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Nitric acid treated phosphate fertilizer from Eppawala apatite in Sri Lanka

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Abstract

A method is described for the production of phosphate fertilizer from a high quality fraction of the apatite ore at Eppawala in Sri Lanka.

Apatite is acidulated with nitric acid (70%) at approximately the stoichiometric level needed to generate dicalcium phosphate. The reaction product when mixed with ground ammonium sulphate yields a dry nonhydroscopic solid containing almost all phosphorus in the "available" form (i.e. ~80% water soluble and ~90%, 2% citric acid soluble). The product can be stored in polythene or gunny bags. Reversion is negligible, as demonstrated by a decrease in water soluble P_2O_5 of less than 1% after 6 months' storage.

Introduction

The reserve of phosphate rock at Eppawala in Sri Lanka is one of the world's largest deposits of apatite (Dahanayake et al., 1988; Dahanayake et al., 1989; Jayawardena et al., 1976; Jayawardena et al., 1986). At the present consumption rate it could provide phosphate fertilizers to the nation for 5–10 centuries (Dahanayake et al., 1988; Dahanayake et al., 1989; Jayawardena et al., 1976, Jayawardena et al., 1986). Eppawala ore is a complex chloro-fluoro apatite of high average P_2O_5 content (~37%) containing significant amounts of hydroxy-apatite and carbonato-apatite (Dahanayake et al., 1988; Dahanayake et al., 1989; Jayawardena, 1976; Jayawardena, 1986). Unfortunately the average ore is not suitable for manufacture of phosphoric acid because of the high chlorine, aluminium oxide and iron oxide content (Jayawardena, 1986). The ore also contains a high quality fraction low in oxides of iron and aluminium which might be used for phosphoric acid production. (Dahanayake et al., 1989). As Sri Lanka has no reserves of elemental sulphur or pyrites needed for production of sulphuric acid, much attention has been focused on benefication techniques independent of sulphuric acid (Amarasekara et al., 1983; Amarasiri et al., 1976; Jayasekara et al., 1978; Tennakone et al., 1978; Tennakone, 1988; Tennakone et al., 1988). In a paper published in this journal we have indicated a method for production of water soluble phosphate fertilizer from Eppawala apatite using hydrochloric acid (Tennakone et al., 1988). Here we report a similar method that uses nitric instead of hydrochloric acid. Because of the hygroscopicity of nitric acidulations which produce calcium nitrate it is necessary to further treat the product with ammonium sulphate. This yields a nonhygroscopic solid containing nearly all phosphorus in an 'available' (2% citric acid soluble) form.

Nitric acid reacts with apatite in the following ways depending on the stoichiometry of the reaction, ie,

$$\begin{aligned} 2Ca_5(PO_4)_3.X + 6HNO_3 &\rightarrow \underset{\text{dicalcium phosphate}}{\underset{\downarrow}{6Ca(HPO_4)}} \\ &+ 3Ca(NO_3)_2 + CaX_2 \qquad (1) \end{aligned}$$

$$2Ca_5(PO_4)_3.X + 12HNO_3 \rightarrow 3Ca(H_2PO_4)_2 + 6Ca(NO_3)_2 + CaX_2 \quad (2)$$

$$\downarrow$$

monocalcium phosphate

$$2Ca_5(PO_4)_3.X + 18HNO_3 \rightarrow 6H_3PO_4 + 9Ca(NO_3)_2 + CaX_2 \quad (3)$$

$$\downarrow$$

orthophosphoric acid

where X = F, Cl or OH.

When the acidulated product is aged for 6h to complete the reaction and mixed with ground ammonium sulphate, the calcium salts undergo the following double decomposition reactions, ie,

$$Ca(NO_3) + (NH_4)_2SO_4 \rightarrow CaSO_4 + 2NH_4NO_3 \quad (4)$$

$$CaHPO_4 + (NH_4)_2SO_4 \rightarrow (NH_4)_2(HPO_4) + CaSO_4 \quad (5)$$

$$\downarrow$$

diammonium phosphate

$$Ca(H_2PO_4)_2 + (NH_4)_2SO_4 \rightarrow CaSO_4 + 2NH_4(H_2PO_4) \quad (6)$$

$$\downarrow$$

monoammonium phosphate

The conversion of calcium nitrate to ammonium nitrate suppresses the hygroscopicity.

Table 1. Composition of the high quality Eppawala ore

Constituent	Percentage
CaO	55.5
P_2O_5 (Citric acid soluble)	4.4
P_2O_5 (Citric acid insoluble)	34.8
SiO_2	0.3
Fe_2O_3	0.3
Al_2O_3	0.3
Cl	2.0
F	1.5

Experimental

In all experiments the high quality ore (composition given in Table 1) was ground and sieved through mesh BS200 (74 μm). The P_2O_5 content (water and 2% citric acid soluble) of the ore and the fertilizers prepared were determined by the vanadomolybdate method. Results were also confirmed by the gravimetric ammonium molybdate method (Jeffery, 1971). The presence of mono, di-and tri-calcium phosphates in the acidulated product, ammonium nitrate and ammonium phosphate after mixing with ammonium sulphate were confirmed x-ray diffractometry (Fig. 1) (Shimadzu XD-7A Diffractometer). To achieve acidulations up to the stoichiometric level of (1), the volume of commercial nitric acid (70% HNO_3. Specific gravity = 1.42) needed per kg of apatite is,

$$[\text{volume } 70\% \text{ } HNO_3] \simeq 0.9 \times 10^{-2}1$$

where x is the percentage of P_2O_5 in the ore. Thus for the ore containing ~39% of P_2O_5, the volume of nitric acid needed for acidulation up to the stoichiometric level of (1) is ~0.36 1 per kg. When the acid treatment is carried up to the level of dicalcium phosphate, the amount of ammonium sulphate required to complete the double decomposition reaction is, $(NH_4)_2SO_4$ weight = $1.7x \times 10^{-2}$ kg per kg of the ore (x = % P_2O_5) in the ore). When x = 39, the ammonium sulphate required per kg of the ore is ~0.66 kg. In our experiments, the following mixtures were prepared.

Mixture. 1 1 kg of apatite (39% P_2O_5) mixed with 0.75 1 of nitric acid (70%) aged for 6h and mixed with 1 kg of ground ammonium sulphate.

Mixture. 2 1 kg of apatite (39% P_2O_5) mixed with 0.50 1 of nitric acid (70%) aged for 6h and mixed with 1 kg of ground ammonium sulphate.

Mixture. 3 1 kg of apatite (39% P_2O_5) mixed with 0.25 1 of nitric acid (70%) aged for 3h and mixed with 1 kg of ground ammonium sulphate.

All the mixtures were dired for five hours at different temperatures (70–150°C) and water soluble, 2% citric acid soluble and the total P_2O_5

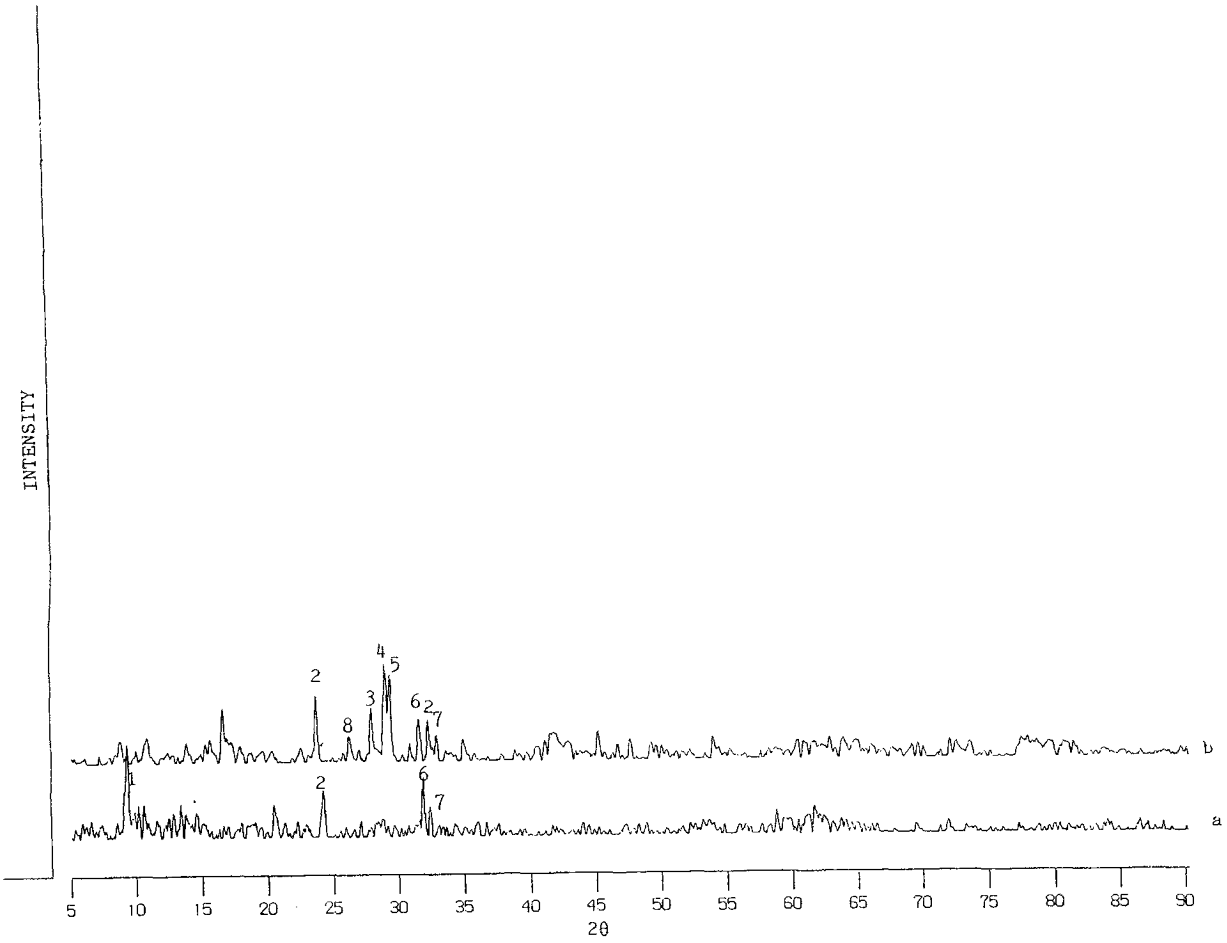

Fig. 1. The X-ray diffraction spectrum of (a) HNO_3 treated apatite (b) HNO_3 treated apatite after mixing with ammonium sulphate (mixing ratios are as in the mixture. 1). 1. Calcium nitrate; 2. Dicalcium Phosphate; 3. Diammonium Phosphate; 4. Calcium Sulphate dihydrate; 5. Tricalcium Phosphate; 6. Monocalcium phosphate; 7. Ammonium Nitrate; 8. Monoammonium phosphate.

content was measured. For determination of total P_2O_5 the product was dissolved in conc. HNO_3. Mixtures dried at 70°C were stored in polythene and gunny bags at 28°C and ~78% humidity.

Results and discussion

Properties of the mixtures

All three mixtures set into a solid form even before drying. The loss in weight on prolonged drying at 70°C was less than 3%. The water in nitric acid is almost completely absorbed by $CaSO_4$ as the water of crystallization ($CaSO_4.2H_2O$ was detected by XRD). The gain in weight of mixture 1 stored in a sealed polythene bag (after heating to 70°C) for one month was ~0.8%. In the case of mixtures 2 and 3 the gain in weight was less than 0.5%. Mixtures 1, 2 and 3 stored in gunny bags showed ~4–6% gain in weight during the same period. However, the product remained in the solid form. The compositions of the fertilizer at different mixing ratios are given in Table 2.

Table 2. Final undried weight (quantities of ingredients as in the (text) and composition of the mixtures 1, 2 and 3 (conversion = P_2O_5) (citric) X 100/total P_2O_5)

	Final Wt/kg	P_2O_5% (Water)	P_2O_5% (Citric acid Soluble)	Conversion % (P_2O_5 citric x 100/P_2O_5 total)	N %
Mixture 1	3.11	13.0	13.5	99	11.9
Mixture 2	2.71	11.5	12.4	86	11.4
Mixture 3	2.36	7.2	10.3	62	10.6

Thermal stability and reversions

Acidulated phosphate fertilizers sometimes undergo reversion reactions, which results in a decrease in the 'available phosphorus' [13]. Generally reversion brings about a decrease in water soluble P_2O_5 followed by a concomitant increase in the 2% citric acid soluble fraction (Sauchelli, 1960). Possible reversion reactions are:

$2(NH_4)(H_2(PO_4) + Ca(NO_3)_2 \rightarrow Ca(HPO_4)$
↓
monoammonium phosphate
$+ (NH_4)_2(HPO_4) + 2HNO_3$ (7)
↓
diammonium phosphate

$2(NH_4)(H_2PO_4) + 3Ca(NO_3)_2 \rightarrow Ca_3(PO_4)_2$
$+ 4HNO_3 + 2NH_4NO_3$ (8)
↓
monoammonium phosphate

Although there is no exothermicity in (7) and (8), HNO_3 is volatile and removal of HNO_3 (e.g., warming) shifts the equilibrium in the forward direction. The decrease in total weight due to loss of HNO_3 brings about an slight increase in citric acid soluble P_2O_5. As reversions increase with a rise in temperature, the change in composition with the increase of drying temperature is a measure of the resistance to reversions. Table 3 shows the changes in the water and 2% citric acid solubilities of the three mixtures when heated for five hours at different temperatures. It is seen that at higher temperatures reversions cause significant decreases in the water soluble P_2O_5. On storage (28°C) for six months, mixture 3 showed a ~4% decrease in water soluble P_2O_5 with a nearly equivalent increase in citric acid soluble P_2O_5. The corresponding values for mixtures 1 and 2 were less than 1%. Reversions that bring about a decrease in citric acid soluble P_2O_5 also occur. A certain amount of apatite could be regenerated via reaction of the form,

$$6(NH_4)_2(HPO_4) + 9Ca(NO_3)_2 + CaF_2 \rightarrow 2Ca_5(PO_4)_3.F + 6HNO_3 + 12NH_4NO_3 \quad (9)$$

It is evident from Table 3. that such reversions become significant at higher temperatures due to the removal of HNO_3. Clearly the reaction (9) leads to a decrease in the 2% citric acid solubility.

Table 3. Water and 2% citric acid solubilities of mixtures 1, 2 and 3 heated for five hours at different temperatures

T/(°C)	Mixture 1 P_2O_5% (water Soluble	$P_2O_5$2% (Citric acid soluble)	Mixture 2 P_2O_5% (water soluble	P_2O_5 (Citric acid soluble)	Mixture 3 P_2O_5% (water soluble	$P_2O_5$2% (Citric acid soluble)
70	13.1	13.6	11.6	12.5	7.2	10.4
100	13.0	13.5	11.5	12.4	6.8	10.4
110	12.0	13.5	10.8	11.9	6.0	10.3
120	11.2	13.4	9.0	10.2	5.9	10.3
130	11.2	13.3	9.0	10.2	5.4	10.0
140	10.0	12.4	8.1	9.4	5.1	10.0
150	8.0	11.0	6.5	8.3	4.6	9.6

Conclusion

The study shows that nitric acidulation of Eppawela Apatite to a level slightly above the stoichiometry needed for dicalcium phosphate (e.g. Mixture 2) and mixing with ammonium sulphate generate a practically useful phosphate fertilizer. This fertilizer is nonhygroscopic and reversions are negligible.

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