

N_2O And NO_x Abatement in Nitric Acid Plant

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ABU QIR FERTILIZERS Co.

“AFC”, is the largest Fertilizer Company in Africa.

AFC was founded as a joint stock company located in Alexandria Province under Egyptian law in 1976 with the market share of close to 70% of the local Egyptian fertilizer market.

The company is ISO 9001/2000 and ISO 14001 certified



ABU QIR

Our Plants

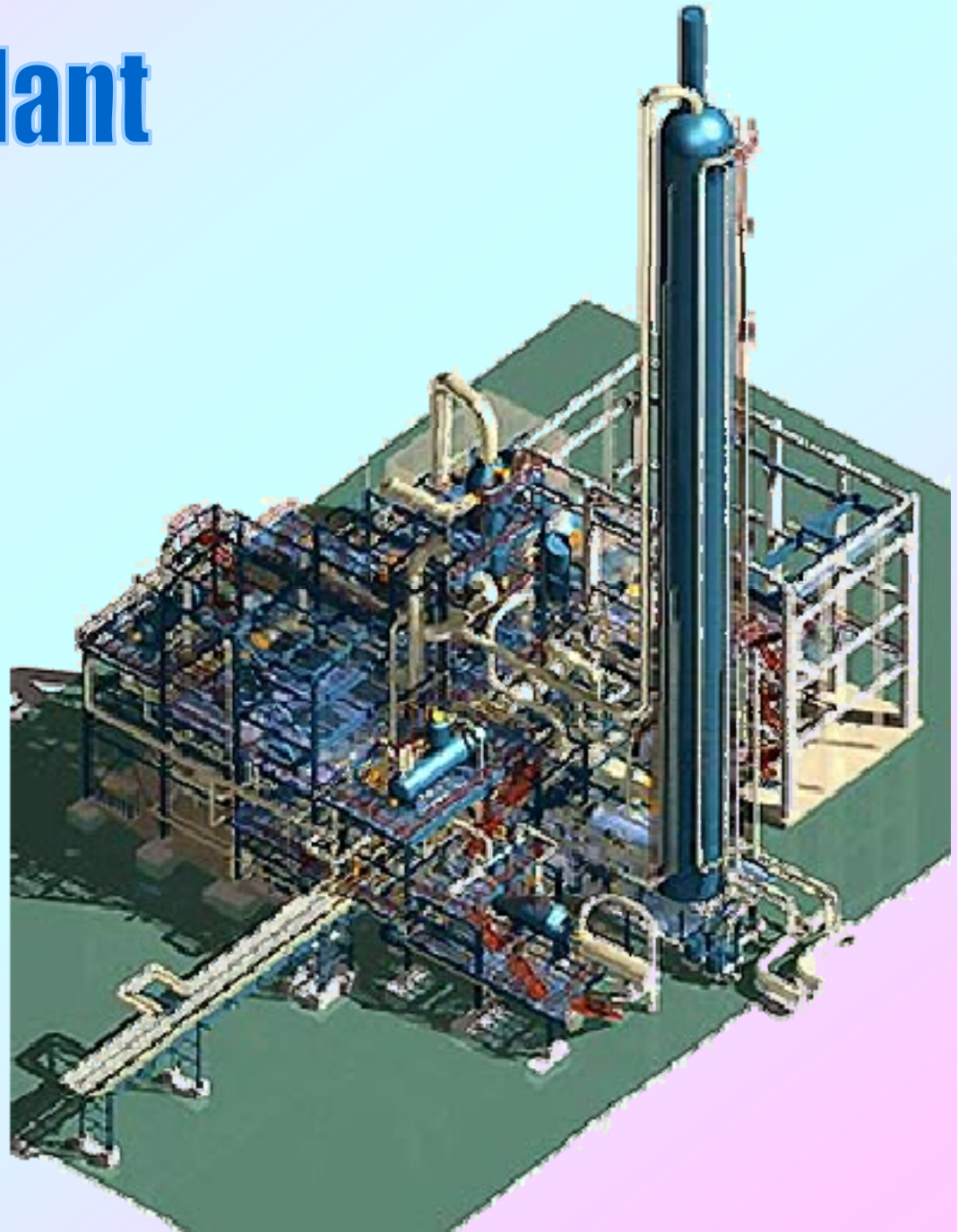


Abu QirPlants

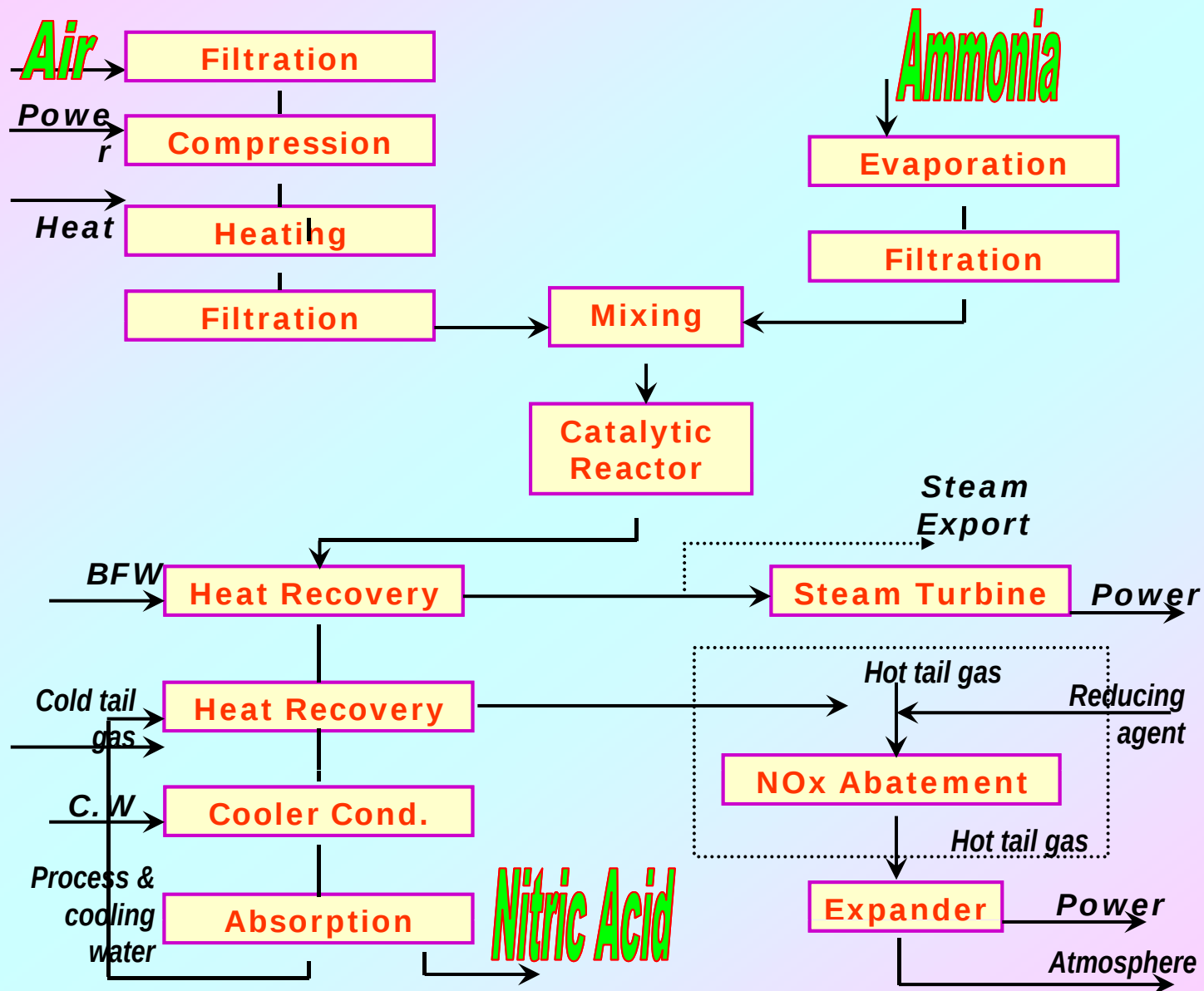
Plant	Start up Production	Capacity ton / day	Products
Abu Qir I			
Urea Plant	September 1979 February 2005	1550	• Prilled Urea 46 % N • Urea Zinc Sulphate 46 % N
Ammonia plant	September 1979	1100	• Ammonia
Abu Qir II			
Ammonium Nitrate Plant	August 1991 December 2004	2400	• Granular Ammonium Nitrate 33 % N • A.N Supplemented with Micro Nutrients 33 % N
Nitric Acid Plant	August 1991	1800	• Nitric Acid Plant
Ammonia plant	August 1991	1000	• Ammonia
Abu Qir III			
Urea Plant	October 1998 February 2004 December 2004	1925	• Granular Urea 46 % N • Granular Urea Ammonium Sulphate 45.5 % N • Granular Urea Magnesium Sulphate 45.5 % N
Ammonia plant	October 1998	1200	• Ammonia
NPK	December 2005	750	• Different Formulas of NPK with Urea or Ammonium Nitrate as Nitrogen Component
UAN	August 2006	1000	• Urea Ammonium Nitrate Solution

The nitric acid plant

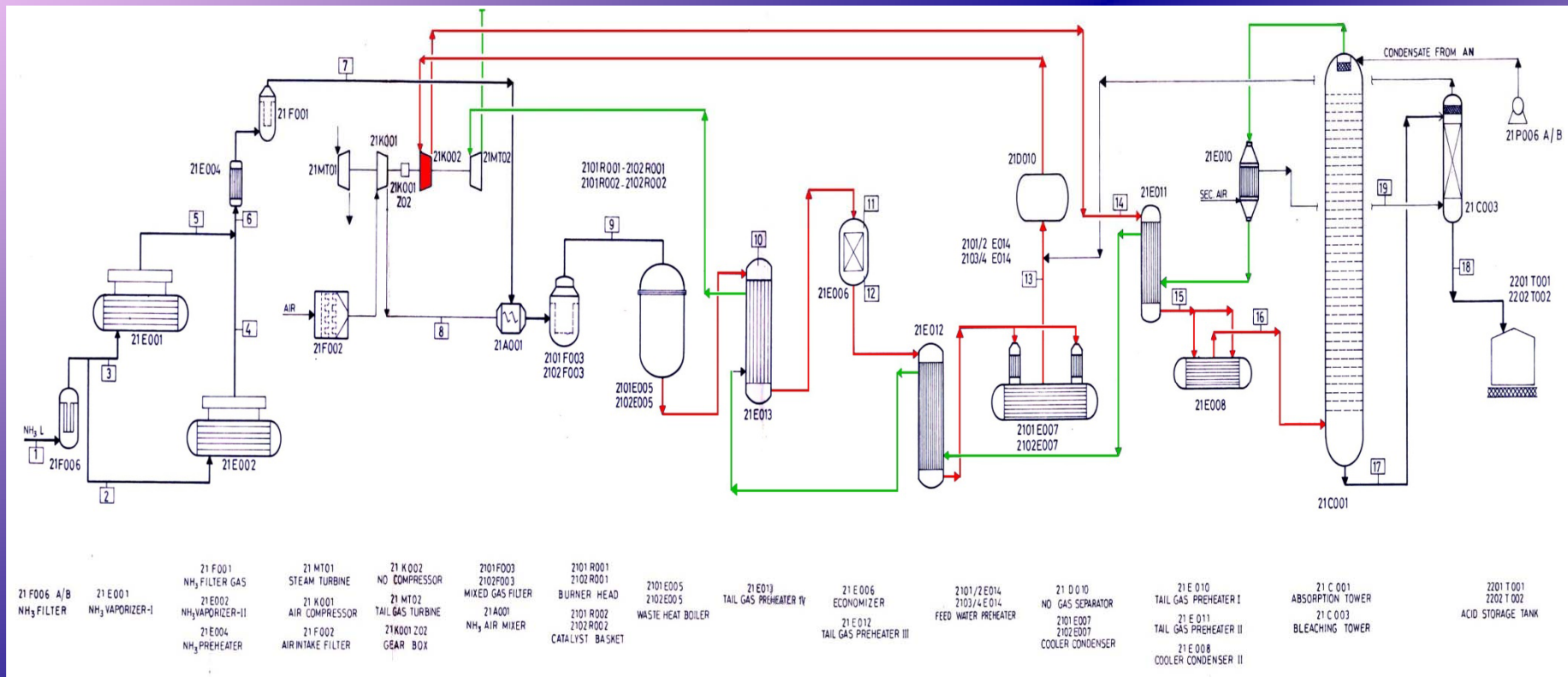
- Constructed by UHDE GmbH, in July 1991
- Capacity of 1,830 tpd
- It is one of the largest nitric acid plants in the world.



Nitric Acid Block Diagram



NA plant - Process flow



NO_x

- Production technology of NA
- Process Description

1- Oxidation of ammonia over catalyst (Pt alloy)



Further Undesired Consecutive Reactions



The amount of N_2O emitted depends on operating condition in ammonia burner and also type of gauzes

It is between (6-8 $\text{kgN}_2\text{O}/\text{ton acid}$)

Ammonia Burners



2- Oxidation of nitric oxide



In presence of further oxygen nitric oxide
converted to NO_2

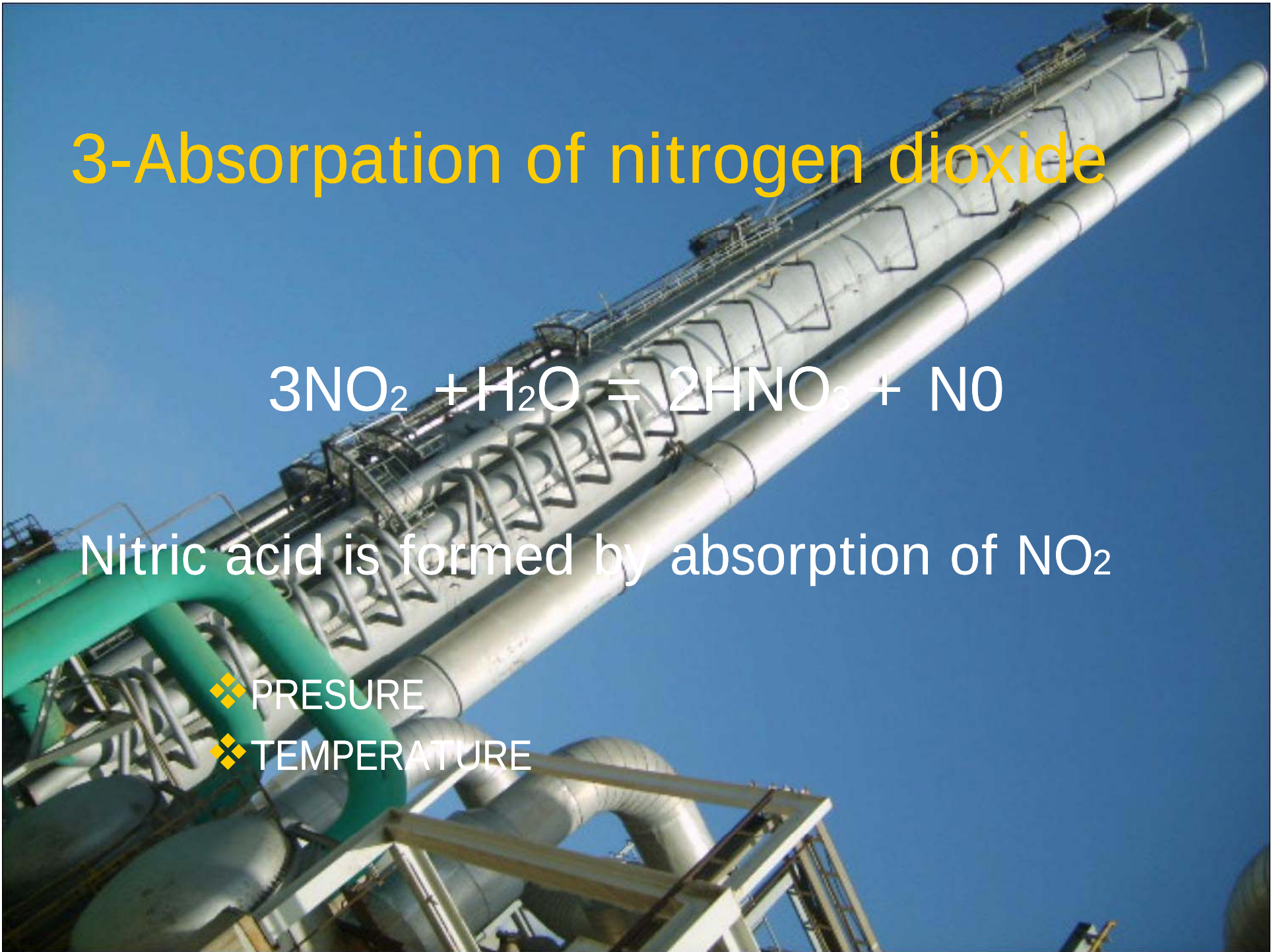
3-Absorption of nitrogen dioxide



Nitric acid is formed by absorption of NO_2

❖ PRESURE

❖ TEMPERATURE





Tail gas specification.

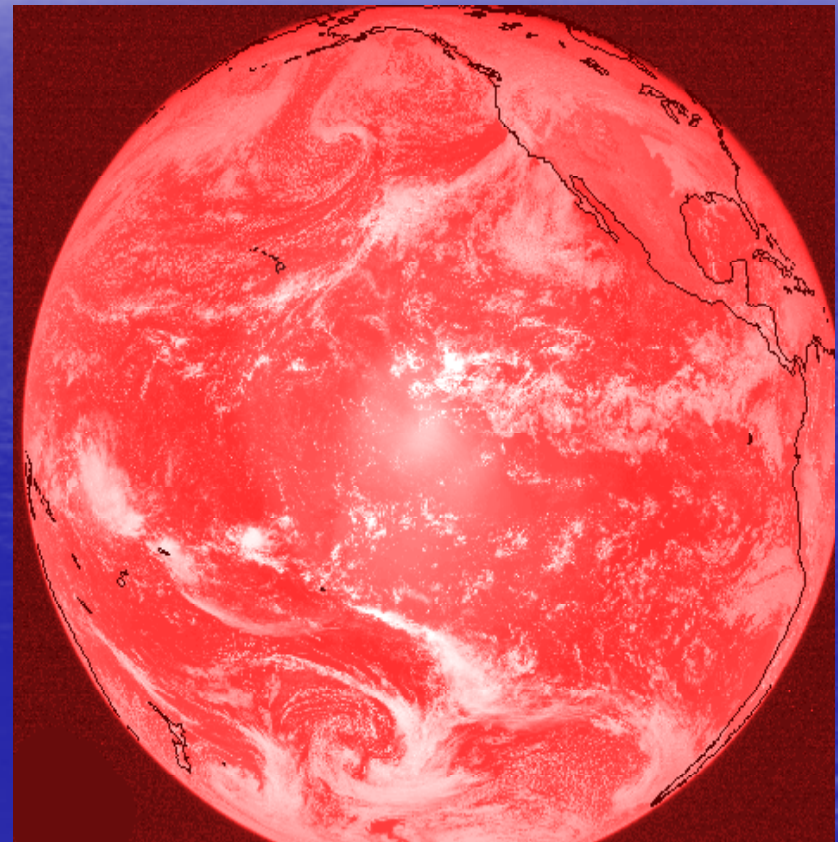
Quantity	250,000 Nm ³ \hr
Pressure	9.5 bar (gauge)
Temp.	> 414 °C

Composition

NO	< 100 PPM
NO ₂	<100 PPM
N ₂ O	1300 PPM

The major Greenhouse gases ?

- Carbon dioxide CO_2
- Methane CH_4
- Nitrous Oxide N_2O
- Hydrofluorocarbon
HFC
- Perfluorocarbon CF_4
- SulfurHexafluoride
 SF_6

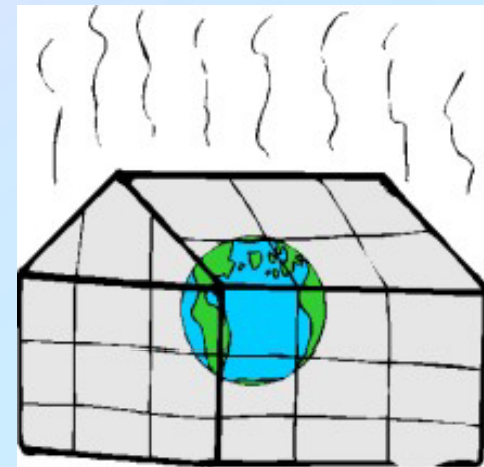


Global Warming Potentials (GWP)

(100 year time horizon)

Greenhouse gases	GWP
Carbon dioxide CO ₂	1
Methane CH ₄	21
Nitrous Oxide N ₂ O	310
Hydrofluorocarbon HFC	1300
Perfluorocarbon CF ₄	6500
Sulfur Hexafluoride SF ₆	23900

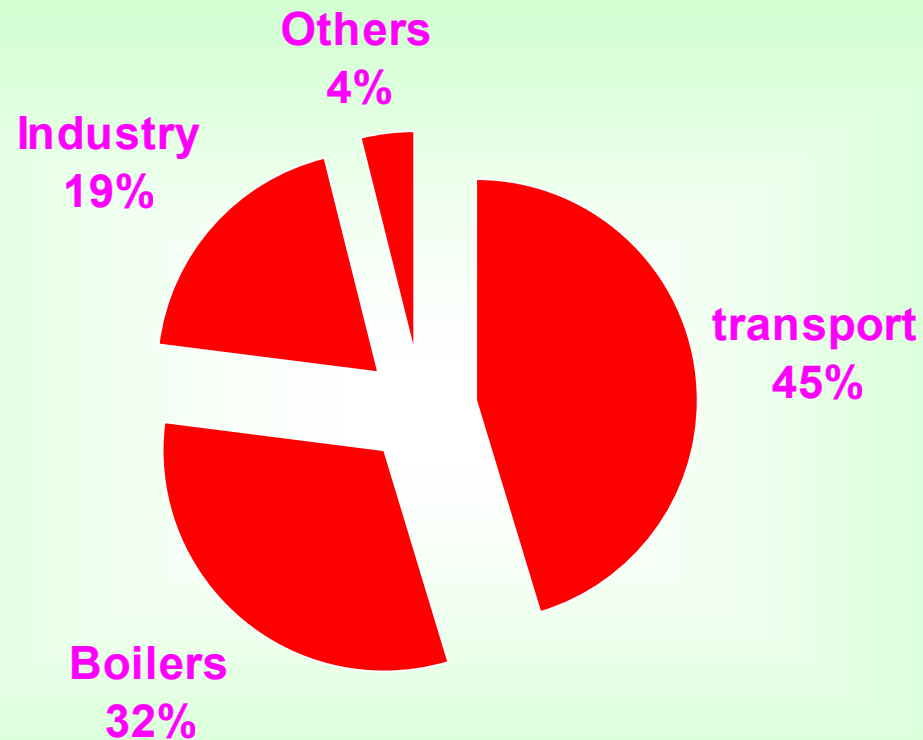
Nitrous Oxide (N_2O)



Sources of N_2O :

- denitrification process for energy production by anaerobic bacteria.
- Nitrification process ($\text{NH}_4^+ \rightarrow \text{NO}_3^-$)
- Fertilizer use
- Biomass burning
- Combustion
- Unknown sources
- *Sink: Photolysis in the stratosphere*

World NO_x Emissions by Anthropogenic Sources



Total NO_x Emission : 50,000,000 tons/year

Atmospheric Concentration in Green House gasses

Gas	Global atmospheric concentration (ppmv)			Atmospheric lifetime (years)	Global warming potential (Kg/ KgCO ₂)
	Pre-industrial	Present. 1992 data	Annual increase		
Carbon dioxide	278	357	0.4%	50-200	1
Methane	0.7	1.71	0.6%	12	21
Nitrous oxide	0.275	0.311	0.25%	120	310
Sulfurhexafluorid	0	32ppbv	0.6%	3200	23900
Perflouromethan	0	70ppbv	1.7%	50000	6500

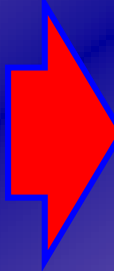
Nitrogen Oxides (NO_x)

NO_x (**7** oxides) :-

NO, NO₂, N₂O, NO₃, N₂O₃, N₂O₄, N₂O₅

- NO (90-95 %)

- NO₂ (5-10 %)



The greater concentration
in Urban & Industrial area

NO + O₂ “Atmospheric”  NO₂

N₂O is a green house gas

NITRIC ACID PRODUCTION

The following reactions occur in the conversion reactor at temperatures of 800°C to 900 °c



Reaction (1) is the desired conversion in the nitric acid process: the formed NO will be oxidized to NO_2 and absorbed in water to form nitric acid.

The formation of N_2O **reaction (2)** and nitrogen N_2 , **reaction (3)** are undesired reactions.

NITRIC ACID PRODUCTION (Contd.)

Conversion % for the 3 reactions are respectively:

94 vol %	conversion to nitric oxide (NO)
4.5 vol %	conversion to nitrogen (N ₂)
1.5 vol %	conversion to N ₂ O

The major greenhouse gas reduction, that can be achieved by removing the N₂O component out of the gas streams in the nitric acid process

NITRIC ACID PRODUCTION (Contd.)

*** For the existing nitric acid production plants, many catalytic N_2O reduction methods have been developed in recent years.**

*** The reduction of N_2O in these methods is realised by decomposing the N_2O to N_2 and O_2 (oxygen) over a suited catalyst.**

Classification According To The Catalytic Reduction Methods

*** There are two types of catalytic reduction**

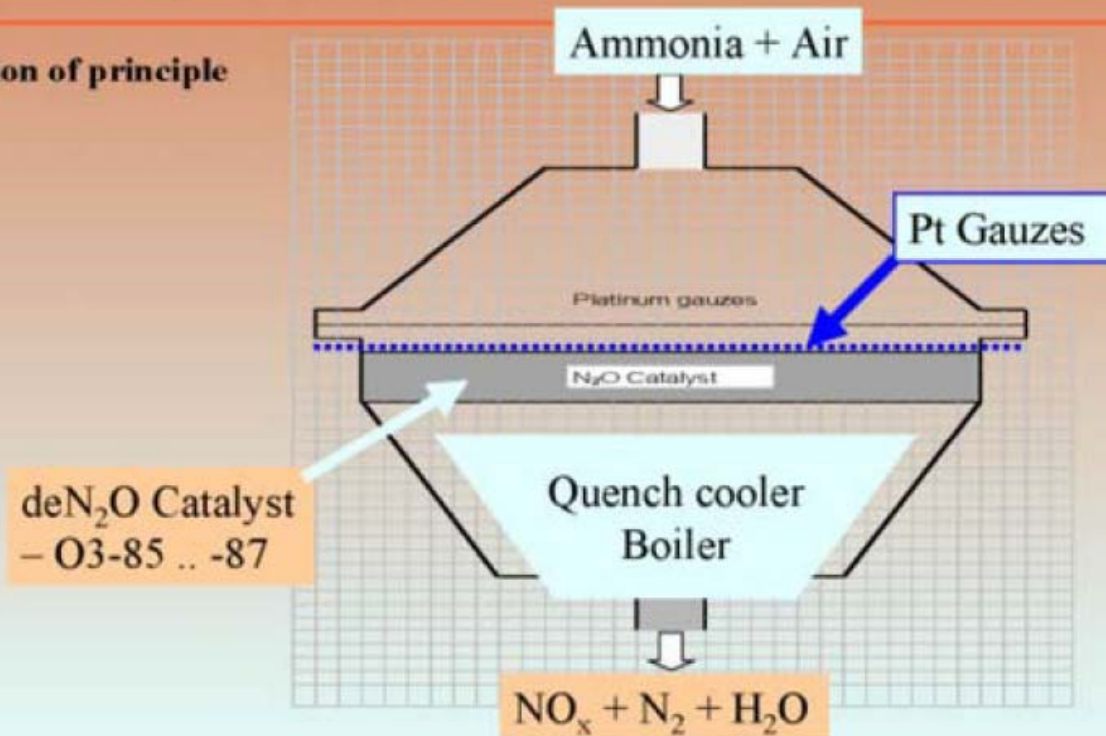
**1- High temperature catalytic reduction
BASF method**

**2- Low temperature catalytic methods
(Tertiary Abatement Measures, UHDE method)**

High temperature catalytic reduction BASF method

O3-85..-87 - N₂O Abatement in HNO₃ plants - Process Set-up

Depiction of principle



BASF 2002, O3-8x presentation

BASF method :-

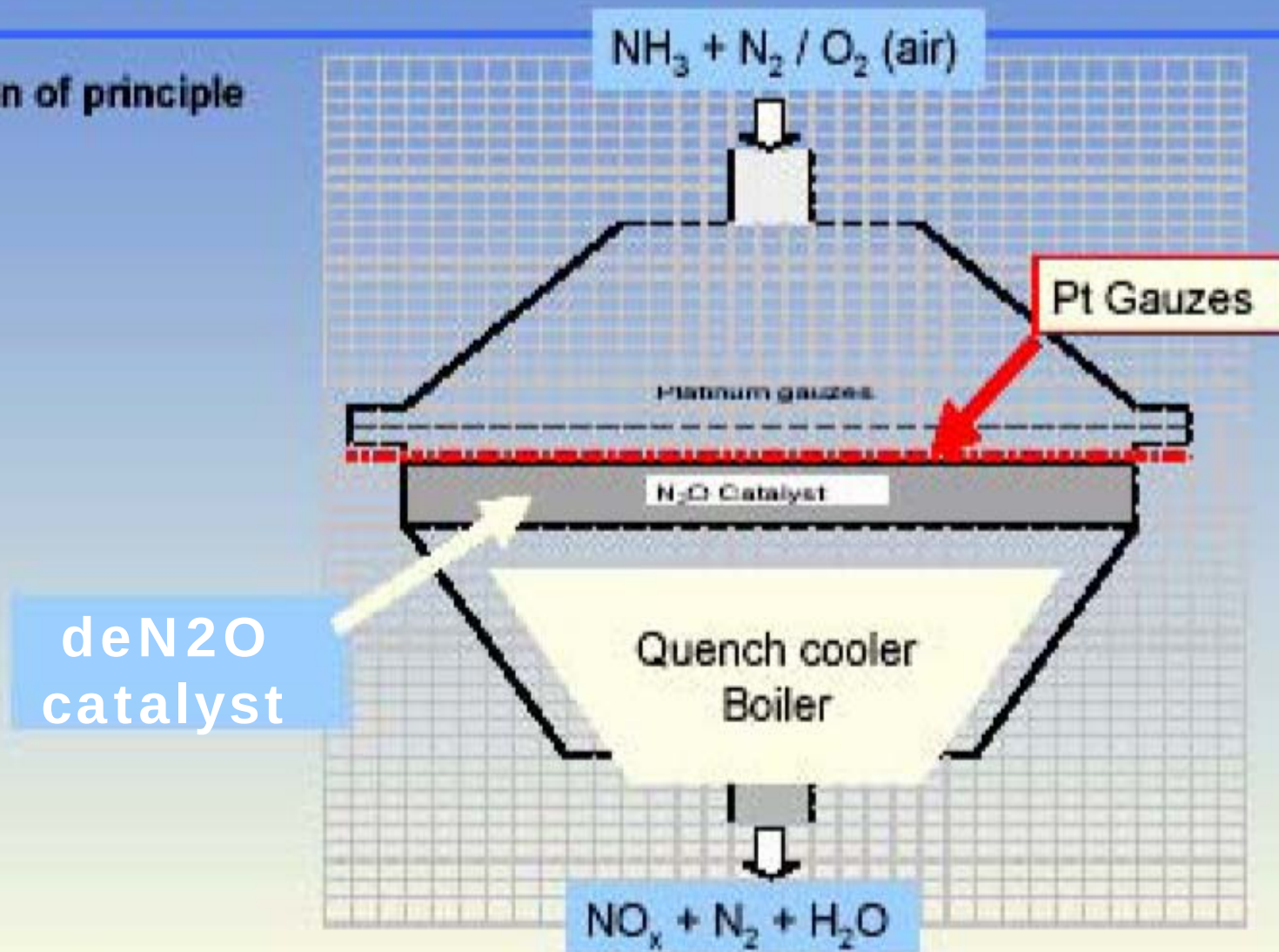
- The methods where the N_2O -reduction catalyst bed is placed under the **Pt / Rh gauzes** of the NH_3 -converter
- It is operated at temperatures of 800°C to 900°C .
- The catalyst is currently in production plants

BASF method (contd.):

- **BASF were able to report an 80 % reduction in N₂O from 1000 down to 200 ppm in an atmospheric combustion plant and a 70 % N₂O reduction down to 350 ppm in the 5.5 bar**
- **The high temperature and water vapour content of the NO_x gas make severe demands on the catalyst.**

O3-85..-87 - N₂O Abatement in HNO₃ plants - Process Set-up

Depiction of principle



BASF

BASF 2002, O3-8x presentation

O3-85..-87 - N₂O Abatement in HNO₃ plants - The Installation



Installing the Catalyst Charge ...

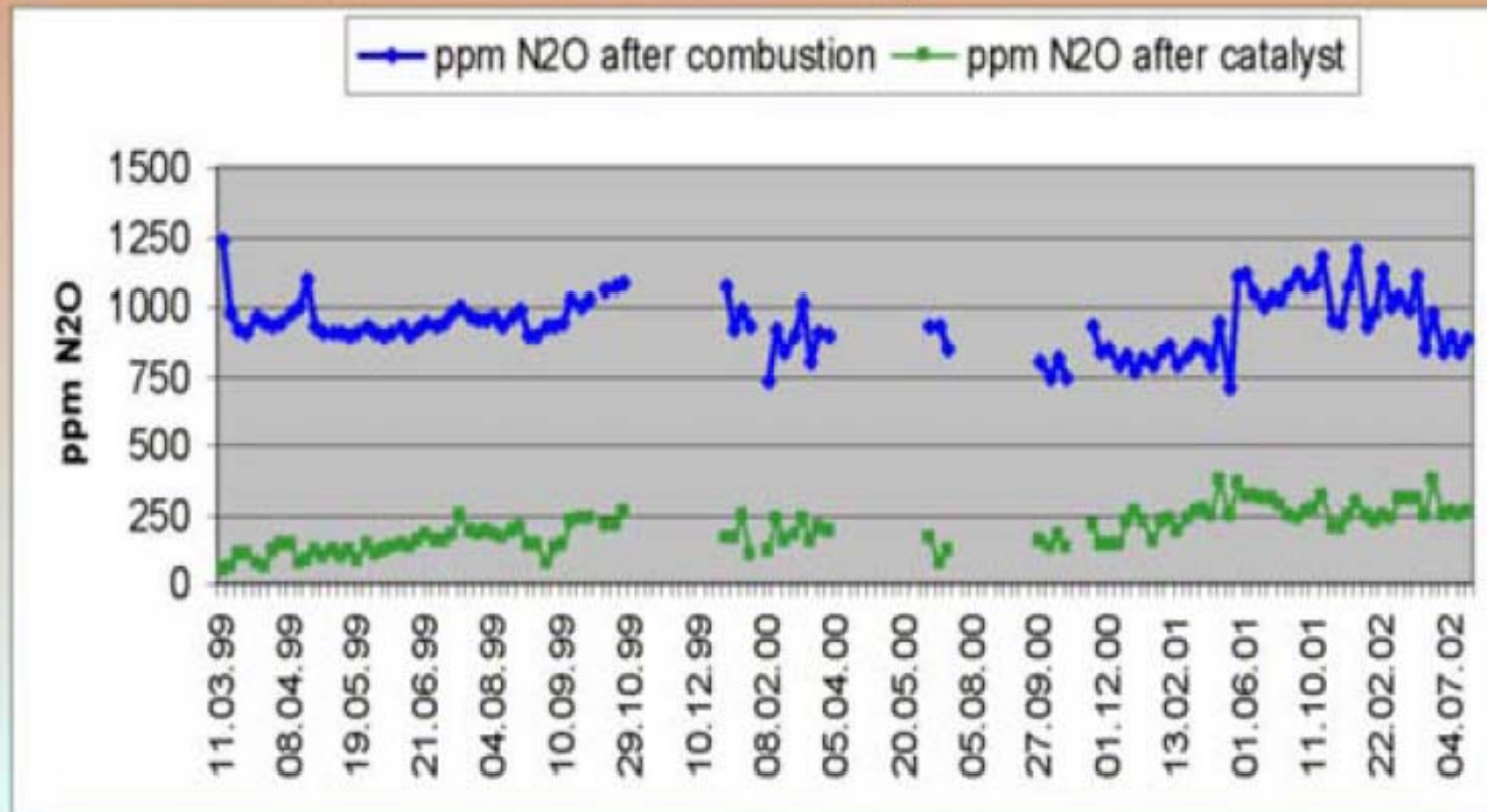
O3-85..-87 - N₂O Abatement in HNO₃ plants - The Installation



Installing the Pt gauze ...

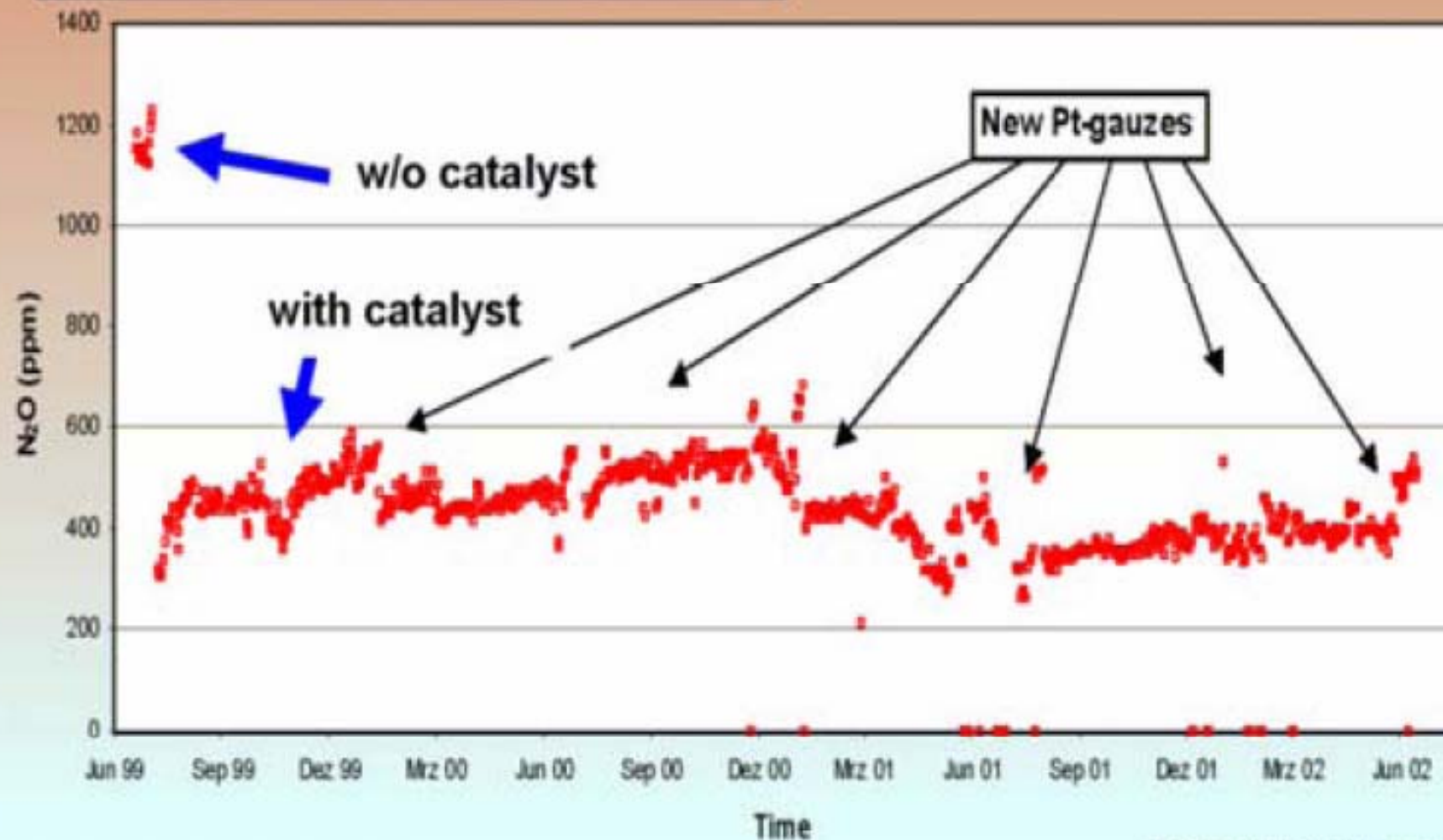
O3-85...87 - N₂O Abatement in HNO₃ plants - references

O3-85 - BASF works, Ludwigshafen



O3-85..-87 - N₂O Abatement in HNO₃ plants - references

O3-85 - BASF works, Antwerp



Low temperature catalytic methods (UHDE method)



UHDE method

- A tertiary abatement system would be installed in the tail gas train at a point between the outlet of the absorber and the inlet of the tail gas expansion turbine
- for catalytic activity, the best location would be at the inlet of the tail gas expansion turbine, as the tail gas temperature here is at its highest, 400°C and more.

UHDE method

- decompose the N₂O downstream the NH₃-converter are called low temperature catalytic reduction methods, because they operate at temperatures of 250 °C to 500°C.
- A high activity above 400°C, not affected by other tail gas components, Tolerant of plant upsets, start-up and shutdown, Low cost, Long life and easy end of use disposal.

Evaluation table for N₂O – reduction methods

	BASF		Krupp Uhde
Reduction method	High temperature selective catalytic reduction	High temperature selective catalytic reduction	Low temperature selective catalytic reduction
Catalyst composition	8wt% CuO, 30wt% ZnO and 62wt% Al ₂ O ₃	Catalyst 03-80 : CuO on an Al ₂ O ₃ carrier.	Iron Zeolite catalysts.
N₂O conversion	Two tests are mentioned : 84.2 % and 80.2 %	Test 1 in Ludwigshafen and test 2 in Antwerp : 58.3 % and 82.1 %	95 %
N₂O inlet concentration	685 and 606 ppm	Test 1 : 1000 ppm , test 2 : 1200 and 1400 ppm	1500 ppm
Gas composition	The catalyst is tested with an artificially created gas stream	Catalyst bed is installed inside a commercially operating plant.	Catalyst bed is installed in the tail gas stream of commercially operating plant
Optimal condition	850 °C and 920 °C , 4-6 bar , residence time: <0.1 sec.	For both plants : 800 °C and 900 °C , 1 Atm. And 5.5 bar	425 °C , 10 bar.
Development stage	Laboratory tests.	Commercial plant scale test.	First commercial scale implementation of the new process successfully started up in sep. 2003 at AMI,Linz,Austria Low temperature catalysts have a longer life time than the high temperature catalysts
Uncertainties to claims	Only two laboratory tests performed.	More than 2 years operational in 2 commercial scale plants,BASF claims no NO conversion with a 0.3 to 0.5 % error	

N₂O

Abatement [CDM Project]

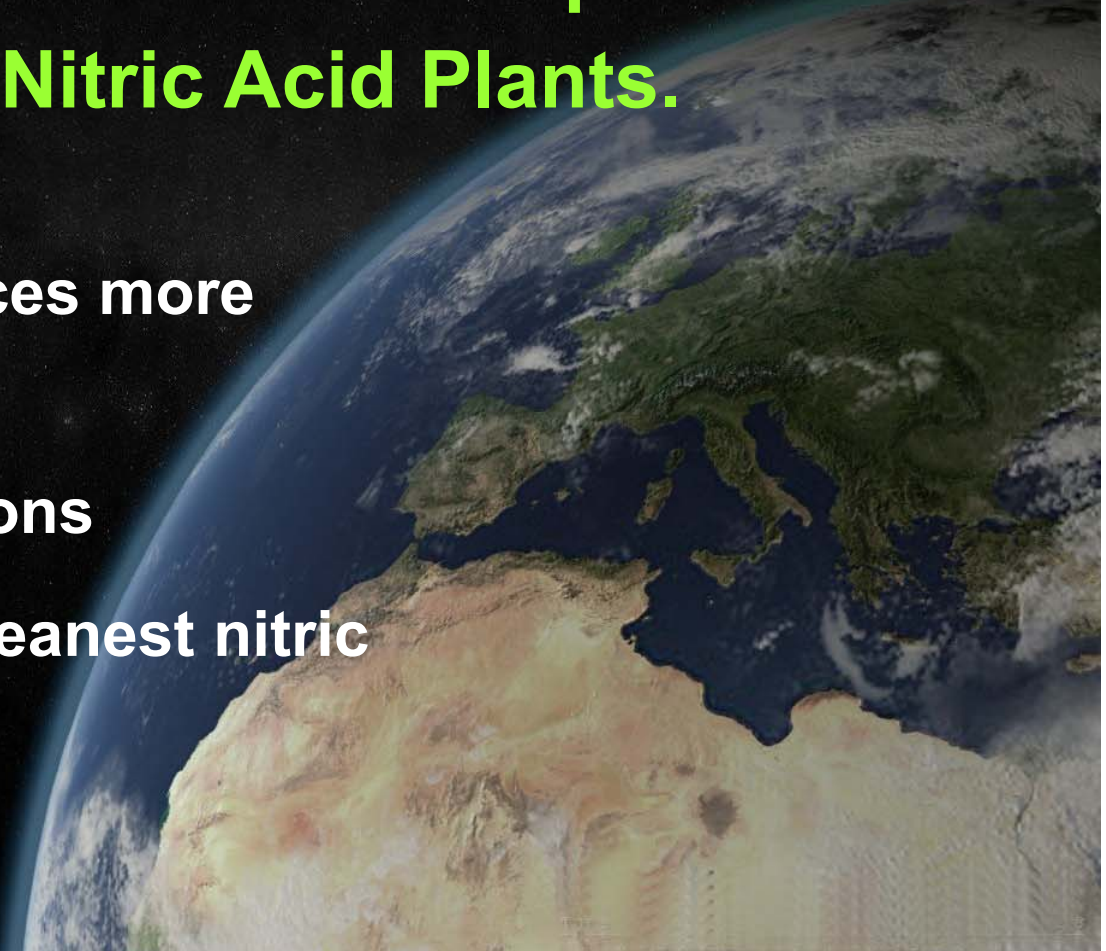

Abu Qir
Fertilizers



N₂O Abatement [CDM Project]

On October ,1 St, 2006,the First “CDM N₂O Abatement Project” Has Started Operation At Abu Qir II - Nitric Acid Plants.

- The CDM project reduces more than 99% of N₂O
- Almost all NO_x emissions
- Makes Abu Qir II the cleanest nitric acid plant worldwide



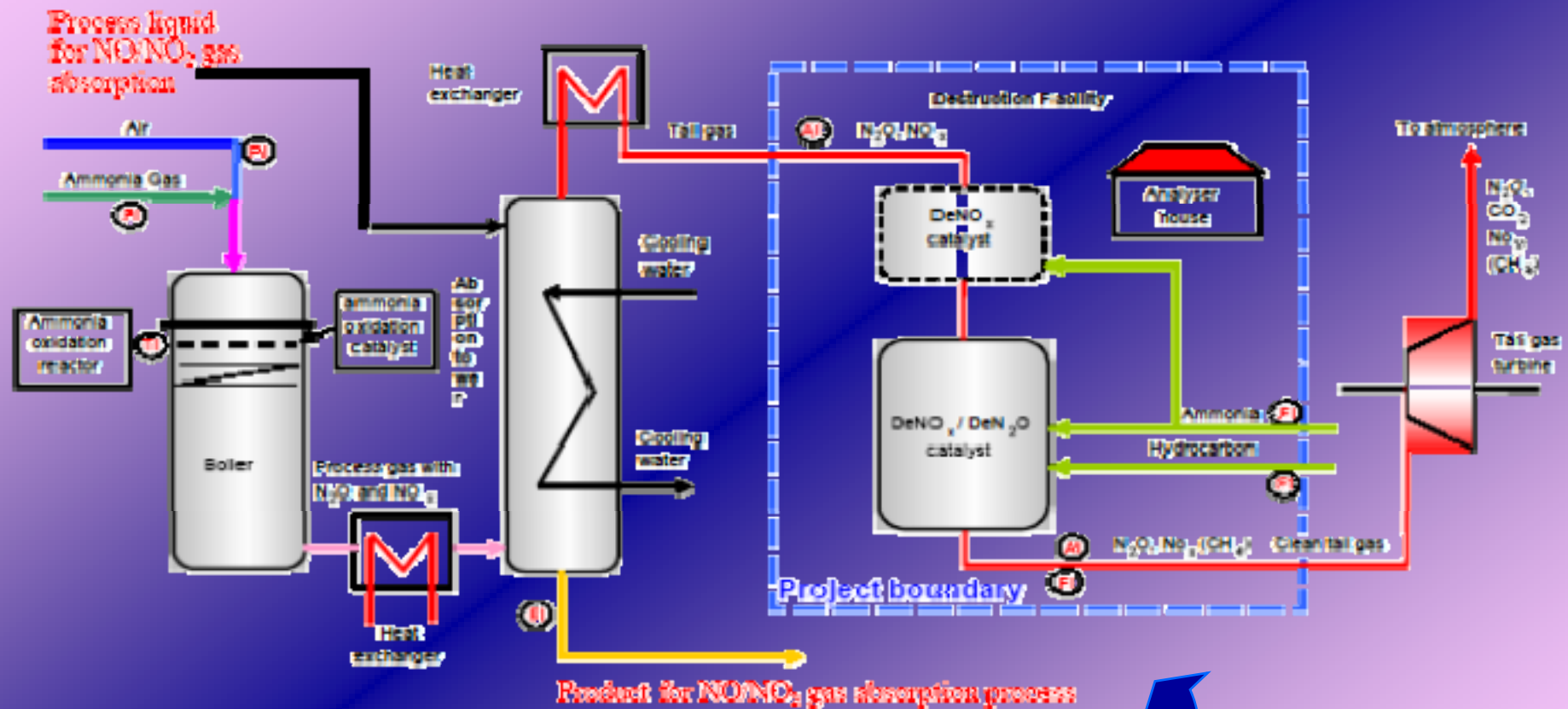
N₂O Abatement [CDM Project]

Our Project is :

- The **LARGEST** CDM Project Worldwide FOR N₂O Abatement
- The **LARGEST** CDM Project in Egypt
- The **LARGEST** CDM project in Africa



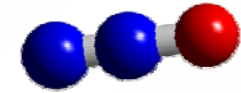
EnviNOx unit in process flow



EnviNOx unit

EnviNOx® System

Baseline Methodology



“Catalytic N₂O destruction in the tail gas of Nitric Acid Plants”



The catalytic reduction of NO_x and N₂O takes place into two stages, the NO_x is with ammonia and the N₂O is with hydrocarbon (natural gas). The reactions takes place over two iron zeolite catalyst beds arranged in series in the reactor.

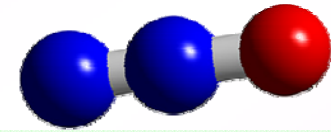


In the 1st bed, the NO_x is efficiently reduced with NH₃ according to the following reactions:

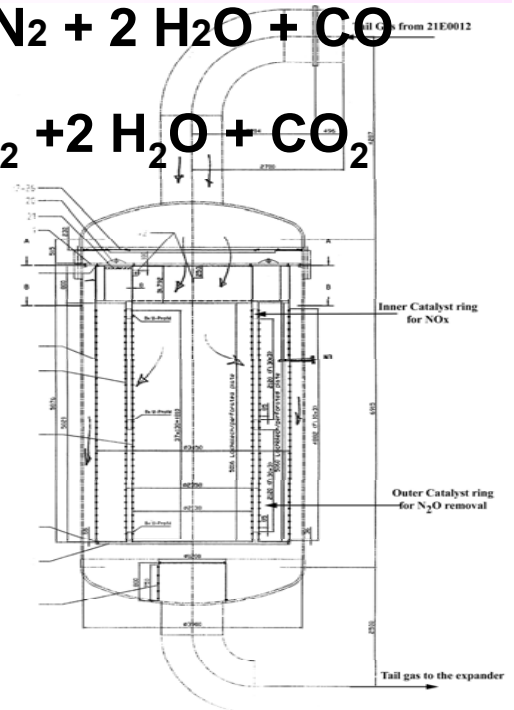
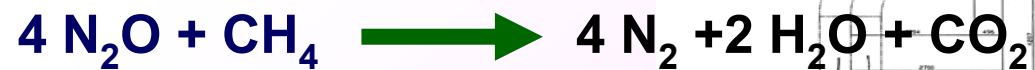


EnviNOx® System

Baseline Methodology



In the 2nd bed, the N₂O is reduced with the natural gas according to the following reactions:



N2O Destruction Project at AFC

Project Description

- Project partner : Abu Qir Fertilizers Co.
- Abu Qir operates 1830 tpd dual pressure NA plant (the biggest plant worldwide)
- Contract between CARBON and AFC has been signed on 24th-27th of September 2005
- CARBON financed developed, developed and implemented the CDM-project at own risk and will pay for the total running costs.

N2O Destruction Project at AFC

Project Description (contd.)

- CARBON EGYPT Ltd. Is the owner and seller of the CERs generated
- Abu Qir Fertilizers Co. will operate the EnviNOx[®] system together with the NA plant and the chemical complex
- CDM project Registration on 6th of October 2006 first issuance of CERs on 31st of May 2007

N₂O – abatement Project at Abu Qir



- ❖ **Project development**
- ❖ **The flexible instrument of the Kyoto Protocol**
- ❖ **Development of the N₂O Abatement project as a CDM**
- ❖ **The project according to Art. 12 of the Kyoto Protocol**

N₂O – abatement Project at Abu Qir

N ₂ O production	2006	2007	2008	2009	2010	2011	2012
NA plant *production	603900	603900	603900	603900	603900	603900	603900
Emissions factor **	8	8	8	8	8	8	8
GWP factor ***	296	296	296	296	296	296	296
Annual CO ₂ e emissions	1430035	1430035	1430035	1430035	1430035	1430035	1430035

- * Based on 330 production days
- ** Kg N₂O / t HNO₃
- ***Global warming potential

N₂O – abatement Project at Abu Qir

N2O Abatement	2006	2007	2008	2009	2010	2011	2012
Total ann. Emissions *	1237082	1237082	1237082	1237082	1237082	1237082	1237082
N2O reduc. efficiency**	80 %	80 %	80 %	80 %	80 %	80 %	80 %
Annual CO ₂ e abetment	1029625	1029625	1029625	1029625	1029625	1029625	1029625

- * Abu Qir On-stream factor expressed to be 90 %
- ** Uhde will guarantee to reduce minimum 80% of the N₂O in tail gas

Summary Emission Reduction 2007-2013

year	Annual emission estimation*
2006	310882
2007	1065881
2008	1065881
2009	1065881
2010	1065881
2011	1065881
2012	1065881
2013	754999

** Reductions in tons of CO₂ eq*



Cost

**Abu Qir will not bear
any costs or
investments by itself.**

Total cost :

16.000.000 Euro

Covered by carbon Austria

In addition to that it will:

- *Share in the selling price of the CERs.*
- *Be compensated for any additional operating costs.*
- *Hold the ownership of equipment (title retention till 2012).*
- *Be offered a production guarantee over stated production levels.*
- *Be the owner of CERs after 2012.*

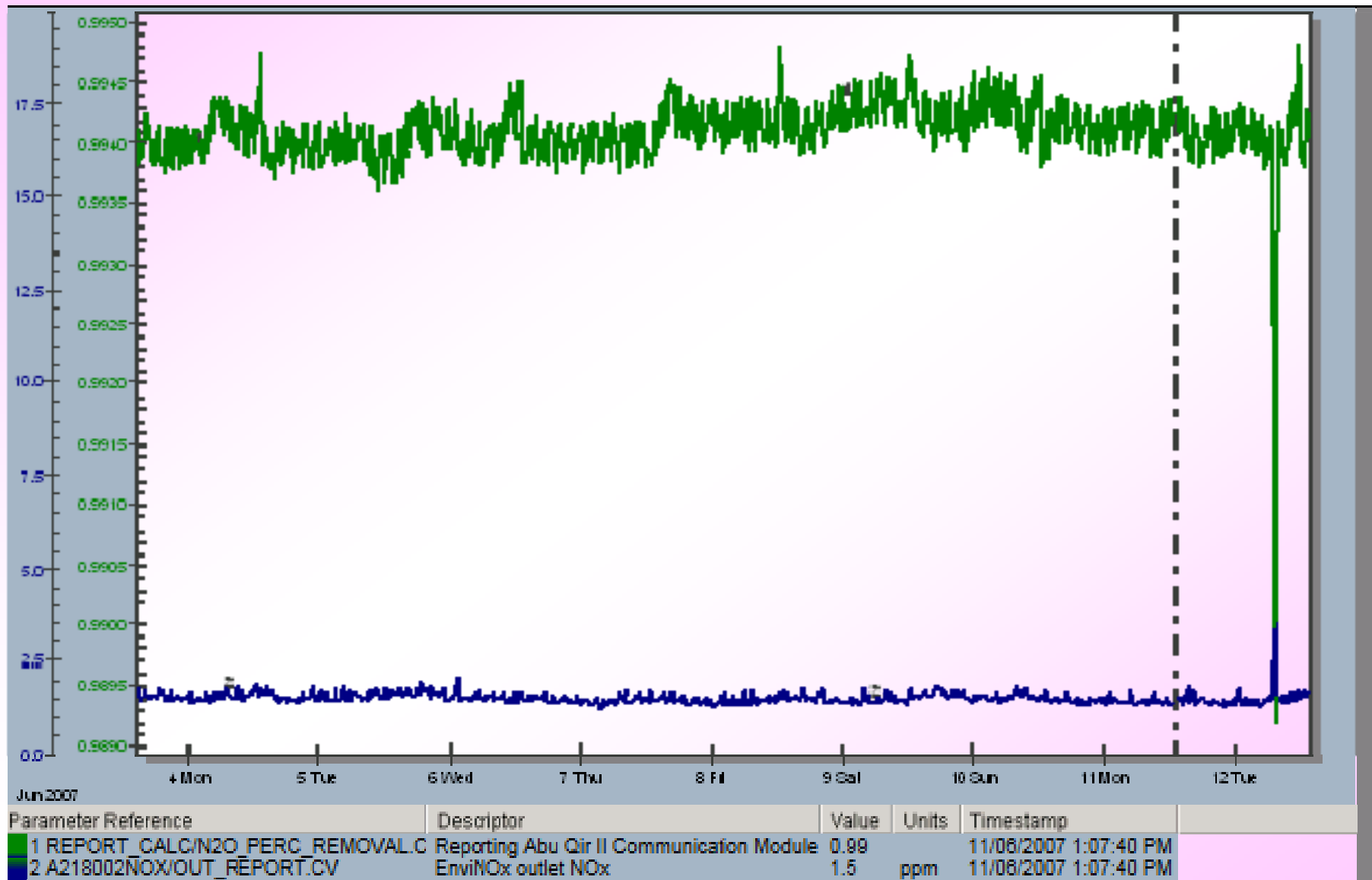


CERs Production and Sales Plan

Base : CERs Issued (416187t CO2 eq.)

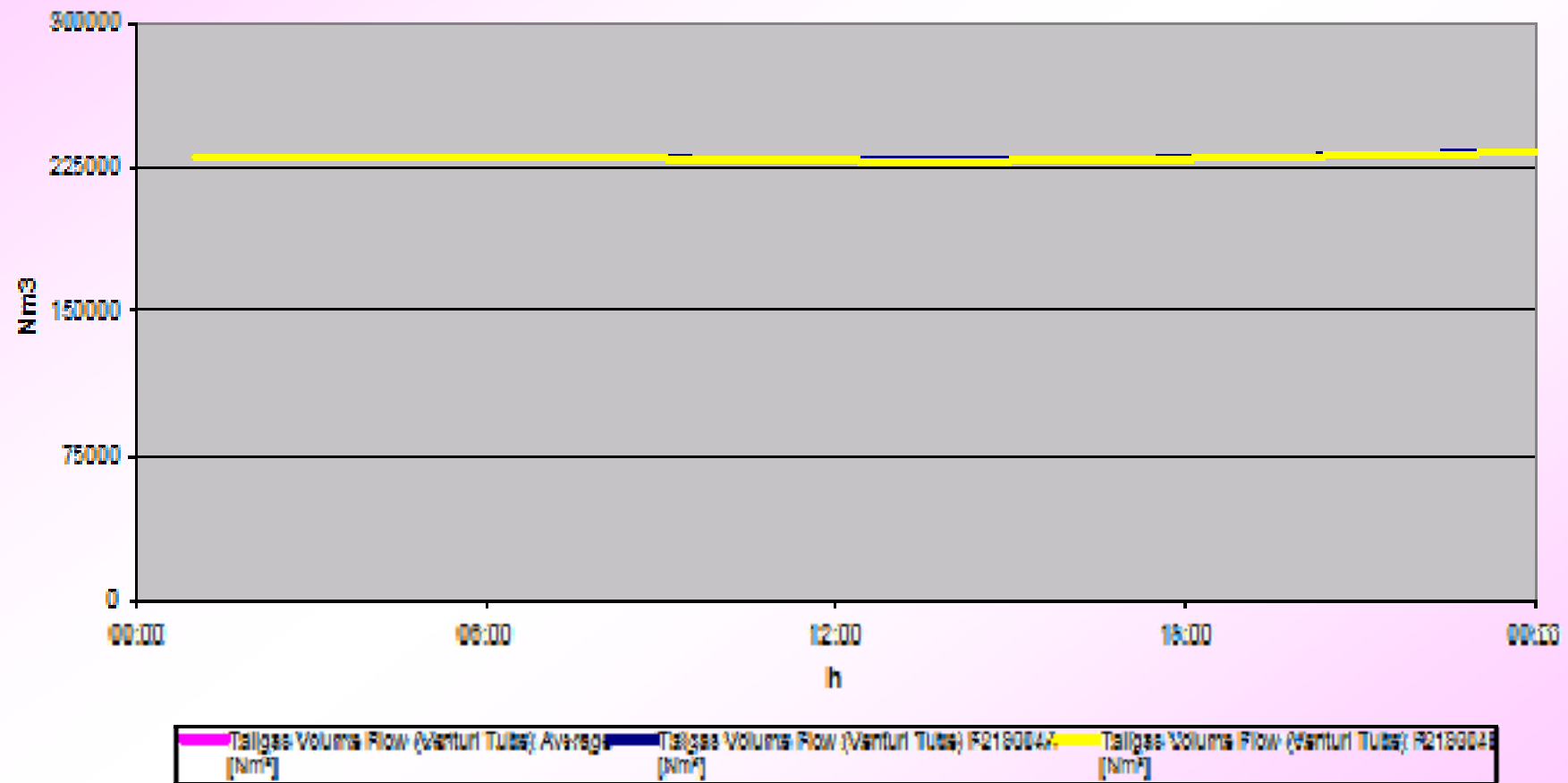
	UNFCC	EEAA	Social Fund	AFC	Carbon	Total
Shares	2 %	6.5 %	3 %	26.55 %	61.95 %	100 %
Quantity	8323.7 4	27052.1 5	12485. 61	110497. 6	2578279.	416187
€	47651	154867	71477	632574	1476005	2382574

Outlet NO_x Concentration



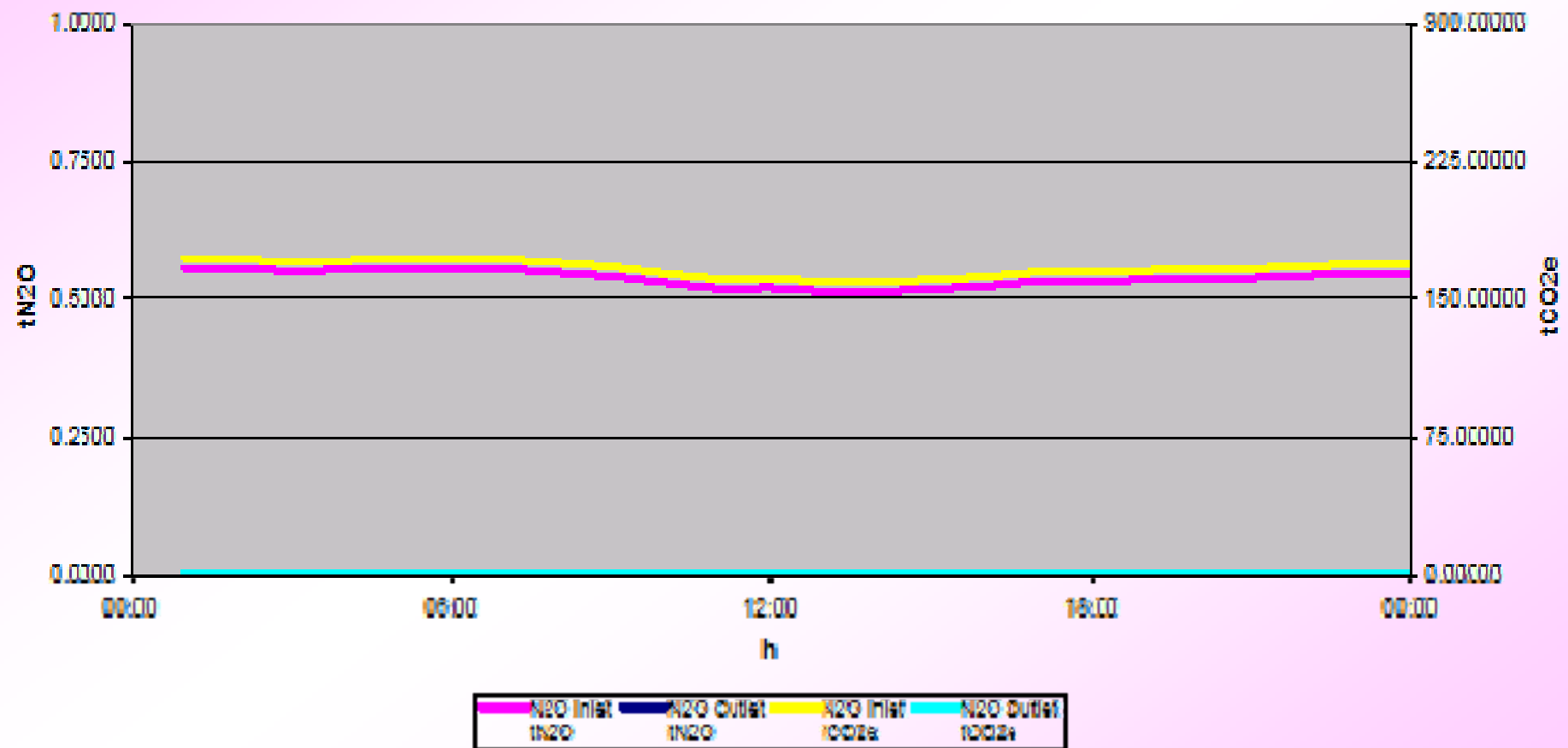
Tail Gas Volume Flow

Daily Chart (Hourly Average)



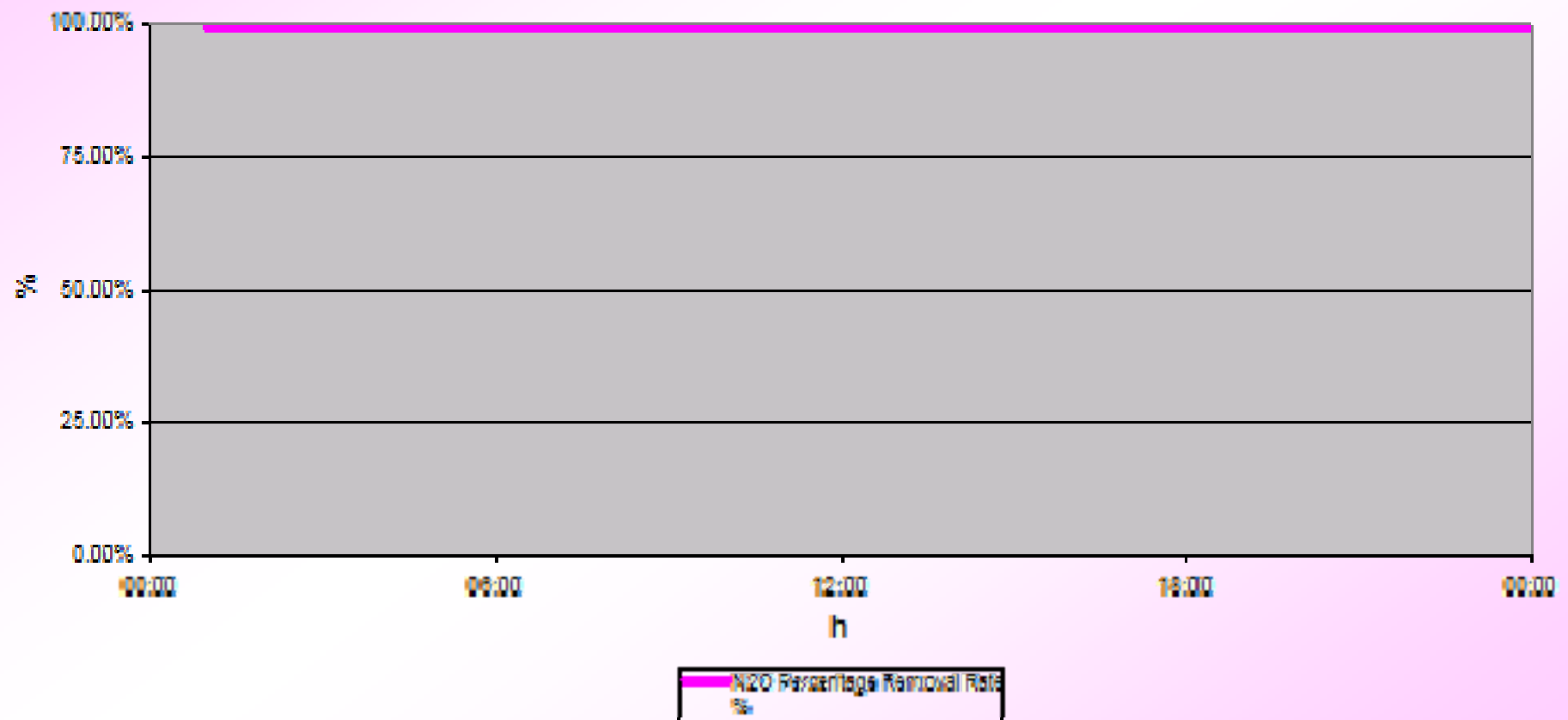
Inlet and Outlet - tN_2O

Daily Chart (Hourly Average)



N₂O Removal Rate %

Daily Chart (Hourly Average)



Thank you ...



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