Technology Section

CHARACTERISTICS OF LAGARBAN PHOSPHATE ROCK FOR THE MANUFACTURE OF PHOSPHORIC ACID BY DIHYDRATE PROCESS

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Characteristics of Lagarban phosphate rock were studied with a view to assess its suitability for the manufacture of phosphoric acid through dihydrate process. Data obtained from bench scale tests are presented. Inspite of high silica, iron, aluminium, magnesium oxide, carbonate and organic matter, slow reactivity and low CaO/P_2O_5 ratio, it is possible to produce phosphoric acid of 25 – 26 percent P_2O_5 concentration from Lagarban rock.

INTRODUCTION

Experimental work was started at NFC Fertilizer Technology Centre Faisalabad to study the characteristics of indigenous rock (Lagarban) for the manufacture of phosphoric acid.

Phosphoric acid is manufactured by the decomposition of phosphate rock with sulphuric acid, the resulting calcium sulphate together with other insoluble impurities is separated from phosphoric acid by filtration. Various processes commonly employed are classified as dihydrate, hemihydrate and anhydrite, depending upon the nature of the calcium sulphate formed.

Dihydrate process for the manufacture of phosphoric acid was selected to be followed because of the relative simplicity of design and operation offered by the process.

Rockphosphate of Lagarban area is generally cherty, dolomitic, medium brownish grey to dark grey, hard and compact. The total inferred reserves of Lagarban area are 13.6 million tons of varying grades having up to 23% P_2O_5 with excessive impurities such as silica, iron oxide alumina and magnesia.

EXPERIMENTAL

250 kg representative sample of Lagarban phosphate rock from north and south areas was supplied by Sarhad Development Authority. Crushing and grinding were done at our laboratory. Chemical composition of the rock sample alongwith Jordan phosphate rock is tabulated below for comparison purposes:

Contents	Lagarban rock	Jordan rock
P_2O_5	26.10 %	32.47 %
CaO	37.5 %	50.17 %
SiO_2	18.40 %	5.63 %
Fe_2O_3	4.40 %	1.87 %
Al_2O_3	1.06 %	0.49 %
MgO	3.30 %	0.25 %
F	2.80 %	3.60 %
Loss on ignition	4.80 %	5.57 %
CaO/P_2O_5 ratio	1.43	1.54
F/SiO_2 ratio	0.15	0.53
R_2O_3	5.46 %	2.36 %

By the chemical analysis the suitability of phosphate rock for the manufacture of phosphoric acid could be assessed fairly, but the combined effect of impurities are different upon reactivity and filterability for each rockphosphate.

The experimental work to be conducted on the Lagarban rock in order to optimise the different variables to find out the conditions for maximum extraction efficiency and best crystal growth for greater filtering rate, was laid down as under:

A. 1) Study of the reactivity of the rock.
   2) Foam stability index of the rock.

B. *Optimization of the variables:*

1) Sulphuric acid and rockphosphate ratio.
2) Degree of agitation.
3) Phosphoric acid (recycled) to rockphosphate ratio i.e. slurry density and percentage solid contents of the slurry.
4) Residence time.
5) Fineness of the rock.
6) Temperature of the reaction suitable for Lagarban phosphate rock.

For comparison purposes similar tests were carried out on standard phosphate rock i.e. Jordan phosphate rock.

A. *Reactivity of the Lagarban Rock*

Reactivity of Lagarban and Jordan phosphate rock was studied by carrying out the following tests.

1. *Reactivity by Rise in Temperature.* Maximum rise in temperature was recorded for both the rocks by mixing continuously 50 g of 90 % − 150 mesh, 5% − 200 mesh rock with 50 % excess of 70 % H_2SO_4 in a glass beaker. Acid and rock before mixing were brought at 50°. Thorough mixing was carried out for two min for both the rocks. Maximum rise 108° respectively. This temperature is proportional to the reactivity of the rock.

2. *Reactivity Index Test.* The test was carried out by reacting the ground rock −200 mesh +240 mesh in a 80 % excess of 30 % phosphoric acid and 30 % sulphuric acid at 70° for 30 min. The percentage dissolution of the rock termed as "Reactivity Index" is measured for both the rocks.

Table 1. Measurement of reactivity index of phosphate rocks.

Phosphate rock	Reactivity Index	
	30% H_3PO_4 %	30% H_2SO_4 %
Lagarban rock	47.9	86.4
Jordan rock	65.8	94.4

The index obtained gives the comparison of the reactivity of the rock. The higher the index the faster the rate of reaction, thus as seen from the Table 1 Lagarban rock has low reactivity.

As the reactivity of the Lagarban rock is low, higher reaction temperature would be favourable for its decomposition.

3. *Foam Stability Index.* This is a comparative test to indicate the extent and stability of foam produced during the acidulation of phosphate rock. −200 mesh +240 mesh ground rock is acidulated in 30 % P_2O_5 phosphoric acid. The height of the foam produced is measured and recorded as a function of time and the foam decay curve is plotted. The area under height − time plot is calculated and termed as "Foam Stability Index", the data of experimental work carried out is given in the graph. For comparison the foam stability index of Jordan phosphate rock is also given in the same graph.
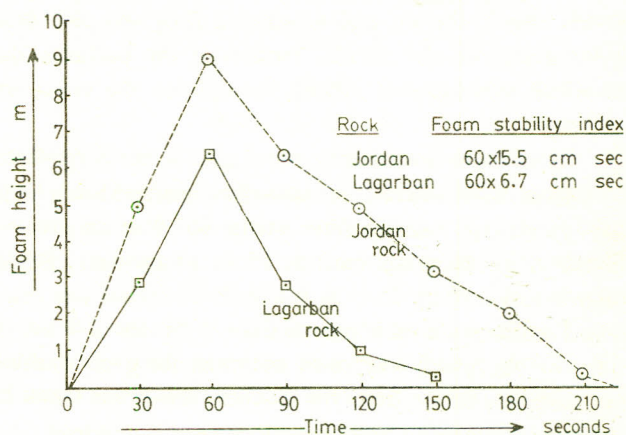

Fig. 1. Foam decay curves and foam stability index.

B. *Optimization of Variables*

Bench Scale Unit Description and operation. The bench scale unit consists of three lead vessels, one reactor and two crystallizers of 260 mm dia and 300 mm height, arranged in series. A schematic diagram of the unit is shown in Fig. 2. After the complete addition of weighed quantities of phosphate rock, recycled phosphoric acid and sulphuric acid, the dissolution (residence time 4 − 6 hours) was provided. Addition of phosphate rock by a screw feeder, recycled phosphoric acid and sulphuric acid through calibrated head container was made, their flow rates were adjusted and sometimes varied to control to foaming and to maintain the required temprature 75 − 80° in the reacting vessel and 62° in the crystallizers. Agitation was provided with lead-coated agitator having four blades of propeller type. Four equally spaced vertical baffles were also fixed with the internal surface of each vessel in order to regulate the agitation and the flow pattern
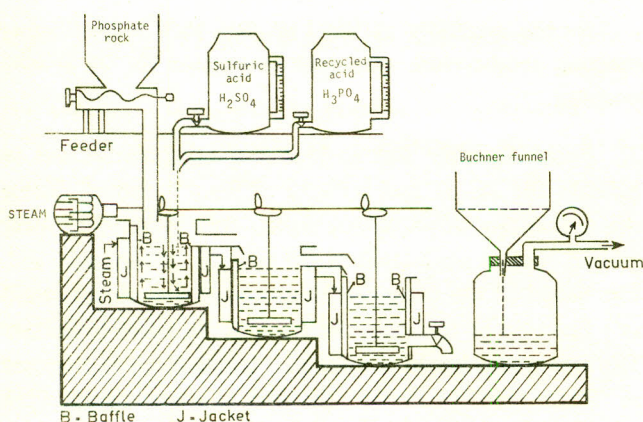
Fig. 2. Phosphoric acid bench unit.

of the slurry. By introducing the vertical baffles in the reaction vessel, the up and downward flow was also developed alongwith the circular motion of the particles, due to which homogenous mixing throughout the vessel was achieved.

Slurry from the reacting vessel goes to the crystallizers by gravity from where it is manually transferred to a buchner funnel type vacuum filter having 507.9 sq cm area for filtration by applying vacuum 15 in of mercury. Before filtration the slurry level in the buchner funnel was maintained up to mark each time, a cake thickness of 4 cm on the filtering funnel was found optimum for good washing. For analysis, slurry from the reaction vessel was taken by vacuum technique to make the adjustment if required.

Bench Scale Tests. In all the tests to be carried out on bench scale unit, 8 kg phosphate rock (fineness 90 % —150# 50 % —200#) with 20 % P_2O_5 phosphoric acid (recycled) and extraction temperature in the reactor 75° — 80° would be used. After the addition of phosphate rock,

recycled phosphoric acid and sulphuric acid, four hours residence was given in all the batch trials.

Effect of Sulphuric Acid to Rock Ratio on P_2O_5 Extraction Efficiency and Filtering Rate. The amount of sulphuric acid used in the following tests is the stochiometric equivalent of CaO contents of the phosphate rock. The little free sulphuric acid contained in the phosphoric acid (recycled) has also been taken into consideration. Actual weight of the sulphuric acid added and the results of the experiments conducted are given in Table 2. Some of the experimental parameters not given in Table 2 are given below:

Quantity of sulphuric acid used, 5.24 kg; Percentage CaO equivalent of the rock, 100 %; 20 % P_2O_5 phosphoric acid recycle, 20 kgs; Extraction temperature, $75 - 80^O$; Residence time (dissolution time), 4 hours; Filtration rate kg P_2O_5/M^2/hour, 83.12; Strength of the product acid; 24.9 %; Free H_2SO_4 in the liquid phase of slurry, 4.9%,

Maximum extraction efficiency achieved in the above experiment was up to 92.4 % even in the presence of high free sulphuric acid i.e. up to 4.9 % in the liquid phase of the slurry. To imporve the extraction efficiency it was decided to find out the optimum degree of agitation needed and thie quantity of sulphuric acid required.

Effect of the Degree of Agitation. To find out the required degree of agitation to get maximum conversion of rock P_2O_5 to water soluble P_2O_5 the degree of agitation was varied from 85 rpm to 151 rpm. Details of the various experiments carried out are given in the following Table 2.

By increasing the degree of agitation from 0.97 m/sec to 1.62 m/sec, extraction efficiency was increased from

Table 2

Agitation		Extraction efficiency	H_3PO_4 filtered			Duration of filtration	Filtering rate kg	Free H_2SO_4	Recovry %age
rpm	Impeller tip speed m/sec	% rock P_2O_5 to W.S. P_2O_5 after 4 hr	Wt. kg	strength % P_2O_5	P_2O_5 kg	min	P_2O_5/M^2/ hr	in product acid %	W.S. P_2O_5 slurry
85	0.97	92.5	15.67	25.0	3.91	56.0	82.48	4.9	89.1
106	1.22	94.8	15.74	25.3	3.98	56.4	83.36	3.4	91.5
127	1.46	97.5	15.83	25.6	4.05	53.8	88.92	1.7	92.8
141	1.62	97.7	15.87	26.2	4.15	53.6	90.78	0.7	93.2
151	1.73	97.8	15.88	26.3	4.17	54.2	90.88	0.6	93.4

92.5 to 97.7 % alongwith it product acid strength 26.2 % P_2O_5 and filtering rate was also increased up to 90.78 kg P_2O_5/M^2/hr respectively. On increasing the degree of agitation more than 1.62 m/sec had a negligible effect upon extraction efficiency and filtering rate. Low contents of free H_2SO_4 up to 0.7 % caused poor dihydrate crystals growth and ultimately less recovery percentage and filtering rate 93.2 % and 90.78 kg P_2O_5/M^2/hr respectively.

Effect of H_2SO_4 on Extraction Efficiency and Filtering Rate. The tests were conducted to determine the effect of varying amount of sulphuric acid from 80 to 120 % CaO equivalent quantities of phosphate rock upon P_2O_5 extraction and filtering rate, while keeping the degree of agitation 1.62 m/sec constant. The results are shown in Table 3.

From the results given in Table 3 it is seen that 5.76 kg H_2SO_4 quantity 110 % CaO equivalent of the phosphate rock with free H_2SO_4 contents 2.9 % has been found optimum because the quantity of acid extraction efficiency of 98.3 % and greater filtering rate 93.83 kg/M^2/hr were achieved.

Increasing the amount of sulphuric acid more than 5.76 kg, the decreased P_2O_5 filtering rate from 92.97 to 92.22 kg P_2O_5/M^2/hr as the product acid contained lower P_2O_5 content (25.4 %) and free H_2SO_4 up to 5.6 % which is high.

On the other hand by decreasing the amount of sulphuric acid, experiment No. 4 and 5 (Table 3), the extraction efficiency decreased and recovery of phosphoric acid decreased up to 89.6 % due to the co-precipitation phenomena in the absence of free H_2SO_4 contents.

Effect of the Amount of Weak Phosphoric Acid (Recycled) Upon Extraction Efficiency and Filtering Rate. The effect of total P_2O_5 contents, density of the slurry and the percentage of the solid particles of the slurry upon extraction efficiency, crystal growth and filtering rate, was studied through a series of tests in which the amount of recycled phosphoric aicd has been varied. (Table 4).

From Table 4 it is seen that conditions most favourable for

Table 3. Effect of varying amount of sulphuric acid on extraction efficiency and filtering rate.

Sulphuric acid		Extraction efficiency	H_3PO_4 filtered			Duration of filtration min	Filtering rate kg P_2O_5/M^2/hr	Free H_2SO_4 %	Recovery efficiency W.S. P_2O_5 %
Quantity kg	CaO eqivalent % age		Wt. kg	strength of of acid % P_2O_5	P_2O_5 filtered kg				
5.28	120	98.4	16.83	25.4	4.20	53.8	90.41	5.6	94.2
5.76	110	98.3	16.3	26.1	4.25	53.5	93.83	2.9	93.6
5.24	100	98.1	15.8	26.5	4.18	54.0	91.44	0.9	92.9
4.71	90	96.2	15.1	26.1	3.94	53.8	86.5	Traces	91.7
4.19	80	94.1	14.5	26.2	3.79	54.0	82.90	Nil	89.6

Recycled H_3PO_4 used = 20 kg.

Table 4. Effect of varying amount of phosphoric acid (recycled) on extraction Efficency and filtering rate.

Recycled phosphoric acid P_2O_5		Density of slurry	Solid particles %	Total P_2O_5 content %	Extraction efficiency %	H_3PO_4 filtered			Duration min	Filtering rate kg P_2O_5 / M^2/hr	Free H_2SO_4 %	Recovery efficiency %
kg	Rock to H_3PO_4 ratio					Stren- gth %	Wt. kg	P_2O_5 filtered				
16	1:2	1.58	34	18.0	98.0	26.7	13.8	3.68	49.0	88.71	1.9	92.9
20	1:2:5	1.53	32	18.2	98.25	26.1	16.1	4.2	52.5	94.49	2.7	93.8
24	1:3	1.50	30	18.5	98.50	24.8	19.16	4.75	50.6	110.83	2.8	93.9
28	1:4	1.44	27	18.7	98.60	24.0	22.5	5.48	57.2	111.50	2.9	94.5

the growth of dihydrate crystals were phosphoric acid recycle (24 kg), slurry density (1.5) and solid particles (30 %) and filtering rate 110.83 kg P_2O_5/M^2/hr. On decreasing the amount of recycled H_3PO_4 as given in experiments 1 and 2 density of the slurry became higher (up to 1.58), the strength of the product acid was increased up to 26.7% P_2O_5 due to higher contents of iron and aluminium oxide (5.46 %) and MgO (3.3 %), the viscosity of the filtering acid was high up to 9.6 % which resulted in poor crystal growth and lowering of the filtering rate (up to 88.7 and 94.9 kg P_2O_5/M^2/hr) and recovery efficiency from 93.9 to 92.9 %. Flow of the slurry caused difficulty in operation due to the settling of the solid particles of higher percentage of solids. Further, on increasing the amount of recycled H_3PO_4 up to 28 kg no marked change in filtering rate was observed, but the strenght of the product acid was decreased from 24.8 to 24 %. So the 24 kg recycled phosphoric acid 20 % P_2O_5 was found to be optimum.

Effect of the Residence Time Upon Extraction Efficiency and Filtering Rate. Suitable residence time required for the dissolution of the phosphate rock was determined by varying residence time from 2 to 8 hours (Table 5).

The results showed (Table 5) that within 2 hours all the phosphate rock was decomposed because the extraction efficiency for 2 hours, 4 hours, 6 hours and 8 hours residence time was the same, but the filtering rate for 2 hours

residence time was low i.e. 98.36 kg P_2O_5/M^2/hr. Further, increasing the residence time for more than 6 hours had no significant effect upon crystal growth and filtering rate. So the six hours residence time was found necessary for the proper dihydrate crystal growth as seen from the filtration results.

Effect of Particle Size upon Extraction Efficiency and Filtration Rate. To find out the suitable particle size, tests were carried out with varying particles sizes 80, 100, 150 and 200 mesh of the rock keeping all the other variables constant.

In case of 80 % −100# and 10 % −100# extraction efficiency was low up to 82.1 % because the conversion of rock P_2O_5 to water soluble P_2O_5 was low due to the coarser rock particles. But the filtering rate was high 133.4 kg P_2O_5/M^2/hr as the bigger silica particles favoured filtration. With the fine rock particles size the extraction efficiency increased with 90 % −150# and 50 % −200# practicle size extraction efficiency and filtration rate obtained were 98.6% and 120.8 kg P_2O_5/M^2/hr respectively. Upon further reduction of particle size up to 80 % −200# and 60 % −250# it was observed that extraction efficiency remained almost the same, but the filtering rate was decreased to 116.67 kg P_2O_5/M^2/hr due to the deposition of very fine silica particles on the filter.

Effect of Temperature. By keeping the previously optimised variables constant, trials were carried out at

Table 5. Effect of residence time upon extraction efficiency and filtering rate.

Residence time hours.	Extraction efficiency (rock P_2O_5 to water soluble 4 hours %)	Wt. kg	H_3PO_4 Filtered Strength %	P_2O_5 filtered kg	Duration of filtration min	Filtering rate P_2O_5/M^2/hr	Free H_2SO_4	Recovery efficiency	Crystals growth under micro-scope
2.00	98.0	19.01	24.4	4.63	55.6	98.36	3.3	92.1	Paste like material
4.00	98.4	19.11	24.8	4.73	50.0	111.75	2.9	94.1	Very small Crystals
6.00	98.5	19.12	25.0	4.78	47.2	119.6	2.8	94.7	Agglomerate rhombic type
8.00	98.5	19.10	25.1	4.79	47.0	120.38	2.8	94.8	Agglomerate rhombic type

Table 6. Effect of particle size upon extraction efficiency and filtration rate.

Finess of rock	Extraction efficiency %	H_3PO_4 Filtered			Duration of filteration min	H_3PO_4 filtering rate kg	Free H_2SO_4 %	Recovery %
		Weight kg	Strength %	P_2O_5 filtered kg				
100% − 80# 10% −100#	82.1	18.52	22.6	4.18	37	133.4	4.6	81.0
90% −100# 20% −150#	87.6	18.78	23.1	4.33	40	127.8	3.9	86.2
90% −150# 50% −200#	98.6	19.2	25.1	4.81	47	120.8	2.9	94.9
80% −200# 60% −250#	98.8	19.3	25.1	4.84	49	116.67	2.9	94.8

Table 7. Effect of temperature.

Temperatures			Extraction efficiency %	Wt. kg.	$H\ PO_4$ filtered		Duration or filtration min.	filtering rate P_2O_5 kg/M²/hr	Free H_2SO_4	Recovery efficiency	Crystal growth
Reactor Max °C	Min °C	Crystalizer °C			Strength %	P_2O_5 Filtered kg.					
75	70	58 − 60	98.3	19.16	24.90	4.77	46.6	120.9	2.7	94.9	Agglomerate type.
80	78	60 − 62	98.7	19.2	25.2	4.83	46.5	122.6	2.8	95.1	− do −
82	78	60 − 62	98.6	19.15	25.1	4.80	45.5	121.9	2.9	95.0	− do −

different ranges of temperature. It was seen that strict temperature control from 78 to 80° in the reaction vessel and from 60 to 62° in the crystallizer favoured the dihydrate crystal growth and also increased the filtering rate.

On the basis of the results of numerous batch scale tests following optimum conditions were chosen:

Variables	Range for Lagarban rock
Quantity of sulphuric acid 100 % for 8 kg phosphate rock.	5.76 kg.
Quantity of phosphoric acid 20 %.	24.00 kg
Agitation impeller tip speed.	1.62 m/sec.
Residence time.	6 hours.
Finness of rock.	90 % −150 mesh. 50 % −200 mesh.
Temperatures.	
Reaction vessel	80 − 75°
Crystallizer	60 − 62°

Keeping all the variables at the above optimum rates, continuous trials on the Lagarban rock and Jordan rock were carried out, detailed data of the same is given on page 40.

CONCLUSION

1. It is possible to prepare phosphoric acid of 25 − 26 % P_2O_5 concentration from Lagarban phosphate rock without its beneficiation.

2. Lagarban phosphate rock is slow reactive, its reactivity index is 47.9 % in 30 % H_3PO_4 and 86.4 % in 30 % H_2SO_4, while the reactivity index of Jordan rock is 60.8% in 30% H_3PO_4 and 94.7% in 30% H_2SO_4. By using fine ground Lagarban phosphate rock 50% − 200 mesh and higher reaction temperature 75 − 80°, extraction efficiency 98% could be achieved against up to 99.5 % extraction efficiency usually obtained for well established phosphate rocks.

3. Inspite of 4.8 % carbonate and organic matter in Lagarban rock, less foaming was found during reaction as compared to that of Jordan rock. This was perhaps due to the high contents of SiO_2 in the Lagarban rock. Also the foam decay rate in case of Lagarban rock is higher than that of

	Lagarban rock	Jordan rock 64
Feed rate of phosphate rock 100 % – 100 mesh	22.2 g/min	13.8 g/min
Feed rate of sulphuric acid 98 %	9 ml/min	7.2 ml/min
Feed rate of recycle H_3PO_4	55.5 ml/min	23.3 ml/min

Operating Conditions.

	Lagarban rock	Jordan rock 64
Degree of agitation, impeller tip speed	1.62 m/sec	1.62 m/sec
Temperature in reacting vessel	$75 - 80^o$	$70 - 75^o$
Temperature in crystallizer	$60 - 62^o$	$60 - 62^o$
Density of slurry.	1.5	1.54
Percentage of solid particles of slurry	30 %	33 %
Total P_2O_5 contents in slurry	18.04 %	18.81 %
Extraction efficiency, rock P_2O_5 to W.S P_2O_5 before filtration.	97.8 %	98.9 %
Free H_2SO_4 in liquid phase of slurry	2.9 %	2.31 %

Filtration Data

	Lagarban rock	Jordan rock 64
Area of filtration.	507.94 cm^2	507.94 cm^2
Product acid strength % P_2O_5	25.01 %	28.9 %
Density of product acid .	1.37	1.31
Viscosity of product amid.	9.3 cP	6.8 cP
Total P_2O_5 filtered in kg.	4.59 kg	2.59 kg
Duration of filtration	45.5 min	25.5 min
Rate of filtration kg P_2O_5/M^2/hr	119.6	136.6 kg
Vacuum applied, inches of mercury	15 in.	15 in.
Density of first wash acid	1.22	1.19
Density of second wash acid	1.09	1.03

Phosphogypsum

	Lagarban rock	Jordan rock 64
Moisture in phosphogypsum	36.0 %	31.2 %
Rock + littice P_2O_5	2.07 %	1.06 %
Water soluble P_2O_5	0.31 %	0.15 %
Recovery efficiency	95.2 %	96.9 %

Efficiency and Consumption

	Lagarban rock	Jordan rock 64
100 % sulphuric acid consumption per kg P_2O_5 in the phosphate rock	2.67 kg (26.1 % P_2O_5 in rock)	2.87 kg 32.47 % P_2O_5 in rock).
100 % sulphuric acid consumed per kg phosphate rock	2.95 kg	0.93 kg
Phosphate rock consumption per kg P_2O_5	3.8 kg	3.08 kg

Jordan rock, suggesting the less consumption of antifoaming agent.

4. Due to lower CaO/P_2O_5 ratio and on the other hand higher quantities of acid insoluble (SiO_2 up to 18.4 %) poor P_2O_5 rock content, the sulphuric acid consumption per kg P_2O_5 is less as compared to Jordan rock.

5. Lagarban rock contains high contents of silica, iron, aluminium and magnesium oxides by which the viscosity of the liquid phase of the slurry becomes very high which affects the crystal growth and filtering rate of the product acid and requires greater filtering area as given below:

	Lagarban rock	Jordan rock
Filtration area requirement of 100 tons P_2O_5/day	35.7 M^2	30.5 M^2
Viscosity of the product acid	9.3 cP	6.8 cP.

6. Strength of the phosphoric acid produced is up to $25-26$ % P_2O_5. It was difficult to achieve the higher concentration H_3PO_4 beacuse due to the low P_2O_5 contents of rock. Density of the slurry becomes high up to 1.57 which results in poor crystal growth and lowering the filtering rate.

7. Due to the low reactivity of the Lagarban rock, slightly higher quantity of free sulphuric acid 2.9 % is needed for this rock as compared to Jordan rock (2.3 % free H_2SO_4) for better crystal growth and minimizing the P_2O_5 losses.

8. Product acid obtained with Lagarban phosphate rock is light green in colour, gives greater sedimentation on standing because of the high contents of R_2O_3 in the phosphate rock as compared to the acid formed from Jordan phosphate rock.