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GP's EXPERIENCE FOR SELECTIVE CATALYTIC REDUCTION IN NITRIC ACID PLANTS

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RESUME

Les unités d'acide nitrique sont la source de fréquentes réclamations à cause des oxydes d'azote (NOx) visibles qu'elles émettent à la sortie des cheminées, caractéristiques d'une "plume" brun rouge qui est due au dioxyde d'azote. Une faible partie de la pollution atmosphérique provient des unités d'acide nitrique, les sources les plus importantes sont les transports motorisés, les chaudières industrielles et thermiques.

Des règlements ont été émis dans les différents pays industrialisés pour protéger l'environnement local et obtenir un impact important sur l'opinion publique pour supprimer ces "affreuses plumes".

Plusieurs types de procédé permettent de réduire ces émissions : Grande Paroisse utilise le procédé de réduction catalytique sélective à l'ammoniac (SCR) sur ses propres unités d'acide nitrique pour respecter les règlements locaux. Elle a développé son procédé et ses catalyseurs. Ainsi, elle a mis en place un nouveau type de catalyseur à base de zéolite sur des unités industrielles depuis plus de 2 ans qui permet d'avoir une haute efficacité, sans ammoniac résiduaire ni formation de N₂O. Des exemples illustreront l'intégration de ce procédé aux unités existantes et donneront les conditions opératoires.

La première unité fonctionne avec succès depuis 1984 ; treize unités sont actuellement opérationnelles utilisant le procédé G.P. et les catalyseurs G.P. Un contrat a été obtenu récemment et plusieurs propositions sérieuses sont en cours.



1. GRANDE PAROISSE S.A.

Grande Paroisse, well known as G.P., was created in 1919. Today, it is an affiliated company of ELF ATOCHEM. It is the largest French fertilizer producer and the largest third in West Europe. In its sites G.P. controls the production of 2 million metric tons of nitric acid.

Continuous improvement of its technology together with productivity development make G.P. one of the most competitive fertilizer manufacturer. A technical team achieves this objective and maintains a world wide reputable technology.

Its nitric acid technology is one of the most efficient, license has been sold in many countries. More than 50 units from 35 metric tons per day to 2000 Mt/d have been erected. The 2000 Mt/d is the largest in the world.

2. NITRIC ACID MANUFACTURE

Three main steps in the nitric acid manufacture:

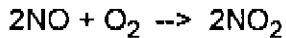
a. Ammonia oxidation:

With oxygen from air, nitrogen monoxide is produced over a heterogeneous catalyst (platinum/rhodium gauzes)



b. Nitrogen monoxide oxidation to nitrogen dioxide:

With remaining oxygen in air, monoxide is changed into dioxide as follows:

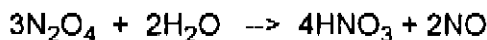


part of this dioxide is the dimer nitrogen tetraoxide



c) Water absorption

Nitric acid is generated by nitrogen dioxide and tetraoxide absorption in water:



Nitrogen monoxide is regenerated and afterwards oxidized for further absorption. Secondary reactions may take place at ammonia oxidation or absorption steps. Oxidation and absorption take place in perforated sieve trays of towers. Demineralised water percolates down while gas travels up. Absorption tower acid produced in trays is cooled by cooling water circulating in coils. Oxidation and absorption take place in each tray of the column.

Partial pressure of NO and oxydation degree of NO₂ decrease regularly when reaching top of absorption tower. To improve oxidation and absorption it is better to run at high pressure (10 to 13 bars) while eliminating calories resulting from exothermic reactions.

Absorption efficiencies in modern plants is over 99.8%. Some nitrogen oxides are discharged to atmosphere at high level stack , composition is:

nitrogen	96% (from initial air)
residual oxygen	3%

Remaining 1% is water, rare gases, and different nitrogen oxides called NO_x.

These oxides are made of colourless NO and brownish NO₂, NO being oxidized into NO₂ with oxygen from air. In old installations colour is deep brown due to high NO₂ concentration.

3. NO_x REDUCTION METHODS

For the past 15 years the industry has been attempting to reduce NO_x atmospheric pollution. In the beginning recovery of nitric acid in exhaust gases allowed investment for NO_x abatement. More than 5000 ppm were released in atmosphere with low capital investment American processes. Over 5% efficiency was lost in absorption phase.

Nowadays depending on the process the gas at the outlet of the absorber may vary within the following limits during stable operation :

NO _x	100 to 2000 ppm volume
N ₂ O	500 to 3500 ppm volume
O ₂	1 to 4% volume
H ₂ O	0.3 to 0.7% volume
N ₂	balance
Flow	3100 to 3300 Nm ³ /t HNO ₃ 100%

Main pollution abatement processes available on the market are listed hereunder in 4 different types:

a. Extended absorption with water

When pressure is over 8 to 10 bars a second absorption tower can be added. Sieve trays allow concentration as low as 200 ppm NO_x and good efficiency.

Many units have been successfully completed in the U.S. during the seventies.

With such a procedure sieve trays number is increased. The dual pressure process allows presently a low pressure of the ammonia converter and a higher pressure in the absorber so dimension can be reduced to one column although larger.

G.P. has completed many such units down to 100 to 200 ppm NO_x level, according to clients requests.

b. Absorption

Silica gel, activated carbon, molecular sieves have important NO_x adsorption capacities. Molecular sieves are considered alone qualified for NO_x economic recovery. They may achieve over 95% efficiency. These materials must be regenerated by the way of desorption: either thermal (expensive) or depressure. This is a discontinuous adsorption/desorption process or a duplication of streams : one adsorbs while the other desorbs.

These processes are not well introduced on the market as many problems remain to be solved:

- . molecular sieve life duration in acid environment,
- . need to dry gases before adsorption,
- . NO not being adsorbed has to be first oxidized to NO₂

c. Chemical absorption

Most of the time it is an alkaline absorption of tail gas by water solution of sodium carbonate or hydroxide. We may also have potassium, magnesium or calcium solutions. Major difficulty is utilisation of resulting solutions more specifically alkaline nitrite and nitrate. When we cannot find immediate usage in a neighbouring unit or sell we transform one pollutant in another different pollutant.

Ammonia can also be utilized but operating conditions are more risky due to ammonium nitrate decomposition.

Urea solutions provide diluted ammonium nitrate solutions which cannot economically be concentrated.

d. Catalytic reduction

There are two different processes:

- non-selective catalytic reduction (NSCR).

Fuel is burnt with remaining oxygen in NO_x flue gases. It may be hydrogen, methane, naphtha, etc. on platinum, rhodium or palladium catalyst. The products are water, carbon dioxide, nitrogen; the nitrogen dioxide is reduced first. In order to reduce nitrogen oxides (NO and N₂O) as well to nitrogen an excess of reduction agent is required.

Depending on the operating conditions and specially high temperatures, other pollutants such as carbon monoxide, cyanhydric acid, hydrocarbons may be released to the atmosphere.

When fuel is reduced, residual oxygen maintained, the NO_2 is converted to NO , and the gas is discoloured as the pollution is present.

The tail gas from the absorber has to be preheated to 300°C minimum with hydrogen, 550°C with methane for good operation of the NSCR catalyst. The reactant gas is mixed with the preheated tail gas and the mixture is passed into a reactor containing the catalytic bed.

This rather costly procedure has been in use in the U.S. for gas discolouration.

The NSCR process is not favoured nowadays for new plants.

- Selective catalytic reduction (SCR)

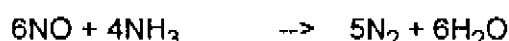
This method is most utilized with ammonia for nitric acid units and described hereunder.

4. NO_x CATALYTIC REDUCTION WITH AMMONIA

As against non-selective catalytic reduction where NO_x is destroyed after total oxygen has disappeared, selective reduction takes place in presence of oxygen and reducing agent which is ammonia.

Ammonia reacts with NO_x components in exhaust gases. Some oxygen may also react.

Main reactions are as follows:



Most favourable conditions are:

- Temperatures: 200 to 350°C Celsius,
- Pressure: highest possible,
- Stoichiometric ratio NH_3/NO_x if NO_2/NO_x is in the range of 50%.

After absorber, gases are pre-heated in heat exchangers and release their energy in expanders (**Appendix 1**). Ammonia is injected in appropriate location where temperature is 200 to 400°C . A static mixer ensures complete mixing. The catalytic converter favours former exothermic reactions. According to NO_x content, temperature increase is small or moderate. High pressure favours conversion efficiency; catalytic reactor will be located before the expander. Less than 50 ppm vol NO_x is achievable with no ammonia leakage.

This process has many advantages:

- It can be adjusted to most existing nitric acid plants,
- It consumes existing ammonia in the site,
- It generates non-polluting gases: nitrogen and water,
- NO and NO_2 are selectively reduced without important oxygen consumption,
- No ammonia slip
- Temperature is moderate,
- Temperature increment is small (about 10°C per 1000 ppm),
- Easy and quick start/stop operation,

- Low pressure drop (50 to 100 millibars),
- No liquid effluent,
- No additional operator,
- Long catalysts life duration (over 5 years),
- Low maintenance cost.

Catalysts are made of precious metals (Pt, Pd, Rh, Ru) over alumina support and also metallic oxides (V, Cr, Fe, Co, Ni, Ti), as well as zeolite more recently.

In the last years, G.P. used such a catalyst based on metallic oxides while developing a new type based on copper-carrying zeolite.

5. G.P. CATALYSTS

a. GPT11

This catalyst is based on iron-chromium-alumina oxides and has an activity which can be compared with other catalysts used in nitric acid plants based on vanadium pentoxides. The first industrial reactor was installed in an existing 270 tpd nitric acid plant at Cubatao in Brazil; commissioning was made in 1984 and it has performed well up to now, after 10 years in operation. The operator purchased a second unit immediately afterwards. Up to the present time 8 plants have been equipped with this type of catalyst (Appendix 3).

- 4 abroad: 2 in Brazil - 1 in Israel - 1 in US
- 4 in France in GP's factories: 2 in Grand Quevilly and 2 in Mazingarbe.

b. GPRN14 and 15

They are based on zeolite materials which have a large internal surface area: copper is carried on zeolite Y by partial exchange of cation with Na^+ or NH_4^+ . These catalysts operate efficiently between 200°C and 500°C with high space velocities and without any ammonia leakage as shown on Appendix 4, in comparison with other usual catalysts.

Tests were made in laboratory as well as on a pilot plant installed in parallel with an existing nitric acid plant in order to check efficiency, ammonia leakage, space velocity influence, temperature effect (Appendices 4, 5, 6). We made also comparisons with catalysts based on vanadium pentoxides, according to data given by literature (Appendix 4). Results were so good that we installed an industrial reactor in an existing 370 tpd nitric acid plant at GP's factory in Grand Quevilly.

Commissioning was made in August 1991 and it has performed very well up to now.

To continue to produce nitric acid in France we had to decrease tail gas pollution with a date limit requested by local authorities or cease operation. So we installed SCR with our zeolite catalyst in 5 additional GP nitric acid units. Some plants are running with inlet temperature lower than 200°C (pilot test shows it is possible to run at 150/170°C with the same performance).

We are starting up some plants at 170°C to minimize pollution without any difficulty. This technology has been sold abroad after all tests were made on our own units. Last year we obtained contracts in Australia and in USA. Two plants by AMC were successful last May and July in obtaining 25 ppm at the outlet of the SCR with no detectable ammonia leakage, demonstrating a NO_x reduction higher than 95%.

Reactor designed by G.P. is either radial or axial ; in this last case it can be vertical or horizontal. As a rough estimate of the capital cost of a SCR unit, a figure of 1,5% of the capital cost of the nitric acid plant can be used.

For a typical reduction from 1000 ppm to 200 ppm of NO_x in tail gas the SCR unit will add 1,1% to the operating cost of the nitric acid unit. The maintenance cost of the SCR unit is typically 2,5% of capital cost.

Analysers used are based on photometry (IR or UV) and chemiluminescence. In many cases we installed "Nicolet" system which uses IRFT and permits to measure on the same analyser NO, NO₂, NH₃ and N₂O instead of having two equipments for measuring all these components.

On one plant where GPT11 was installed, we put additional GPRN15 catalyst to decrease tail gas content; efficiency was very good and ascertained by measurements made by official authorities.

Tail gas inlet in NO_x: 852 ppmv
 " " " " outlet: 49 ppmv
 Ammonia leakage: < 0,27 ppmv

c. Conclusion

Zeolite catalysts have many benefits:

- Good efficiency with no ammonia slip,
- No formation of N₂O after SCR (N₂O is considered as a contributor to global warming and ozone depletion),
- Wide temperature range: from 170°C to more than 500°C,
- High ammonia adsorption capacity.

6. REGULATIONS

Nitric acid manufacture is not a major NO_x pollution source. In the U.S., it is only responsible for one percent of NO_x emission. Nevertheless NO_x pollution may happen to be locally important and visible from very far away.

NO₂ is 30% to 50% of total NO_x emitted, hence the colour in nitric acid plant stack exhaust. In power plant stack exhaust, NO₂ is only 5% and colourless.

EEC Commission is defining new regulations applicable to each member state. Presently regulations are different (**Appendix 2**).

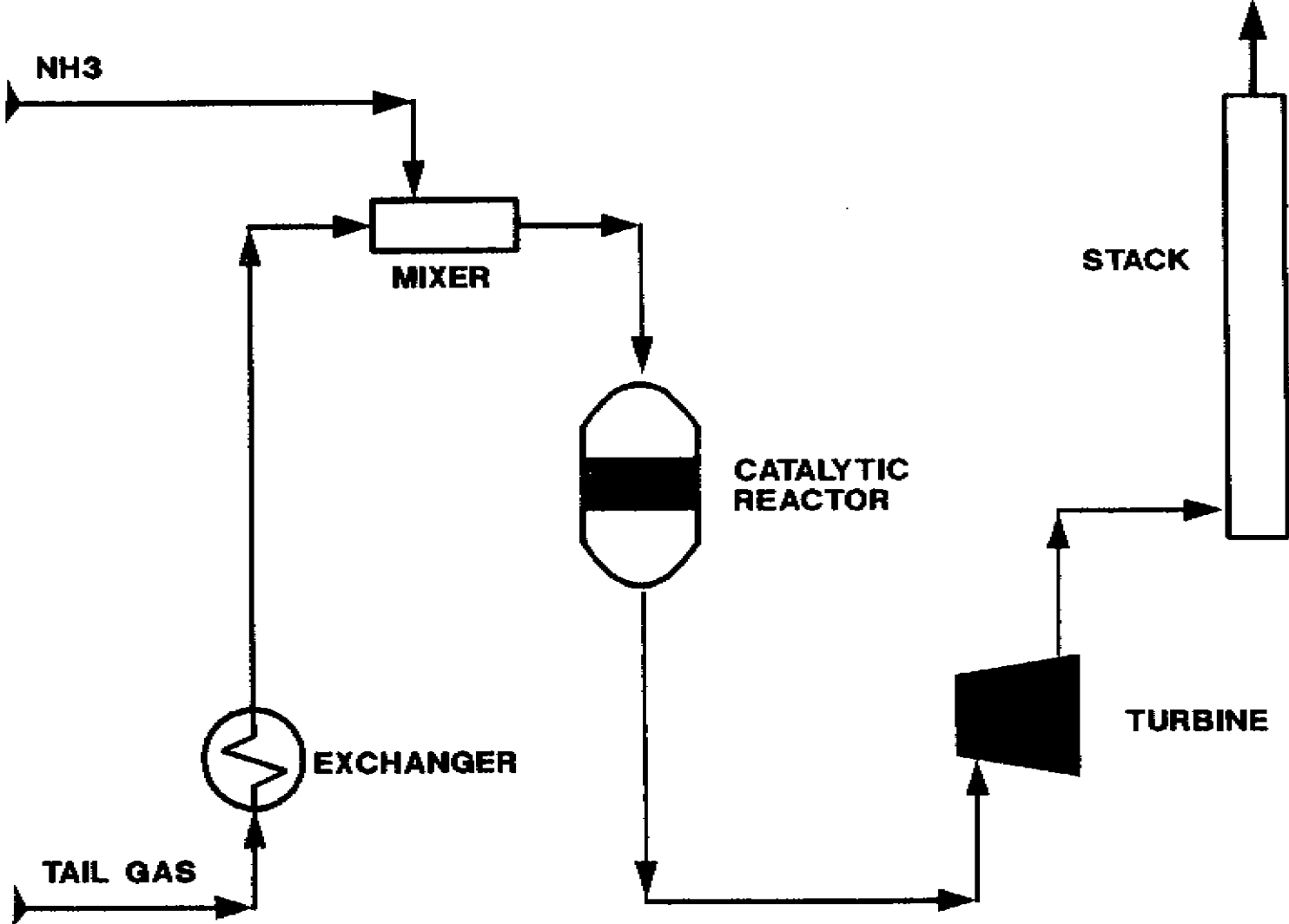
In the US, the limit is 1.5 kg NO₂ per metric ton of nitric acid solution counted as 100% for new plants (3 lb/ton). E.P.A. has to update this regulation every 4 years. This has never been done as nitric acid capacities have been decreasing for the past years; in addition applicable regulations are different from one state to another.

To evaluate these regulations one has to bear in mind the other pollution sources. Car exhausts are by far the most important NO_x pollution source. In France, they constitute about 70%. Agriculture and chemical industry being responsible for 13% and nitric acid manufacture for 1.3%.

More over, for the past 15 years transport pollution has been increased by 1.4 fold as against the chemical industry and agriculture which decreased by 1.6 fold.

Air pollution by nitric acid plants can be substantially reduced with some investment on existing processes. It is nevertheless important to define a reasonable level of NO_x to be emitted by nitric acid manufacturers, (in the range of 200 ppm). When establishing this regulation, important other pollutants must be considered. They tend to ignore large amounts of invisible nitrogen oxides. Nitric acid manufacturers should not be penalised only because of the unfortunate brown colour of their stack gas which is visible from long distances.

GRANDE PAROISSE DE-NO_x PROCESS



APPENDIX 2

COUNTRY Date of publication	NEW PLANTS				EXISTING PLANTS			
	Limit value	Averaging time	Date of implementation	Excursions	Limit value	Averaging time	Date of implementation	Excursions
BRD 2/1986	450 µg/m ³ dry NO _x expr.in NO ₂ (# 219 ppbv)	24 h	3/1986	< double < 24 time	450 µg/m ³ dry NO _x expr.in NO ₂ (# 219 ppbv)	24 h	Low - med.press. 3/1986	
F 7/1974	4.5 kg HNO ₃ /t HNO ₃ 100%		7/1974	< 400 h/y < 48 h con.sec < 6 kg/t	4.5 kg HNO ₃ /t HNO ₃ 100%			flexible approach case by case
I								
NL > 500 t/d 8/1987	220 ppbv (NO _x)	1 h	8/1987	no limit shut- down & start-up	600 ppbv (> 220 ppbv)	1 h	1992	
B								
L								
UK 5/1987	200 ppbv BPM 24 (1987)		5/1987	limit not to be exceeded at any time for normal operation	1000 ppbv		1992	limit not to be exceeded at any time for normal operation
IRL					200 ppbv (NO _x)		1976	
DK	Limit values will be set for each plant (General regulations is in preparation. 200-225 ppe NO _x is expected)				Limit values are set for each plant			
GR	5 kg NO _x /t HNO ₃ 100%							
B 2/1975	3 kg NO _x /t HNO ₃ 100% 1.5 kg/t	2 h	... 1975 ... 1980		20 kg NO _x /t HNO ₃ 100%	2 h		
P project	400 µg/m ³ N (NO ₂) (24 02)							

Table AV(a)
Summary of Emission Limits in EC Member States

APPENDIX 3

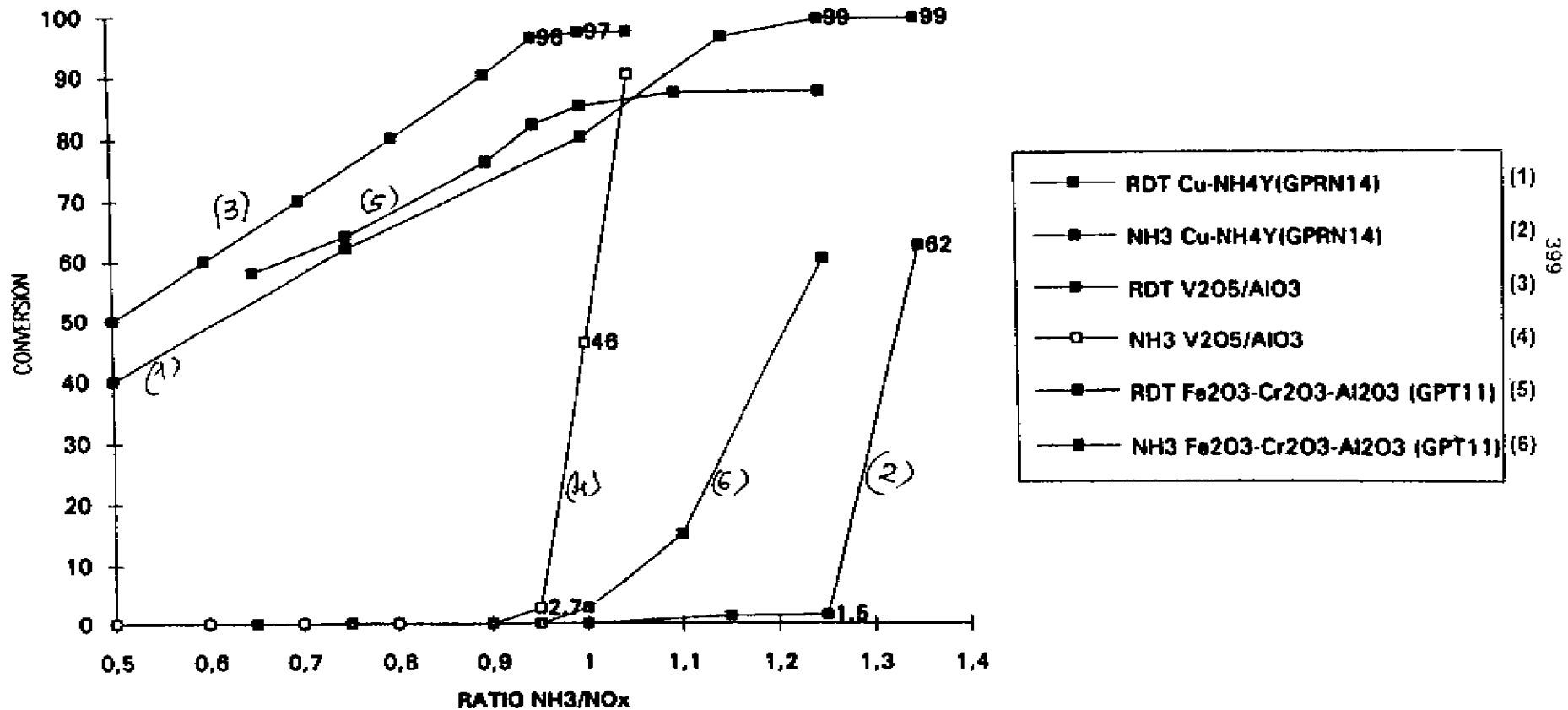
POLLUTION ABATEMENT PROCESS
REFERENCE LIST

Year of Commissioning	Customer	Location	Capacity t/d absorption (atmos)	Catalytic or extended inlet	ppm NOx outlet	**ppm NOx
1995	CSBP AND FARMERS	Perth, (Australia)	500	Catalytic Zeolithe	1000	50
1995	GRANDE PAROISSE	Mazingarbe, (France)	420	Catalytic Zeolithe	700	150
1994	AMC	Verdigris, (USA)	1000	Catalytic Zeolithe	1000	50
1994	AMC	Verdigris, (USA)	1000	Catalytic Zeolithe	600	50
1993	GRANDE PAROISSE	Mazingarbe, (France)	280	Catalytic Zeolithe	1150	90
1993	GRANDE PAROISSE	Toulouse, (France)	210	Catalytic Zeolithe	1000	160
1992	GRANDE PAROISSE	Toulouse, (France)	200	Catalytic Zeolithe	1100	200
1992	GRANDE PAROISSE	Toulouse, (France)	360	Catalytic Zeolithe	1500	150
1992	MISSISSIPPI CHEMICAL CORPORATION	Yazoo City, Mississippi, (USA)	500	Catalytic	1000	200
1991	GRANDE PAROISSE	Mazingarbe, (France)	212	Catalytic	1700	175
1991	GRANDE PAROISSE	Mazingarbe, (France)	280	Catalytic	1100	135
1991	GRANDE PAROISSE	Grand Quevilly 5, (France)	360	Catalytic Zeolithe	940	150
1991	GRANDE PAROISSE	Grand Quevilly 6, (France)	360	Catalytic	940	150
1991	GRANDE PAROISSE	Grand Quevilly, (France)	1000	Catalytic Zeolithe	1000	100
1990	HAIFA CHEMICALS	Haifa, (Israel)	240	Catalytic	2300	850
1989	HAIFA CHEMICALS	Haifa, Israel	385	6,5	1500	390
1988	UTRAFERTIL	Cubatao, (Brazil)	220	Catalytic	790	150
1986	PAKARAB FERTILIZER	Multan, (Pakistan)	180	7.7	6000	400
1984	ULTRAFERTIL	Cubatao, (Brazil)	270	Catalytic	2300	75
1984	U.S. ARMY	Radford, Virginia, (USA)	370	7.9	6400	75
1983	NORSK HYDRO FERTILIZER Ltd	Immingham, (England)	675	9.25	8900	600
1979	FERTICA	Costa Rica	250	7.4	9310	1000
1976	COMINCO AMERICAN	Beatrice, Nebraska, (USA)	420	8	4800	400
1976	KAISER AGRICULTURAL	Cincinnati, Ohio, (USA)	240 or 108	7.4 or 7.8	1500 or 9500	260 or 380
1976	KAISER AGRICULTURAL	Tampa, Florida, (USA)	115	9.1	1730	200
1975	MISSISSIPPI CHEMICAL CORPORATION	Yazoo City, Mississippi, (USA)	270	7.3	2970	400
1973	MISSISSIPPI CHEMICAL CORPORATION	Yazoo City, Mississippi, (USA)	330	9	1700	200

** Variable NOx output are requested by customers according to local regulations

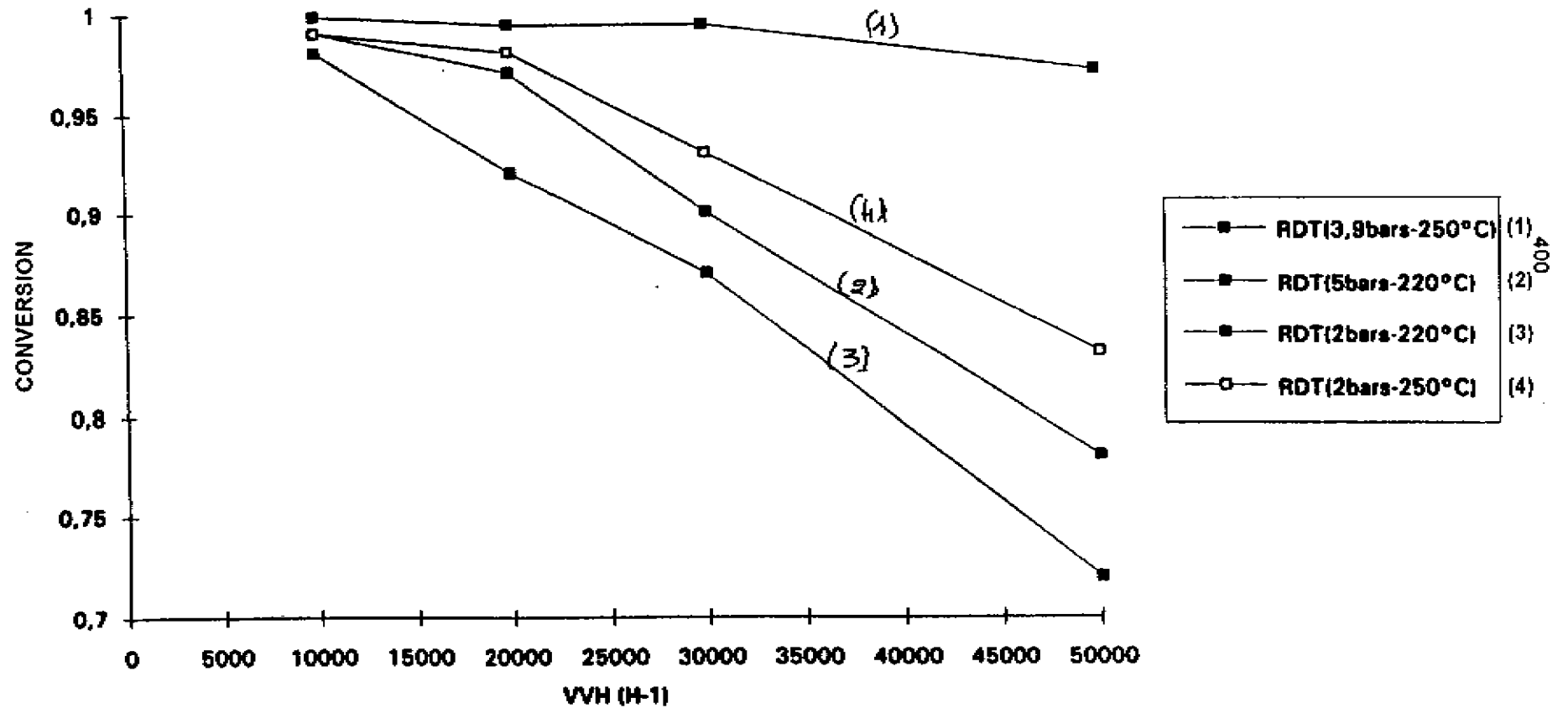
APPENDIX 4

Trend in the rate of production, of ammonia loss in relation to the NH_3/NO_x ratio
 (V/VH:10000H-1; T°:210°C ; P:3 bar; NOx:2000ppm)



APPENDIX 5

TREND OF THE RATE OF CONVERSION IN RELATION TO THE VVH FOR VARIOUS OPERATIONAL CONDITIONS (NO_x:1000 ppm)



APPENDIX 6

TREND OF THE RATE OF CONVERSION IN RELATION TO TEMPERATURE
(NOX: 1500 ppmv; VVH: 20000H-1)

