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Preliminary Laboratory Studies on Eppawela Apatite - II

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Abstract: Investigations carried out earlier showed that the phosphate in Eppawela apatite can be converted into a citric acid soluble form by treatment with soda ash. In the present series of experiments apatite obtained from the grinding plant at Eppawela was used. Calcination of this powdered apatite at 1400°C, complete conversion of P_2O_5 to citric acid soluble form was obtained. The chemical and the energy dispersive spectrometer analyses of the powdered sample of apatite showed that it contains alumina, iron oxide and silica as main impurities. These impurities favoured the conversion of P_2O_5 in apatite to citric soluble form. Treatment of pure apatite with red clay containing alumina, iron oxide and silica also showed a positive effect on the conversion of P_2O_5 to citric soluble form.

1. Introduction

Laboratory studies carried out on the beneficiation of Eppawela apatite showed that by calcining a mixture of apatite and soda ash the phosphate (P_2O_5) in Eppawela apatite can be converted into citric acid soluble form.

X-ray diffraction studies of the calcined product showed the formation of sodium calcium phosphates (*eg.* $NaCaPO_4$, $Na_3Ca_6(PO_4)_5$ etc.). The product has been reported to be substantially more effective than superphosphate on several acid tropical soils, because of its alkalinity and resistance to fixation by the soil.[4] In some crops or soils the sodium or soil-soluble silica may be beneficial.

In the present investigation attempts were made to develop a product with high citric soluble phosphate (P_2O_5), without addition of alkali salts in the process of calcination.

2. Experimental

2.1 Starting Material

The term commercial apatite is given to the sample obtained from grinding factory and pure apatite for sample obtained from primary deposit.

Both samples were ground to pass BS 100 mesh sieve and used in the present investigation.

Chemical analysis of both starting materials were carried out according to standard method.[3]

2.2 Calcination

Calcination experiments were carried out upto 1400°C in platinum crucibles in temperature controlled furnaces. The experiments were carried out in duplicate.

The calcined products were analysed for 2% citric acid solubility according to official method of analysis AOAC,[2] P_2O_5 content was determined by a spectrophotometric method using ammonium vanadate reagent.

2.3 Differential Thermal Analysis

Differential thermal analysis curves of both samples and the clay used were taken by using model spectromom 190 A, Derivatograph.

2.4 XRD Studies

X-ray diffraction patterns of the samples were taken using JEOL JDX-8S, type X-ray diffractometer fitted with graphite monochrometer.

2.5 Scanning Electron Microscope

Scanning Electron Microscope microphotographs of the samples were taken using a JSM T-200, JEOL Scanning Electron Microscope.

3. Results and Discussion

3.1 Preliminary Studies

3.1.1 Chemical Analysis

Given below were the results of the chemical analyses carried out on pure apatite and commercial apatite (Table I).

Table 1. Chemical Composition of the Apatite Sample used

Constituent	Commercial Apatite % w/w	Pure Apatite % w/w
CaO	48.11	55.52
P_2O_5	31.65	39.35
SiO_2	1.96	0.35
Fe_2O_3	6.14	0.27
MgO	0.19	0.10
Al_2O_3	3.20	0.63
Loss on ignition	0.95	0.21
Moisture	3.94	—

The effectiveness of these apatite samples as a phosphatic fertilizer were determined as 2% citric acid soluble P_2O_5 content and results obtained were as follows (Table 2).

Table 2. Citric Acid Solubility of Apatite Samples

Sample	2% Citric Acid soluble P_2O_5 %	Total P_2O_5 %	%Conversion P_2O_5 to Citric Acid soluble form
Pure apatite	5.18	39.35	13.16
Commercial apatite	4.63	31.65	19.61

3.1.2 X-ray Diffraction Analysis

X-ray analysis showed that Eppawela Apatite is mainly in the form of hydroxyl apatite $Ca_5(PO_4)_3(OH,Cl,F)$ with a little amount of fluorapatite $Ca_5(PO_4)_3F$ (Figure 1) In the case of commercial apatite peaks due to small amounts of α-quartz, goethite was observed.

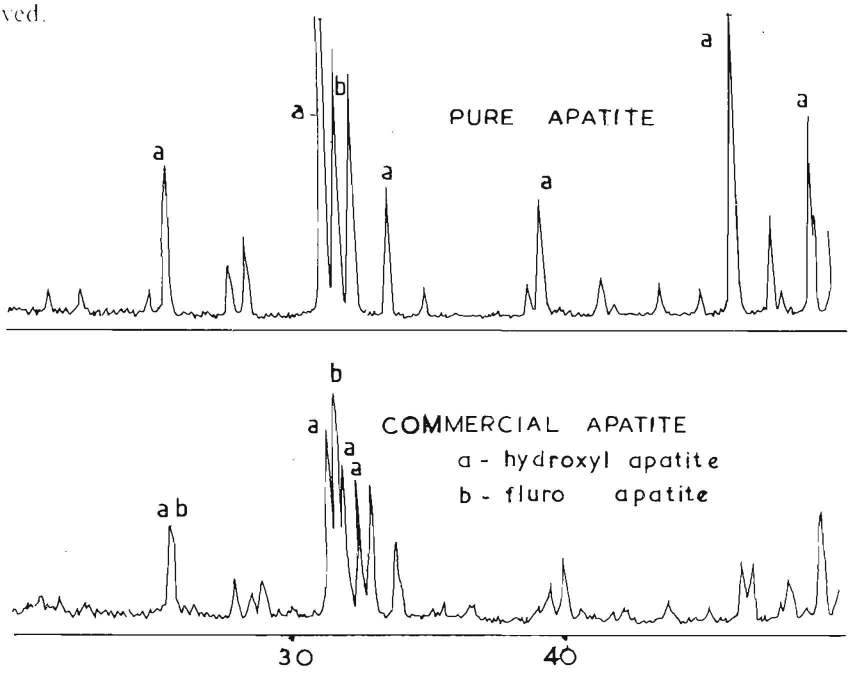

Figure 1. XRD Patterns of Apatite

From this it was clear that pure apatite consists mainly of apatite material and commercial apatite contains small amounts of clay, goethite, silica sand as impurities along with apatite materials.

3.1.3 Scanning Electron Microscopic (SEM) Studies

SEM photographs taken on a apatite rock are given in Figure 2. The white patches indicate the presence of impurity in the rock.

The SEM microphotograph of the sample used for Energy Dispressive Spectrometer (EDS) studies is given in Figure 3.

The EDS analysis of the top surface of the rock labelled as 'A' showed that it consists mainly of clay and 'B' of pure apatite with silica as impurity.

These results clearly show that the green surface 'B' is pure apatite and the brown surface 'A' from matrix of the deposit. Brown surface consists of mainly alumino silicates (from clay).

From this preliminary analysis we can conclude that:

(a) Greenish pure apatite contains mainly apatite materials such as hydroxyl apatite and fluorapatite.

(b) Commercial Apatite contains alumino silicates, goethite and silica as impurities. These impurities have come to apatite material from the brown surface on the green apatite rock material.

3.2 Calcination of Apatite

Calcination of commercial and pure apatite samples upto 1400°C were carried out and the citric solubility of the samples were determined. The results are shown in Figure 4.

It is clear that the citric acid soluble P_2O_5 percentage rapidly increase with the calcination temperature for commercial apatite. It was observed that the reason for this was the formation of $[Ca_3(PO_4)_2]$ calcium phosphate which is readily soluble in citric acid.

The XRD patterns of the calcined products are given in Figure 5.

XRD studies also showed that the major constituents in the residue after dissolving calcined commercial apatite (1400°C) in 2% citric acid was unreacted apatite and clay. Calcination of pure apatite at 1400°C resulted in the formation of stoichiometric hydroxyl apatite. Formation of hydroxyl apatite did not increase the citric acid solubility of pure apatite at high temperatures.

Figure 2. Sem Microphotographs of Apatite

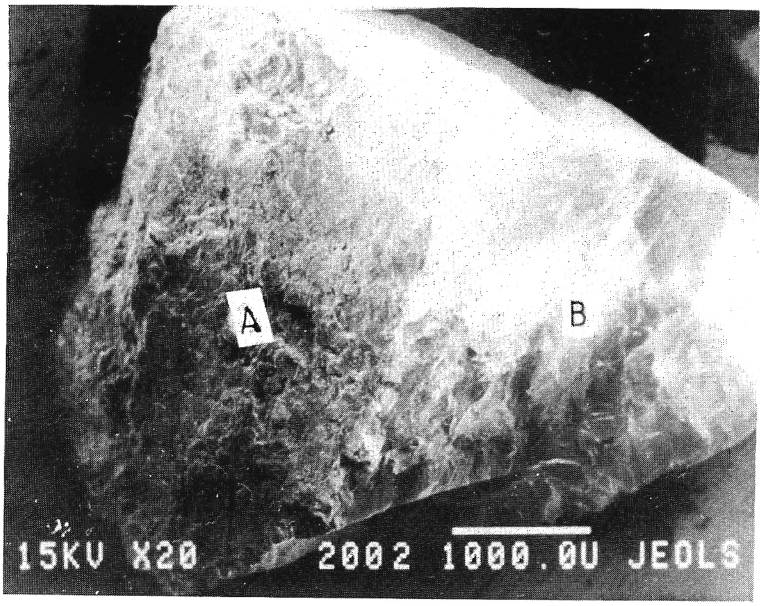

Figure 3. Rock Apatite used for eds analysis

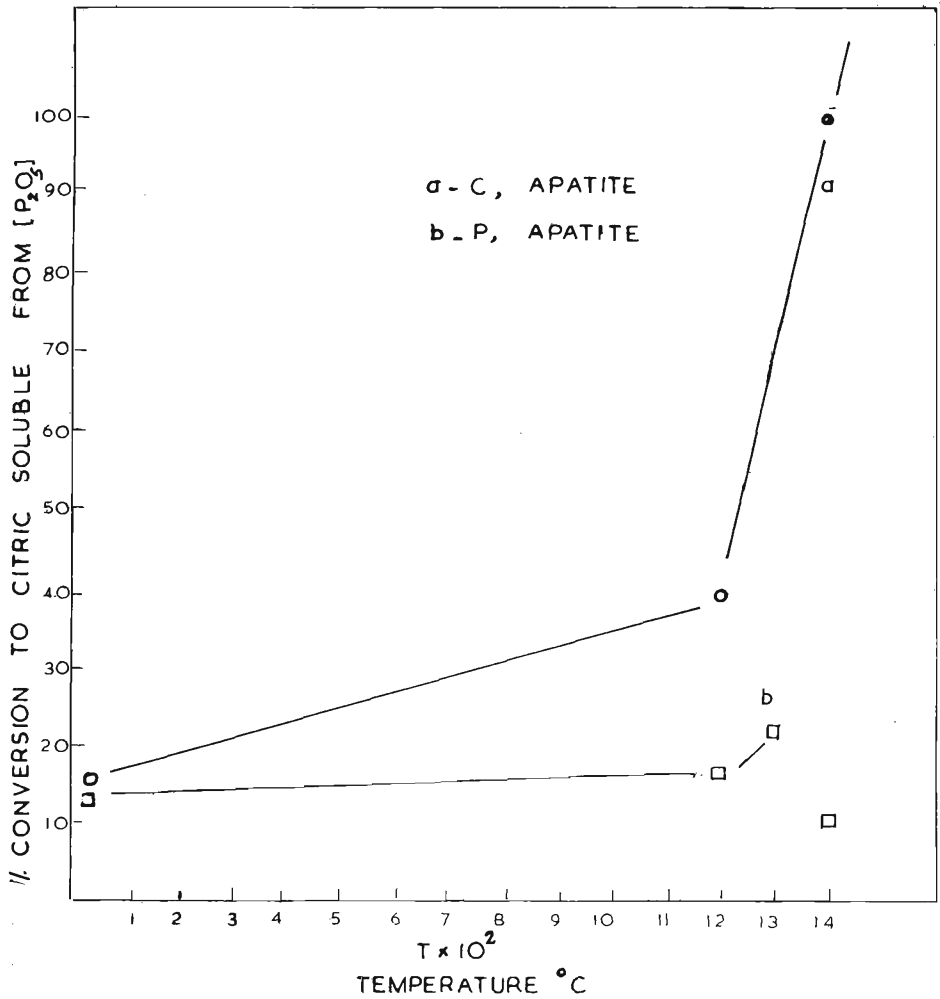

Figure 4. Effect of temperature on citric solubility of Apatite

The preliminary investigation clearly shows that,

(a) Increase of citric acid solubility in calcined samples is due to the presence of appreciable amounts of silica, alumina in commercial grade of apatite which would have come to the sample from gangue material clay or from free silica.

(b) These impurities had influenced the formation of citric acid soluble $Ca_3(PO_4)_2$ from the hydroxylapatite.

(c) Corresponding results for pure apatite were very low, due to the absence of these impurities and hence formation of purely crystalline hydroxyl apatite.

Further experiments were carried out on commercial apatite samples by calcining with powdered silica sand (100 mesh) from Nattandiya to investigate the effect of free silica on the conversion of P_2O_5 to citric acid soluble form.

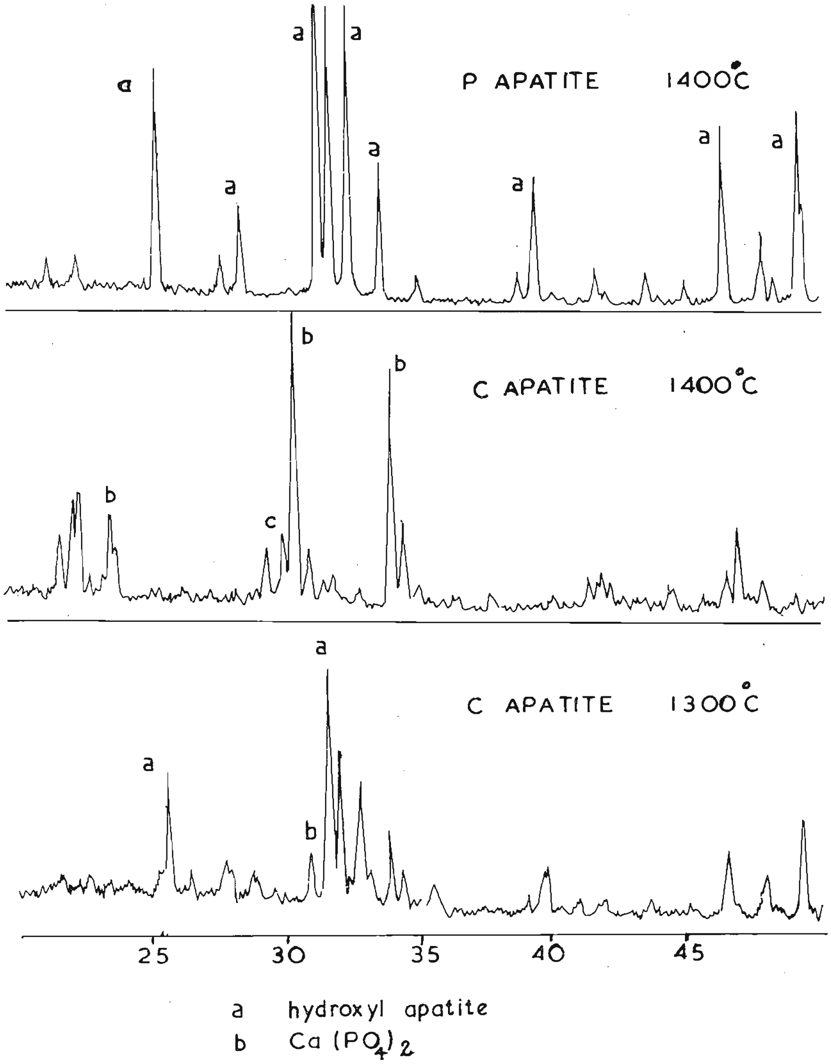

Figure 5. XRD Patterns of calcined apatite.

3.3 Calcination of Commercial Apatite with Silica Sand

3.3.1 Preliminary Analysis of Silica Sand

3.3.1.1 Chemical Analysis

Following were the results of the chemical analysis on Nattandiya sand used. (Table 3)

Table 3. Chemical Analysis of Nattandiya Sand

Constituent	% w/w
SiO_2	99.02
Fe_2O_3	0.18
Al_2O_3	0.88

3.3.2 Calcination Studies – Commercial Apatite and Silica

Calcination of commercial apatite with different proportions of finely powdered silica sand were carried out up to temperature 1300°C. Figure 6 represents the effect of addition of silica sand to commercial apatite on the citric solubility.

Calcination of pure apatite with silica sand has already showed that the solubility could not be increased.

XRD patterns of these samples showed apart from unreacted apatite the presence of $Ca_5(PO_4)_2SiO_2$ which is not soluble in citric acid.

It was clear that

(a) There is no correlation between the citric acid soluble P_2O_5 content and amount of silica added to the samples.

(b) The samples obtained by adding extra silica to commercial apatite gave lower citric acid soluble P_2O_5 content than that obtained by calcining alone.

(c) Increased citric acid soluble P_2O_5 content of the commercial apatite alone was not due to the presence of free silica in the sample.

3.4 Calcination with Clay

3.4.1 Preliminary Investigation of Clay

Clay from Biyagama area was selected for the investigations. Figure 7 gives the DTA of Biyagama clay.

DTA curve of the clay used show three endothermic peaks at temperatures around 110°C, 300°C and 530°C and a weak exothermic peak at 900°C. Normally kaolinitic clays show a weak peak below 200°C and endothermic peak around 570 - 580°C and exothermic at 970°C. Ferruginous materials (mainly goethite) show an endotherm around 350°C but the peak temperature may vary according to the crystallinity of the material. Kaolinite - gibbsite clays show an endotherm around 320°C and other kaolinite peaks at 580°C (endotherm) and 970°C (exotherm).

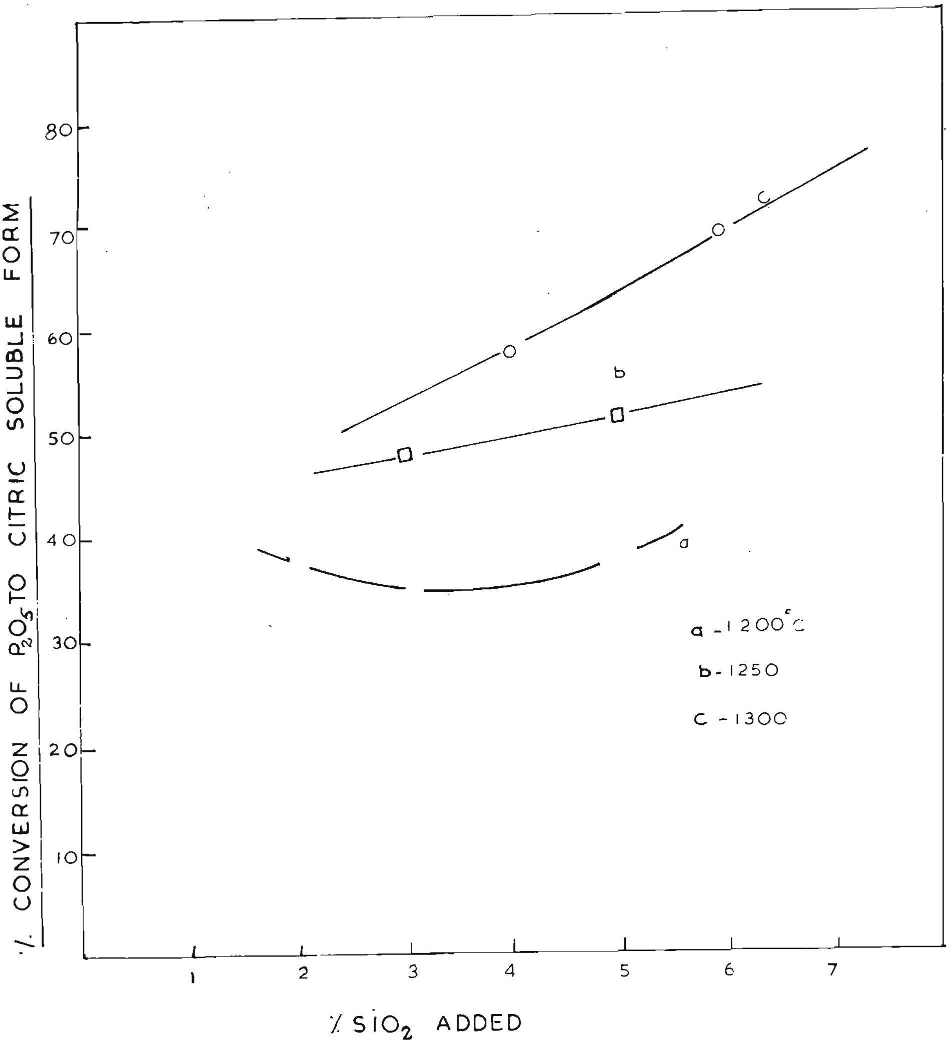

Figure 6. Effect of addition of SiO_2 on citric solubility of commercial apatite at different temperatures.

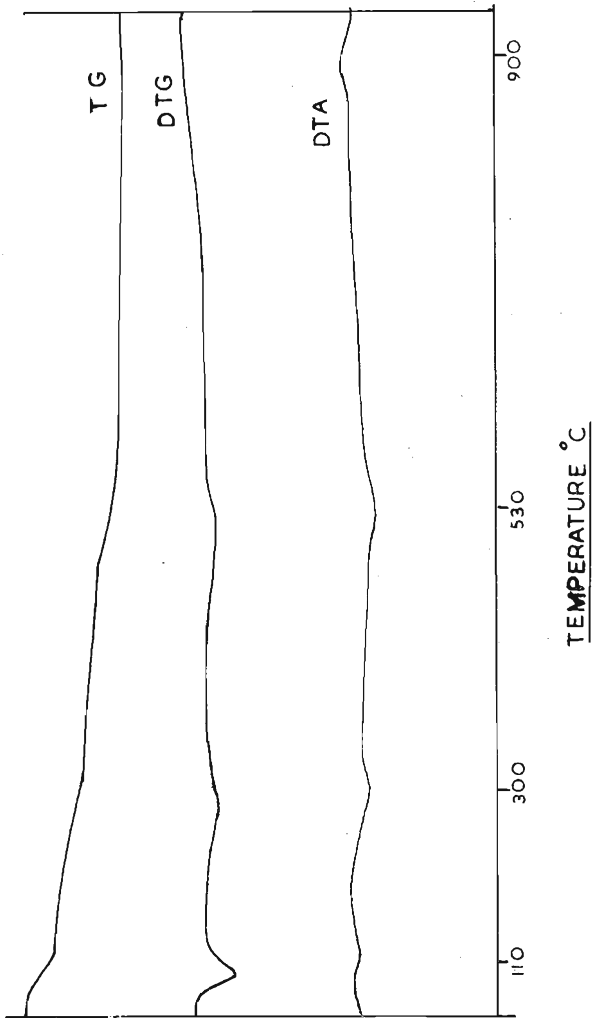

Figure 7. DTA curve of Biyagama clay.

XRD study (Figure 8) of clay show the presence of kaolinite, quartz, gibbsite and goethite. Hence the clay used is a kaolinite - gibbsite - goethite type clay.

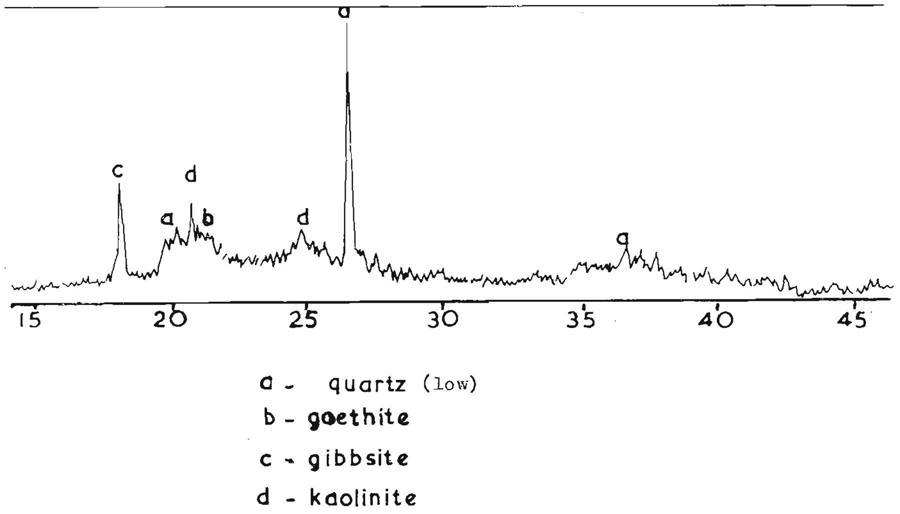

Figure 8. XRD pattern of Biyagama clay.

3.4.2 calcination

Pure apatite samples were calcined with different proportions of clay and citric acid soluble P_2O_5 contents were determined. The results are shown in Figure 9.

Phases present in these samples were analysed using X-ray Powder Diffractometer (Figure 10).

From these it is clear that,

(a) Apatite could be converted to citric acid soluble form by fusing with clay.

(b) Citric acid soluble P_2O_5 content increased with increasing temperature.

(c) Citric acid soluble constituent in these calcined products is mainly $Ca_3(PO)_{4\,2}$.

(d) With increase of apatite to clay ratio beyond 10:4 the solubility decreases. This is due to unreacted clay remaining in the sample.

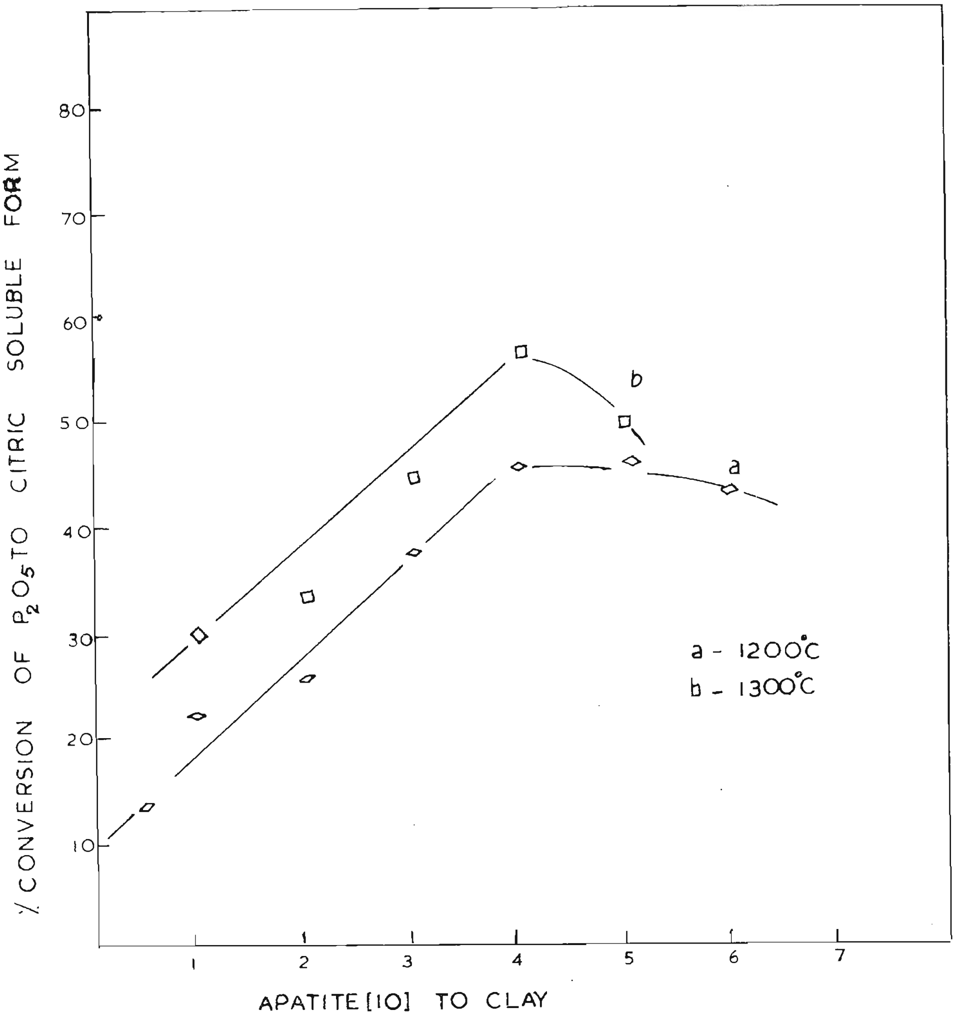

Figure 9. Effect of clay on citric solubility of pure apatite.

4. Conclusion

(1) Commercial grade Eppawela Apatite and Pure Apatite are not suitable as fertilizers since they have a low citric acid soluble P_2O_5 percentage.

(2) Commercial Apatite can be converted to a product having almost all the phosphorous in citric acid soluble form by calcining it at 1400°C.

(3) Pure Apatite cannot be converted to a more citric acid soluble form like commercial grade, by simply calcining to high temperature.

(4) Reason for higher citric acid soluble phosphorous in calcined **commercial apatite** is the presence of alumino silicates, which acts as a flux.

(5) Pure **apatite** also could be converted to more citric acid soluble form by calcining with clay at high temperature (above 1200°C)

(6) In all experiments the citric acid soluble phase obtained was $Ca_3(PO_4)_2$.

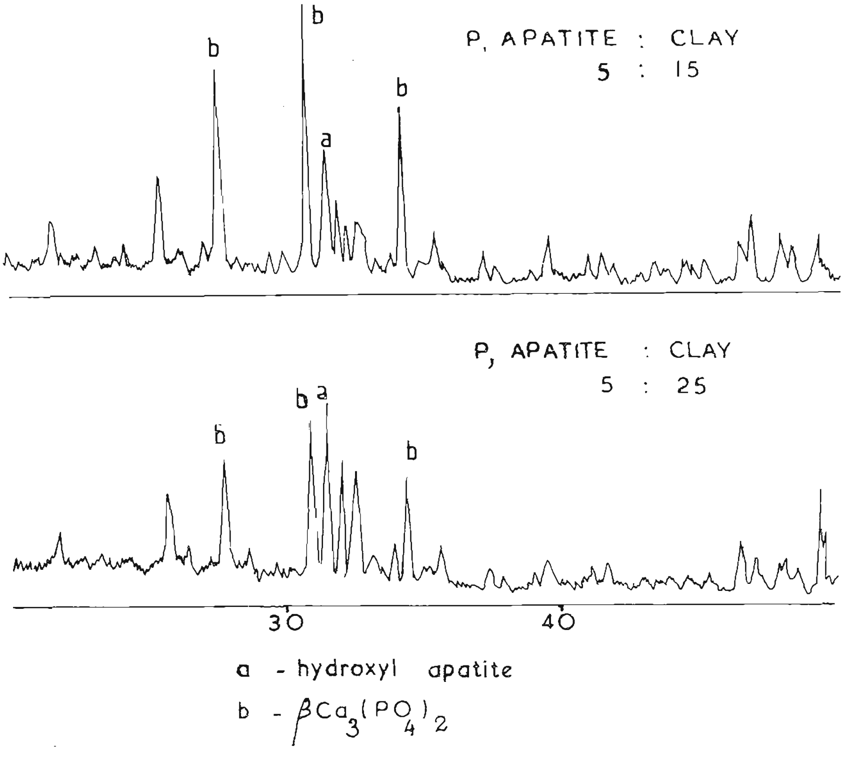

Figure 10. XRD patterns of calcined apatite with clay.

References

1. AMARASEKERA J., SOORIYAKUMARAN R & ISMAIL M. G. M. U. (1981) *"Preliminary Laboratory Studies on Eppawela Apatite" J. Natn. Sci. Coun. Sri Lanka* 9 (1).

2. Association of Official Analytical Chemists. (1975). *Official Methods of Analysis.*

3. JEFFRY P. G. (1970). *Chemical Methods of Rock Analysis*, Pergamon Press, Oxford.

4. WERNER W. (1969). *"Die Bedeutung Kalk and Silikathaltiger fur die Dungung Von Latosolen" Der Tropenlandwrit,* 57 - 81.