

IFA Technical Conference

Port El Kantaoui, Tunisia 12-15 September 1986 SOLVING NO $_\chi$ POLLUTION PROBLEMS IN NITRIC ACID MANUFACTURING PLANTS J. ROIRON, Rhône Poulenc Chimie de Base, France

SUMMARY

The NO_X content of tail gases from a standard nitric acid manufacturing plant depends on the absorption efficiency; in other words, mainly on the pressure factor.

Initially, the NO_X cleansing problem was tackled simply by increasing the absorption pressure; although it is an efficient method, it cannot be applied to old plants and it demands a high energy input.

Various processes were then proposed for solving the problem of old plants, that is, low-pressure absorptions. Only selective catalytic destruction of NO_X with ammonia is used on an industrial scale today.

Although efficient with respect to pollution control, this method involves a loss of ammonia yield which is not insignificant; in order to reduce this loss, RHONE POULENC have developed a High Efficiency Absorption, based on a liquid-phase oxidation of NO $_{\rm X}$ and used in combination with the catalytic destruction: these two techniques used together enable the most stringent standards for NO $_{\rm X}$ levels to be met in each case and at minimum cost.

BACKGROUND TO NO. EMISSIONS

 $NO_{\mathbf{x}}$ emissions cannot be disregarded as recent estimates

show that 500 million tonnes are discharged annually into the atmosphere.

Most of these emissions, approximately 90%, originate from natural phenomena (organic matter decomposition, thunderstorms, etc.), the remainder originating from unnatural sources such as internal combustion engines, power stations and chemical industries.

Although NO_X emissions from the chemical industry represent only a very small fraction of the total (Ref. (1), (2)), reducing them became essential because of their relative concentration on the one hand and because of their localization near large urban populations on the other.

Therefore, RHONE POULENC being a producer and user of nitric acid and also a seller of nitric processes, has had to undertake studies on the reduction of NO_X emissions from nitric acid manufacturing units, and has developed original pollution-control technologies which are particularly well suited for nitric acid plants, but which can also be used for other sources of NO_X emission whether they are in other chemical processes or alternatively in fumes from power stations which contain both nitrogen and sulphur oxides.

NO_x EMISSION FROM NITRIC ACID PLANTS

Most of the nitric acid used in the world is produced in the diluted form (concentration: 58 to 68% by weight) and is used in the manufacture of fertilizers.

It is produced from ammonia, according to the overall reaction below:

$$NH_3 + 202 \longrightarrow HNO_3 + H_2O$$
 (1)

All processes employed are based on this oxidation, they only vary in respect of pressure levels. Three fundamental

stages can be distinguished (see flow diagram in Figure 1):

High-temperature combustion of ammonia in air, in the presence of a catalyst:

$$NH_3 + 5/4 0_2 \longrightarrow NO + 3/2 H_2O + Q \longrightarrow (2)$$

Oxidation of NO by air: NO + 1/2 $\theta_2 \longrightarrow N\theta_2 + Q \longrightarrow$ (3)

Absorption of NO₂ in water at low temperature NO₂ + 1/3 H₂O $\xrightarrow{---}$ 1/3 NO + 2/3 HNO₃ + Q $\xrightarrow{---}$ (4)

In practice, reactions (3) and (4) are simultaneous and incomplete: as a result, after absorption, the gases emitted still contain NO_X and usually have the following characteristics:

Flow rate = $3,200 \text{ to } 3,500 \text{ Nm}^3/\text{t HNO}_3$

Oxygen ≈ 2 to 4% by volume

NO $_{\rm X}$ = 200 to 3,000 ppm by volume (30% of which is in the form of NO $_{\rm Z}$)

Thus, for a standard nitric acid plant, the emission of smoke containing 1,000 ppmv of NO $_{\rm X}$ is equivalent to discharging approximately 9.5 kg of HNO $_{\rm X}$ (in the form of NO $_{\rm X}$) to the atmosphere, per tonne of nitric acid produced.

At present, the generally agreed international standard for modern plants is 1.9 kg of HNOz (in the form of NO $_{\rm X}$) per tonne of acid produced, which amounts to approximately 200 ppmv of NO $_{\rm X}$, which necessitates either carrying out a final absorption under high pressure or the installation of a supplementary cleansing cell.

It should be noted that the colour of the smoke originates from NO2 only, NO being colourless: the same total NO $_{\rm x}$ content may give rise to very different colour

intensities; smoke containing less than 150 ppmv of NO₂ will be practically invisible.

OPTIMIZATION OF CONVENTIONAL ABSORPTION

The first logical step for reducing NO_X emission from nitric acid plants involves finding ways for optimizing the operation of conventional absorption, that is, Studying the effect of the main parameters involved.

The conventional absorption is carried out in plate columns in which gases flow in the direction opposite to the liquid; the recovery of NO_X in the form of dilute nitric acid makes use of reactions (3) and (4) mentioned above, reactions which are carried out in the following order:

Oxidation of NO in the gaseous phase in the space between plates, with a reaction rate which is relatively slow and which increases with decreasing temperature.

Absorption of NO2 in the liquid phase on the plates.

This is an exido-absorption, the overall efficiency of which is related to the thermodynamics and the kinetics of these reactions, in other words, to the operating conditions (especially pressure) and to the column technology (especially volume present).

The simulation of a concrete industrial example (see Figures 2, 3 and 4) leads to the following general observations:

More than 95% of NO_X present at the start of absorption are recovered in the first third of the column: the efficiency decreases considerably when the NO_X level is below 5,000 ppmv. The absorption volume required to reach 1,000 ppmv is twice that required for the decrease from 60,000 to 5,000 ppmv.

It will be seen later that this loss of efficiency related to the kinetics of NO oxidation in the gaseous phase, which becomes very slow at low partial pressures and at low oxidation levels, may be limited by means of a new absorption technique.

- * A very small change in pressure has a significant effect on the final NO_X level: it is therefore advisable to minimize losses of plant load (omission of valves or unnecessary monitoring devices, cleaning the filters) and to find out an optimum point of operation of the rotating machine.
- Lowering the temperature of the cooling water over the entire absorption also has a significant effect: but, the practical implementation would involve prohibitively high costs (supply of approximately 300,000 kilogram calories per tonne of acid produced).
- * Increasing the oxygen level by injecting additional air (and not pure oxygen) does not have a significant effect because the partial pressures of NO_X are reduced by dilution and the losses of load are increased.
- * A lowering of the concentration of acid produced has more effect the higher the initial concentration: in practice, a drop of the order of 1% may often be achieved by improving the "cleaning" part of the plant so as not to strip the NO_X contained in the crude acid, but to convert them into acid.
- * A drop in production leads to a drop in pollution due to the simultaneous effect of an increase in the cooling and an increase in the residence time (parameters beneficial to the kinetics of reaction (3)).
- * The injection level of condensates (mean HNO₃ concentration: 30 to 35%) produced upstream of the

absorption should be chosen judiciously: too low an injection modifies the acid profile of the column significantly and increases the NO $_{\rm X}$ level by approximately 10%, whereas too high an injection has very little effect.

This study leads to the decisive conclusion that under average pressure, the critical level of 200 ppmv of NO_X cannot be achieved by the optimization of the conventional parameters for regulating absorption and even resorting to solutions which are not economically sound.

In order to be sure of achieving this objective, it is essential to carry out the absorption under a pressure greater than 10 bars absolute; but this high pressure, which constitutes the first industrial solution to the $NO_{\rm x}$ pollution problem, does not represent the universally ideal solution because:

Firstly, it can only be envisaged for old plants which operate under low or medium pressure and which cannot be altered.

Secondly, when applied to future plants, it involves an additional consumption of compression energy and necessitates, if a satisfactory ammonia yield of the plant is to be maintained, changing from a single pressure process to a two-pressure process, which involves greater investment costs.

Since 1975, RHONE POULENC has undertaken a study to review the various processes which are likely to solve the problem of ${\rm NO}_{\rm X}$ emissions from nitric acid plants which operate at low or medium pressure.

TECHNIQUES FOR CONTROLLING NO POLLUTION

The treatment of NO_X effluents raises a large number of problems related to the complexity of the chemistry of nitrogen oxides, to the extreme diversity of the NO_X emissions (in quality and quantity of NO_X) and to the analytical problems encountered; the large number of patents related to this subject is the proof thereof.

In the more restricted area limited to effluents from nitric acid manufacturing plants, a multiplicity of processes are to be found; they may be classified into three large categories according to the fate of NO_X:

- a. Process which decomposes NO_v into nitrogen and water.
- b. Process which recovers NO, in the form of nitric acid.
- c. Process which converts NO, into secondary products.

The last category, which corresponds for example to scrubbing with an alkaline solution, eliminates the gaseous effluent by creating a liquid effluent. Therefore, this process has few industrial applications, except in some specific cases where the liquid effluent can be upgraded.

The second category, which covers both the improvement of absorption by regulating the parameters mentioned above as well as the use of the absorption/adsorption-desorption cycle, leads to a limited performance or prohibitively high operating costs.

Only the first category seems to be capable of guaranteeing a satisfactory industrial efficiency under all circumstances today.

PROCESSES INVOLVING THE DESTRUCTION OF NO.

These processes, in combination with a "reducing agent", carry out the destruction of the NO $_{\rm X}$ molecule into N $_{\rm 2}$ and O $_{\rm 2}$, at high temperature and in the presence of a catalyst.

After a first generation of non-selective catalysts, that is catalysts with which it was necessary to burn the exygen present before the destruction of NO_X , all the present industrial processes are of the type "selective catalysis in the presence of ammonia".

Gaseous ammonia is injected into the tail gases; the mixture passes over a catalytic bed (in general, vanadium oxide) and the following reactions take place:

$$^{2} \text{ NH}_{3} + ^{3} \text{ NO} \longrightarrow ^{3} \text{ H}_{2}^{0} + ^{5/2} \text{ N}_{2} + ^{2} \text{ (5)}$$

$$4 \text{ NH}_3 + 3 \text{ NO}_2 \longrightarrow 6 \text{ H}_2 \text{O} + 7/2 \text{ N}_2 + Q \longrightarrow (6)$$

Considering the selectivity of the reaction, the reagent quantities are very small (hence, a low heat output) and $100\ \text{vpm}$ of $N0_x$ is easily achieved.

But there are two types of constraint:

Constraint of operation.

The reactivity of the catalyst remains effective only over a restricted range of temperature, generally 230° to 330° : hence the necessity to provide a preheating of the gases, in many old plants.

Profitability constraint.

Ammonia consumption quickly becomes prohibitive: for a standard nitric acid plant, lowering NO_X from 2,200 to 200 vpm involves a reduction in the ammonia yield 2.1%, resulting in an increase in the cost of production of the acid of approximately 2%:(see Figure 8).

Therefore, RHONE POULENC has developed a selective catalysis in the presence of ammonia, the only effective industrial solution in order to meet the most stringent anti-pollution standards under all circumstances, but seeking to eliminate the constraints above, and especially the need to operate at relatively high temperatures.

RHONE POULENC CATALYST FOR THE REDUCTION OF NO.

The RHONE POULENC catalyst, designated as DN 110 (Ref. (3)), contains 10% by weight of vanadium pentoxide deposited on 3 mm-diameter alumina beads; it is employed in the form of a 0.2 to 0.5 m thick bed over which passes the gas to be treated into which the required amount of ammonia has been injected.

The reaction mechanism proves to be more complex (Ref. (6)) than described by the two theoretical reactions mentioned above and involves the formation of the intermediate HNO2; this is shown by:

A reactivity and an ammonia consumption closely related to the NO_2/NO_{χ} ratio.

A change in this ratio compared with its original value (see Figure 5).

The conversion rate obtained, that is, the ratio:

$$\frac{\text{NO}_{X} \text{ input - NO}_{X} \text{ output}}{\text{NO}_{X} \text{ input}}$$

depends on various parameters such as temperature, pressure, oxygen level, NO_2/NO_x ratio, quantity of catalyst, etc.; it is observed that it proves necessary to restrict this level to values generally less than 90% in order to avoid the emission of residual ammonia (see Figure 6).

The advantages offered by the RHONE POULENC ON 110 catalyst, related to the optimization of the controlled porosity of the catalyst are:

Minimum operating temperature of 170° (instead of the usual 230°), hence the possibility of use in most of the old plants without the need for heating the gases to be treated (see Figure 7).

Increased activity over a wide temperature range, from 170°C to 380°C .

The first industrial plant was put into operation in 1981; in this unit, the same catalyst load has been in use continuously for 5 years without any sign of loss of activity. 7 industrial units have already been installed in EUROPE and several projects are currently under study (see list of references).

Nitric	acid	units	equipped	with	the
RHONE	POULE	NC (DC	N) cataly	tic c	ell

Starting date	Country	Pressure blabs.	Gas flow rate Nm³/ȟ	Temperature	NO Level *ppmv input/output
1981	GREECE	3.5	30,000	210	1200/200
1985	GREECE	4.1 3.6 4.0	30,000 15,000 30,000	180 210 280	1300/200 1500/200 1200/200
1986	FINLAND	3.7	42,000	215	1200/200
1986*	FINLAND	4.2	34,000	210	1500/200
1986*	GREE'CE.	4.1	28,000	190	1000/200

^{*} not yet in operation

Therefore, the catalyst DN 110 enables the NO $_{\rm X}$ content of the effluents from the old nitric acid plants to be reduced to below 200 ppmv; nevertheless, the ammonia consumption quickly becomes prohibitive when the gases to be treated have a high NO $_{\rm X}$ content. Figure 8 shows a deterioration in the total ammonia yield of a standard nitric acid plant when a catalytic cell is installed to achieve 200 ppmv NO $_{\rm X}$.

In fact, at a given point on the graph, the overall ammonia balance sheet for 1 tonne of acid produced is as follows:

	Conventional absorption		
NO _X content, plant outlet (ppmv Ammonia consumption (kg)) 2200	200	
Combustion	278.2	278.2	
Absorption loss	5.8	5.8	
Injection into DCN	0	6.0	
Total	284.0	290.0	
Total ammonia yield %	<u>95</u>	93	

In order to prevent this loss of ammonia yield, RHONE POULENC then supplemented the DCN reactor with a high efficiency absorption which recovers a part of the NO $_{\rm X}$ in the form of HNO $_{\rm X}$.

HIGH EFFICIENCY ABSORPTION

The HEA (High Efficiency Absorption) technique, patented by RHONE POULENC results from studies on the fundamental mechanisms controlling the oxido-absorption of nitric acid in the region of low NO_{χ} partial pressures: it is based on the formation and oxidation of the intermediate HNO2 in the liquid phase, without an external oxidizing agent.

Without going into the theoretical details of the HEA system (Ref. (5)), it is pointed out that the passage through the intermediate HNO₂ seems to be fundamental because it introduces a totally new concept to the final absorption:

In conventional absorption, the plates are increasingly spaced out, in order to promote oxidation in the gaseous phase (reaction 3): hence a very large column height.

In HEA absorption, this height is divided by 2 or 3 because the increase in efficiency is obtained by promoting the oxidation in the Liquid phase, and not that in the gaseous phase (see Figure 9).

In fact, it has been demonstrated that reaction (4), in some areas (pNO $_{\rm X}$, NO/NO $_{\rm Z}$), is the sum of two reactions in the liquid phase:

$$^{\text{H}}_{2}^{\text{O}}$$
 + NO + NO₂ ---> 2HNO₂ (4a)
2 HNO₂ ---> 2/3 HNO₃ + 4/3 NO + 2/3 H₂O (4b)

and that it is possible to increase the production of acid without NO being evolved, by promoting the oxidation of HNO2 in the liquid phase according to the reaction

$$2 \text{ HNO}_2 + 0_2 \longrightarrow \text{HNO}_3$$
 (7)

Concretely, by means of a well-suited technology which forms the subject of the patent Ref. (4), reaction (7) is promoted at the expense of reaction (4b); this leads to the following advantages compared with a conventional absorption:

For an equal plant volume, improved efficiency.

For an equal absorption efficiency, plant volume two
to three times smaller.

(Pressure 3.5 b abs)			dard HEA ion absorp	
Column volume	(m ³)	٧	0.35 V	٧
Inlet NO _X concentration	(ppmy)	2500	2500 2	500
Outlet NO _x concentration	(ppmv)	1800	1800 1	300

Additionally, the oxidation level of the gases (NO $_2$ /NO $_x$ ratio) is strongly reduced at the outlet of the HEA column, which reduces the intensity of the colour of the smoke.

Five industrial columns of this type have already been installed in EUROPE, for pressures ranging from 2 to 8.5 bars absolute and gas flow rates of 15 to 65,000 ${\rm Nm}^3/{\rm h}$.

ADVANTAGES AND APPLICATIONS OF THE RHONE POULENC PROCESS

By coupling an HEA cell and a DCN reactor, RHONE POULENC is then capable of providing an optimum solution to the problem of NO_X emission from nitric acid plants, by guaranteeing the observance of the most stringent anti-pollution standards, for a minimum of operating costs (see Figure 10).

The integration into an existing plant is easy: the HEA column is placed in series with the existing absorption and the DCN cell is placed just upstream of the decompression turbine.

The increase in ammonia yield brought about by this solution greater in magnitude the higher the initial $NO_{\mathbf{X}}$

concentration; for example, in the case dealt with above, it is observed that the HEA column enables the initial yield to be recovered without the BCN reactor (see Figure 8a).

Furthermore, the "HEA + DCN" as a whole, leads to a certain number of other advantages:

- * Stabilization of the NO_X concentration at the reactor inlet, which facilitates the regulation of ammonia injection.
- * Possibility of treating gases with a high NO_X concentration without the need to use reactors with several superimposed beds, with multiple ammonia intiections.
- Relative decrease in the NO2 concentration, hence lowering of the colour intensity of gases and of ammonia consumption in the reactor.
- Reduced pollution, even during the initial stages of starting up of the plant (whereas the DCN reactor can only be put into operation after plant stabilization)
- * Possibility of increasing the concentration of the acid produced or the production capacity of the plant.

Balance Sheet (for 1 tonne HNO ₃)	Standard plant	Equipped with DCN	Equipped with (HEA + DCN)
Plant outlet NO. concentration (pomv) 2200	200	200
Ammonia consumption (Combustion Absorption Loss Injection into DCN	kg) 278.2 5.8 0	278,2 5.8 6.0	278.2 3.1 3.0
Total	284 - 0	290.0	284.3
Total ammonia yield %	95	93	94 .9

A cost analysis carried out within the European context demonstrates the cost-effectiveness of the combination "HEA + DCN" compared with the DCN reactor on its own for a standard single-pressure dilute nitric acid plant of capacity 350 t/day: depending on the initial NO $_{\chi}$ level, the investment costs corresponding to the HEA column are recovered in 1 to 3 years (see Table 1).

The first industrial plant incorporating such a unit was built in 1981 and since then various other plants have been sold (see Table II) and many projects are currently under study.

CONCLUSION

A detailed knowledge of the mechanisms related to the chemistry of the HNO2 intermediate has enabled RHONE POULENC to tackle problems of NO_X reduction systematically, and to arrive at the economical solution best suited for each case, by optimizing the operating range of the techniques available:

In the case of the revamping of old plants, after optimizing the existing absorption, choice according to the initial quality of the gases (pressure, oxidation level, oxygen content, etc.), and the economical context, from the following solutions:

DCN reactor (low pressure)

Combination of HEA + DCN (medium pressure)

HEA column alone (high pressure)

For new plants, incorporation into the conventional absorption of a high efficiency absorption part, leading to a gain of approximately 20% on the total height of the column, irrespective of the operating pressure: hence, reduced investment costs.

TABLE I Comparison of profitability between "HEA column + DCN reactor" and DCN reactor alone

Existing plant outlet for 2200 ppm			bban No.X	NO _x 3200 ppmv NO _x		
1 tonne HNO ₃ produced	10	"HEA + DC	n" "DCn"	"HEA + DCN"	"Z-bed DCN	
<u>Performance</u>						
Outlet NO x	(væqq)	200	200	200	200	
HNO ₃ recovered	(kg)	9,4	0	15.1	0	
Ammonia injected	(kg)	3.0	6.0	4.2	9.2	
Total pressure loss	(bar)	0,23	0.06	0.23	0,12	
t in DCN	(°C)	13	26	16	31	
Operating costs (FF)		·		· ·		
Acid recovered		-7.05		-11.32		
Ammonia		5.10	10.20	7,14	15.30	
Energy		0.90	-1,90	0,50	-2.40	
Total		-1.05	8.30	-3.68	12.90	
Relative gain from the "HEA + DCN" solution		9.35	F/c HNO 3	<u>16.58</u> F/t	нио3	

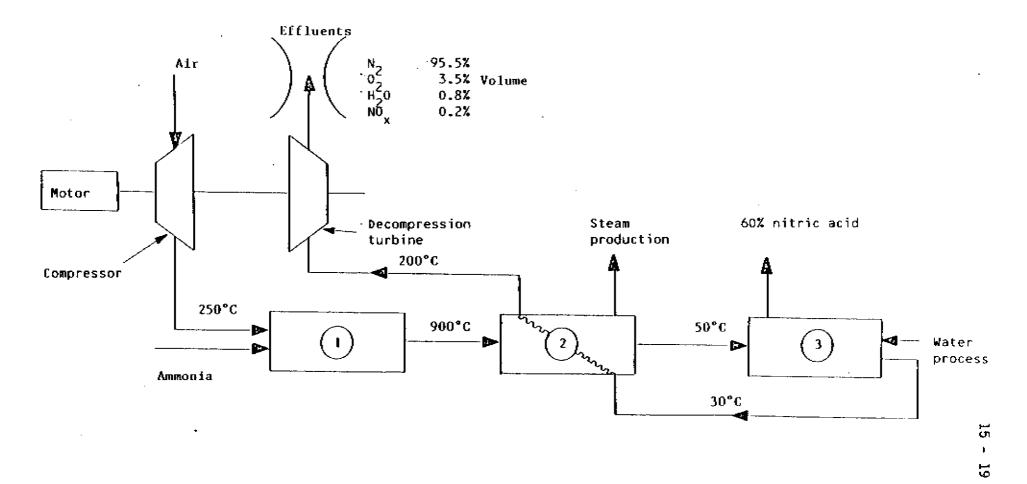
TABLE II ${\tt RHONE\ POULENC\ process\ for\ reducing\ NO}_{\chi}$ Industrial applications in nitric acid units

Date of			Tail gas	Pressure	ppm v NO _x	
starting up	Country	Process	flow rate No.3/h	bar abs:	Inlet/outlet	
1981	GREECE	HEA + DCN	30,000	3.5	2500/200	
1983	FRANCE	ΗEĄ	65,000	2.0	3000/1800	
1984	SPAIN	HEA	41,000	8,5	3800/800	
1985	GREECE	DCN	30,000	4.1	1300/200	
		DCN	15,000	3.6	1500/200	
		DCN	30,000	4,0	1200/200	
1986	FINLAND	HEA + DCN	42,000	3.7	2500/200	
1986*	FINLAND	DCN	34,000	4.2		
1986*	GREECE	HEA + DCN	28,000	4.1	1800/200	

^{*}Not yet in operation

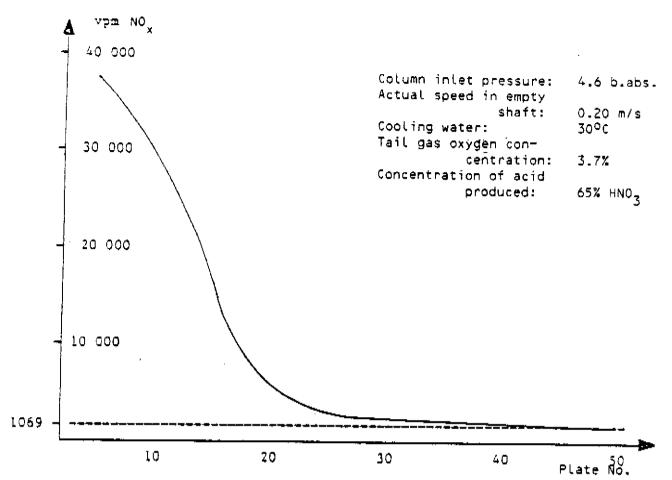
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- (2) R. BOUSCAREN, Colloquium AQA, PARIS, October 1985.
- (3) French Patent 2,450,784: Catalyseur d'élimination des oxydes d'azote contenus dans un courant gazeux.
- (4) French Patent 2,486,513: Procédé de traitement d'un courant gazeux contenant des oxydes d'azote et de l'oxygène.
- (5) J. ROIRON, Nitrogen 86, 10th British Gas Int. Conf. AMSTERDAM, April 1986.
- (6) F. LUCK and J. ROIRON, 7th Franco-Soviet colloquium on catalysis, STRASBOURG, September 1986.

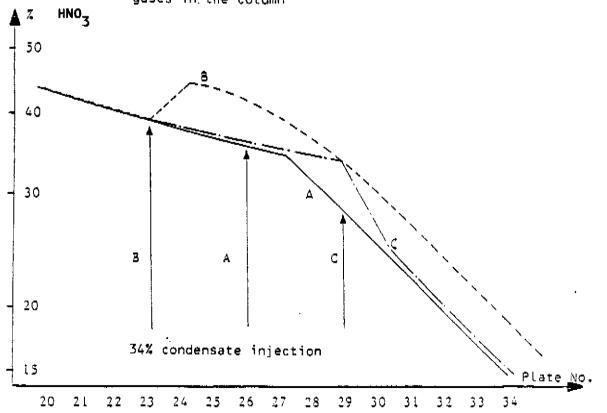


- () Ammonia combustion
- $\binom{2}{2}$ NO oxidation and $H_2O + HNO_3$ condensation
- $\binom{3}{2}$ NO oxidation and NO₂ absorption

(Fig. 1) - Flow diagram illustrating the principle of single-pressure (4b.abs.) dilute nitric acid plant

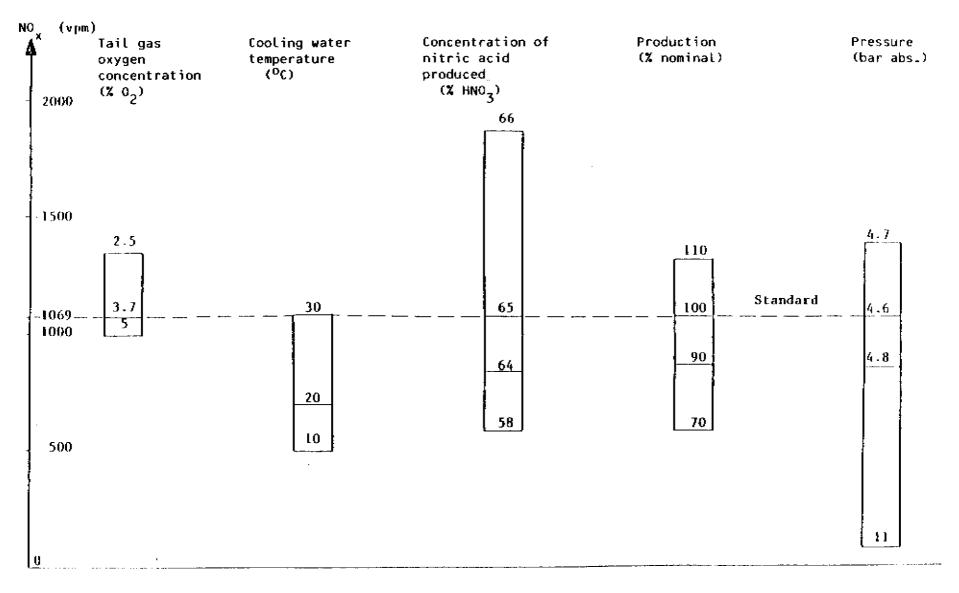


(Fig. 2) - Nitric acid absorption: changes in the NO concentration of gases in the column

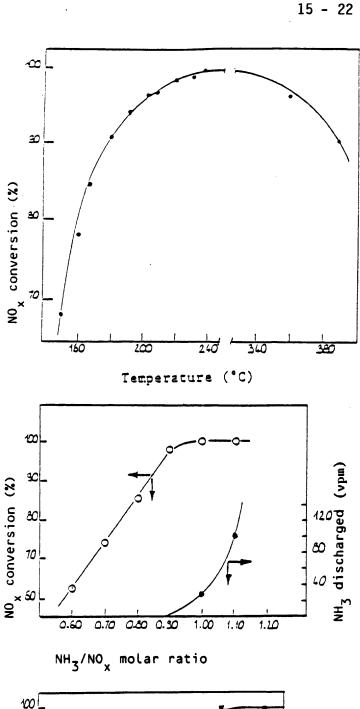


(Fig.3) _ Nitric acid absorption: effect of the condensate injection level on the acid profile.



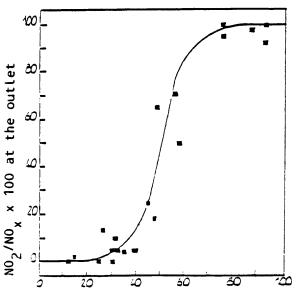


(Fig. 4) – Conventional NO absorption: effect of various parameters on the NO concentration of tail gases



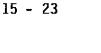
(Fig. 7) - Activity of the DN 110 catalyst as a function of gas inlet temperature (pressure: 2.5 bar abs. spatial velocity: 8000 h⁻¹).

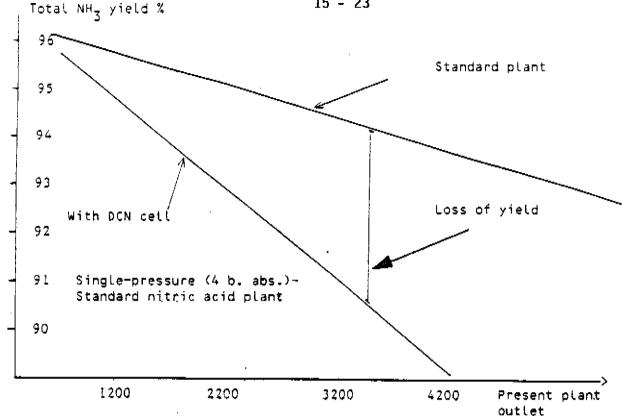
(Fig. 6) - Activity of the DN 110 catalyst as a function of the NH_3/NO_x molar ratio (temperature 210° C)



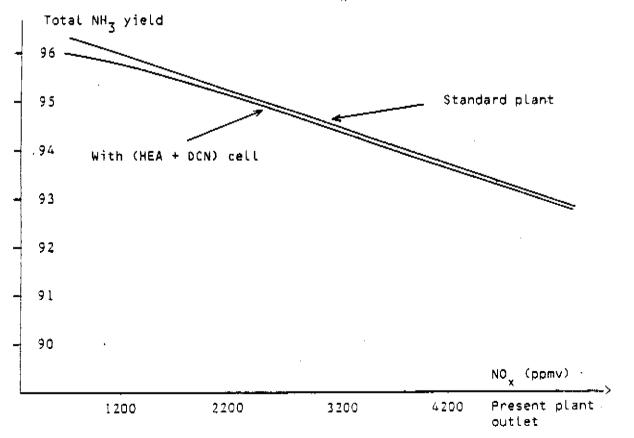
 $N0_2/N0_x \times 100$ at the inlet

(Fig. 5) - Changes in the NO_2/NO_X ratio between the inlet and the outlet of the DN 110 catalyst (Pressure: 1.5 to 5.0 bar abs.)

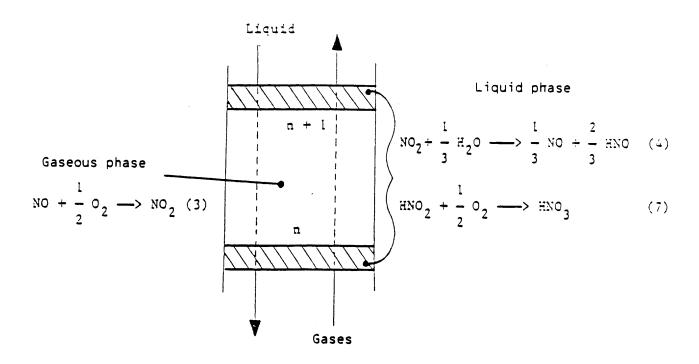




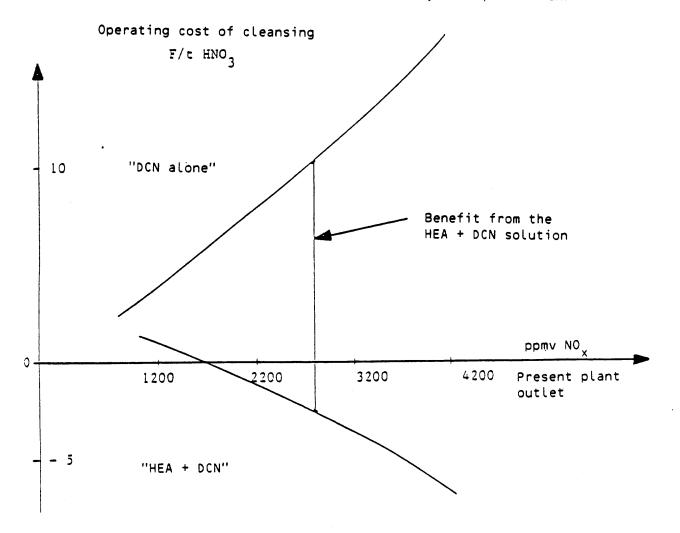
(Fig. 8) - DCN cell: changes in ammonia yield of the plant as a function of the level of NO $_{\rm x}$ to be treated to achieve 200 vpm NO $_{\rm x}$



(Fig. 8a) - (HEA + DCN) cell: changes in ammonia yield of the plant as a function of the level of NO_x to be treated to achieve 200 vpm NO_x .



(Fig. 9) - Principle of High Efficiency Absorption (HEA)



(Fig. 10) - Cleansing cell operating cost to achieve 200 ppmv NO in a single-pressure (4 b. abs.) standard nitric acid plant.

TA/86/15 Solving NOx pollution problems in nitric acid manufacturing plants by J. Roiron, Rhône Poulenc Chimie de Base, France

DISCUSSION: (Rapporteur T. Loyer, COFAZ SA, France)

- Q Mr. P. ORPHANIDES, Duetag, France
 - 1. Have you applied, in a new plant, your concept of 20% more compact column? Is the comparison made with actual offers of competitors?
 - 2. Can you also compare the pressure drop in the column?
 - 3. It is often stated that, to avoid the formation of nitrites and nitrates, one should operate at 210°C minimum in the catalyst and avoid the simultaneous presence of NOx and ammonia. What are the risks of operating at 170°C?
 - 4. What is the distance between plates and the height of liquid on each plate?
- A 1. There is no difficulty to incorporate a high efficiency part in the column of a new plant. We have no such achievement, but we studied it for a 1500 t/d dual pressure plant.

The conventional column would be about 60 m high to reach 200 ppm under 11 bar; in that case we propose a 43 m column.

- 2. The pressure drop in the high efficiency column is equal or 5-10% inferior to a conventional column.
- 3. 210° C seems a very high temperature. The limit would rather be 120-110° C for the activity of a catalyst.

The temporary excess of ammonia can be avoided by controlling NH3 flowrate, NH3/NO2 ratio, by continuous analysis of NOx at the entrance and exit, and by a continuous monitoring of temperatures in the catalyst bed.

- 4. The distance between plates is imposed by manufacturing problems (welding). It is linked with the reactions in liquid phase according to a patented liquid/gas contact technology.
- w Mr. B. CHRISTENSEN, Superfos, Denmark
 - 1. How does the liquid phase oxidation proceed?
 - 2. What is the investment cost for a 3.5 bar absorption plant and 35,000 Nm3/hr tail gas?
- A 1. The liquid phase reaction is promoted by avoiding the destruction of HNO2.

External oxidizers could be added, according to our own patents, with extra cost, but this is only of interest for small amounts of effluents.

- 2. For a 300 t/d plant, 40-45,000 Nm3/hr and a reduction from 2,500 to 200 ppm, the package column-reactor erected and commissioned would cost about 4-5 million F. The cost varies according to pressure, quality of the actual absorption and NO/NO2 ratio.
- Q Mr. BAROUNI RAOUF, SAEPA, Tunisia
 - 1. The DCN process for destroying NOx with ammonia has no advantage in comparison with thermal cracking. Why did you choose it?
 - 2. Can the effluent gases be recovered in the ammonia production process?
- A 1. The thermal cracking needs the addition of an oxidizing substance which uses the existing oxygen, then the NOx. It is a boiler operating at 400° C and the steam produced should be valorized.

The destruction of ammonia is selective and ppms of NH3 should be added in relation to ppms of NO3. The temperature produced is limited. To destroy 1.000 ppm NOx, the gas temperature differential is $10-15\,^\circ$ C.

- 2. The effluent gases contain 97% N2, 2-4% O2, 200 ppm NOx and some N2O. We do not know if they can be used in the NH3 process.
- Q Mr. D.C. OOSTERWIJK, DSM, Netherlands
 - 1. To reduce the NOx concentration of a small plant from 2,500 to 600 ppm at a 3.5 b pressure, is the combination HEA + DCN advantageous in comparison with DCN alone?
 - 2. If so, what would be the investment corresponding to HEA to process 40,000 m3/hr?
- A 1. This plant must be treating by a combination of column-reactor, unless local economic conditions are different. If, for example, the price of ammonia is low and that of energy is high, the reactor only can be used.
 - 2. The column has its limits and, in that case, the cost of a column used alone would be prohibitive. The reactor can also be used to remove the peaks which the column could not absorb. The column could also be limited to 1,200 ppm in view of its discolouring effect on NO2 and the reactor could operate to produce 1000 ppm totally invisible gases.