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GAS SCRUBBING SYSTEMS IN FERTILIZER INDUSTRY

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1. INTRODUCTION

The units in which fertilizers: powder and/or granule superphosphates, ammonium nitrates, ammonium nitrophosphates, NP, NPK, PK are produced, generate gaseous effluents which cause raw material losses and environmental pollution unless they are adequately treated.

Scrubbing installations have been conceived for a long time as auxiliary and secondary equipment, which resulted in operating troubles, poor efficiency and pollution transfer from gaseous to liquid effluents.

AZF, which has been operating for several decades, plants producing all these types of fertilizers, obviously met with these problems.

In a first stage, it has equipped its plants with gas scrubbing treatment procured from other specialized firms and big amounts have consequently been invested in this sector. More frequently, the results were unsatisfactory, feeble and, in some cases, disastrous. This can be explained by the fact that such equipment did not cope with characteristics specific to fertilizer industry, did not run satisfactorily (sprayer clogging, scrubber and demister incrustation, deposition, settling of precipitates) and could not be actually integrated into operating processes without causing serious troubles.

Very often, it happened that these installations became disabled or that their operating principle was entirely modified. For example, a scrubber previously designed to recover ammonia by scrubbing with phosphoric acid was finally operated with lost water to transfer ammonia losses and fluorine compound emissions to sewer.

AZF, which was developing its own processes to produce any types of fertilizers, inferred from these unfortunate attempts that it should conceive as part of its processes, gas treatment equipment like plain reactors perfectly consistent with the production unit into which they should fit.

2. SELECTION OF THE TYPES OF EQUIPMENT

Industrial expertise gained in many plants using various equipment which evidenced unfitness for fertilizer industry, erroneous conception of design or sizing, mistakes in the construction and, in particular, in the choice of materials, has been complemented by:

- pilot studies on transparent models,

- mathematical modelings of fluid mechanics and of materials and energy transfer.

AZF gas treatment system consists of elements which have been known for long but calculated, designed, sized, assembled and equipped with specific accessories by fertilizer producers to be used in fertilizer production:

a) cyclones - AZF design program allows their size to be determined as a function of expected efficiency and treatment feed gas characteristics. They are equipped with adequately located inspection doors, easy to operate, which facilitate both surveillance and maintenance. Cyclones and their receiving hoppers are fitted with automatic cleaning systems.

b) venturis - AZF venturis comprise a single liquid atomizer of special design, nonclogging, which delivers a solid jet of water with an angle of 15 degrees at outlet of the divergent section. They are so designed that the pressure drop is none or very small, and, in some cases, they can have a slightly driving effect. Their selection is a function of optimum distribution of energy between gases and the liquid.

c) cyclonic spray tower - In AZF system, cyclonic spray towers are twofold: complementary transfer of material downstream the venturi (which can be coaxial - figure 5), and efficient demisting preventing the scrubbing liquid from being entrained to stack.

d) liquid-gas separators - AZF has designed two types of separators. One of them is intended to receive the gas/liquid mixture discharged from venturis. This is the separator currently installed in the gas scrubbing system designed for DAP-NPK units (figure 1). It also acts as scrubbing liquid reserve.

The other is a cyclonic separator which can be installed directly at bottom of a stack to ensure the demisting of an existing installation which let liquid droplets be discharged with gases (figure 7).

e) accessories - It is of importance that accessories to a gas scrubbing system be efficient. AZF was thus led to very carefully study the design of scrubbing liquid supply systems, piping supports, the selection of valves, pumps, control and measuring devices (pHmeters) and to conceive nonclogging spray nozzles.

These types of equipment are used separately or jointly in function of the problems met. Assemblies more frequently used in AZF units or at AZF licensors' are described below.

3. GRANULATION UNITS (figures 1, 2, 3, 4, 5)

More often, the AZF system installed in DAP, NPK, PK, and also, supertriple granulation units, consists of two venturi scrubbers, a separator and a cyclonic spray tower.

Gases discharged from the granulator (and from phosphate attack tank in the case of supertriple slurry granulation) are exhausted in a venturi. Gases are separated from the scrubbing liquid in a compartment of the separator, and discharged into the final cyclone tower by a blower. The second venturi delivers the dry gases to the second separator compartment. Scrubbed gases are then sent to the final cyclonic spray tower.

The same scrubbing liquid stored in the separator is sprayed into the two venturis. Plant water and heat balances can thus be easily optimized as gases delivered by the dryer are dry with a high evaporative, and, then, cooling efficiency whereas gases received from the granulator and from the reactor mainly are water vapour.

The liquid present in the separator is strongly agitated by venturi jets and the high delivery rate of the pump. No deposition or plugging hazards exist.

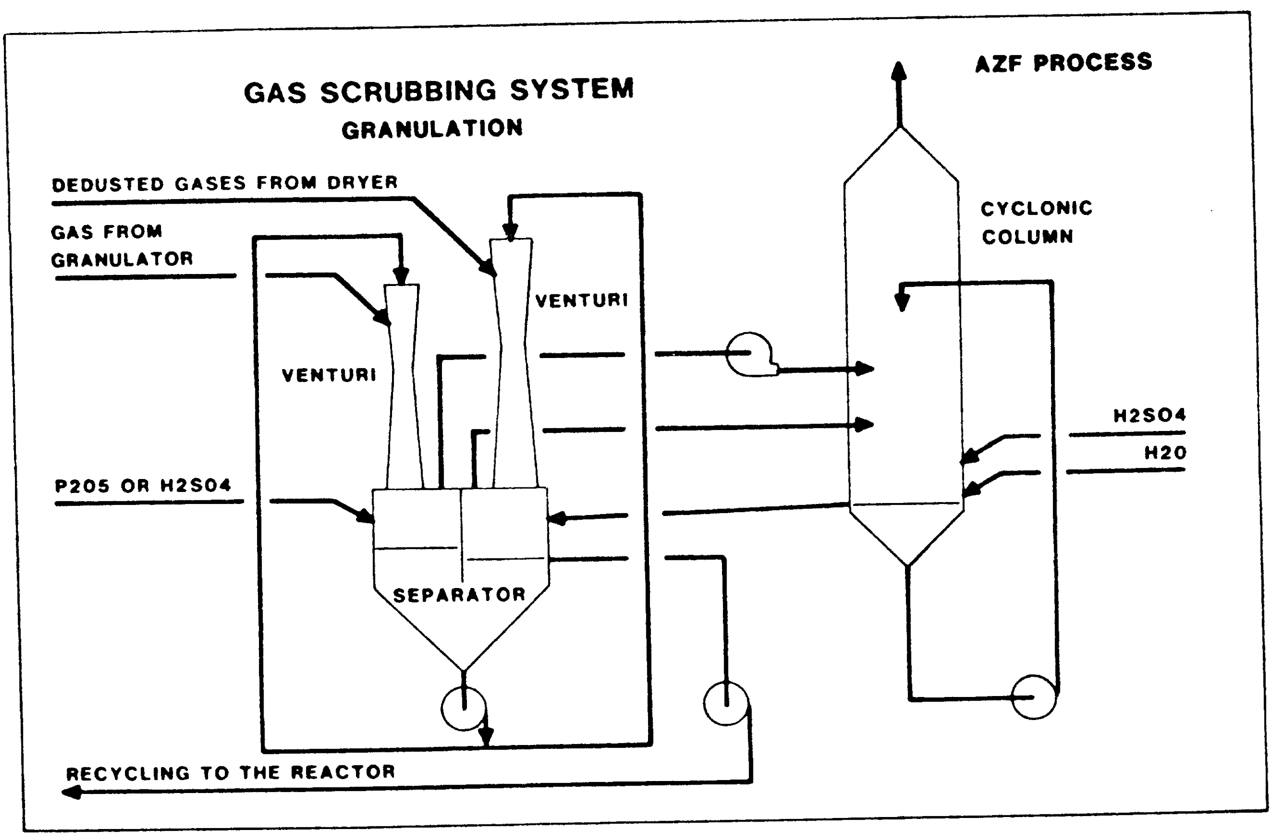

Fig. 1

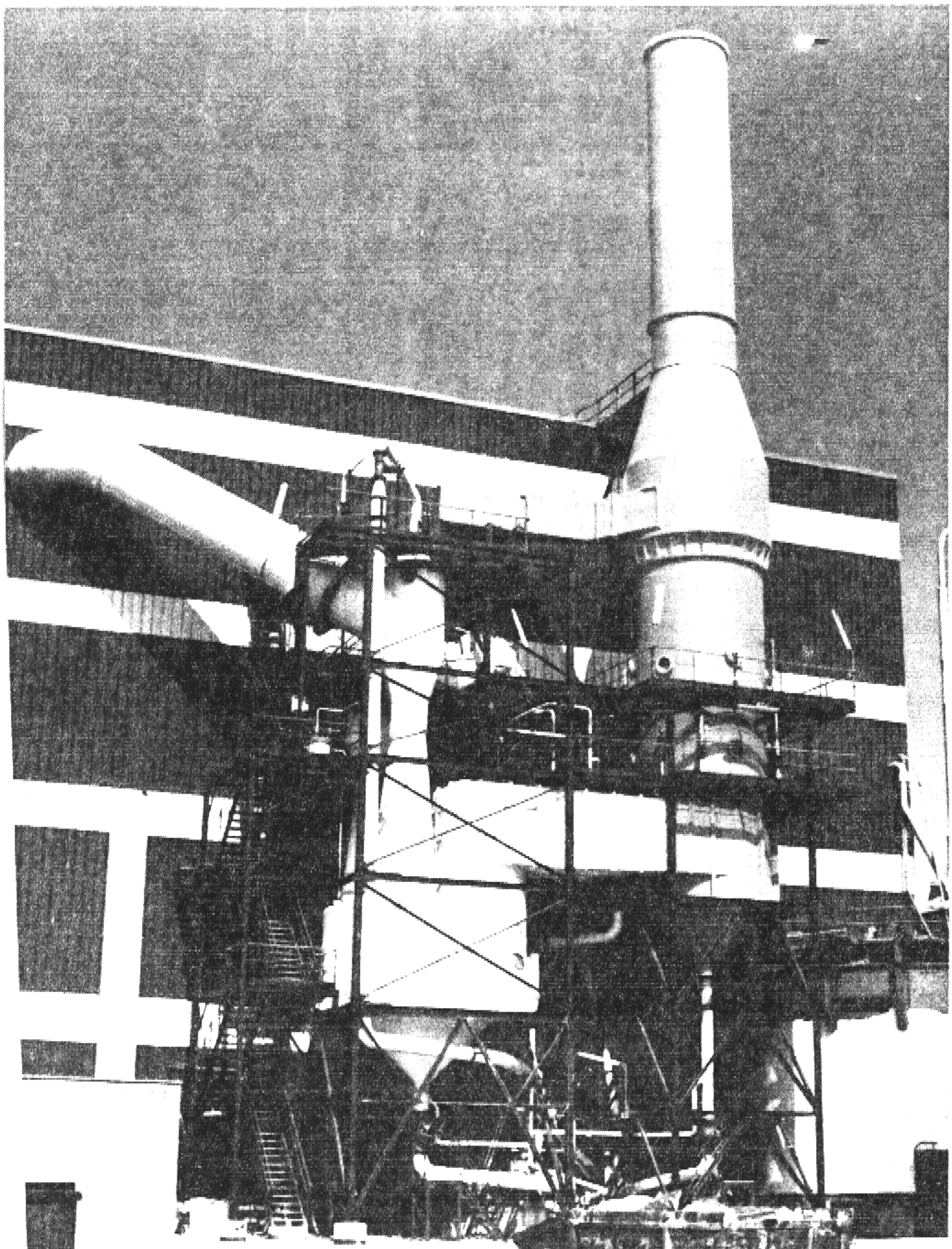

Figure 2 : AZF's plant in L'OSERAIE (FRANCE)

For granulation of DAP or ammonium phosphate-based fertilizer, the scrubbing liquid used in venturis is an ammonium phosphate solution of which N/P molar ratio is kept automatically at a value near 1.4 through a makeup supply of phosphoric acid under control of an in-line pHmeter.

This ratio value has been selected by AZF after numerous inlab and pilot studies as it allows the fluorine compound gaseous emissions to be limited to very low values while achieving good recovery of ammonia not fixed during granulation. AZF units have been so operated for many years.

Cyclonic spray tower carries out a complementary absorption of the ammonia warranting to the assembly described above an ammonia captation yield of above 95%.

It is sprayed with a diluted acid solution of which pH is controlled by means of phosphoric, sulfuric or nitric acid depending on the type of product manufactured in the granulation unit, and of available acid. For DAP production, sulfuric acid required by the formula equilibrium is generally introduced into this tower as also the quantity of water corresponding to the water balance equilibrium and to densities in the gas scrubbing unit.
The excess scrubbing liquid produced in the spray tower gravity flows into the venturi stage, and the venturi scrubbing liquid is sent to the pipe-reactor of the granulator.

No liquid effluent is discharged.

A granulation unit operated according to the AZF process, with two pipe - reactors and equipped with the third reactor represented by AZF gas scrubbing system, warrants an overall ammonia yield of about 99%.

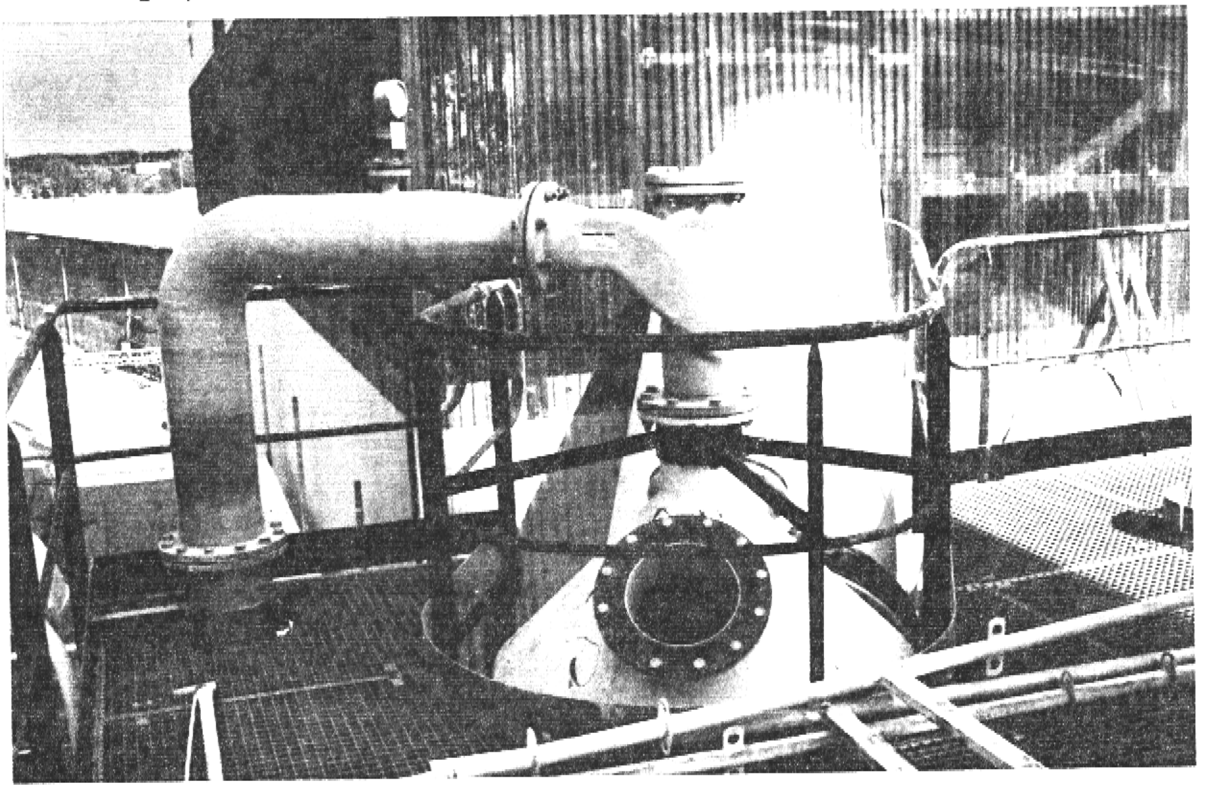

Figure 3 : Sprayer on the top of venturi

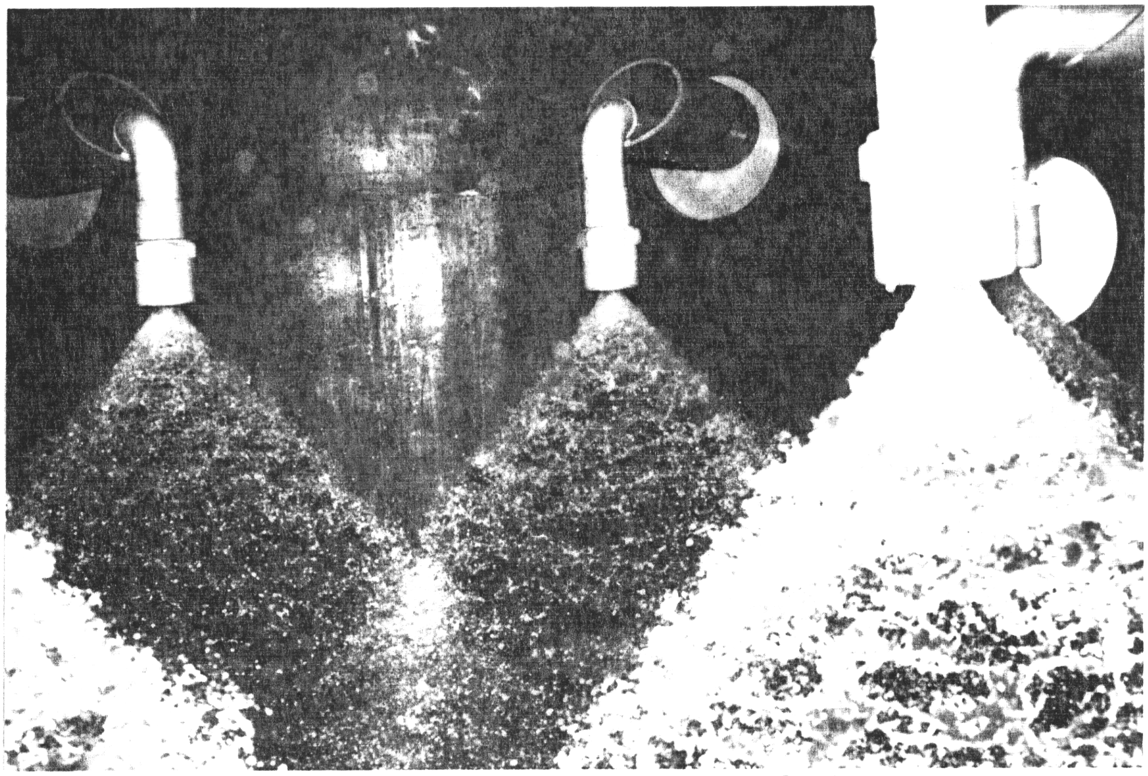

Figure 4 : Sraying in a clyclonic tower

Figure 5 shows a variant to this system. It consists of a cyclonic spray tower housing a coaxial venturi fitted with a centrifugal disperser at its lower end. This venturi represents the first scrubbing stage, the tower body through which gases delivered from the venturi flow according to a cyclonic path acting as the second stage. In the second stage, exhaust gases from an external venturi in which gases from another system have been treated in a first stage, can be injected tangentially.

This system can be installed in preference to the first system in cases where the layout or special arrangements need it. When gases from a granulation unit have to be treated, the venturi inside the tower receives gases from the dryer, the external venturi treating gases from the granulator.

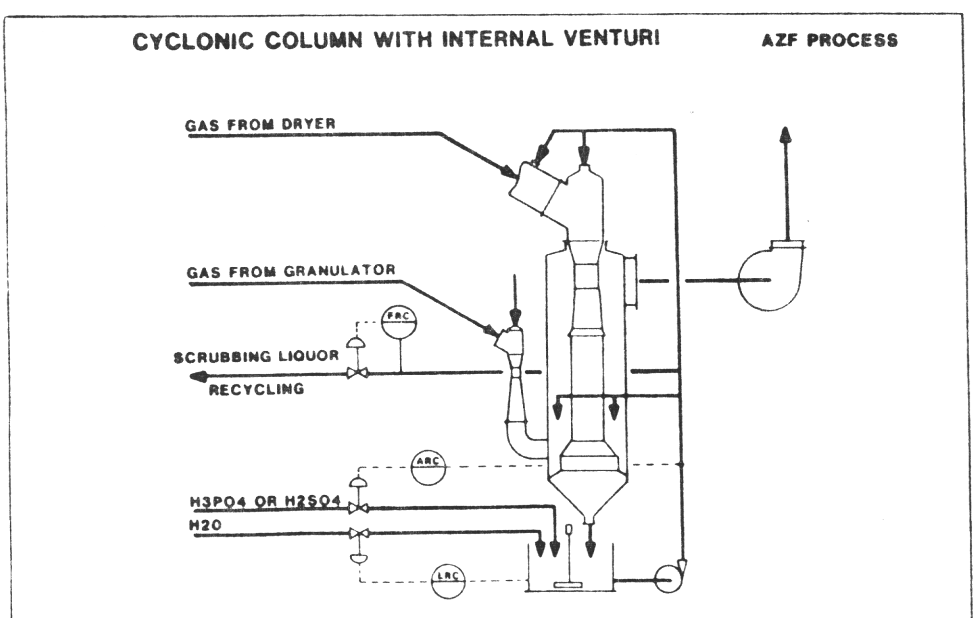

Fig. 5

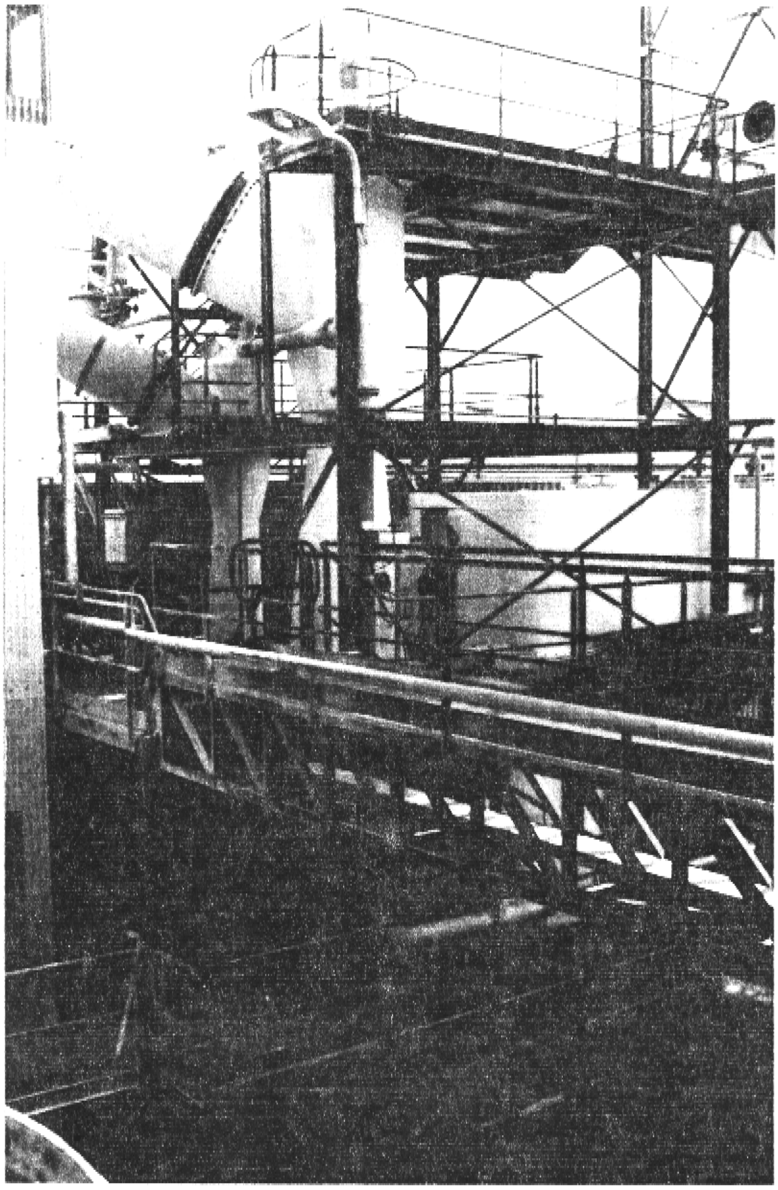

Figure 6 : Venturis

CYCLONIC SEPARATOR

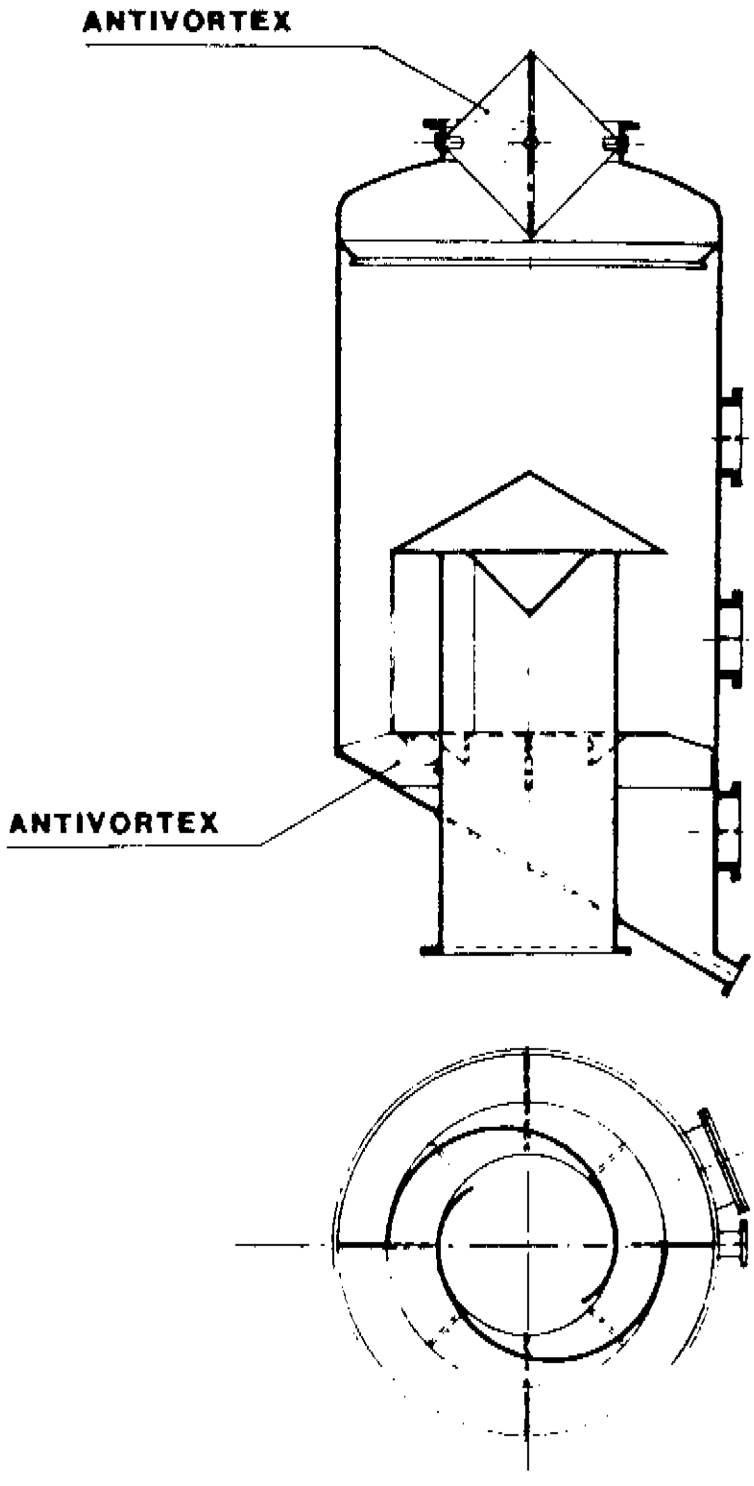

Fig. 7

4. POWDER SUPERPHOSPHATE PRODUCTION UNITS (figures 8, 9, 10)

AZF has developed two processes for production of simple, double or triple powder superphosphate. A process uses a rotary den, and the other, a curing belt. Whichever the process, attack of natural tricalcium phosphate containing calcium fluoride with an acid releases HF + SiF_4 fluorine compounds.

Acid release is particularly high when simple superphosphate is produced and the phosphate attack carried out using 70-76% H_2SO_4 sulfuric acid. In this case, and depending on the quantity of reactive silica present in phosphate, SiF_4 gas whose absorption in water makes colloidal silica precipitates according to the reaction:
$3\ SiF_4 + 2\ H_2O \longrightarrow 2\ H_2SiF_6 + SiO_2$
is released in preference.

Silica precipitation, which occurs inside the gas scrubbing system, is highly prejudicial as it tends to clog all liquid and gaseous circuits unless the plant has been specially designed to avoid these troubles.

All producers of simple superphosphate are well aware of this problem and pay attention to it.

To avoid these difficulties, it is of importance that silica precipitates within a turbulent liquid mass instead of on walls not sprayed permanently.

AZF system accounted for these phenomenon as well as for administrative requirements, sometimes more exacting than those of the US agency, E.P.A., however very strict.

It generally consists of three stages, each of them made up of a venturi and a tower. The scrubbing liquid flows systematically from a stage to another countercurrently with gases. Water is introduced into the third stage and a solution with a 10% (or more) fluorine concentration can be obtained in the first stage while gases delivered from stack still have a fluorine content of the order of from 10 to 20 mg/m3

This fluosilicic acid concentrated solution produced in the first scrubbing stage can be filtred and used to produce sodium or potassium fluosilicates, or recycled to the mixer simultaneously with phosphate and sulfuric acid, which allows saving about 3 % of sulfuric acid.

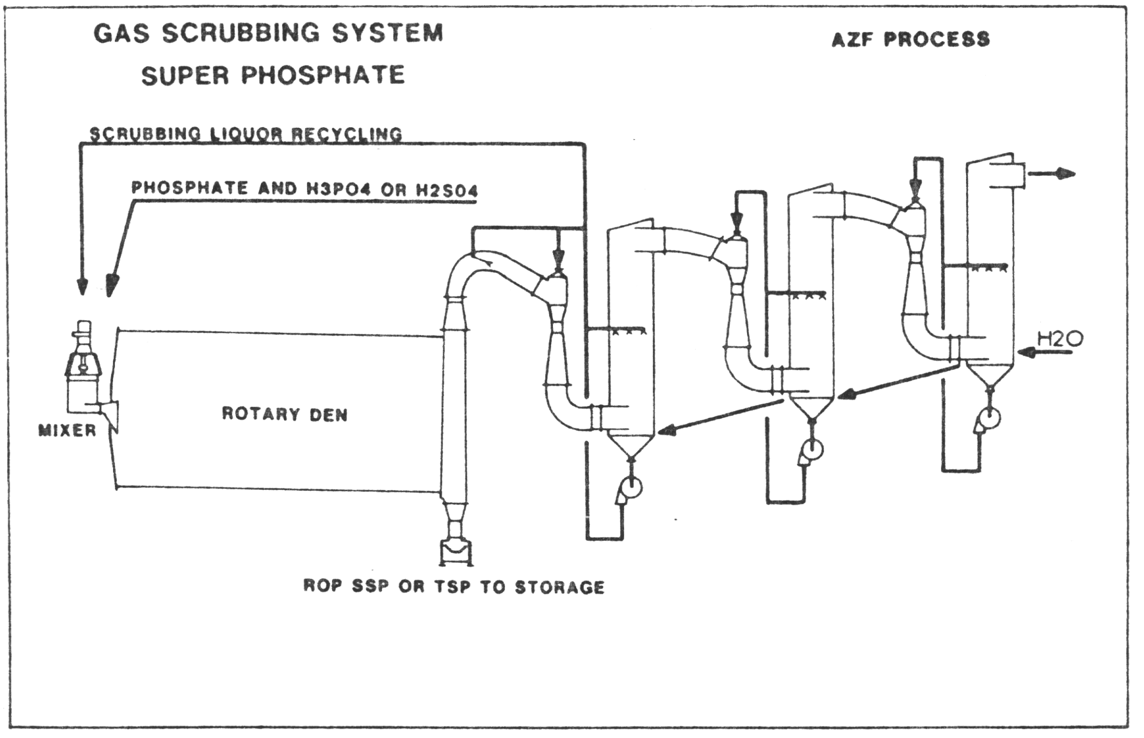

Fig. 8

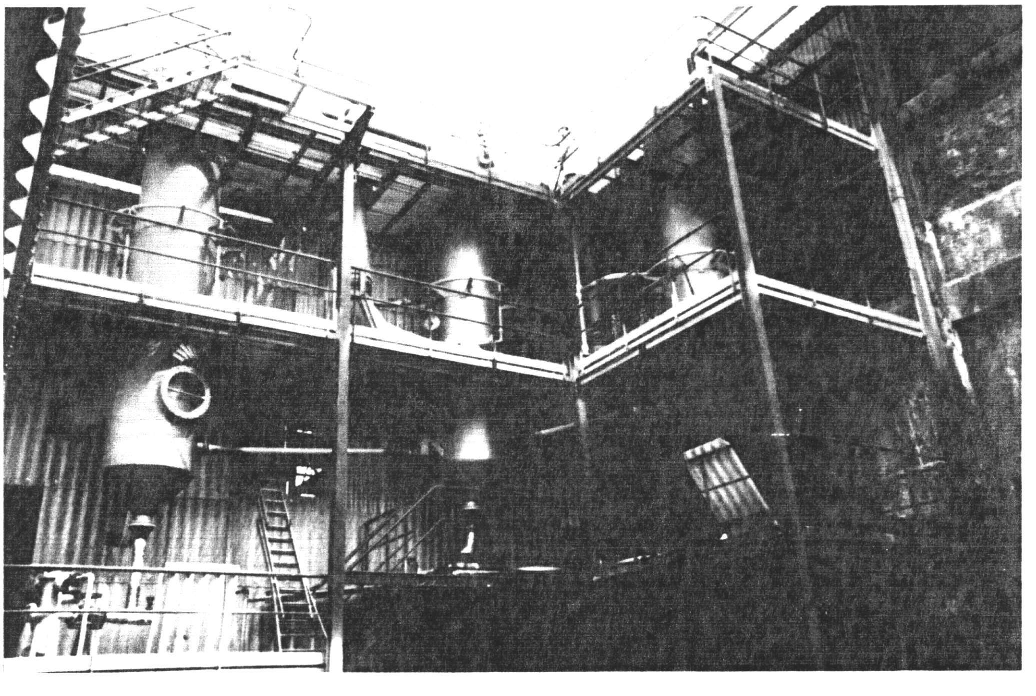

Figure 9 : Superphosphate Plant (NANTES) cyclonic towers

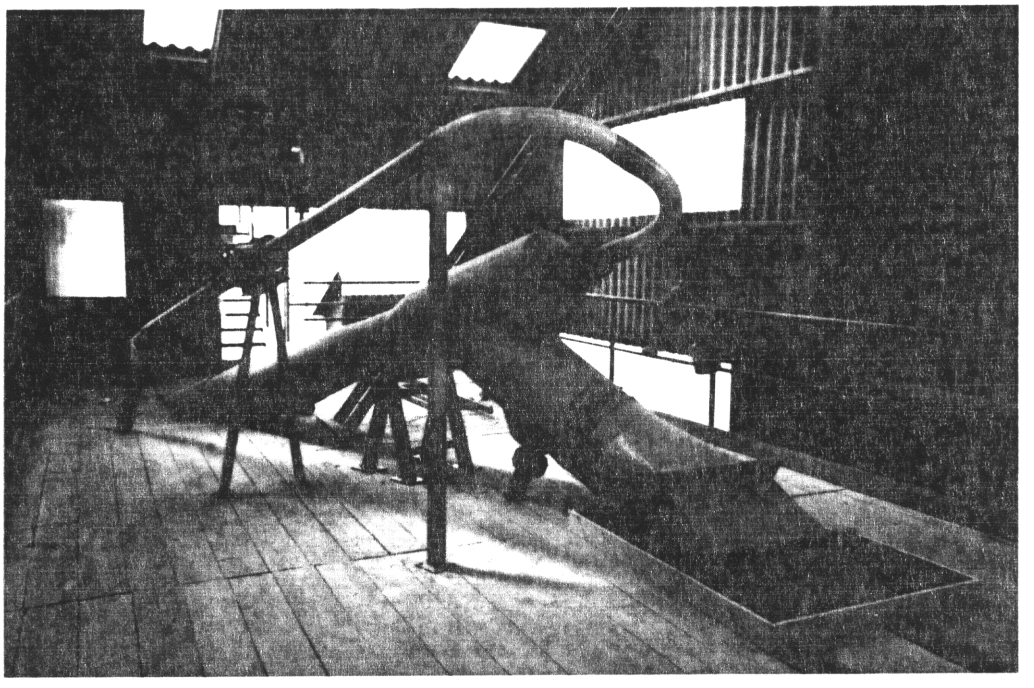

Figure 10 : Superphosphate Plant (NANTES) First venturi

5. PRODUCTION OF AMMONIUM NITRATE SOLUTIONS (figure 11)

The venturi cyclonic spray tower unit has also been efficiently used to reduce ammonia and nitrate losses in the production of ammonium nitrate solutions, and to avoid the production of polluted condensate.

The scrubbing system for mists sprayed with a 30% nitrate acid solution is set between the neutralizer and the first exchanger where ammonia required in the process is evaporated by exchanging calories with the vapour.

Condensate with a nitrate content of less than 0.1 g/l can thus be obtained which can perfectly be used as process water in the nitrate acid unit.

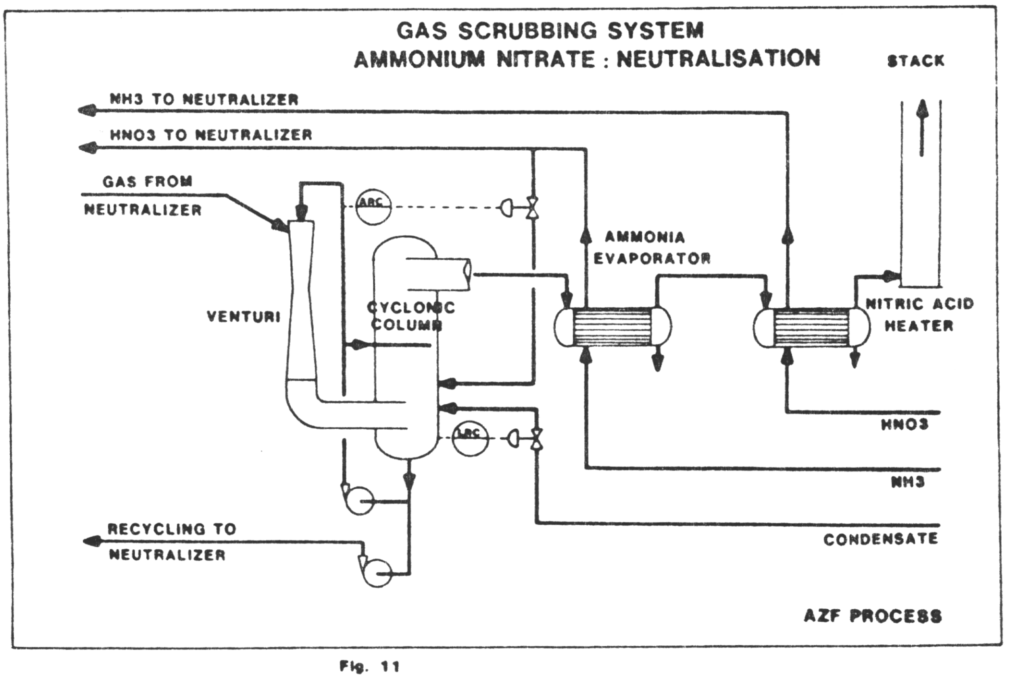

Fig. 11

6. EXAMPLES OF REALIZATIONS

a) AZF simple superphosphate production unit in NANTES;
In 1980, AZF had to install in this plant a rotary den to produce simple superphosphate. The administrative authorization was function of the compliance with very exacting requirements about pollution:
- no polluted liquid effluent,
- delivery to atmosphere of less than 0.45 kg/h fluorine.

The unit capacity was to be 35 t/h, using:
* 16.250 tons of MORROCO phosphate,
* 4.130 tons of SENEGAL phosphate,
* 18.230 tons of 72% sulfuric acid

per hour. In view of the fluorine content of phosphates used, of in-lab tests and of AZF industrial expertise, the amount of fluorine released by this production was estimated at 300 kg/h.

The number of transfer units can be expressed as follows :

$$NUT = \frac{r}{r-1} \, Log \, \frac{Ye - m\,Xs}{Ys - m\,Xe}$$

where r is the extraction coefficient, Xe and Ye, the quantities of polluting agent at liquid and gases inlet, Xs and Ys, the same elements at outlet.

This expression can be simplified since, in the present case, r is higher than 10^6, and fluorine vapour pressures in H_2SiF_6 solutions at a temperature of about 70±C, very low. It can thus become:

$$NUT = Log \, \frac{Ye}{Ys} \quad or \quad \frac{Ys}{Ye} = e^{NUT}$$

The table of correspondences between the NUT and the resulting fluorine absorption yields is as follows :

NUT	1	2	3	4	5	6	7
R%	63.2	86.5	95.0	98.2	93.3	99.75	99.9

The number of transfer units required by the Administration for the rotary den gas scrubbing installation was consequently 6.5.

Theoretical studies, pilot tests and industrial experience gained in other installations resulted in the definition of a set of three venturis and three towers according to the diagram in figure 8, the fluosilicic acid solution with a concentration of about 10% obtained in the first stage being recycled back to the mixer.

The number of transfer units required had to be distributed over the three stages in the following way: 1.5 - 2.0 - 3.0. The delivery rate selected for suitable cleansing of the rotary den, the mixer and the first section of superphosphate conveyor, 15 000m3/h, was to result in a fluorine content of gases delivered through stack of 30mg/m3.

The installation has been built according to this procedure and the fluorine content measured at stack outlet ranges from 10 to 20mg/m

b) Scrubbing of gases from the biggest granular fertilizer plants in the world in USSR (IFA - Technical Congress 1984 - 2)

Soviet standards to be complied with,regarding gaseous effluents from this enormous units (130t/h 17.17.17) built to AZF process were drastic:
- ammonia .... 10 kg/h maximum
- fluorine .... 1.5 kg/h maximum

These gaseous effluents were subjected to a treatment in venturi-cyclonic tower units sprayed with an ammonium sulfate acid solution and, then, in venturi-cyclonic tower units sprayed with lime milk.

Below are the calculation elements applied for the venturi-tower unit in which ammonia present in gases from the granulator and from the reactor is treated.
Gases entering a gas scrubbing unit have the following composition in kg/h:

- dry air 33 500
- H2O vapour 12 434
- fluorine 15.3
- NH3 .... 1 197

which corresponds to a volume flow rate of 56,465m3/h at 91±C.

Calculation of the average molecular weight of scrubbing liquid:

$$M = \frac{\rho}{\frac{a}{Ma} + \frac{\rho - a}{18}}$$

where ρ = 1,200 kg/m3
a = 480 kg/m3
Ma = 132

$$M = \frac{1\ 200}{\frac{480}{132} + \frac{1\ 200 - 480}{18}} \times 27.5$$

Calculation of L (liquid flow rate in kmoles) :

$$L = \frac{1 \times \rho}{M}$$

The spraying pump capacity is 125.3 m3/h

$$L = \frac{125.3 \times 1\ 200}{27.5} = 5\ 428$$

Calculation of G (gaseous flow rate in kmoles)

$$G = \frac{11.79\ .X}{(273 + t)} = \frac{11.79\ (33\ 500 + 15.3 + 1\ 197)}{0.94\ (273 + 91)} = 1\ 196$$

$$\frac{L}{G} = 4.6$$

Calculation of the required number of transfer units

It is determined from in and out ammonia contents.

$$\text{At inlet we have } \frac{(1\ 197)\ 10^{-3}}{56\ 465} = 21.2\ g/m3$$

$$\text{where } Ye = \frac{mg\ 10^{-6}}{Ma.G} = \frac{21\ 200 \times 56\ 465}{17 \times 1\ 196 \times 10^{6}} = 58.875.10^{-3}\ \text{mole/mole dry air}$$

Exit gases should have the following composition in kg/h:
- dry air 33 500
- H2O vapour......... 10 045 t = 76.5°C
- fluorine 2.6
- NH3 .... 7.33

which corresponds to a volume flow rate of 49,215m3/h :

$$Ys = \frac{m'\ g'\ 10^{-6}}{Ma.\ G} = \frac{149 \times 49\ 215}{17 \times 1\ 196 \times 10^{6}} = 0.361.\ 10^{-3}\ \text{mole/mole dry air}$$

The in-lab study of 40% ammonium sulfate solutions demonstrated that the vapour pressure of ammonium in solution is negligible. The term mXe can thus be eliminated from the formula applied to obtain the depletion efficiency which becomes:

$$EG = \frac{Ye - Ys}{Ye} = \frac{58.875 - 0.361}{58.875} = 0.993$$

The number of transfer units is obtained by writing

$$NUT = Log \frac{1}{1 - EG} = 4.96$$

Pilot tests and measurements made in industrial-scale plants have shown that the assembly defined for this unit should allow five transfer units to be easily reached.

A similar calculation has been performed for fluorine absorption.

During a guarantee test in MELEOUS unit, the results were as follows:

	guaranteed values	values obtained
ammonia	10 kg/h	5.5 kg/h
fluorine	1.5 kg/h	0.17 kg/h

7. CONCLUSION

Many studies have been carried out, and are still developed, for the purpose of getting full control of the various problems met with gas scrubbing in fertilizer industry. They allowed AZF to conceive a complete system taking into account gas scrubbing from all its angles and backed up by theoretical studies, mathematical modelling, and also, and principally, industrial expertise: a system conceived by fertilizer producers for fertilizer production.

TA/80/19 Gas scrubbing systems in fertilizer industry by P. Chinal, J.F. Priat & Ph. Segard, CdF Chimie AZF, France

DISCUSSION : (Rapporteurs Messrs A. Bourgot & M. Sart, Prayon-Rupel, Belgium)

Q - Mr. P. BECKER, COFAZ SA, France

Concerning the exhaust gases and the recycling in the case of SSP, what is the H2SO4 concentration in the recycled 10% solution, for ex. 98% H2SO4 or do you adjust it?

- In the system with three consecutive venturis, is the liquid the driving force or do you have a ventilator? What the KW consumption? What is the pressure drop of the whole system?

- How many NTU per unit of venturi?

A - For SSP we use 70% H2SO4. Scrubbing liquors represent a very small part and result in slight savings on the acid consumption f.ex., at the BASSE-INDRE plant, for a production of 35 t/hr, we recycle about 0.5 m3/hr of liquids.

- The gas scrubbing system includes an extraction ventilator downstream; the pressure drop is almost nil since we put preferably the energy at the level of scrubbing liquid sprayers, about 3.5 bars. It is the design of our venturis. One must find the good compromise between the energy put on gases and on scrubbing liquids. For example, a system including a venturi + a cyclonic tower has a pressure drop of 80-100 mm wg. Thus, the three stages at BASSE-INDRE have a total pressure drop of 250-300 mm wg.

- At BASSE-INDRE the total NTU is 7.5, hence about 2.5 NT/stage

- Consumption of electricity (excluding rock grinding): 3.2 kW/t SSP.

Mr. P. BECKER

I think that the concentration of 70% H2SO4 is obtained after mixture with the recycling, as it is difficult to produce SSP with a 70 acid with later dilution.

In our plant, with 40 t/hr production, the recycling is 2 m3/hr. The figures should be revised.

<u>Answers given later</u>:

- For 35 t/hr the recycling is 1.5 to 2 m3/hr

- The 70-72% concentration is, indeed, after dilution with recycled scrubbing liquors.

Q - Mr. T. NURMI, Kemira Oy, Finland

Your first flowsheet showed the exhauster was placed between venturi and spray cyclonic column in quite dirty conditions. Have you had any leakage problems with the exhauster?

A - Yes, for the granulator gas circuit, the ventilator is located between the venturi scrubber and the cyclonic tower and it thus receives gases still containing particles, dust, ammonia, etc... but these gases are saturated since they are cooled in the first stage: we have no particular problem in so far as the connecting pipes between the first and the second stages are as short as possible, with the right slope and equipped with auxiliary sprayers which can be used if necessary.

Q - Mr. M.H. JENNEKENS, DSM Fertilizers, Netherlands

In case of DAP production, what is the temperature of the scrubber liquid? Is this liquid a solution or a slurry?

A - In the case of 18-46-0 DAP production, the solution in the cyclonic tower is acidified with H2SO4, and is used in the formulation; the temperature of the scrubbing liquors in the last scrubber is about 40-45° C. For the first stage the scrubbing liquor is made of a solution of ammonium sulphate phosphate; its temperature is about 60-65° C.

It is a scrubbing liquor with a density of 1.350, pH 4-5, N/P=1.4. Thus it is not a slurry but a true solution.

Q - Mr. B.O. PERSSON, Supra, Sweden

In the DAP production the NH3:P2O5 ratio in the scrubber is claimed to be 1.4. What is the concentration? What is the NH3-loss in that case?

A - In the case of DAP production (AZF produces 50,000 t/yr in N° 5 plant at Rouen + several seasons at Avignon and Sas van Ghent) the ammonia losses for the first seasons represented 15 to 18% of the ammonia supplied. Since then progress was made and, presently, for DAP, 12 to 13% of the ammonia used for production enters in the scrubbing system. As the scrubbing plant efficiency is 90 to 95%, this enables to guarantee for the plant an overall recovery equal or above 99% for ammonia.

Q - Mr. M. BARLOY, SCPA, France

Since the fluorine contained in the gas is recycled with the scrubbing liquors in the granulator and ends in the finished product with a new equilibrium in the gases:

- What is the equilibrium fluorine content at the scrubber inlet, with reference to a waste water scrubbing system and for several productions?

- In what form is fluorine in the finished product?

A - For SSP the F content of gases in a balanced system is about three times the conventional value. From investigations made at BASSE-INDRE for 35 t/hr SSP production, the F content in the exhaust gases of the den is about 4 g/m3 if scrubbing liquors are not recycled and about 11 g/m3 when they are recycled.

- In the finished production F is in the form of calcium fluoride.