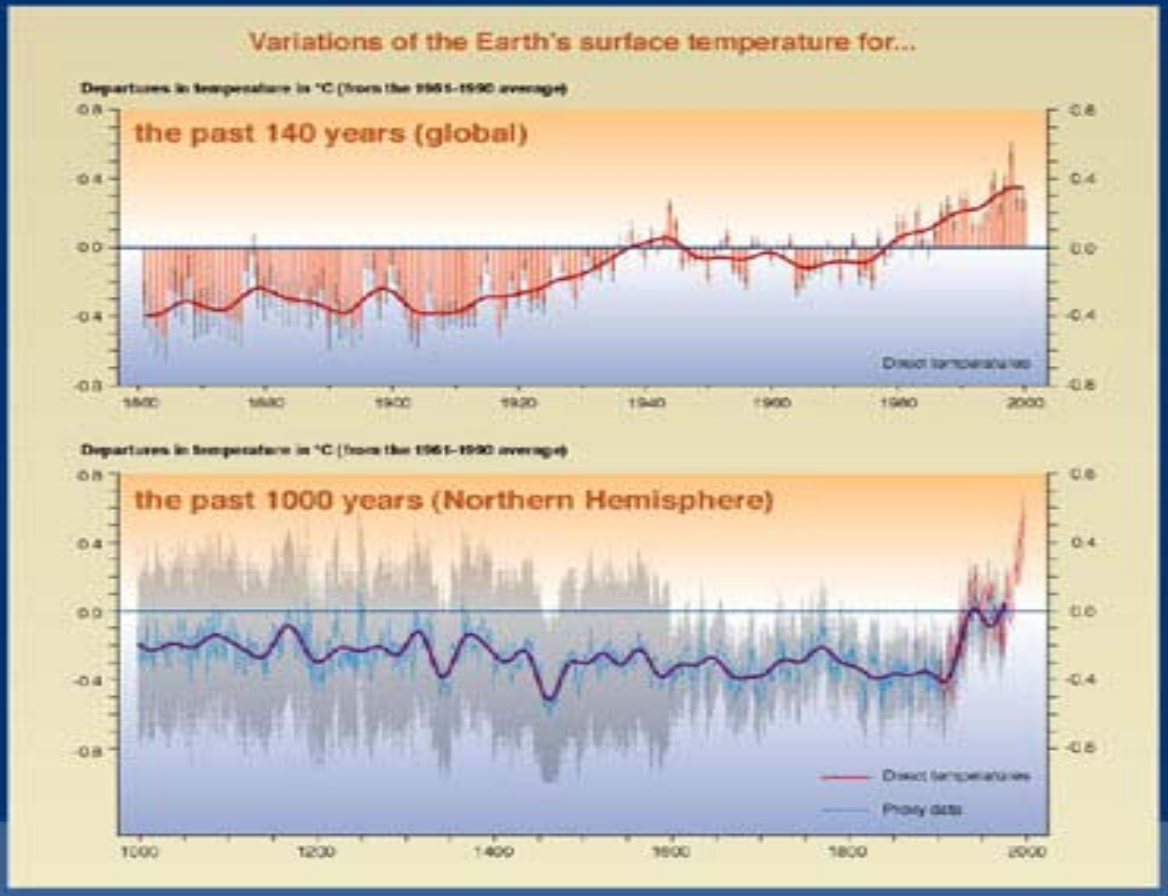
New Süd-Chemie Off-gas Catalysts for the reduction of NO and N_2O from Nitric Acid plants:

A Significant Contribution against Global Warming

The Chem Show, New York City, October 31, 2007

New Süd-Chemie off-gas catalysts for the reduction of NO and N_2O from Nitric Acid plants: a significant contribution against global warming

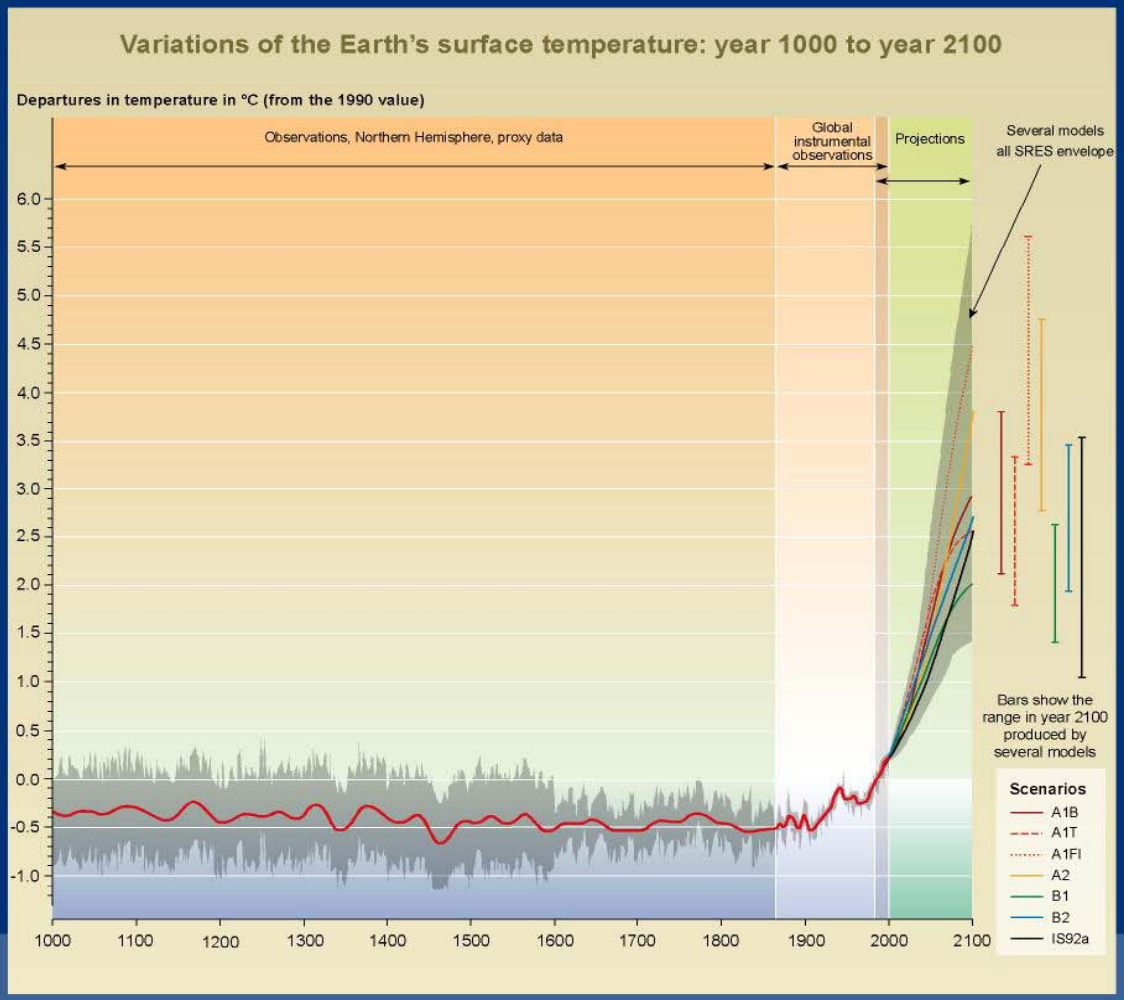
- ➔ atmospheric introduction
- ➔ Zeolites: nice and useful
- ➔ DeN_2O-process by Uhde
- ➔ Industrial Experience
- ➔ Summary



SYR - FIGURE 2-3

IPCC
INTERGOVERNMENTAL PANEL ON CLIMATE CHANGE

WMO UNEP

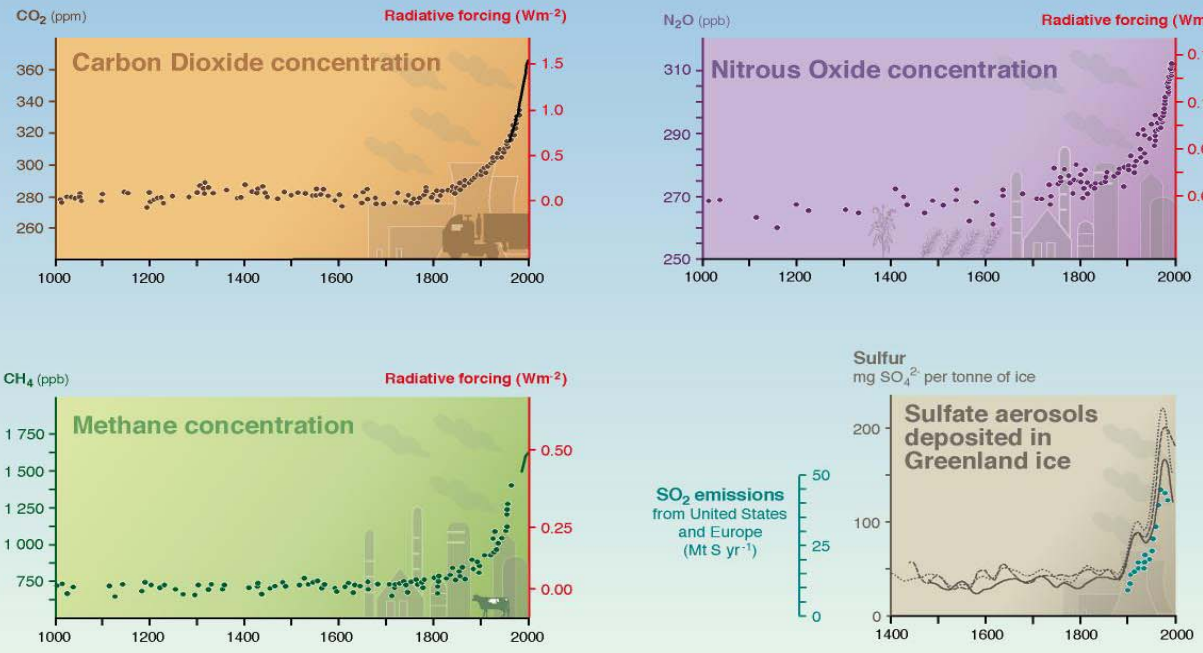


SYR - FIGURE 9-1b

IPCC
INTERGOVERNMENTAL PANEL ON CLIMATE CHANGE

WMO UNEP

Indicators of the human influence on the atmosphere during the Industrial era



SYR - FIGURE 2-1
WG1 FIGURE SPM-2

IPCC
INTERGOVERNMENTAL PANEL ON CLIMATE CHANGE
WMO UNEP

Actual contribution of gases to the atmospheric greenhouse effect

Greenhouse gas	Contr.	GWP100	Residence time
water vapour (H_2O):	61,4 %		days
carbon dioxide (CO_2):	20,5 %	1	50-200 a
methane (CH_4):	7 %	23	9-15 a
laughing gas (N_2O):	6,8 %	310	120 a
ozone (O_3):	2,3 %		
others (FCKW, SF_6, ….):	2,0 %	22.000/SF_6	3200 a/SF_6

Source: Bayerisches Amt für Umweltschutz + IPCC

→ **For the reduction of one of the most harmful atmospheric greenhouse gases - N2O - Sud-Chemie offers zeolite catalysts !**

N_2O; where does it come from ?

N_2O contributes by about 6.8 % to atmospheric global warming

Main sources are;

- Agriculture (major source)
- Adipic Acid production (significantly reduced by new catalysts)
- Automotive off-gas (three way catalysts)
- Nitric acid production (now largest industrial source)
  - 700 plants worldwide
  - 400,000 tpa N_2O or the equivalent of 125,000,000 tpa CO_2

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General Formula of Zeolites

Crystalline hydrated aluminosilicates:

➔ General formula: $M_{x/n}[(AlO_2)_x(SiO_2)_y]\cdot wH_2O$
M = cation of valence
n, w = number of water molecules.

➔ The ratio of AlO_2 to SiO_2 represents the framework composition.

➔ Tayloring of properties by synthesis or post treatment
- pore size (0,3 to 1,2 nm)
- acidity (amount of sites and strenghts)
- hydrophobicitiy, hydrophilicity
- metal exchange,….

Natural Zeolite: Erionite

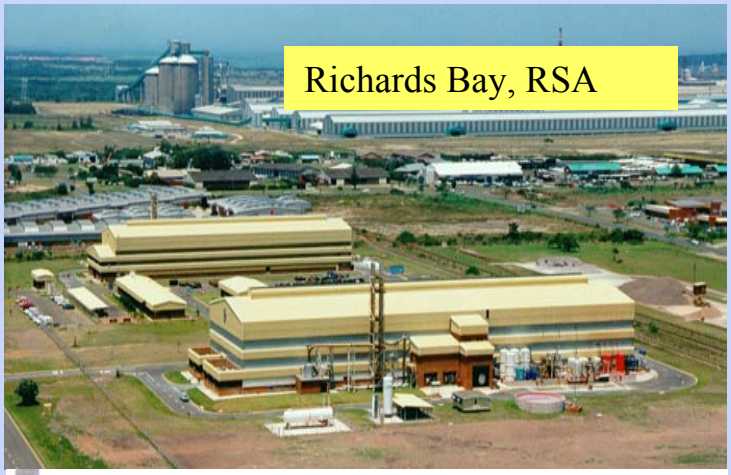
Zeolite production of Süd-Chemie

- 2 modern plants in RSA
  + aquisition of Tricat Zeolites Bitterfeld/Germany in 10/2006

- Capacity > 2000 tpa for Powders and 1000 tpa catalysts

- Full production lines for
  - Iron Zeolites powders and
  - Iron Zeolite catalysts

Sud-Chemie DeN$_2$O catalysts are mainly zeolite based !!



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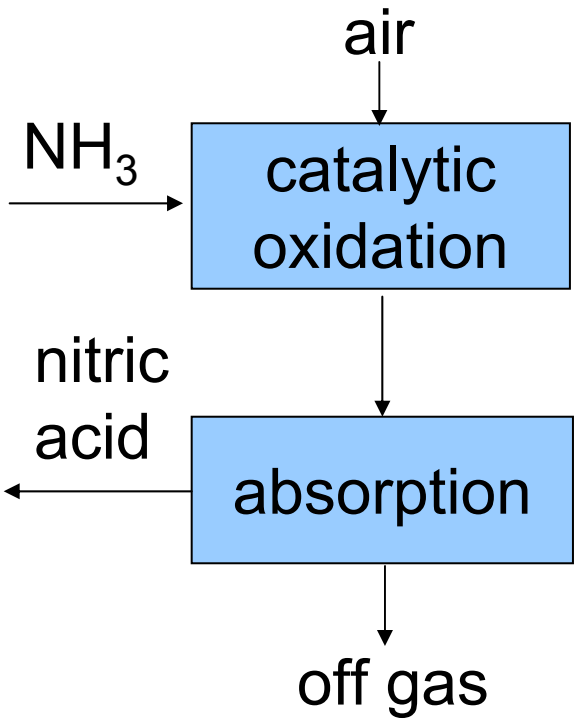
NO_x/N_2O formation in nitric acid production



(1) $4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$ ~96 % — desired

(2) $4\ NH_3 + 3\ O_2 \rightarrow 2\ N_2 + 6\ H_2O$ ~2 %

(3) $4\ NH_3 + 4\ O_2 \rightarrow 2\ N_2O + 6\ H_2O$ ~2 %

} undesired

(4) $4\ NO + 3\ O_2 + 2\ H_2O \rightarrow 4\ HNO_3$

1000 - 2000 ppmv N_2O; 200 - 600 ppmv NO_x

Amount of N_2O formed: on average 7 kg N_2O / t HNO_3

World wide emissions ~ 400,000 t N_2O / a ; corr. 124 Mio t CO_2

HNO_3 production now largest industrial process source of N_2O

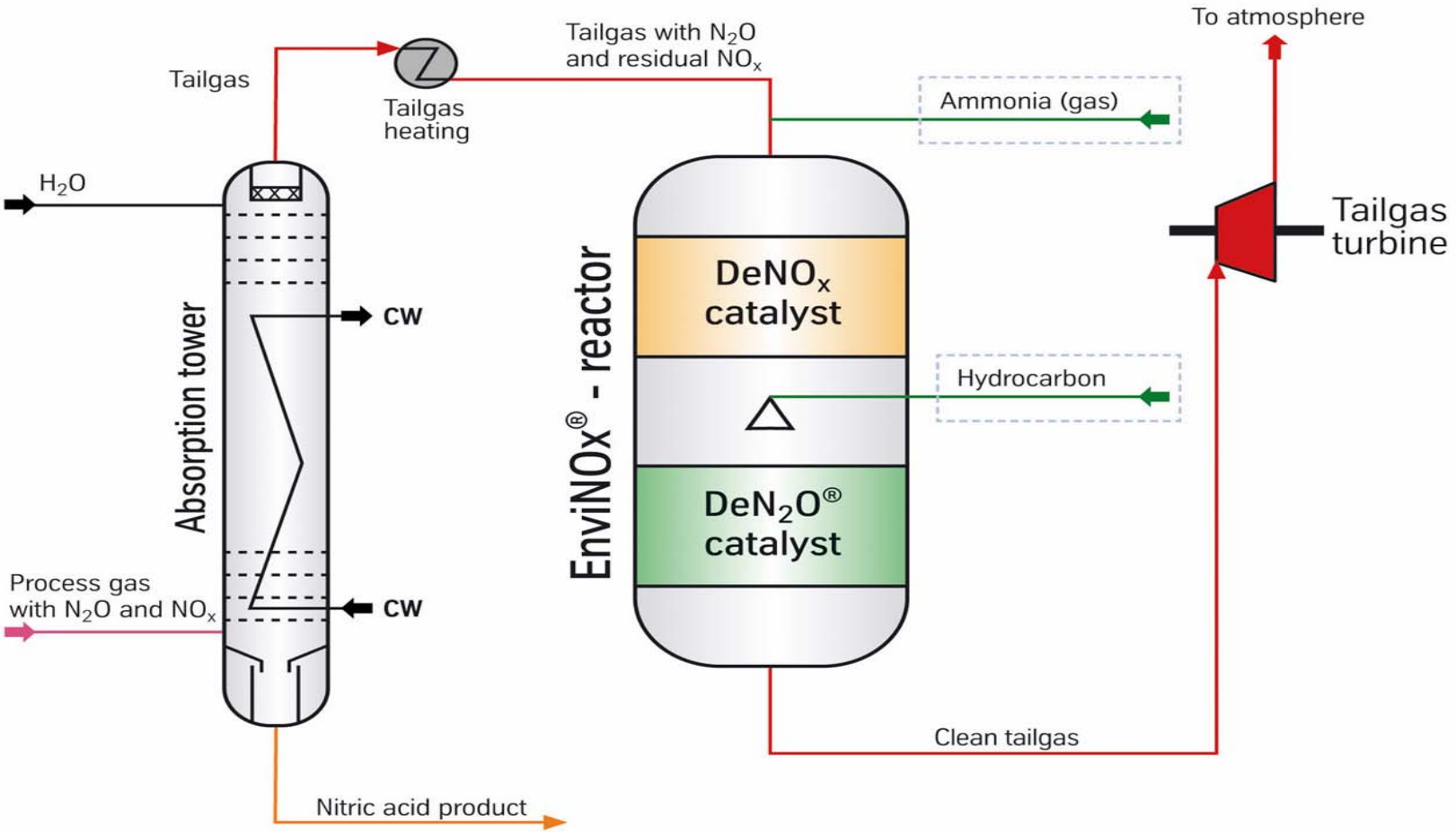
GWP-Factor of N_2O=310 (N_2O/CO_2)

Possibilities to reduce N_2O at Nitric acid plants

Primary:	**N_2O is prevented from forming. Alternative catalysts necessary, which may suffer from lower selectivity.**
Secondary:	**N_2O once formed, is removed anywhere between the outlet of the ammonia oxidation gauzes and the inlet of the absorption tower. Influences the process.**
Tertiary (end of the pipe):	**N_2O is removed from the tail gas downstream of the absorption tower by catalytic destruction.**
Advantages are:	**→ no interference with the nitric acid production itself** **→ well accepted by plant operators** **→ process suitable for destroying N_2O and NOx**

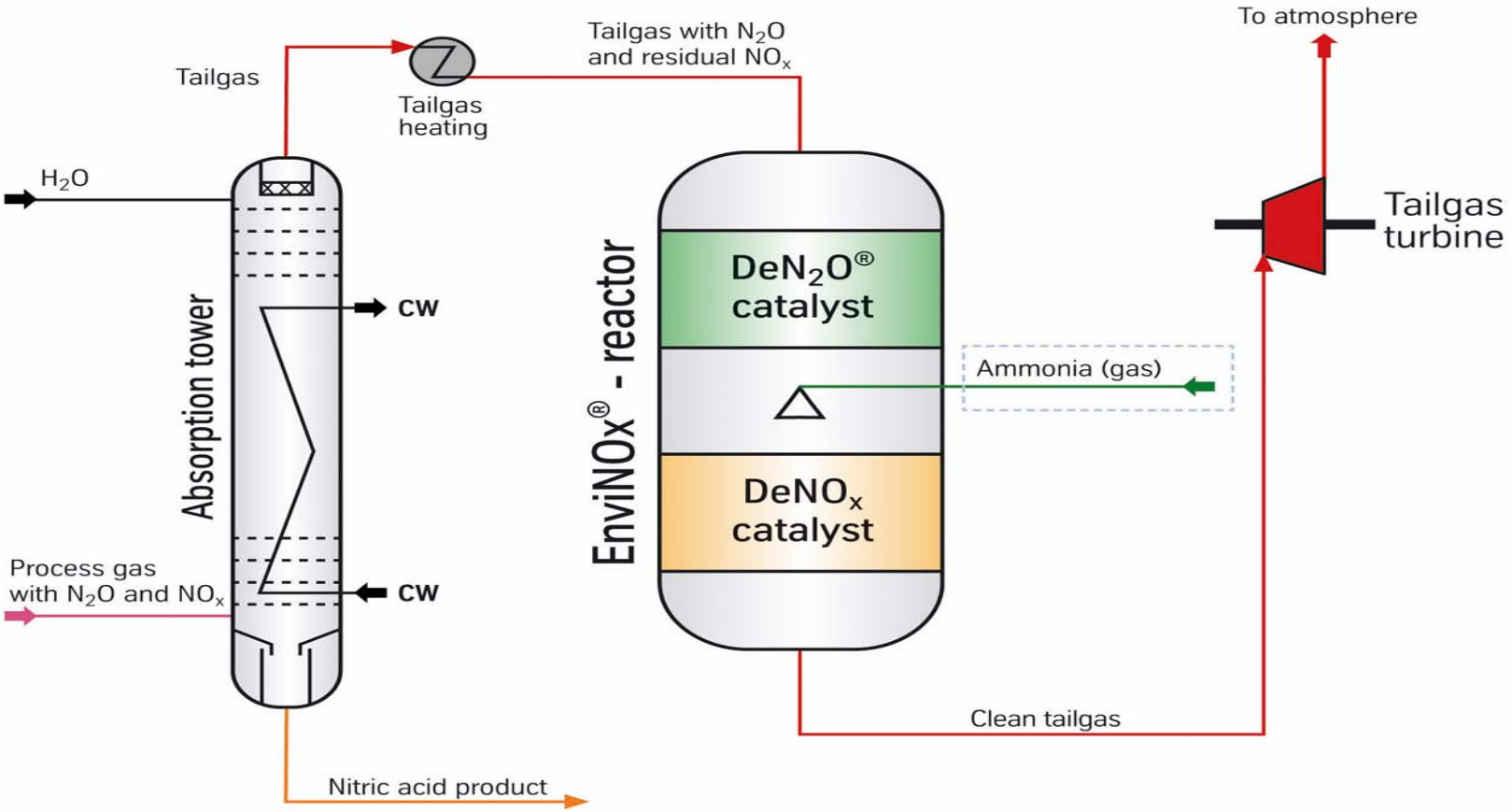
EnviNOx® (Uhde) Process Variant 1

NO_x reduction by ammonia / N_2O reduction by HC



EnviNOx® (Uhde)Process Variant 2

NO_x reduction by ammonia / N_2O removal by decomposition



Catalytic N_2O/NO destruction methods
(end of the pipe) only schematic

Catalytic N_2O decomposition (catalyst Fe-zeolite)

$$2\ N_2O \rightarrow 2\ N_2 + O_2$$

Catalytic N_2O reduction with Hydrocarbons (catalyst Fe-zeolite)

$$C_xH_y + z\ N_2O \rightarrow a\ CO + b\ CO_2 + c\ H_2O + d\ N_2$$

Catalytic NO reduction with NH_3 (catalyst Fe-zeolite or $V_2O_5/TiO_2/WO_3$)

$$a\ NH_3 + b\ NO + (O_2) \rightarrow c\ N_2 + d\ H_2O$$

Catalytic N_2O reduction with Hydrocarbons

Case CH_4 as reducing agent

$$CH_4 + 3\ N_2O \rightarrow CO + 2\ H_2O + 3\ N_2$$

$$CH_4 + 4\ N_2O \rightarrow CO_2 + 2\ H_2O + 4\ N_2$$

Case C_2H_6 as reducing agent

$$C_2H_6 + 5\ N_2O \rightarrow 2\ CO + 3\ H_2O + 3\ N_2$$

$$C_2H_6 + 7\ N_2O \rightarrow 2\ CO_2 + 3\ H_2O + 7\ N_2$$

Case C_3H_8 as reducing agent

$$C_3H_8 + 7\ N_2O \rightarrow 3\ CO + 4\ H_2O + 7\ N_2$$

$$C_3H_8 + 10\ N_2O \rightarrow 3\ CO_2 + 4\ H_2O + 10\ N_2$$

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1st commercial scale realization by Uhde

Site:	**Linz / Austria**
Company:	**Agrolinz Melamine International (AMI)**
Variant 2:	**Decomp. + NH_3 -SCR**
Capacity:	**1,000 t/d HNO_3**
Tailgas:	**120,000 Nm^3/h**
Temperature:	**430°C**

Greenhouse effect:
> 600.000 tpa CO_2

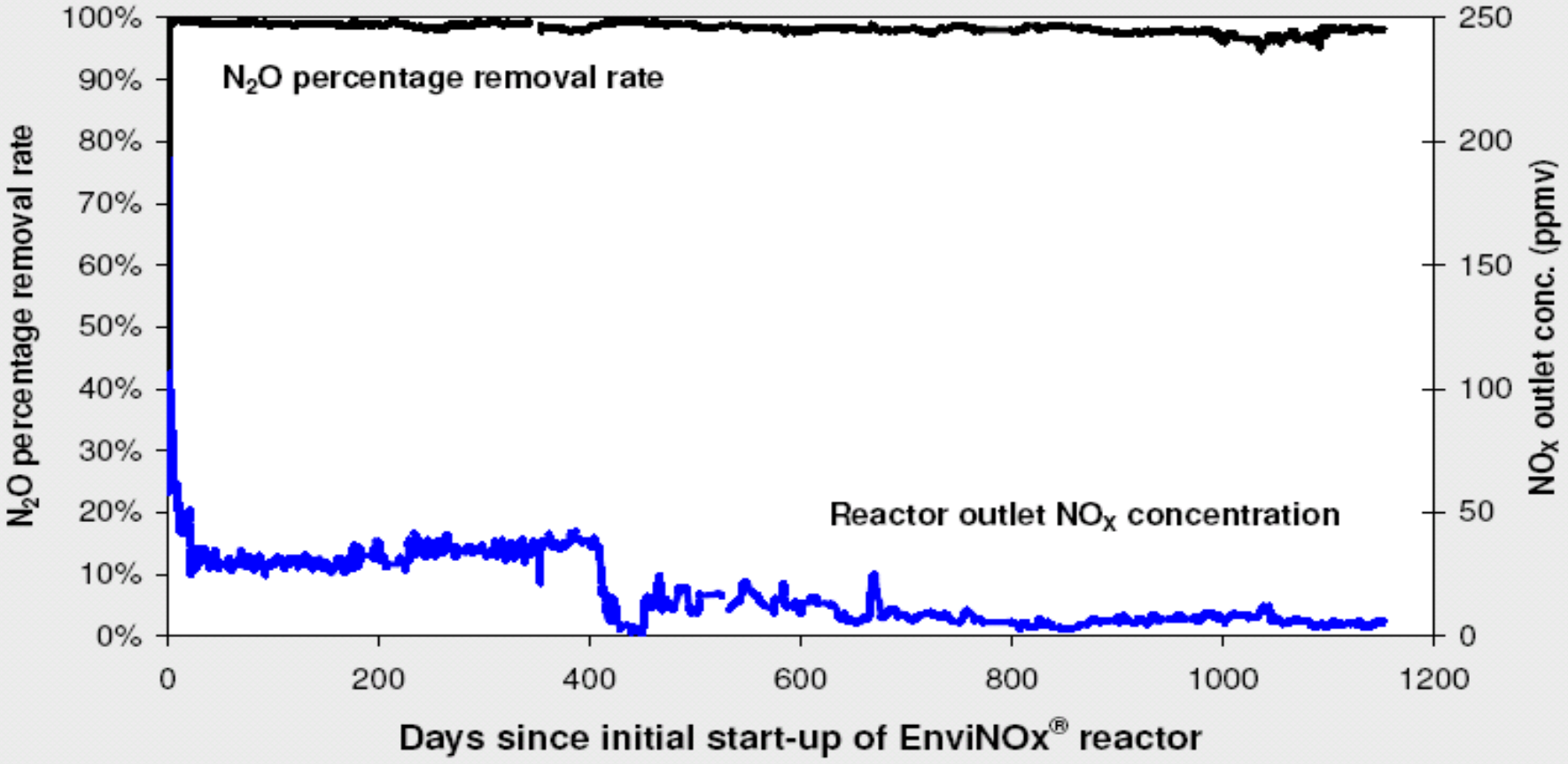
98 - 99 % conversion

Start up: 29-09-2003

EnviNOx® Process

Plant operating data

AMI HNO_3 Plant Line E - Uhde EnviNOx® Process Variant 1
N_2O Removal Rate and NO_X Exit Concentration



2nd commercial scale
Realisation by Uhde

Site:	Abu Qir, Egypt
Company:	Abu Qir Fertilizers
Variant 1:	NH_3-SCR + CH_4-SCR
Capacity:	1870 t/d HNO_3
Tailgas:	225.000 Nm3/h
Temperature:	410°C

Greenhouse effect:
1.400.000 tpa CO_2

➢ 99 % N_2O conversion

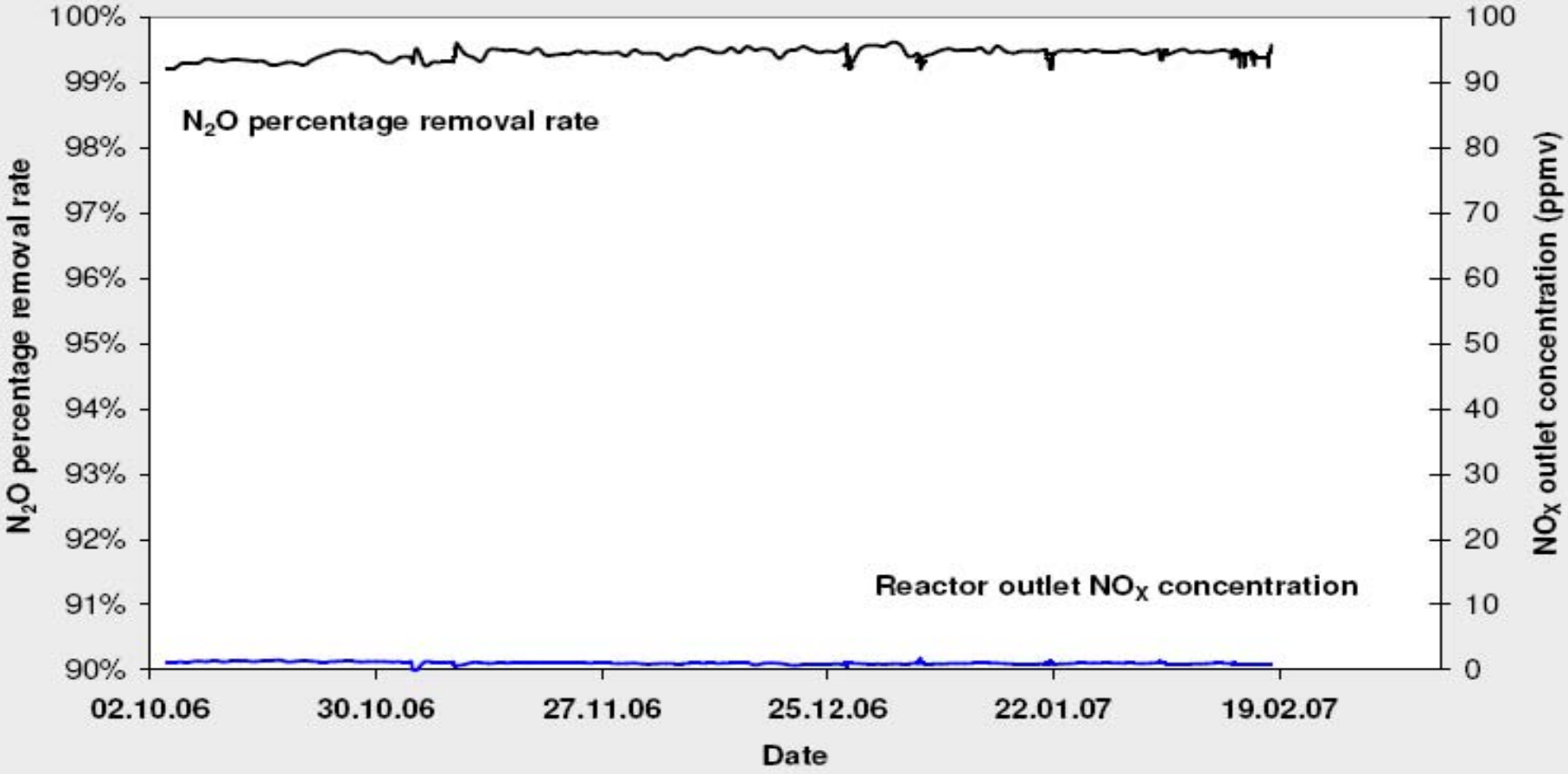
NOx < 1 ppm

Start up: 30-09-2006

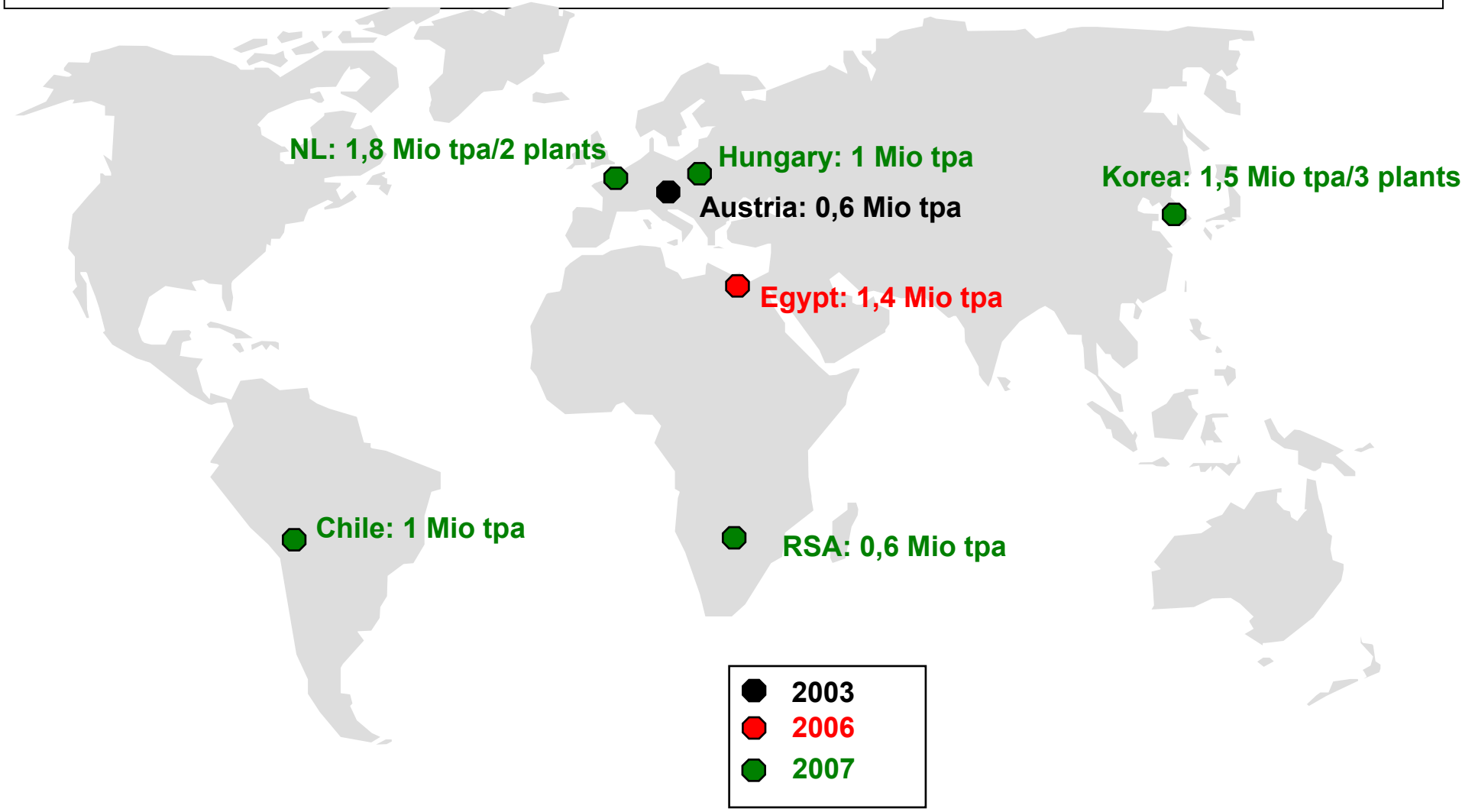
EnviNOx® Process

Plant operating data

Abu Qir 2 HNO_3 Plant, Egypt - Uhde EnviNOx® Process Variant 2
N_2O Removal Rate and NO_X Exit Concentration



CO_2 equivalent reduction in De-N_2O off-gas units in HNO_3-plants realized end 2007 by Uhde/SCAG



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Conclusions

Forced by such environmental regulations as the „Kyoto Protocol“ and the economic incentives as exist with CO2 trading, a major part of the worldwide existing Nitric acid plants will be equipped with N2O destruction units. For new Nitric Acid plants a N2O destruction technology will be obvious.

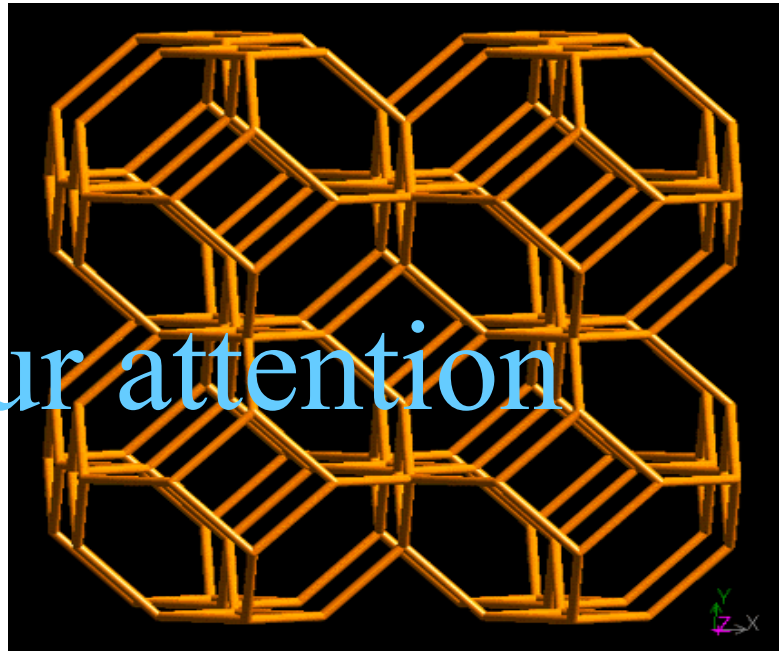
This will contribute significantly to global environmental protection.

Early zeolite applications in Egypt arround 1330 BC

Lapislazuli

Mainly Lasurit / Sodalite-Group.

Coulour by (S_3^-) in the Sodalite-Cage



Thank you for your attention