JNSF 9-1-55

J. Natn. Sci. Coun. Sri Lanka 1981 9 (1) :

Preliminary Laboratory Studies on Eppawela Apatite

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(Date of receipt : 18 August 1980)

(Date of acceptance : 23 January 1981)

1. Introduction

Eppawela apatite deposit was discovered during systematic geological mapping of the Anuradhapura area in North Central Province of Sri Lanka by the Geological Survey Department in 1971. This deposit spread around an area of 3 sq miles, but was most predominantly concentrated in an area of 576 acres in the northern region of the deposit and most of the investigations have been carried out in this region

This is a firm reserve of 25 million tons of apatite having P_2O_5 content of 30% to 35%. The inferred reserve for the entire deposit is around 40 million tons and it is estimated to be about 30 million tons of 90% apatite material, and it will last for 500 years at present demand rate.

Eppawela rock phosphate by itself can only be used as a fertilizer for long term crops. It cannot be directly applied to short term crops since it releases phosphate very slowly. For short term crops superphosphate is used. It is projected that in 1980 the country will require 50,000 tons of concentrated superphosphate and 46,000 tons of rock phosphates.[3]

Chemical analysis of Eppawela apatite deposit was carried out by both local and foreign institutions, and it is given in Table 1.

Table 1 – Chemical Analysis of Eppawela Apatite (From ref. 4)

		percentage by weight
CaO	—	55·30
P_2O_5	—	40·75
SrO	—	1·18
SiO_2	—	0·14
Fe_2O_3	—	0·07
MnO	—	0·01
MgO	—	0·01
F	—	1·78
Cl	—	2·29
		101·53
Less O, F, Cl	—	1·27
		100·26

Though the P_2O_5 content of Eppawela apatite is higher than that of imported superphosphate to Sri Lanka (Table 2), the citric solubility is low when compared to other types of phosphates (Table 3).

Table 2 – Comparison of major constituents between Eppawela Apatite and imported superphosphate

Constituent	Eppawela Apatite % (by wt)	Imported Super-Phosphate % (by wt)
SiO_2	0·1 — 0·5	5·0 — 6·0
P_2O_5	30 — 35·0	28·0 — 29·0
Fe_2O_3	1 — 4	1 — 2
CaO	50 — 55	47
Cl	3·0	3·0
F	1·7 — 2·4	2·8

Table 3 – Comparison of citric acid soluble P_2O_5 in Eppawela Apatite and other fertilizers

Fertilizer Material	Citric Acid Solubility % P_2O_5
Eppawela Apatite	1·0 — 3·0
Imported rock phosphate	3·4
Imported super phosphate	9·0
Rhenania phosphate	18·9

Thus, although the citric acid solubility which is used as an index of the effectiveness of rock phosphate to the soil of the local material is about 50% less than imported phosphate, it is not suitable to use as a direct fertilizer. Further a report from Tennessee Valley authority[6] states that the Eppawela apatite is not recommended for direct application and is not considered suitable for superphosphate manufacture unless beneficiated. Hence research work had been carried out in Sri Lanka on beneficiation of Eppawela apatite.[1, 5, 8]

Since Eppawela apatite contains an appreciable amount of Cl (as well as F), it can cause corrosion in wet process beneficiation. Besides, sulphuric acid has to be imported for use in the manufacture of superphosphate fertilizer. Therefore the beneficiation method, that is most suitable for Sri Lanka would be a dry process.

To achieve this goal the Mineral Technology Section of the Ceylon Institute of Scientific and Industrial Research had carried out a series of laboratory experiments on Eppawela Apatite to produce an effective fertilizer by using locally available materials as far as possible, in a dry process

Calcination experiments were carried out at high temperatures with local minerals such as quartz, dolomite, feldspar, normal salt and with alkali salts like soda ash, hydrated lime, sodium hydroxide and also with paddy hull ash. It was found that beneficiation with soda ash gave a product having about

27·00% to 30·00% of P_2O_5 in citric acid soluble form. Hence this product which is actually a thermophosphate can be used for short term crops of Sri Lanka instead of imported phosphate fertilizers by saving valuable foreign exchange which our country needs for other development work. Field trials are presently being carried out to evaluate the effectiveness of this product as a fertilizer.

The main differences between this product and Rhenania type[12] fertilizer which is made out of apatite, soda ash and silica are the method of preparation and temperature of calcination. This product is made by calcining apatite with soda ash alone at a low temperature of 1150°C than that of Rhenania phosphate (1300°C to 1400°C). Also, this has higher citric acid solubility than Rhenania phosphate.

2. Experimental

In all the experiments, the powdered samples brought from the factory at Eppawela were used. Treatments were carried out in platinum crucibles with duplicates in temperature controlled electric furnaces. Treated samples were quenched in air rapidly by immersing the crucible in a water surface. In some fusions that were carried out to find the quenching effect, experiments with sodium carbonate, quenching was done in water by immersing rapidly the platinum crucible with hot sample in water. Calcination studies of samples were carried out by using weight ratios of apatite and material at a given condition as given in respective tables. Each sample was analysed for its 2% citric acid solubility according to official methods of analysis A O A C.[2] P_2O_5 content was determined by a spectrophotometric method using ammonium vandate reagent.[9] DTA analysis of raw apatite was done by using "Spektromom 190 A" derivatograph and X- ray analysis of samples were done by using "JEOL JDX-8S" X-ray powder diffractometer.

Initially a preliminary analysis was carried out on apatite rock by DTA, X-ray diffractometer and chemically. Later fusions were carried out at high temperatures (above 1000°C) with locally available minerals and alkali salts.

Cell dimensions of sodium carbonate fused apatite samples were determined from X-ray powder diffraction patterns, taken using Cu target under following conditions, scanning ½°/min, sollar slit 1° divergence slit1° receiving slit 0·4 mm, time constant 2sec. For this purpose peaks due to (211) and (300) planes of samples were taken.

3. Results and Discussion

3·1 Preliminary Investigation

3·1·1 *Chemical Analysis*

Chemical analysis showed the powdered rock sample which was used for these experiments has 34·00% of total P_2O_5 out of which only 9·70% is in citric acid soluble form (citric acid soluble P_2O_5 3·30%).

3·1·2 *X–ray Analysis*

X–ray analysis showed Eppawela apatite is mainly in the fluorapatite form with small amounts of chlorapatite, hydroxyapatite, α quartz, goethite (Fig 1 (A).

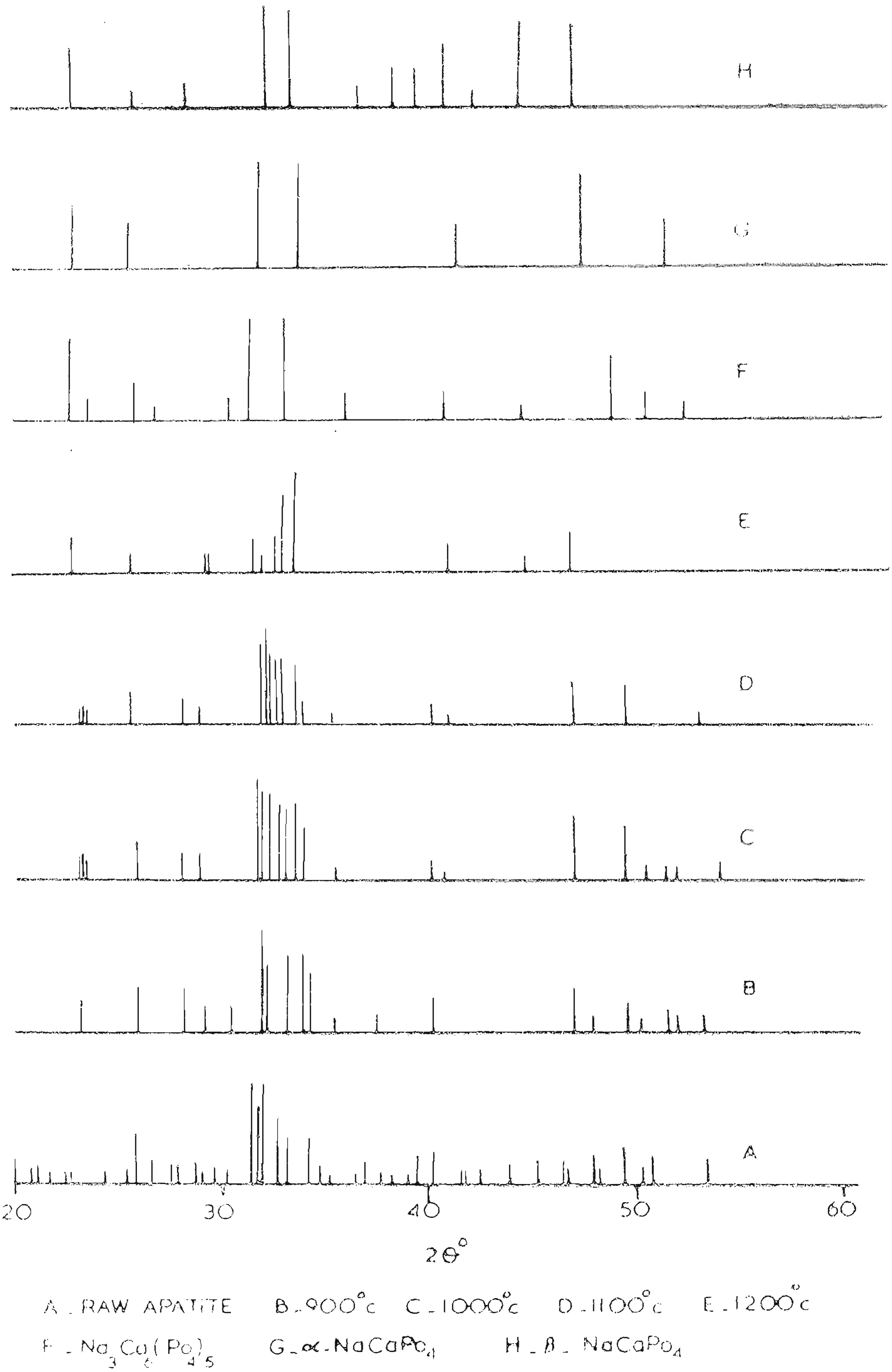

Figure 1 XRD patterns of Row Apatite and Calcined Apatite samples with Na_2CO_3 in the ratio 100 : 20 for 3·0 hrs duration.

Apart from the peaks of the above mentioned constituents, several other shifted apatite peaks were observed. These may be due to frankolite ($Ca_5(PO_4\ CO_3\ OH)_3\ F$) a polymorph of fluor-chlor and hydroxy-apatite. A firm conclusion cannot be achieved due to the unavailability of X-ray data of fran-

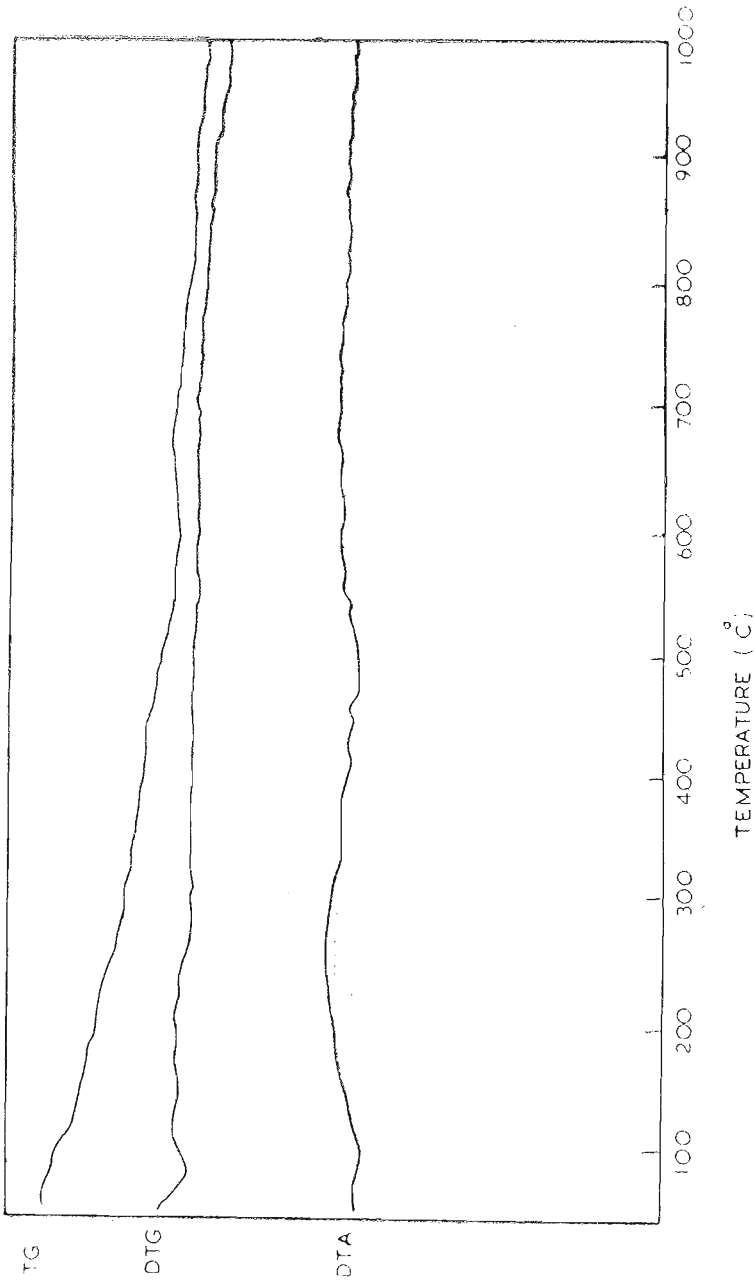

Figure 2 – DTA of Apatite

kolite. By taking X-ray peaks d = 2·828 A° (211) and d = 2·704 A° (300), lattice constants of Eppawela apatite was calculated and found to be a=9·4572 A° and b = 6·6786 A°.

3·1·3 *Differential Thermal Analysis*

Differential thermal analysis of apatite upto 1000° C did not show any apparent peaks (Figure 2).

This indicates that there is no chemical or physical changes taking place during heat treatment upto 1000°C. Therefore any changes in solubility cannot be expected below 1000°C.

3·2 Calcination of Apatite

The results of heat-treatment of apatite alone above 1000°C is given in Table 4

Table 4 Effect of heat treatment on citric acid solubility of Apatite

Temperature (°C)	Treatment duration (hrs)	citric acid solubility% P_2O_5
Room Temperature	—	3·33
1000	0·50	3·35
1100	0·50	3·40
1200	0·50	3·60
1000	1·0	3·40
1100	1·0	3·52
1200	1·0	3·75

These results shows clearly that the heat treatment alone will not increase solubility in citric acid considerably by changing the temperature or duration of treatment of apatite.

3·3 Calcination with some locally available minerals

Calcinations at high temperatures were carried out randomly with the following powdered minerals; (a) Dolomite (b) Feldspar (c) Kaolinite (d) Normal Salt (e) Quartz. Results obtained are given in Table 5.

The above results reveals that minerals like Kaolin, Dolomite, Feldspar, Common Salt or combination of these cannot be used for successful beneficiation of apatite even at temperatures 1100°C, since the conversion of P_2O_5 for citric soluble form is only about 17% to 19%.

It was also observed that quartz gave a 30% conversion on rock apatite when calcined at 1100°C. Hence further studies were carried out by using quartz as a mineralizer.

TABLE 5_EFFECT OF CITRIC ACID SOLUBILITY OF APATITE WHEN CALCINED WITH DIFFERENT MINERALS

RATIO			TEMPERATURE OF TREATMENT °C	DURATION OF TREATMENT Hrs	CITRIC ACID SOLUBLE P_2O_5 %	% CONVERSION P_2O_5 TO CITRIC SOLUBLE FORM
APATITE	MINERAL(1)	MINERAL(2)				
100	DOLOMITE (30)	KAOLINE (20)	1000	2,00	6,00	17,64
100	DOLOMITE (40)	QUARTZ (20)	1200	2 00	6,00	17,64
100	FELDSPAR (40)	-	1100	2,00	6,50	19,11
100	SALT (30)	QUARTZ (20)	1100	2,00	6,50	19,11
100	QUARTZ (10)	-	1100	2,00	10,40	30,58
100	QUARTZ (20)	-	1100	2,00	10,00	29,41

3.4 Calcination with Quartz and Paddy hull Ash

The results obtained by calcination of apatite samples with quartz at different temperatures and for different time duration are given in Table 6, 7 and 8.

Table 6 - Effect of temperature of treatment on citric acid solubility of Apatite when calcined with constant amount of quartz for constant time duration

RATIO		Temp. °C	Duration (hrs)	Citric acid solubility % P_2O_5	% Conversion of P_2O_5 to citric acid soluble form
Apatite	Quartz				
100	10	1000	2·00	8·00	23·52
100	10	1100	2·00	10·40	30·58
100	10	1150	2·00	11·40	33·52
100	10	1200	2·00	11·50	33·82

Table 7 – Effect of duration of treatment on citric acid solubility of Apatite when calcined with constant amount of quartz at constant temperature.

RATIO		Temp. °C	Duration (hrs)	Citric acid solubility % P_2O_5	% Conversion of P_2O_5 to citric acid soluble form
Apatite	Quartz				
100	10	1150	2·00	11·40	33·52
100	10	1150	2·50	12·00	35·29
100	10	1150	3·00	12·10	35·58

Table 8 – Effect of amount of quartz used on citric acid solubility of Apatite when calcined at constant temperature for constant time duration.

RATIO		Temp. °C	Duration (hrs)	Citric acid solubility % P_2O_5	% Conversion of P_2O_5 to citric acid soluble form
Apatite	Quartz				
100	0	1150	2·50	3·80	11·17
100	10	1150	2·50	12·00	35·29
100	20	1150	2·50	11·40	33·52
100	30	1150	2·50	9·50	27·94

The above results show that by increasing temperature of treatment, about 35% of conversion can be obtained. Increasing of quartz percentage in treatments shows a lowering of citric acid soluble P_2O_5 percentage. Also it shows that about 2 to 3 hrs. treatment (Table 7) is sufficient for complete reaction to take place, between quartz and apatite.

Further experiments were carried out by using paddy hull ash obtained by burning paddy hull at 650°C. This paddy hull ash contains about 95% silica in the amorphous state. The results obtained are given in Table 9 10 and 11.

Table 9 – Effect of temperature of treatment on citric acid solubility of Apatite when calcined with constant amount of paddy hull ash for constant time duration

RATIO		Temp. °C	Duration (hrs)	citric acid solubility % P_2O_5	% Conversion of P_2O_5 to citric acid soluble form
Apatite	PHA				
100	30	1000	2.00	6.50	19.11
100	30	1100	2.00	8.00	23.52
100	30	1200	2.00	10.00	29.41
100	10	1000	2.00	10.50	30.88
100	10	1100	2.00	11.00	32.35
100	10	1150	2.00	11.50	33.82
100	10	1200	2.00	11.60	34.11

Table 10 – Effect of duration of treatment on citric acid solubility of Apatite when calcined with constant amount of Paddy hull Ash at 1150°C

RATIO		Temp. °C	Duration (hrs)	Citric acid solubility % P_2O_5	% Conversion of P_2O_5 to citric acid soluble form
Apatite	PHA				
100	10	1150	2.0	10.50	30.88
100	10	1150	2.5	12.00	35.29
100	10	1150	3.0	12.20	35.88

Table 11 – Effect of Apatite : Paddy hull Ash ratio used for calcination on citric acid solubility

RATIO		Temp. °C	Duration (hrs)	Citric acid solubility % P_2O_5	% Conversion of P_2O_5 to citric acid soluble form
Apatite	PHA				
100	10	1150	2.50	12.00	35.29
100	20	1150	2.50	11.40	33.52
100	30	1150	2.50	10.50	30.94
100	10	1100	2.0	11.00	32.35
100	30	1100	2.0	8.00	23.52
100	50	1100	2.0	8.00	23.52
100	60	1100	2.0	9.00	26.47
100	100	1100	2.0	8.00	23.52

From the above results obtained on calcination experiments of apatite with quartz and PHA, effect of temperature of treatment, effect of duration of treatment and effect of ratio of constituents used for treatments are plotted (in Figures 3, 4 and 5) and variation of citric acid solubility is clearly seen.

From these results it is clear that:

a) By increasing the temperature and duration of treatment or by varying the amount of apatite to material used the highest possible citric soluble P_2O_5% that can be obtained is 12·0%, irrespective of silica material used (whether quartz or paddy hull ash). That is percentage conversion of P_2O_5 in rock apatite is 35·29%.

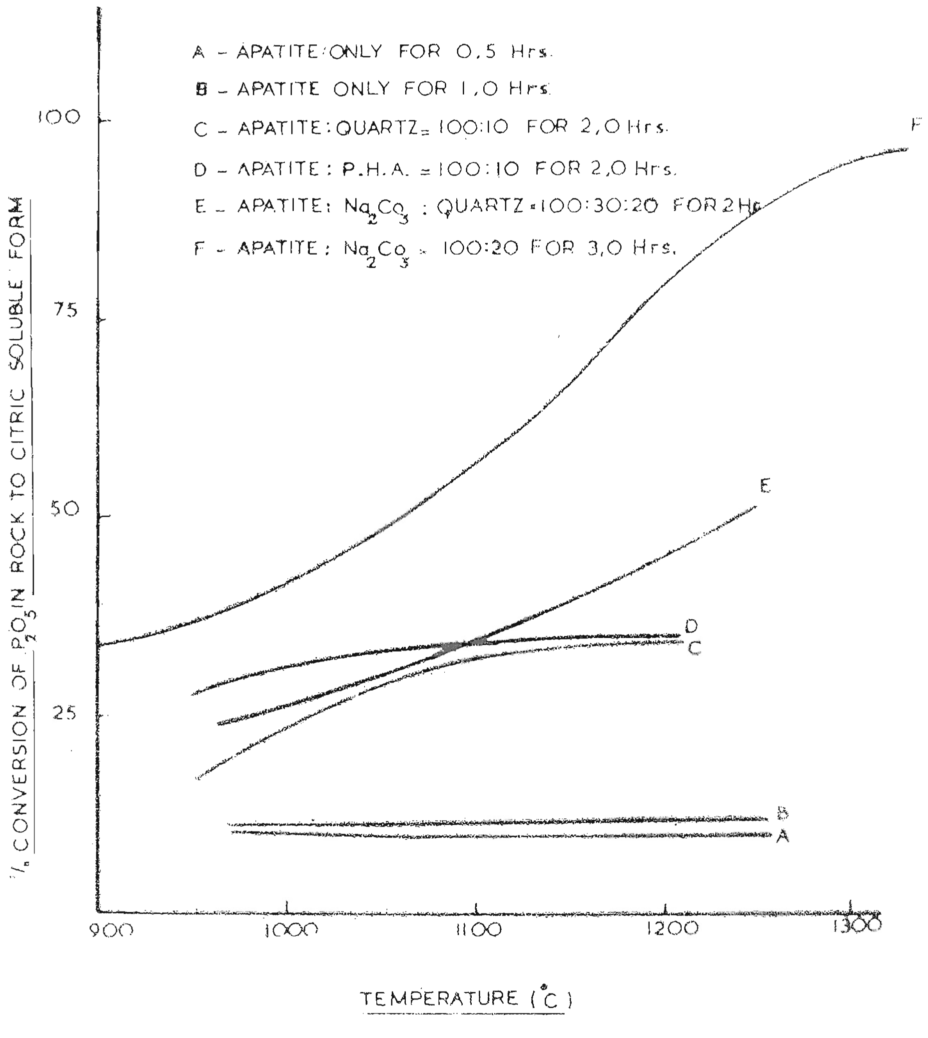

Figure 3 — Effect of temperature on percentage conversion of P_2O_5 in Apatite to Citric Acid soluble form when calcined with different mineralizers.

b) To attain complete reaction between Paddy hull Ash or Quartz with apatite at high temperatures 2·50 to 3·00 hrs is sufficient (Figure 4).

c) From Table 8 (and Figure 5) it is clear that there is an optimum apatite : Paddy hull Ash or quartz ratio that gives the highest citric soluble $P_2O_5\%$.

d) According to Figure 3 it is clear that we could not expect a higher citric soluble P_2O_5 % than the maximum value obtained (12·00%), by increasing temperature of treatment above 1200°C.

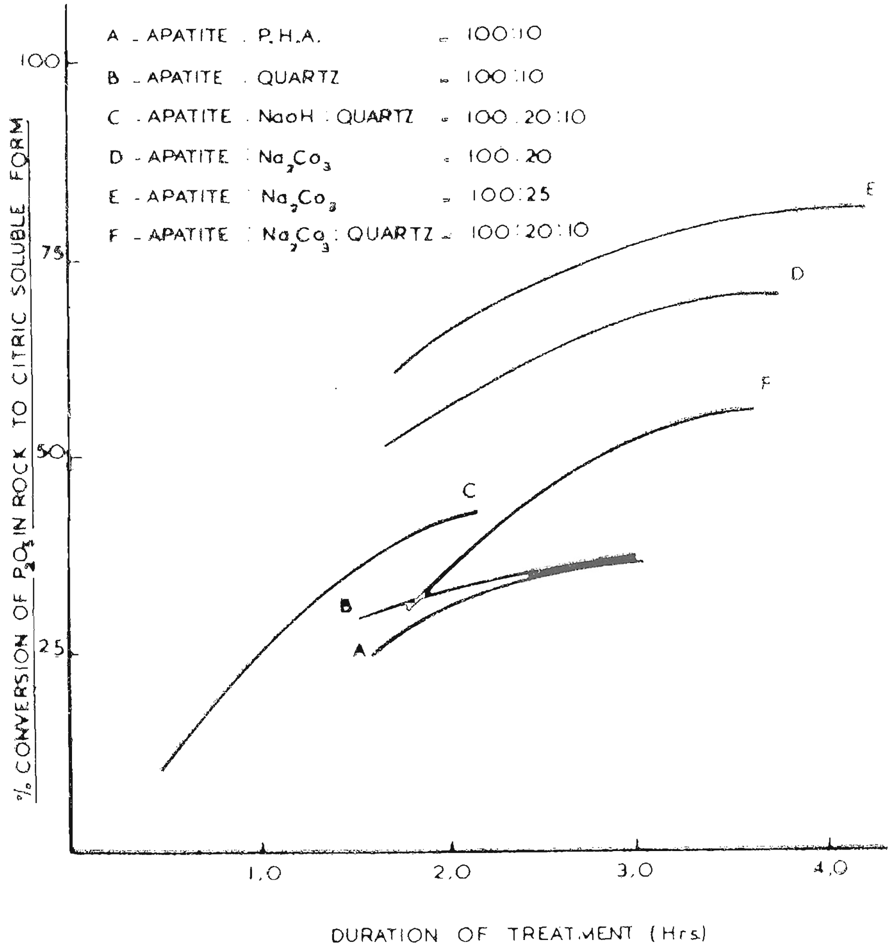

Figure 4 — Effect of duration of calcination on percentage conversion of P_2O_5 in Apatite to Citric Acid soluble form when calcined with different mineralizers.

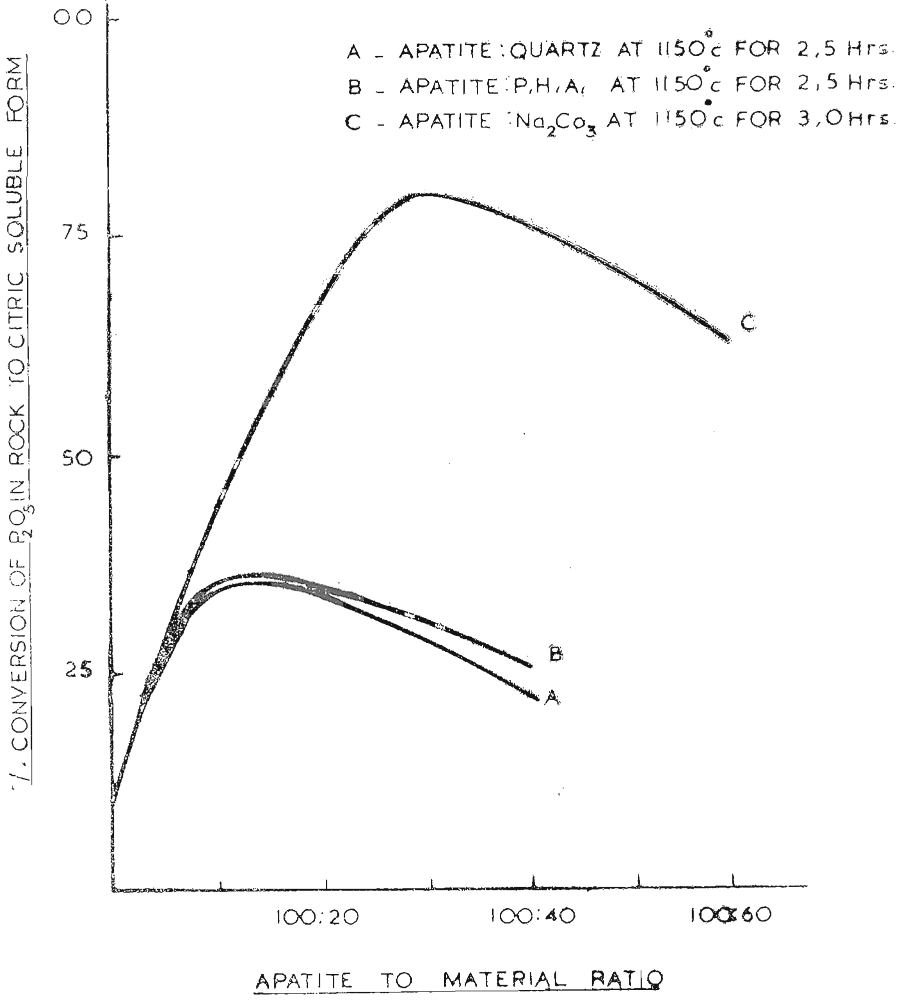

Figure 5 — Effect of mineralizer ratio used in calcination on percentage conversion of P_2O_5 in Apatite to Citric Acid soluble form.

Further experiments were carried out with quartz and other materials such as alkali salts to find out whether those substances would act as better mineralizer on calcination with quartz.

3.5 Calcination with alkali compounds

Calcinations were carried out with apatite and quartz along with NaOH, $Ca(OH)_2$ and Na_2CO_3. Following are the results obtained: Table 12, 13, 14 and 15.

Table 12 – Effect of NaOH on apatite : quartz calcination Effect of Duration of treatment on citric acid soluble P_2O_5%

RATIO			Temp. °C	Duration (hrs)	Citric acid solubility % P_2O_5	% Conversion of P_2O_5 to citric acid soluble form
Apatite	Quartz	NaOH				
100	10	20	1000	0·50	3·40	10·00
100	10	20	1000	1·00	10·40	30·58
100	10	20	1000	2·00	13·40	39·41

Table 13 – Effect of amount of $Ca(OH)_2$ used in calcination of Apatite : Quartz on citric solubility

RATIO			Temp. °C	Duration (hrs)	Citric acid solubility % P_2O_5	% Conversion of P_2O_5 to citric acid soluble form
Apatite	Ca $(OH)_2$	Quartz				
100	30	10	1000	2·00	3·50	10·29
100	30	20	1000	2·00	4·00	11·76
100	50	20	1100	2·00	4·00	11·76

Table 14 – Effect of temperature on citric solubility of Apatite when calcined with Na_2CO_3 and quartz

RATIO			Temp. °C	Duration (hrs)	Citric acid solubility % P_2O_5	% Conversion of P_2O_5 to citric acid soluble form
Apatite	Quartz	Na_2CO_3				
100	20	30	1000	2·00	9·00	26·47
100	20	30	1100	2·00	12·00	35·29
100	20	30	1200	2·00	15·70	46·17

Table 15 – Effect of duration of treatment on citric solubility of apatite when calcined at 1150°C with Na_2CO_3 and quartz

RATIO			Temp. °C	Duration (hrs)	Citric acid solubility % P_2O_5	% Conversion of P_2O_5 to citric acid soluble form
Apatite	Quartz	Na_2CO_3				
100	10	20	1150	2·00	12·00	35·29
100	10	20	1150	2·50	15·50	45·58
100	10	20	1150	3·00	17·00	50·00

From these results it is evident that NaOH and $Na_2 CO_3$ has a better effect on apatite than $Ca (OH)_2$ in rendering it to more citric soluble form. By increasing duration of treatment it is clear that NaOH and Na_2CO_3 would give high citric soluble P_2O_5 content (Figure 4).

But in Sri Lanka since the price of NaOH is high, the use of NaOH is not economical. Hence further experiments were carried out using Na_2CO as a mineralizer.

3.6 Calcination with Na_2CO_3

Table 14 and Figure 3 show that when temperature is increased by keeping Apatite : $Na_2 CO_3$: Quartz ratio constant, citric acid soluble $P_2 O_5$ % is also increasing. Table 15 and Figure 4 show that reaction comes to near completion when sample is heated for 3 hrs.

The product obtained by this calcination may be of rhenania type PO_4 [12] Hence the possible reaction is

$$Ca_5 (PO_4)_3 F + 2 Na_2CO_3 + SiO_2 \longrightarrow 3 Ca NaPO_4 + Ca_2SiO_4 + 2 CO_2 + NaF$$

By this way $P_2 O_5$ in Eppawela Apatite can be converted to 50 % citric soluble form and can be used as a fertilizer.

Further calcination studies were carried out with $Na_2 CO_3$ alone to find ou the influence of $Na_2 CO_3$ and quartz separately on apatite. The results obtained are as follows (Table 16.).

Table 16 -- Effect of duration of treatment on citric acid solubility when apatite is calcined with Na_2CO_3 at 1150°C

RATIO		Temp. °C	Duration (hrs)	Citric acid solubility % $P_2 O_5$	% Conversion of $P_2 O_5$ to citric acid soluble form
Apatite	Na_2CO_3				
100	20	1150	2.00	19.50	57.35
100	20	1150	2.50	21.25	63.23
100	20	1150	3.00	23.00	67.64
100	25	1150	2.00	22.00	64.70
100	25	1150	3.00	26.00	76.47
100	25	1150	4.00	27.60	81.17

By comparing results of Table 16 and 15, it is clear that $Na_2 CO_3$ alone has a better effect on apatite than No_2CO_3 and quartz in beneficiation. Also it shows that 81% of $P_2 O_5$ in apatite can make citric soluble by this type of calcinations.

Further experiments were carried out by varying the temperature of treatment by keeping the molecular ratio and duration of treatment constant (Table 17) and also varying the Apatite : Na_2CO_3 ratio by keeping temperature and duration of treatment constant (Table 18). Results were as follows:

Table 17 – Effect of Temperature of treatment on citric acid solubility of apatite by keeping the material ratio and duration of treatment constant

RATIO		Temp. °C	Duration (hrs)	Citric acid solubility % P_2O_5	% Conversion of P_2O_5 to citric acid soluble form
Apatite	Na_2CO_3				
100	20	900	3·00	12 41	36·50
100	20	1000	3·00	14·31	42·08
100	20	1100	3·00	16·46	48·41
100	20	1150	3·00	23·00	67·64
100	20	1200	3 00	27·35	80·44
100	20	1300	3·00	32·78	96·41

Table 18 – Effect of Apatite : Na_2CO_3 ratio on citric acid solubility by calcining at 1150 °C for 3.0 hrs

RATIO		Temp. °C	Duration (hrs)	Citric acid solubility % P_2O_5	% Conversion of P_2O_5 to citric acid soluble form
Apatite	Na_2CO_3				
100	15	1150	3·00	16·46	36·50
100	20	1150	3·00	23·00	67·64
100	25	1150	3·00	26·00	76·47
100	30	1150	3·00	27·20	80·00
100	35	1150	3·00	26·46	77·87
100	40	1150	3·00	25·77	73·79
100	45	1150	3·00	25·08	73·76
100	50	1150	3·00	22·7	66·76
100	100	1150	3·00	17·15	50·44

The variation of citric acid solubility of Eppawela apatite, when calcined with Na_2CO_3 can be clearly seen in Figures 3, 4 and 5. From X-ray powder analysis studies of these products (Figure 1) and results that had been obtained following conclusions can be achieved.

a) Increase of temperature of treatment will increase the citric soluble P_2O_5 % considerably when Apatite to Na_2CO_3 ratio was kept constant (Figure 3). X-ray studies (Figure 1) showed the formation of various sodium calcium phosphates[10] (Table 19).

Table 19 – Various phases present in calcined product of apatite with Na_2CO_3 at different temperatures by keeping apatite: Na_2CO_3 = 100 : 20 and for duration of 3 hrs.

Temperature °C	Phases present in the product	Phases present in the residue after dissolving in 2% citric acid
900	$Na_3Ca_6(PO_4)_5$ (ie. 2·4 CaO. 0·6 Na_2O. P_2O_5) Fluorapatite (unreacted)	Fluorapatite
1000	$Na_3Ca_6(PO_4)_5$ + α – Na Ca PO_4 (2 CaO. Na_2O. P_2O_5)	Fluorapatite
1100	$Na_3Ca_6(PO_4)_5$ + α – Na Ca PO_4 + β – Na Ca PO_4	Fluorapatite
1150	— do —	Fluorapatite
1200	β – Na Ca PO_4	Fluorapatite (distorted)
1300	β – Na Ca PO_4	Fluorapatite (distorted)

This means that,

i. At lower temperatures low Na_2O / CaO phosphates are formed by reacting with lesser amount of Na_2O from Na_2CO_3.

ii. At higher temperatures high Na_2O / CaO phosphates are formed with higher amount of Na_2O from Na_2CO_3.

All these phosphates are in citric soluble form. Pure fluotapatite found in the residue may be from unreacted rock and this amount decreased with increasing temperature.

b) Increase in duration of treatment will increase the citric acid solubility considerably until it reaches a treatment duration of 3 – 4 hours. Hence reaction with Na_2CO_3 is complete only after 3 hrs. (Figure 4)

c) Highest citric acid soluble P_2O_5 % can be obtained by using 30 - 40 parts of Na_2CO_3 to that of 100 parts of Apatite (by weight) on calcinations at 1150°C. This is clearly shown in Figure 5. Increase or decrease of

Na_2CO_3 ratio at 1150°C lower the citric soluble P_2O_5 percentage in tha final product. X-ray studies of the products obtained (Figure 6) showed the presence of various sodium calcium phosphates (eg. $NaCaPO_4$, $Na_3Ca_6(PO_4)_5$ etc.). The residue obtained after dissolving in 2% citric acid contained only pure fluorapatite (Figure 7 (A)), if Na_2CO_3 ratio is less than 30 - 35 to 100 parts by weight of apatite.

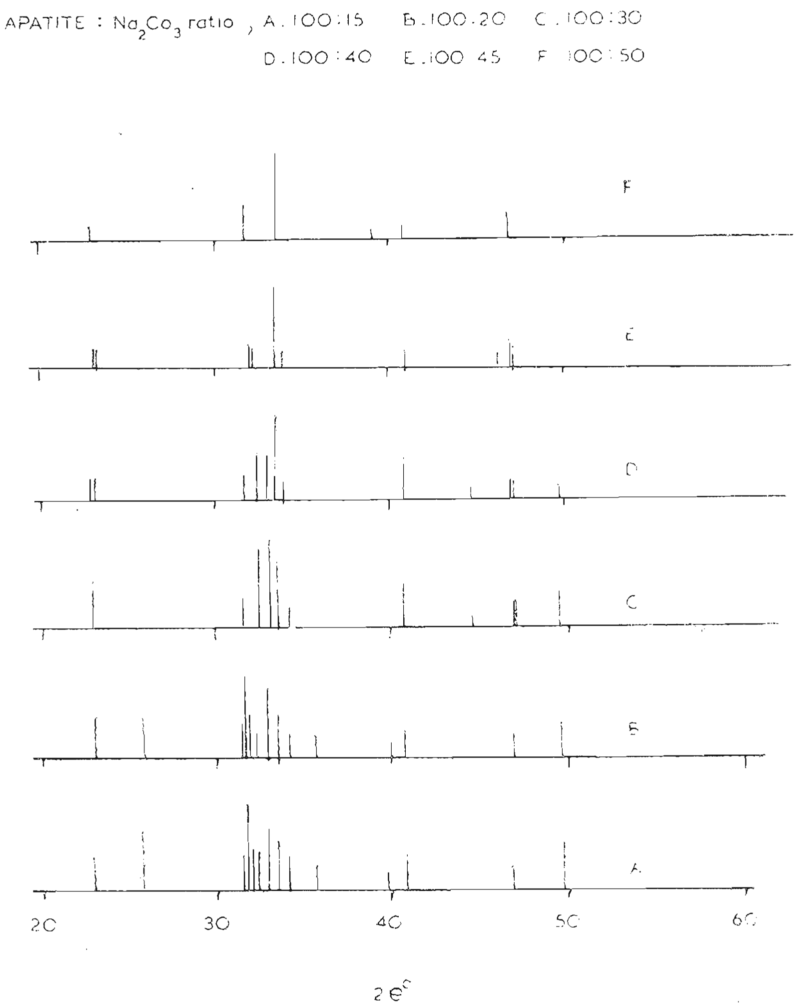

Figure 6 — XRD patterns of products obtained when apatite is calcined at 1150°C for 3·0 hrs with varying amounts of Na_2CO_3

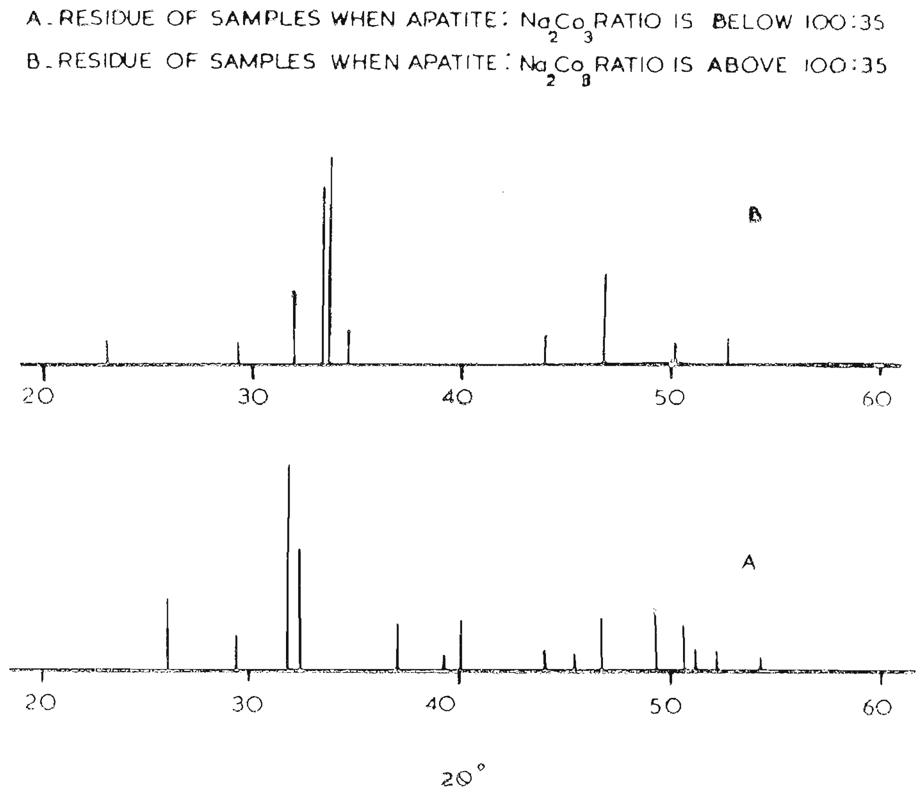

Figure 7 — XRD patterns of residue obtained after dissolving the $Na_2 CO_3$ + Apatite calcined samples in 2% citric acid.

This means that at low $Na_2 CO_3$ ratios, Na_2O from $Na_2 CO_3$ is reacting exclusively first with chlorapatite and then with fluorapatite of the rock to form $Na Ca PO_4$ or other related phosphate which is soluble in 2% citric acid. (Also X-ray patterns do not show the presence of unreacted $Na_2 CO_3$ or $Na_2 O$). This can be clearly seen by calculating percentage $P_2 O_5$ and percentage CaO reacted to form the citric soluble compound with percentage $Na_2 O$ from added Na_2CO_3. (Table 20) (Calculations were done by considering Eppawela apatite has 50% CaO and 34% total P_2O_5. With each sample percentage CaO that was reacted to give citric soluble compound was calculated from its citric soluble $P_2 O_5$% and $Na_2 O$% was calculated by considering that all Na_2CO_3 was reacting with apatite to give a citric soluble product).

Table 20 – Ratio of CaO: Na_2O : P_2O_5 in the citric acid soluble product that had formed with low Na_2CO_3 ratios at 1150 °C for 3 hrs duration.

Reacting Materials		Citric soluble P_2O_5%	Weight Ratio		
Apatite	Na_2CO_3		CaO	Na_2O	P_2O_5
100	15	16·46	1·47	0·530	1
100	20	23·00	1·47	0·50	1
100	25	26·00	1·47	0·56	1
100	30	27·20	1·47	0·594	1

From Table 20 it is clear that until Apatite : Na_2CO_3 ratio is 100 : 30, the CaO : Na_2O : P_2O_5 ratio of citric soluble sodium calcium phosphate, is nearly equal. This means that constant amount CaO and P_2O_5 from rock is reacting with all of Na_2O to form the citric soluble compound. Rest of CaO and P_2O_5 will be in the product as fluorapatite itself. This is evident from X-ray results and cell dimension values of residue fluorapatite obtained (Figure 8).

The XRD patterns of the residual fluorapatite showed a shifting of peaks with the increase of sodium carbonate (Figure 7 (B)). This may be due to the substitution of excess Na^+ in the fluorapatite lattice.

The cell constants of the residual fluorapatite obtained after dissolving in 2% citric solution is plotted in the Figure 8. The cell constants are nearly same upto a sodium carbonate to apatite ratio of 100 : 30. Beyond this cell constant "a" decreases and "b" increases with the increase of Na_2CO_3 percentage. Also the percentage of citric soluble P_2O_5 in the final product decreases.

Colour and the form of the product

The colour of the products varies from brown to grey when Na_2CO_3 ratio is increased at 1150°C and the samples which give high citric solubility had a sintered appearence.

Effect of quenching

It was observed when carrying out experiments that rapid air quenching is needed to get better citric acid solubility in a given condition. Since the product obtained had low water solubility (Table 21) further experiment was carried out with calcined samples by quenching into water. The citric solubility of this sample was very low compared to air quenched sample and X-ray patterns showed the sample had more unreacted fluorapatite.

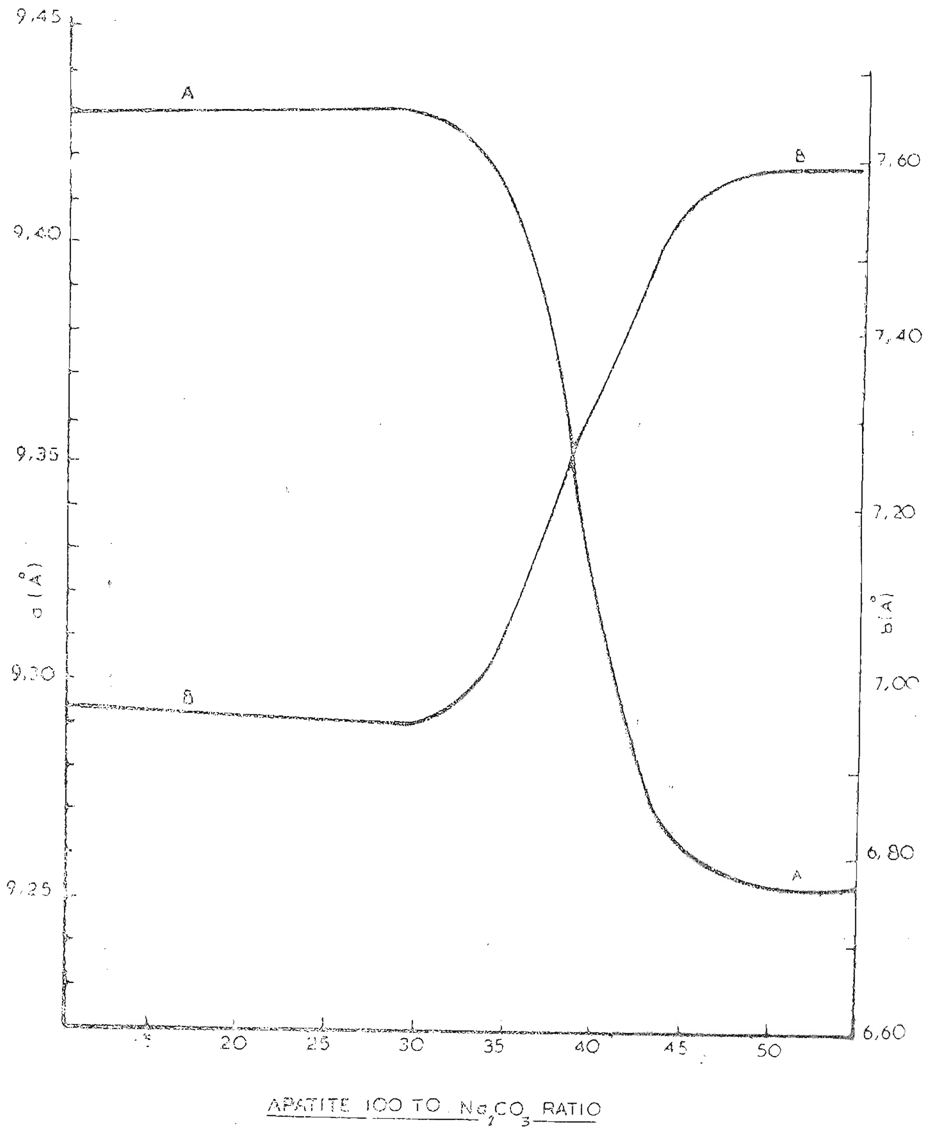

Figure 8 — Variation of cell dimensions of unreacted fluorapatite when raw apatite is calcined with varying amounts of Na_2CO_3 at 1150°C for 3 hours.

A — Variation of cell dimension a

B — Variation of cell dimension b

Table 21 – Effect of water quenching and air quenching on citric soluble $P_2O_5\%$ on Na_2CO_3 calcined Apatite.

RATIO		Temp. °C	Duration (hrs)	Air Quenching		Water Quenching
Apatite	Na_2CO_3			water sol. $P_2O_5\%$	citric sol. $P_2O_5\%$	citric soluble $P_2O_5\%$
100	20	1150	3·00	3·17	23·00	6·44

Hence it is clear that to obtain high citric soluble P_2O_5 content with calcinations with soda ash at 1150° C, apatite to Soda ash ratio must be in the range of 100 : 30 - 35 and duration of treatment is 3 hrs. The sample should be quenched rapidly in air.

Conclusions

1) Eppawela apatite itself is not suitable as a fertilizer since it has low citric soluble P_2O_5 percentage. (ie. out of 34% P_2O_5 available only 3% is in citric soluble form).

2) It can be converted to a product having more PO_4 in citric soluble form by calcining with sodium carbonate, quartz or paddy hull ash. With sodium carbonate 80% of P_2O_5 can be made citric soluble whereas with quartz and paddy hull ash only 50% can be converted. Calcination of a mixture Apatite + Quartz + Na_2CO_3 will also give 50% conversion.

3) Soda Ash calcination has to be done with controlled amounts of apatite and soda ash to get high citric soluble value and less soda ash consumption. It was found at 1150°C a ratio of Apatite : Na_2CO_3 of 100 : 30 — 35 at a duration of treatment for 3 hrs, would give best results.

4) If apatite is calcined with controlled amounts of Na_2CO_3 at temperatures above 1300° C, over 95% P_2O_5 in rock can be converted to citric soluble form. For example when a charge consisting of 100 parts of rock apatite, 20 parts of soda ash was calcined at 1300°C for 3 hours a product of 96% citrate soluble P_2O_5 was obtained.

5) There is a possibility to use this product as a phosphate fertilizer for short term crops instead of imported superphosphates, since this type of sodium thermophosphates are presently being used as fertilizers in many countries of the world. But before coming to a firm conclusion one has to carry out field trials with the product.

Acknowledgement

The authors wish to express their gratitude to the Director and the Deputy Director of the C. I. S. I. R. for their encouragement and the staff of the section of Mineral Technology of C. I. S. I. R. for their help in preparing this paper.

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