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Formulation of single super phosphate fertilizer from rock phosphate of Hazara, Pakistan

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Abstract

Phosphorus deficiency is wide spread in soils of Pakistan. It is imperative to explore the potential and economics of indigenous Hazara rock phosphate for preparation of single super phosphate fertilizer. For the subject study rock phosphate was collected from Hazara area ground at 160 mesh level with 26% total P_2O_5 content for manual preparation of single super phosphate fertilizer. The rock phosphate was treated with various concentrations of sulfuric acid (98.9%, diluted or pure) in the field. The treatments comprised of 20 and 35% pure acid and diluted with acid-water ratios of 1:5, 1:2, 1:1 and 2:1 v/v for acidulation at the rate of 60 liters 100 kg^{-1} rock phosphate. The amount was prior calculated in the laboratory for complete wetting of rock phosphate. A quantity of 150 kg rock phosphate was taken as treatment. The respective amount of acid was applied with the spray pump of stainless steel or poured with bucket. After proper processing, chemical analysis of the products showed a range of available P_2O_5 content from 9.56 to 19.24% depending upon the amount of acid and its dilution. The results reveal at that 1:1 dilutions gave the highest P_2O_5 content (19.24%), lowest free acid (6 %) and 32% weight increase. The application of acid beyond or below this combination either pure or diluted gave hygroscopic product and higher free acids. The cost incurred upon the manual processing was almost half the prevailing rates in the market. These results lead to conclude that application of sulfuric acid at the rate of 60 liters 100 kg^{-1} with the dilution of 50% (v/v) can yield better kind of SSP from Hazara rock phosphate at lower prices.

Keywords: *Hazara rock phosphate, single super phosphate, phosphorus content, acidulation*

Introduction

The P deficiency is wide spread in soils of Pakistan (Rashid, 2005). Pakistani soils contain less than 10 mg kg^{-1} available P (Memon, 1986), hence application of phosphatic fertilizers are recommended for better crop production. To combat the deficiency, annually 565.7 thousand nutrient tons of P fertilizers are imported against its requirement of 759 (Agri. Statistics, 2009). The continuous price hike in various P fertilizer was observed after year 2003-04. The trend of increase in prices became sharper during the years 2007-08 and 2008-09 when 107 and 232% increase over the year 2003-04 was recorded, respectively. The price of widely used DAP hiked from Rs. 997 to Rs. 1934 and Rs. 2787 with an increase of 93.9% and 179.5%, during the years 2007-08 and 2008-09 as compared with year 2003-04, respectively (Agri. Statistics, 2009). The price hike in P fertilizers ultimately affected the amount of consumption negatively by 35.7% and 53% during the years 2007-08 and 2008-09, respectively, as compared with year 2006-07. The decrease in consumption could be more drastic, negatively affecting the crop yields in the years, but the increase in procurement/ support prices (46.5% and 52%) compensated the grower. As a result, declining trend was observed in the wheat production. The unbalanced use of fertilizers particularly phosphatic fertilizer below the recommended dose is one of the reasons for decline in wheat production in Pakistan during 2007-08 (Aujla *et al*., 2010).

Pakistan is well blessed by the Almighty Allah with rock phosphate deposits in Hazara area of Khyber Pukhtunkhwa province of Pakistan. It is basically tri-calcium phosphate [Ca_3 $(PO_4)_2$] insoluble in water and unavailable to plant (Brady, 1980; Das, 2005). The reserves are widespread in Hazara, Taranawai as schists, shales or limestones at Kakul, Guldaman, and Legerban villages of district Abbottabad in the forms of dolomites or phosphorites, and in Thandiani in the form of orthoquartizites and limestones (Javed *et al.*, 2008). The so far reported exploration indicates that total reserves are about 35.7 million tons including inferior and proven quality (PMDC, 2006).

Keeping in view the huge foreign exchange incurred on the import of P fertilizers and the available rock phosphate reserves in the country, it is imperative to explore the extent of P_2O_5 release, the amount of acid required for complete

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acidulation and its economics for manual preparation of single super phosphate.

Materials and Methods

Rock phosphate was collected from Tarnawai area of Hazara division, ground at 160 mesh level having total P_2O_5 content of 26%. The chemical reaction that occurs in the manufacturing of SSP when rock phosphate is mixed with sulphuric acid may be represented by the following equation:

$$Ca_3(PO_4)_2 + 2H_2SO_4 + H_2O \rightarrow$$
$$Ca(H_2PO_4)_2 . H_2O + 2CaSO_4 + 108.44 \text{ k cal}$$

(Fertilizer Manual, 1979)

The rock phosphate was treated with various dilution and amounts of sulphuric acid. Before using the various concentrations of acid for acidulation, the amount of acid required for complete contact was determined. It was concluded that 60 liter acid was sufficient for complete contact with 100 kg rock phosphate. In the first two treatments (T1 and T2), acid was applied at the rate of 20 and 30 liters (pure) to 100 kg rock phosphate, respectively. In the remaining treatments, the acid was diluted as; T3 = 1:5 (16.6%), T4 = 1:2 (33.3%), T5 = 1:1 (50%) and T6 = 2:1 (66.6%) applied at the rate of 60 liters to 100 kg rock phosphate and obtained SSP of higher P_2O_5 content with minimum input cost. The acid dilutions were the first step and done very carefully specially beyond 1:2 acid-water. Intense precautionary measures were adopted for the laborers during the acidulation process. An amount of 250 kg rock phosphate was spread in a stainless steel pan (2.5×2.5 m) and the required amount of acid (pure or diluted) was applied to the respective treatments with the help of stainless steel spray pump followed by thorough mixing. The amount of acid, where it was enough for thorough wetting of the rock phosphate, was poured slowly with the help of stainless steel bucket other than spray pump. After application of the required acid, the material was mixed thoroughly so as to get maximum rock phosphate-acid contact, and covered with the used plastic sacs followed by polythene sheet. The mixture was kept for 24 hours in the same pan to conserve evolving heat, enhance reaction and solidify the slurry/mixture.

The clods made up were kept in used plastic sacs, internally lined with the polythene bags for incubation/ curing at room temperature for 40 days. The product (SSP) made clods at first and then changed into disintegrated form with good dispersion, as the reaction completed in the respective treatments. The product was analyzed for available P_2O_5 content by Quinoline molybdophosphate titrimetric method (Bassett *et al.,* 1978). The data on free acid content in the product was also recorded with the time span of 8 days upto 40 days and was determined with the titration method (Pakistan Standards, 1967).

Results and Discussion

Available phosphorus concentration

There are three main factors which influence the amount of available P_2O_5 release from rock phosphate; the amount of total P_2O_5 content in the rock, the particle size of the ground rock phosphate, and the amount concentration of acid required for the reaction (Fertilizer Manual, 1979). The chemical analysis (after 40 days) of the products made up from various treatments showed a range of available P_2O_5 content from 9.56 to 19.24% depending upon the amount of acid and its concentration. The highest P_2O_5 content (19.24%) was recorded in T_5 where 1:1 acid-water (v/v) dilutions was applied while lowest (9.56%) in T_3 where diluted acid of 1:5 was applied (Figure 1). The sequence of available P_2O_5 in various treatments ranked as $T_5 > T_4 > T_1 > T_6 > T_2 > T_3$ in the experiment. Generally, weight increase of various percentages over rock phosphate were noted in all the treatments according to the amount of acid applied. The T_5 gave a weight increase of 32% in the dried product. This weight increase might be due to the higher specific density of H_2SO_4 (1.84 g cm^{-3}) applied for acidulation. The application of acid higher than 1:1 combination either pure or diluted gave hygroscopic product and incomplete reaction might be due to the higher free acids concentration. The hygroscopic products did not dry even if kept in oven. The available P_2O_5 content in these hygroscopic treatments also remained lower as compared with T_5. This might be due to the higher density of the product due to excessive application of acids and more moisture content.

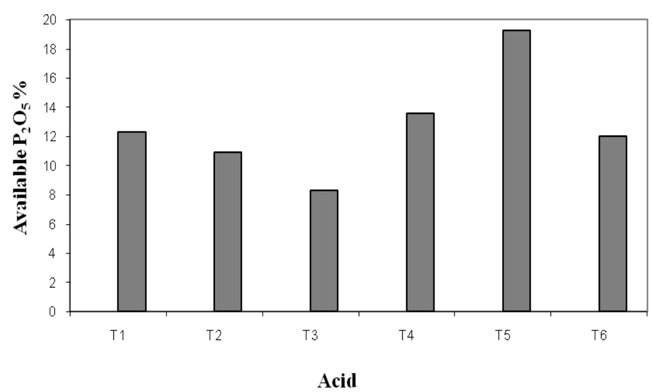

Figure 1: Release of phosphorus from rock phosphate for SSP preparation

Time span effect on P_2O_5 availability

The reaction of rock phosphate and acid for preparation of single super phosphate generally proceeds in two stages;

in the first stage, sulphuric acid reacts with rock phosphate to form phosphoric acid (H_3PO_4) and calcium sulfate ($CaSO_4$) and in the second step; the H_3PO_4 reacts with more rock phosphate to form monocalcium phosphate or Single Super Phosphate. The first stage completes rapidly while the second stage continues for several days or weeks (Fertilizer Manual, 1979). Hence, after acidulation with various concentrations of acid, the mixture was kept for incubation/curing so as to complete both the reactions. The time span effect on the availability of P_2O_5 after acidulation process remained ascending up to the day 32. The increase in P_2O_5 content between day 32 and day 40 remained constant especially in desired treatment of 1:1 (Figure 2).

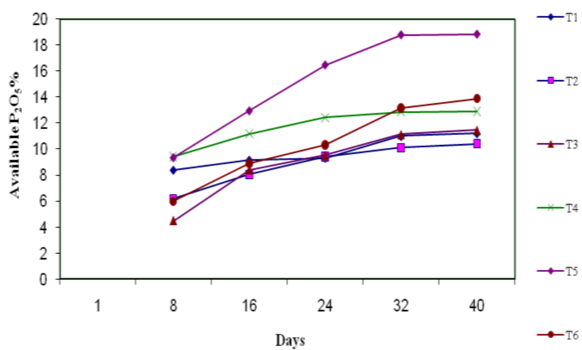

Figure 2: Effect of time span on P_2O_5 release

Free acid contents

The amount of free acids in single super phosphate depicts extent of proceeded reaction and is directly affected by the amount and concentration of acid applied for acidulation. The lesser the free acids content in single super phosphate, the better the quality of the product is considered and the higher the free acids content, the more will be moisture content and density of single super phosphate (Fertilizer Manual, 1979). The results of this experiment revealed that free acids content in the product after 40 days of incubation ranged from 15.20% to 2.43% showing various dispersion patterns during the time. About 6.0% free acids were recorded in the treatment where acid was applied with the 1:1(T_5) acid-water ratio (Figure 3) which showed better reaction with good dispersion of acid and rock phosphate mixture. This confirms the optimum level of H_2SO_4 concentration and amount required for solubilizing higher economical P_2O_5 from rock phosphate. In the treatments where dilution and concentration varied from this optimal range and amount, showed more free acids which consequently gave hygroscopic nature of the product and more density. The higher the density of product, the lower will be the P_2O_5 content in it. The decrease in free acids due to excessive dilution might show that sulphuric acid amount was lesser for rock phosphate to release maximum P_2O_5.

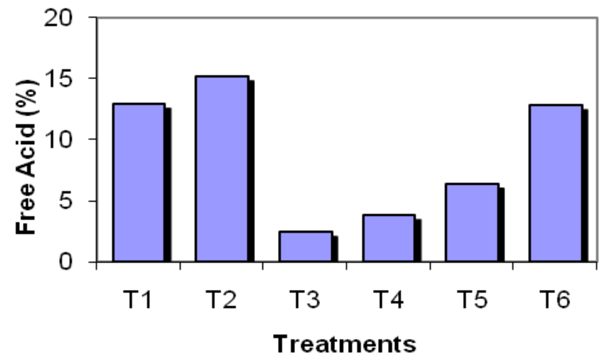

Figure 3: Acidulation of RP for preperation of SSP

Granulation

Granulation of SSP involves much heat energy that is why it contributes a significant cost in SSP production. It depends upon the personal preferences whether SSP should be granulated or powdered. Generally, granulation does not enhance any phosphorus content of the SSP. However, it might help in physical activities like broadcasting. The granulation at industrial level is carried out by meshing in disintegrator, application of water spray, drying in dens, and ultimately automated screening. After incubation/ curing, some samples with good dispersion during reaction were spread in the plane pan. A light spray of water was applied on well dispersed powdered SSP and then kept for drying for further 3 hours in the sunlight of summer. The product was then passed through 6 mesh size inclined screen, the remaining part was again meshed and sprinkled with water and the same procedure was adapted for granulation.

Economics for SSP production

The Self prepared cost of SSP was almost half as compared with market prevailing rates.

Input Cost

Price of RP (one kg)	Rs. 4.70
Transportation charge (one kg)	Rs. 1.00
Price of RP at station (one kg)	Rs. 5.70
Price of commercial H_2SO_4 (one kg)	Rs. 9.00
Price H_2SO_4 (one liter)	Rs. 15.56
Transportation charges (one liter)	Rs. 1.00
Price of H_2SO_4 per liter at station	Rs. 16.56

Preparation of SSP from 100 kg RP

Price of 100 kg RP	Rs. 570.00

30 liter H_2SO_4	Rs. 496.80
Total input cost	Rs. 1066.80
Prepared SSP come out	132 kg
(specific gravity of $H_2SO_4$1.84 g cm^{-3})	
Input cost per 50 kg bags (1066.8÷132×50)	Rs. 404.00
Bagging cost per bag	Rs. 15.00 L
Labour charges per bag	Rs. 50.00
Total cost of SSP bag (50 kg)	Rs. 469.00

The self produced single super phosphate has an edge that it contained 19% P_2O_5 while a commercial SSP analyzed showed 16% P_2O_5 content. The inputs for the SSP preparation like rock phosphate and acids were purchased in fewer amounts, therefore the prices and transportation charges were comparatively high. In case of acids purchased in tankers and RP transportation in big trucks can save the cost further more. All the procedure /methodology for SSP preparation were manual and the equipments were temporary made according to experiment need. Mechanization and large scale SSP preparation can save handsome amount from labour and transportation charges.

Conclusion

Good quality single super phosphate can be prepared from the indigenous Hazara mined rock phosphate subject to higher total P_2O_5 content in the rock phosphate. Commercial sulphuric acid is the best and cheaper reactant to release maximum phosphorus from rock phosphate. Sixty liter sulphuric acid diluted at 50 % level (volume/volume) is optimal dose to release maximum phosphorus from 100 kg rock phosphate. The process is simple, cost effective but necessary precautionary measures are required to be adopted. The cost involved in such type of single super phosphate is almost half as compared with prevailing market prices.

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