

IFA Technical Conference

Venice, Italy
2-4 October 1990

NOx CATALYTIC REDUCTION BY AMMONIA IN NITRIC ACID PLANT

P. GRY and M. PRAT

Société Chimique de la Grande Paroisse, France

1. BACKGROUND : SOCIETE CHIMIQUE DE LA GRANDE PAROISSE

SCGP known as GP was created in 1919, and it is today an affiliated company of ATOCHEM. The Company is the largest French fertilizer producer and is the third largest in Europe.

It sells more than 6 million metric tons/year of fertilizers.

GP controls the production of 2 million metric tons of nitric acid.

Continuous improvement of its technology together with productivity development make GP one of the most competitive fertilizer manufacturers.

A technical team helps to achieve this objective and maintains a world wide reputable technology.

Its nitric acid technology is one of the most efficient; licences have been sold in many countries. More than 50 units from 35 metric ton per day to 2000 Mt/d have been erected.

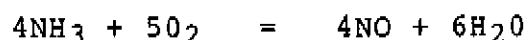
The 2000 Mt/d/unit is the largest in the world.

2. NITRIC ACID MANUFACTURE

The three main steps in the nitric acid manufacture are :

a) Ammonia oxidation :

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



b) Monoxide oxidation to nitrogen dioxide :

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

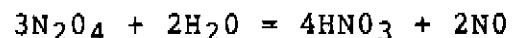
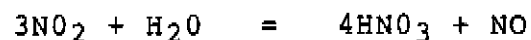


Part of this dioxide is the dimer nitrogen tetraoxide



c) Water absorption

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



Monoxide is regenerated and afterward 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 degree of oxidation 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 NOx.

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. NOX REDUCTION METHODS

For the past 15 years the industry attempts to reduce NOx atmospheric pollution.

In the early days recovery of nitric acid in exhaust gases was profitable to allow investment for NOx abatement.

More than 5000 ppm were released into the atmosphere from the low capital investment American processes. Over 5 % efficiency was lost in absorption phase.

Main pollution abatement processes available in the market are listed below :

The 4 different types are :

a) Secondary absorption

When pressure is over 8 to 10 bars a second absorption tower can be added. Sieve trays reduce efficiently concentration of NOx to as low as 200 ppm.

Many units had been successfully completed in the US during the seventies.

With such a procedure sieve trays number is increased. The dual pressure process allows a low pressure on the ammonia converter and a higher pressure in a single enlarged column.

GP has completed many such units which reduce NOx levels down to 100 to 200 ppm in accordance to the clients' requests.

b) Use of Absorption materials

Silica gel, activated carbon, molecular sieves have good NOx adsorption capacities.

Molecular sieves per se are adequate for NOx economic recovery. They may achieve over 95 % efficiency.

These materials must be regenerated by desorption : either thermal (expensive) or depressure. So it is discontinuous adsorption/desorption process or duplication of streams : one adsorbs while the other desorbs.

These processes are not widely used in the market as many problems are not yet solved :

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

c) Chemical absorption

Most widely used is an alkaline absorption of tail gas by water solution of sodium carbonate, or, potassium, magnesium and calcium hydroxide solutions may be used. Major difficulty is utilisation of resulting solutions, more specifically, alkaline nitrite and nitrate.

When there is no immediate sale or usage in a neighbouring unit, it merely transforms one pollutant to a different pollutant.

Ammonia can also be utilized but operating conditions are more risky due to possible ammonium nitrite decomposition. Urea solution provides diluted ammonium nitrate solutions which cannot be economically concentrated.

d) Catalytic reduction

There are two different processes :

- non-selective reduction.

Fuel is burned with remaining oxygen in NO_x flue gases. It may be hydrogen, methane, naphtha etc... on platinum or palladium catalyst.

In presence of steam, carbon dioxide, nitrogen, oxygen is burned initially to reduce NO_x but this is not obvious.

Depending on temperature level other pollutants may be generated such as :

carbon monoxide, cyanhydric acid and hydrocarbons.

When fuel is reduced, residual oxygen is maintained and the NO₂ is converted to NO. The gas is discoloured but pollution is still there.

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

- Selective reduction

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

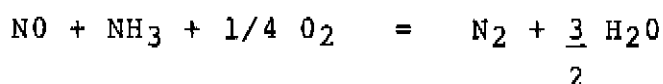
4. NO_x CATALYTIC REDUCTION WITH AMMONIA

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

Ammonia reacts with NOx components in exhaust gases.

Some oxygen may also react.

Main reactions are as follows :



Most favourable conditions are :

- Temperatures : 200 to 350 ° Celsius,
- Pressure : highest possible,
- Stoichiometric ratio NH₃/NOx

After passing through the absorber, gases release their energy in the heat exchangers and expanders.

Ammonia is injected at appropriate location where temperature is 200 to 350 ° C.

A static mixer ensures complete mixing. The catalytic converter favours former exothermic reactions. Depending on the NOx content, temperature increase is small to moderate.

High pressure favours conversion efficiency ; the catalytic reactor must be located close to the absorber and before the expander.

Less than 200 ppm of NOx by volume can be achieved with minimal residual ammonia.

If NOx content has to be decreased, residual ammonia must be increased.

This process has many advantages :

- It can be adapted to most existing nitric acid plants,
- It consumes existing ammonia in the site,
- It generates non polluting gases : nitrogen and water,
- NO and NO₂ are selectively reduced without large oxygen consumption,

- 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 catalyst life duration (over 5 years)
- low maintenance cost,

catalyst is made of precious metals (Pt, Pd, Rh, Ro) over alumina support.

Metallic oxides (Va, Cr, Fe, Co, Ni, Ti) take an increasing part in this catalyst manufacture.

This process is presently the most efficient costwise (5 to 15 Million FF for a 1000 Metric Ton /Day unit).

Operating cost is a function of ammonia and catalyst cost as well as NOx content.

GP has three operating units according to this process. Two are operating in Brazil (one of them, for more than six years with the original catalyst load).

Another unit is operating in Grand Quevilly France for nearly two years.

During the last quarter of 1990 a unit will be started in Israël. In 1991 four units will be started in France, in GP nitric acid plants.

5. REGULATIONS

Nitric acid manufacture is not a major NOx pollution source. In the US it is only responsible for one percent of NOx emission.

Nevertheless NOx pollution may happen to be locally important and visible from very far away.

NO₂ makes up from 30 % to 50 % of total NOx emitted, hence the colour in nitric acid plant stack exhaust.

In the power plant stack exhaust, NO₂ constitutes only 5 % and is colourless.

EEC Commission is defining new regulations applicable to each member state.

Presently regulations are different (ref. Appendix 2) : in the US the limit is 1.5 kg NO₂ per metric ton of nitric acid solution and is set as a standard of 100 % for the 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.

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 it contributes about 70 % of the NO_x pollution .

Agriculture and chemical industry are responsible for 13 % of the NO_x pollution.

Nitric acid manufacture is responsible for only 1.3 % of NO_x pollution.

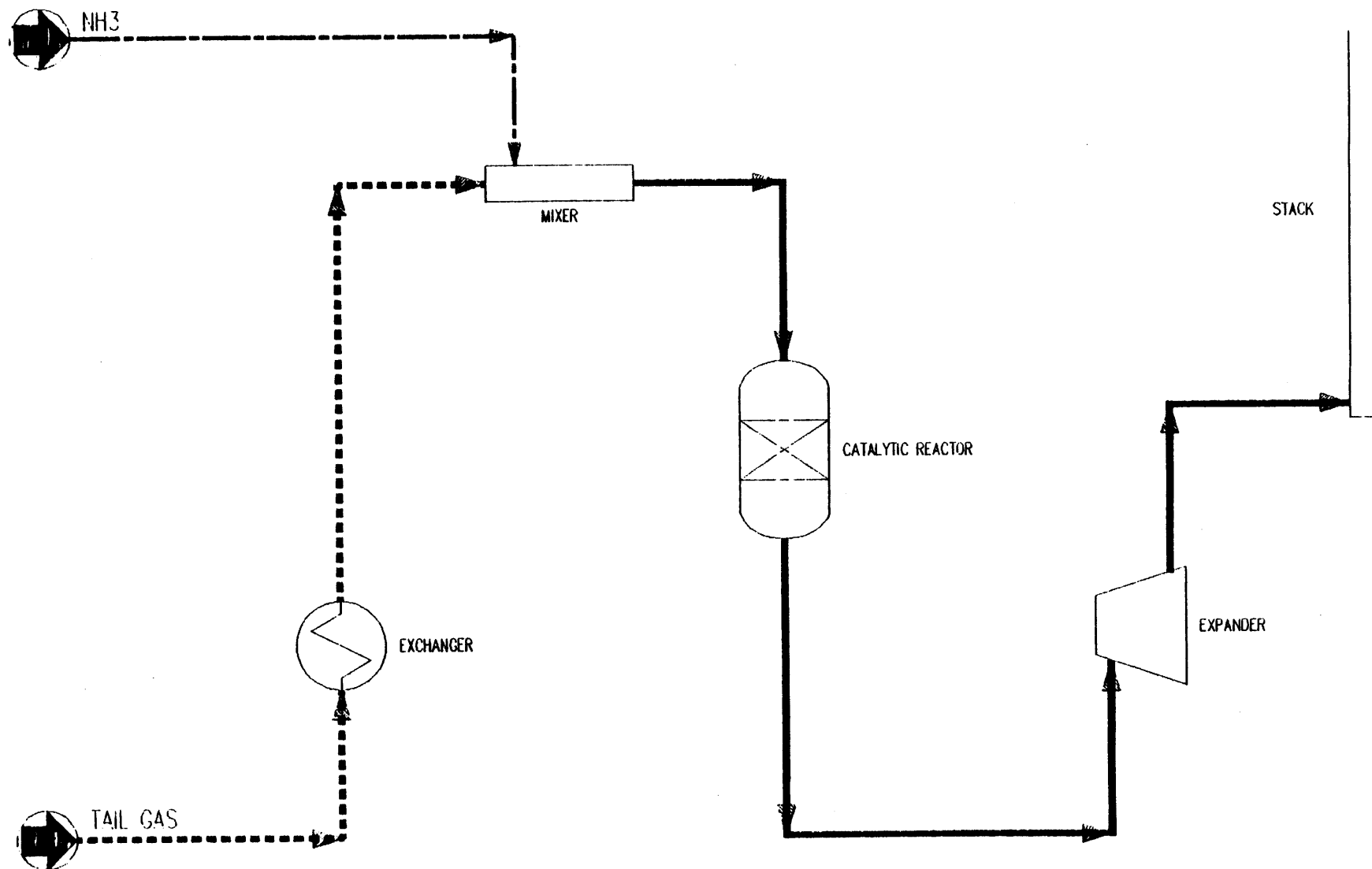
Moreover, for the past 15 years transport pollution has increased by 140 % as against the fertilizer industry and agriculture which have been reduced by 60 %.

Air pollution by nitric acid plants can be substantially lowered with existing processes, but with some investment.

It is nevertheless important to define a reasonable level of NO_x to be emitted by nitric acid manufacturers in Europe.

When establishing this regulation, major other polluters must be considered. They, reject high levels of the invisible nitrogen oxides.

Nitric acid manufacturers should not be singled out for penalty because of the brown colour of their stack gas which is visible from long distances.



APPENDIX 2

COUNTRY DATE OF PUBLICATION	NEW INSTALLATIONS			EXISTING UNITS		
	THRESHOLD VALUE	DATE OF ENFORCEMENT	DEROGATIONS	THRESHOLD VALUE	DATE OF ENFORCEMENT	DEROGATIONS
GERMANY february 86	450 MG/m3 sec NOx expressed as NO2 # 219 ppmv	March 86	lower than double, during less than 2 % of time	450 mg/m3 sec	March 1996	
FRANCE July 74	4,5 KG NOx/t acid 100% NOx expressed as NO2	July 74	lower than 400 h/an less than consecutives 48h - less than 6 kg/t			flexible approach case by case
NETHERLAND Sup. 500 t/d August 87	220 ppmv (NOx)	August 87	no limit to stop and start	600 ppmv	1992	
GREAT BRITAIN May 87	200 ppmv	May 87	limit not to be trespassed in any moment during normal operation	100 ppmv	1992	limit not to be trespassed in any moment during normal operation
GREECE	5 KG NOx/t acid 100%					
SPAIN February 75	3 KG NOx/t acid 100% 1,5 kg/t	1975 1980		20 kg NOx/t acid 100%		
PORTUGAL	400 mg/Nm3 (NO2) (2% O2)					