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**LARGE NITRIC ACID PLANTS USING GRANDE PAROISSE PROCESS -
IMPROVEMENTS AND EXPERIENCE**

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1 - A B S T R A C T

In addition to the advantages of reduced specific capital and labour costs per tonne of product which are a general benefit of large-scale chemical plants, very large single-stream nitric acid plants also have improved thermal efficiency in comparison with smaller units. The greatest overall efficiency, in terms of nitrogen conversion, catalyst consumption and environmental control, can be achieved by using the dual-pressure type of process, with ammonia combustion at an intermediate pressure and absorption under high pressure. This type of process was pioneered by Société Chimique de la Grande Paroisse from 1958, and the company has exploited the inherent advantages of this type of process in a number of extremely large plants in various parts of the world in recent years.

On present time, considering large nitric acid units designed according to the Grande Paroisse process, 15 are larger than 900 mt/day, 13 being today into operation with a very high reliability. No other licensor has such an experience with plants in operation at capacity larger than 900 mt/day on one single line ; it is the result of years of development of the process both as manufacturer of nitric acid and as leading plant designer.

2 - NOTE ON SOCIÉTÉ CHIMIQUE DE LA GRANDE PAROISSE

Société Chimique de la Grande Paroisse, usually known by the abbreviation "GP" was founded in 1919 and was a subsidiary of Air Liquide until October 31st, 1987.

On November 1st, 1987, Cdf. Chimie AZF has brought to Société Chimique de la Grande Paroisse most of its fertilizer activities and related assets, which have kept their original brand name.

The shareholding of the new Société Chimique de la Grande Paroisse is Cdf Chimie 70%, Air Liquide a little under 20% and other shareholders slightly over 10%. Société Chimique de la Grande Paroisse retained its stock exchange listing.

As a result of the merger, Société Chimique de la Grande Paroisse is now the number one as French fertilizer company and ranks second in Europe. Three main fertilizer plants are located in Grand-Quevilly, Toulouse and Grandpuits ; other sites, in France, are Mazingarbe, Waziers, Carling, Ottmarsheim, Montoir de Bretagne and also in the Netherlands Sas van Gent.

The merger also left out six small fertilizer plants, producing P & PK fertilizers ; these are managed independently by AZF and located in France : in Brest, Grandville, Basse Indre, Fenouillet, Bordeaux and in Belgium, Rieme.

The installed annual capacity of nitric acid of the Société Chimique de la Grande Paroisse is nowadays of 2,2 millions metric tons.

In addition to the manufacture of nitrogenous fertilizers GP has activities of engineering in the same field, in France and abroad, for which it has a well established reputation for technical competence and thoroughness. This activity has been particularly demonstrated in the area of nitric acid since 1958, when GP constructed the first medium unit for its own use and then commercialized its nitric acid process (single and dual pressure), which have now been used in more than 50 units with capacities ranging from 35 to 2000 MTPD.

3 - HISTORY OF GP PROCESS FOR LARGE NITRIC ACID PLANTS

GP has been a pioneer in the process of large single stream nitric acid plants after many tests and improvements in its own factories since 1958 with the dual pressure process.

1 - Based design

It was made in 1956 and based on dual pressure process with an oxydation under medium pressure instead of atmospheric pressure as it was on other plants at this time. One plant with a capacity of 160 MTPD was commissioned in 1958 at Fraix Marais in the GP Group ; it was duplicated at Lievin close to Fraix Marais which was in the GP Group at that time.

They had the following design characteristics :

- dual pressure process
- ammonia oxydation at 3,5 bar
- absorption at 6,5 bar
- concentration at 58%
- tail gas content of 700 ppm.

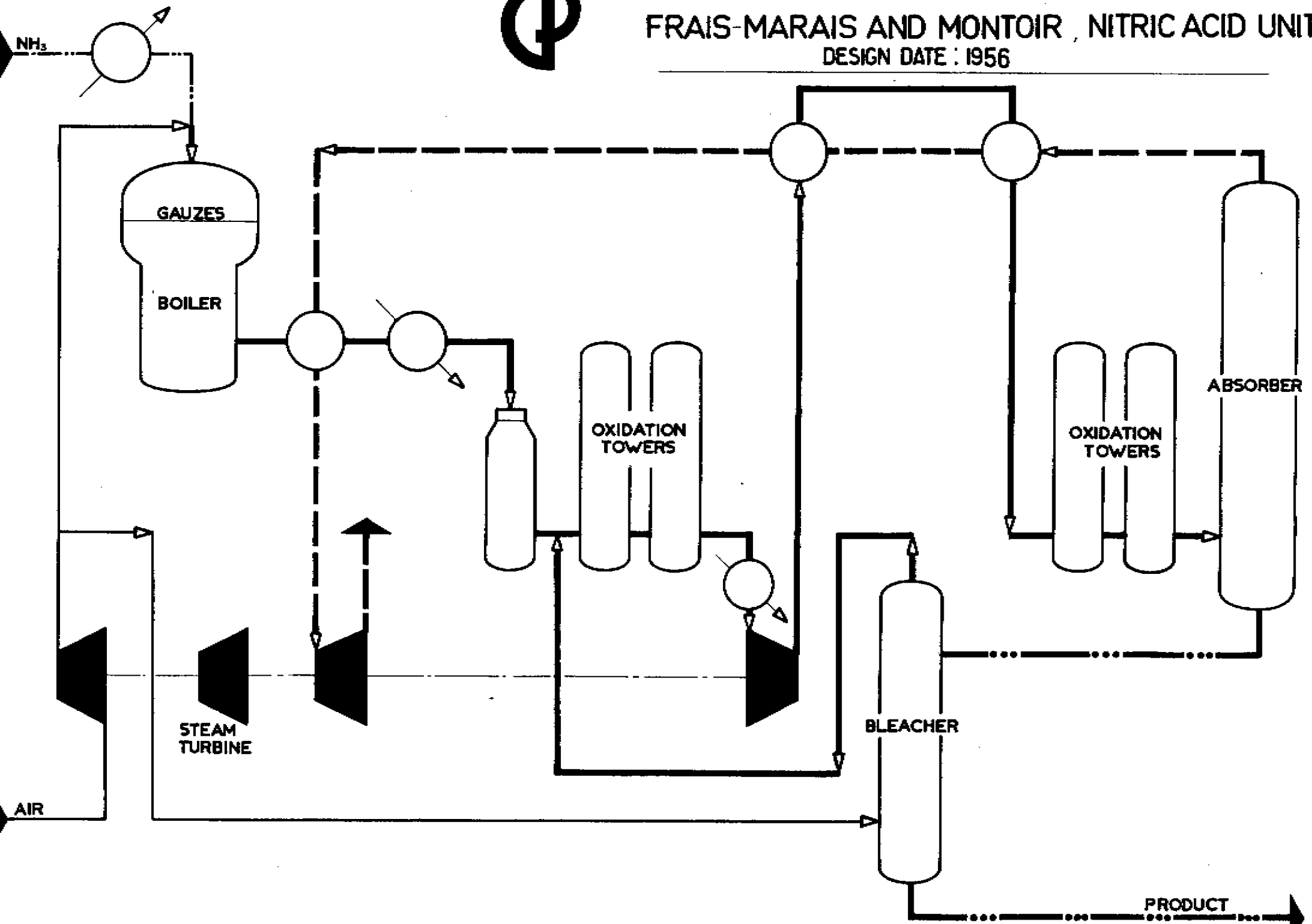
A basic flow diagram is shown in the annexed figure. We used four oxydation towers on these units, two on medium pressure and two on high pressure. As it was a success, our management decided in 1960 to build three identical plants with the expansion of our fertilizer production, once again in the Northern Group at Fraix Marais and two in the Western Group at Montoir de Bretagne which was created at this date. These plants were commissioned in 1963.

2 - 925 MT PD design

Afterwards in 1965, due to our great success in nitric acid production, our management has proposed a big plant for the German Democratic Republic at Schwedt. They needed 925 MTPD HNO₃ in order to produce calcium ammonium nitrate. Instead of the six lines identical to precedent lines (160 MTPD) running in our own factories, we proposed them only one line and they accepted to do it. Due to some delays in construction, this plant was commissioned in 1968. It was again a great success after some minor modifications on gas-gas exchanger as it had vibrations on tubes. This plant was at that time the largest plant all over the world.

FRAIS-MARAIS AND MONTOIR, NITRIC ACID UNITS

DESIGN DATE : 1956



10 - 4

Characteristics were similar to our own plants and as follows :

- ammonia oxydation at 3,5 bar with four burners
- absorption at 9 bar
- two oxydation towers, one on oxydation and one on absorption
- sieve trays on absorption tower for the first time.

Very close after designing and before commissioning, two plants of same capacity were reproduced in Poland and one for ourselves in Grandpuits.

A basic flow diagram is shown on the annexed figure.

3 - 1100 MT PD design

Again in 1970, we have increased the capacity for a plant to be built in Bulgaria, at Varna, till 1100 MT PD ; it became the largest plant all over the world.

Design was very similar but with no oxidation tower. It was the result of calculations and tests made in our own plants ; before designing this plant, we did it on two smaller plants and the result confirmed our calculations.

Absorption pression was increased till 13 bar in order to get 400 PPM on tail gas content.

4 - 1250 MT PD design

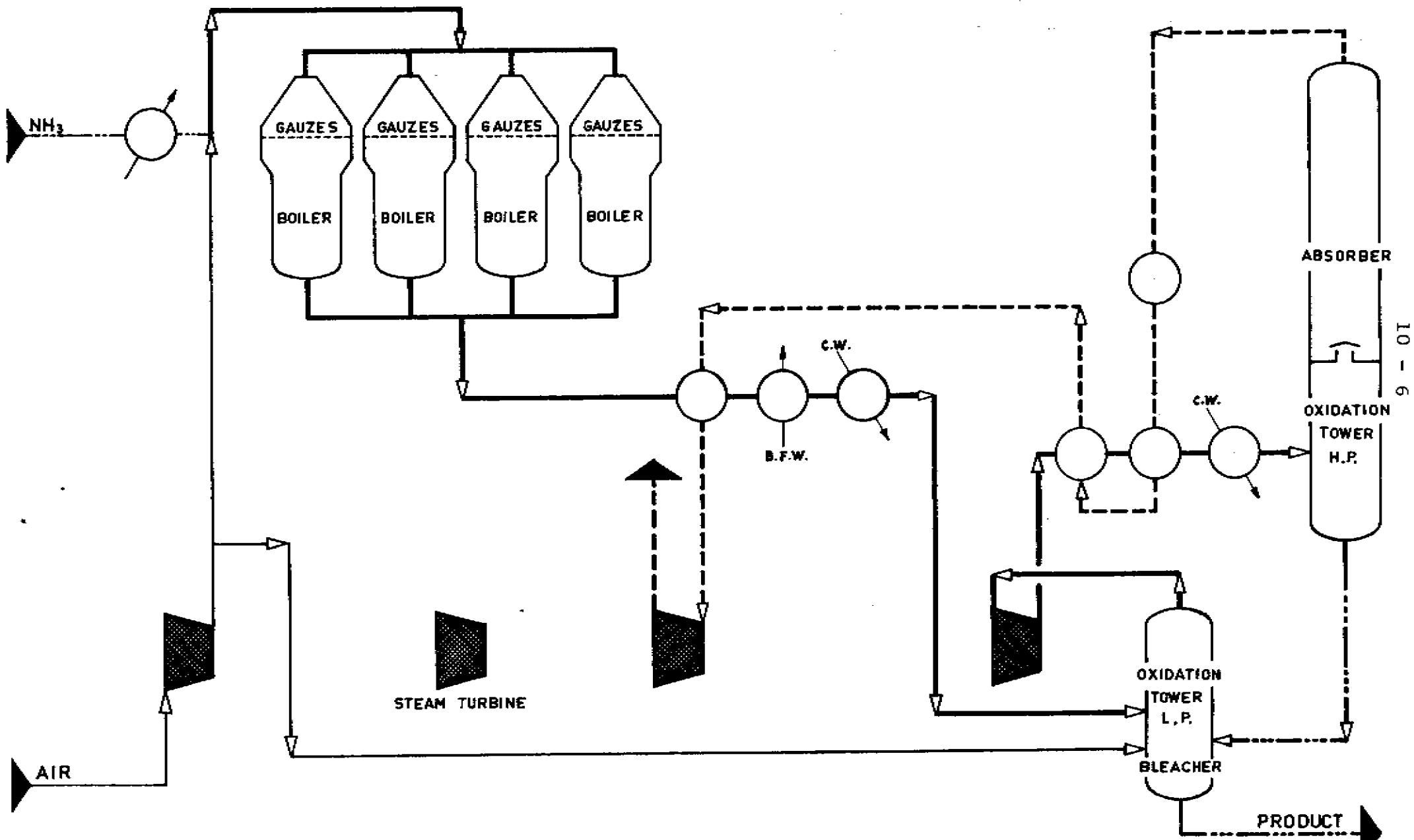
In 1975, NSM intended to build one nitric acid plant for a capacity of 1250 MT PD ; as they were very anxious to have only one line for this capacity, we invited them to visit Varna. They were very impressed and immediately afterwards they have ordered us the nitric acid plant, becoming again the biggest plant all over the world. They decided to have a direct contract with GP in order to discuss carefully with the suppliers of equipment and to order what they wanted ; so we made all the detailed engineering as well as the purchasing services. We made the orders on behalf of NSM. We supervised the construction in workshops, the erection and the start up of the plant.

The basic flow diagram is shown in the annexed figure.



S.E.I.F. NITRIC ACID UNIT

DESIGN DATE: 1967



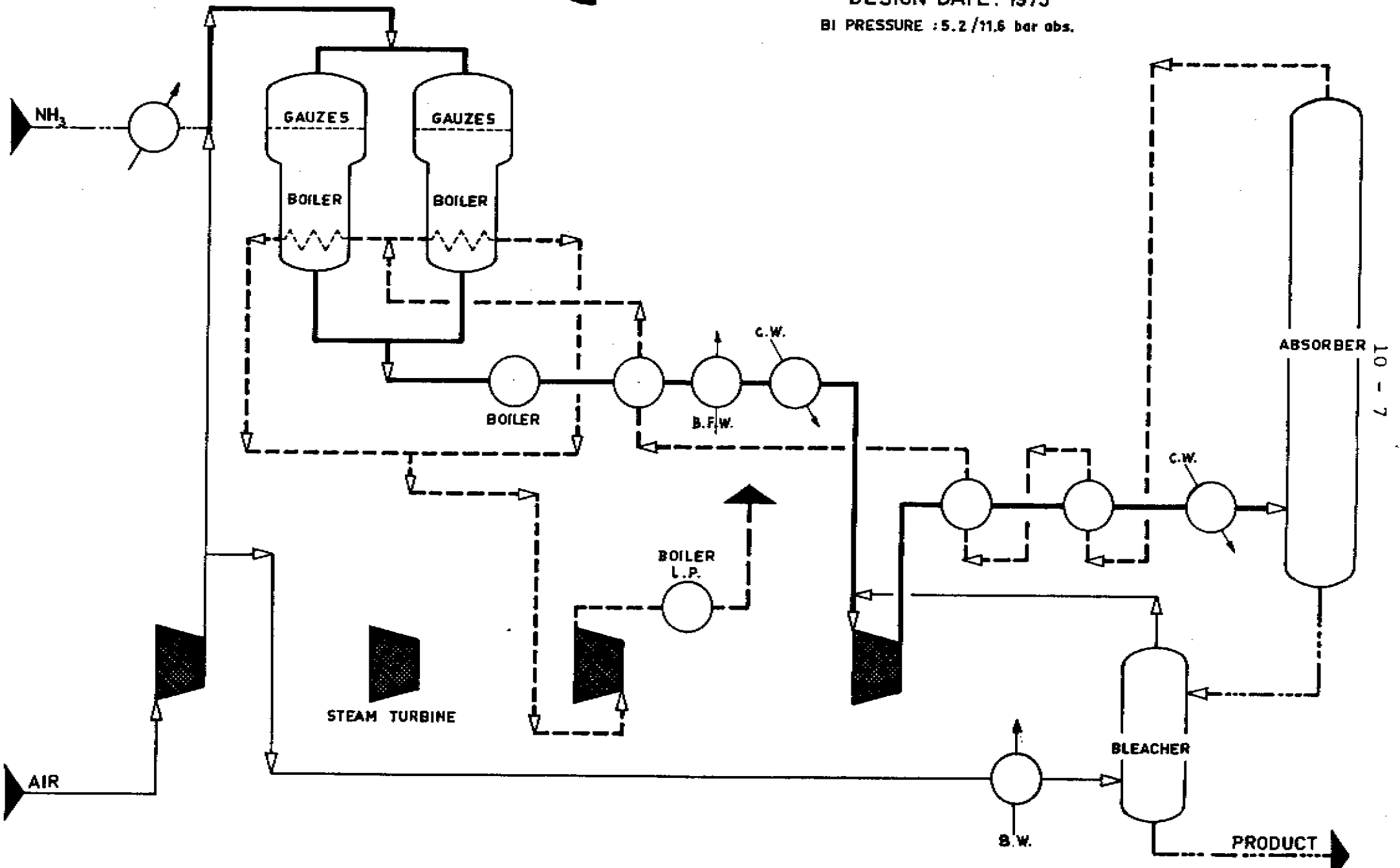


_ SLUISKIL _ HOLLAND _

1250 M.T.D. HNO₃ 100 %

DESIGN DATE : 1975

BI PRESSURE : 5.2 / 11.6 bar abs.



Main design characteristics are as follows :

- ammonia oxydation at 5,2 bar
- absorption at 11,6 bar
- concentration at 60%
- tail gas content lower than 200 ppm.

Comparing to 1100 MTD Varna plant, there are only two burners which are again to-day the biggest in this field with a diameter of about 5 m. After the 1973 oil crisis , energy recovery had to be optimized so a higher number of exchangers.

This plant has been revamped and the capacity increased till 1600 mt/day.

5 - 1800 MT PD design

In 1984, NSM decided to increase its capacity of fertilizers and so to build a nitric acid plant with a nominal capacity of 1800 MTPD, using our new improvements.

This plant has been commissioned on June 1986 and within a few weeks of set up had successfully passed its performance tests. For this second unit, we provided to NSM with basic engineering and technical assistance for detailed engineering, purchasing and start up while NSM staff took the responsibility of general contractor.

The plant was designed very close to the first one but with a higher energy recovery ; the burners were the same and so the investment for gauzes as spare parts smaller.

Concerning the equipments and specially for the critical ones, they have been supplied by the same vendors as the first unit so Man GHH of German Federal Republic for the turbo set, Fives Cail Babcock of France for the waste heat boiler and AKF of Netherlands for the absorption column which was erected in one piece.

The basic flow diagram is shown in the annexed figure.

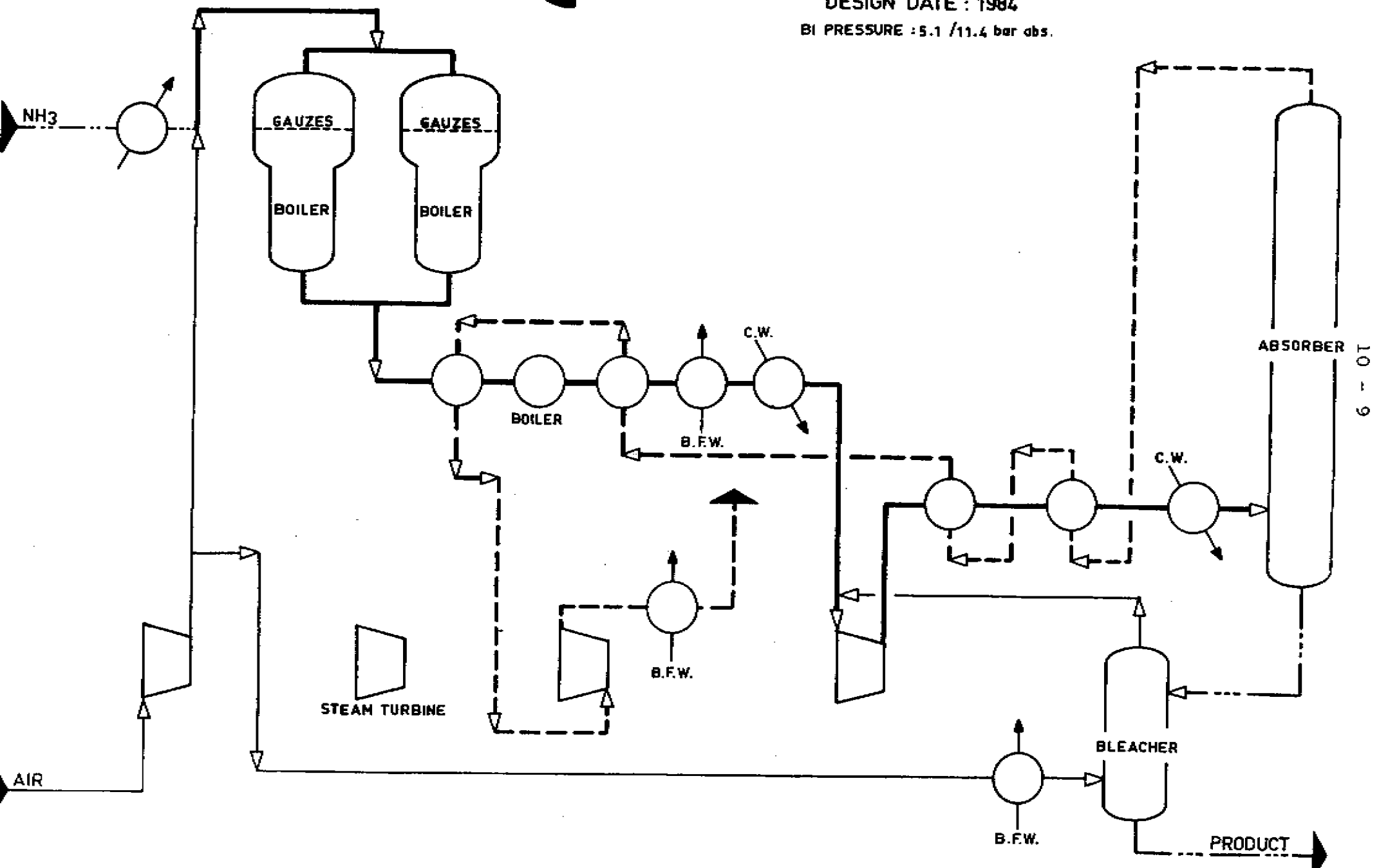
This plant became the largest plant all over the world and, after minor modifications, capacity has been increased till 2000 MTPD.

6 - List of references for plants larger than 900 MT PD

GP over the last twenty years has been associated with the installation of very large single train nitric acid plants with capacities larger than 900 MTPD, such as :



_N.S.M. _ SLUISKIL _ HOLLAND _
2 x 1800 M.T.D. HNO₃ 100 %
DESIGN DATE : 1984
BI PRESSURE : 5.1 / 11.4 bar abs.



COMMISSIONING DATE	CUSTOMER	LOCATION	CAPACITY MTPD
1968	DIA CHEMIE AUSRUSTUNGEN	Schwedt/Oder GDR	925
1970	SEIF	Grandpuits France	925
1972	POLIMEX	Wloclawek Poland	2 x 900
1973	TECHNOIMPORT	Varna Bulgaria	1 100
1977	DU PONT DE NEMOURS	Victoria Texas - USA	907
1977	NSM	Sluiskil Netherlands	1 250
1984	INDUSTRIEANLAGEN IMPORT	Rostock GDR	2 x 1 200
1984	ICI	Billingham U.K.	1 000
1986	NSM	Sluiskil Netherlands	1 800
1987	CNTIC	Lu Cheng China	2 x 902
1989	Société Chimique Grande Paroisse	Grand Quevilly France	1 000 (removal & revamping)
1991	TAGAS	Mersin TURKEY	1 200

Many of these plants have been revamped with the aim of increasing the capacity while the tail gas content should be in conformity with all the environmental standards :

- SEIF till 1.150 MT PD
- NSM (1) till 1.600 MT PD
- NSM (2) till 2.000 MT PD.

Some others are under feasibility study such as DU PONT DE NEMOURS and INDUSTRIEANLAGENIMPORT.

7 - Experience in large plants

GP is not only involved in designing of nitric acid plants but also as manufacturer and seller of fertilizers and as manufacturer of nitric acid accordingly.

We have experience in large plants not only for our clients but also in our own factories ; as an example, we made many tests before proposing any improvement on the plant built in Grandpuits, owned 100% by GP, where we :

- increase the capacity up to 1150 MT PD,
- increase the energy recovery to save steam consumption,
- solve corrosion problem in tail gas preheater,
- increase the reliability of the plant,
- install a digital centralized system.

This plant belongs to the first generation of large plants from the design point of view as described hereabove ; however its optimization has been improved continuously. There are constant relations between Engineering Department and engineers involved on this nitric acid plant on site. And so, we are able to give the benefits of our improvements to our clients.

TA/88/10 Large nitric acid plants using the Grande Paroisse process: Improvements and experience by P. Gry, Société Chimique de la Grande Paroisse, France.

DISCUSSION (Rapporteur Mr. A.F. Porneuf, Grande Paroisse, France).

Q - Mr. G. KONGSHAUG, Norsk Hydro, Norway.

The problem of tail gas colour increase with increasing plant capacity due to larger stack diameter. How do GP meet the requirements of colourless tail gas from large acid plants ?

A - The problem was raised in England and in Scotland where regulations are 1000 ppm colourless gas. Hence, we had to solve that problem first at ICI and, taking account of the capacity of 1000 t/d, from our calculations, the tail gas content was 120 ppm. In Scotland, at Scottish Agricultural Industries, with a 500 t/d capacity, tail gases contained 130 ppm, so that we complied with the existing rules and gases were colourless. As a result, the higher the capacity, the lower the content of the tail gases, since the colour is due to the NO₂ content.

Q - Mr. T. LAINTO (Kemira Oy, Finland)

1/ Would it be possible to build a single line nitric acid plant with a larger capacity than 2000 t/d ? What are the critical design factors ?

2/ Can you tell us what is the difference in thermal efficiencies between a nitric acid plant with a capacity of 500 t/d and one with a capacity of 1500 t/d ?

A - 1/ I believe it is possible to build plants of more than 2000 t/d capacity, but it is not only a problem of process. There is a problem of equipment, in particular with regard to the diameter of the burner. The burner is voluminous and it raises a transport problem.

There is also a problem of machines which we are now considering with the suppliers of equipment. It is an important point. We cannot only develop the process by itself, but we must do it in association with the suppliers.

2/ There is no difference between a 500 and a 1500 t/d capacity plant, if they are built according to the same process, the double pressure. But one could build a 500 t/d single pressure plant and a 1500 t/d double pressure plant. There, we may find differences. We now build 500 t/d plants based on single pressure, but, in some cases, we might use double pressure. It depends on the operational costs, investments, payback, etc. We recently made a survey in the US for a 600 t/d plant and found that double pressure is more economical than single pressure; each case must be considered separately.

Q - Mr. P. ORPHANIDES (Duetag, France)

1/ What is the maximum burner capacity you have so far designed for a double pressure HNO₃ plant ?

2/ What is the catalyser net effective diameter for such a burner ?

3/ What are the limiting factors to increase further the burner capacity in double pressure plants ?

.../.../...

A - 1/ It relates to a single burner 1000 t/d plant, but the design for a 1200 t/d is being completed.

2/ The cloth diameter is 5.5 m.

3/ There are mainly construction problems.

Q - MR. S.K. MUKHERJEE (Khrisco, India)

Would you like to comment on adopting design based on extended absorption tower against relatively smaller absorption tower followed by catalytic combustion in both cases to obtain emission standard at below 200 ppm max NO_x, and large capacity nitric acid plants of approximately 1000 t/d (100% basis). The comparison may be on relative investment cost and ammonia efficiency ?

A - It depends on the existing situation; it is necessary to carry out a complete survey to see if one absorption tower is sufficient. There are several possibilities. There is not only one absorption tower. One can have one absorption tower, one catalytic combustion or one small absorption tower followed by a catalytic absorption, it depends on the cost of raw materials and on the existing installation, in particular its pressure. If that pressure is not sufficient, the absorption tower will not be recommended. The solution would be one absorption tower and one catalytic combustion or a catalytic combustion alone. On the other hand, in the US, in the 70's, we installed 7 or 8 absorption towers. There was enough pressure - 7 to 10 bars. Consequently, nitric acid was recovered and the tail gas content was reduced from 4000 ppm to 200 or 400, according to the regulations in the country. There, the absorption tower was interesting but there is no systematic answer. Each case must be studied with all the factors involved.

Q - Mr. S. ORMBERG (Norsk Hydro, Norway)

You indicated moving and revamping one HNO₃ plant in France in 1989. What is the saving in investment compared to building a new plant ?

A - We did not have the money to build a new 1000 t/d plant and the actual budget saving is about 30-40%, since part of the equipment to be used in that plant, which will be completely changed, will be recovered. All the compressor line - a single pressure unit operating at 5 bars; for the oxidation we are going to replace the burner. There were three burners, we are going to install one. The three existing absorption towers will not be transported and will be replaced by two and, since the pressure is not sufficient, we are going to install two absorption towers followed by a catalytic combustion to fall below the French standards. The line of exchangers remains the same. Hence, only the burner and absorption tower will be replaced, saving about 30-40% investment.