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Enhancement of P_2O_5 Content in SSP Made from Local Rock Phosphate of Pakistan

Hina Arshad[1], Shahid Raza Malik[1], Muhammad Usman Tahir[2], Waqar Ali Khan[1], and Muhammad Usman[3]

[1]Department of Chemical Engineering,
NFC Institute of Engineering and Fertilizer Research,
Faisalabad, Punjab, Pakistan

[2]School of Chemical Engineering,
The University of Faisalabad,
Faisalabad, Punjab, Pakistan

[3]Production Department,
Rafhan Maize Products Co. LTD (INGREDION, USA),
Faisalabad, Pakistan

ABSTRACT: The Phosphorus content is a necessary part of fertilizers used in Pakistan and is readily available in single super phosphate fertilizer. Pakistani rock phosphate being of low grade cannot be used by conventional method to prepare good quality SSP. This rock however, can be used by some unconventional techniques for preparing some better quality fertilizer. For the subject study rock phosphate samples were collected from Hazara, Pakistan and were ground to 150 mesh level containing 24% total phosphate pentoxide (P_2O_5) content and were treated with different ratios of sulphuric acid (H_2SO_4) and phosphoric acid (H_3PO_4). Seven samples with composition comprising of fix weight of rock phosphate i.e. 100 gm were prepared by treating it with H_2SO_4 (diluted to 65%) and H_3PO_4 (of 85% purity) in w/w ratios of (13:1, 13:2, 4:1, 11:4, 2:1 and 3:2) were manually prepared and analyzed through spectro-photometric method before and after a curing period of two weeks. The results obtained showed that there was enhancement in P_2O_5 up to 22.9% total and 19.9% available P_2O_5 content by addition of H_3PO_4 and H_2SO_4 (in weight ratios of 3:2) to the conventional formulation of single super phosphate (SSP) containing the rock phosphate and H_2SO_4 only. The results lead to conclude that the phosphorus content in SSP made from low quality local rock phosphate can be effectively enhanced and a market grade SSP(with 18% available P_2O_5) can be prepared using the local rock without any need to import rock phosphate from other countries.

KEYWORDS: P_2O_5 Enhancement, Hazara Pakistan, Rock phosphate, Single Super phosphate, H_2SO_4 and H_3PO_4.

1 INTRODUCTION

Phosphates are necessary elements in the fertilizers used to supply food and feed for human beings. Currently in the world, there is no alternate for phosphate rock as a raw material for the production of phosphate fertilizer. The demand for phosphate increases as the world population increases. Phosphate rocks are complex raw materials and are mainly used in the production of phosphate fertilizers. The composition of these rocks varies from one deposit to another. Therefore phosphate rocks from different sources are expected to behave differently in acidulation process [1].

In agricultural soils (cultivated land) readily available phosphorous is an important nutritional element and controls the growth of plants [2]. Even normal soils with intermediate fertility possess 0.4 – 1.2 g of phosphorous per kilo gram of soil. About 95 – 98% of this P is in the form metallic chelates and is insoluble hence difficult to utilize [3]. Therefore about all soils which are used for agricultural purposes are fertilized with compounds containing soluble phosphorous [4].

In many countries, rock phosphate was first finely ground and applied directly to soil as fertilizers [5]. Rock phosphate is a natural, cheap and clean compound but unfortunately it is a poor phosphorous fertilizer since its solubilization is too slow to satisfy agricultural requirements [6]. It was soon recognized that treatment of these phosphate minerals with sulfuric acid (H_2SO_4) increased the availability and efficiency of the phosphate for agricultural purposes. At present, acidulation with Nitric Acid (HNO_3) or strong Phosphoric acid (H_3PO_4) or H_2SO_4 gives enhanced fertilizer values.

For the purpose of this available phosphorous acidulation of rock phosphate with H_2SO_4 is important now days. Triple Supper Phosphate (TSP) with 45 – 50% available Phosphorous Pentoxide (P_2O_5) and Single Supper Phosphate (SSP) with 16 – 18% of available P_2O_5 are manufactured by the reaction of phosphate rock with H_3PO_4 and H_2SO_4 respectively [7]. These are used to provide necessary phosphorous to crops and also balancing phosphorous contents of soils in agricultural areas.

Pakistan is blessed by rock phosphate deposits in Hazara area of KPK province in Pakistan. This is basically a tri-calcium phosphate [$Ca_3(PO_4)_2$] which is insoluble in water and not directly available to the plants [8]. These reserves are spreaded in Hazara, Tranawai, in the form of shist, shales and limestone, at Kakul, Guldaman and Lagerban villages of districts Abbotabad in the forms of dolomite and phosphorites, also at Thandiani in the forms of limestones Looking at the huge amounts of foreign exchange incurred on the imports of phosphatic fertilizers it is suggested to explore and exploit the local phosphate rock reserves and to enhance the extent of P_2O_5 release [9, 10].

In this research work, H_3PO_4 was used during the synthesis of SSP and observed that the P_2O_5 contents increased.

2 MATERIALS AND METHODS

2.1 PROCUREMENT OF RAW MATERIALS

Rock Phosphate was collected from Tarnawai area of Hazara division (Khyber Pukhtunkhwa), Pakistan. Rock phosphate was ground at 150 mesh level with a total P_2O_5 content of 24 %. H_2SO_4 and H_3PO_4 were purchased from Sigma Aldrich of purity 98% and 85% respectively. Distilled water was used for the dilution of the acid.

The ground rock was then treated with different ratios of acids to prepare samples. It was initially calculated that a total 40 % (70gm) of liquid (acid) is enough to wet a 100 gm. of solid (rock).

2.2 EXPERIMENTAL METHODS

100 grams of Rock phosphate ground at 150 mesh level was weighed and carefully taken in a Pyrex glass beaker. H_2SO_4 obtained from market was diluted to 65% by careful addition of distilled water. Now 65 grams of diluted H_2SO_4 and 5 grams of H_3PO_4 obtained from market were added into the rock and stirred with the help of glass stirrer. The sample was handled carefully and placed in oven at 80^oC for one hour before analysis. Other samples of SSP were prepared by using different amounts of acids are shown in table 1.

Table-1: Single Super Phosphate Samples

Sample #	Composition
1	100g rock + 65g H_2SO_4
2	100g rock + 65g H_2SO_4 + 5g H_3PO_4
3	100g rock + 65g H_2SO_4 + 10g H_3PO_4
4	100g rock + 60g H_2SO_4 + 15g H_3PO_4
5	100g rock + 55g H_2SO_4 + 20g H_3PO_4
6	100g rock + 50g H_2SO_4 + 25g H_3PO_4

2.3 PRODUCT ANALYSIS

Standard methods of Pakistan Standards Quality Control Authority were adopted for the analysis of samples to get accurate values of the contents present in samples. Following were the testing procedures adopted to analyze the samples for various types of phosphorus contents.

2.3.1 TEST FOR WATER SOLUBLE P_2O_5 CONTENT

1 gram of each sample was separately added in 250 ml round bottom flask, filled with distilled water and then was stirred on magnetic stirrer for 30 minute to assure complete dissolution. Then filtered and collected the filtrate, 2 ml of filtrate was further diluted in 100 ml volumetric flask by adding distilled water.

20 ml of Molybdovanadate reagent was added in each sample and these samples were analyzed in spectrophotometer (Model Company) set at wavelength of 405 nm, maximum absorbance. After that results were calculated for all the samples separately.

2.3.2 TEST FOR TOTAL P_2O_5 CONTENT

Samples were analyzed for the total P_2O_5 content present in them, 1 gm of every sample was digested with concentrated HCl and concentrated HNO_3 in a ratio of 3:1 to dissolve samples completely, heated it till boiling in fume cupboard and when was about to dry it was diluted using distilled water and made up 1000 ml volume. Filtered the solution and 5 ml of filtrate was further diluted in 100 ml volumetric flask then 20 ml of Molybdovanadate reagent was added and every sample was analyzed through 405 nm wavelength of spectrophotometer, maximum absorbance measured and results were further calculated.

2.3.3 CITRATE SOLUBLE P_2O_5 CONTENT

Samples were analyzed for citrate soluble P_2O_5 content, they were treated for un-reacted P_2O_5 content and was further used to calculate the citrate soluble P_2O_5. 0.5 gm of every sample was separately treated with 100 ml of neutral ammonium citrate ($C_6H_{17}N_3O_7$) solution, shook it and heated in water bath at 65^oC for one hour. Filtered it and the residue left on filter paper was ignited in furnace at 550^oC completely. The residues of furnace were further digested in conc. HCl and conc. HNO_3 in 3:1. When it was about to dry was diluted again by adding 40 ml of distilled water. Finally filtered it again and 2ml of filtrate taken in flask and was diluted to 100ml by adding distilled water and 20 ml of Molybdovanadate reagent. Then analyzed through spectrophotometer at 405 nm, the maximum absorbance, and un-reacted P_2O_5 calculated. Citrate soluble P_2O_5 was then found out by using formula:

$$\text{Citrate soluble } P_2O_5 = \text{Total } P_2O_5 - \text{Water soluble } P_2O_5 - \text{Un-reacted } P_2O_5$$

2.3.4 ESTIMATION OF AVAILABLE P_2O_5 CONTENTS

The available P_2O_5 contents in samples were estimated using the formula:

$$\text{Available } P_2O_5 = \text{Water soluble } P_2O_5 + \text{Citrate soluble } P_2O_5$$

3 RESULT AND DISCUSSION

3.1 EFFECT OF COMPOSITION ON TOTAL P_2O_5 CONTENTS

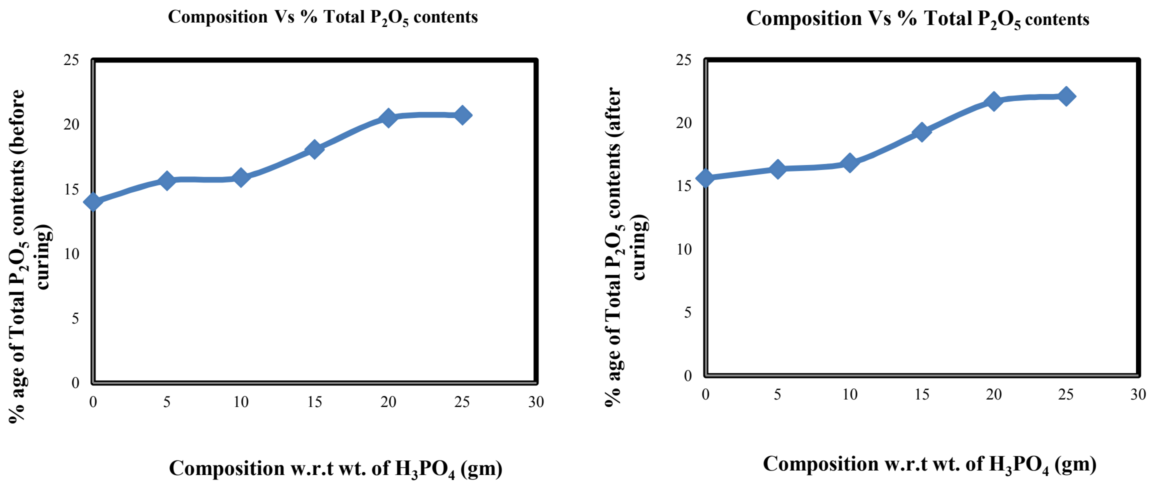
(a) Before curing

The samples prepared using different additives to the conventional formulation of SSP showed that the available P_2O_5 content varied with varying the composition markedly by increasing the ratio of H_3PO_4 as compared to the ratio of H_2SO_4.

The % total P_2O_5 contents increased as the H_3PO_4 was used in the samples as show in figure 1(a). When there was no H_3PO_4 in the sample the % total P_2O_5 contents were 14% which increased up to 20.73% total P_2O_5 contents with use of 25 gm H_3PO_4.

(b) After curing

After curing the samples for two weeks the maximum value of total P_2O_5 contents obtained was in the sample containing maximum percentage of H_3PO_4 and approached to the value up to 22.09 % by adding 25 gm H_3PO_4 as shown in Figure 1(b).This shows the direct relationship between total P_2O_5 content and H_3PO_4.



(a) (b)

Figure-1: ***Relation between single super phosphate samples with % total P_2O_5 contents (a) Before curing (b) After curing***

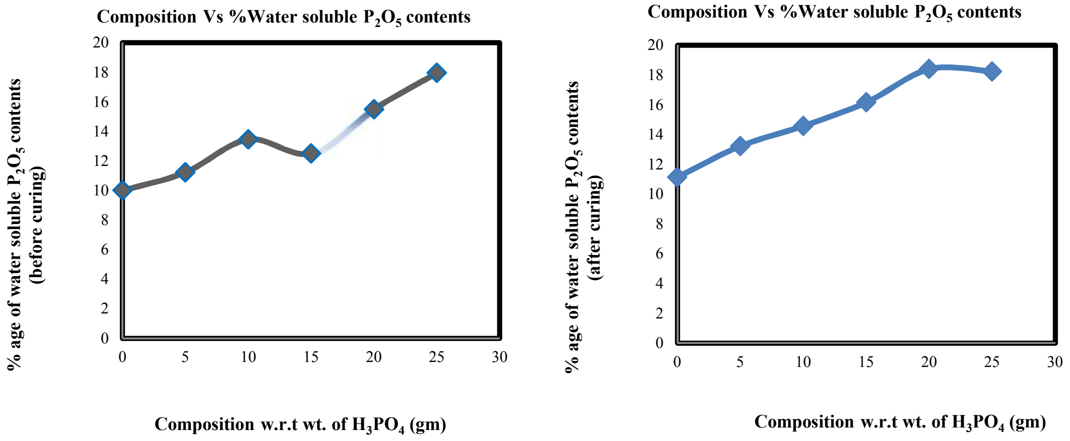
3.2 EFFECT OF COMPOSITION ON WATER SOLUBLE P_2O_5 CONTENTS

(a) Before curing

The water soluble phosphorus content had an increasing trend as the amount of H_3PO_4 increased in the samples as shown in figure 2(a). The sample with no H_3PO_4 showed 10 % water soluble P_2O_5 contents. In comparison the sample that contained the maximum amount (25 gm) of H_3PO_4 had a very prominent value of 17.95% water soluble P_2O_5 contents.

(b) After curing

There was a remarkable enhancement in the water soluble P_2O_5 contents after curing the fertilizer ranging from 11.14% with no H_3PO_4 to 18.23% with 25 gm of $H_3PO_4$for various samples as shown in figure 2(b).



(a) (b)

Figure-2: Relation between single super phosphate samples with % water soluble P_2O_5 contents (a) Before curing (b) After curing

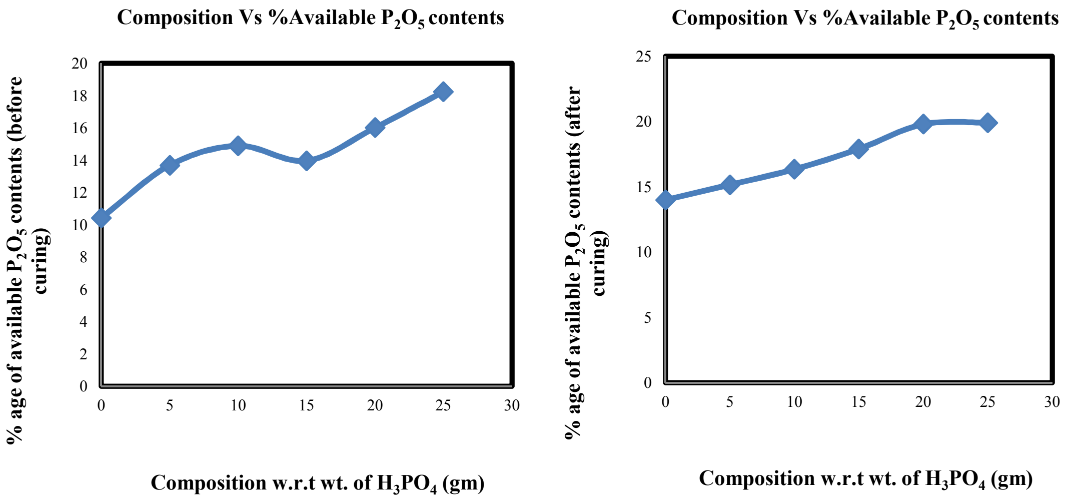
3.3 EFFECT OF COMPOSITION ON AVAILABLE P_2O_5 CONTENTS

(a) Before curing

The available P_2O_5 contents which is actually that amount of phosphorus content which is readily available for the plant to be up taken, showed linear relationship with the amounts of H_3PO_4 added to various samples and approached a maximum value of 18.52% for the sample containing 25 gm of the H_3PO_4 added in comparison to it the sample that had no H_3PO_4 added showed a total value of available P_2O_5 contents as 10.43 % as shown in figure 3(a).

(b) After curing

After giving a curing time of two weeks to the samples to complete the chemical reactions taking place, the maximum available P_2O_5 contents reached a value of 19.90% with the sample having maximum amount of the H_3PO_4 and in comparison to it the other samples with lesser H_3PO_4 showed lower available P_2O_5 contents as shown in figure 3(b).

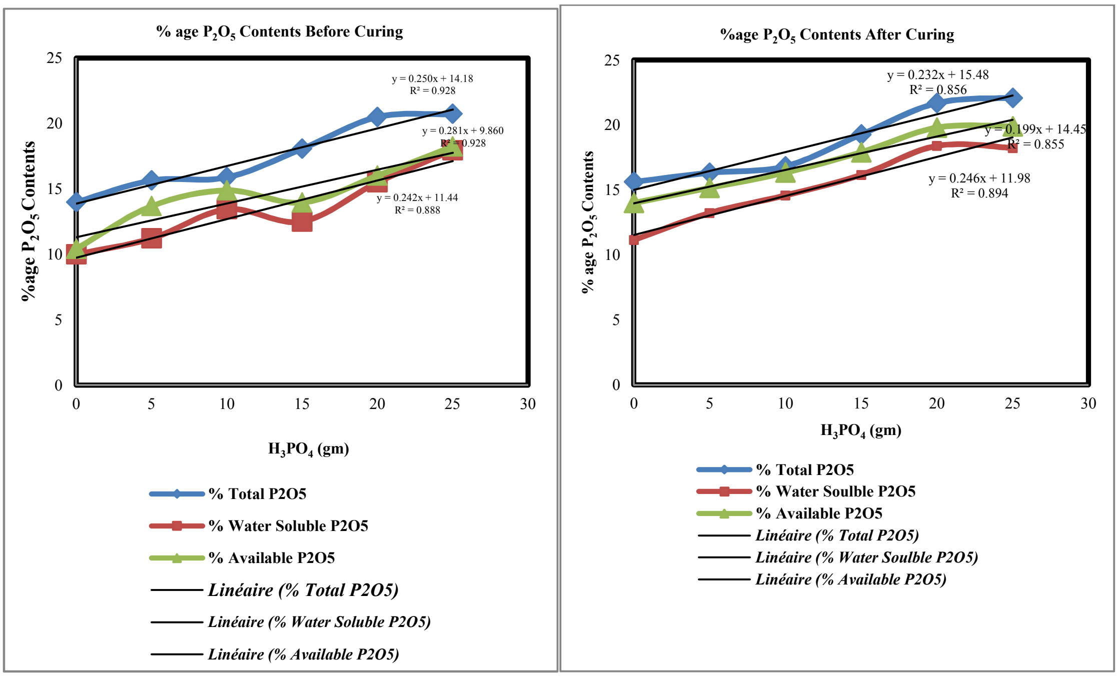


(a) (b)

Figure-3: Relation between single super phosphate samples with % Available P_2O_5 contents (a) Before curing (b) After curing

3.4 LINEARITY OF DATA

Figure 4(a) and 4(b) show the best fit lines for the curved data. And the R squared values for these lines. The R squared values being very close to “1” shows that the data is presenting closer to linear relationship of the observed parameters.



(a) (b)

Figure-4: Technical analysis of the data. (a) Before curing (b) After curing

The self-prepared SSP has an edge that it can contain up to 19.9% and even above available P_2O_5 contents (depending on amount of H_3PO_4 added) while the SSP commercially available when analyzed showed only 16% P_2O_5 content.

The self-made SSP with 18% available P_2O_5 content costs Rs. 878/50 Kg of fertilizer which is quite low than the price of same grade SSP available in market.

4 CONCLUSIONS

This study aims to examine the possibilities of the phosphates of low grades valorization in the manufacture of good quality SSP. The results demonstrate the possibility of production of market grade SSP from the low grade phosphate rocksat lower price rates. A fine quality SSP can be prepared by using the inferior quality local rock phosphate by the addition of H_3PO_4 to the conventional formulation of SSP. By increasing the concentration of H_3PO_4 the available P_2O_5 contents of the resulting SSP increases from 14% (without H_3PO_4) to up to 19.9% (by adding 25 gm. H_3PO_4). SSP of market grade or having 18% available P_2O_5 content can be manufactured from the same low quality rock phosphate with lesser cost than the same grade SSP available in market made from expensive imported rock.

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