International
Fertilizer Industry
Association

IFA Technical Conference

The Hague, The Netherlands
6-8 October 1992

SPEICHIM / RHONE POULENC PROCESS:

MAIN PROCESS FEATURES AND THE LATEST IMPROVEMENTS OF THE PHOSPHORIC ACID PROCESS

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SUMMARY

During the 1990 IFA Technical Conference, we highlighted the latest improvements of the Rhone-Poulenc process. This paper presents the industrial applications of these improvements.

We shall describe in the following order:

- Environmental consideration: in strict accordance with EPA standards and absence of any fluorinated liquid effluent as relating to environmental performance of the process.

- Energy saving: as exemplified by the heat recovery from sulfuric acid unit to phosphoric acid concentration unit.

- Simple process: well known as a simple process, improvements set the following simplifications to a much simpler process: saving the filtrate separator and having phosphoric acid pump feed the filter by overflow.

1. INTRODUCTION

A phosphoric acid process, known today as "SPEICHIM / RHONE POULENC Process", was developed by RHONE POULENC and transferred to SPEICHIM Eng. The latter had been collaborating for many years with RHONE POULENC for the improvements of this process and related fields. The research and development program of the dihydrate process continues. RHONE POULENC chemical engineers previously in charge of this program are now with SPEICHIM. All research in raw materials, phosphate rocks and laboratory tests are now SPEICHIM property. So the same team will continue to do its best to improve this process and its application for licensors, buyers of phosphate rocks and producers of phosphoric acid. Further, the industrial development remains.

2. MAIN PROCESS FEATURES

SPEICHIM / RHONE POULENC set the following goals in the development of its process :

- Simplicity and ease of operation due to:

  . simplicity of equipment and layout,
  . ease of operation,
  . flexibility (with an operating factor up to 90%)

- Reduction in investment, operating and maintenance costs.

- Protection of the environment by reducing effluents with fluorine recuperation and the implementation of techniques for the evacuation of phospho-gypsum.

The main features of the SPEICHIM / RHONE POULENC process are as follows:

- A single, non-compartmented attack reactor with a single central agitator and air cooling.
- A flat, rotating, table filter (UCEGO) for the separation of gypsum from the acid.
- A forced circulation loop for the concentration of the dilute acid.

The main equipment comprises:

- A high performance scrubbing system for the gases leaving the reactor which meets the most stringent effluent regulations.
- A simple and economic system for applying vacuum to the concentration loop.
- A high performance fluosilisic acid recovery unit.

The SPEICHIM / RHONE POULENC dihydrate process is available in two versions:

- the single tank process **(figure 1)**
- the DIPLO process **(figure 2)**

These had already been described in 1979 (1), 1984 (2), 1987 (3), 1990 (4).

3. ENVIRONMENTAL CONSIDERATION

The SPEICHIM / RHONE POULENC process has gained wide recognition for many years for its simplicity and clean technology. They are based upon SPEICHIM engineering skills and RHONE POULENC experiences as a phosphoric acid producer and buyer of phosphate.

Two fields are described below:

- gas effluent : to meet the U.S. EPA standards,
- liquid effluent : none.

3.1 Gas effluent

3.1.1 Scrubbing of fluorinated gases leaving the attack tank:

The air leaving the reactor is generally saturated and its temperature close to that of the phosphoric acid slurry. This is because of high efficiency of the air cooling technique, with following characteristics:

- very simple to operate,
- low in operating and investment costs,
- high efficiency.

The reactor is cooled by a current of air circulating on the surface. Good contact between air and slurry is ensured by patented small surface coolers, which project droplets of slurry into the airflow. A temperature difference of 10 to 15°C between air and reaction medium is obtained, which minimizes the air flow to be treated downstream. **(figures 3 & 4)**

The gas flow leaving the tank is mainly contaminated by HF, SiF_4 and CO_2. The relativ composition of the gas depends on the phosphate rock used, the temperature of the slurr and the phosphoric acid concentration. The saturated air leaving the reactor contains abou 5 % of the fluorine present in the phosphate.

Phosphate dusts and droplets of slurry could leave the reactor with the gas flow but the lov speed design of the air flow and the raw material feeding avoid any entrainment. Into th scrubbing section, the gas meets a fluosilisic acid solution which absorbs HF and SiF_4.
A global and theoretic equation of these chemical reactions are:

$$3\,SiF_4 + 2\,H_20 \longrightarrow 2\,H_2SiF_6 + S_i0_2 \quad (K = 5{,}4 \times 10^{-27})$$

$$6\,HF + Si0_2 \longrightarrow H_2SiF_6 + 2\,H_20 \quad (K = 0{,}65 \times 10^{-6})$$

A good knowledge of liquid-vapor equilibrium, HF/SiF_4 ratio into the gas, HF, SiF_4, H_2(partial pressures help to find the best design for a gas scrubbing unit (5).

The SPEICHIM / RHONE POULENC process uses two types of scrubbers:

- The Venturi scrubber, with the following characteristics

  . high efficiency,
  . low investment and maintenance costs

- The cyclonic column, with the following characteristics:

  . high efficiency of coalescence and demisting
  . low investment and maintenance costs
  . low pressure drop. **(figure 5)**

The calculation method is based on number transfer unit concept. It consists in th determination of the number of theoretical stages to meet the required fluorine discharg standards.

From the knowledge of liquid and gas flowrate and their fluorine content, we define th number transfer unit for each equipment by the following equation:

$$NUT = Log\,\frac{Y_1 - Y_1^*}{Y_2 - Y_2^*} \quad \text{where}$$

Y_1 = fluorine content in gas inlet

Y_2 = fluorine content in gas outlet

Y^* = equilibrium fluorine in gas in contact with liquid.

Furthermore, we deduce from fluorine equilibrium diagram the partial pressure of HF anc SiF_4 to calculate:

$$Y^* = \frac{P_{HF} + 4P_{SiF_4}}{P_{total}}$$

This calculation is accurate enough for a good design of the scrubbing equipment.

The full pressure at the cone sprayers must be reached in order to get a spray pulverizatior and thus optimizes the specific surface suitable for a good absorption. However, this i limited to avoid entrainment and also not to disturb the cyclonic effect given by the inle location. The ring installed before the outlet close to the shell of the cyclonic column break the fine layer.

To be able to design the scrubbing section of the units, SPEICHIM / RHONE POULENC has developed its original method of calculation which have been verified at pilot and industrial scale.

By using scrubbing recycled water into the washing section to the filter, it means that the SPEICHIM / RHONE POULENC process does not generate any liquid effluent from the attack and filtration section.

3.1.2 Recent industrial applications

In future, all phosphate projects using the RHONE POULENC process, anywhere in the world, will have to match industrial performances withand environmental protection. Moreover, most of our clients consider it as essential this subject for any new project.

For example, in China, environmental protection is a way of life. Each new Chinese project undergoes many technical exchanges on this point. Lately, SPEICHIM started up with success a new phosphoric acid plant (Guixi, China). This unit, designed for 440 mtpd P_20_5, using Yunnan phosphate rock in order to meet with EPA standards, has been fitted with a scrubbing section including in series:

- a Venturi scrubber,
- a single stage cyclonic column
- a double stage cyclonic column (figure 5)

During test run, a Chinese team checked the efficiency of the scrubbing section:

- EPA standard: 10 g / t P_20_5 feed
- Test results: 4 to 7 g / t P_20_5 feed (figure 6)

3.2 No fluorinated liquid effluent

The acid produced in the attack filtration section usuall has a concentration between 28 to 32% P_20_5. For industrial use, the required concentration generally stands between 40 to 54 %. It thus follows that the acid has to be concentrated. During the concentration, the fluorine given off with the steam can be recovered in the form of fluosilisic acid, which is the raw material in the manufacture of sodium and potassium fluosilicate and aluminium fluoride.

The installation thus consists of:

- A forced circulation loop comprising:
  . a flash chamber
  . a heat exchanger
  . a circulation pump
- A fluosilisic acid absorber
- A contact condenser ensuring, at the same time, the application of vacuum over the whole unit.

(figure 7)

The device has been designed to use the mechanical energy of the condensing water in the barometric leg to remove the incondensable gases in the vapor.

The water temperature will increase about 10°C. Two cases may happen:

- Use cooling water, usually from a river or sea, or **(figure 8)**
- Use a cooling tower in order to recycle the required condensing water. **(figure 9)**

Unfortunately, these two systems generate fluorine discharge. In the first case, if the concentration unit is not fitted with absorbers (located between the evaporator and the condensor) all the fluorine leaving the flash chamber will be lost into the condensing water. In the second case, the fluorine evolved at the top of the cooling tower in the air could be about 2 kg/h which is higher than the U.S. EPA regulation. For this reason, an indirect condensation system has been evolved.

The required condensing water is recycled on the condenser but is cooled before by an heat exchanger feeded with an independant water supply. These two water loops are independant and assure an absolute no fluorine outlet. **(figures 10 & 11)**

4. ENERGY SAVING: HOT WATER CONCENTRATION

4.1 Principle

Absorption and formation of sulfuric acid by reaction with process water envolve an exothermic reaction. Heat needs to be eliminated by circulating sulfuric acid through a column and a cooling system.

Heat removal depends on:

- the rate of the unit,
- composition and gas temperature inlet of the absorption tower,
- H_2SO_4 content in the acid,
- gas temperature outlet of the absorption tower (supposed to be in equilibrium with the circulation acid temperature).

In order to remove the heat of reaction, the acid circulating through cast iron heat exchanger is sprayed with a water loop cooled by atmospheric heat exchanger.

Phosphoric acid concentration is carried out through graphite heat exchanger blocks heated with steam at a pressure of 4 bars.

Process principle is to take the available hot water from the anhydrous, feed it to the concentration unit and use it in a heat exchanger instead of steam. **(figure 12)**

4.2 Industrial example: SICNG

Process principle described below is a hot water concentration unit which was operational at SICNG (Greece) since July 1991.

Original design modified according to the new process is composed of:

- Tube heat exchanger instead of classical coolers to cool down the circulating acid through absorption tower,
- Hot water loop which feed the concentration unit,
- A new heat exchanger and a circulating pump in order to produce concentrated phosphoric acid 45% and 54 % P_2O_5.

Main changes:

- Hot water loop: the loop is fitted with a plate cooler on line with the concentration heat exchanger in order to regulate the thermal balance. In case when a concentration unit shuts down or if the heat transfer coming from the sulfuric unit is lower than needed for the phosphoric acid concentration, the plate heat exchanger will use the cooling water coming from the atmospheric cooler.
- Phosphoric concentration unit modifications: the concentration loop is equipped with a VICARB tubes heat exchanger:

  Material: SANICRO 28 from SANDVIK
  Area: 285 sqm

A new circulating pump gets a flow big enough through the tubes to avoid plugging and scaling inside.

Performances achieved:

	43% P_2O_5 acid	
Acid concentration inlet	(% P_2O_5)	29.5
Acid concentration outlet	(% P_2O_5)	43
Density acid inlet	(kg/m^3)	1 362
Density acid outlet	(kg/m^3)	1 573
LMTD	(°C)	15
Evaporated water capacity	(T water/h)	7.6
Steam saving	(T steam/d)	218
Saving	(KFF/d)	14

	53% P_2O_5 acid	
Acid concentration inlet	(% P_2O_5)	27.5
Acid concentration outlet	(% P_2O_5)	53
Density acid inlet	(kg/m^3)	1 293
Density acid outlet	(kg/m^3)	1 654
LMTD	(°C)	7.7
Evaporated water capacity	(T water/h)	6.1
Steam saving	(T steam/d)	126
Saving	(KFF/d)	8

5. TOWARDS A MUCH MORE SIMPLE PROCESS

The SPEICHIM / RHONE POULENC process has widespread international success because of its great simplicity and ease of operation. All technological improvements evolved lately had the same goal: simplicity.

The new tested developments available are:

- the suppression of the slurry pump and the filter feeding by overflow
- the suppression of the gas liquid separator under the filter.

Two innovations having important effects on:

- the equipment number
- the civil work cost.

Installed between the vacuum box and filtrate pumps, the separator knocks down water an gas. Its overall dimension is about 2.5 m. **(figure 14)**

Now, it is possible to save this equipment and to connect directly by single pipes the aci filtrate pumps to the vacuum box without any seal tanks. So it is today possible to decreas the filter table level. The filter can be feeded by overflow.

These improvements reduce the cost of the required civil work.

In the classic layout the table level is about 11 meters from the ground. Then the slurry is fe by pumping, the acid filtrate pumps are fitted with blade impellers, have a constant speed and are driven by belt and pulleys. These are self-regulating output pumps but require suction pipe five meters height in order to ensure the expected flexibility.

The first evolution allows the decrease of the table level to 8 m from the ground. The filtrat acid pumps are fitted with vortex impellers, have a constant speed and are driven by bel and pulleys: they have a suction pipe three meters height but they only really required suction pipe 1.5 meter height.

The pumps are directly connected to the vacuum box without the previous single separator.

Since May 1989, this filter is fed by direct overflow from the reactor, without any pumping Henceforth SPEICHIM / RHONE POULENC propose to install the filtration table at abou 6.5 m from the ground. Then, the filter is fed by direct overflow from the reactor without th necessity to raise this one and the vacuum box is directly connected to the pumps. Thes acid filtrates pumps are fitted with vortex impellers, have a constant speed and are drive by belt and pulleys: then have the expected operating flexibility and only require a suctio pipe 1.5 meter height. Eventually it would be possible to use pumps fitted with blad impellers but with a direct driving and a speed variator.

Due to the reduction of the civil work as explained, the dimensions of the building enclosin the filter are thus also reduced.

So, reduction of:

- installation costs, (civil work),
- maintenance costs, (equipment number). **(figures 15 & 16)**

These improvements have industrial applications and are operated at:

- Guixi (CNTIC, China),
- Rieme (RP, Belgium).

6. CONCLUSION

This study shows that the SPEICHIM / RHONE POULENC process is constantly evolving not only through laboratory developments (Ref. 4), but also industrial applications. These improvements have affected several fields such as:

- environment,
- energy saving,
- reduction of civil work and maintenance costs,

and they arise out of necessity to improve productivity and meeting environmental standards.

During each stage of a project, in collaboration with the clients, an examination of the new performance and amount of effluents from the new unit is carried out.

The goals are to reduce raw materials consumption and energy consumption for all licensors of SPEICHIM / RHONE POULENC process.

REFERENCES

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(3) The DIPLO process, an excellent opportunity for revamping a phosphoric acid plant - AIChE - Clearwater - May 1987.

(4) RHONE POULENC process : its latest improvements with various phosphate rocks - B. SATIER - IFA Technical Conference, 1990.

(5) Absorbing fluorine compounds from waste gases - DJOLOLIAN & BILLAUD - Chemical Eng. Process - November 1978.

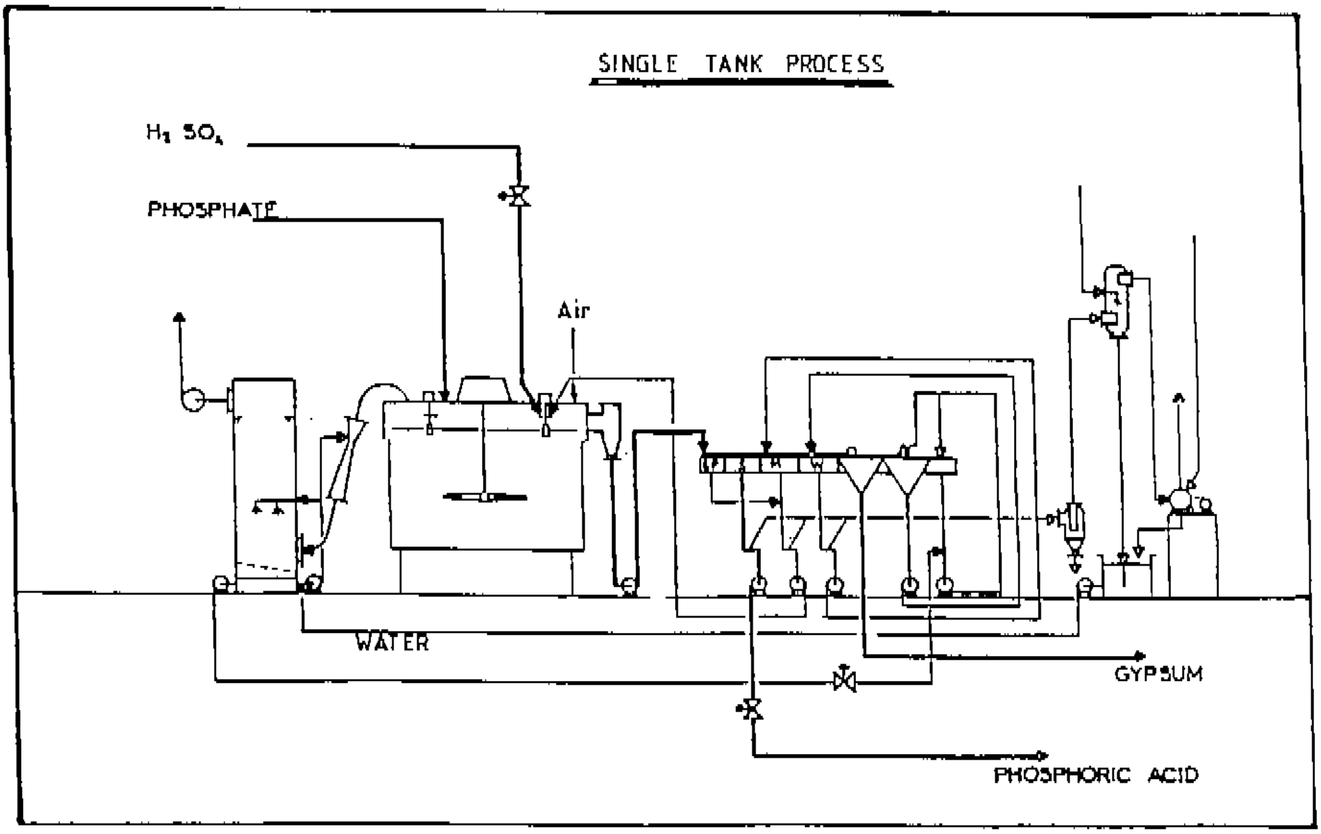

Figure 1 - Single tank process

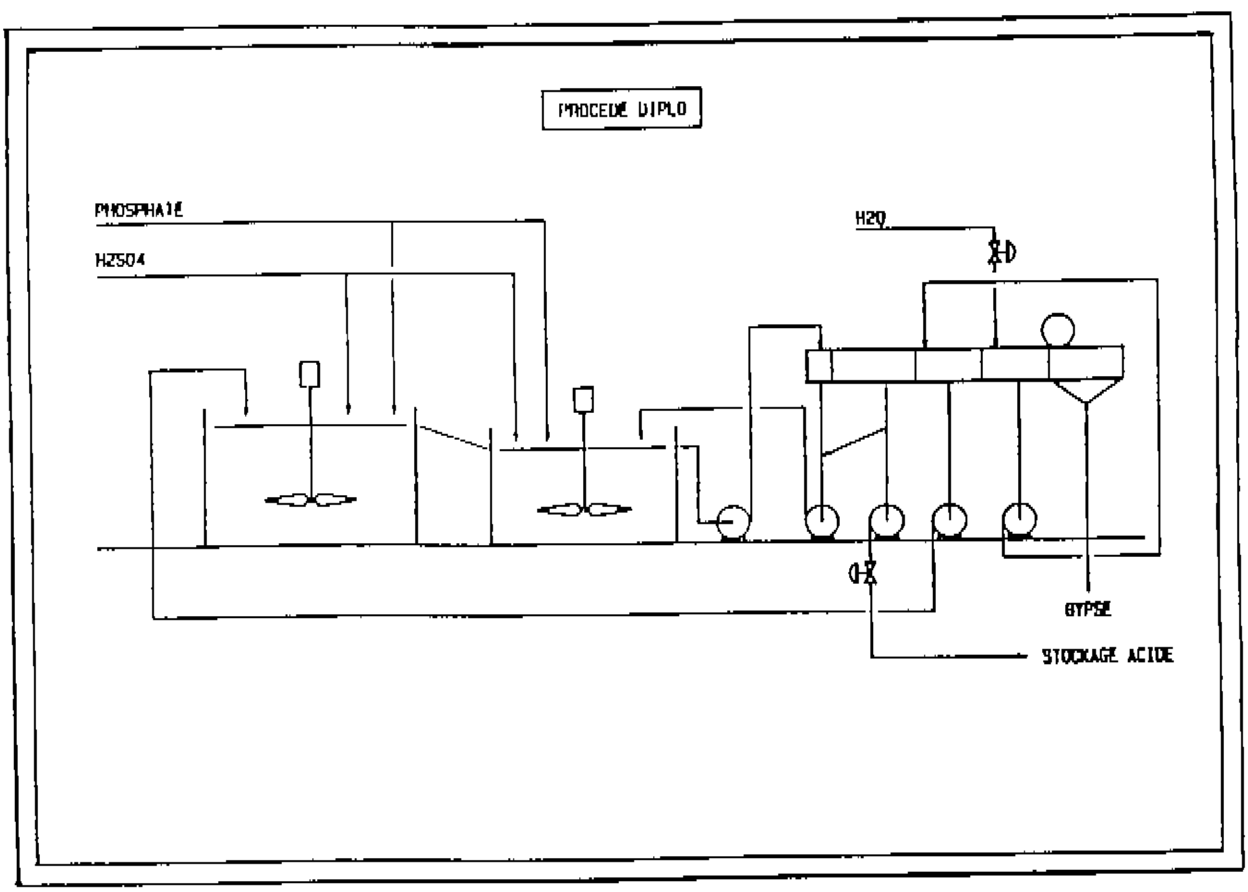

Figure 2 - DIPLO Process

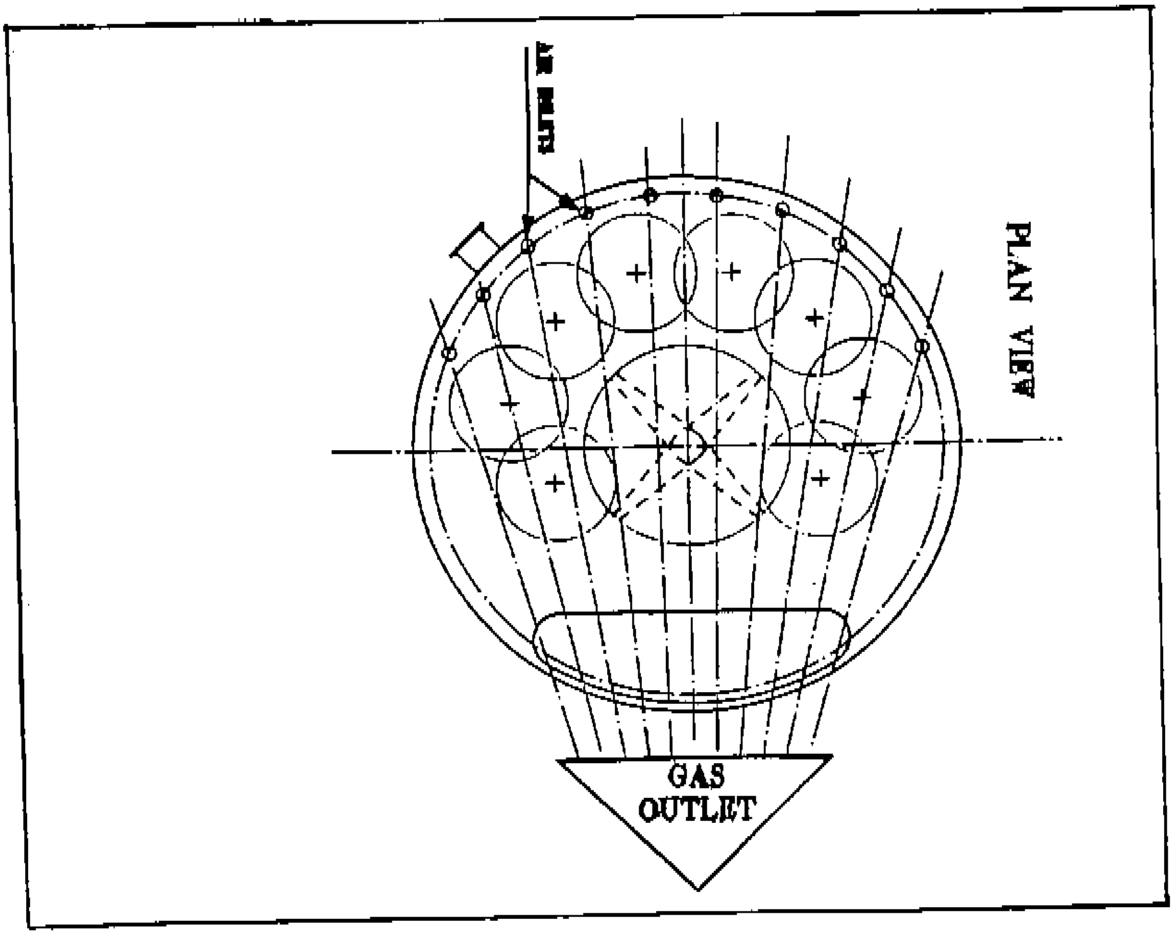

Figure 3 - Cooling system reactor

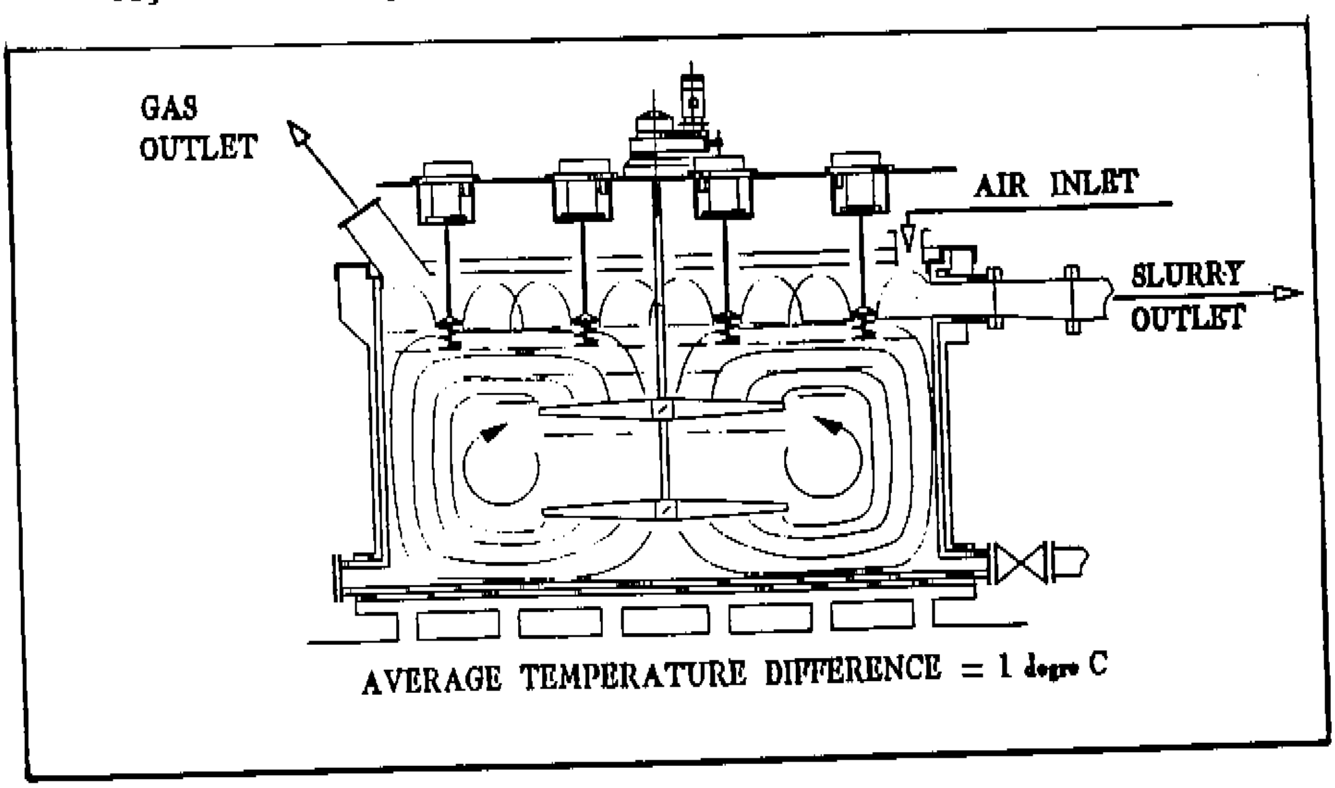

Figure 4 - Cooling system reactor

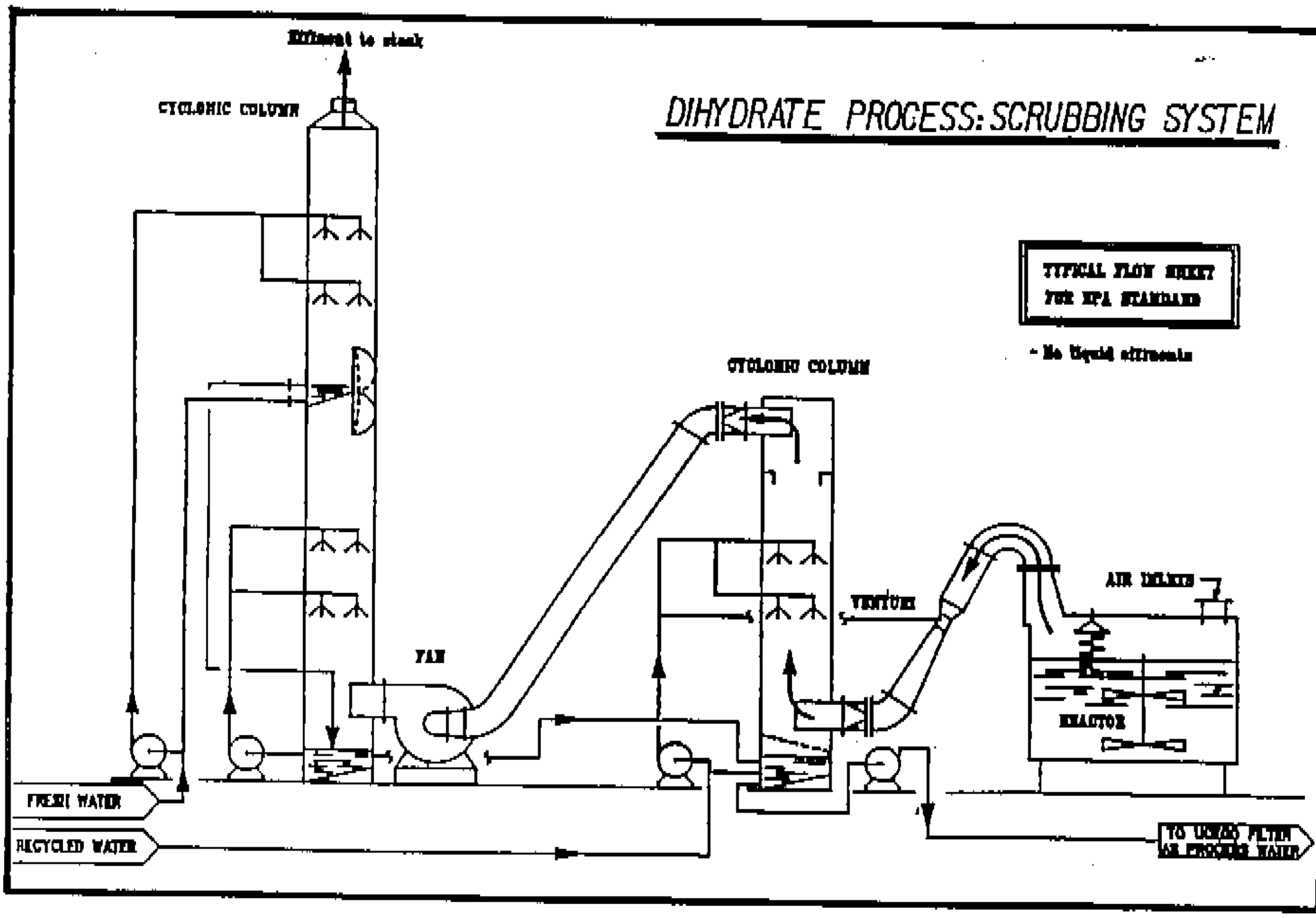

Figure 5 - Scrubbing system - typical flowsheet for EPA standard

SCRUBBING SECTION PERFORMANCE

PLANT LOCATION Commission date			GUDQ CHINA 1991
Daily P_2O_5 output		(mtpd)	436
Rock Analysis	P_2O_5	(%)	31.5
	F	(%)	3.10
F evolving from tank		(kg/h)	90.5
Venturi scrubber			oui
NTU			2.5
Ye/Ys		(kg/h)	90.5/7.93
1st cyclonic column			oui
			1er étage
NTU			1.5
Ye/Ys		(kg/h)	7.93/2.19
2nd cyclonic column (1st stage)			oui
NTU			1.5
Ye/Ys		(kg/h)	2.19/0.55
2nd cyclonic column (2nd stage)			oui
NTU			1.5
Ye/Ys		(kg/h)	0.55/0.13
F discharge			
EPA		(g/t P_2O_5)	10
Garanteed		(g/t P_2O_5)	10
Design		(g/t P_2O_5)	7
Measured		(g/t P_2O_5)	4

Figure 6 - Scrubbing system - example

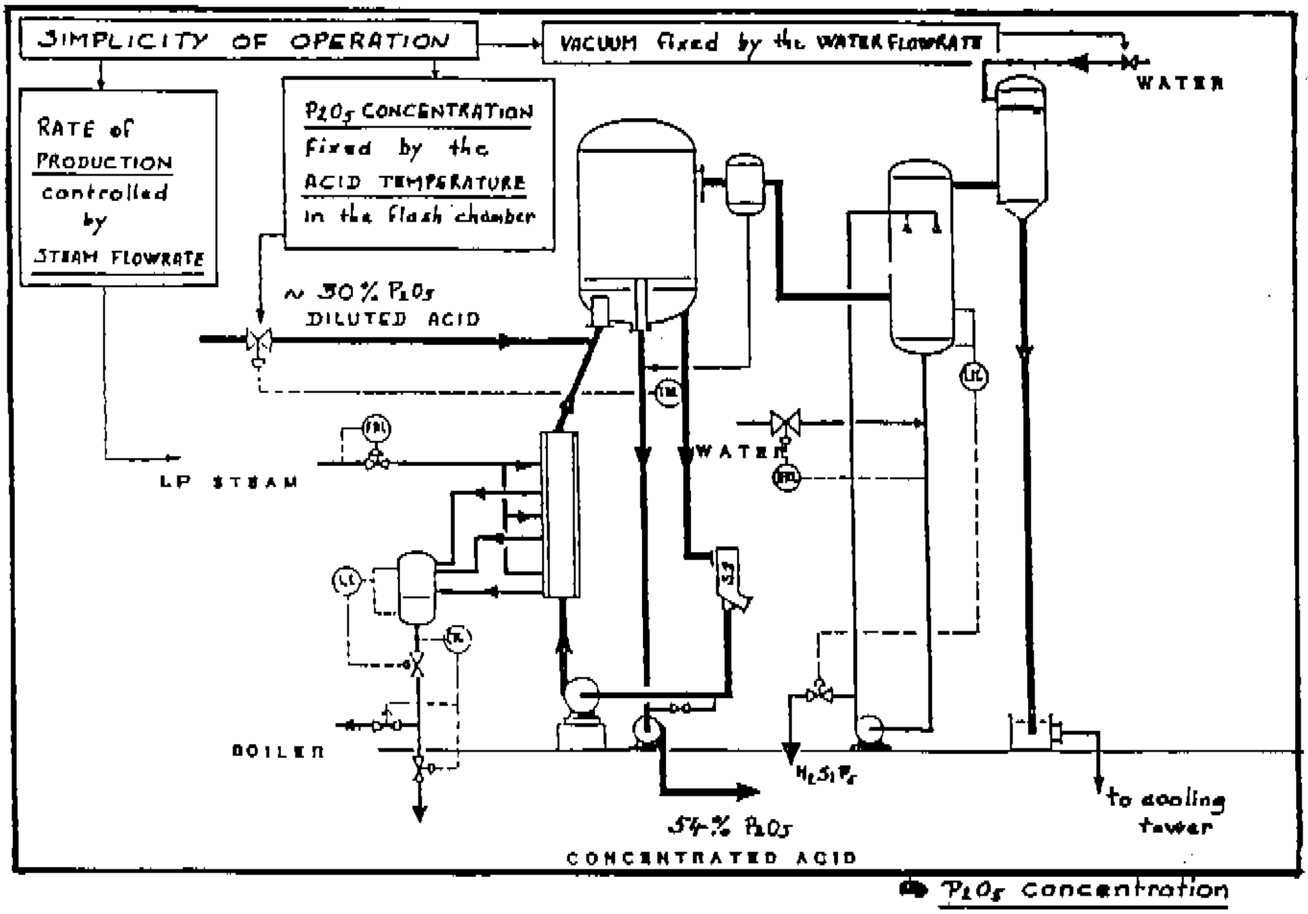

Figure 7 - Concentration unit

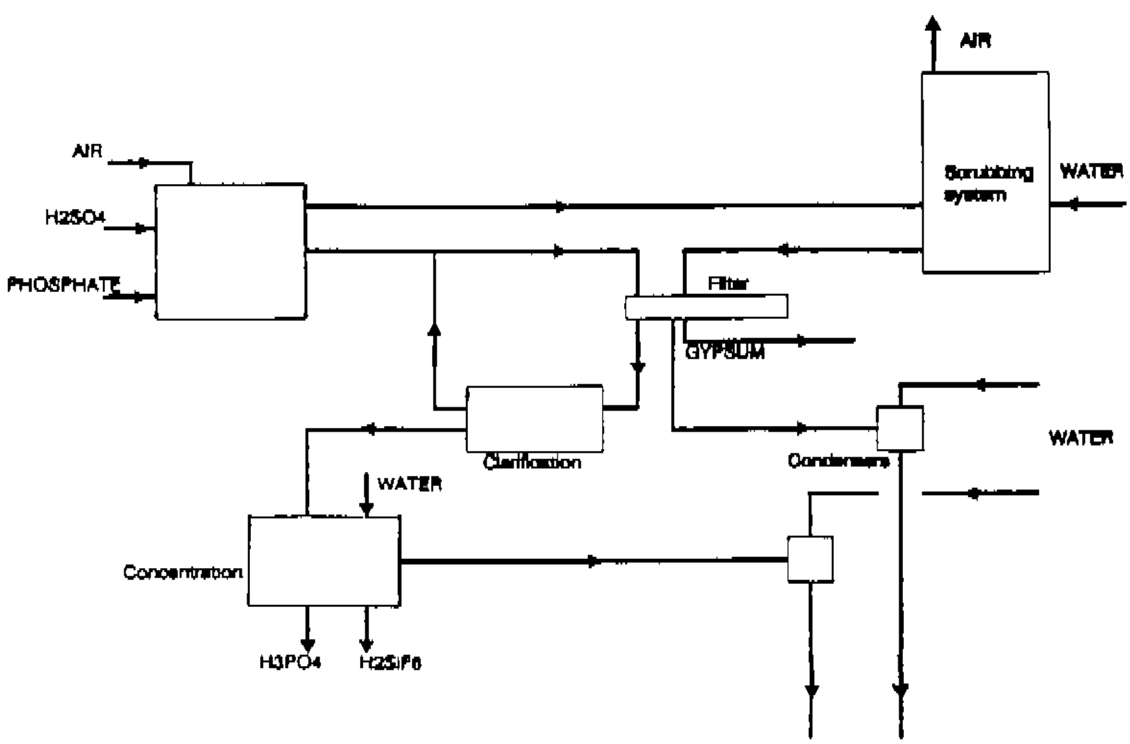

Figure 8 - Condenser using one through cooling water

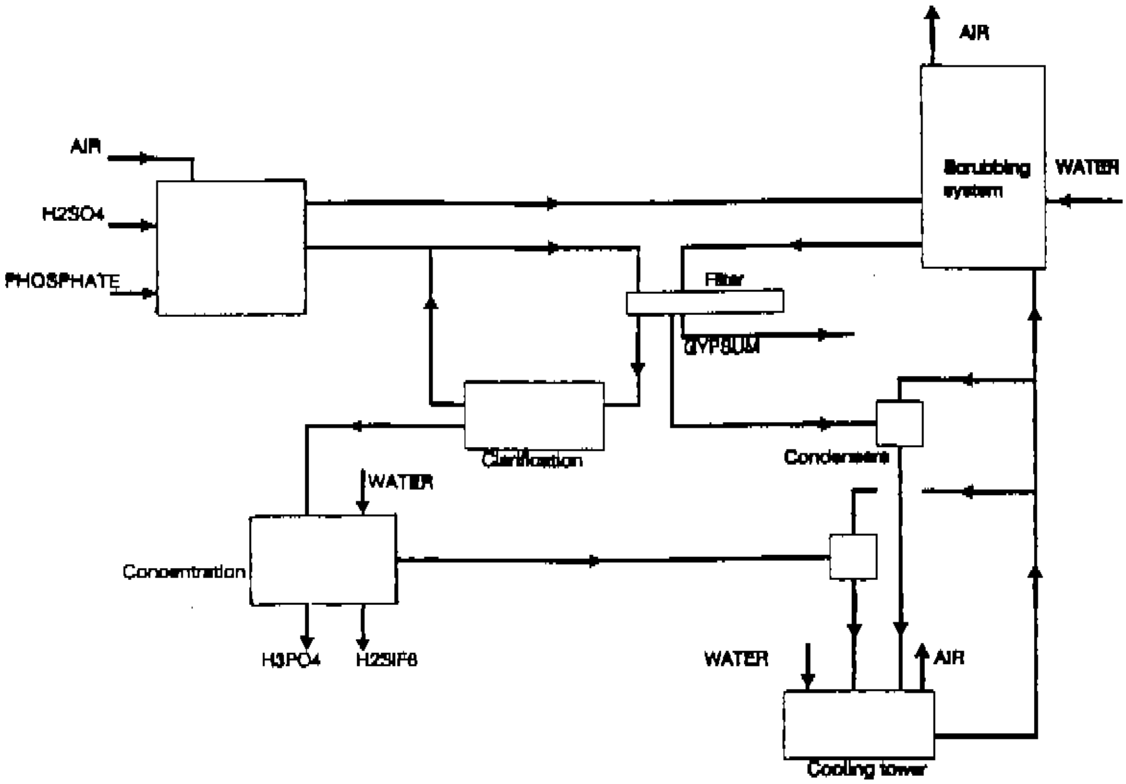

Figure 9 - Condenser using water from cooling tower

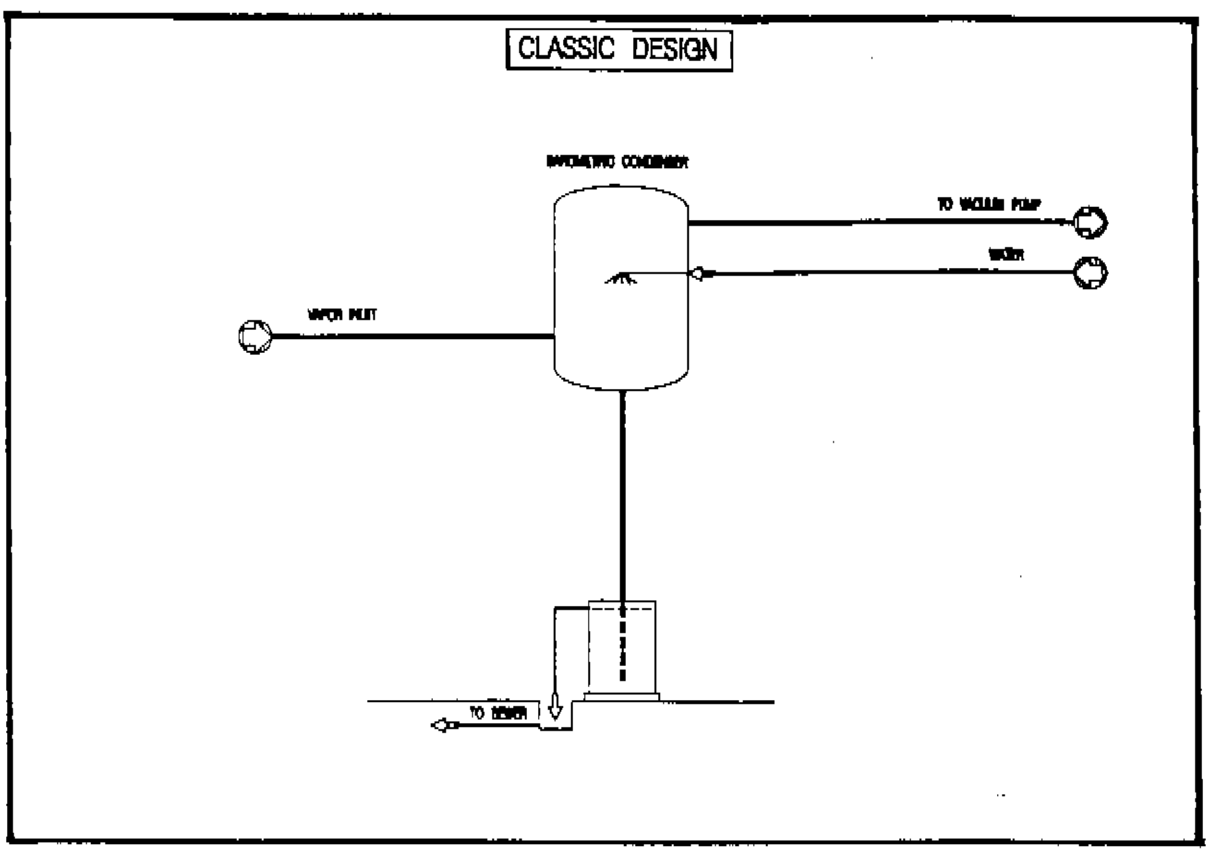

Figure 10 - Typical condenser flowsheet

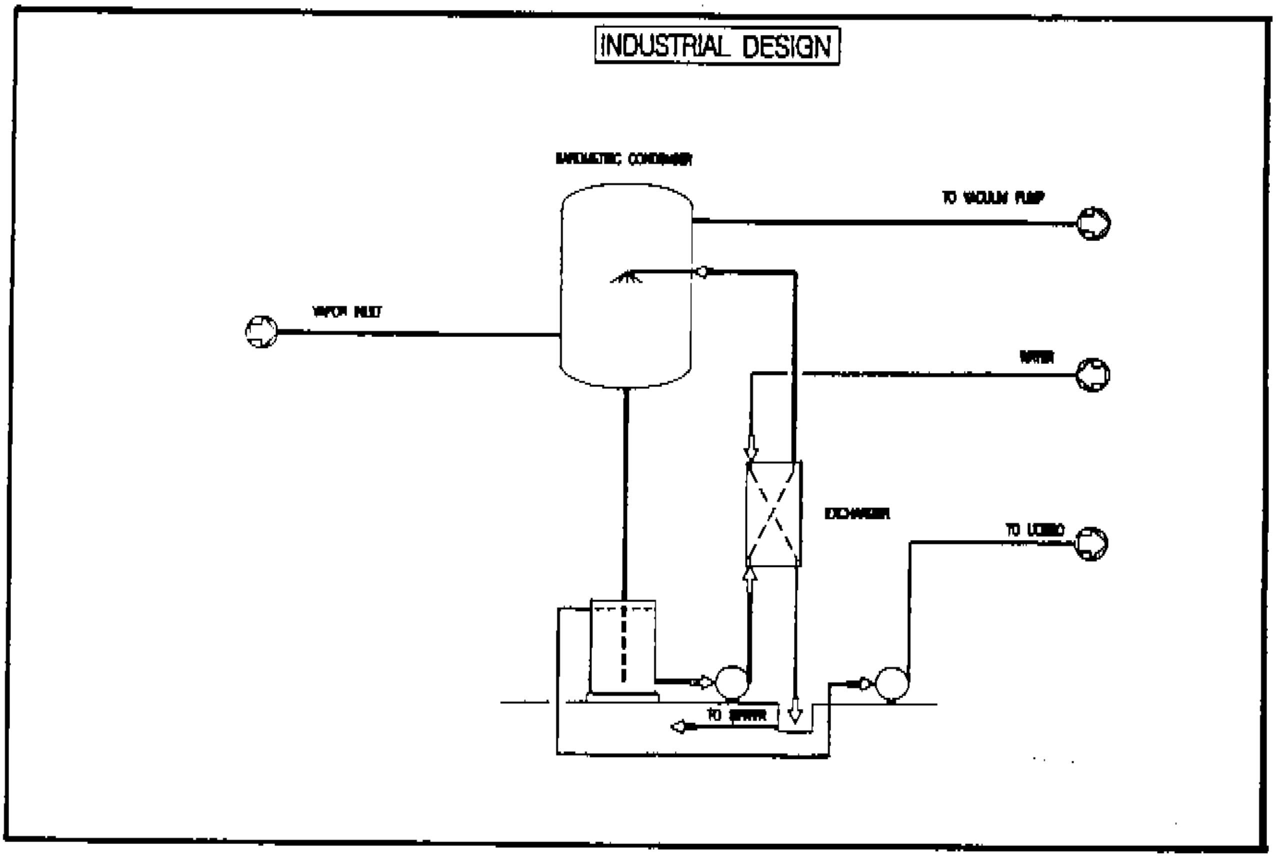

Figure 11 - Indirect condenser flowsheet

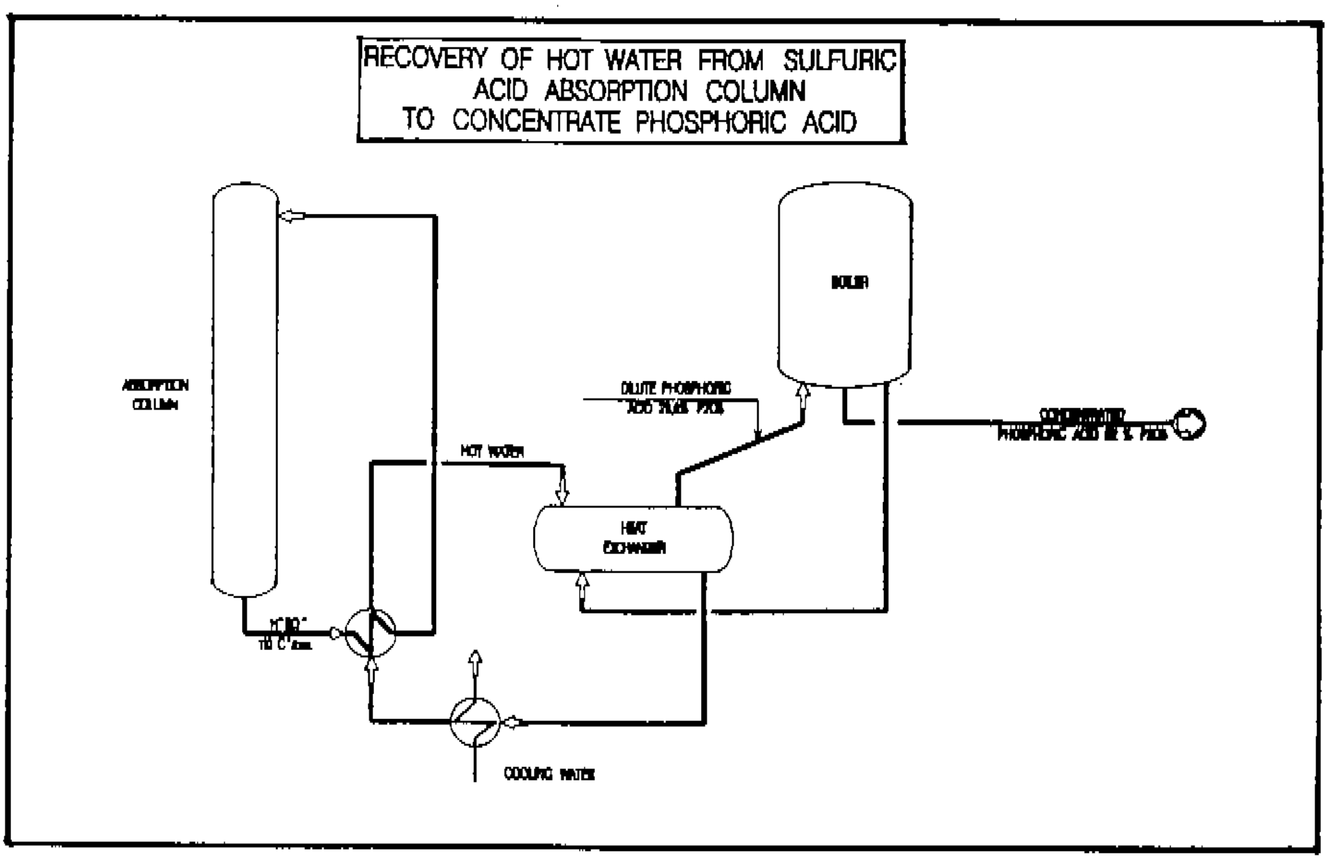

Figure 12 - Hot water concentration flowsheet

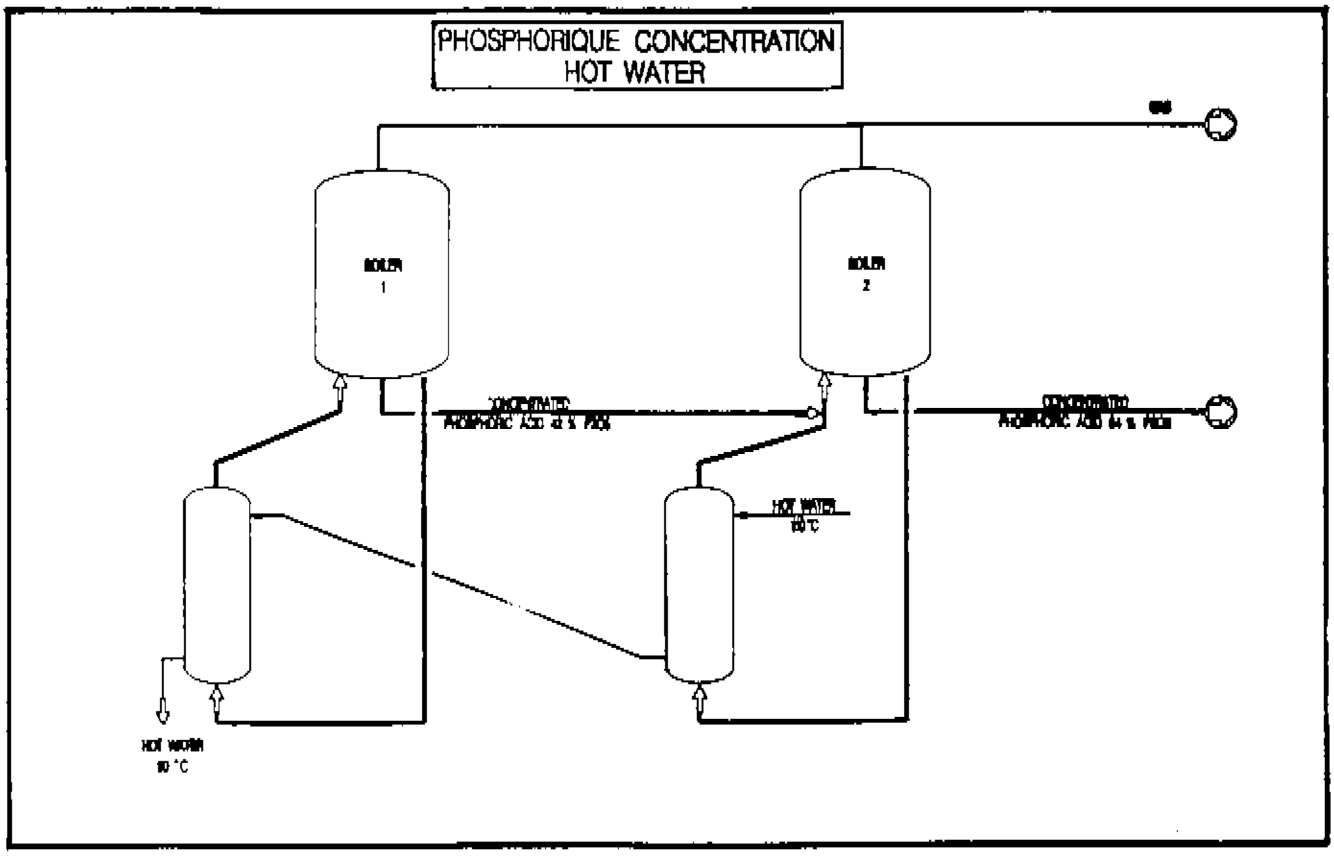

Figure 13 - Hot water concentration flowsheet

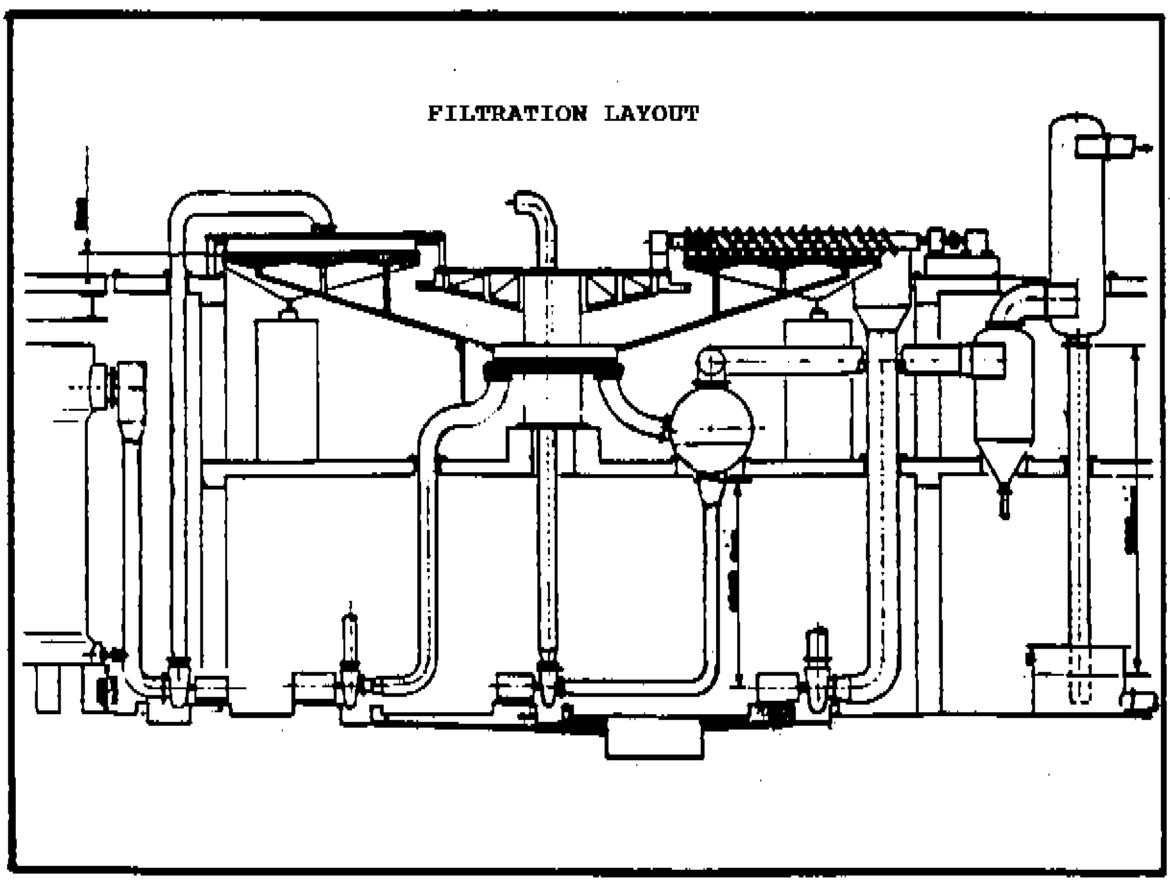

Figure 14 - Typical filtation unit layout

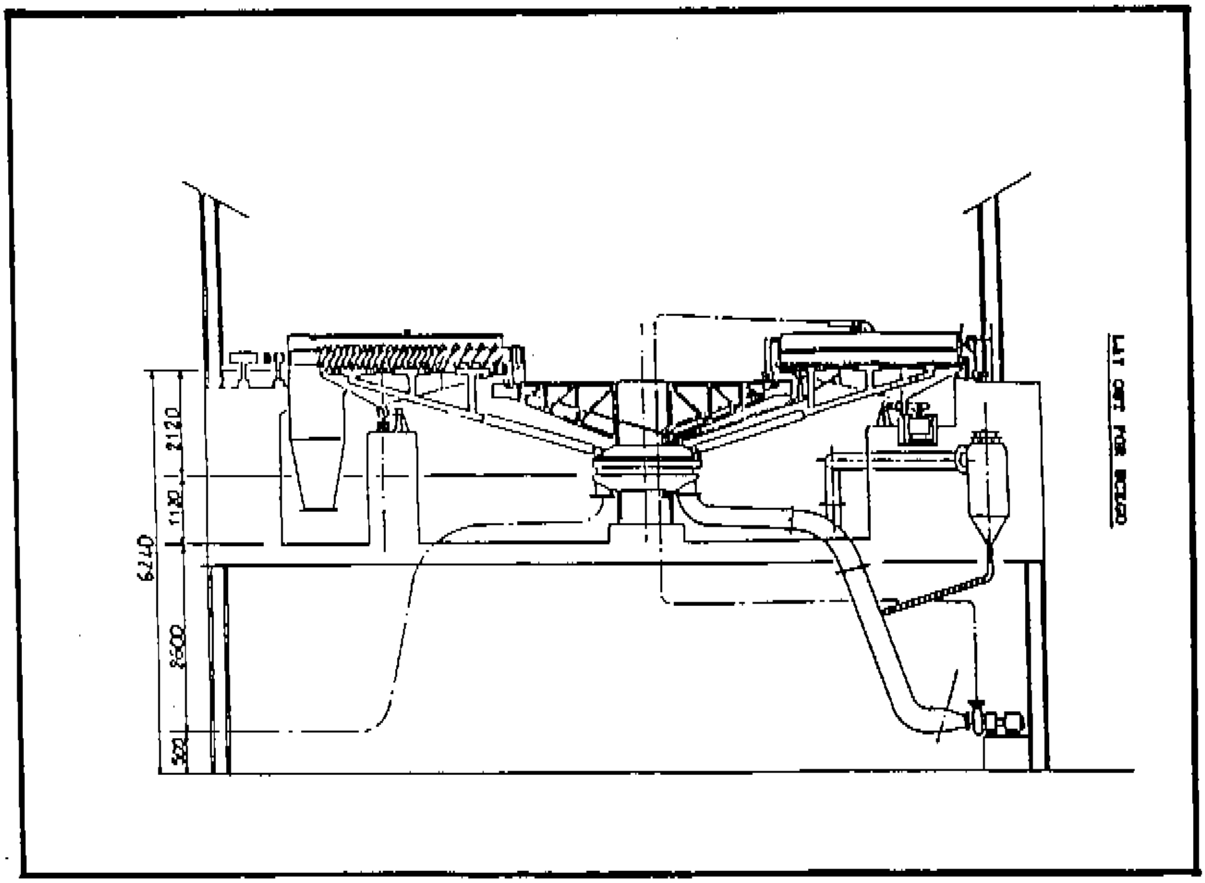

Figure 15 - New filtration unit lay out

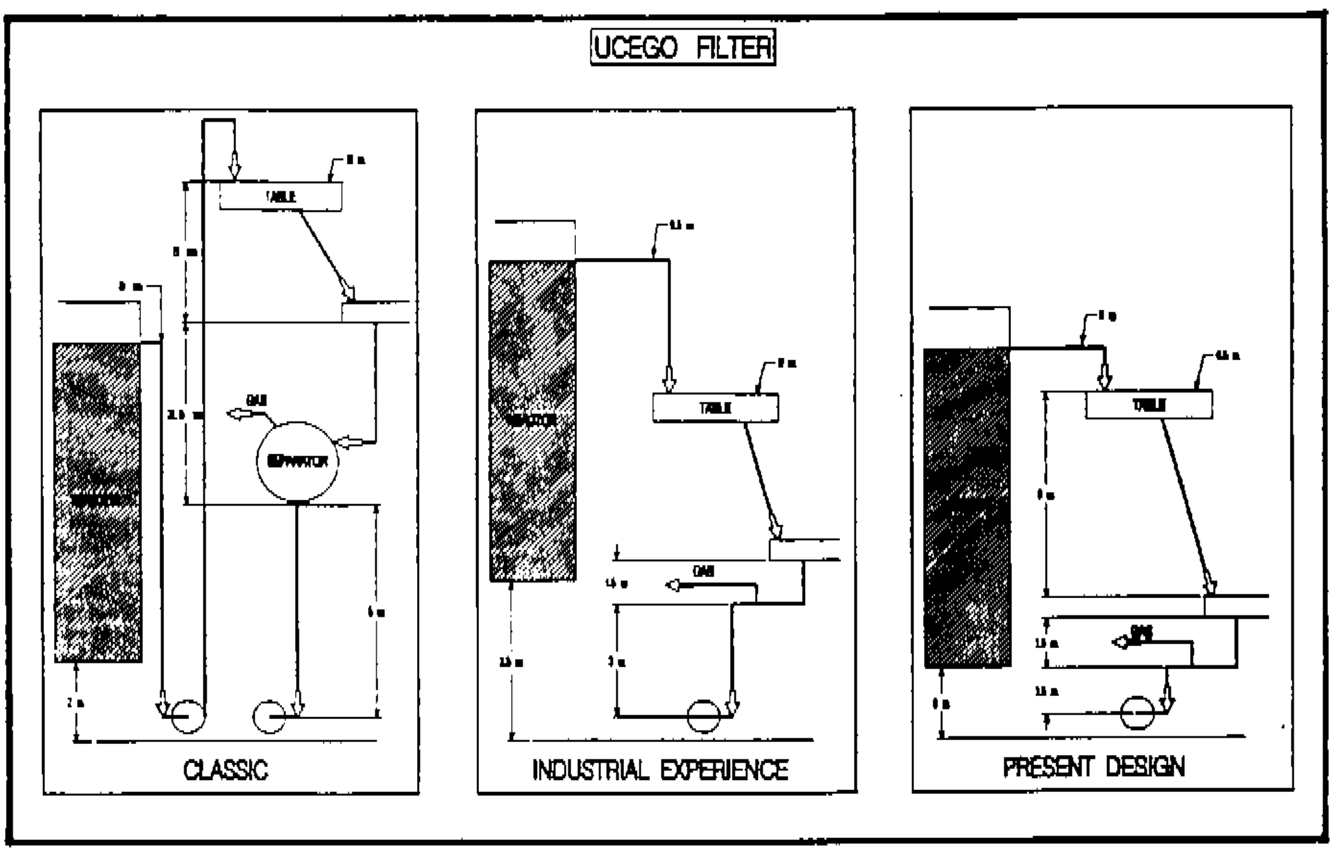

Figure 16 - Filtration unit lay out evolution