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Effect of Combinations of Phosphate Rock and Superphosphate on Dissolution of Phosphate Rock in Water

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Abstract: **Most of the agricultural lands in the tropics are highly weathered and depleted of plant nutrients, particularly phosphorus resulting in a decline in crop production. Phosphate rock can be used to correct the phosphorus levels but its effectiveness is generally low compared to water-soluble phosphate fertilisers such as single superphosphate or triple super phosphate due to its low solubility in soils. Incubation and glasshouse studies have shown that physically mixing phosphate rock and water-soluble phosphate fertiliser can significantly improve its solubility and has been attributed to phosphoric acid produced from the hydrolysis reaction in the soil of monocalcium phosphate in superphosphate dissolving the phosphate rock. However, the phosphoric acid could also be dissolving iron and manganese minerals in soil which subsequently lowers the dissolved phosphorus levels from phosphate rock by precipitation reactions, thus the need to carry out further experiments in other systems like water to investigate as to whether the increased phosphorus levels in the mixtures is due to dissolution of phosphate rock by phosphoric acid or increased phosphorus levels from increased amounts of superphosphate. Effect of combinations of a commercially available water-soluble phosphate fertiliser (single superphosphate) and gafsa phosphate rock material in the ratios of gafsa phosphate rock to superphosphate of 1:1, 1:4, and 4:1 in 25 mL and 100 mL deionized water were set up. The findings of this study were that superphosphate was found to be responsible for the increase in the extractable phosphorus concentrations. This was due to the fact that there was enhanced dissolution of gafsa phosphate rock in the mixture from the hydrolysis reaction of monocalcium phosphate by phosphoric acid and with the pH values increasing as both the extractable calcium and phosphorus decreased an indication that both metal solutions affected the dissolution through the formation of metal precipitates.**

Keywords: **Superphosphate, Gafsa Phosphate Rock, Dissolution, water.**

I. INTRODUCTION

Phosphorus is the second important nutrient after nitrogen to plants and although soil phosphorus exists in various chemical forms including organic phosphorus and inorganic phosphorus which differ widely in their behavior and fate in soils (Shand and Smith, 1997; Turner et al., 2003a, 2003b; Hansen, et al., 2004) in relation to bioavailability, these forms can undergo cycling at different rates and get retained in soils or made available to plants (Chen et al., 2003; De Brouwere et al., 2003; Nwoke et al., 2003). Phosphorus is one of the major nutrients that have been identified as a limited resource that would end up earlier than predicted at the rate of current consumption (Malavipathirana et al., 2013), and its deficiency is a major constraint to plant productivity in many soils of the world particularly those of the humid tropics and acidic savannas (Oberson et al., 2006). In these soils however, P can be strongly adsorbed by soil minerals and (or) precipitated with free ions in the soil solution (Al^{3+}, Fe^{2+}, Ca^{2+}) (Smith 2002). Because of this problem, high rates of phosphate fertilizers are required to achieve normal plant growth (Hue and Fox 2010). Moreover, the use of synthetic water-soluble P fertilizers is limited in developing countries due to the significant product and associated transportation costs (Sagoe et al. 1998; Van Kauwenbergh 2006) coupled with the fact that these fertilisers are expensive particularly to resource poor farmers usually involved in small-scale subsistence agriculture and the prohibition for use by organic farming standards. As a result, locally available sources of raw phosphate rock have been recognized as alternative P fertilizers (Arcand and Schneider 2006; Van Straaten 2007). Although, the effectiveness of most of these materials are limited by their very low dissolution rate (Yusdar et al., 2007;Hamdali et al., 2010), there is an increasing interest in developing strategies to improve the effectiveness of phosphate rock as a phosphate fertilizer in tropical soils (Msolla et al., 2005; Randhawa et al., 2006; Ojo et al., 2007; Shrivastava et al., 2007; Bhatti and Yawar 2010) thus, conventional water-soluble phosphate fertilisers such as superphosphate or triple superphosphate are usually added to soils to improve phosphorus levels and hence soil fertility.

Direct application of phosphate rock is considered a cheaper alternative to the more expensive high solubility phosphate fertilisers in managing phosphorus deficiency (Mahimairaja et al., 1995). Although several studies have been conducted over the years regarding phosphate rock as an alternative source of phosphorus, the problem limiting its use in agricultural systems is its low solubility in soil (Khasawneh and Doll, 1978).

Physical mixtures of the rock material and water-soluble fertiliser such as superphosphate may be a cheaper technology of lowering the cost of using the more expensive superphosphate while at the same time improving the solubility of the phosphate rock (Thibaud et al., 1993; Ng'eno et al., 2008). Chepkwony et al., (2005) reported that extractable phosphorus levels of superphosphate – Minjingu- phosphate rock mixtures increased with increasing proportion of superphosphate in the mixtures in two acid soils.

In all the above studies, it has been suggested that the strongly acidic triple point solution of phosphoric acid (pH 1.5) resulting from the hydrolysis reaction of the monocalcium phosphate component in the superphosphate (Lindsay and Stephenson, 1959), reacts with apatite in phosphorus rocks material rather than with the soil thereby enhancing the phosphate rock solubility and hence availability in soil (Kundu and Basak, 1999; Chien et al., 1987) as indicated in the equations 1 and 2 below:

$Ca(H_2PO_4)_2 \cdot H_2O + 2H_2O \rightleftharpoons CaHPO_4 + H_3PO_4 + 3H_2O$---------------------------------------(1)

$Ca_{10}(PO_4)_6F_2 + 14H_3PO_4 + 10H_2O \rightarrow 10Ca(H_2PO_4)_2.H_2O + 2HF$----------------------------------(2)

On the other hand, Ngeno et al., (2008) used a wide range of mixtures of superphosphate to Minjingu phosphate rock to investigate the effect of the mixtures on the solubility of Minjingu phosphate rock, and on concentrations of iron and manganese in three acid soils. The study showed that the solubility of Minjingu-phosphorus rock in the mixtures increased with increasing proportion of superphosphate component in the mixtures in all the soils and suggested that the monocalcium phosphate in superphosphate underwent hydrolysis reaction to produce phosphoric acid, which subsequently dissolved the phosphorus rock material. Additionally, their results also indicated that the phosphoric acid not only dissolved the phosphate rock material but also iron and manganese in the soils. The extractable iron and manganese concentrations increased, and soil pH concomitantly decreased with increasing proportion of superphosphate in the mixtures in all soils. Further results also showed that application of the phosphate fertilisers decreased extractable iron and manganese levels in all the soils, suggesting that the dissolved iron and manganese might have precipitated with the dissolved phosphorus in solution as insoluble iron and manganese phosphates. But results from phosphate rock study using soil systems did not clearly show as to whether the increased extractable phosphorus values with increasing proportion of superphosphate in the mixtures were due to increased amounts of superphosphate in the mixtures or solubilization of phosphate rock by phosphoric acid. Hence, it was necessary to carry out further studies using systems such as water other than soil to monitor phosphorus release and extent of dissolution of phosphate rock in mixtures of superphosphate and the rock fertilisers.

II. MATERIALS AND METHODS

One reactive phosphate rock material gafsa phosphate rock (GPR) from Tunisia and a commercially available soluble P fertiliser- single superphosphate (SSP) were used. The two fertilisers were ground separately to pass through a 100 mesh (≤ 2mm) sieve in order to improve their surface area. They were then mixed in various ratios on the basis of their total P contents.

The mixtures were made by combining appropriate amounts of the two sets of the fertilisers in the percentage ratios of GPR to SSP of 1:1, 1:4 and 4:1. Total P in the fertiliser samples was determined by digesting 25g of the fertiliser samples with 5 mL of the prepared digestion mixture, together with a reagent blank and then digested at 360^{o}C for 3 hours in an electric hot plate then allowed to cool. Into each tube, 25 mL distilled water was added respectively and mixed well till no more sediment dissolved, then filtered through a Whatman No. 42 paper to remove any suspended matter that would cause interference. The filtrates were then transferred into 50 mL volumetric flasks and topped to the mark, Okalebo et al., (1993). The concentrations of P in the extracts were determined calorimetrically using UV/visible Spectrophotometer at a wavelength of 882nm after colour development using ascorbic acid.

Appropriate amounts of the fertiliser samples were mixed on the basis of their total P contents in three ratios with each of the weighed fertiliser samples put into clean 200 mL beakers. 10 mL of 10 ppm iron and manganese solutions were added to some of the fertiliser samples followed 25 mL and 100 mL of deionized water. The samples were carefully covered with Whatman no. 42 filter papers and left to stand for twelve hours. They were subsequently shaken on an end-to end shaker for one hour and then filtered into clean 250 mL conical flasks before determining pH, calcium by AAS and phosphorus contents by UV/Visible spectroscopy.

III. RESULTS

The data below show the results of the effect of combining Gafsa phosphate rock and superphosphate on dissolution of Gafsa phosphate rock in 25mL and 100mL DI water respectively as represented by $\overline{X}_1$ and $\overline{X}_2$.

Table I: Effects of added 0 ppm of Fe/Mn on the pH of P sources and P rates

P source	P rate	P ratio	$\overline{X}_1$	$\overline{X}_2$	STDEV	95% CI of $\overline{X}$
SSP	200	0:1	4.74	4.79	0.04	0.02
	500	0:1	4.72	4.76	0.03	0.01
GPR	200	1:0	6.50	6.54	0.03	0.01
	500	1:0	6.47	6.5	0.02	0.01
GPR+SSP	200	1:1	4.70	4.77	0.05	0.02
		1:4	4.39	4.50	0.08	0.04
		4:1	4.83	4.90	0.05	0.02
	500	1:1	4.65	4.73	0.06	0.03
		1:4	4.33	40.4	0.05	0.02
		4:1	4.76	4.81	0.04	0.02

LSD ($P< 0.05$) = 0.0000

The results of this analysis showed that SSP had a lower pH than the Gafsa PR at all rates of application. But when the fertiliser components were mixed, the pH decreased over both SSP and Gafsa PR components. This could be because of the effect of SSP in lowering the pH. For all the fertiliser samples there was significant difference (increase) between the pHs when 25 mL of water was added and after 100 mL, since the p-values were less than $P = 0.05$.

Table II: Effects of added 10 ppm Fe on the pH of P sources and P rates

P source	P rate	P ratio	$\overline{X}_1$	$\overline{X}_2$	STDEV	95% CI of $\overline{X}$
SSP	200	0:1	2.48	2.54	0.04	0.02
	500	0:1	2.46	2.51	0.04	0.02
GPR	200	1:0	5.30	5.35	0.04	0.02
	500	1:0	5.28	5.31	0.02	0.01
GPR+SSP	200	1:1	3.20	3.27	0.05	0.02
		1:4	3.17	3.25	0.06	0.03
		4:1	3.30	3.38	0.06	0.03
	500	1:1	3.16	3.47	0.22	0.10
		1:4	3.10	3.27	0.12	0.05
		4:1	3.22	4.61	0.98	0.44

LSD ($P< 0.05$) = 0.0372

The pH of the mixture was higher in a 4:1 ratio compared to ratio 1:1 while lower for a 1:4 ratio. This could be because of the Gafsa PR in the fertiliser component probably neutralizing the acidic nature of SSP. At higher rate of fertiliser application, the pH decreased could be due to the increased acidity being contributed by the superphosphate component and partly by the 10 ppm iron solution releasing more H^+ ions.

Table III: Effects of added 10 ppm Mn on the pH of P sources and P rates

P source	P rate	P ratio	$\bar{X}_1$	$\bar{X}_2$	STDEV	95% CI of $\bar{X}$
SSP	200	0:1	2.48	2.54	0.04	0.02
	500	0:1	2.46	2.51	0.04	0.02
GPR	200	1:0	6.29	6.46	0.12	0.05
	500	1:0	6.16	6.37	0.15	0.07
GPR+SSP	200	1:1	4.63	4.69	0.04	0.02
		1:4	4.31	4.39	0.06	0.03
		4:1	4.82	4.89	0.05	0.02
	500	1:1	4.61	4.67	0.04	0.02
		1:4	4.29	4.36	0.05	0.02
		4:1	4.75	4.78	0.02	0.01

LSD ($P<0.05$) = 0.0000

When the fertiliser components were treated with 10 ppm manganese solution, the generally trend in the pH for all the P sources were significantly lower than the untreated samples and the iron treated samples but almost insignificant for the SSP alone. This could explain the reason that manganese is slightly acidic compared to iron and that it was the SSP that was responsible for driving the pH drift and not Gafsa PR. On dilution, it increased indicating the weakening of the strength as more water was being added, because the dilution was neutralizing the overall solution.

Table IV: Effects of added 0ppm Fe/Mn on calcium of P sources and P rates

P source	P rate	P ratio	$\bar{X}_1$(µg/g Ca)	$\bar{X}_2$(µg/g Ca)	STDEV	95% CI of $\bar{X}$
SSP	200	0:1	10.80	11.29	0.35	0.16
	500	0:1	11.63	11.86	0.16	0.07
GPR	200	1:0	8.50	8.78	0.20	0.09
	500	1:0	8.70	8.92	0.16	0.07
GPR+SSP	200	1:1	9.76	9.89	0.09	0.04
		1:4	9.81	9.85	0.03	0.01
		4:1	10.44	10.52	0.06	0.03
	500	1:1	10.01	10.14	0.09	0.04
		1:4	10.22	10.29	0.05	0.02
		4:1	10.37	10.46	0.06	0.03

LSD ($P< 0.05$) = 0.0013

At all rates of application the extractable calcium increased with increased rate due to the fact that more was extracted at higher rates of application while the increase on dilution was probably because dilution favours higher extraction of calcium.

There was an increase in the extractable calcium in the mixtures at higher rates of application and could be attributed to increased unit per weight. Comparing the results in table IV with those of table II above, with regards to increased rate of application, the amount of extracted calcium increased as pH decreased. Therefore it can be concluded that at lower pH, the calcium activity increased when the Gafsa PR ratio was increased in the P sources and can be attributed to the high solubility of the PR at lower pH.

Table V: Effects of added 10ppm Fe on calcium of P sources and P rates

P source	P rate	P ratio	$\bar{X}_1$(µg/g Ca)	$\bar{X}_2$(µg/g Ca)	STDEV	95% CI of $\bar{X}$
SSP	200	0:1	8.67	8.77	0.07	0.03
	500	0:1	8.73	8.82	0.06	0.03
GPR	200	1:0	10.43	10.50	0.05	0.02
	500	1:0	10.51	10.56	0.04	0.02
GPR+SSP	200	1:1	10.29	10.34	0.04	0.02
		1:4	10.32	10.36	0.03	0.01
		4:1	10.11	10.18	0.05	0.02
	500	1:1	10.31	10.36	0.04	0.02
		1:4	10.39	10.41	0.01	0.00
		4:1	10.14	10.22	0.06	0.03

LSD ($P < 0.05$) = 0.0000

The extractable calcium decreased at all the rates of application compared to the untreated samples (see table IV above). This could be as a result of precipitation taking place where much of the extracted calcium get held up as precipitates rather than being freed into solution. As such dissolution of Gafsa PR was low and could be attributed to the fact that dissolution of PR is not only controlled by pH but also exchangeable calcium. However, on dilution, there seemed to be an increase in calcium content extracted. The increased could be as a result of calcium continuing to dissolve. The pH value of both fertiliser sources decreased as the extractable calcium concentration increased with rate of application. This suggested that dissolution may not have occurred much due to presence of the cations precipitating out calcium in the solution. The pH value of both fertiliser sources decreased as the extractable calcium concentration increased with rate of application. This suggested that dissolution may not have occurred due to presence of the cations precipitating out calcium in the solution.

Table VI: Effects of added 10 ppm Mn on calcium of P sources and P rates

P source	P rate	P ratio	$\bar{X}_1$(µg/g Ca)	$\bar{X}_2$(µg/g Ca)	STDEV	95% CI of $\bar{X}$
SSP	200	0:1	10.12	10.18	0.04	0.02
	500	0:1	10.16	10.20	0.03	0.01
GPR	200	1:0	10.78	10.83	0.04	0.02
	500	1:0	10.83	10.99	0.11	0.05
GPR+SSP	200	1:1	10.32	10.46	0.10	0.04
		1:4	10.36	10.43	0.05	0.02
		4:1	10.19	10.26	0.05	0.02
	500	1:1	10.37	10.49	0.08	0.04
		1:4	10.44	10.50	0.04	0.02
		4:1	10.28	10.32	0.03	0.01

LSD ($P < 0.05$) = 0.0001

Comparable trends were observed for the addition of manganese as was for the iron. The values for manganese were a little higher though. This could be because manganese does not have a higher affinity to precipitate calcium as much as iron does.

Table VII: Effects of added 0 ppm Fe/Mn on phosphorus of P sources and P rates

P source	P rate	P ratio	$\bar{X}_1$(μg/g P)	$\bar{X}_2$(μg/g P)	STDEV	95% CI of $\bar{X}$
SSP	200	0:1	10.83	10.9	0.05	0.02
	500	0:1	12.55	12.69	0.10	0.04
GPR	200	1:0	7.71	8.16	0.32	0.14
	500	1:0	8.54	9.18	0.45	0.2
GPR+SSP	200	1:1	11.40	11.73	0.23	0.1
		1:4	13.10	13.37	0.19	0.08
		4:1	11.83	12.33	0.35	0.16
	500	1:1	11.80	12.09	0.21	0.09
		1:4	13.57	13.78	0.15	0.07
		4:1	12.27	12.52	0.18	0.08

LSD ($P< 0.05$) = 0.0001

Extracted P increased with rate of application, when the superphosphate component was increased in the mixture and on dilution could be due to increased amount of P in each case while more dissolve on dilution.

Table VIII: Effects of added 10 ppm Fe on phosphorus of P sources and P rates

P source	P rate	P ratio	$\bar{X}_1$(μg/g P)	$\bar{X}_2$(μg/g P)	STDEV	95% CI of $\bar{X}$
SSP	200	0:1	7.92	7.77	0.11	0.05
	500	0:1	8.32	8.02	0.21	0.09
GPR	200	1:0	6.19	5.91	0.2	0.09
	500	1:0	6.34	6.21	0.09	0.04
GPR+SSP	200	1:1	9.76	9.48	0.20	0.09
		1:4	10.18	9.81	0.26	0.12
		4:1	8.55	8.47	0.06	0.03
	500	1:1	10.47	10.23	0.17	0.08
		1:4	10.64	10.52	0.08	0.04
		4:1	9.90	9.74	0.11	0.05

LSD ($P< 0.05$) = 0.0000

The P extracted increased with rate and with the increased rate of the superphosphate in the mixture. Nonetheless, compared to the values of untreated samples, the P values decreased probably because of the formation of the metal iron precipitates in solution due to the fixation reactions of P in solution in form of precipitates because of the prevailing acidic conditions created by the addition of 10 ppm iron solution (Campbell *et al*., 2001). The effect of precipitation may have also influence dissolution as more water was added hence the decreased trend.

Table IX: Effects of added 10 ppm Mn on phosphorus of P sources and P rates

P source	P rate	P ratio	$\bar{X}_1$(μg/g P)	$\bar{X}_2$(μg/g P)	STDEV	95% CI of $\bar{X}$
SSP	200	0:1	8.11	7.94	0.12	0.05
	500	0:1	8.36	8.2	0.11	0.05
GPR	200	1:0	6.28	6.18	0.07	0.03
	500	1:0	6.49	6.36	0.09	0.04
GPR+SSP	200	1:1	10.25	10.02	0.16	0.07
		1:4	10.4	10.27	0.09	0.04
		4:1	8.91	8.74	0.12	0.05
	500	1:1	11.23	10.67	0.40	0.19
		1:4	11.49	10.75	0.52	0.23
		4:1	10.89	10.46	0.30	0.13

LSD ($P< 0.05$) = 0.0014

The trend of extracted P at all rates of application and with the increased rate of the superphosphate in the mixture was observed to be similar as the case in iron treatment. They too increased due to increased P. Compared to the values for iron addition, addition of manganese solution though affected extractable P, the values were slightly higher than for iron. This could be because the precipitates formed by manganese did not bind P so much compared to iron, hence the observed values.

IV. CONCLUSION

The result of this study demonstrated a positive effect of superphosphate in increasing the extractable calcium and phosphorus concentrations of the Gafsa PR- superphosphate fertilizer samples, an indication that dissolution occurred. Dissolution of the PR fertilisers also increased with increased rate of application and was attributed to the increased amount of the fertiliser materials per unit weight.

When mixtures were treated with iron and manganese solutions, the pH values increased as both the extractable calcium and phosphorus decreased an indication that these metal cations had an effect on dissolution as they form metal precipitates hence stopping dissolution. When the fertiliser materials dissolve, the resultant chemical reaction may have converted the soluble P within the material granules into phosphoric acid and a less soluble form of P, di-calcium phosphate and with the prevailing acidic conditions caused by the metal cations addition, the P from the granules could therefore have been transformed into low solubility phosphates precipitates of the metals.

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