Stationary Emissions and Control

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Representative stationary sources


Coal-fired P/Ps


Oil-fired P/Ps


Natural gas-fired P/Ps

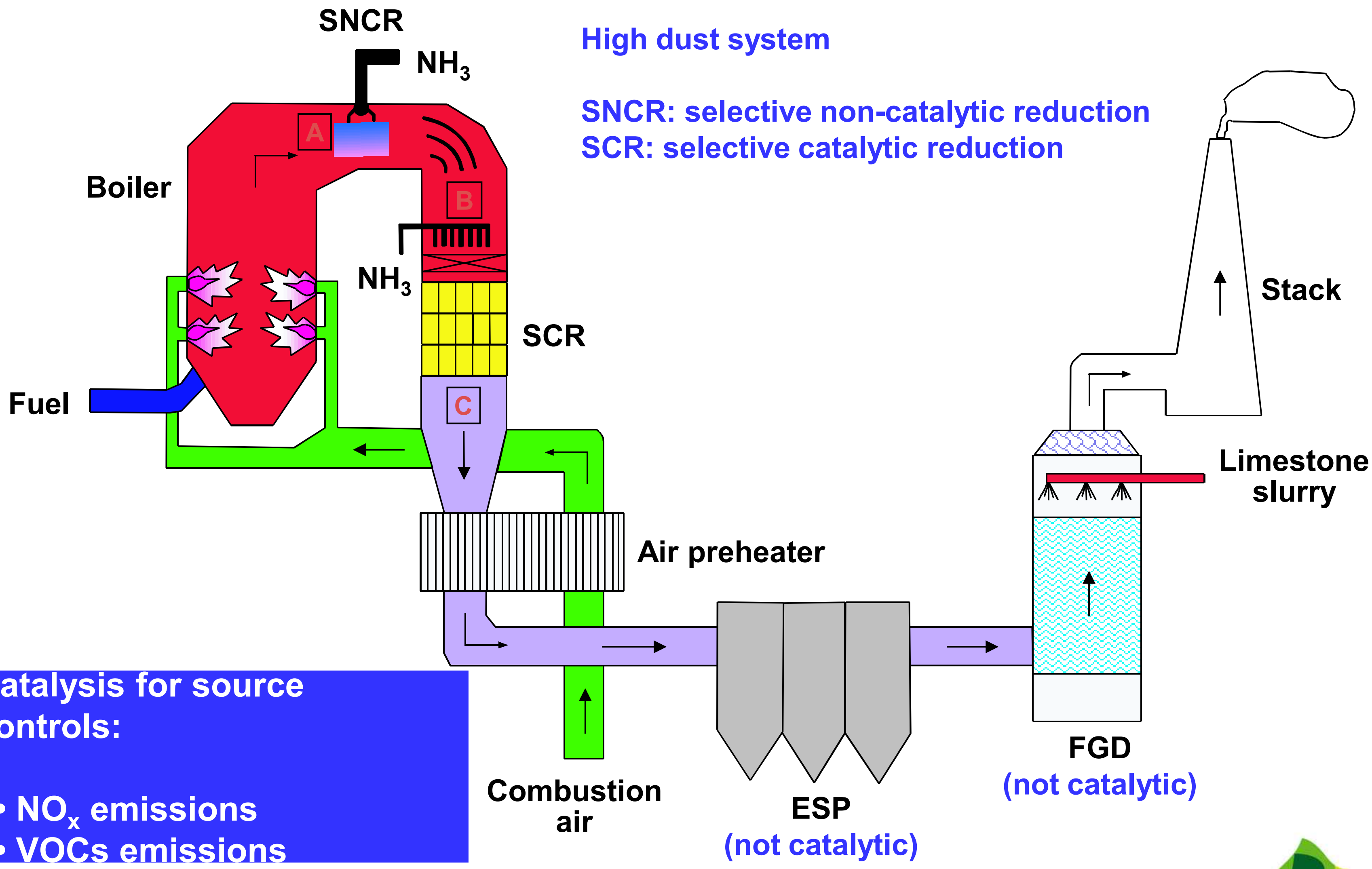

Steel making plants


Chemical plants


Cement plants


Waste incinerators

An example of stationary source controls



High dust system

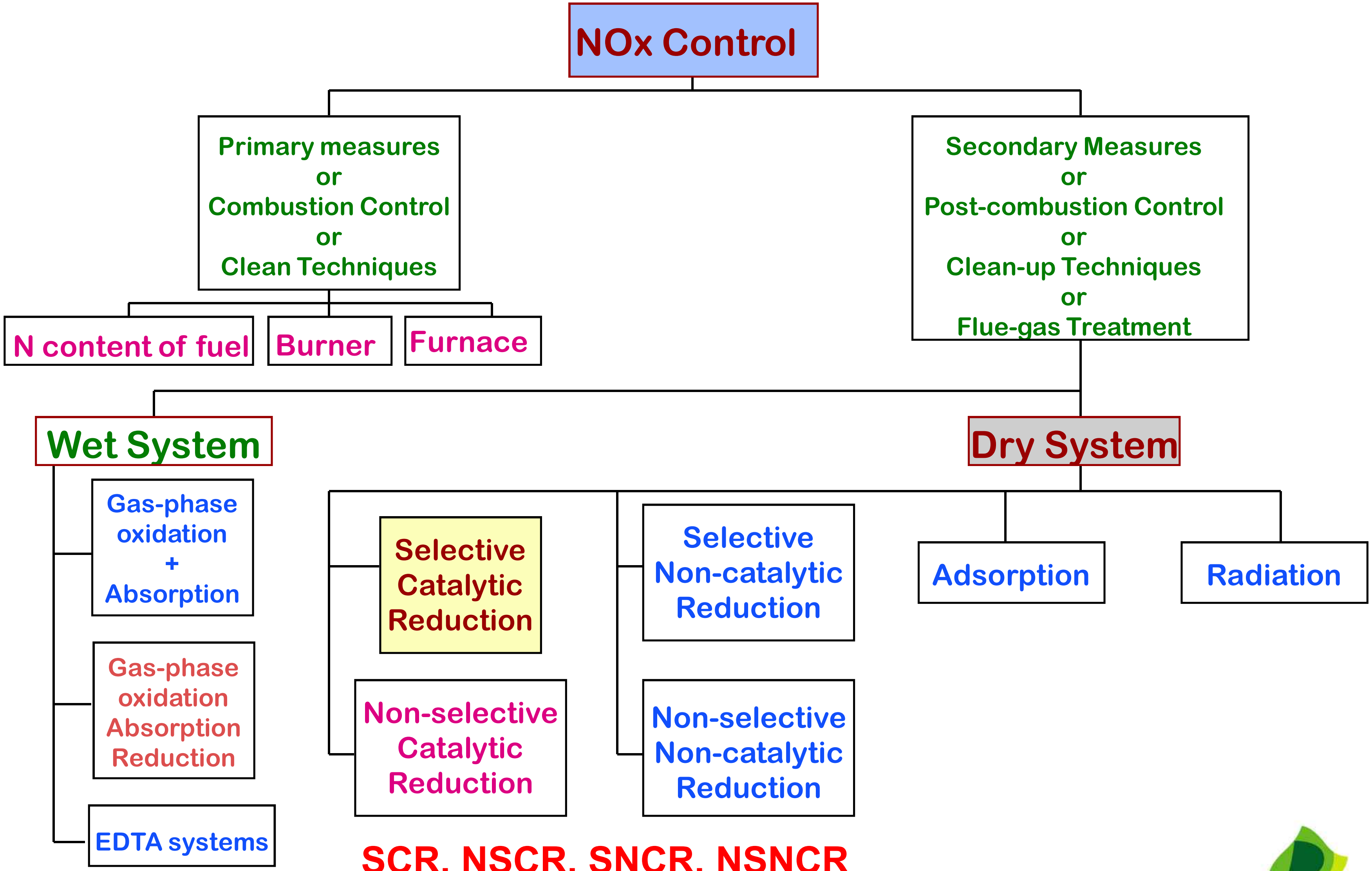
SNCR: selective non-catalytic reduction
SCR: selective catalytic reduction

Catalysis for source controls:

- NO_x emissions
- VOCs emissions

Introduction to NO_x Emissions and Control

NOx control technologies



SCR, NSCR, SNCR, NSNCR

Mechanism forming NOx in fuels combustion

Nitrogen oxides	Regions of formation	Mechanism/ Reaction	Dependent Mainly on
Thermal NO_x (Zeldovich NO_x)	• Flames • After burner • All kinds of fuel	• With an excess oxygen: $O + N_2 = NO + N$ $N + O_2 = NO + O$ • Under fuel-rich conditions: $N + OH = NO + H$	• Concentration of O atoms from O_2 • Residence time ($T_{flame} > 1300^oC$)
Prompt NO_x (Fenimore NO_x)	• Flames • All kinds of fuel	• $CN + H_2 = HCN + H$ • $CN + H_2O = HCN + OH$ • $CH + N_2 = HCN + N$	• Concentration of O atoms from O_2 • O_2 concentration fed
Fuel NO_x	• Flames • Coals, heavy oils	• *via* CN-compounds	• N concentration • Residence time

Combustion control measures:

- Peak **TEMPERATUREs** at flame regions
- Residence **TIME** at the peak temperatures
- Feed air **TURBULANCE** associated with O_2 conc.

DeNOx SCR technologies

- **NH_3-SCR**

$$NO_x + NH_3 \xrightarrow[Catalyst,O_2]{} N_2 + H_2O$$

- **Urea-SCR**

$$NO_x + NH_2CONH_2 \xrightarrow[Catalyst,O_2]{} N_2 + H_2O + CO_2$$

Thermal decomposition: $NH_2CONH_2 \longrightarrow NH_3 + HNCO$

Hydrolysis: $HNCO + H_2O \longrightarrow NH_3 + CO_2$

- **HC-SCR**

$$NO_x + C_nH_m \xrightarrow[Catalyst,O_2]{} N_2 + H_2O + CO_2$$

NH_3-SCR deNOx processes

- ☞ Commercially-proven process
  (first installed in the late 1970s, Japan)
- ☞ High $DeNO_x$ efficiency even in commercially-available scales
- ☞ Relatively expensive
- ☞ NH_3 slip
- ☞ Highly corrosive
- ☞ Relatively delicate feed system of NH_3
- ☞ Formation of ammonium salts

Urea-SCR deNOx processes

- ☞ High $DeNO_x$ activity
- ☞ Non-toxic solid-phase reductant
- ☞ Easier handling, transportation and storage
- ☞ Applicable to stationary and mobile sources (Power plants and ships)
- ☞ Diesel engine-equipped heavy duty vehicles
- ☞ Difficulty in homogeneously feeding urea
- ☞ NH_3 slip
- ☞ Infrastructure of urea supply

HC-SCR deNOx processes

☞ New emerging technology

☞ Applicable to stationary and mobile emissions

(Alternative to conventional NH_3-SCR and TWC)

☞ DeNOx reaction w/o an additional reductant

☞ Lean-burn gasoline engine (AFR = 18 ~ 22)
Gas turbine
Diesel engine

☞ Relatively low DeNOx performances

☞ Precursors for urban photochemical smog reaction

NH_3-SCR $DeNO_x$ Technology

NH_3-SCR DeNOx reactions

☞ NO reduction reactions

$$6NO + 4NH_3 \longrightarrow 5N_2 + 6H_2O$$ (1st priority)

$$6NO_2 + 8NH_3 \longrightarrow 7N_2 + 12H_2O$$ (Undesired)

$$4NO + 4NH_3 + O_2 \longrightarrow 4N_2 + 6H_2O$$ (2nd priority)

☞ NH_3 oxidation reactions

$$4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$$

$$4NH_3 + 4O_2 \longrightarrow 2N_2 + 6H_2O$$

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$

$$4NH_3 + 7O_2 \longrightarrow 4NO_2 + 6H_2O$$

☞ Side reactions

$$2NH_3 + H_2O + 2NO_2 \longrightarrow NH_4NO_3 + NH_4NO_2$$

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

$$2NH_3 + SO_3 + H_2O \longrightarrow (NH_4)_2SO_4$$

Representative commercial deNOx SCR catalysts

- Noble metals-based catalysts

  Pt, Ru, etc

- V_2O_5/TiO_2-based catalysts (first patented by Engelhard Corp., and first commercialized by IHI Corp., Japan)

  Additives: WO_3, MoO_3, BaO, CaO, etc

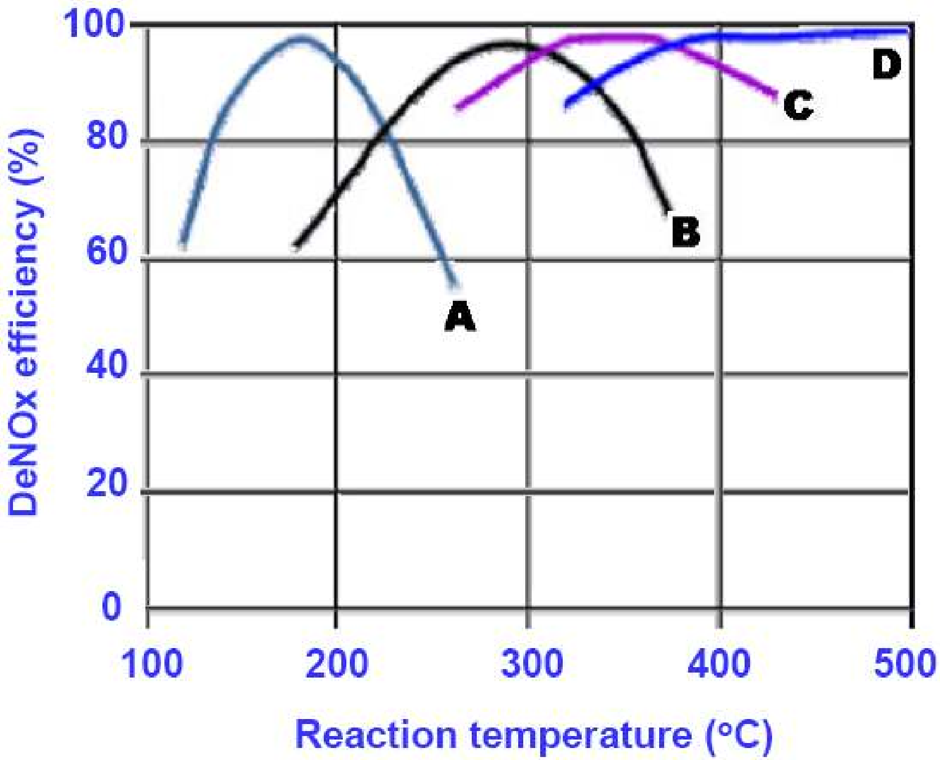
- Cu- and Fe-zeolite catalysts (developed in USA and FRG)

  Prevention of an immediate increase in NH_3 slip when being overdosed

- Fe_2O_3-based catalysts (developed in FRG)

  Iron oxide particles with thin crystalline surface cover of iron phosphate; can be mixed with chromic oxide; can be melted along with normal iron at a steel plant

Typical behaviors in activity vs. temperature



Criteria that determine which types of catalyst should be used:

- **Flue gas temperatures**
- **NO_x reduction efficiencies required**
- **Acceptable NH_3 slip**
- **Permissible oxidation of SO_2**
- **Concentration of pollutants in the inlet flue gases**
- **Homogeneity of a flue gas flow**

A: Pt-based catalysts

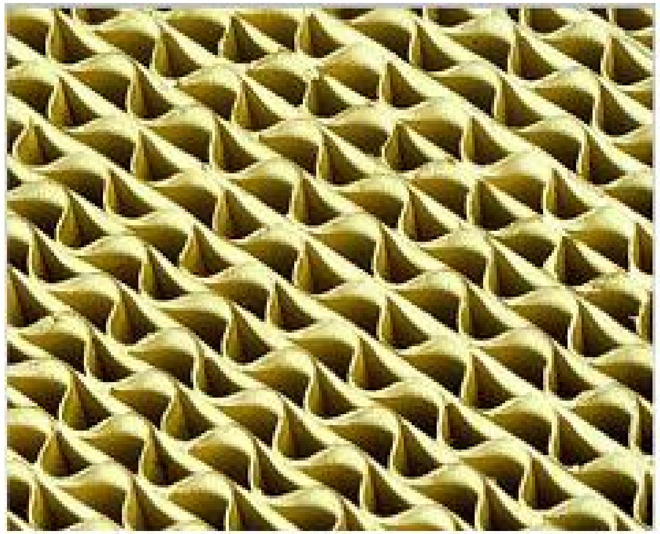
B: Modified Pt-based catalysts

C: V_2O_5/TiO_2-based catalysts

D: Metal-exchanged zeolites catalysts

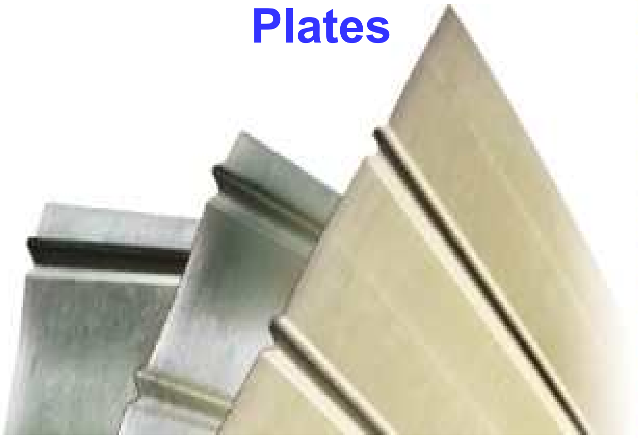
Common shapes of deNOx SCR catalysts

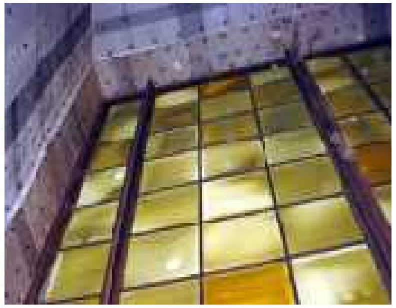
Corrugates



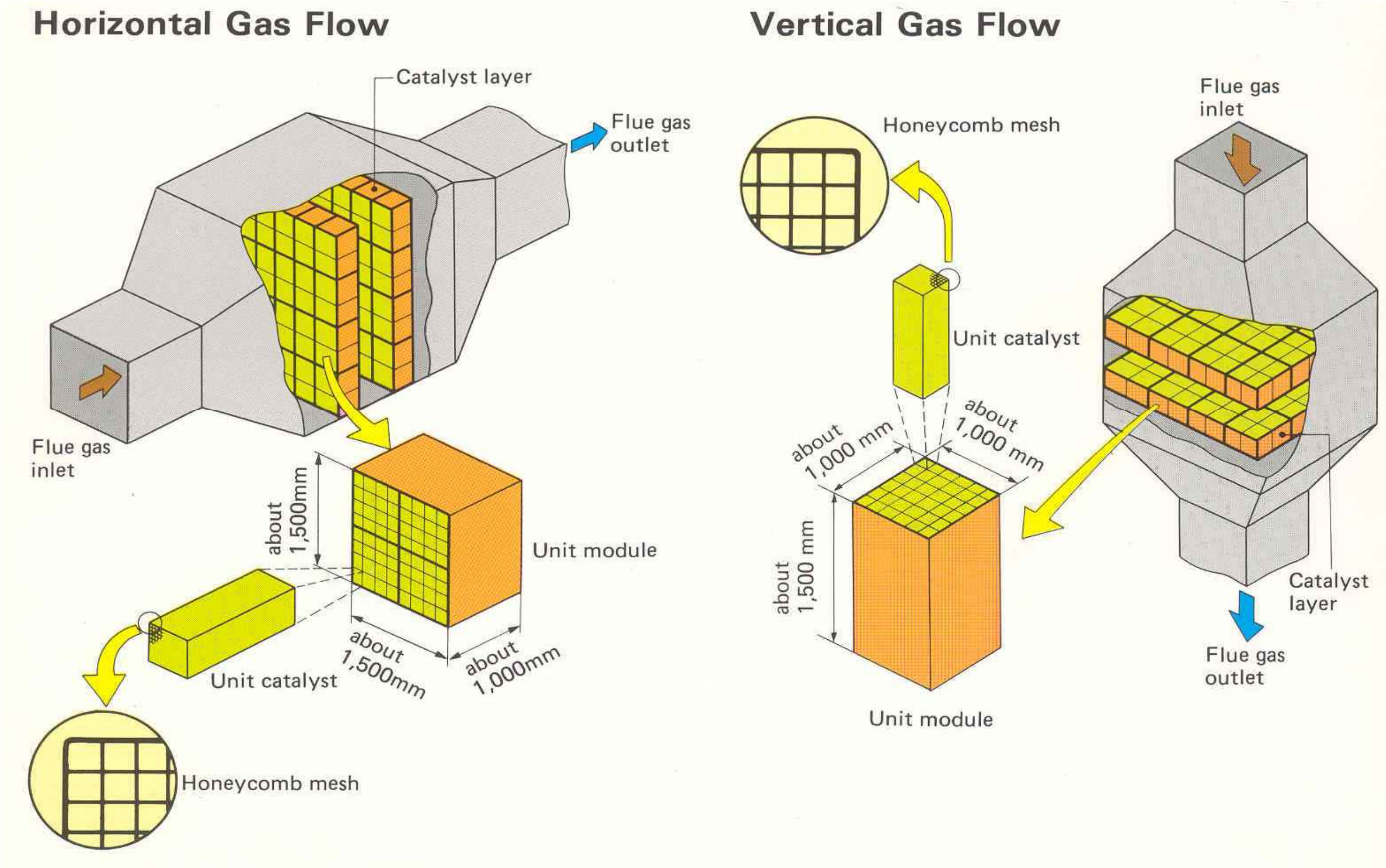
Honeycombs

Plates





Flue gas flow designs in deNOx SCR processes



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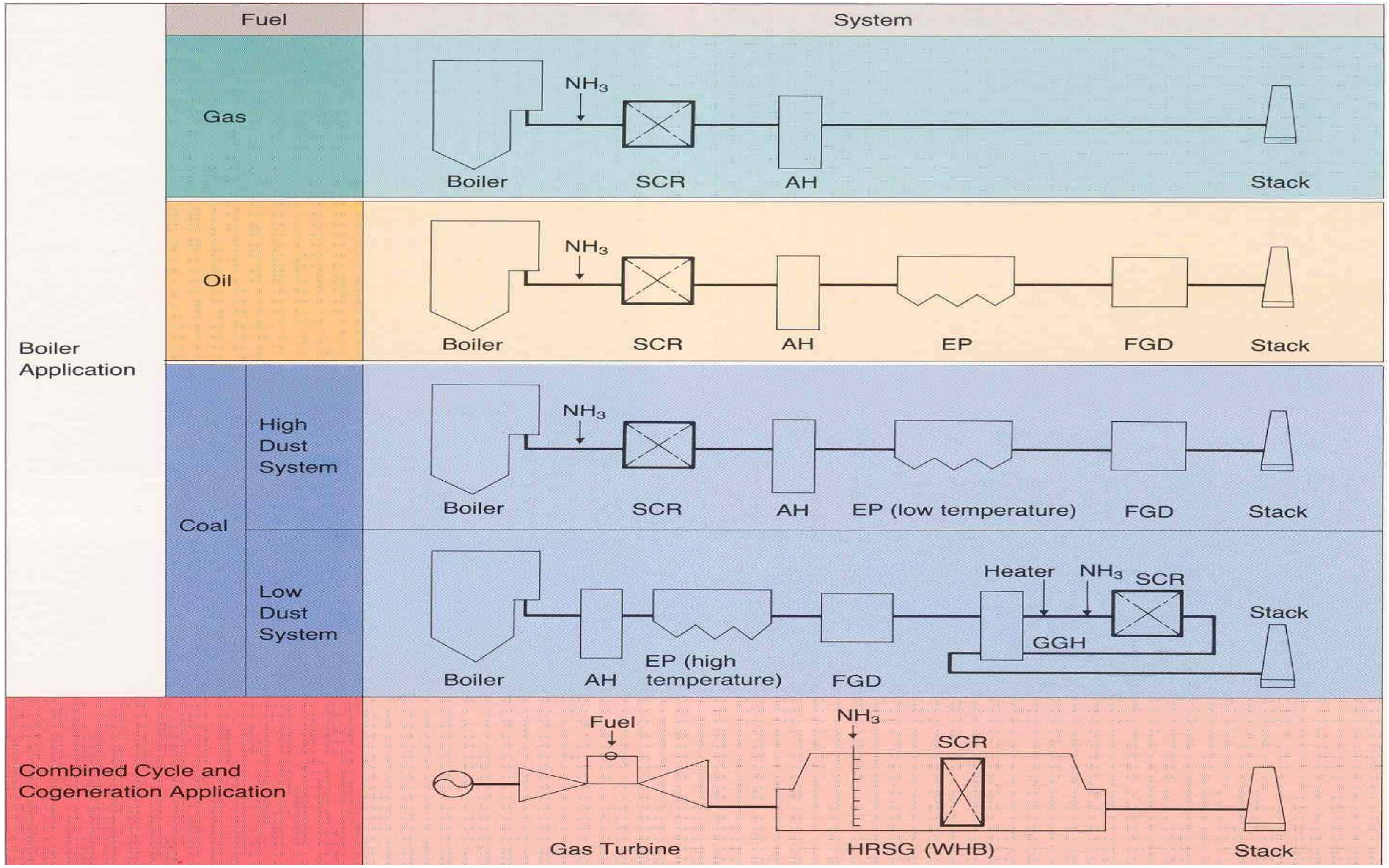
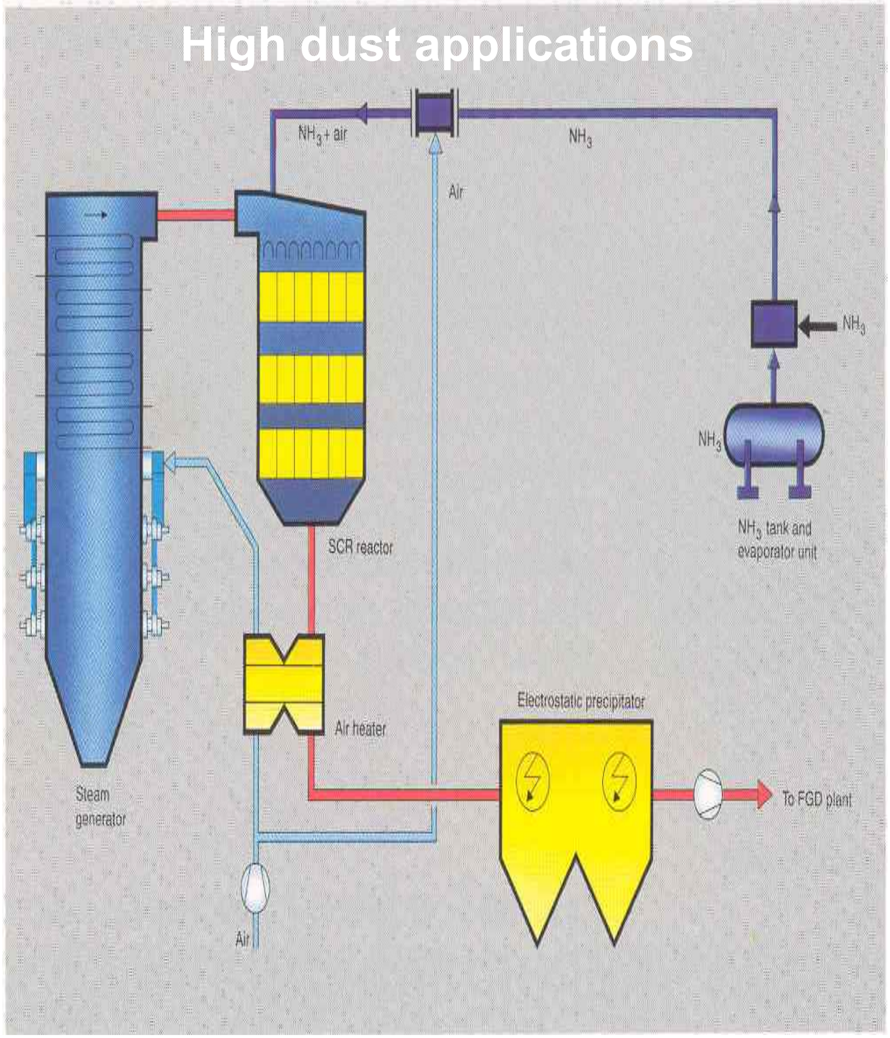
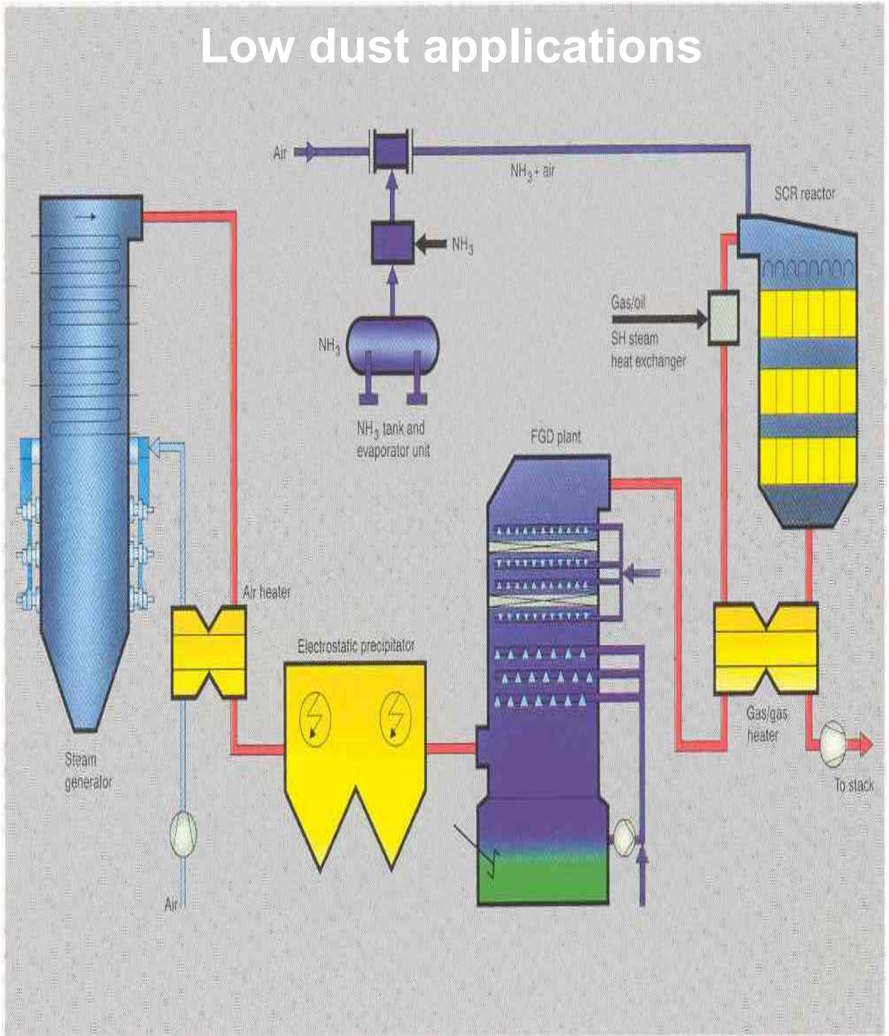
DeNOx process configuration



High dust and tail-gas systems



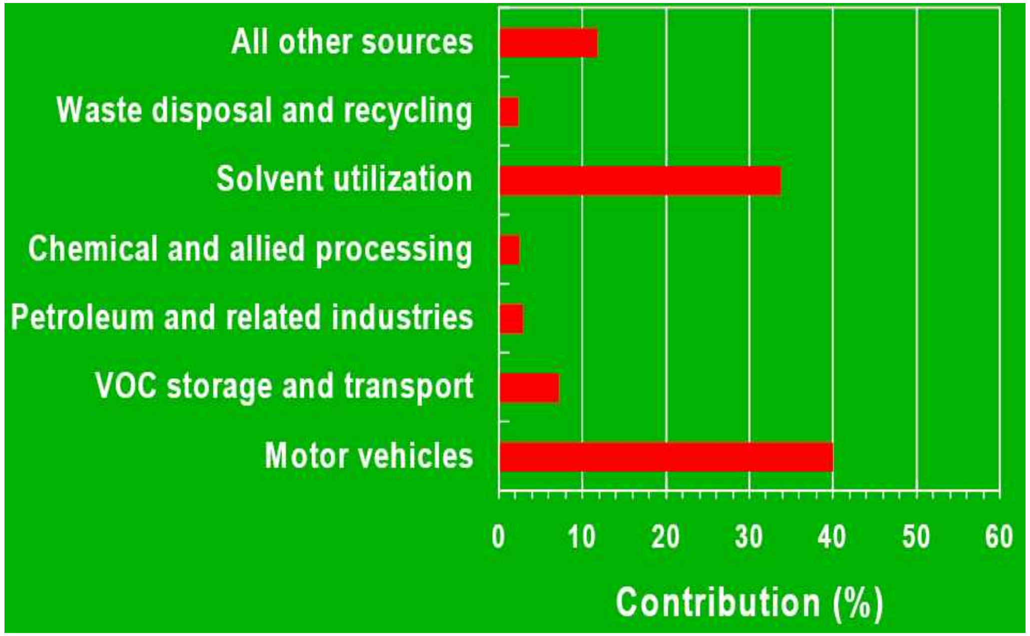


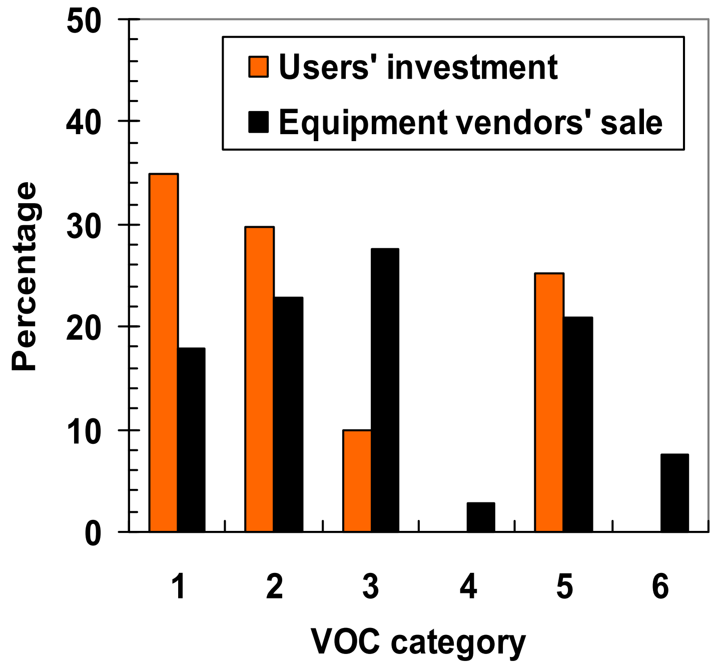
Stationary
VOCs Emissions and Control

Representative deVOCs applications

- Solvent utilization facilities
- Degreasing and solvent washing processes
- Can, paper and fabric coatings chemicals
- Manufacture of organic chemicals (cumene, caprolactam, maleic anhydride, etc)
- Plywood manufacturing
- Tire and rubber processing and production
- Fish meal processing
- Offset printing
- Evaporants from waste water treatment plants
- Volatiles from urine
- Automotive exhaust
- Evaporants from oil stations and storages
- Asphalt production and blowing
- Miscellaneous

Estimates of VOCs emissions and their categories





- **Vehicles emissions controls: TWCs and DOCs**
- **Remaining sources controls:**

  - Recovery and reuse as a feedstock

  - Use of 2nd fuels

  - Suitable reduction processes

1: Aliphatic HCs

2: Aromatic HCs

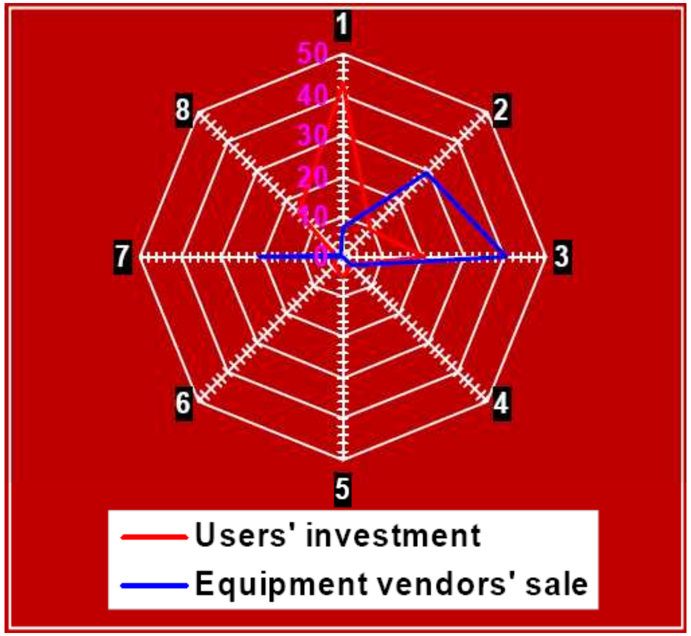
3: Halogenated HCs

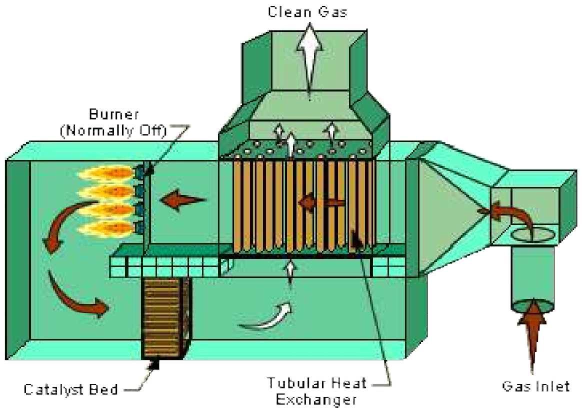
4: Ketons and aldehydes

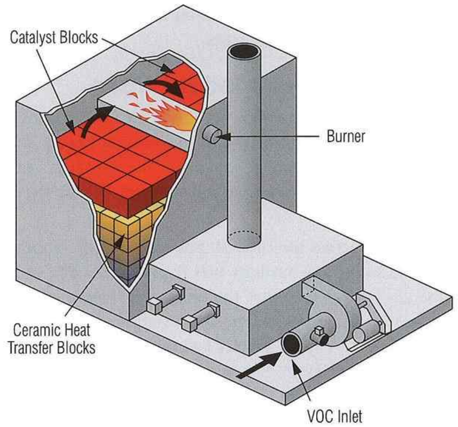
5: Alcohols, ethers and phenols

6: Others

DeVOCs technologies and system designs



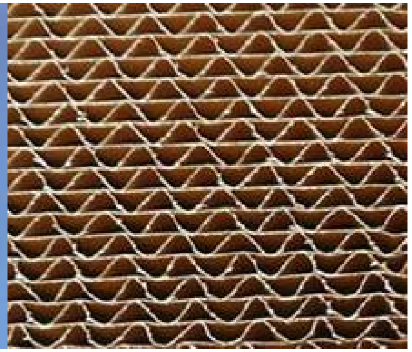




1: Thermal oxidation
2: Catalytic oxidation
3: Adsorption
4: Absorption
5: Process heaters
6: Flares
7: Biofiltration
8: Others

Representative deVOCs catalysts

- Pt/Al_2O_3 washcoated on honeycombs
- Pd/metal meshs or honeycombs
- Hopcalites (amorphous $CuMn_2O_4$)
- TiO_2-coated monoliths
- Supported and unsupported NiO
- V_2O_5-promoted TiO_2/monoliths
- Multi-components ($TiO_2/V_2O_5/WO_3/SnO_2/Pt$)
- Miscellaneous



Stationary and Mobile N_2O Emissions and Control

Which gases result in global warming

- Primary green house gases (GHGs):

  - Carbon dioxide (CO_2)
  - Nitrous oxide (N_2O)
  - Methane (CH_4)
  - Fluorinated gases, chlorofluorocarbons, particulates, clouds

- All fossil fuels contain carbon and when burned release CO_2 into the atmosphere.

- Combustion of fuels also release emissions of N_2O and CH_4 as well as criteria pollutants.

GHG	Global warming potential (GWP)
CO_2	1
CH_4	21
N_2O	310
HFCs	1,300
PFCs	7,000
SF_6	23,900

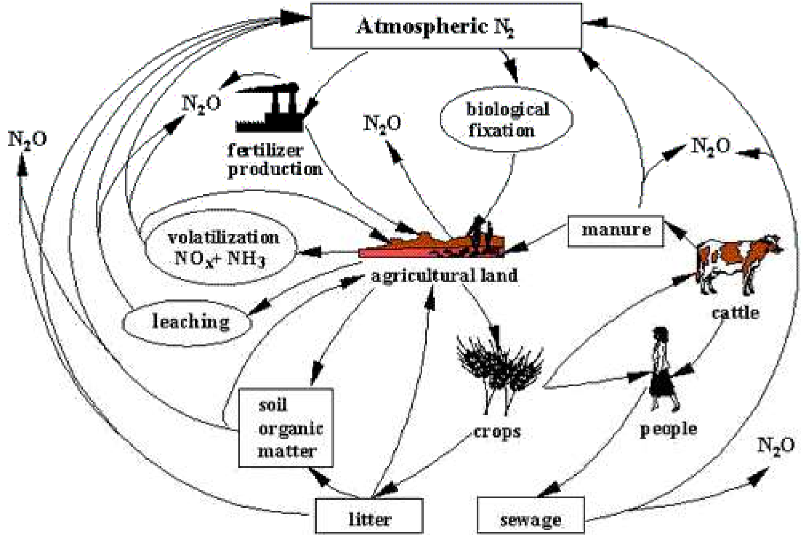
- CO_2, N_2O and CH_4 are the primary greenhouse gas emissions responsible for global warming.

N_2O emission sources

Source	Emissions (Mt/y)	Contribution (%)
Agricultural activity (including fertilizers)	3.5	44.3
Nitric acid production	0.4	5.1
Adipic acid production	0.1	1.3
Fossil –fuels combustion	1.4	17.7
Biomass combustion	1.0	12.7
Sewage treatments	1.5	18.9
Total	7.9	100

Source: Perez-Ramirez et al., Appl. Catal. B, 44 (2003) 117.





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Large anthropogenic N_2O emission sources

Automotives w/ TWCs

FBC plants

SCR processes in P/Ps

Nitric acid plants

Adipic acid plants

Caprolactam production plants

Emission controls of N_2O from adipic acid plants

The most common technology is catalytic decomposition.

. Use of metal-zeolites and metal oxides (*i.e.*, noble metals, precious metals)

. High temperatures (300~620°C)

. High hydrothermal stability in the presence of H_2O

. High stability and activity in the presence of O_2

. Low hydraulic resistance to catalyst bed

Catalyst	Temp. (°C)	DeN_2O efficiency (%)	Developed by
$CuAl_2O_4/Al_2O_3$, Ag-CuO/Al_2O_3, Ag/Al_2O_3	480~550	> 99[a]	BASF
CoO-NiO/ZrO_2	400	98.5[b]	DuPont
CuO/Al_2O_3	620	> 99.5[c]	Asahi
Co-, Fe-zeolites[d]	300~600	-	Air Products

Note. "-": no data or not applicable.

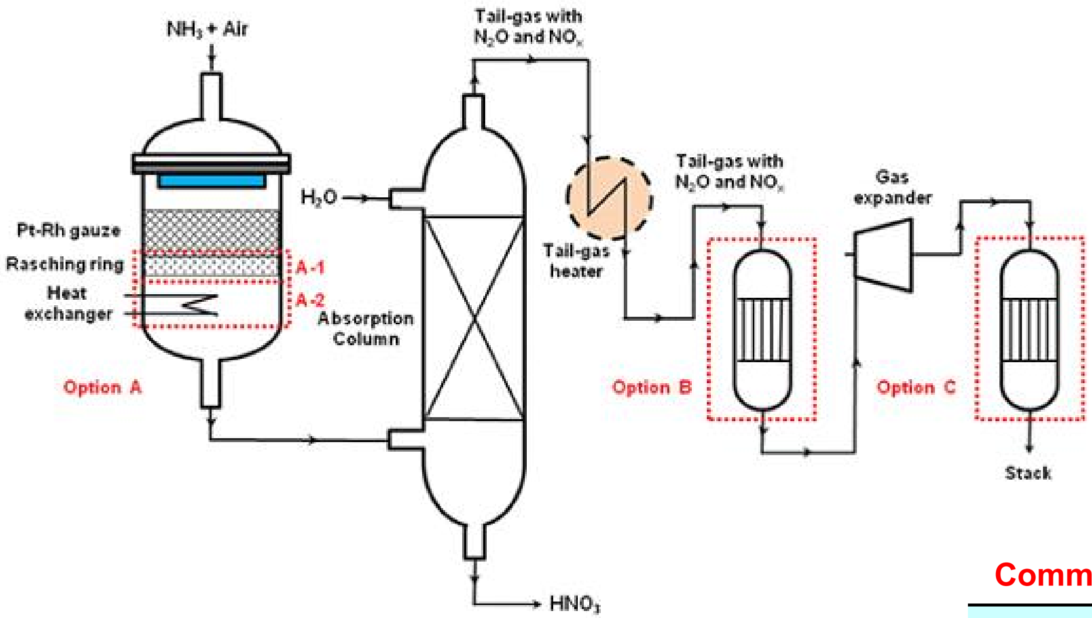
[a] Under an off-gas consisting of 23% N_2O, 17% NO_2, 47% N_2, 7.5% O_2 and 3.0% H_2O.

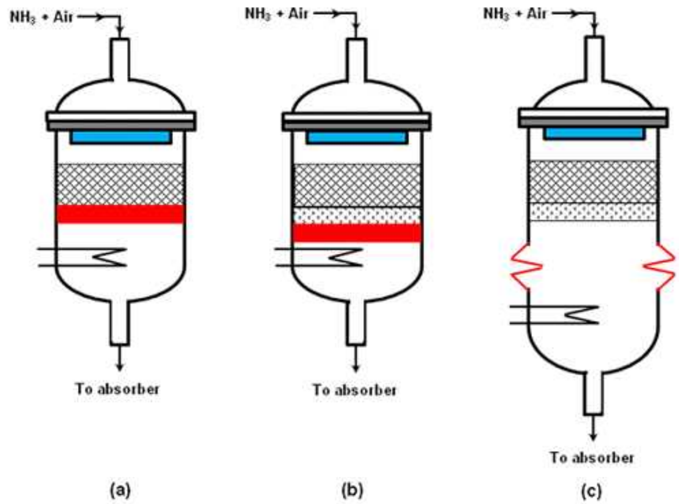
[b] With a flow of 100% N_2O.

[c] In a realistic stream containing 34% N_2O.

[d] With small amounts (0.2~0.6%) of precious metals to lower light-off temperatures.

Emission controls of N_2O from nitric acid plants





Stream	N_2O (ppm)	NO (ppm)	O_2 (%)	H_2O (%)
Process-gas	1.5~2.5[a]	95~97[a]	-	-
Tail-gas	300~3,500	100~3,500[b]	1~4	0.25~3

Note. "-": no data or not applicable; NO_x: NO + NO_2.

[a] In %.

[b] As of NO_x with NO_2/NO ratios near 1.

Commercial decomposition catalysts for Option A-1

Catalyst	Temp. (°C)	Commercialized by
CuO/Al_2O_3	800~950	BASF
Co_2AlO_4/CeO_2	800~950	Yara International
$La_{0.8}Ce_{0.2}CoO_3$	800~950	Johnson Matthey
Co_3O_4/CeO_2	890	Norsk Hydro Agri
Supported Rh, Pd	800~950	Heraeus

Emission controls of N_2O from nitric acid plants

Commercial deN_2O catalysis for Option B

Technology	Catalyst	DeN_2O (%)	Requirements and problems	Commercialized by
Decomposition	Fe-zeolites	> 80	. Medium temperatures (430~500°C) . Catalysts stability at such temperatures	Uhde[a] and Sud Chemie
NSCR	Pd/Al_2O_3	> 70	. Reducing agents, representatively CH_4 . High temperatures (450~650°C) . Large CO_2 and CO emissions . Catalysts stability at such temperatures . Exotic materials for a gas expander . High energy and maintenance costs	CRI[b]
SCR	Fe-zeolites	~40	. Medium temperatures (390~450°C) . Reducing agents such as NH_3, CH_4, etc . CO_2, CO and unburned hydrocarbons emissions	Uhde[a] and Sud Chemie

[a] In the ThyssenKrupp Group.

[b] In the CRI/Criterion that is an affiliate of Royal Dutch Shell Group.

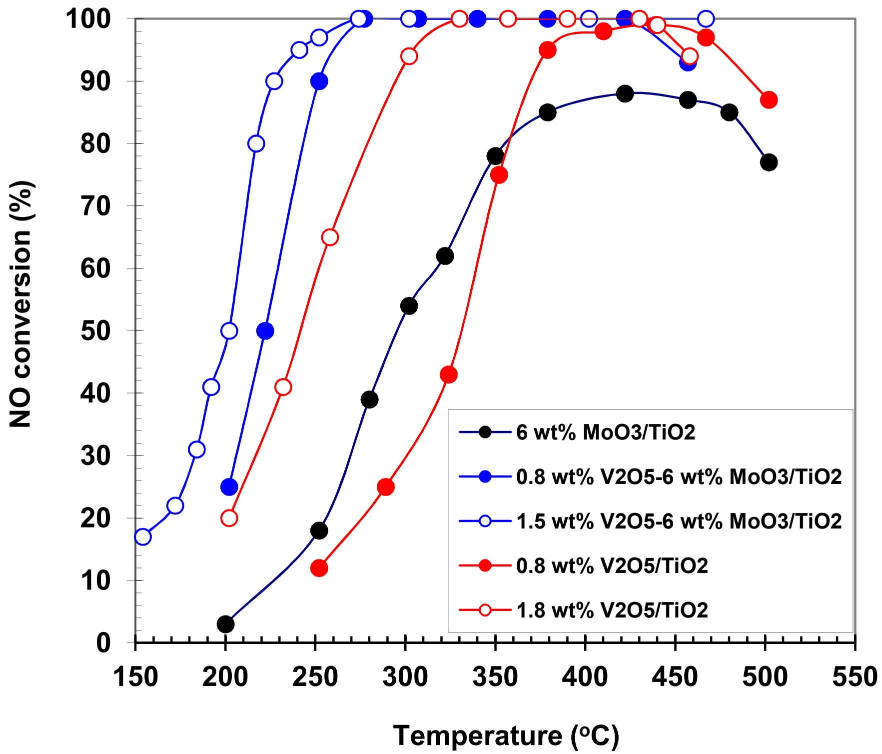
N_2O emissions from SCR processes

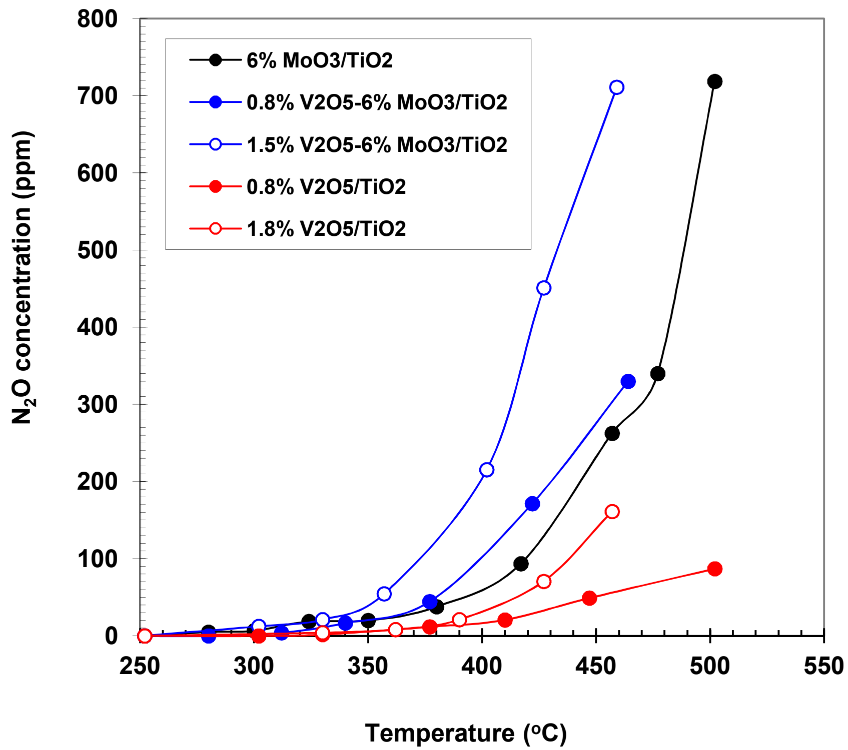
Emission source	Concentration (ppm)
$DeNO_x$ processes	
NH_3 (or urea)-SCR	20 ~ 65
NH_3 (or urea)-SNCR	2 ~ 250
Coal combustion boilers	
Pulverized coal (PC)	0.5 ~ 5
Fluidized bed combustion (FBC)	20 ~ 200
Natural gas combustion boilers	< 2
Diesel combustion boilers	0 ~ 5

Source: Perez-Ramirez et al., Appl. Catal. B, 44 (2003) 117; Gutierrez et al., Waste Manage. Res., 23 (2005) 133; Madia et al., Appl. Catal. B, 39 (2002) 181; Sjovall et al., Appl. Catal. B, 64 (2006) 180.

N_2O formation on V_2O_5/TiO_2-based catalysts

- **Reaction conditions: [NO] = 800 ppm; [NH_3] = 800 ppm; [O_2] = 0.9%.**





Source: Lietti et al., J. Catal., 187 (1999) 419.

- $8NO_2 + 6NH_3 \rightarrow 7N_2O + 9H_2O$
- $4NO_2 + 4NH_3 + O_2 \rightarrow 4N_2O + 6H_2O$
- $8NO + 2NH_3 \rightarrow 5N_2O + 3H_2O$
- $4NO + 4NH_3 + 3O_2 \rightarrow 4N_2O + 6H_2O$
- $2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O$