Nitric acid treated phosphate fertilizer from Eppawala apatite in Sri Lanka

K. Tennakone^{1,2} & U.T. Weragama¹

¹Institute of Fundamental Studies, Kandy, Sri Lanka ²Department of Physics, University of Ruhuna, Matara, 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. $\sim 80\%$ water soluble and $\sim 90\%$, 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 carbonatoapatite (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. (Dahanavake et al., 1989). As Sri Lanka has no reserves of elemental sulphur or pyrites needed for production of sul-

phuric 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,

monocalcium phosphate

$$2Ca_{5}(PO_{4})_{3}.X + 18HNO_{3} \rightarrow 6H_{3}PO_{4}$$

+ 9Ca(NO_{3})_{2} + CaX_{2} (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,

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

$$CaHPO_{4} + (NH_{4})_{2}SO_{4} \rightarrow (NH_{4})_{2}(HPO_{4}) + CaSO_{4} \qquad (5)$$

diammonium phosphate

monoammonium phosphate

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

Experimental

In all experiments the high quality ore (composition given in Table 1) was ground and sieved through mesh BS200 (74 μ m). The P₂O₅ 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

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	0.3
Fe ₂ O ₃	0.3
Al ₂ O ₃	0.3
Cl	2.0
F	1.5

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% HNO₃. Specific gravity = 1.42) needed per kg of apatite is,

[volume 70% HNO₃] $\simeq 0.9 \times 10^{-2}$ 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