



## OPTIMIZATING WATER AND SULFURIC ACID RATES FOR DISSOLUTION OF HAZARA ROCK PHOSPHATE

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### Abstract

Hazara Rock Phosphate ores are the only workable phosphate deposits in Pakistan. The direct application of Hazara rock phosphate (HRP) could be the sole substitution of costly commercial P fertilizers. However, it is of immense value that the optimum levels of water and sulfuric acid required for its dissolution be determined for economical and effective utilization of this non-renewable natural resource. For this purpose, the Rock phosphate (RP) was obtained from Kakul ores of district Hazara and was evaluated for its total P content, solubility and release of P in different volumes of water and H<sub>2</sub>SO<sub>4</sub> in the laboratory of Soil and Environmental Sciences, The University of Agriculture Peshawar, Pakistan. It was found that RP contained > 30 % P<sub>2</sub>O<sub>5</sub> on dry weight basis which realized its suitability for direct application as P fertilizer. Dissolution of HRP in water alone showed a linear relationship with amount of water used for its dissolution up to 1:600 but no significant increase in release of P was observed with further addition of water. Hence it was concluded that 1:600 could be the optimum ratio of HRP and water for maximum possible release of P. The concentrations of P released from HRP with H<sub>2</sub>SO<sub>4</sub> at 1:2, 1:1 and 1:0.5 were not significantly different which suggested that HRP 50% H<sub>2</sub>SO<sub>4</sub> could be the adequate acidulation level for desired P-releases. Though 25% H<sub>2</sub>SO<sub>4</sub> on volume basis (1:0.25) released 21.08% P<sub>2</sub>O<sub>5</sub> from HRP, which was less than that released with 1:0.5, it was still higher than that of single super phosphate (SSP). The recovery of P from HRP lagged markedly behind HPR25% H<sub>2</sub>SO<sub>4</sub> (1:0.25) but was still 20 times more than that released with water alone. Owing to the socio-economic conditions of the poor farmers, it was recommended that HPARP 25% H<sub>2</sub>SO<sub>4</sub> could be the most practical and economical level of acidulation, potent enough to reduce the input cost without compromising on crop yields.

### INTRODUCTION

Generally, Phosphorus deficiencies have been reported in all types of soils all over the World (McDowell and Stewart, 2006). Phosphorus is the essential macronutrient and plants need adequate supply of this nutrient for their optimum growth and development (Marschner, 1993). It is usually the main constraint in crop production in alkaline and calcareous soils. When a water soluble P fertilizer is added to calcareous soils it is either absorbed by plant roots or is adsorbed on surfaces of inorganic soil constituents or precipitated with lime. (Javid and Rowell, 2003). In most of the developing countries the WSP fertilizers are imported and their sky high rates and limited accessibility result into negligible application to the soils by the poor farmers. Reduction, in P supplementation, causes a drastic decrease in crop yields on national level. In this context availability of relatively cheaper P sources could enable the poor farmers to supplement their soils with optimum P levels and obtain better returns from their crops. For

developing countries endowed with Rock phosphate (RP) deposits the direct application of RP could be the most suitable alternative of costly commercial fertilizers.

Rock phosphate is a non-renewable natural resource which contain Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH, F, Cl) in the apatite in insoluble form. The apatite can be named as hydroxyl apatite, fluor- apatite or chloro-apatite depending on the end number (Rogers and Wolfram, 1991). Most of the rock phosphates have low P concentrations and are thus unsuitable for commercial utilization (A.E Johnston, 2000). According to the estimates, about 60 % of the phosphorus used as WSP fertilizer comes from rock phosphate (Cordell, 2010; Smit et al., 2009) while the remaining 40 % is recycled from organic residues.

For commercial utilization in fertilizer industry, phosphate rock or its concentrates preferably should have about 30% phosphorus P<sub>2</sub>O<sub>5</sub> (Klein et al., 1985). Phosphoric acid is reacted with phosphate rock to produce the fertilizer triple super phosphate (TSP) or with anhydrous ammonia to produce the ammonium

phosphate fertilizers. Single super phosphate (SSP) is commercially obtained by treating RP with sulfuric acid. Approximately 90% of phosphate rock production is used for fertilizer and animal feed supplements and the balance for industrial chemicals (Phosphate AMIR Report, 2007).

In Pakistan, Hazara phosphorite deposits are the main sources of raw material for phosphate fertilizer production. These deposits are located in Hazara division of Khyber Pakhtunkhwa in five different localities and have been estimated at 6.9 million tons (Fertilizer Related Statistic, NFDC, 1989) of which 4.58 million tons are considered as recoverable. Unfortunately, due to low grade of indigenous RP, most of the commercial water soluble phosphorus (WSP) fertilizers are imported and used widely as P-fertilizers in the country. In spite of huge subsidy about Rs.2000/- per bag paid by the government, the prices of these fertilizers are high enough for farmers to be purchased and applied in optimum levels. Along with high prices, the timely supply is also a main hindrance in its timely application which ultimately lowers the crop yields. Therefore the direct application of Hazara rock phosphate (HRP), a sole substitute to expensive commercial P fertilizers, has been gaining much importance for researchers all over the country.

However, the direct application of untreated RP is not recommended because of its slow P releases and needs some amendments for dissolution prior to its application. The agronomic effectiveness of RP can be increased with physical, biological and chemical means. Among all these measures the chemical means (Partial acidulation of RPs) for releasing available P from RP is the most practical and efficient way (FAO, 2004).

Research work in this department has shown that addition of RP with equal amount of  $H_2SO_4$  could replace the expensive DAP (Bashir, 2008). Though it was economical if compared to commercial P fertilizers with huge subsidy paid by the government but still the amount of acids seemed to be extraordinarily high and might result into useless expenditures. This research was planned to determine the effect of different levels of water and  $H_2SO_4$  on P-release from RP to optimize the level of water and  $H_2SO_4$  for partial acidulation of Hazara RP.

## MATERIALS AND METHODS

Finely ground rock phosphate (RP) was obtained from Kakul, Hazara and was analyzed both for water solubility with different volumes in relation to RP and by treating with different levels of  $H_2SO_4$ . The study was conducted in the laboratory of Dept. of Soil and Environmental Sciences, NWFP Agricultural University, Peshawar.

**RP solubility in Water:** RP solubility in water was determined by two methods. In first method, 1, 2, 3, 4, 5, 10 and 15 g RP was shaken with 200 mL distilled water for 1 hr and then diluted to 1 L. In the second

spell, the same amount of 0.25 g RP was shaken with 50, 100, 150 and 200 mL water for 1 hr on to and fro horizontal shaker and then analyzed for P concentration in the solution. In both cases, the P concentration was calculated on the basis of P recovery on dry weight basis of RP. The ratio of RP and Water that released higher P on dry weight basis of RP was assumed to be the most appropriate proportion of RP to water.

**RP solubility in  $H_2SO_4$ :** The RP solubility in  $H_2SO_4$  was also determined in two spells. In first instance, 2 g RP was added to 4, 2, 1 and 0.5 mL concentrated  $H_2SO_4$  in the presence of 4 mL distilled water. The reactants were then diluted to 200 mL with addition of distilled water and shaken for 1 hr on horizontal to and fro shaker. Two ml of the solution were then diluted to 100 ml (dilution factor = 50) and then analyzed for P concentration. In the second spell, 2 g of RP were treated with 0.5, 0.25 and 0.12 mL  $H_2SO_4$ , making the ratio of acid more lower to find out the effect of lower level of acid on P release from RP. Just like the first spell, the acid were added in the presence of initial 4 mL water and diluted to 200 mL, which upon shaking were further diluted by the factor of 50 for P analysis on spectrophotometer. In analogy to water solubility, the P concentration was also calculated on dry weight basis of RP to estimate the release of P from RP.

**Determination of P in solution:** The phosphorus was determined in both water and acid solutions by ammonium molybdate color complex method whereas measuring the absorption of light at 880 nm through spectrophotometry (Shimadzu, UV-1700). In this method 1 ml of the sample or concentrations of 0, 2, 4, 6, 8, 10 mg  $P L^{-1}$  were added with 4 ml distilled water and 5 ml P-color complex which were finally further diluted to 25 ml with addition of 15 ml water. A calibration curve was obtained by plotting concentration of standards solutions against their respective absorbance which was used for calculation of P concentration in unknown solution.

## RESULTS AND DISCUSSION

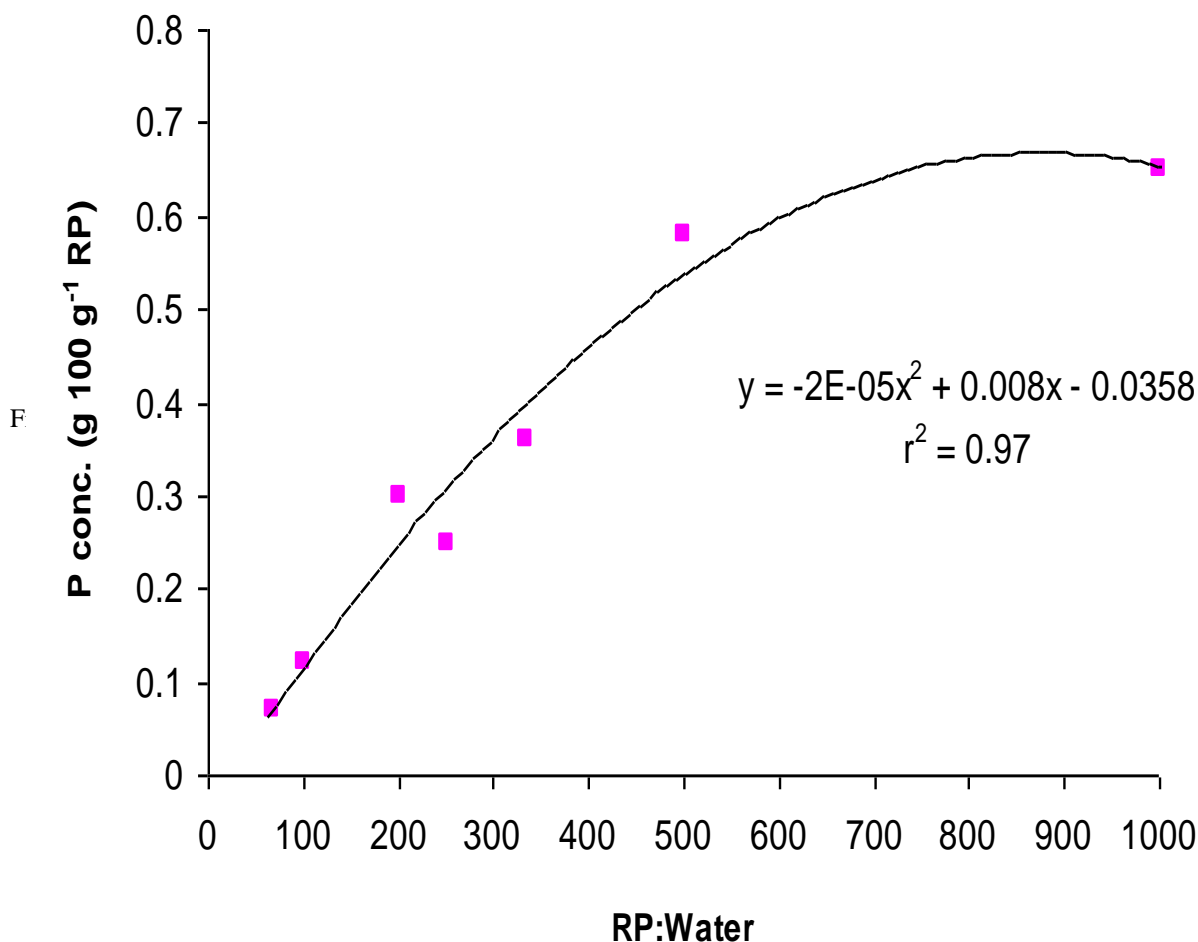
**Total phosphorus in RP:** The rock phosphate was analyzed for total P by treating with concentrated  $H_2SO_4$  and combination of  $HNO_3+HF$  (3:1) followed by heating for 30 minutes. In case of  $H_2SO_4$  0.25 g RP was treated with 5 ml  $H_2SO_4$  which in case of  $HNO_3+HF$  the same amount of RP (0.25 g) was treated with 5 ml concentrated  $HNO_3$  plus 3 ml concentrated HF. Results showed that the RP contained 33.0 and 34.6 %  $P_2O_5$  on dry weight basis for  $H_2SO_4$  and  $HNO_3+HF$  digestion, respectively. The little difference between the two procedures suggested that  $H_2SO_4$  alone or  $HNO_3+HF$  could be used. However, due to easy handling and availability, the digestion of RP with  $H_2SO_4$  is could be preferred. It was concluded that Hazara RP (> 30% P) could be considered as suitable for manufacture of commercial fertilizers as well as direct application.

**Table 1 Total P in RP treated either with concentrated H<sub>2</sub>SO<sub>4</sub> or combinations of HNO<sub>3</sub>+HF**

Treatments	-----P conc. (g P 100 g <sup>-1</sup> RP)-----			
	R1	R2	Mean	SD
H <sub>2</sub> SO <sub>4</sub>	15.72	14.46	15.09	0.89
HNO <sub>3</sub> +HF	14.76	14.05	14.41	0.50
	-----P conc. (g P <sub>2</sub> O <sub>5</sub> 100 g <sup>-1</sup> RP)-----			
H <sub>2</sub> SO <sub>4</sub>	36.01	33.12	34.56	2.04
HNO <sub>3</sub> +HF	33.81	32.19	33.00	1.14

**Recovery of P from RP dissolved in water:** Different amounts (weights) of RP were treated with the same amount of water with the ratios of RP to water from 1:1000 to 1:66 (Table 2). The result showed that as the ratio of RP to water decreased from 1:1000 to 1:500 the mean P concentration became almost double with values of 2.82 and 5.06 mg P L<sup>-1</sup>, respectively. However, further decrease in the RP to water ratio did not show significant variations which revealed that at 1:500 RP to water ratio, the solution attained the maximum P saturation. The P recovery decreased with further decrease in the ratio of RP to water. The maximum P recoveries as 0.28 or 100 %

1 P or 0.65 g P<sub>2</sub>O<sub>5</sub> 100 g<sup>-1</sup> RP were observed in the solution of 1:1000 RP:water. This value was slightly higher or almost equal to P concentrations observed in RP and water solution of 1:500 which suggested that both 1:1000 and 1:500 ratio of RP and water could release the maximum water soluble P from RP. The quadratic equation showing the P concentrations in RP in different ratios of RP:water with r<sup>2</sup>= 0.97 also suggested that the 1:500 ratio of RP:water could be the optimum combination of RP with water (Fig. 1).



**Table 2** The P recovery from RP treated with addition of distilled water stirred for one hr on horizontal shaker

Treatments		-----P conc. (mg L <sup>-1</sup> )-----			
RP (g)	RP: Water	R1	R2	Mean	SD
1	1:1000	2.72	2.92	2.82	0.14
2	1:500	5.49	4.62	5.06	0.62
3	1:333	4.11	5.38	4.75	0.90
4	1:250	4.48	4.2	4.34	0.20
5	1:200	6.10	6.96	6.53	0.61
10	1:100	4.68	5.46	5.07	0.55
15	1:67	5.21	4.36	4.79	0.60
		-----P conc. (g P 100 g <sup>-1</sup> RP)-----			
1	1:1000	0.27	0.29	0.28	0.01
2	1:500	0.27	0.23	0.25	0.03
3	1:333	0.14	0.18	0.16	0.03
4	1:250	0.11	0.11	0.11	0.00
5	1:200	0.12	0.14	0.13	0.01
10	1:100	0.05	0.05	0.05	0.01
15	1:67	0.03	0.03	0.03	0.00
		-----P conc. (g P <sub>2</sub> O <sub>5</sub> 100 g <sup>-1</sup> RP)-----			
1	1:1000	0.62	0.67	0.65	0.03
2	1:500	0.63	0.53	0.58	0.07
3	1:333	0.31	0.41	0.36	0.07
4	1:250	0.26	0.24	0.25	0.01
5	1:200	0.28	0.32	0.30	0.03
10	1:100	0.11	0.13	0.12	0.01
15	1:67	0.08	0.07	0.07	0.01

In the second trial (Table 3) where the same amount of 0.25 g RP was shaken with different volumes of water producing RP and water ratios 1:200, 1:400, 1:600 and 1:800 showed that P concentrations in solution increased with increase up to 600 and then decreased

at 1:800 of RP and water. The same trend is also shown in Fig. 2 suggesting that 1:600 could be the optimum ratio of water and RP for maximum release of P from HRP.

**Table 3** Phosphorus recovery from RP dissolved in different amounts of water and stirred for one hr on horizontal shaker

Water	RP: Water	-----P conc. (mg L <sup>-1</sup> )-----			
mL		R1	R2	Mean	SD
50	1:200	3.55	2.49	3.02	0.75
100	1:400	4.3	5.17	4.74	0.62
150	1:600	5.2	4.92	5.06	0.20
200	1:800	3.24	3.37	3.31	0.09
		-----P conc. (g P 100 g <sup>-1</sup> RP)-----			
50	1:200	0.07	0.05	0.06	0.01
100	1:400	0.17	0.21	0.19	0.02
150	1:600	0.31	0.30	0.30	0.01
200	1:800	0.26	0.27	0.26	0.01
		-----P conc. (g P <sub>2</sub> O <sub>5</sub> 100 g <sup>-1</sup> RP)-----			
50	1:200	0.16	0.11	0.14	0.03
100	1:400	0.39	0.47	0.43	0.06
150	1:600	0.71	0.68	0.70	0.03
200	1:800	0.59	0.62	0.61	0.02

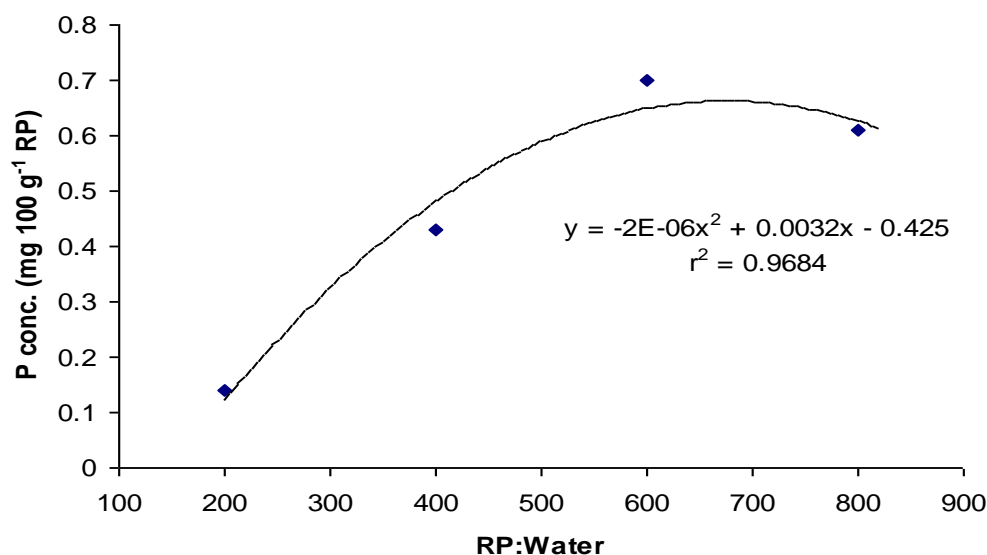


Figure 1. Different volumes of water

**Recovery of P from RP treated with H<sub>2</sub>SO<sub>4</sub>:** In this trial 2 g RP was treated with different amounts of H<sub>2</sub>SO<sub>4</sub> and shaken for 1 hr on horizontal shaker. Results showed that P concentrations in the solution were higher at 1:2 and 1:1 of RP and H<sub>2</sub>SO<sub>4</sub> solutions which were 24.12 and 24.72 mg P L<sup>-1</sup>, respectively (Table 4). Phosphorus concentrations at 1:0.5 and 1:0.25 RP: H<sub>2</sub>SO<sub>4</sub> were low as compared to 1:2 and 1:1 of RP and H<sub>2</sub>SO<sub>4</sub> but the concentrations calculated in g P<sub>2</sub>O<sub>5</sub> 100 g<sup>-1</sup> RP were still at par or even better than the P concentrations usually found in the commercially

available single super phosphate (SSP). These results suggested that RP treated with 25% H<sub>2</sub>SO<sub>4</sub> (RP 25% H<sub>2</sub>SO<sub>4</sub>) on basis of W/V could be as effective as commercially available SSP in the final trial (Table 5) same amount of RP (2g) was treated with different levels of acids 1:0.25, 1:0.125, 1:0.05 which released the mean concentrations, 16.09, 9.05, 4.31 mg P l<sup>-1</sup>, respectively. Statistical analysis of these result showed that there was no significant difference in the availability of P from HRP.

**Table 4** Phosphorus concentrations in RP treated with different amounts of commercially available H<sub>2</sub>SO<sub>4</sub>.

Treatments		-----P conc. (mg L <sup>-1</sup> )-----			
H <sub>2</sub> SO <sub>4</sub> (mL)	RP: H <sub>2</sub> SO <sub>4</sub>	R1	R2	Mean	SD
4	1:2	24.87	23.37	24.12	1.06
2	1:1	25.19	24.25	24.72	0.66
1	1:0.5	22.97	21.27	22.12	1.20
0.5	1:0.25	18.41	19.89	19.15	1.05
-----P conc. (g P 100 g <sup>-1</sup> RP)-----					
4		12.44	11.69	12.06	0.53
2		12.60	12.13	12.36	0.33
1		11.49	10.64	11.06	0.60
0.5		9.21	9.95	9.58	0.52
-----P conc. (g P <sub>2</sub> O <sub>5</sub> 100 g <sup>-1</sup> RP)-----					
4		28.48	26.76	27.62	1.21
2		28.85	27.77	28.31	0.76
1		26.30	24.36	25.33	1.38
0.5		21.08	22.78	21.93	1.20

**Table 5 Phosphorus concentrations in RP treated with different amounts of commercially available H<sub>2</sub>SO<sub>4</sub>**

Treatments		-----P conc. (mg L <sup>-1</sup> )-----			
H <sub>2</sub> SO <sub>4</sub> (mL)	H <sub>2</sub> SO <sub>4</sub> (mL)	R1	R2	Mean	SD
0.5 mL	1:0.25	15.7	16.5	16.09	0.51
0.25 mL	1:0.125	8.6	9.5	9.05	0.63
0.1 mL	1:0.05	4.4	4.2	4.31	0.11
		-----P conc. (g P 100 g <sup>-1</sup> RP)-----			
0.5 mL	1:0.25	7.87	8.23	8.05	0.25
0.25 mL	1:0.125	4.30	4.75	4.52	0.31
0.1 mL	1:0.05	2.19	2.12	2.15	0.06
		-----P conc. (g P <sub>2</sub> O <sub>5</sub> 100 g <sup>-1</sup> RP)-----			
0.5 mL	1:0.25	18.01	18.84	18.43	0.58
0.25 mL	1:0.125	9.85	10.87	10.36	0.72
0.1 mL	1:0.05	5.03	4.84	4.94	0.13

## CONCLUSIONS

Hazara phosphate obtained from Kakul area contain more than 30% P and can be considered as suitable for direct application to soils as P fertilizer. However, HRP does not contain water soluble P and all the P is in apatite form. Therefore it needs certain amendments (biological, physical or chemical) prior to application, for its dissolution and release of available P. The optimum level of water for its dissolution and release of maximum possible P is 1:600, but the total P recovery is much lower than that released with H<sub>2</sub>SO<sub>4</sub>. The best level for partial acidulation of RP with H<sub>2</sub>SO<sub>4</sub> is 1:0.5. PAHRP 50% H<sub>2</sub>SO<sub>4</sub> has the potential to replace the costly SSP. However, owing to the socio-economic conditions of the poor farmers of Pakistan, PAHRP 25% H<sub>2</sub>SO<sub>4</sub> can be utilized confidently for sustainable crop production as it contains 21.08 % P<sub>2</sub>O<sub>5</sub>. The relative agronomic efficiency of these partially acidulated Hazara rock phosphates (PAHRPs), needs to be evaluated through greenhouse and field experiments to set recommendations for a given set of conditions in different agro-ecological zones of the country.

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