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COMPARATIVE ACIDULATION STUDIES OF THE MATRIX AND THE SINGLE CRYSTALS OF THE EPPAWELA APATITE AND XRD IDENTIFICATION OF BYPRODUCTS

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ABSTRACT

Acidulation studies on the two major fractions of the Eppawela rock phosphate, viz. primary apatite crystals and the matrix, have been carried out to determine the optimum conditions for manufacturing single super phosphate fertilizer. The optimum conditions observed were the use of 70% sulphuric acid and a curing time of four weeks. Available phosphate as determined from the citric acid solubility reaches ca. 28% for the Eppawela rock phosphate (ERP) and 30% for the high grade Eppawela rock phosphate (HERP) under these optimized conditions. XRD data reveal that HERP is exclusively hydroxyl apatite while ERP is comprised of hydroxyl apatite as the major phase along with francolite and chlorofluoroapatite. The acidulated products are quite different for the two fractions where ERP gives calcium monohydrogen phosphate ($CaHPO_4$) while HERP gives calcium dihydrogen phosphate (CaH_2PO_4) as the major product and calcium hydrogen phosphate as a minor product.

1. INTRODUCTION

Eppawela rock phosphate reserve in Sri Lanka is considered as a chlorofluoroapatite with the general formula, $Ca_5(PO_4)_3X$ (X= Cl, F). Although this deposit was discovered in 1971, its detailed geology was not reported until 1987. Dahanayake et al. discovered[1] that this deposit comprises of two components: (i) primary apatite crystals consisitng of mainly hydroxychlorfluorapatite, chlorfluorapatite and fluorapatite (ii) secondary phosphate matrix dominated by carbonate fluorapatite with appreciable amounts of aluminous, ferruginous and siliceous materials. The primary crystals have a much lower R_2O_3 (R=Fe,Al) content of <0.5%, while for the weathered matrix this is around 12% and has a slightly higher fluoride content.

There is a worldwide shortage of phosphate resources and it is important to utilize even low-

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grade phosphate rock to produce superphosphates. Here, in addition to $Ca(H_2PO_4)_2.H_2O$ and role

in the agronomic effectiveness of the products[2]. Two of the commonest water insoluble compounds found in single superphosphate (SSP) fertilizer produced by acidulation with sulphuric acid are, $FeNaH_5(PO_4)_3.H_2O$, $(FeAl)_3H_9(PO_4)_6.6H_2O$. In addition, their analogues where Na is substituted with ions such as K^+ or NH_4^+ may also be present depending on the composition of the initial phosphate rock and their formation represents a lowering of the soluble phosphate content of the resultant fertilizer. Thus, it is important to compare the agronomic effectiveness of the SSP produced from the two fractions of the Eppawela rock phosphate.

Acidulation with H_2SO_4, H_3PO_4, HCl and HNO_3 have been used[3,4] to convert rock phosphates to more soluble fertilizers. Out of these, single superphosphate and triple superphosphate (TSP) are the commonest phosphate fertilizers manufactured. TSP is the fertilizer of choice when transport over long distances is considered. However, SSP plants are still economical when the transport distances are relatively short. Its manufacture produces no liquid effluent and also provides sulphur as a nutrient in the form of $CaSO_4$ for sulphur deficient soils. Hence, SSP is the phosphate fertilizer of choice for Sri Lanka[5].

Complete acidulation and partial acidulation studies with hydrochloric and sulphuric acids of Eppawela rock phosphate has been reported[3]. Acidulation with 50% sulphuric acid produces partially acidulated rock phosphate (PARP-50) containing 17% (by weight) of available P_2O_5 while complete acidulation yields 21% (by weight) of available P_2O_5. Acidulation with nitric acid[4] yielded similar products and partial acidulation is the preferred choice here since the products are highly hygroscopic.

Previous studies on acidulation have been carried out on a weathered matrix with relatively high R_2O_3 content (R= Fe, Al) and a higher fluoride content. Thus, it is important to compare the behaviour of these of these two fractions during acidulation since this has a bearing on any future development of this deposit for producing soluble phosphate fertilizer. The present study is aimed at determining the optimum conditions of acidulation and curing time for producing SSP from Eppawela rock phosphate and to identify the products obtained during acidulation of ERP and HERP.

2.0 MATERIALS AND METHODS

2.1 Sample

Two types of Eppawela rock phosphate samples were used in the present study; these were Eppawela rock phosphate (ERP) and high grade Eppawela rock phosphate (HERP), both of which are commercially produced by Lanka Phosphate Ltd. These samples were crushed, powdered and sieved through a 100 mesh sieve. The resultant powders were dried in an oven at 80-90 °C and kept in a desiccator prior to use.

2.2 Acidulation studies

Fifty gram samples of each type of rock phosphate, ERP and HERP were mixed with 20 $cm^3$of sulphuric acid solutions of varying compositions from 40-80% and kept in air at room temperature. One gram samples of the resultant solid were taken at different time intervals into 50 ml conical flasks, 25 cm^3 of 2% citric acid was added and stirred for 30 minutes. The resultant suspensions were filtered and 1 cm^3 of the extracted solution was diluted to 100 cm^3.

The phosphate concentration in the solution was determined colorimetrically using the vanadomolybdate method[6] (Genesis Colorimeter, model 253 at 460 nm). Samples were taken every week for a period of 5 weeks.

2.3 XRD measurements

XRD data on the reactants and the acidulated samples were obtained using a Siemens D5000 X-ray diffractometer. The scan range was from 3.0 to 80.0 degrees 2-theta with a 0.02 degrees 2-theta step and a dwell time of 1 s. Cu-K_α radiation generated at 40 kV and 30 mA was employed. The raw diffraction data were processed using JCPDS database using PCPDFWIN software and the peaks were identified using the ICDD powder Diffraction File (release 1999).

3. RESULTS AND DISCUSSION

3.1 Acidulation studies

Figures 1 & 2 give the variation of the available P_2O_5 (solubility in 2% citric acid) with acid concentration for varying curing times for ERP and HERP respectively. It is clear that the optimum concentration of sulphuric acid for producing SSP is 70% and beyond this there is a decrease in the extent of the reaction. This is consistent with the work of others[3] where the Optimum concentration of acid for complete acidulation with H_2SO_4 was found to be in the range of 65-70% and a decrease in available P_2O_5 observed thereafter. It is also clear that a four week curing period is essential to produce optimum results and beyond this period, available P_2O_5 content decreases. Similar results have been obtained in other investigations and this has been attributed to the formation Fe-Al-P compounds formed when low grade phosphate rocks are acidulated[7].

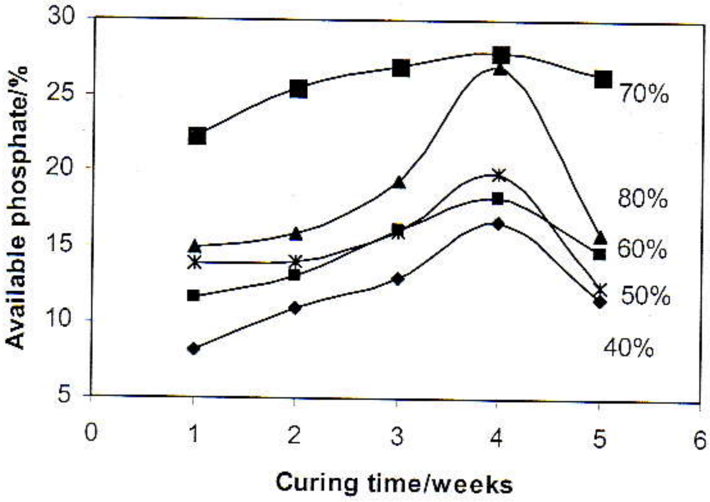

Fig. 1. Variation of available phosphate with curing time for ERP acidulated products at different H_2SO_4 concentrations.

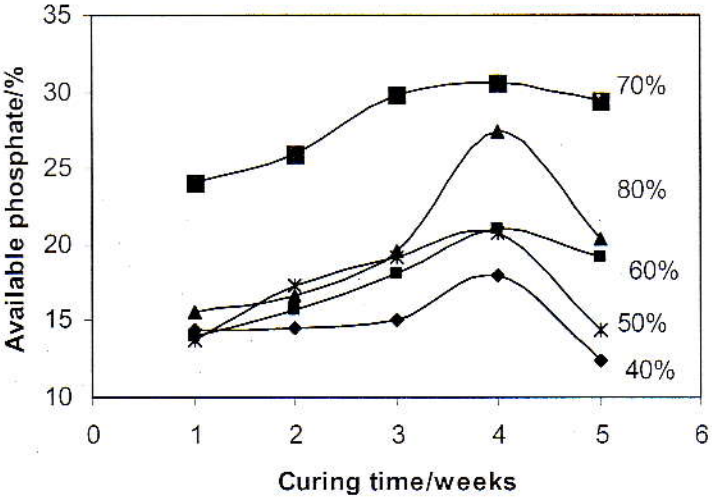

Fig. 2. Variation of available phosphate with curing time for HERP acidulated products at different H_2SO_4 concentrations.

3.2. XRD studies

XRD patterns observed for ERP, HERP and their acidulated products are given in Figures 1-4. The constituents identified from the major diffraction peaks are given in Table1. At least three spectral lines were used to positively identify a phase without interference from peaks of other phases. Both HERP and ERP had XRD peaks at 0.181, 0.184 and 0.343 nm, which can be attributed to hydroxyl apatite, $Ca_{10}(OH)_2(PO_4)_6$ with ERP showing lower intensities compared to HERP. There are some differences in the XRD patterns of ERP and HERP in that the peaks identified as hydroxyl apatite , $Ca_5(PO_4)_3(OH)_2$ in HERP at 0.181, 0.184 and 0.282 nm are noticeably weaker in ERP where peaks at 0.316, 0.279 and 0.270 nm can be identified as due to francolite which is patterns of ERP also show the presence of hydroxylchlorofluorapatite as a minor phase.

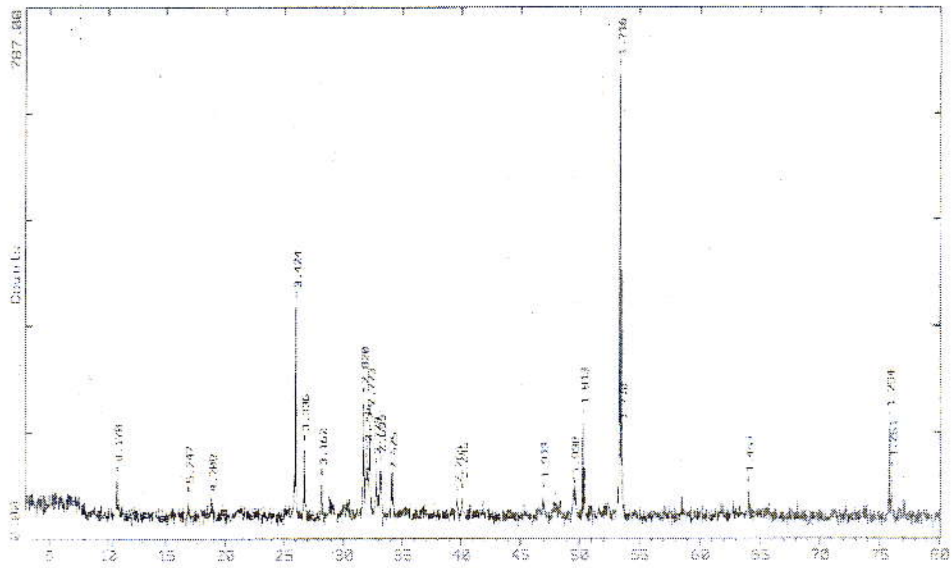

Fig. 3. XRD pattern of ERP

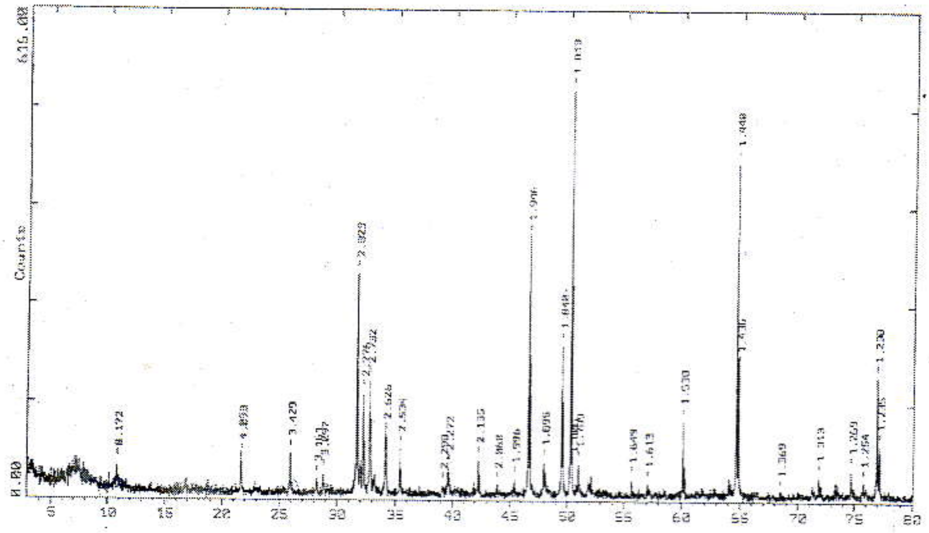

Fig. 4. XRD pattern of HERP

found as a secondary phosphate mineral in the matrix of the ore. In addition, XRD also supports this conclusion where it has been reported that single crystals of HERP are pure hydroxyl apatite and the weathered rock (ERP) can be described as comprised of hydroxyapatite, fluorapatite, carbonate fluorapatite, crandallite, wardite and fuellite.

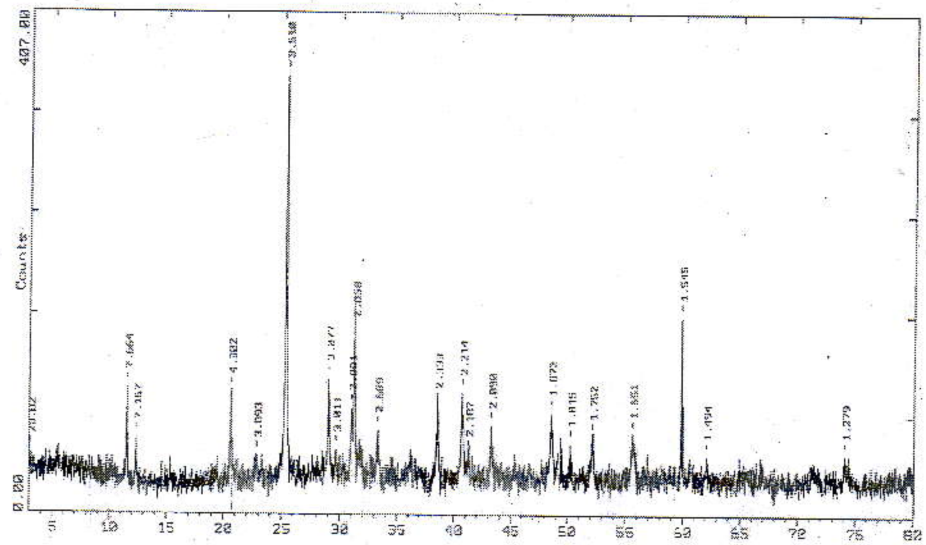

Fig. 5. XRD pattern of the acidulated product from ERP

A major difficulty in analyzing the XRD data is that of overlapping peaks and some peaks due to chlorofluoroapatite are almost identical to those of carbonate-hydroxyl apatite, $Ca_{10}(PO_4,CO_3)_6(OH)_2$. Previous work[8] using high resolution electron microscopy The XRD patterns of acidulated products are dominated by the forms of calcium sulphate. Anhydrite ($CaSO_4$), bassanite ($CaSO_4.0.5H_2O$) and gypsum($CaSO_4.2H_2O$) can be identified as dominating the XRD patterns of the acidulated products of both ERP and HERP (table 1). However, there are noticeable differences in the calcium phosphate products obtained with HERP which gives

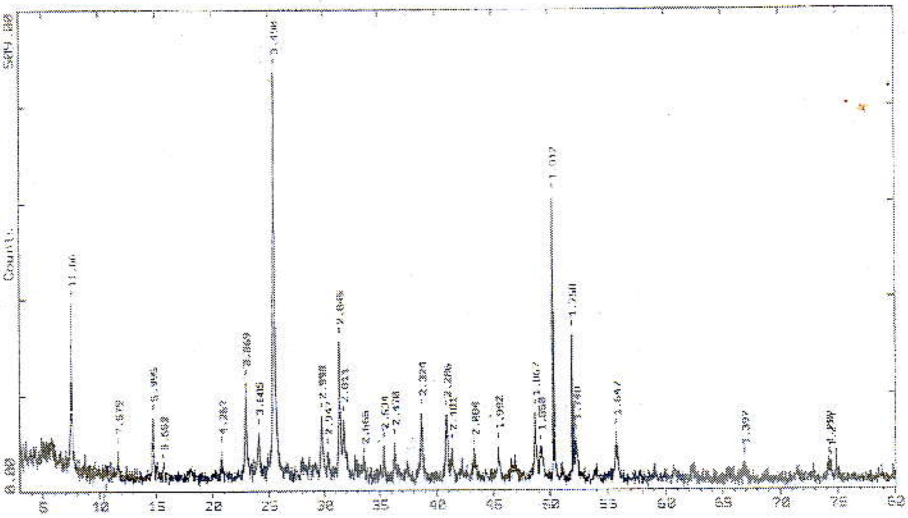

Fig. 6. XRD pattern of the acidulated product from HERP

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Table 1: Identification of phases in ERP, HERP and their acidulated products from XRD data.

XRD peaks (nm)	Phase	Chemical formula
ERP		
0.171, 0.262, 0.227, 0.213	hydroxyl apatite	$Ca_{10}(OH)_2(PO_4)_6$
0.181, 0.184, 0,282	hydroxylchlorofluoroapatite	$Ca_5(PO_4)_3(OH,Cl,F)$
0.316, 0.279, 0.270	francolite	$Ca_{10}(PO_4)_6(F,CO_3)$
HERP		
0.181, 0.184, 0.282	hydroxylchlorofluoroapatite	$Ca_5(PO_4)_3(OH,Cl,F)$
0.279, 0.262, 0.184	hydroxyl apatite	$Ca_{10}(OH)_2(PO_4)_6$
Acidulated ERP		
0.351, 0.285, 0.233	anhydrite	$CaSO_4$
0.758, 0.427, 0.306, 0.285	gypsum	$CaSO_4.2H_2O$
0.301, 0.185, 0.282	bassanite	$CaSO_4.0.5H_2O$
0.756, 0.427, 0.306, 0.268	calcium hydrogen phosphate	$CaHPO_4.2H_2O$
Acidulated HERP		
0.349, 0.281,0.232	anhydrite	$CaSO_4$
0.427, 0.758, 0.285	gypsum	$CaSO_4.2H_2O$
0.301,0.185, 0.281	bassanite	$CaSO_4.0.5H_2O$
1.166, 0.599,0.387,	Monocalcium hydrogen phosphate dihydrate	$Ca(H_2PO_4)_2.2H_2O$
0.758, 0.427, 0.308, 0.267	Calcium hydrogen phosphate	$CaHPO_4.2H_2O$

$Ca(H_2PO_4)_2.2H_2O$ as the major component with only a minor amount of $CaHPO_4.2H_2O$ in the SSP produced while ERP gives $CaHPO_4.2H_2O$ as the major product. This is a significant finding since calcium dihydrogen phosphate, $Ca(H_2PO_4)_2.2H_2O$ is highly water soluble while calcium hydrogen phosphate, $CaHPO_4$, is water insoluble but citric acid soluble, still making it available to plants. However, there may be a difference in the agronomic effectiveness of the two acidulated products originating from HERP and ERP particularly for basic soils. We were unable to detect any insoluble phosphate containing phases such as $Fe_3(K,Na,H)H_8(PO_4)_6.6H_2O$ and $CaAlH(HPO_4)_2.2H_2O$ which are reported[7] as the main water insoluble phosphates formed during SSP production.

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