UMONS
Université de Mons

Techniques de déNOx:
Etat de l'art & Nouvelles tendances
DeNOx processes:
State-of-the-art & New trends

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POLYTECH MONS

Atmos'Fair
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NOx Stationary Sources

- **Combustion units**
- **HNO_3 manufacture plan**
- **Reactors using nitric acid**

3 specific mechanisms generating NOx

***NO: 95%**

NO_2 : 5%

NOx Regulation for Combustion Units

		Puissance (MWth)	Comb. Solide	Comb. Liquide	Comb. Gazeux	
U.Europ.	Dir 2001/80/CE Anciennes et installations 01/07/87 < < 7/11/2002 > 01/01/2016	50 - 500 >500 50 - 500 >500	600 500 600 200	450 400	300 200	

U.Europ.	Dir 2001/80/CE N^{elles} installations > 27/11/2002	50 - 100 100 - 300 > 300	400 200 200	400 200 200	150 150 100	50 (GN) 120 (L-G)

1 **ppm** NO_2 = 2.044 **mg** NO_2 **/Nm^3**

NOx reduction techniques for combustion units

Main factors:

- flame temperature
- oxygen concentration
- fuel N content
- fuel residence time at high t
- mixing fuel/air
- …

PRIMARY Techniques
Combustion Modifications

SECONDARY Techniques
Post-combustion

Flue Gas Treatment
Clean-Up techniques

Action principles of primary techniques:

- choice and quality of fuel
- better design of burners
- fuel staging
- air staging
- reburning
- recirculation (recycling) of fumes

Low NOx Burners (LNB) Technology

Combination of several NOx reduction principles

NOx reduction techniques for combustion units

PRIMARY Techniques
Combustion Modifications

SECONDARY Techniques
Post-combustion

Flue Gas Treatment
Clean-Up techniques

Dry Techniques
SCR
SNCR
Radiation
Adsorption

Wet Techniques
Oxidation-Absorption

Procédé SCR = Selective Catalytic Reduction

Desired reaction :

$4\ NO + 4\ NH_3 + 3\ O_2 \rightarrow 4\ N_2 + 6\ H_2O$

Reactants:

- NH_3
- $(NH_2)_2CO$
- $(HOCN)_3$

Operating Conditions:

- **temperature : 160 - 350 C**

= function (F.G. conditions, catalyst type)

Optimum cata/t for >> NOx reduction

<< SO_2 to SO_3 conversion

- **NH_3 concentration :** **NH_3/NOx <~ 1**

! Limit = « NH_3 slip »

Modular building of the SCR catalytic bed reactor

uniform velocities, good injection and mixing of NH_3

Element

Module

Layer

Advantages of SCR

- a very efficient process

  → performances of NOx abatement up to **90-95 %**
- the most mature post-combustion technology
- a wide variety of applications
- flexibility of the process and tailored technology

Drawbacks of SCR

- cost of the catalyst
- limited lifetime of the catalyst
- pressure drops
- large plot place:

  SCR design < [Nm^3/h (flue gas) / m^3 (cata)] ~ **3000 – 10000 h^{-1}**

SCR - More recent developments:

Catalysts:

- improved for **lower operating temperatures**
- destroying **dioxins** and **furans**
- for **simultaneous removal** of carbon monoxide CO and volatile organic compounds (VOC)

SNCR Process
= Selective Non Catalytic Reduction

Reactants:

- NH_3 *(Thermal DeNOx process)*
- $(NH_2)_2CO$ *(NOxOUT process)*
- $(HOCN)_3$ *(RAPRENOx process)*

Reduction: the same reactions reducing NOx than for SCR

Non Catalytic: Reactant injected in the furnace/convective cavities

Furnace = chemical reactor

SNCR reactions

Selective… requiring several conditions:

- a narrow temperature window: 950-1100 C

Outlet NOx content vs Temperature

Advantages of SNCR

- lower capital investment
- low space required

Drawbacks of SNCR

NOx Reduction vs Stoechiometry (ratio NH_3/NOx)

Practically: achievable NOx reduction efficiency:

40-50%

New developments for SNCR

- Injection nozzles for a rapid and excellent mixing of the reductant
- Simultaneous injections:
  - of H_2 with NH_3
  - of additives with urea
  - of Na_2CO_3
    - → shift of the t° window → lower t°
    - → side effects ??

Hybrid SNCR + SCR

- Reduction of SCReactor size (cost, Δp…)
- Aiming at achieving a higher NOx reduction with lower NH_3 slip
- …

Electron Beam Process (EBP)

- Simultaneous removals of SO_2 and NOx
- High efficiencies 95% for SO_2 and 70% for NOx
- Generation of valuable by-products → NPK fertilizers
- 2 industrial installations (China and Poland)

NOx reduction techniques for nitric acid plants

PRIMARY Techniques

Absorption Process Modifications (t°, pressure, volume, additional reactant…)

SECONDARY Techniques:

- SCR (NH_3)
- NSCR (H_2, HC)
- Adsorption (activated carbon, molecular sieves…)

NOx reduction techniques for reactors using nitric acid

Various specific solutions depending on:

process, NOx concentration and composition ([NOx-NO]/NOx), …

Applicability of wet techniques:

← lower flow rates

← favourable NOx composition

→ example

Example : NOx reduction in off-gases issued from the production of catalysts for vehicle exhaust pipes

Procédé :

1°) attaque : 3 Ni + 8 HNO_3 (42%) -> 3 $Ni(NO_3)_2$ + 2 NO ↗

2°) Immersion support poreux dans solution de $Ni(NO_3)_2$

3°) cata / $Ni(NO_3)_2$ -> calcination (250-450°C) -> cata / NiO avec NOx ↗

N_2O emerging problem

Greenhouse effect : $GWP_{N2O} = 300xGWP_{CO2}$ + Ozone layer depletion
Sources: nitric acid and adipic acid plants

N_2O Reduction Techniques

Primary abatement techniques for HNO_3 units**:**

- Modification of the ammonia oxidation catalyst
- Homogeneous decomposition

Flue gases treatment :

- Catalytic decomposition

N_2O heated, compressed then fed into fixed bed reactor ∋ catalyst

- Thermal decomp. at high t° (800-1000°C)

$N_2O \rightarrow N_2 + O$; $N_2O + O \rightarrow N_2 + O_2$; $N_2O + O \rightarrow 2\ NO$

- Selective Catalysis (SCR) in presence of a reducing agent

Ex: Fe-ZSM-5 and propane

- NSCR (with H_2, CH_4, … on Pd/Al_2O_3)

Conclusions

Process generating NOx:
Concentration of NOx
Composition of NOx

Choice of technology:
Performances required
Secondary impacts
Costs
….

LABORATORY

PILOT

INDUSTRIAL

AOP (UV/H_2O_2)

+… ???

EBT
Adsorption
Simultaneous removal of NOx and SOx

Primary:
Process modifications
Secondary:
SCR
SNCR
NSCR

Good performances
Some improvements

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THANKS FOR YOUR ATTENTION

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Locations of SCR in the flue gas train

High Dust arrangment

+ Operating temperatures in the optimum range
- Salts formation and precipitation; erosion

Low Dust Crude Gas Arrangement

+ Flue gas temperatures usually sufficient without further heating
- Salts formation and precipitation

Tail End Arrangement –

+ Longer service life for th
- Too low temperature lev

Schematic diagram of the low-dust purified gas configuration

SNCR reactions

With ammonia:

Desired

$$\mathbf{4\ NO + 4\ NH_3 + 3\ O_2 \rightarrow 4\ N_2 + 6\ H_2O} \quad \mathbf{(1)}$$

$$\mathbf{2\ NO_2 + 4\ NH_3 + O_2 \rightarrow 3\ N_2 + 6\ H_2O} \quad \mathbf{(2)}$$

To avoid

$$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O \quad (3)$$

With urea:

$$2\ NO + CO(NH_2)_2 + 0.5\ O_2 \rightarrow \mathbf{2\ N_2 + CO_2 + 2\ H_2O}$$

Electron Beam Technique

In Poland – some figures:

2 boilers: 2 x 65 MWe (100 MWth)
G = 270 000 Nm^3/h
4 accelerators: 4 x 700 keV / 260 kW beam power each
In operation > 2500 h
X 1000 tons of by-products = NPK fertilizer

Adsorption (charbon actif, tamis moléculaires)

Example 2: reduction of NOx in flue gases of a pickling unit by addition of H_2O_2