania the first two methods would require the use of imported materials hence making them expensive. Therefore the interest is to find the possibility of using locally available materials in improving the solubility of

Minjingu and Panda PRs. Areas to explore are the use of geologic materials to enhance PR solubility. Geologic materials reported elsewhere to influence the solubility of PRs include zeolites (Lai and Erbel, 1986) and pyrite (Gupta and Mishra, 1978; Mishra *et al.*, 1980), the former acts as Ca^{2+} sink whereas the latter as supplier of H^+ in the PR dissolution process. The first two methods would require the use of imported materials hence making them expensive. Therefore the use of locally available materials in improving the solubility of minjingu and Panda PRs might be most appropriate. Apart from the use of organic materials other areas to explore is the use of geologic materials.

In Tanzania limited study have been done on the use of zeolite (Mnkeni *et al.*, 1994) and none was done on the use of pyrite. High quantity of pyrite is found at Sammena hill in Geita. According to Britton (1976) the deposit contains about 190 million tons of the ore which could supply 28.5 million tons of sulphur. This study was conducted to test the effect of pyrite rock from Sammena on the solubility of Minjingu and Panda phosphate rocks.

Materials and methods

Two phosphate rocks one of sedimentary and another of igneous origin and pyrite rock were used in this study. The PR of sedimentary origin was obtained from Minjingu in Arusha, PR of igneous origin was obtained from Panda hill in Mbeya whereas Pyrite rock was obtained from Sammena hill in Geita. Some of the chemical properties of the rocks used in this study is shown in Table

1. The soil used was obtained from the upper 30cm of the Rhodic ferralsols from Mlingano, Tanga. Some of the chemical composition of the soil is shown in Table 2.

treatments. Each PR/pyrite mixture amounted to 200 g. The amount of PRs and pyrite mixed were calculated basing on total P and S contents respectively. Thereafter, 50g of soil was added in each

Table 1: Chemical composition of Minjingu, Panda phosphate rocks and Sammena pyrite.

Content	Minjingu PR (%)	Panda PR (%)	Pyrite rock
Total P ₂ O ₅	34.8	18.00	
Citric acid soluble P	2.86	1.6	n.d
CaO	46.4	26.7	2.24
MgO	3.4	1.3	0.80
Na ₂ O	0.84	1.94	n.d
K ₂ O	1.4	4.1	n.d
SiO ₂	10.4	48.1	47.91
F	2.8	n.d	n.d
AL ₂ O ₃	2.3	15.1	10.80
Fe ₂ O ₃	1.0	12.4	18.91
p(H ₂ O)	9.0	5.8	n.d
SO ₃	n.d	n.d	35.28

Note: The soil properties of the soil used in this study is shown in Table 2.

Table 2: Initial soil characteristics

PH (H ₂ O)	PH (KCl)	OC (%)	TN (%)	Avail.P (mg/kg)	CEC (cmol/kg)	Ca (cmol/kg)	K (cmol/kg)	Mg (cmol/kg)	Na (cmol/kg)
6.0	5.2	2.1	0.19	1	12.9	4.4	3.5	0.9	0.1

Method

The effect of pyrite rock on PR solubility was tested in the laboratory. This was done in PR/pyrite mixture of P:S ratios of 3:1, 2:1, 1:1, 1:2, 1:3 and 1:4, making a total of 6 mixtures for each of the phosphate rock. Also the treatment of PR alone was included. The treatments were tested in 2 replicates.

The PRs and pyrite rock were ground and passed through a 0.045 mm sieve. PRs and pyrite rock were mixed according to

treatment to act as a source of chemolithotropic bacteria responsible for oxidation of S bound in pyrite to sulphuric acid. The contents were thoroughly mixed, put in volumetric container and moistened. The mixtures were incubated at 25°C for 11 weeks. A sample of 5 g was taken weekly from the mixtures, soaked in 20 mls of distilled water for 4 hours and latter stirred and filtered with 42 Whatman filter paper. Then pH and the amount of dissolved P, Al and Mn were determined in the filtrate.

Results and discussion

Both phosphate rocks responded to the addition of pyrite rock. Incubation of phosphate rocks with pyrite rocks resulted to the drop in pH and increase in P solubility. However the extent of these effects varied between the phosphate rocks tested. The response of pH to P:S ratios and the period of incubation is illustrated in Figures 1 and 2. Solutions from phosphate rock/pyrite mixtures had lower pH values than that of phosphate rock alone. The drop of pH values of the solutions corresponded with the increase in pyrite rock in the mixtures. The lowest pH was obtained in solution from the mixtures with highest amount of pyrite rock. The drop in pH values ranged between 0.5 to 4 units. At lower P:S ratios the drop in pH ranged between 3.5 to 4 units. At higher P:S ratios, the solution from Panda rock mixtures showed a very big drop than that of Minjingu phosphate rock mixtures. Unlike Minjingu PR/pyrite mixtures, increasing the amount of pyrite

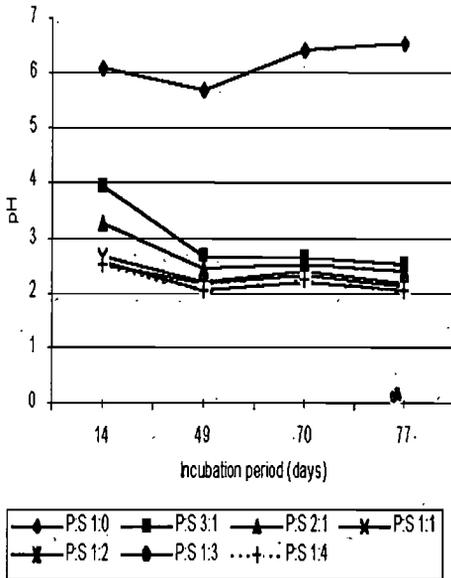


Figure 1: Effect of Panda RP/Pyrite mixture and incubation period on pH

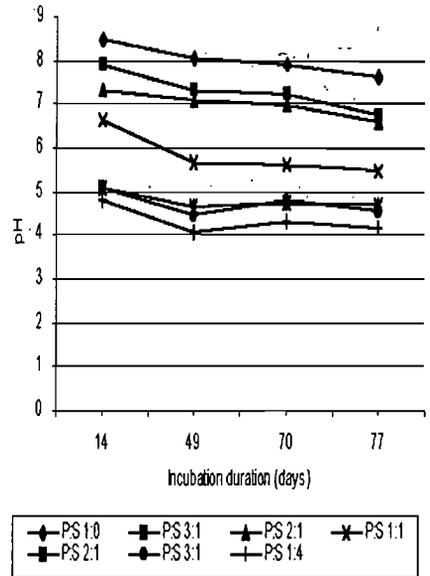


Figure 2: Effect of Minjingu RP/Pyrite mixture and incubation period on pH

in the Panda phosphate rock mixtures resulted to very little extra drop in pH. The effect of P:S ratios on pH differed in the first 49 days afterwards all ratios behaved the same way. The extent of pH drop in the solution of Minjingu phosphate rock mixtures differed between the P:S ratios, increasing with the amount of pyrite in the mixtures. Generally the pH in all treatments in the first 49 days were dropping with time. The effect of incubation time on pH of the phosphate rock and pyrite mixtures was not observed.

Figures 3 and 4 show the effect of P:S and period of incubation on the solubility of PRs. The solubility of PRs in the PR/pyrite mixtures during the early stages of incubation was very low. Solubilization was not observed in Minjingu as well as in Panda phosphate rock in the first 7 days for all P:S ratios. Latter the PR solubility increased steadily with time

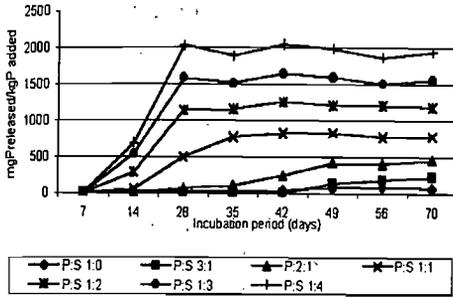


Figure 3: Effect of Panda RP/Pyrite mixture and incubation period on P solubility

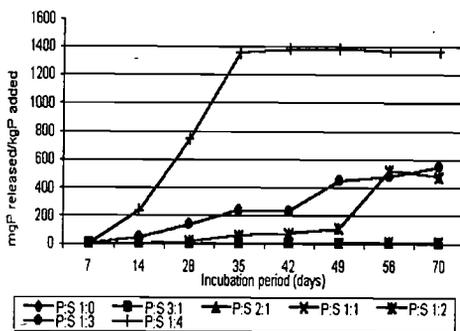


Figure 4: Effect of Minjingu PR/Pyrite mixture and incubation period on P solubility

to the maximum after which no more increase was observed. The period of incubation at which this was attained varied with P:S and the phosphate rock in the mixture. Solutions from the mixtures with P:S ratios 1:3 and 1:4 were observed to have soluble P after the first 7 days. The amount of P solubilized expressed as mgP released/ Kg P added increased with time of incubation

and attained maximum values after 28 days in Panda phosphate rock mixtures. The solubilization in mixtures of P:S 1:1, 2:1 and 3:1 was observed in latter stages of incubation, after 14, 28 and 42 days respectively. The maximum amount of P solubilized increased with the amount of pyrite in the mixtures. The release of P from PR/pyrite mixtures corresponded well with the decrease in pH in the first 28 days of incubation particularly with Panda PR. Beyond day 28 to day 49 there was no relationship between P release and decrease in pH in PR/mixtures of P:S higher than 1. With Minjingu phosphate rock P release increased with the amount of pyrite in the mixture. Highest solubility was observed in mixtures with P:S 1:4. The solubility increased steadily with time to a certain point where it then increased sharply to the maximum. At the P:S 1:4 the sharp increase was obtained after 28 days of incubation and the maximum was attained after 35 days of incubation. The solubility in mixtures with P:S less than 1:2 was not different from that of minjingu phosphate rock alone. High release of P from PR/pyrite mixtures between the 7th and 35th day of incubation could be from easily weatherable fraction in the mineral.

As solubilization proceeded the surfaces of PR and pyrite were coated by the byproduct of reaction thereby slowing down the solubilization process. Also the accumulation of reaction products, Ca and P may have limited the rate of solubilization reaction resulting to a steady release of P. The effect of pyrite in mixtures was more pronounced on Panda RP than on Minjingu RP. This difference could be attributed to the difference in chemical composition of these rocks. Minjingu RP have higher amount of Ca and Mg than Panda RP. These two cations might have neutralized acids produced upon the oxidation of pyrite hence leaving

only little amount of acid in the solution. Also Minjingu RP has higher pH value than Panda RP, reflecting higher neutralizing value. One would expect that as Ca and Mg are released from the PR to neutralize acids produced by pyrite more P will be solubilized from the PR. Contrary to this expectation only very little amount of P was solubilized in Minjingu PR/pyrite mixtures except at low P:S ratios of 1:4. This indicates that apart from apatite there are other sources in Minjingu phosphate rock which supply Ca and Mg. The similar observations were reported by Lowell and Weil (1995) on PR from Minjingu, Dorowa (Zimbabwe) and Tunduru (Malawi). The possibility that there are carbonate minerals associated with these sedimentary PR was thought as the reason for little P release. These carbonates also take part in neutralization of acids released upon the oxidation of pyrite. The pyrite in PR/pyrite mixtures oxidizes gradually with time producing acids which solubilize PRs. In this study pH of the mixtures dropped gradually in the first 49 days of incubation and afterwards stabilized to a constant value. This shows that after 49 days the production of acids is reduced to a greater extent possibly by oxides precipitating/coating the surface of pyrite particle.

The amount of Al solubilized was determined by the amount of pyrite in the mixture, type of phosphate rock and the duration of incubation (Fig. 5 and 6). With Panda phosphate rock Al was found in soil solution after one week of incubation (day 7) for the P:S 1:1 and below. The effect of incubation period was irregular but there was a sharp increase in levels of Al solubilized in the seventh week of incubation (day 49). Generally Al levels were lower in the first six weeks of incubation than the following weeks of incubation. This pattern of Al release partially explains the trend of P release. The process of P release was increasing when Al levels were

low and there was no increase in P levels when Al levels were high. The released Al might have formed oxides which coated the surfaces of PRs and pyrite and prevented further dissolution reaction hence maintaining constant levels of P in the solution. Since there was no decrease in P levels during the incubation process the precipi-

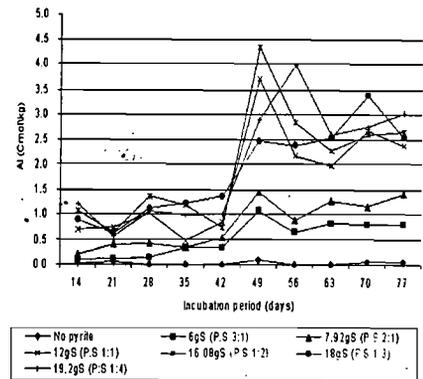


Figure 5: Effect of Panda RP/Pyrite mixture and incubation period on Al solubility

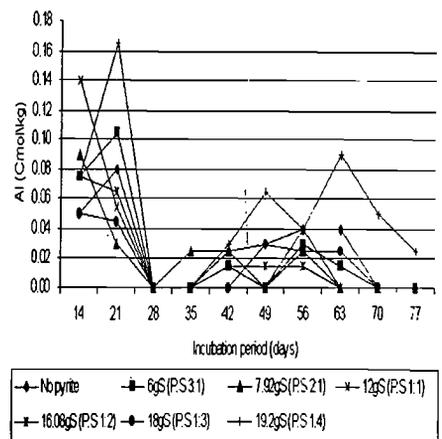


Figure 6: Effect of Minjingu PR/Pyrite mixture and incubation period on Al solubility

tation of P by Al might be very minimal if any. The amount of Al solubilized in minjingu phosphate rock was very little and almost similar in all treatments. The amounts solubilized correspond well with Al contents in these PRs (Table 1).

The effects of P:S and duration of incubation on Mn solubility in the PR/pyrite mixtures are shown on Fig. 7 and 8. The mixing of pyrite and panda phosphate rock increased the amount of Mn solubilized in all P:S ratios. There was a sharp release of Mn in the third week of incubation (between day 14 and day 21). Afterwards the pattern of Mn release with incubation period became irregular. The P:S in Panda PR/pyrite mixtures had no effect to Mn release. In Minjingu PR/pyrite mixtures very little Mn was solubilized at P:S ratio 1:2 and below. There was no relationship between the levels of Mn and the released P.

Conclusion

The solubility of PRs can be increased by mixing and incubating them with pyrite. The amount of pyrite needed to enhance the

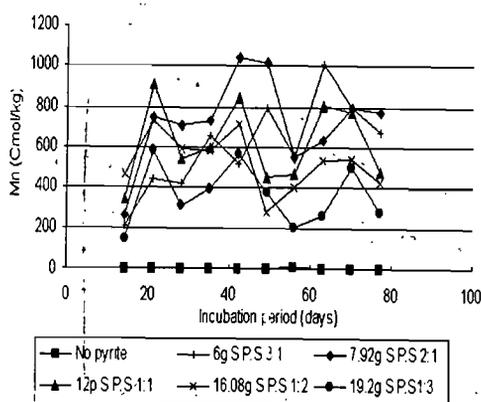


Figure 7: Effect of Panda RP/Pyrite mixture and incubation period on Mn solubility

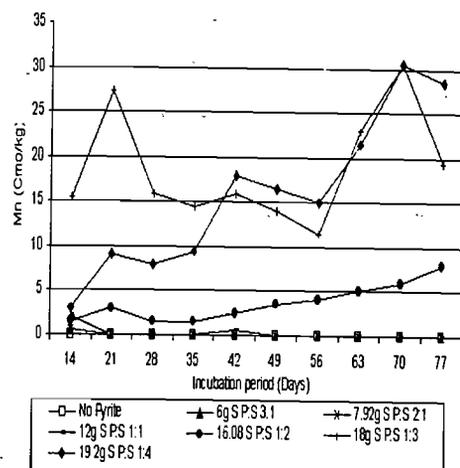


Figure 8: Effect of Minjingu RP/Pyrite mixture and incubation period on Mn solubility

solubility of PRs is determined by the composition of the PRs. Phosphate rocks with high neutralizing values like Minjingu PR need to be mixed at lower P:S ratios than PRs with low neutralizing values. Therefore the use of pyrite in enhancing PR solubility would be more appropriate to Panda PR than to Minjingu PR. However the dissolution of Panda PR is accompanied by release of high amount of Al and Mn which can have negative effect to the soils and plants. Therefore, more work is needed to investigate the effect of PR/pyrite mixture on the soil properties and crop performance.

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