

## STUDIES ON COMPLETE AND PARTIAL ACIDULATION OF EPPAWELA APATITE

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**Abstract :** Acidulation of Eppawela apatite with hydrochloric acid and sulphuric acid has been investigated in an attempt to convert this rock phosphate to an acceptable P-fertilizer using a simple and low cost method. Although direct acidulation with hydrochloric acid leads to a highly hygroscopic product, physical condition of this material can be improved by subsequent treatment with ammonia. Hydrochloric acid acidulation with 15-20% HCl followed by pH adjustment using an alkali, leads to the precipitation of dicalcium phosphate,  $\text{CaHPO}_4$ , which can readily be used as a P-fertilizer. Use of ammonia and ammonium salts has an added advantage in that the product contains nitrogen in addition to phosphorus. Physical condition of  $\text{H}_2\text{SO}_4$ -acidulated material is superior and the fertilizer value of this product is dependent on the extent of acidulation. Since the cost of this product depends mainly on the cost of  $\text{H}_2\text{SO}_4$ , partial acidulation with sulphuric acid seems to be a potentially useful and economical method. 50% acidulation with sulphuric acid to produce partially acidulated phosphate rock (PAPR-50) containing 17% wt available  $\text{P}_2\text{O}_5$  and 25% wt total  $\text{P}_2\text{O}_5$  appears to be suitable.

### 1. Introduction

Rock phosphate reserves<sup>6</sup> at Eppawela in Sri Lanka can be represented as chlorfluorapatite<sup>3</sup>  $\text{Ca}_5(\text{PO}_4)_3(\text{Cl},\text{F})$ . It has been reported<sup>8</sup> that the use of Eppawela apatite as a phosphatic fertilizer is limited due to its very low solubility. Its water solubility is about 0.5% wt  $\text{P}_2\text{O}_5$ , while 2% citric acid solubility<sup>3</sup> is in the range 5-6% wt  $\text{P}_2\text{O}_5$ . Thus, it is not generally recommended for direct application especially for short term crops such as paddy. As such, attempts have been made to convert this mineral to more soluble phosphate fertilizers by low temperature sintering methods.<sup>3,4,5</sup>

Acidulation is one of the common methods<sup>10</sup> to convert rock phosphate to more soluble phosphate fertilizers. Most commonly rock phosphate is treated with either  $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$  to produce singlesuperphosphate (SSP) or triplesuperphosphate (TSP) respectively. SSP contains about 20% wt available  $\text{P}_2\text{O}_5$  while TSP possesses much higher available phosphorus content ( ~ 45% wt  $\text{P}_2\text{O}_5$ ).

Eppawela rock phosphate is believed to be of igneous origin<sup>6</sup> and contains more chlorine<sup>3</sup> than fluorine. Its total  $\text{P}_2\text{O}_5$  content is rather high, the average being about 36%. It has a relatively high and a variable content

(4–10%) of total  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . Although these special chemical features of Eppawela apatite could make it difficult to use it for conventional acidulation processes, it is of interest to investigate the basic aspects of its acidulation reaction with locally produced mineral acids such as hydrochloric and sulphuric acids.

In the present study complete and partial acidulation of Eppawela apatite with hydrochloric acid and sulphuric acid has been investigated in an attempt to convert Eppawela rock phosphate to a more soluble fertilizer grade phosphate material.

## 2. Experimental

Two rock phosphate samples labelled I and II have been used in the present study. Sample I was collected from one of the hillocks in the northern part of the "leached zone" of the apatite deposit at Eppawela, Sri Lanka. This rock sample was crushed, powdered and sieved (100 mesh) for subsequent investigation. Sample II is a sample of commercially available powdered (90% passing through 100 mesh) Eppawela rock phosphate.

### 2.1 Chemical analysis

Analysis of the metallic elements and silicon has been performed using a X-ray fluorescence spectrometer. Total  $\text{P}_2\text{O}_5$  has been determined by the X-ray fluorescence as well as by the vanadomolybdate method.<sup>9</sup> Analyses for fluoride have been made using Orion model 94–09 fluoride ion electrode<sup>1</sup> against a Beckman type R.L.B. calomel reference electrode. The samples were dissolved in 5M hydrochloric acid for this analysis. Chlorine analyses were made by dissolving the samples in 1:1 nitric acid and titrating it with standard 0.05M silver nitrate to a potentiometric end point. Table 1 shows the results of chemical analysis of the two samples for their major constituents and trace elements. Phases present in some products were identified by using powder X-ray diffraction with Cu  $K\alpha$  radiation.

### 2.2 HCl acidulation

Rock phosphate samples were treated with hydrochloric acid of known strength and stirred vigorously for 30 minutes in beakers. The resulting slurry was allowed to stand for 6 hours and then transferred to porcelain dishes for curing. After curing period, the product was dried at 100°C.

For dicalcium phosphate precipitation, the rock samples have been mechanically stirred with hydrochloric acid for 6 – 8 hours. The pH of the resulting solution was adjusted in the range 5 – 7 using aqueous sodium

Table 1. Analytical data of Eppawela apatite

(i) Partial Chemical Analysis: (in wt%)

|                                | Apatite (I) | Commercial apatite (II) |
|--------------------------------|-------------|-------------------------|
| CaO                            | 46.60       | 43.50                   |
| P <sub>2</sub> O <sub>5</sub>  | 35.30       | 32.80                   |
| Fe <sub>2</sub> O <sub>3</sub> | 3.80        | 5.00                    |
| Al <sub>2</sub> O <sub>3</sub> | 0.74        | 2.60                    |
| Cl                             | 2.20        | 2.03                    |
| F                              | 1.70        | 1.60                    |
| SiO <sub>2</sub>               | 0.43        | 0.79                    |
| SrO                            | 0.38        | 0.34                    |

(ii) Trace Elements Analysis: (in ppm)

| Element | I    | II   | Element | I   | II   |
|---------|------|------|---------|-----|------|
| K       | 300  | 500  | Cu      | 307 | 157  |
| Ba      | 316  | 1178 | La      | 470 | 438  |
| Co      | 8    | 10   | Mn      | 500 | 2300 |
| Cr      | 20   | 21   | Ti      | 10  | 200  |
| Mg      | 300  | 400  | Na      | 600 | 1100 |
| Zn      | 309  | 239  | Zr      | 9   | 12   |
| Y       | 94   | 108  | Ni      | 23  | 26   |
| Sr      | 3217 | 2936 | W       | 8   | 5    |
| As      | 23   | 27   | Pb      | 111 | 140  |
| V       | 46   | 81   |         |     |      |

NOTE: I – A representative sample from the 'leached zone' at Eppawela.

II – A sample of commercially available powdered Eppawela apatite.

hydroxide, lime or ammonia. After the precipitation is complete, the product was filtered under suction and dried at 100°C prior to analysis.

### 2.3 H<sub>2</sub>SO<sub>4</sub> acidulation

Sulphuric acid acidulation was performed similar to hydrochloric acid acidulation but in this case drying was not necessary. During the curing period the acidulated product gradually transforms into a dry powder.

### 2.4 Estimation of phosphorus

Water and 2% citric acid soluble P<sub>2</sub>O<sub>5</sub> contents of the samples have been determined<sup>11</sup> by using about 1g samples. These were extracted in 250 ml reagent bottles with 100 ml of distilled water or 2% citric acid solution using a mechanical shaker operating at about 250 oscillations per minute for 30 minutes. The total P<sub>2</sub>O<sub>5</sub> contents have been determined by extracting the samples with conc. HCl. The extracts were analysed for phosphorus by the vanadomolybdate<sup>9</sup> method using Corning colorimeter model 253 at a wavelength of 460 nm.

## 3. Results and Discussion

### 3.1 Direct acidulation with HCl

Acidulation reaction for the complete (100%) acidulation of apatite may be represented as follows.



Several side reactions may also occur depending on the other components and the impurities present in the rock. As such, the acid requirement for acidulation in general is calculated by considering the nature and amounts of impurities present and the total P<sub>2</sub>O<sub>5</sub> content of the rock.

Variation of available P<sub>2</sub>O<sub>5</sub> with the acid concentration for 100% and 60% acidulations is shown in Figure 1. In both cases the available P<sub>2</sub>O<sub>5</sub> increases with increase in concentration up to about 18% and further increase in concentration does not have any effect on the available phosphorus content. Thus, the optimum concentration for HCl acidulation is in the range 15 – 20%. Therefore, it appears that dilute hydrochloric acid solution could be conveniently used for the acidulation process. Completely acidulated product of rock sample I contains ~ 19% available P<sub>2</sub>O<sub>5</sub> while

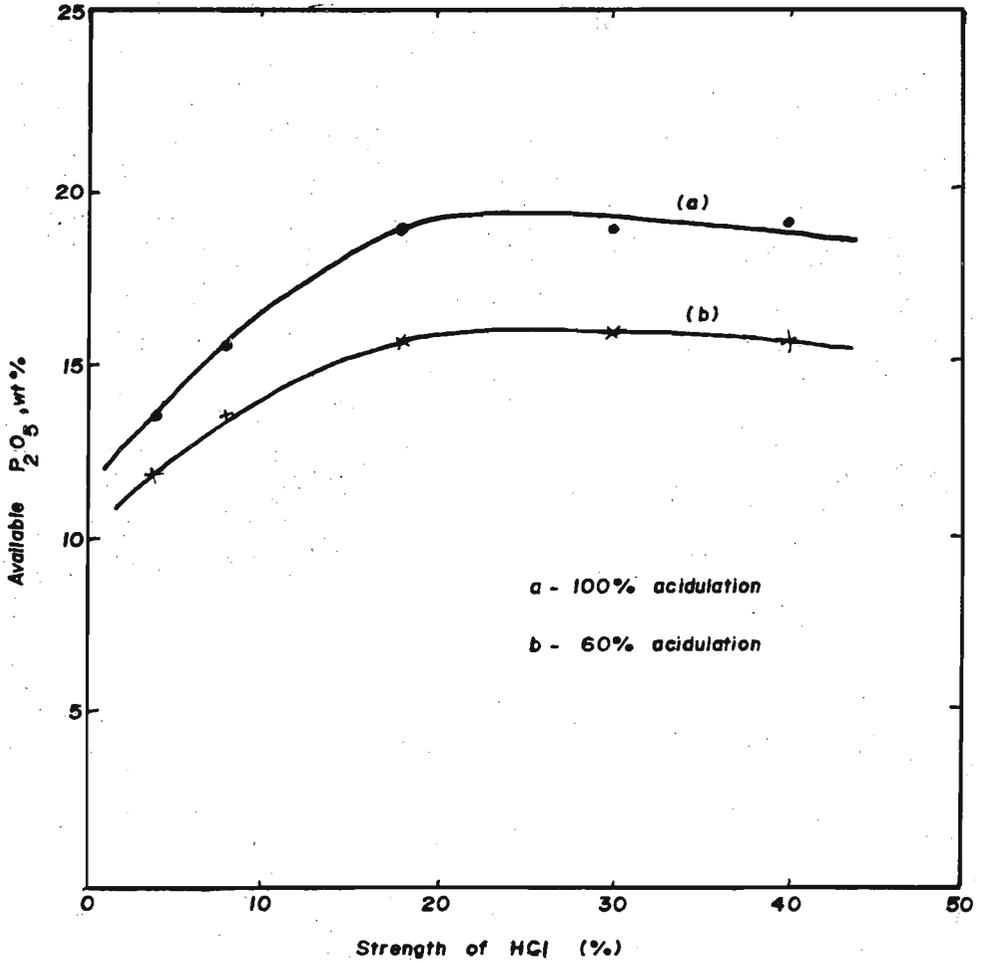


Figure 1. Variation of available phosphorus content of HCl-acidulated product with the acid concentration.

commercial apatite (sample II) gave a product containing  $\sim 17\%$  wt  $P_2O_5$ . However, a product containing a maximum of  $\sim 20\%$  available  $P_2O_5$  can be obtained by increasing the amount of acid added. On the other hand partially acidulated (60%) product contains 14 – 16% wt available  $P_2O_5$ .

Major problem of HCl acidulation is due to the fact that the product contains a large amount of highly hygroscopic calcium chloride. The presence of calcium chloride leads to problems of drying, storage and transport of the fertilizer. However, it has been observed in the present study that the hygroscopic nature of the product can be considerably reduced and the physical properties improved by the treatment of the HCl acidulated product with aqueous ammonia or a suitable ammonium salt.

Since both monocalcium phosphate,  $Ca(H_2PO_4)_2$ , and calcium chloride are highly water soluble it is rather difficult to separate one from the other by a simple and inexpensive technique. As an alternative, it may be possible to convert apatite to dicalcium phosphate ( $CaHPO_4$ ) which is water insoluble (Table 5) but citric acid soluble making its phosphorus available to the plants. Thus, extremely water soluble calcium chloride can be conveniently removed from the product.

### 3.2 $CaHPO_4$ precipitation

The optimum conditions suitable for the precipitation of dicalcium phosphate,  $CaHPO_4$ , from acidic phosphate solutions have been determined<sup>7</sup> previously. The optimum pH for this precipitation is found to be in the range 5 – 7. The variation of available  $P_2O_5$  of the product with the precipitation pH is shown in Figure 2. This confirms the optimum pH for the precipitation as 5 – 7. The precipitation begins around pH 4 and when the pH is increased beyond 7, citric acid solubility of the product decreases indicating the conversion of  $CaHPO_4$  to  $Ca_3(PO_4)_2$ .

pH adjustment in the acid extracts has been done using aqueous NaOH lime or ammonia. Table 2 shows the results of dicalcium phosphate precipitation after 60% and 100% acidulation followed by pH adjustment using aqueous NaOH. Both sets of results show that there is an increase of 2% citric acid solubility of the product with increase in acid concentration up to 18%. 60% acidulation with 18% HCl followed by neutralization with aqueous NaOH yielded a product containing 23–25% available  $P_2O_5$ . The rock sample II, however, yielded a product containing slightly lower ( $\sim 21\%$ ) available  $P_2O_5$  content. The major constituent in the dried product was identified as dicalcium phosphate ( $CaHPO_4$ ) by powder X-ray diffraction. Tricalcium phosphate,  $Ca_3(PO_4)_2$ , and apatite also have been identified in the product.

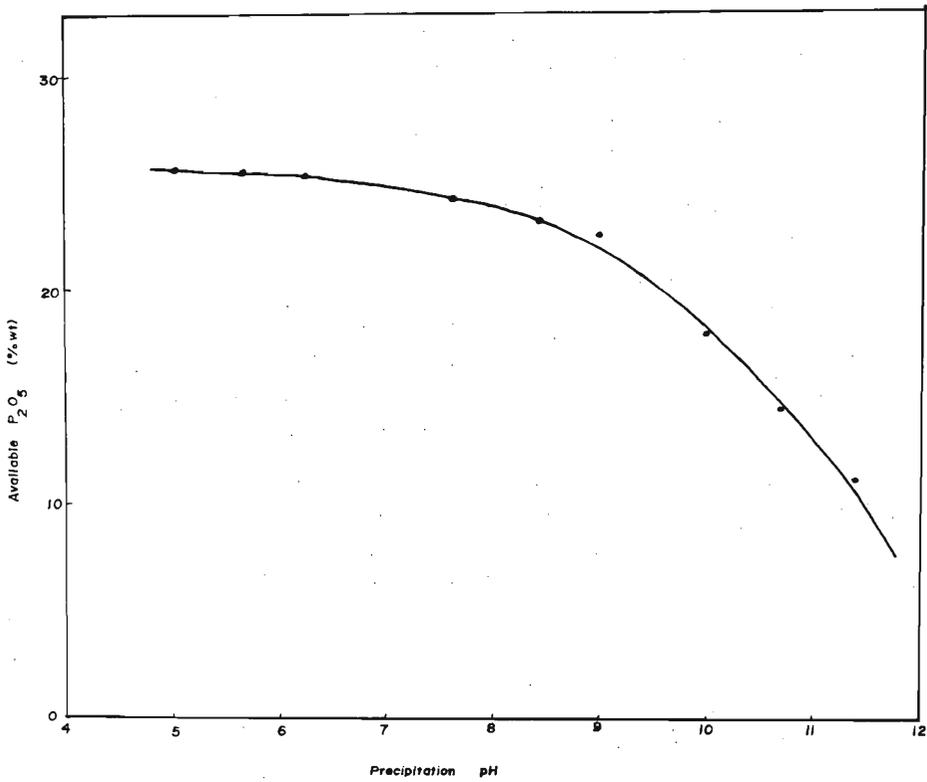


Figure 2. Effect of precipitation pH on the available phosphorus content of the precipitated product.

Table 2. Results of HCl acidulation followed by precipitation.

| Strength of acid | Extent of acidulation | 2% citric acid soluble P <sub>2</sub> O <sub>5</sub> wt. % | P <sub>2</sub> O <sub>5</sub> wt. % in the filtrate |
|------------------|-----------------------|--|---|
| 4%               | 60%                   | 21.3   | 0.5   |
| 8%               | 60%                   | 22.2   | 1.6   |
| 18%              | 60%                   | 22.9   | 1.9   |
| 4%               | 100%                  | 23.6   | 1.2   |
| 8%               | 100%                  | 24.5   | 1.8   |
| 18%              | 100%                  | 24.8   | 1.7   |

Note: Base used is aqueous sodium hydroxide

Possibility of using lime to adjust the pH has been attempted. But in this case the product was found to contain about 16% available P<sub>2</sub>O<sub>5</sub>. Relatively large quantities of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and hydroxyapatite in addition to CaHPO<sub>4</sub> have been observed in the product obtained using lime. Thus it is rather difficult to control the reaction for the preferential precipitation of CaHPO<sub>4</sub> in the presence of lime. On the other hand, ammonia was found to be an acceptable pH controlling agent. It has an added advantage in that the product contains appreciable amount of nitrogen in addition to phosphorus ( ~ 26% wt available P<sub>2</sub>O<sub>5</sub>). The following reaction may occur during the ammoniation facilitating the precipitation of CaHPO<sub>4</sub>.



### 3.3 Acidulation with sulphuric acid

Figure 3 shows the variation of the extent of conversion with the concentration of H<sub>2</sub>SO<sub>4</sub> used in the acidulation. All three curves representing 100%, 75% and 50% acidulation reactions show a maximum around 70% H<sub>2</sub>SO<sub>4</sub>. Thus the optimum concentration for complete and partial acidulation of apatite with H<sub>2</sub>SO<sub>4</sub> is in the range 65 – 70%. As such, all the H<sub>2</sub>SO<sub>4</sub> acidulation experiments have been performed using 70% sulphuric acid in the present study.

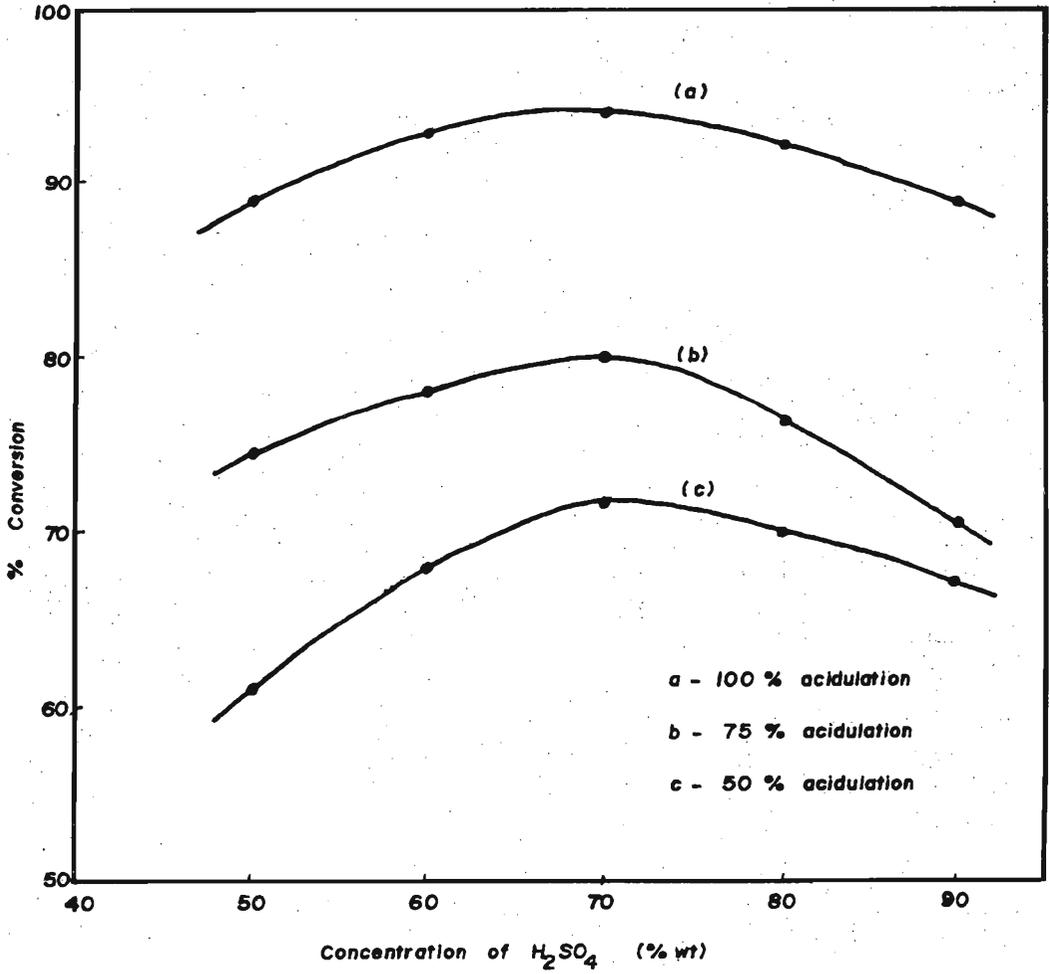


Figure 3. Effect of concentration of H<sub>2</sub>SO<sub>4</sub> on the extent of conversion.

Table 3. Variation of available  $P_2O_5$  content with the extent of  $H_2SO_4$  acidulation.

| Extent of acidulation | Total $P_2O_5$ % wt. | Water soluble $P_2O_5$ % wt. | 2% citric acid soluble $P_2O_5$ % wt. |
|-----------------------|----------------------|------------------------------|---------------------------------------|
| 100%                  | 21.7                 | 19.6                         | 20.8                                  |
| 80%                   | 22.6                 | 16.3                         | 19.0                                  |
| 60%                   | 24.4                 | 12.1                         | 18.0                                  |
| 50%                   | 25.6                 | 10.5                         | 17.1                                  |
| 30%                   | 28.6                 | 6.1                          | 14.8                                  |

Note: Original rock phosphate contained 35.3% wt. total  $P_2O_5$ ; curing period = 4 weeks

$P_2O_5$  contents of the products obtained by complete and partial acidulation of Eppawela apatite are given in Table 3. The variation of total, available and water soluble  $P_2O_5$  contents with the extent of acidulation are shown in the Figure 4. SSP produced (100% acidulation) from apatite contains 20.8% available  $P_2O_5$ , of which 19.6% is water soluble. The available  $P_2O_5$  contents decrease with decrease in the extent of acidulation. 50–60% acidulated product contains a reasonably high value of available  $P_2O_5$  (17–18% wt), although the amount of acid added is reduced by 40–50%. Furthermore, partially acidulated product contains much higher total  $P_2O_5$  content (Figure 4) which will eventually be available to the soil and to the plants.

Available  $P_2O_5$  contents of the product obtained after different curing periods are shown in Table 4. Effect of curing period on the product for 100% and 60% acidulations are shown in Figure 5. The results indicate that for 60% acidulation the optimum curing period is about 3–4 weeks while for SSP production 5–6 weeks curing is required. Thus, partial acidulation has an added advantage of having a less curing period.

50% acidulated product was found to contain unreacted apatite, monocalcium phosphate and trace amounts of dicalcium phosphate by powder X-ray diffraction. The product was not found to be sticky. However, a suitable treatment may be necessary if the product obtained in a commercial scale preparation is found to be sticky.

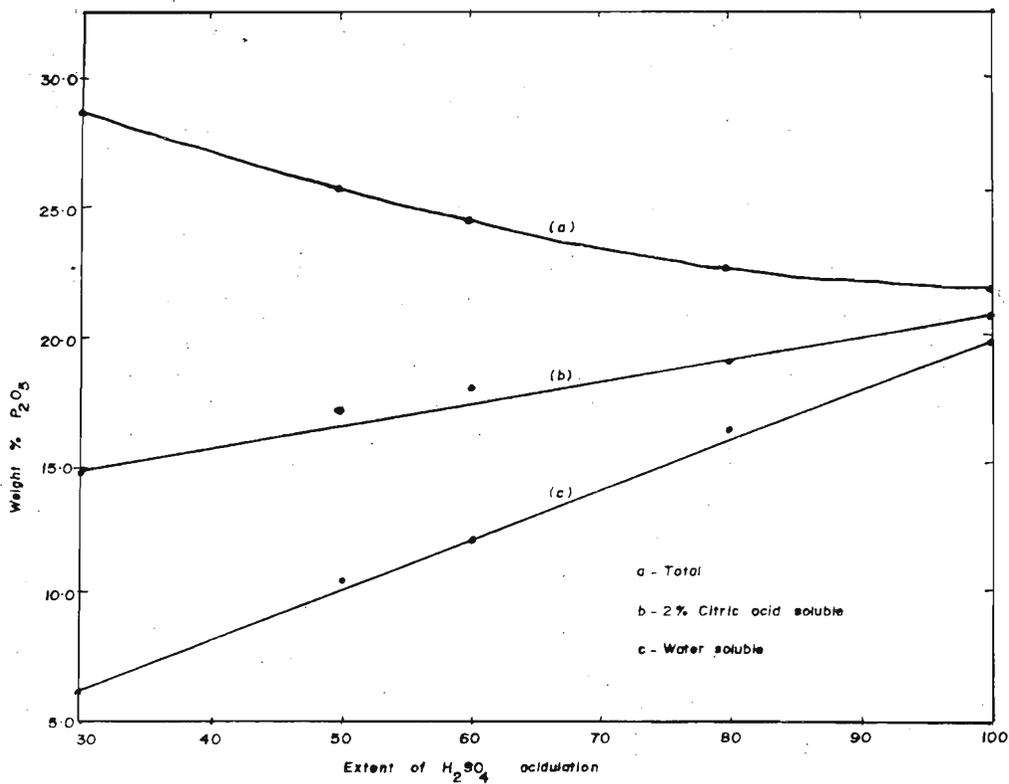


Figure 4. Variation of total, available and water soluble phosphorus contents with the extent of  $H_2SO_4$ -acidulation.

Table 4. H<sub>2</sub>SO<sub>4</sub> acidulation : Effect of curing time on the available P<sub>2</sub>O<sub>5</sub> content.

| Curing period | 2% citric acid soluble P <sub>2</sub> O <sub>5</sub> wt % |                 |
|---------------|---|-----------------|
|               | 100% acidulation  | 60% acidulation |
| 34 hrs        | 12.3  | 13.0            |
| 1 week        | 15.2  | 15.8            |
| 2 weeks       | 17.8  | 17.2            |
| 3 weeks       | 18.9  | 17.8            |
| 4 weeks       | 20.1  | 18.0            |
| 5 weeks       | 21.3  | 18.0            |
| 6 weeks       | 21.1  | 17.9            |

Table 5. Phosphorus contents of some calcium phosphates

| Sample  | Total P <sub>2</sub> O <sub>5</sub><br>wt % | Water soluble<br>P <sub>2</sub> O <sub>5</sub> wt % | 2% citric acid<br>soluble P <sub>2</sub> O <sub>5</sub> wt % |
|---|---|---|--|
| Rock phosphate I  | 35.3  | 0.5   | 5.8  |
| Rock phosphate II   | 32.8  | 0.4   | 5.2  |
| Hydroxyapatite<br>Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH      | 42.3  | 0.7   | 16.2   |
| Monocalcium phosphate<br>Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> | 60.6  | 58.3  | 60.4   |
| Dicalcium phosphate<br>CaHPO <sub>4</sub>                                 | 52.1  | 1.3   | 44.4   |
| Tricalcium phosphate<br>Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>   | 45.8  | 0.9   | 34.0   |

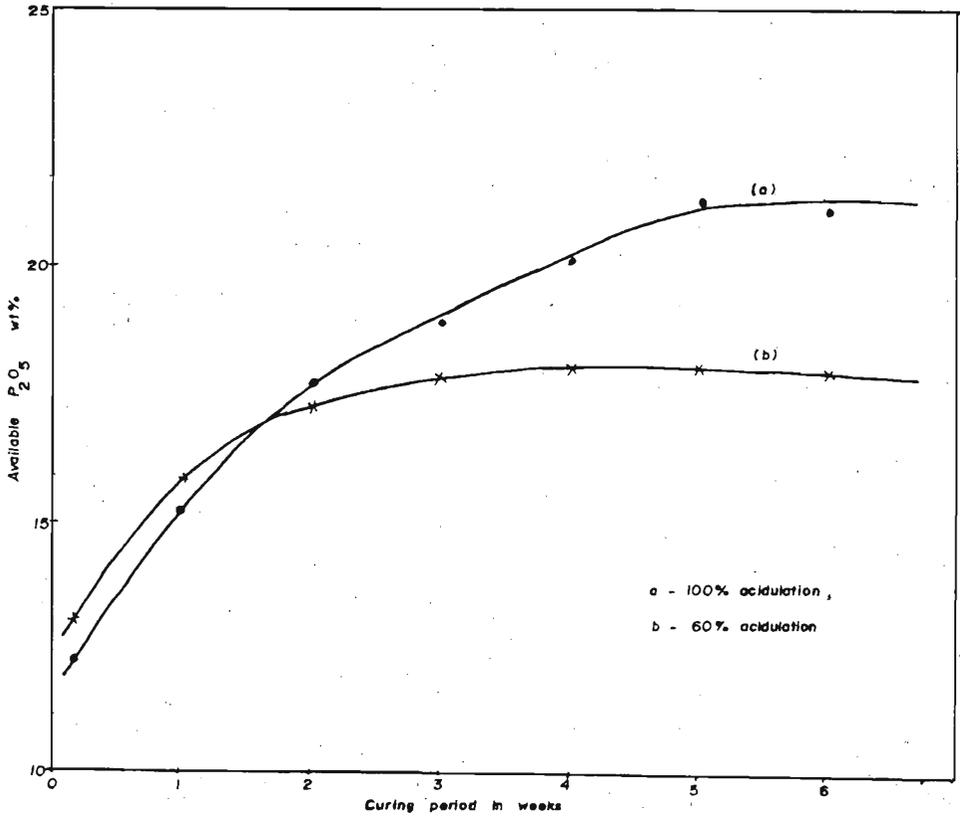


Figure 5. Effect of curing period on the available phosphorus content of the H<sub>2</sub>SO<sub>4</sub>-acidulated product.

#### 4. Discussion

Phosphorus contents of the starting materials are compared with those of the major constituents in the fertilizer products in Table 5. Conditions of acidulation of Eppawela apatite are summarised in Table 6. For the production of 50% acidulated product, 30 kg  $\text{H}_2\text{SO}_4$  (100% basis) diluted to 70% is required for 100 kg powdered apatite.

Direct acidulation of Eppawela rock phosphate with HCl to produce SSP is not feasible owing to the presence of large amounts of highly hygroscopic calcium chloride in the product. However, physical conditions of this product may be improved considerably by the subsequent treatment with ammonia or ammonium salts. A similar situation is anticipated in nitric acid acidulation to produce nitrophosphates. Nevertheless, HCl acidulation followed by alkali treatment produces  $\text{CaHPO}_4$  which can readily be used as P-fertilizer. Use of  $\text{CaHPO}_4$  may be advantageous in areas where there is considerable leaching of phosphates.

Although lime is the cheapest alkali available, the use of lime in the pH adjustment is not recommended. Ammonia is an efficient neutralization agent because it facilitates the formation of dicalcium phosphate and the product contains another important plant nutrient, N. However, considering the availability and economic factors aqueous NaOH seems to be the most suitable.

In the case of sulphuric acid acidulation the major factor seems to be the cost of sulphuric acid. The cost of the final product will be dependent mainly on the cost and the amount of sulphuric acid used (extent of acidulation) in the process. When the extent of acidulation is less the cost will be lower and the total  $\text{P}_2\text{O}_5$  content of the product will be more. On the other hand, the available  $\text{P}_2\text{O}_5$  content or the fertilizer value increases with increase in the extent of acidulation.

On account of the large saving due to cutting down of acid requirement, and due to the presence of reasonably high phosphorus content of the partially acidulated product, this material can be considered as a potentially useful and economical phosphate fertilizer for Sri Lanka. Thus, 50% acidulation of Eppawela apatite with  $\text{H}_2\text{SO}_4$  to produce partially acidulated phosphate rock (PAPR) containing about 17% wt available  $\text{P}_2\text{O}_5$  and 25% total  $\text{P}_2\text{O}_5$  appears to be suitable.

Free phosphoric acid content in the acidulated product plays an important role in fixing phosphates as aluminium and iron phosphates. Since the free phosphoric acid content is minimal in the partially acidulated product, the effect of the presence of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  is negligible in

Table 6. Methods of acidulation of Eppawela Rock Phosphate

| Acid                           | Strength of acid | Extent of acidulation | * Ratio of raw materials  | Available P <sub>2</sub> O <sub>5</sub> of the product (wt. %) | Total P <sub>2</sub> O <sub>5</sub> (wt. %) | Machinery                                |
|--------------------------------|------------------|-----------------------|---|--|---|--|
| HCl                            | 20%              | 100%                  | 100 kg apatite<br>46 kg HCl<br>(100% basis)                                       | 19%  | 24%   | Acidulation plant                        |
| HCl                            | 20%              | 50%                   | 100 kg apatite<br>23 kg HCl<br>(100% basis)                                       | 15%  | 26%   | Acidulation plant                        |
| HCl                            | 20%              | 50%—100%              | 100 kg apatite<br>23—46 kg HCl<br>(100% basis)<br>aqueous NaOH or NH <sub>3</sub> | 22—25%   | 26—28%                                      | Acidulation plant & crystallization tank |
| H <sub>2</sub> SO <sub>4</sub> | 70%              | 100%                  | 100 kg apatite<br>60 kg H <sub>2</sub> SO <sub>4</sub><br>(100% basis)            | 21%  | 22%   | Acidulation plant                        |
| H <sub>2</sub> SO <sub>4</sub> | 70%              | 50%                   | 100 kg apatite<br>30 kg H <sub>2</sub> SO <sub>4</sub><br>(100% basis)            | 17%  | 25%   | Acidulation plant                        |

N.B. \* These ratios are calculated assuming that the total P<sub>2</sub>O<sub>5</sub> of the rock phosphate is about 35% wt. Curing period is 4 weeks.

comparison with 100% acidulation to produce SSP.

Presence of high chlorine content in Eppawela apatite leads to corrosion problems in an industrial acidulation process. As such, mechanical mixers and the acidulation tanks should be lined with corrosion resistant material. Furthermore, pollution factors also should be taken into consideration in deciding the location of acidulation plants.

Although chemical tests and laboratory evaluations indicate that these products can be used as P-fertilizers, it is essential to examine the crop response of the products and the financial viability of these processes. Therefore, pilot plant trials together with comprehensive financial evaluation of the processes and long-term field trials have to be carried out prior to commencement of any commercial production.

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