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UTILISATION OF LOW GRADE ROCK PHOSPHATES IN THE MANUFACTURE OF PHOSPHORIC ACID

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ABSTRACT

As a result of increasing availability of low grade rock phosphates and high costs associated with beneficiation processes, it has become necessary to develop suitable processes for utilizing low grade ores abundantly available. Such low grade rocks containing high percentages of silica, feral and other impurities cannot be directly used in above processes due to their well known adverse effects.

Manufacturing wet process phosphoric acid from such low grade rocks requires a different technique. A two stage filtration is incorporated. By using mixtures of phosphoric acid and H_2SiF_6 or phosphoric acid and HNO_3 , the P_2O_5 in the rock is selectively extracted leaving the impurities with residual filter cake in the first stage. The filtrate of this stage is treated with H_2SO_4 to form crystallised gypsum of high purity, which is filtered in the second stage. The product phosphoric acid containing 22 to 27% P_2O_5 is isolated from the recycled stream and concentrated to 54% P_2O_5 . The H_2SiF_6 or HNO_3 is recovered and recycled to the process. The salient features of the process described in this article are a two stage filtration, the first to remove silica and unextracted impurities and the second to separate gypsum of high purity with minimum P_2O_5 loss.

1. INTRODUCTION

Technical grade phosphoric acid manufactured by the "Wet Process" requires the use of rock phosphate with low levels of silica, R_2O_3 , carbonate and other impurities. The supply of such grade of phosphate rocks is dwindling all over the world or the processing of low grade rocks into suitable quality by washing and beneficiation is becoming increasingly expensive necessitating renewed efforts for the utilisation of low grade rock phosphates, with higher levels of inerts and impurities.

Low grade rock phosphates have various impurities such as SiO_2 , Fe_2O_3 , Al_2O_3 , etc. which cause processing difficulties in conventional phosphoric acid plants such as high grinding cost, higher viscosities of slurry, poor filtrability of gypsum and lower recovery of P_2O_5 . The quality of the byproduct phosphogypsum further deteriorates making it unsuitable for its conventional uses.

Beneficiation processes to increase percentage P_2O_5 for upgrading rocks suffer from the inherent disadvantage of loss of P_2O_5 in the tailings. They require a large quantity of water and energy and are expensive.

This paper describes a new process for the manufacture of commercial phosphoric acid from low grade phosphates having high silica and feral impurities. The process is based upon selective chemical extraction of P_2O_5 by leaching the rock with mixture of phosphoric acid, hydrofluosilicic acid or nitric acid. The reaction mass is filtered to remove silica and feral impurities, which are discarded, and the filtrate is acidified with sulphuric acid to precipitate gypsum. The product containing 22-27% P_2O_5 is taken from the recycle stream of mixed acids and concentrated to 52-54% P_2O_5 . H_2SiF_6 or HNO_3 are recovered and recycled to the process and gypsum of high purity is obtained as a valuable byproduct. The process has been investigated in detail in laboratory and tested stagewise on pilot plant on low grade rock phosphates from the Indian mines at Jhabua and Sagar of Madhya Pradesh and Maton rock from Rajasthan. The results of our above studies are the subject matter of this paper (References 3 to 9).

2. LOW GRADE ROCKS

The analyses of Jhabua, Maton and Sagar rocks used in our process are given in Table 1. For comparison the analysis of standard Morocco rock is also included in above table.

Table 1 - Chemical Analyses of Rock phosphates (Dry Basis)

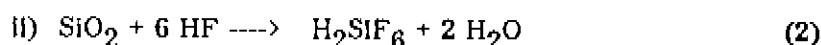
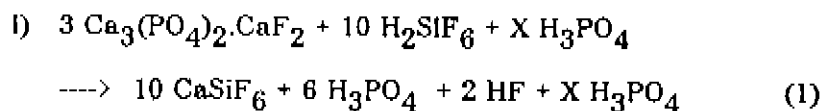
Constituents (Wt. %)	JHABUA (M.P.)	MATON (RAJASTHAN)	SAGAR (M.P.)	MOROCCO
P ₂ O ₅	28.603	24.47	26.77	33.4
CaO	41.848	34.55	36.48	50.6
SiO ₂	19.65	33.80	22.53	1.92
F	3.00	2.29	1.953	3.97
CO ₂	0.75	0.95	1.322	4.51
Al ₂ O ₃	1.924	0.71	3.17	0.43
Fe ₂ O ₃	1.15	1.832	7.57	0.20
MgO	0.052	0.21	0.41	0.33
Na ₂ O	0.047	0.05	0.04	0.70
K ₂ O	0.184	0.072	0.361	0.09
Organics	0.32	0.28	0.551	0.26
SO ₃	0.058	Traces	Traces	1.62
Cl	0.006	0.0025	0.006	0.028
Zn	0.04	0.013	0.019	0.028
Cu	0.0032	0.0024	0.0034	0.0032
Mn	0.056	0.54	0.083	0.0022
Pb	0.013	0.0125	0.0113	0.0097

Jhabua and Maton rock phosphates used in our process consist of mineral apatite and fall in the category of siliceous rock phosphate, and the Sagar rock is not only siliceous but is also high R₂O₃ bearing. The silica in both the cases is mostly present as quartz and R₂O₃ is present as their hydrous oxides. Iron is mostly present as magnetite. The presence of only silica in the rock phosphate lowers the BPL grade but not necessarily their chemical quality but the presence of feral impurities not only lowers the BPL grade but also has a very pronounced effect on the suitability of rock phosphate in phosphoric acid process.

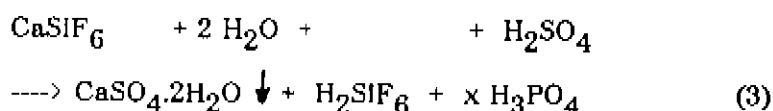
3. CHEMISTRY AND FLOWSHEET OF THE FLUOSILICATE PROCESS

The chemistry of the fluosilicate process can be summarised by following set of chemical equations:

A) Reaction



B) Crystallization of Gypsum



Referring to Figure 1 of the Fluosilicate process for the manufacture of merchant grade phosphoric acid and gypsum of higher purity, coarsely ground (-8 +25 mesh) low grade rock phosphate (1) is reacted in a stirred reactor (3) with a recycle acid mixture (15) of fluosilicic acid and phosphoric acid at a temperature of 65 to 70°C for a maximum period of 2 hours, when the phosphatic and fluorine content of rock phosphate are substantially solubilised. The resulting slurry is filtered in a vacuum filter (4) to remove insoluble impurities and silica (5) which is discarded. The clear filtrate (6) and washings are fed to a crystallizer (7) containing seed crystals of gypsum slurry at about 65°C along with 98% H₂SO₄ (2), with a residence time of 3 hrs. White crystalline dihydrate gypsum (9) is obtained and fluosilicic acid is regenerated after filtration in the second filter (8). The filtrate and washings containing fluosilicic acid and phosphoric acid are divided into two unequal portions, the smaller portion (11) is concentrated to give 52-54% P₂O₅ product phosphoric acid (14) and recovered H₂SiF₆ (13) is mixed with the larger stream (10) for recycling (15) to the reactor (3).

4. LABORATORY EXPERIMENTS ON FLUOSILICATE PROCESS

These experiments were carried out by using 200 gms. of coarser fractions of (-8 +25 B.S.S.) of Jhabua rock with recycled acid mixtures in a three litre flask supported on a heating mantle and fitted with an overhead stirrer, thermometer and dropping funnel at 70°C for two hours. The filtration was carried out at 500 mm Hg vacuum in a porcelain buchner funnel of 14 cm. dia. and the filtrate was collected in a 3 litre filtration flask. The results are summarised below:

- 4.1 The composition of recycle acid mixture was fixed up as 20 + 2% P₂O₅, 10 to 12% H₂SiF₆ and 0.5% (max.) H₂SO₄ taking into consideration the factors like solubility of CaSiF₆ in max. concentration of phosphoric acid and stability of the solution - In view of the fact that CaSiF₆·2H₂O is known to exist in two forms A and B, the A form is soluble but metastable and slowly gets converted to the stable form which is insoluble in the media. The presence of free H₂SiF₆ in the reaction media somewhat stabilizes the soluble form of CaSiF₆ formed in the reaction. It has been found that excess of free H₂SO₄ over and above 0.5%, results in lowering of P₂O₅ extraction from coarser rocks due to the phenomenon of coating of rock particles with gypsum. The solubility of fluoride compounds in various concentrations of phosphoric acid at 25°C is given in Table 2 (Ref. 1).

Table 2 - Stability of fluoride compounds from wet process phosphoric acid

	Solubility, wt. (%) 25°C				
	30% P ₂ O ₅ + gypsum	15% P ₂ O ₅ acid	5% P ₂ O ₅ acid	Pond water + gypsum	Distilled water
Na ₂ SiF ₆	0.20	0.69	0.87	1.11	0.50
K ₂ SiF ₆	0.25	0.24	0.21	0.23	0.14
NaKSiF ₆	0.26	0.5	0.68	1.13	0.72
CaSiF ₆ ·2H ₂ O	1.80	15.0	23.6	28.8	31.4
MgSiF ₆ ·6H ₂ O	4.0	21.8	32.8	35.2	36.0
Na ₃ AlF ₆	0.4	0.26	0.08	0.51	<0.02
NaK ₂ AlF ₆	0.50	0.19	<0.10	0.36	<0.03
Ca ₃ (AlF ₆) ₂ ·4H ₂ O	0.2	0.15	<0.09	0.36	<0.02
MgNaAlF ₆ ·2H ₂ O	0.5	0.15	0.07	<0.25	<0.04
Ca ₄ SO ₄ AlSiF ₁₃ ·10 H ₂ O	0.2	0.2	0.2	<0.01	<0.04
CaF ₂	0.1	0.12	0.07	<0.01	0.04
MgF ₂	0.5	0.37	0.23	0.31	<0.02

- 4.2 Though the extraction of P₂O₅ from coarser rock with above recycle acid mixture can even be achieved at ambient temperature (30°C) within a period of 2 hrs., the process was operated at 70°C in order to improve rate of filtration of silica mud obtained after the reaction. Also the recycle acid obtained after gypsum crystallization is at a temperature of 65°C. It has been observed by us that the % of P₂O₅ and F dissolution from the rock is identical (more than 95%) confirming to the presence of mineral fluorapatite (3Ca₃(PO₄)₂·CaF₂) in case of rock phosphates of Indian origin tested by us.
- 4.3 The time required for -25 mesh and -60 mesh rock for 95% extraction of P₂O₅ and F is only 15 minutes. For -8 +25 mesh rock 2 hrs. time is required.
- 4.4 Since the rock does not contain appreciable quantities of organics and carbonates, there was no frothing.
- 4.5 R₂O₃ dissolution was to the extent of 50% only.
- 4.6 The optimum ratio of P₂O₅ in rock to P₂O₅ in recycle acid was 1 : 6.
- 4.7 The rates of filtration of silica mud and gypsum at 60°C on the filter in the fluosilicate process were as follows:

1. Filter 1 Silica and R_2O_3 mud = 6.8 Tonnes $P_2O_5/M^2/day$
(Cake thickness - 4 mm)
2. Filter 1 Silica and R_2O_3 mud = 6.8 Tonnes $P_2O_5/M^2/day$
with 10% gypsum as filter aid
3. Filter 2 Gypsum = 6.5 Tonnes $P_2O_5/M^2/day$
(Cake thickness - 25 mm)
(Crystal size 150x500 microns)

The clear filtrate develops turbidity due to the precipitation of $CaSiF_6 \cdot 2H_2O$ and other fluorine compounds at $60^\circ C$ and below, and must not be stored beyond 3 hours.

- 4.8 Unlike conventional process there is little effect of % free H_2SO_4 in the crystallizing slurry on the losses of lattice P_2O_5 in the gypsum. The lattice P_2O_5 of gypsum was 0.26% for a crystallization period of 3 hrs. at $66^\circ C$. Free H_2SO_4 was maintained in the slurry at 0.5%
- 4.9 The gypsum obtained in this process has good filtrability and is dazzling white in nature with minimum 98% purity (Table 3).

TABLE 3

Analysis of By product Gypsum from DMCC Processes (Wt.%)
using Jhabua and Sagar rock phosphates

Component	Fluosilicate Process (Jhabua)	Nitric Acid Process (Sagar)	Conventional Dihydrate Process (Morocco Rock)
Appearance	Dazzling white	Dazzling white	Off white
$CaSO_4 \cdot 2H_2O$	98.0 min.	98.0 min	90% min.
Total P_2O_5	0.4	0.57	1.2
W/S P_2O_5	0.2	0.26	1.0
SiO_2	Traces	Traces	3.5 to 4.0
F	0.15	0.28	1.5
R_2O_3	<0.02	<0.025	0.2 to 0.3

4.10 The P_2O_5 losses based upon P_2O_5 input in rock are as follows in fluosilicate process.

- 1) Unreacted P_2O_5 : 3.5%
(First stage - mud)
- 2) Soluble P_2O_5 : 1.32%
(First stage - mud)

3) Co-crystallised P_2O_5 : 1.21%
(Second stage - gypsum)

4) Soluble P_2O_5 : 0.4%
(Second stage - gypsum)

4.11 Product stream concentration of phosphoric acid and recycle of acid mixture

The filtrate and washings of gypsum crystallization is divided into two streams A & B. The smaller stream A equivalent to product P_2O_5 consisting of approximately 22% P_2O_5 is concentrated by evaporation at approx. 90°C, at 100 mm Hg vacuum to 52-54% P_2O_5 product phosphoric acid and the recovered H_2SiF_6 is mixed with the larger stream B for recycling the acid mixture back to the reaction stage. The overall recovery of P_2O_5 from rock is 93% only. The analysis of product phosphoric acid obtained is given in Table 4 along with typical analysis of concentrated acid from conventional dihydrate plant based on Morocco rock.

TABLE 4

Analysis of Phosphoric Acid from DMCC Processes (Wt.%)

Component	Fluosilicate Process (Jhabua)	Nitric Acid Process (Sagar)	Conventional Dihydrate Process (Typical)
P_2O_5	54.5	55.6	54.5
H_2SO_4	1.5	4.0	3.0
HNO_3	-	1.06	-
Al_2O_3	1.5	1.7	0.85
Fe_2O_3	0.95	2.7	1.0
F	0.8	0.38	0.4

4.12 Dazzling white, very high purity gypsum produced as a byproduct is suitable for a number of specialised applications such as in the manufacture of white cements and plaster boards, and as a part substitute for costly titanium dioxide filler in paper manufacture (Ref.2).

4.13 Limitations of the Fluosilicate Process

(1) It is not possible to process low grade rocks containing higher than 3% feral impurities by this process, since the passivation of feral impurities in this process is not more than 50% and the presence of higher concentration of such impurities makes the process "unstable" due to the losses of fluorine values in the form of $CaSiF_6 \cdot 2H_2O$, and other fluorine compounds, along with the silica mud. The product phosphoric acid obtained from rocks with higher R_2O_3 is very impure and shows sludge formation during concentration at 40% P_2O_5 only.

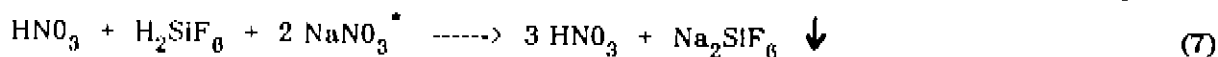
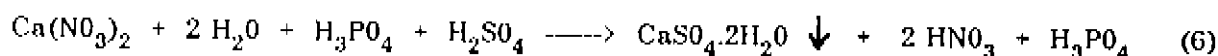
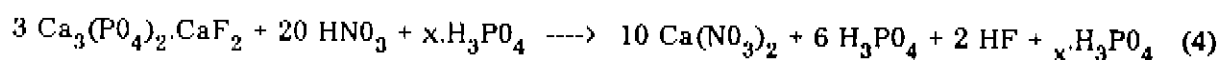
- (2) The process involves two stages of filtration, but this drawback can be overcome if the high purity byproduct white gypsum can be marketed. It is more than off-set by the saving in costs associated with beneficiation of rock.
- (3) In this process a dilute acid of 20-22% P_2O_5 strength is obtained along with 10% H_2SiF_6 after gypsum filtration whereas in conventional dihydrate process 28 to 30% P_2O_5 acid is obtained with only 3% H_2SiF_6 . The steam required for concentration to 54% P_2O_5 is higher than that in conventional plants.
- (4) The ratio of P_2O_5 in rock to P_2O_5 in recycle acid is 1 : 6 which is higher than that in conventional plants.

5. NITRIC ACID PROCESS

5.1 The limitation of ferrous content stipulated for fluosilicate process is partly solved by substituting hydrofluosilicic acid with nitric acid in the process. The presence of nitric acid in the recycle acid gives following advantages to the process compared to the fluosilicate process:

- (1) P_2O_5 concentration could be raised from 20-22% level to 25- 27% level.
- (2) R_2O_3 passivation could be raised from 50% to minimum 80%. By prior calcination to $950^\circ C$. It could be increased to 90%.

5.2 Chemistry and flowsheet of nitric acid process



*In place of $NaNO_3$ other sodium salts like Na_2CO_3 , Na_2SO_4 can also be used. $NaCl$ is prohibited due to generation of corrosive HCl .

5.3 The Nitric Acid process is described with reference to Figure 2.

The sample of low grade Sagar rock phosphate (1) of BSS -60 mesh (less than 0.25 mm) size is reacted in a well stirred reactor (3) with a recycle acid mixture (12) comprising of 25-27% P_2O_5 , 10-12% HNO_3 , 3% H_2SiF_6 and 2% H_2SO_4 at a temperature of around $70^\circ C$, for a period of 15 minutes only. This results in more than 98% dissolution of P_2O_5 and only a maximum of 20% dissolution of R_2O_3 impurities from the rock. The resulting reaction slurry is treated with a small quantity (100 ppm only) of flocculating agent (4) and filtered (5) so as to remove the silica and insolubles in the form of a red mud (6) which is discarded.

The clear filtrate (7) is then fed to crystallizer (9) maintained at a temperature of $60-65^\circ C$ and reacted with 98% H_2SO_4 (8) for period of 3 hrs. The slurry of white gypsum crystals along with the regenerated HNO_3 is vacuum filtered (10) and washed counter currently with leach liquors and water. The filtrate from (10) is divided into two streams: A (12) and B (13). The stream A (12) is recycled to reaction (3) along with make-up HNO_3 (2).

Stream B (13) is concentrated (14) to product phosphoric acid of 54% strength (15).

The HNO_3 and H_2SiF_6 evolved are absorbed in a scrubber (16) with recycled acid (17) and sent to a precipitation tank (18) to react with NaNO_3 (19) or any other suitable sodium salt to precipitate insoluble byproduct Na_2SiF_6 (22), which is recovered by filtration (20). The filtrate (21) containing recovered HNO_3 is recycled to the reactor (3).

6. LABORATORY EXPERIMENTS ON NITRIC ACID PROCESS

- 6.1 These experiments were carried out by using 200 gms. of coarse fractions of (-60 mesh B.S.S.) Sagar rock with reaction mixture containing by weight 25% P_2O_5 , 12% HNO_3 and 2% H_2SO_4 in a manner similar to that followed for fluosilicate process.
- 6.2 The quantity and composition of recycled acid was fixed up by the ratio of P_2O_5 in rock to P_2O_5 in recycled acid as 1 : 6. HNO_3 requirement was calculated as per equation No.4.
- 6.3 A short residence time of 15 minutes was given for the first stage so as to achieve maximum dissolution of P_2O_5 from the rock and minimum dissolution of feral impurities.
- 6.4 The strength of P_2O_5 in recycled acid was maintained between 25 to 27% so as to crystallise out the gypsum as dihydrate from the mixture of phosphoric acid and regenerated 12% HNO_3 at 60-65°C temperature in the second stage of the process.
- 6.5 The rates of filtration of silica + feral mud and gypsum at 60°C were as follows:
- | | | |
|---|---|--|
| 1) Filter 1 Silica + feral mud
(cake thickness 7 mm) | = | 2.0 Tonnes $\text{P}_2\text{O}_5/\text{M}^2/\text{day}$ |
| 2) Filter 1 Silica + Feral mud
(with 10% gypsum as filter aid) | = | 3.0 Tonnes $\text{P}_2\text{O}_5/\text{M}^2/\text{day}$ |
| 1) Filter 2 Gypsum
(cake thickness 12 mm) | = | 6.2 Tonnes $\text{P}_2\text{O}_5/\text{M}^2/\text{day}$
(crystal size 50 x 150 microns) |
- 6.6 The analysis of product phosphoric acid obtained by nitric acid process is given in Table 4 alongwith that of conventional dihydrate process acid.
- 6.7 The gypsum analysis is given in Table 3 and compared with conventional dihydrate process gypsum.
- 6.8 The make-up nitric acid requirement of the process is max. 150 kg./tonne of P_2O_5 . The breakdown of losses is as follows:

Process step	% loss of HNO_3 over stoichiometry
1. Filter 1 + Filter 2	0.95
2. Product acid	0.7
3. In scrubbing (90% efficiency)	1.3
4. Handling loss	1.5

Total losses are 4.45% of 3.3 tonnes of HNO_3 required i.e. = 147 kgs.

6.9 The P_2O_5 losses based upon input in Sagar rock are as follows:

- 1) Unreacted P_2O_5 : 0.76%
(First stage - mud)
- 2) Soluble P_2O_5 : 64.23%
(First stage - mud)
- 3) Co-crystallised P_2O_5 : 0.95%
(Second stage - gypsum)
- 4) Soluble P_2O_5 : 0.65%
(Second stage - gypsum)

7. ADVANTAGES AND LIMITATIONS OF THE NITRIC ACID PROCESS OVER THE FLUOSILICATE PROCESS

- 7.1 Low grade coarse rock with high silica and feral impurities can be used, since the degree of passivation of R_2O_3 impurities is higher at 80%. With calcined rocks, the degree of passivation can be as high as 90%.
- 7.2 The problem of losses of F values in silica mud and the subsequent imbalance of the process are completely eliminated.
- 7.3 As in the case of Fluosilicate process the ratio of P_2O_5 in rock to P_2O_5 in recycle acid is high as 1:6. If the ratio is lowered to 1 : 3 the gypsum passes to hemihydrate phase, making the process complicated.
- 7.4 The process involves two stage filtration but as in the case of fluosilicate process this is compensated by high purity gypsum.
- 7.5 Complete recovery of HNO_3 and its recycle is the key to the success of this process.

8. PILOT PLANT STUDIES AND FURTHER PROGRAMME

We had installed a 1 TPD pilot plant for studying the above processes with respect to material of construction, reaction and filtration rates and the quality of phosphoric acid and gypsum obtained from above low grade rocks. Rock was fed from a hopper by means of a vibrofeeder at the rate of 150 kg/hr to 2 reactors in series (MS/RL and PP/FRP) and the reaction slurry was filtered through a set of tray filters (MS/RL, 2 M² filter area) under 500 mm Hg vacuum. The filtrate was collected in a storage tank (MS/RL) from where it was pumped to 3 gypsum crystallizers (MS/RL & SS316) arranged in series. The gypsum slurry was filtered through another set of tray filters (MS/RL, 2 M² filter area). The filtrate was stored in a tank (MS/RL). Later on a plug flow reactor (SS-316) was also installed for studying the reaction of rock with recycle acid for shorter residence time of 5 to 15 minutes. In above pilot plant trials no major difficulty was faced and laboratory results for the reaction and filtration rates at both the stages were confirmed. The high purity gypsum produced on pilot plant was sent to Regional Research Laboratory, Hyderabad (India) for trials in the use as a paper filler for part substitutions of costly Titanium dioxide pigments and was approved.

9. SUMMARY AND CONCLUSIONS

With the availability of large quantities of low grade rocks and the increasing need for phosphate fertilizers, particularly in developing countries, ways and means are to be found sooner than later for making optimum usage of available raw materials and resources by each country. It is obvious that for manufacturing phosphoric acid from low grade, unbeneficiated rock phosphate containing varying percentages of silica feral and other impurities, they have to be processed in two stages. The impurities are to be removed by reacting with a suitable acid mixture in a premixer with a short residence time so as to leach out maximum P_2O_5 from such low grade rocks. The clear filtrate is to be processed to give purer quality white gypsum, with better outlets and higher price than conventional phosphogypsum of wet process phosphoric acid plants. The phosphoric acid obtained by DMCC process is of a suitable quality for the manufacture of such phosphatic fertilizers like TSP and ammonium phosphates. After purification by known methods such phosphoric acids can even be used for making industrial phosphates like STPP and sodium hexametaphosphates.

10. ACKNOWLEDGEMENT

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REFERENCES

1. "Chemical behaviour of Fluorine in the production of Wet Process Phosphoric Acid" by A. William Frazier, James R. Lehr and Ewsell F. Dillard - TVA.
2. Phosphorus & Potassium No.133, Sept-Oct., 1984, p.36.
"Phosphogypsum - Use in the paper industry turns over a new leaf"
3. Patent on Phosphoric Acid Process - India.
Complete specification No.154778 dated 27.2.1981.
Title - "An improved process for manufacture of phosphoric acid and gypsum from rock-phosphate.
4. Patent on phosphoric acid process - India.
Complete specification No.155760 dated 22.10.1982.
Title - "An improved process for manufacture of phosphoric acid and gypsum from rock phosphate".
5. Patent on phosphoric acid process - U.K.
Complete specification No.2094282 B dated 30.8.1984.
Title - "Process for the manufacture of phosphoric acid and cement grade gypsum".
6. Patent on Phosphoric acid process - European countries.
Complete specification No. 0087323 dated 3.9.1986.
Title - "Process to manufacture commercially acceptable phosphoric acid and gypsum from rock phosphate".
7. French translation of the above European patent at Belgium patent office, dated 5.11.86.

8. German translation of the above European Patent at Austrian patent office, No. E 21882 dated 12.9.1988.
9. Patent on Phosphoric acid process - Indian.
Patent Application No.227/BOM/87 dated 8.7.1987.
Title - "A process for manufacture of commercial phosphoric acid and high purity gypsum as principal products and other fluorine chemicals as byproducts from rock phosphate containing high percentages of silica and feral impurities".

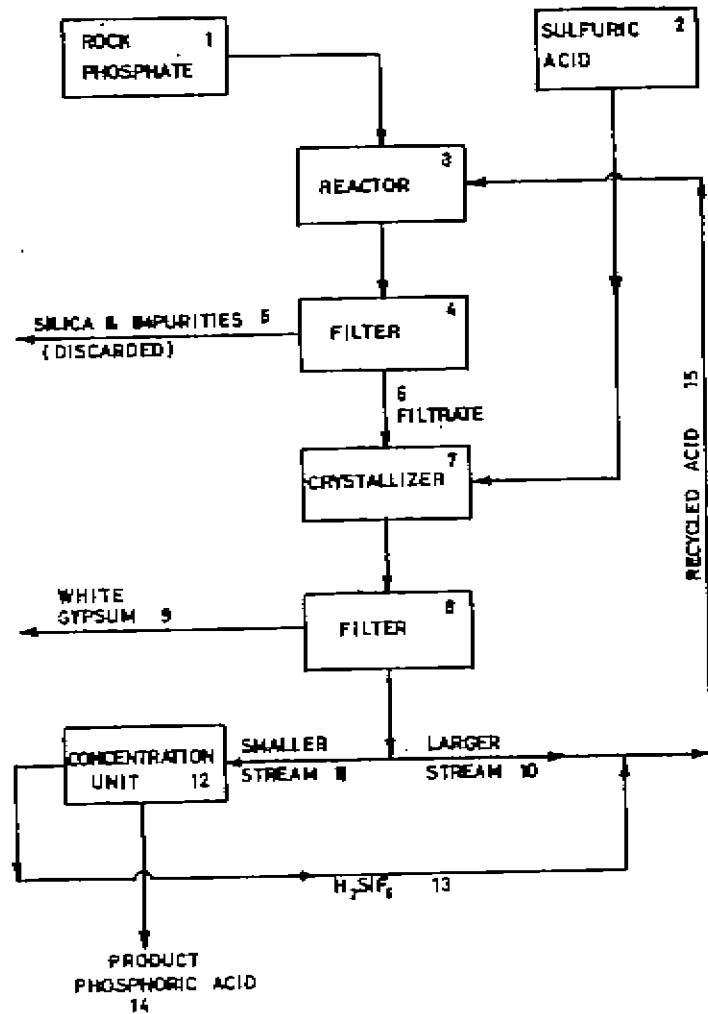


FIG. 1 FLUOSILICATE PROCESS

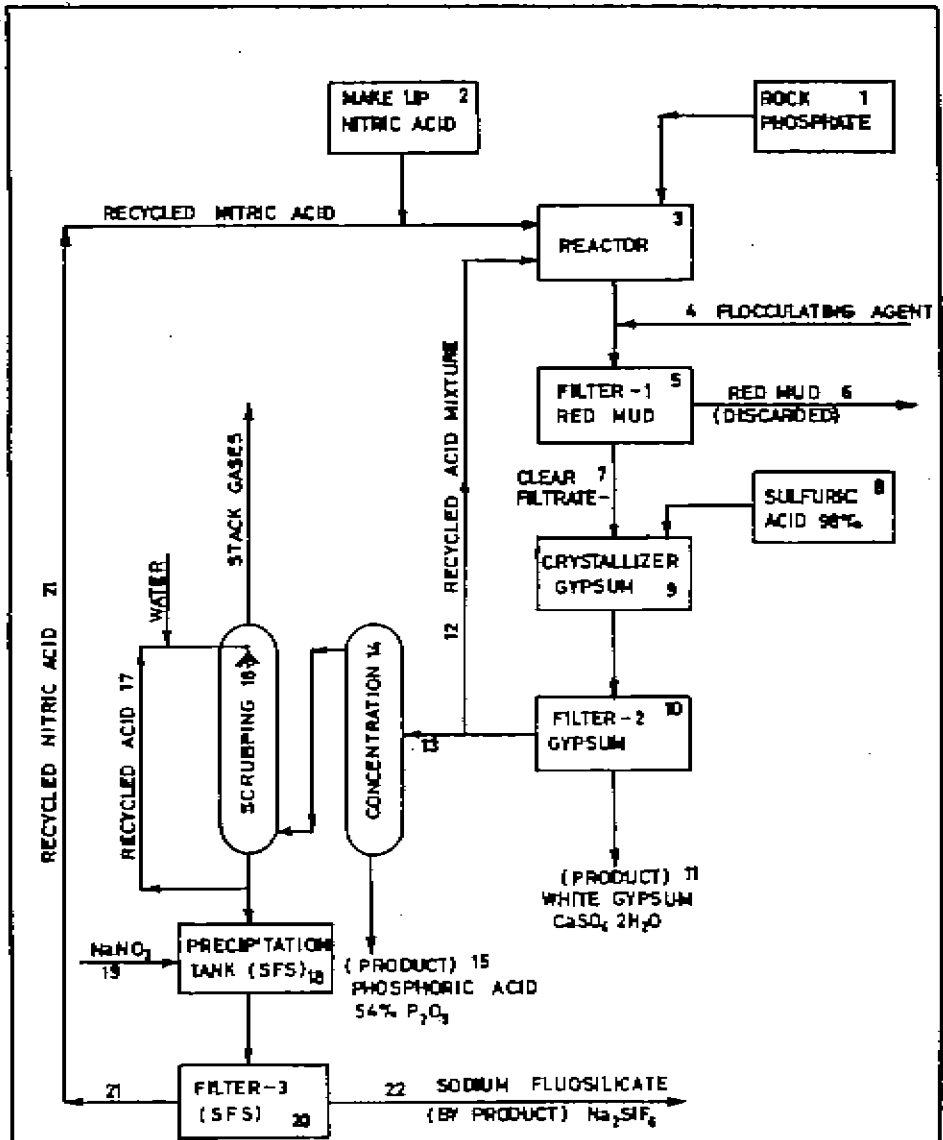


FIG. 2 NITRIC ACID PROCESS