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# THE RHÔNE-POULENC PHOSPHORIC ACID PROCESS AND THE ENVIRONMENT

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## 1.0 - INTRODUCTION

The RHÔNE-POULENC Phosphoric Acid Process was originally designed in 1953. Since then it has been constantly upgraded through the experience of more than 70 operating plants either within RHÔNE-POULENC or its licensees worldwide, representing about 20% of the present world capacity. Among these, the JORF LASFAR plant in Morocco should be mentioned as it is the largest phosphoric acid production facility in the world (eight trains of 500TPD $P_2O_5$) and will start in 1986.

RHÔNE-POULENC has also designed and developed an original filter, a rotating vacuum table filter, the UCEGO - RHÔNE-POULENC filter. Eighty-one of these have so far been constructed during the last 20 years (seven in the USA, six of which are in Florida).

The various aspects of the process and equipment have been already described in the past, particularly:

- The single reactor concept for the attack (1)
- The air cooling of the attack (2)
- The performance of the evaporation (3)
- The DIPLO process (4)

More recently modification and improvement of the RHÔNE-POULENC process has been presented (5, 6), especially in respect of energy saving and process optimization.

In this paper the environmental aspect of the process, and especially the fluorine discharge will be emphasized. We also will present an original way to recycle the fluorine back into the process. It is called the Internal Fluorine Valorisation process or the "VIF" process.

At the present time, Florida's phosphoric acid industry is undergoing a crisis brought about by declining fertilizer demand and stiffened foreign as well as domestic, competition. RHÔNE-POULENC'S prosphoric acid technology is uniquely well suited to present Florida conditions. Its ability to meet present EPA (Florida DER) environmental requirements, its low capital investment cost, as well as low total energy consumption and its ability to process a variety of rock feed make the RHÔNE-POULENC process a serious candidate for any plants that may be built in Florida in the future.

## 2.0 - FLUORINE DISCHARGE IN THE ACID PLANT

In the dihydrate process, the fluorine present in the phosphate (2-4% depending on the phosphate) is shared among:

- The gypsum (20-50%).
- The concentrated phosphoric acid (10-25%).
- The vapor produced during the concentration (40-60%).
- The emmissions from the attack reactor.

Only the last two items create specific environmental problem of fluorine discharge.

We will first review these two items and then present the process choice made by RHÔNE-POULENC. Then we will present the overall fluorine balance of a phosphoric unit taking into account all of the recycling.

As an example, the unit at DAROU, Senegal will be described. This plant which started in 1984, has been selected because, according to the site constraint, necessitating that the water circuit runs in a closed loop without using a pond system.

In conclusion of this chapter, we will discuss the different alternates of the process with the environmental advantages and drawbacks.

## 2.1 - Attack reactor cooling and gas treatment

There are two types of techniques for the heat removal of the sulfuric acid attack which are used:

- The air swept cooling.
- The vacuum cooling.

The first system is much simpler at the attack level but an air scrubber is required.

In the second system the vapor has to be condensed with water, this creates a large quantity of liquid effluent that leaves the system at 30-35°C and contains dissolved fluorides.

We are going to describe the first system which is at our opinion the best optimization of investment capital and operating cost, as well as presenting less of an effluent problem. In addition, it is particularly well adapted to the RHÔNE-POULENC process using a single tank reactor running at atmospheric pressure.

### 2.1.1 - Principle of air cooling

Special small agitators called "surface coolers" allow a good contact between the cooling air stream, circulating at the liquid surface and the agitated slurry. By so doing, we obtain saturated air at a temperature of 10 to 12°C below that of the slurry which is being cooled.

For example for a 900 MT/D $P_2O_5$ unit, (1000 ST/D $P_2O_5$) to maintain the reactor at 80°C, we need an air flow rate of 200,000 $m^3/h$ (110,000 ACFM) (Humidity 80%, temperature 32°C). The saturated air leaving the reactor contains about 5% of the fluorine existing in the phosphate which is scrubbed before being released.

2.1.2 - Scrubbing system

RHÔNE-POULENC process uses two kinds of scrubbers:

- The venturi scrubber with the following features:
  - High efficiency (2-3 transfer units).
  - Low investment and maintenance cost.
  - High pressure drop (0.3-0.4 PSI).

- The cyclonic column with the following features:
  - High efficiency of coalescence and demisting.
  - Low investment and maintenance cost.
  - Low pressure drop.
  - Limited efficiency (0.5-1.5 transfer units).

The type and quantity of this equipment is derived following analysis of the environmental standards to be met in order to design the scrubbing section of the plants, RHONE-POULENC has had to develope a new method of calculation which have been verified at both pilot and industrial scales (7).

2.1.3 - Results obtained in several RHÔNE-POULENC designed units

In the table of appendix 1, we report the results obtained in the three latest units designed recently by RHÔNE-POULENC (block diagram of the unit in appendix 2). It shows that:

1. The new calculation method we have developed has proven very accurate for the good design of the scrubbing equipment.

2. In the case of the AQABA unit which is the largest single train dihydrate plant in the world, the fluorine emission (0.01) lb/t of $P_2O_5$ in the air is lower than the American EPA standards (0.02 lb/t of $P_2O_5$).

2.1.4 - Typical design for a 900 MT/D $P_2O_5$ unit (1000 STPD)

In the case of a plant of 900 MT/D running with a conventional phosphates (Morocco, Florida, North Carolina...), in order to meet the American EPA standards, the scrubbing section would include in series: (see in appendix 3).

- A venturi scrubber.
- A single stage cyclonic column.
- A double stage cyclonic column.

This equipment design may be modified to facilitate the optimization of investment and operating cost.

### 2.1.5 - Operating conditions

The operating conditions are such that any precipitation of fluorine salt or silica are avoided due to the low pH of the scrubbing water through the system. Thus, as no scaling occurs, this section does not need any process washing, specific control, or maintenance. All of the scrubbing water used in these two systems is recycled into the washing section of the filter.

We will consider later the complete fluorine and water balance of the whole phosphoric plant. Meanwhile, we can conclude at this point that due to the air cooling system the RHÔNE-POULENC process does not generate any liquid effluent from the attack or filtration sections.

## 2.2 - Concentration

The acid produced in the attack of the dihydrate process contains 50 to 80% of the fluorine existing into the phosphate before its concentration from 26-32% to 40-54% $P_2O_5$.

Depending on the final concentration, about 60 to 90% of the fluorine contained in the dilute acid goes into the vapor phase which is con densed in a contact condenser fed with cold water. So the concentration step generates a large amount of warm water containing between 40 to 70% of the total fluorine existing in the phosphate. This water cannot be discharged without treatment and is recycled into the process after being cooled.

In order to reduce the fluorine concentration in the water, RHÔNE-POULENC recommends the recovery of the fluorine by an absorber located between the evaporator and the condenser. By so doing, we recover up to 80% in one step or 90% in two steps of the fluorine existing in the vapor (i.e. 35 to 60% of the fluorine existing in the phosphate). Therh byproduct of the absorber is a 20-25% fluosilicic acid solution which can be used for manufacture of fluosilicate, cryolite or aluminum fluoride.

In that case, the amount of fluorine discharged into the water circuit drops from the previous 40 to 70% to 10 to 15% of the total fluorine existing in the phosphate and as a result the fluorine concentration in water is much lower.

## 2.3 - Overall fluorine balance

### 2.3.1 - Typical example

Appendix (4) shows a typical simplified process flow sheet with $P_2O_5$, water and fluorine balance in the case of a unit of 900 MT/D $P_2O_5$ (1000 STPD $P_2O_5$) running with Florida rock.

The phosphoric acid process is a net consumer of water: in that case it requires about 180 T/h of fresh water which are fed:

- into the scrubber.
- as a make up in the cooling circuit.

The outlet of the concentration condenser is recycled after being cooled:

- Either by a cooling pond.
- Or by a cooling tower.

The choice between these two techniques depends on technical and economic criteria, one of the most important factor being the concentration of fluorine in the water because of its impact on:

- The corrosion problem.
- The scaling problem.
- The gaseous discharge.

In case one, previously considered, the concentration in the water recirculating loop would be around 3-5 g/l of fluorine which is low enough to use the cooling tower technique without corrosion problems.

Choice of cooling tower

The fluorine evolved at the top in the air will be about 2 kg/h i.e. 0.12 lb/t $P_2O_5$ which is higher than the American E.P.A. regulation. All the water will be recycled so there is no liquid effluent.

Choice of cooling pond

The size of the required pond will be about 200-300,000 $m^2$ (50-70 acres). The gaseous emissions from the pond are difficult to estimate: sensible assumption (8) (9) leads to a figure ranging between 5 to 20 kg F/h (0.3 to 1.2 lb F/t $P_2O_5$). The water balance will depend on the atmospheric conditions. In case of excess rain fall, water treatment may be needed.

Note: Comparison with other processes

In the processes using vacuum to cool the attack reactor, the condensation of the vapor coming from the vacuum cooler generates a water outlet containing fluorine (about 1700 T/h of water for a 900 MT Day $P_2O_5$).

This additional effluent goes to the cooling circuit increasing the fluorine level of the water. In general this level reaches about 10-12 g/l of fluorine.

So the vacuum cooling has the following drawbacks.

- Need of additional cooling capacity in the water circuit (either pond or cooling water) of about 65%.

- More severe problems of corrosion and scaling.

The different possible situations are well described in the paper of B. WALTMAIER (10).

2.3.2 - Industrial experience of DAROU (Senegal)

Appendix (5) shows the simplified process flow sheet of DAROU (Senegal). This unit of 720 T/Day $P_2O_5$ capacity was commissioned in 1984. As water is scarce in this site, the following choices have been made:

- Dry discharge for the gypsum.
- Closed circuit for the water with a cooling tower.
- Recovery of $H_2SiF_6$.

Industrial results

The fluorine concentration of water loop ranges between 3 to 10 g/l according to the functioning of fluorine absorbers (from 40% to 80%).

The total fluorine evolvement is:

- 1 kg/h from the air scrubber.
- 2 kg/h from the cooling tower.

i.e., a total of 0.22 lb/t $P_2O_5$.

which is much lower than any site using a cooling pond.

## 3.0 - RECYCLING OF FLUOSILICIC ACID

As the use of fluosilicic acid or its derivated products is limited, this flow may become an effluent which has to be eliminated at the lowest cost and without harm to the environment. This is why RHÔNE-POULENC is presently developing a new process which consists in using fluosilicic acid for acidulation of phosphate. It is called the Internal Valorisation Fluorine Process or "VIF" Process.

## 3.1 - Chemical approach

The attack of phosphate by $H_2SiF_6$ leads to many complexes which more or less precipitate and are often very difficult to filtrate (among them the following complexes could be mentioned according to the Na and Mg content in the rock:

- $Na_2SiF_6$ Sodium fluosilicate.
- Mg Na $AlF_6$, $2H_2O$ Ralstonite.
- $CaSO_4$ $CaSiF_6$ $Ca_2$ (OH) $AlF_6$, 12 $H_2O$ Chukhrovite
- $CaF_2$ Calcium bifluoride.
- $PO_4H_2Ca$ Monocalcium phosphate.

Several attempts of fluosilisic attack have been achieved. For instance, in a sequential attack, BANNING (11) obtained mainly $CaF_2$.

In our pilot study, we have run continuous attack with the following objectives:

- Maximum $P_2O_5$ yield.
- Best fluorine insolubilisation.
- Best filtration rate.

We found that the best insoluble complex which answer the above objective is:

<u>THE CHUKHROVITE</u>

The precipitation conditions of Chukhrovite is the reactor tank is:

- $P_2O_5$ concentration 27-30%.

- Ration $Ca/PO_4$ = 0.4 (in fact, it is more accurate to put cation/anion = 0.4).

- Temperature 75°C (max. 80°C). The reaction is almost athermic.

- Long residence time (6-8 hours).

Depending on the type of phosphate, alumina and sulfuric acid have to be added to the tank to obtain the Chukhrovite crystals. The $Ca/PO_4$ ratio involves a recycling of dilute phosphoric acid coming from the sulfuric attack.

So the final process scheme is as described in appendix (6) where we have two lines:

- The main line with sulfuric attack.
- The side line with fluosilicic attack.

They are connected at three levels:

- Recycling of dilute phosphoric acid from sulfuric attack to fluosilicic attack in order to obtain the good ratio $Ca/PO_4$.

- Recycling of solution from fluosilicic attack to the main line. As the calcium content in the first one is rather high, a desulfatation of the main flow occurs.

- Recycling of fluosilicic acid from concentration to fluosilicic attack.

3.2 - Results:

Appendix (7) shows the pilot results obtained with different phosphates (Taiba, Togo, Morocco K., Florida).

- $P_2O_5$ yield: Optimum has not yet been received for Morocco K, and Florida rock. Nevertheless these losses (10-15%) correspond to about 1% of the total $P_2O_5$ throughout.

- Filtration rate: The chukhrovite filtration rate is rather higher than the gypsum filtration rate.

- Fluorine precipitation: The fluorine remaining in solution is recycled to the concentration and back to the fluosilicic attack. So the rather low yield does not correspond to a loss.

- Saving of sulfuric acid: It comes from the addition of two factors:

  - Saving due to the replacement of sulfuric acid by fluosilicic acid (3-4%).

  - Saving due to the fact that fluosilicic attack produces a phosphoric solution which has a high content in calcium. At the mixing of this flow with the main flow containing free sulfuric, a precipitation of gypsum and chukhrovite occurs. So all the free sulfuric is used to produce phosphoric acid which causes an additional saving of about 2% compared to the conventional process.

3.3 - "VIF" process advantages

3.3.1 - Environment

The whole fluorine of the phosphate ends:

- Either in the gypsum.

- Either as a solid complex which can be discharged with the gypsum.

- Either in concentrated phosphoric acid.

3.3.2 - Sulfuric savings

The specific consumption of sulfuric acid for phosphate attack drops by 5 to 7% thus a potential saving of 7 to 10 $/t P2O5 on sulfur (valued at 150 $/t).

3.3.3 - Quality of phosphoric acid

Compared to the conventional process, the final concentrated acid contains:

- More calcium: 0.2 to 0.5% instead 0.02 to 0.05%.
- Less sulfate: 0.5% instead of 3-4%.
- The same amount of fluorine 0.3-0.4%

The low content of sulfate is an important advantage for two reasons:

- The phosphoric acid can be concentrated up to 60% without problem.

- After concentration, there is no post precipitation of gypsum.

Notes:

- The additional investment for this "VIF" process corresponds to 15 to 20% of the total investment of a classical unit and the pay back based on sulfuric acid saving is about two years.

- This process is patented (US patent no. 4, 557, 915 issued on 12/10/85).

## 4.0 - CONCLUSION

The constant effort of RHÔNE-POULENC to minimize the fluorine discharge from phosphoric acid manufactures has led to a process with the following characteristics:

Liquid effluent

Attack filtration step
Thanks to the air cooling system and the recycling of the water used in the associated scrubbers, there is no liquid effluent.

Concentrated step

Thanks to the new process of Internal Valorisation of Fluorine ("VIF" process), the fluosilicic acid can be recycled into the process. The small amount of fluorinated water coming from the final condensation can be easily recycled. So liquid effluent can be completely avoided.

Gaseous effluent

Attack filtration concentration

Fluorine discharge lower than 0.02 lb/t $P_2O_5$.

Water recycling

Fluorine discharge depending upon the cooling system.

- With a cooling tower it can be maintained at a level of 0.1 lb/t $P_2O_5$.
- With a cooling pond the level reaches 0.2 to 1 lb/t $P_2O_5$.

With these very good environmental features the RHÔNE-POULENC process is one of the cleanest processes in existence, and easily meets all of the current E.P.A. standards.

# REFERENCES


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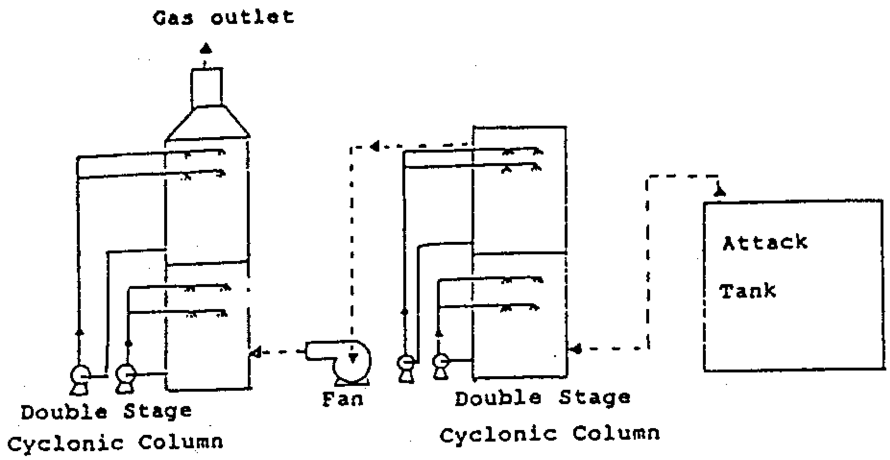
# — PERFORMANCE OF OPERATING PLANTS —

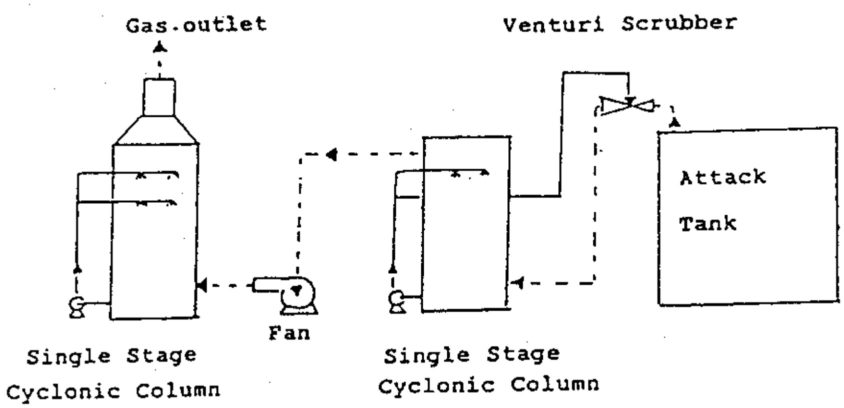
| PLANT LOCATION<br>Commission date | JORDAN<br>AQABA<br>1982 | SENEGAL<br>DAROU<br>1984 | SCOTLAND<br>LEITH<br>1982 |
|---|---|---|---|
| Daily P205 output MTPD | 1250 | 720 | 150 |
| (STPD) | (1378) | (794) | (165) |
| Rock analysis P205 % | 33.2 | 36.5 | 36.5 |
| F % | 3.9 | 3.5 | 3.8 |
| **Running conditions** | | | |
| F evolving from tank (kg/h) | 330 | 180 | 34 |
| (lb/h) | 728 | 400 | 77 |
| **Results of calculations** | | | |
| Venturi scrubber | | | |
| Throat velocity (m/s) | - | 53.6 | 47.6 |
| L/G (kg/kg) | - | 1 | 1 |
| NTU | 0 | 2.5 | 2.5 |
| Cyclonic column | | | |
| 1st cyclonic column | | | |
| Stage number | 2 | 1 | 1 |
| L/G (kg/kg) | 2.4 | 1 | 2.1 |
| Number of spray level | 2 | 1 | 1 |
| NTU | 3.2 | 0.45 | 0.6 |
| 2nd cyclonic column | | | No |
| Stage number | 2 | 1 | - |
| L/G (kg/kg) | 2.45 | 2 | - |
| Number of spray level | 2 | 2 | - |
| NTU | 3.25 | 0.95 | |
| **Total calculated NTU** | 6.45 | 3.9 | 3.1 |
| **Results of measurement** | | | |
| F at stack discharge | | | |
| kg/h | 0.230 | 2 | 0.50 |
| lb/h | 0.507 | 4.4 | 1.1 |
| lb/T P205 | 0.009 | 0.15 | 0.16 |
| NTU back calculated from measurement | 7.3 | 4.4 | 4.1 |

- AQABA SCRUBBING SECTION DIAGRAM

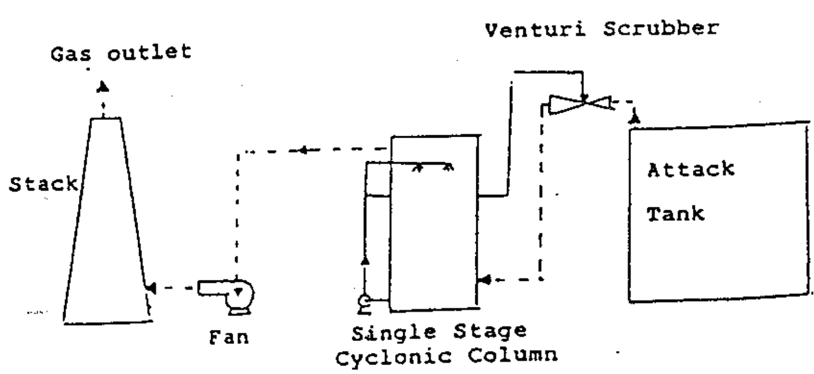
APPENDIX 2

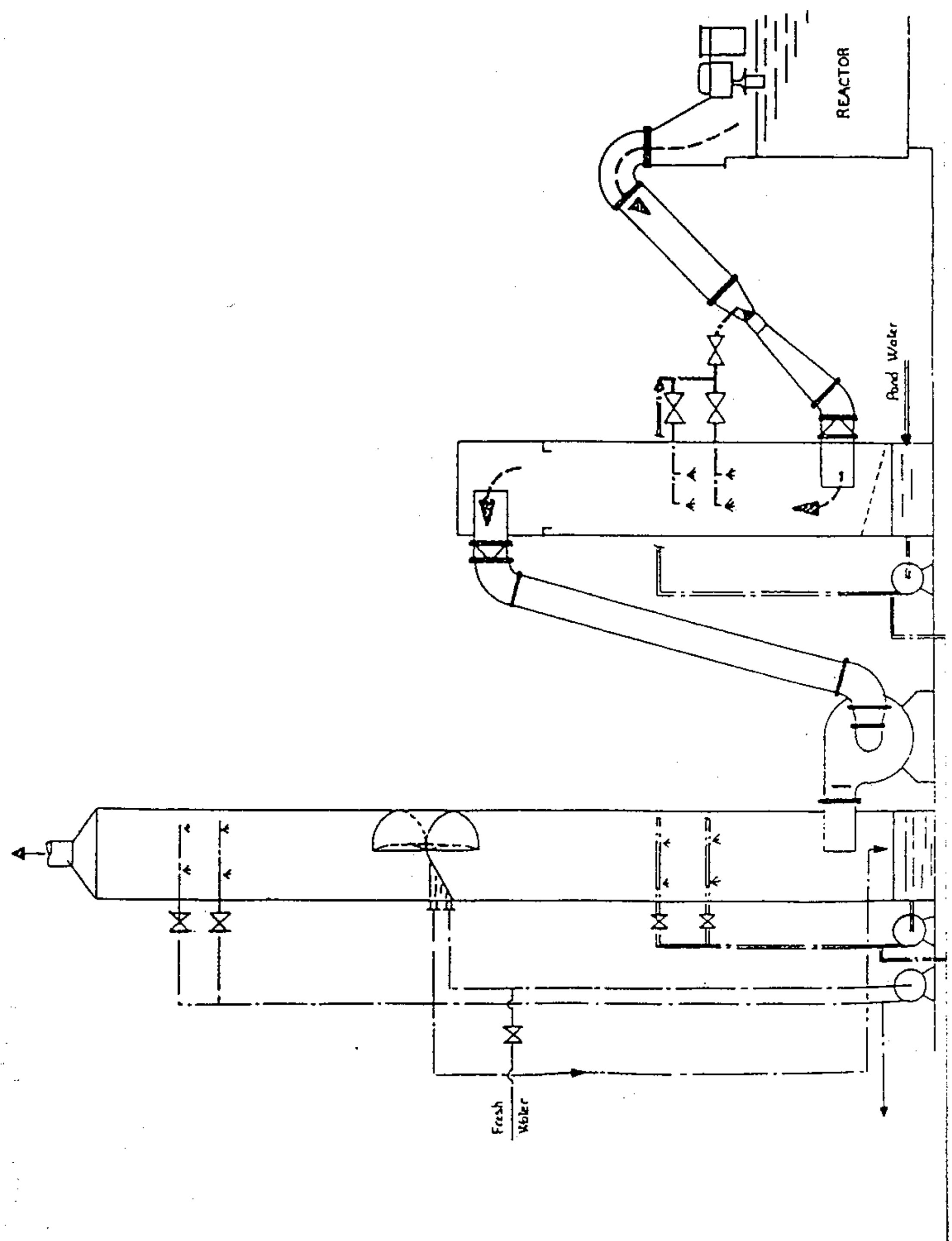



- DAROU SCRUBBING SECTION DIAGRAM

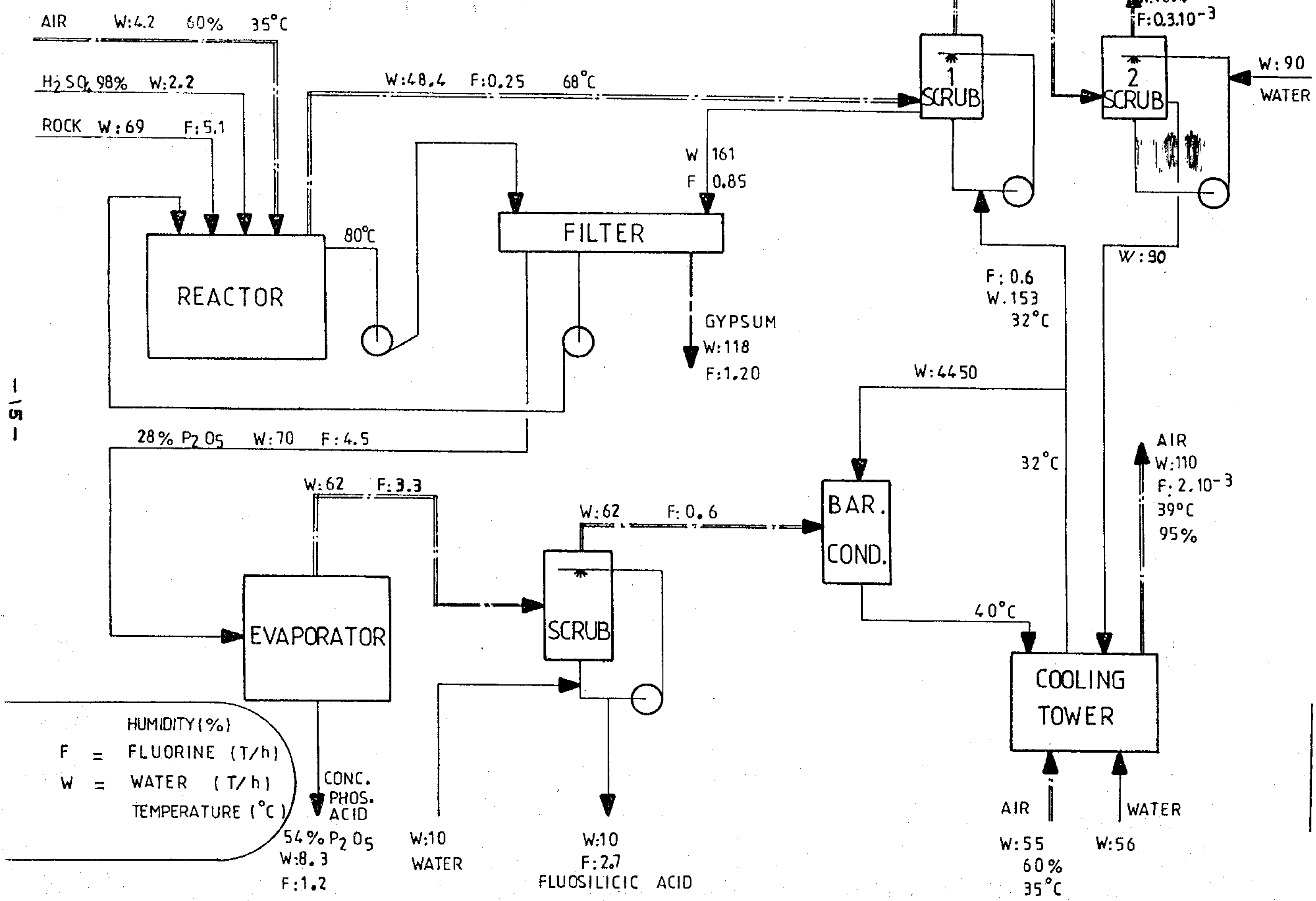



- LEITH SCRUBBING SECTION DIAGRAM



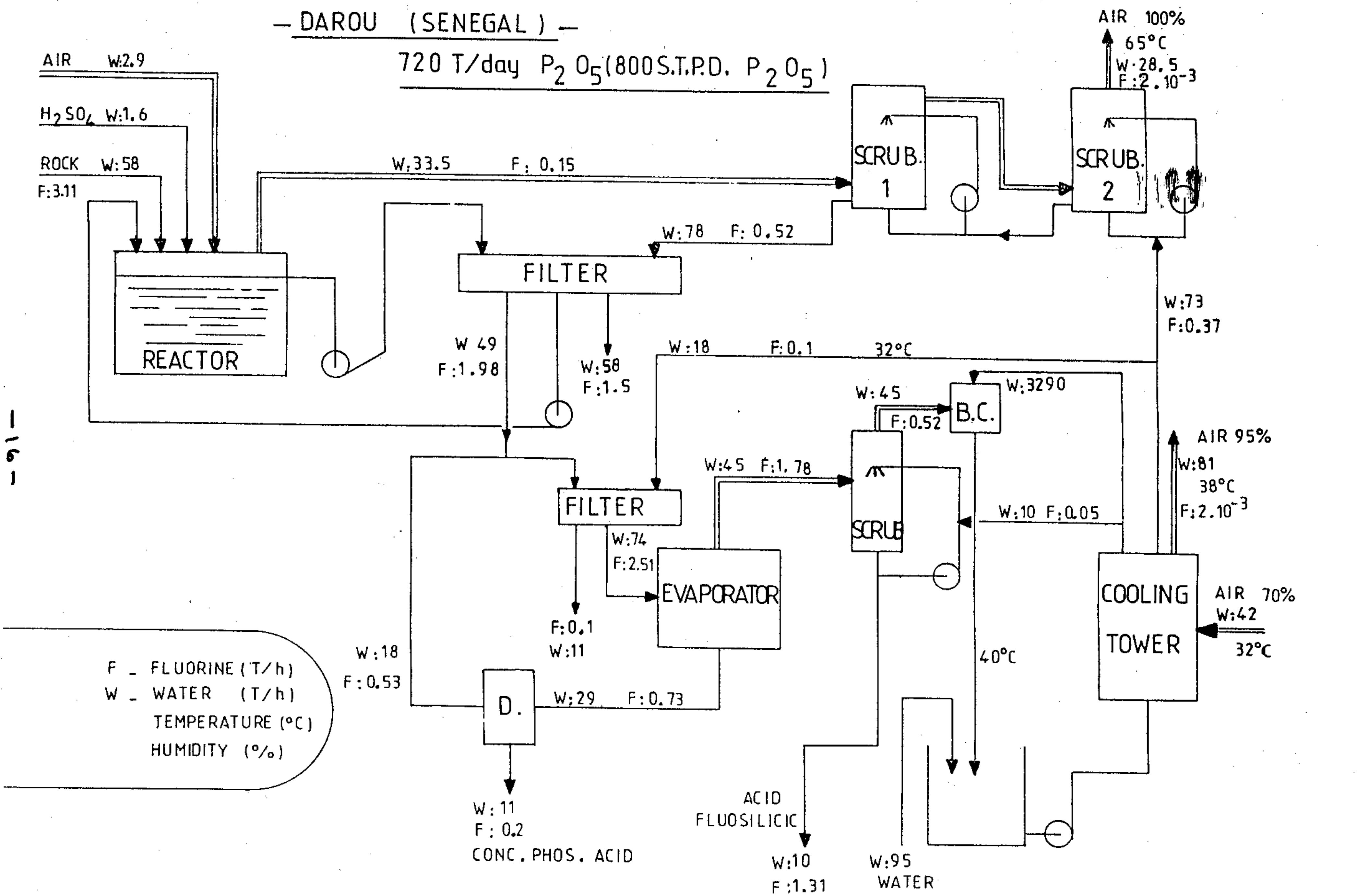

REACTOR
Pond Water
Fresh Water

## — FLORIDA — 900 T/day $P_2O_5$ (1000 S.T.P.D. $P_2O_5$) —



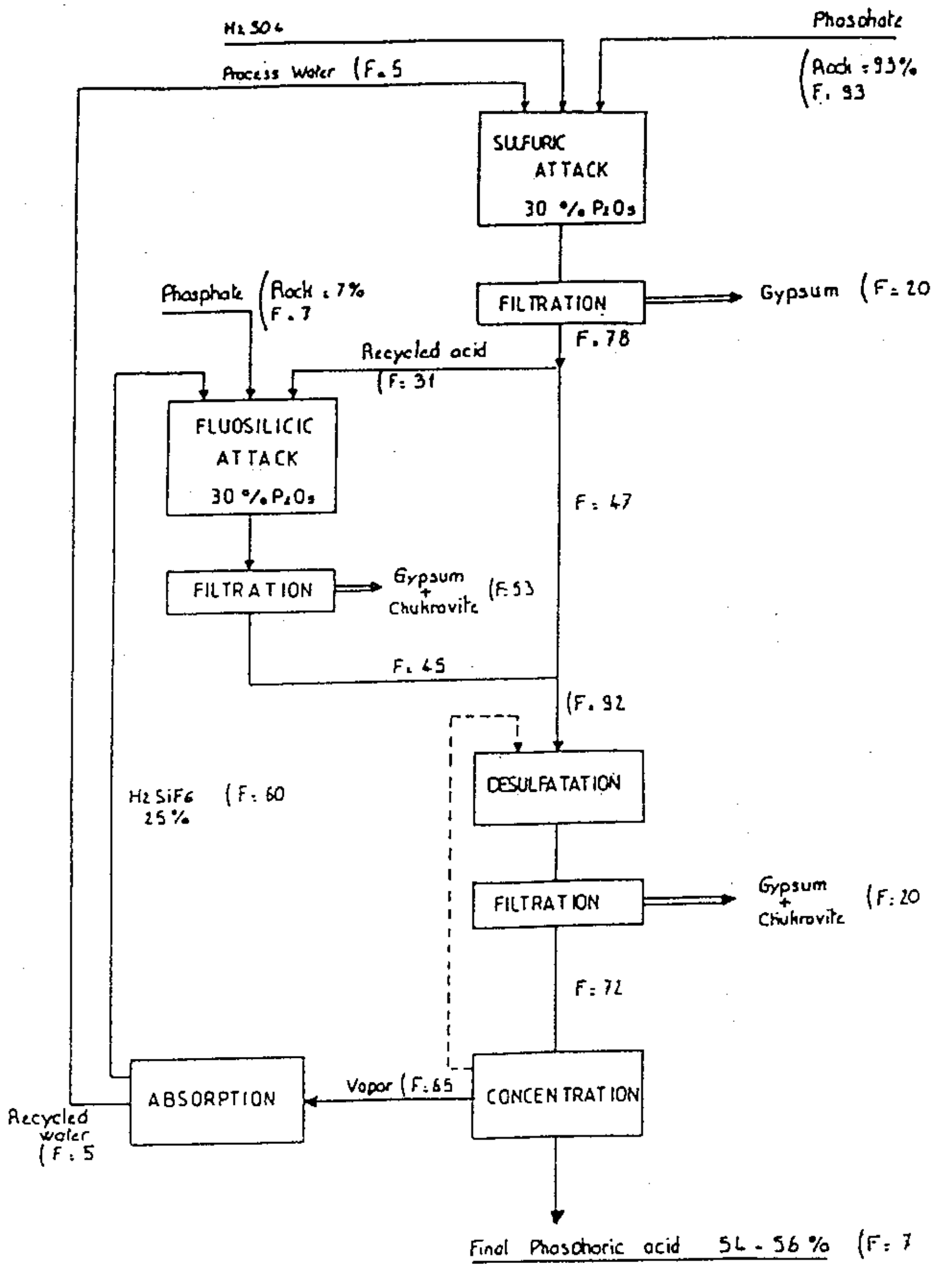
## — DAROU (SENEGAL) —

## 720 T/day $P_2O_5$ (800 S.T.P.D. $P_2O_5$)



**APPENDIX 6**

# SULFURIC AND FLUOSILICIC ATTACK



## V.I.F. PROCESS

| | TAIBA | TOGO | MOROCCO K | FLORIDA |
|---|---|---|---|---|
| $P_2O_5$ attack Yield % | 94 | 96 | 89.6 | 85 |
| Filtration rate Kg $P_2O_5/h.m^2$ | 300 | 450 | 740 | 380 |
| Ratio $\frac{\text{F precipitated}}{\text{F contained in } H_2SiF_6}$ % | 67 | 53 | 49 | 88 |
| Saving of sulfuric acid % Reported to the total sulfuric consumption | 6 | 6 | 5 | 7 |