THERMAL AND CATALYTIC CONVERSION - NOx

General principles

- Chemical conversion of pollutants **at high temperature** in products with lesser environmental impact

- Typical applications
  - NO_x reduction to N_2 (combustion activities)
  - VOC oxidation (combustion) to CO_2 and H_2O (industrial gaseous streams)

- Process configuration
  - **thermal conversion** at higher T levels (750°C – 1200°C), with or without heat recovery
  - **catalytic conversion** at low T levels (300°C – 500°C)

General principles

- **Process alternatives**
  - selective reduction to atmospheric nitrogen through thermal or catalytic systems
  - both processes require proper additions of reducing reagents: ammonia or urea

- Selective Non Catalytic Reduction: **SNCR**
  - high temperature conversion: addition of reactant directly in combustion chamber or before heat recovery section
  - reactions of interest

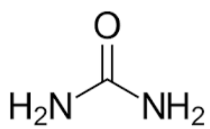
- Selective Catalytic Reduction: **SCR**
  - The best temperature range is from 300°C to 400°C.
  - Reduction is done in a dedicated tower with a V_2O_5 (vanadium pentoxide) catalyst

NOx reduction: reactions

ammonia

$$4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ \mathbf{N_2} + 6\ H_2O \text{ ("Standard SCR")}$$
$$6\ NO + 4\ NH_3 \rightarrow 5\ \mathbf{N_2} + 6\ H_2O \text{ ("Slow SCR")}$$
$$6\ NO_2 + 8\ NH_3 \rightarrow 7\ \mathbf{N_2} + 12\ H_2O \text{ ("}NO_2\text{ SCR")}$$
$$NO + NO_2 + 2\ NH_3 \rightarrow 2\ \mathbf{N_2} + 3\ H_2O \text{ ("Fast SCR")}$$

Oxidation state of N
II or IV + -III $\rightarrow$ 0



urea

$$2\ CO(NH_2)_2 + 4\ NO + O_2 \rightarrow 2\ CO_2 + 4\ \mathbf{N_2} + 4\ H_2O$$
$$4\ CO(NH_2)_2 + 6\ NO_2 \rightarrow 4\ CO_2 + 7\ \mathbf{N_2} + 8\ H_2O$$

- Ammonia is very soluble in water, but this could be dangerous for volatility.
- The efficiency with urea or ammonia is similar, but urea costs more.
- The industrial production of urea was firstly described by Wohler (1828)

NOx reduction: undesired secondary reactions

$$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$$
$$2\ NH_3 + 2\ NO \rightarrow 2\ N_2 + 2\ H_2O + H_2$$
$$2\ NO + H_2 \rightarrow N_2O + H_2O$$

Nitrous oxide (greenhouse gas)

If HCl is present another undesired reaction can occur:

$$NH_{3\,(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)}$$

Ammonia chloride

The reaction is exotermic. Increase in temperature decreases the equilibrium constant

Prevention to reduce ammonia chloride:

- Low HCl concentration
- High temperature

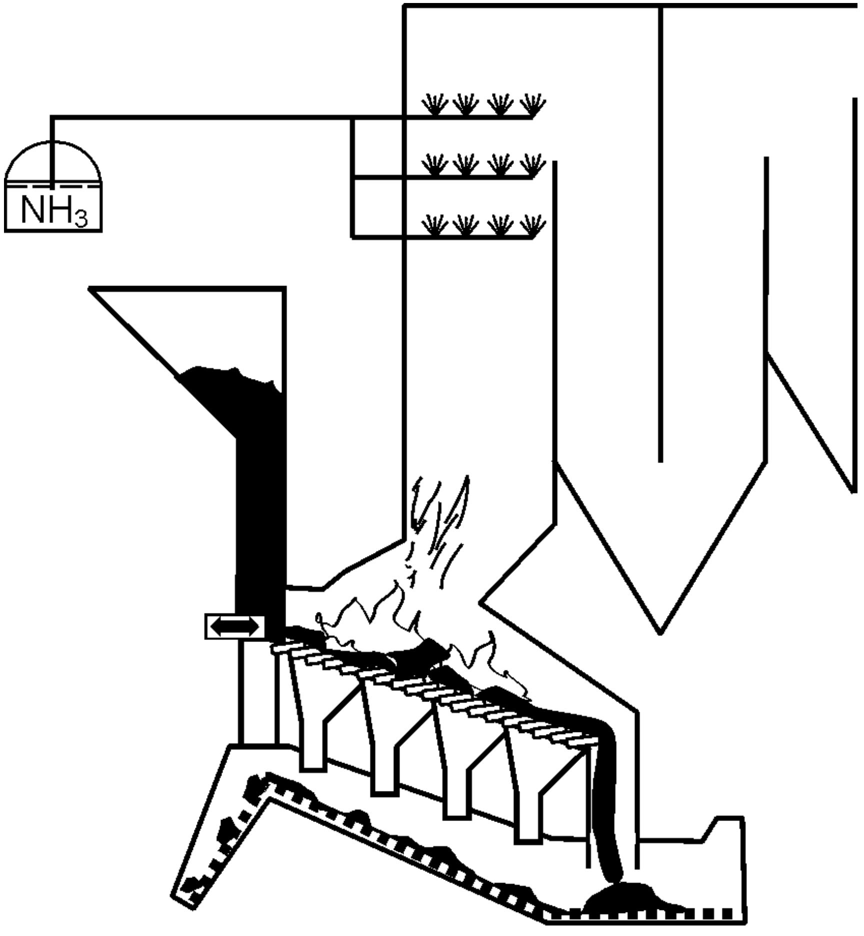
There is a similar problem with sulphur removal. Ammonium sulphate can be formed.

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

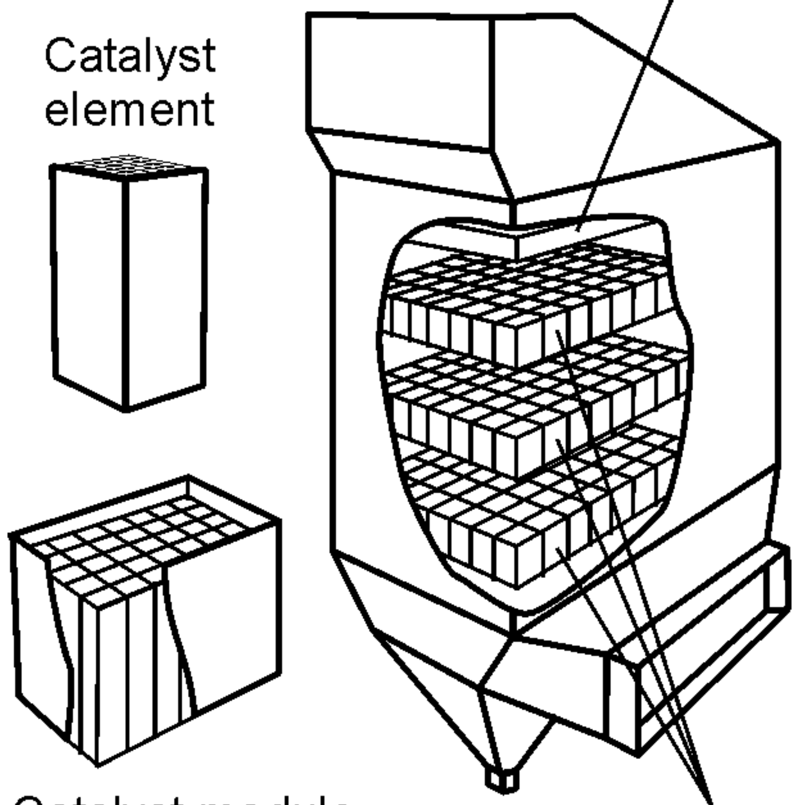
(solid salts deposit formations in the surface of catalyst) → Secondary formation of duts in the atmosphere

NOx reduction: SNCR and SCR

NO_x removal: SNCR

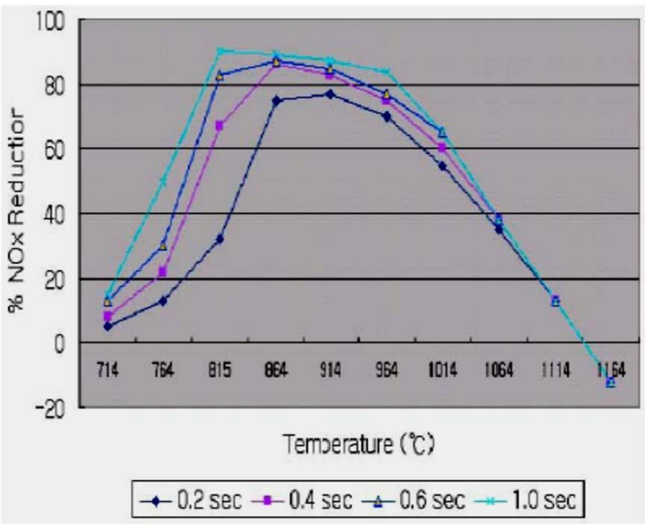


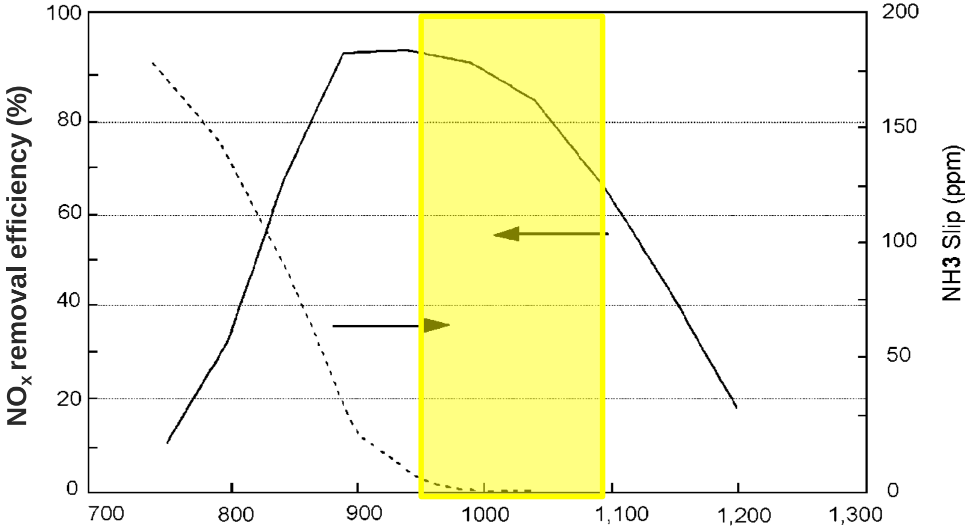
NO_x removal: SCR



SNCR process design and operating parameters

- reaction temperature: optimal range between 950°C - 1100°C
  - lower T: reduced efficiency, higher reactant release (ammonia slip) with potential formation of scaling salts and undesired ammonia stack emissions
  - higher T: increasing intervention of unwanted reactions (direct oxidation of ammonia to NO and N_2) with efficiency loss
- adequate gas residence time in optimum T window



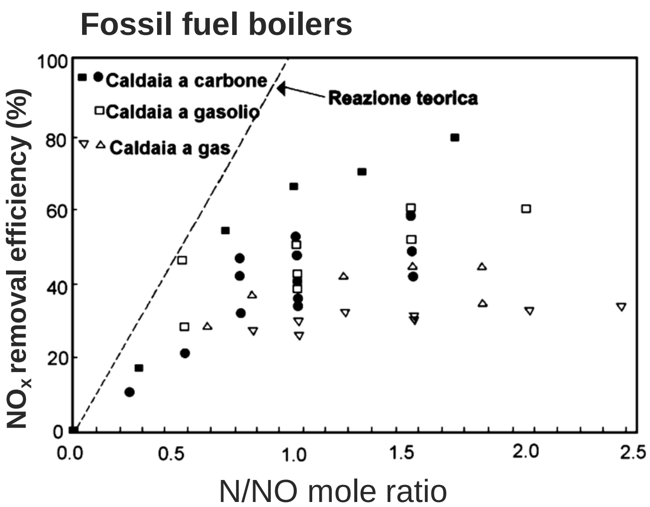


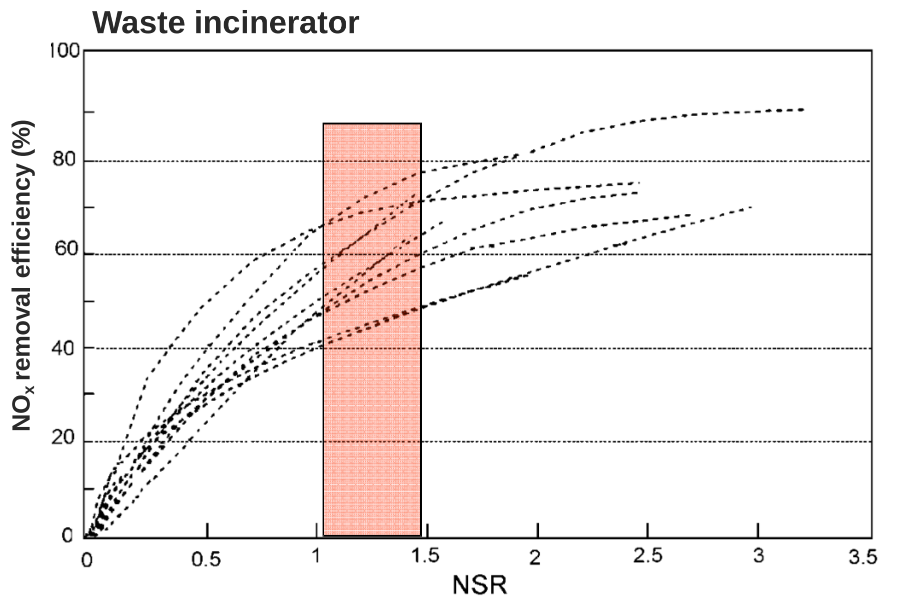
SNCR process design and operating parameters

Excess reactant addition: evaluated through normalized stoichiometric ratio (NSR), defined as

$$NSR = \frac{\left(\text{moles reagent added}/\text{moles } NO_x \text{ input}\right)}{\left(\text{stoichiometric mole ratio reagent}/NO_x\right)}$$

(stoichiometric mole ratio = 1 for ammonia and 0.5 for urea)

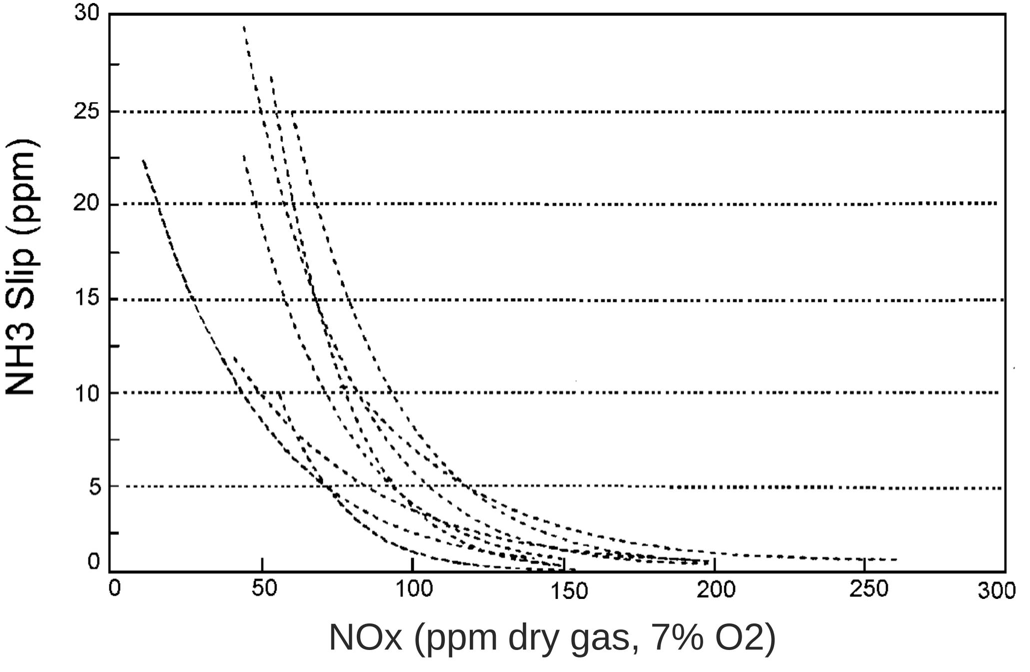




No significant effect of higher excess dosage on removal efficiencies beyond certain values, due to the limiting effect of mixing and residence time

SNCR process design and operating parameters

Ammonia slip: increase with increasing NO_x removal efficiencies (higher NSR required)



NH_3 slip and undesired secondary reactions (salts formation) limit high NSR adoption in SNCR systems for obtaining elevated removal efficiencies

- $NH_3 + HCl \rightarrow NH_4Cl$ (ammonia chloride)
- $2NH_3 + SO_2 + H_2O \rightarrow (NH_4)_2SO_3$ (ammonium sulphite)

SNCR process design and operating parameters

N_2O emissions (Nitrous oxide)

- ammonia: up to 15% NO_x conversion to N_2O
- urea: up to 30% NO_x conversion to N_2O
- expected stack levels: 20-60 mg/m³

WTE urea based SNCR (T = 950 - 1000°C)

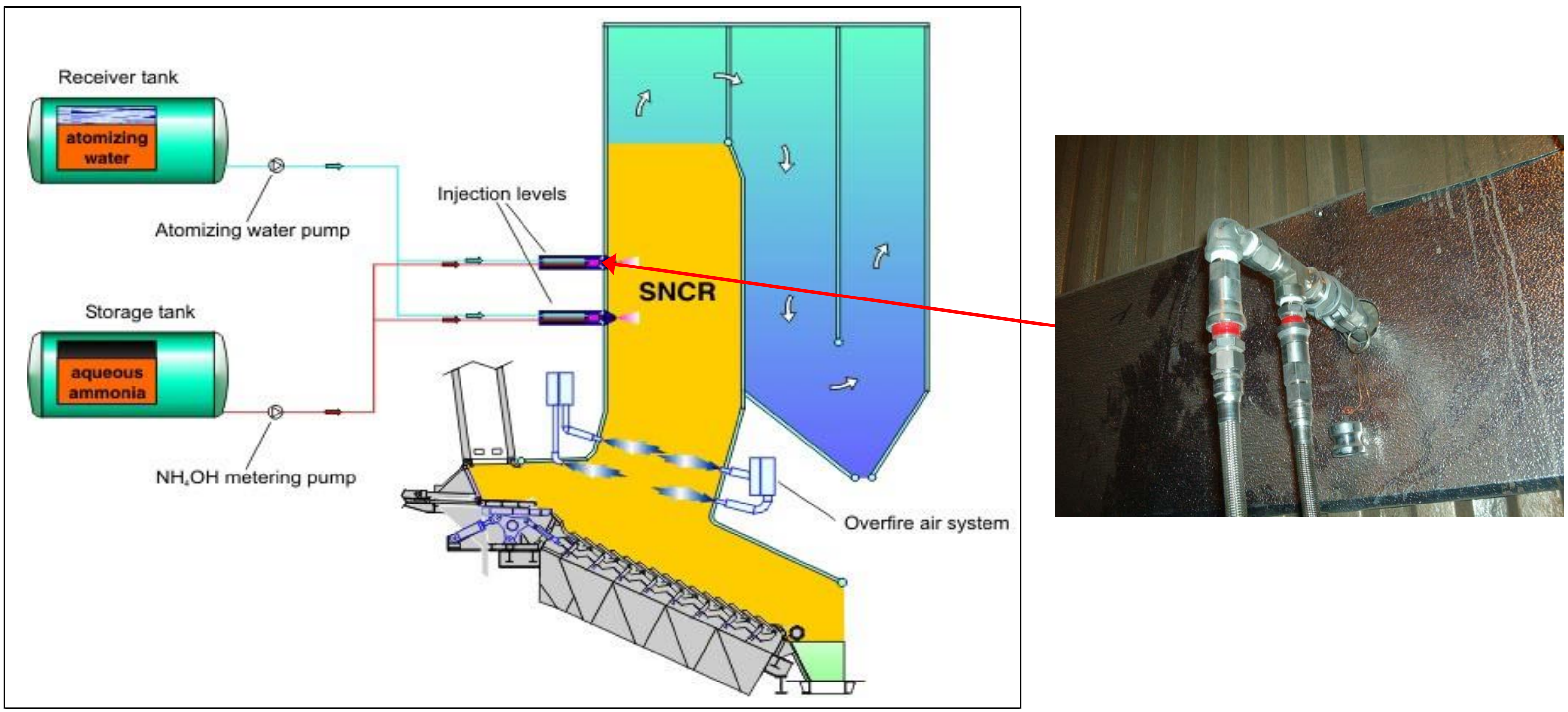
		Line 1	***Line 2***	***Line 3***
Average	*mg/m³ₙ*	16,1	19,2	14,9
Standard deviation	*mg/m³ₙ*	4,48	5,29	3,22
Maximum	*mg/m³ₙ*	25,6	29,6	22,3
Minimum	*mg/m³ₙ*	10,1	12,5	9,1

WTE low T SCR (operating T = 180°C)

		Line 2	***Line 3***
Average	*mg/m³ₙ*	0,9	0,3
Standard deviation	*mg/m³ₙ*	0,16	0,26
Maximum	*mg/m³ₙ*	2,0	1,9
Minimum	*mg/m³ₙ*	0,7	0,1

SNCR system configuration

- reactant storage
- atomization system (water, steam)
- multiple injection level nozzles



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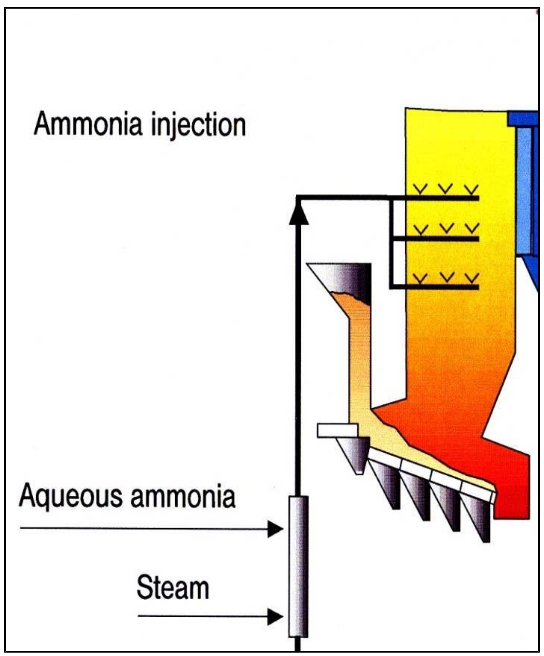
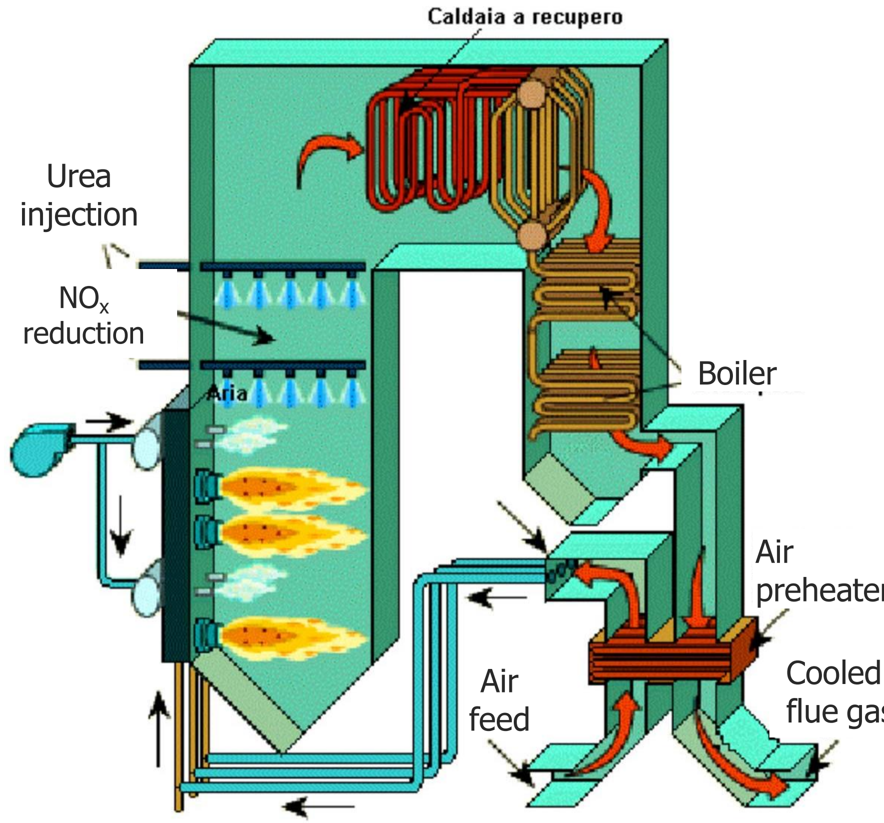


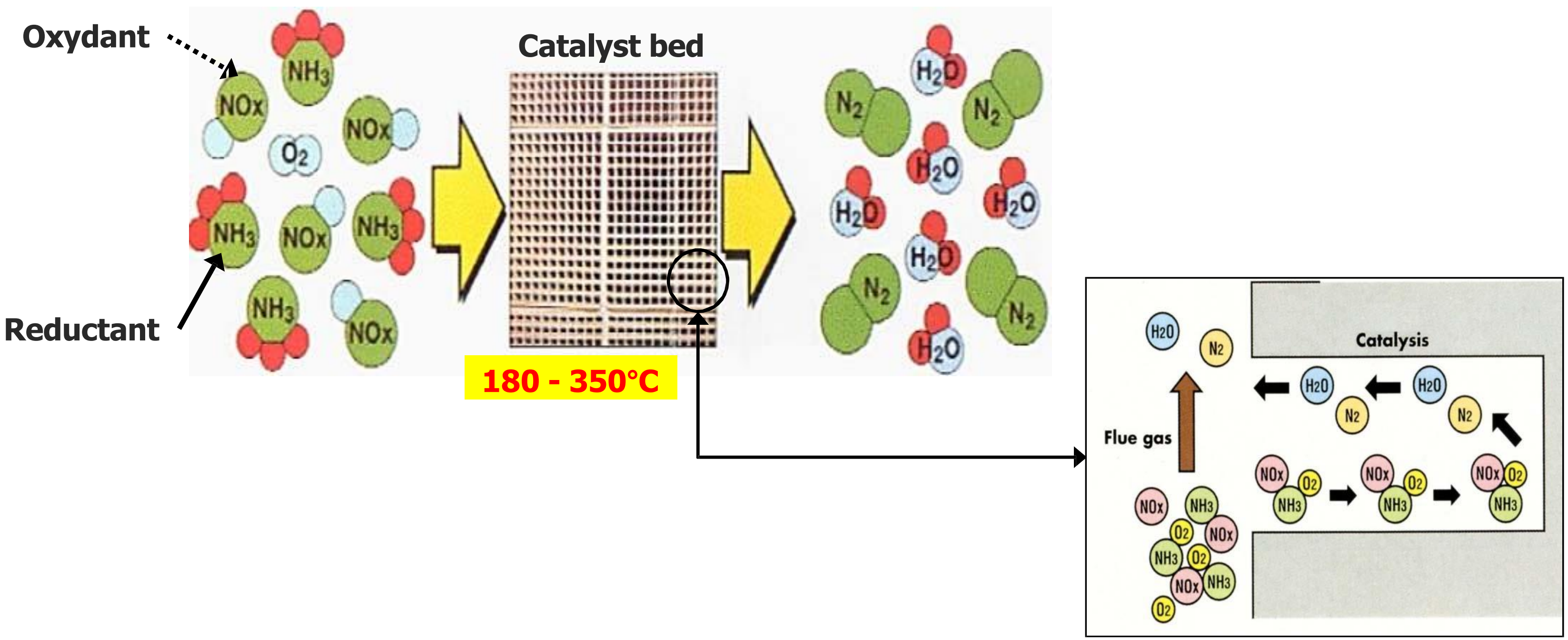


SNCR process main features

- NO_x average conversion efficiencies in the range **35-50%** (upper end until 70%)
- lower complexity: contained capital and operating costs
- available for retrofit and for combined (hybrid) systems with SCR
- significant **ammonia slip** for higher efficiencies (salts deposition downstream, NH_3 emissions significance for secondary fine particulates formation, flyash and solid residues quality)
- **higher reactant dosage** with respect to SCR systems (NH_3/NOx ratio = 1.5-2.5 for SNCR and 1-1,05 for SCR)
- not applicable in gas turbines or engines (residence time /temperature window requirements not available)
- not adequate as BAT for large stationary combustion sources (power plants, waste incinerators)
- **potential significance of N_2O** (nitrous oxide) emissions, particularly for urea feed systems

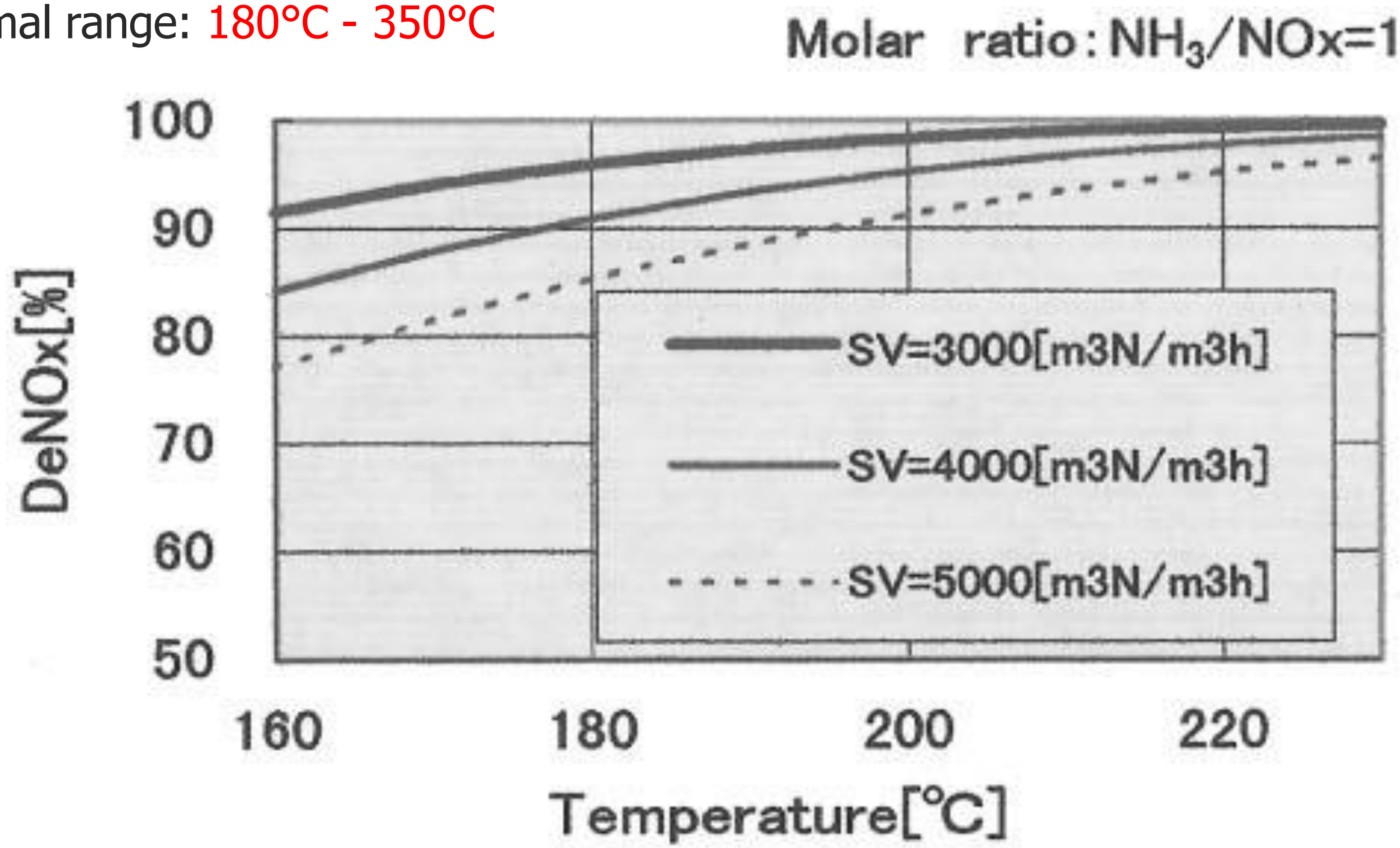
SCR process characteristics

- NO_x reduction to N_2 promoted by a catalyst
- lower T range: 180°C - 350°C
- same sequence of conversion reactions as for SNCR



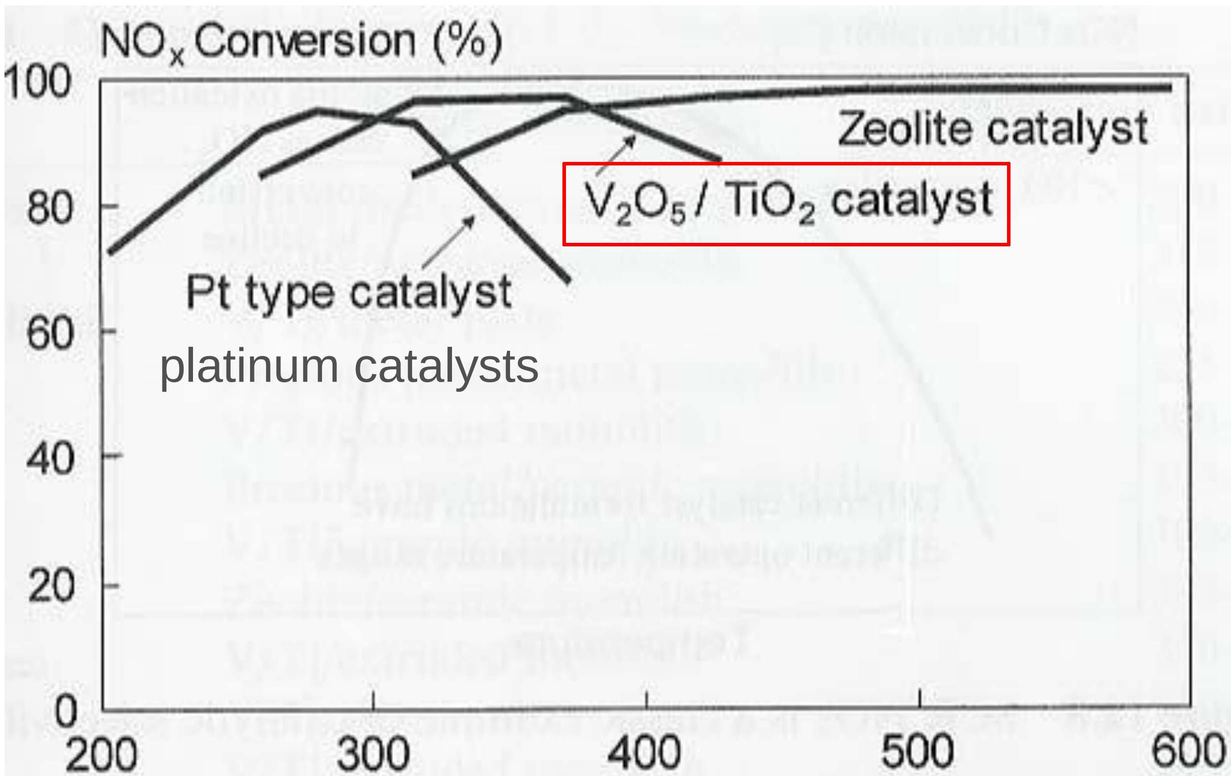
SCR process characteristics

T optimal range: 180°C - 350°C



SCR process characteristics

catalyst active substrates: vanadium supported on titanium dioxide



SCR process characteristics

Temperature: optimal range between 180°C - 350°C

higher T

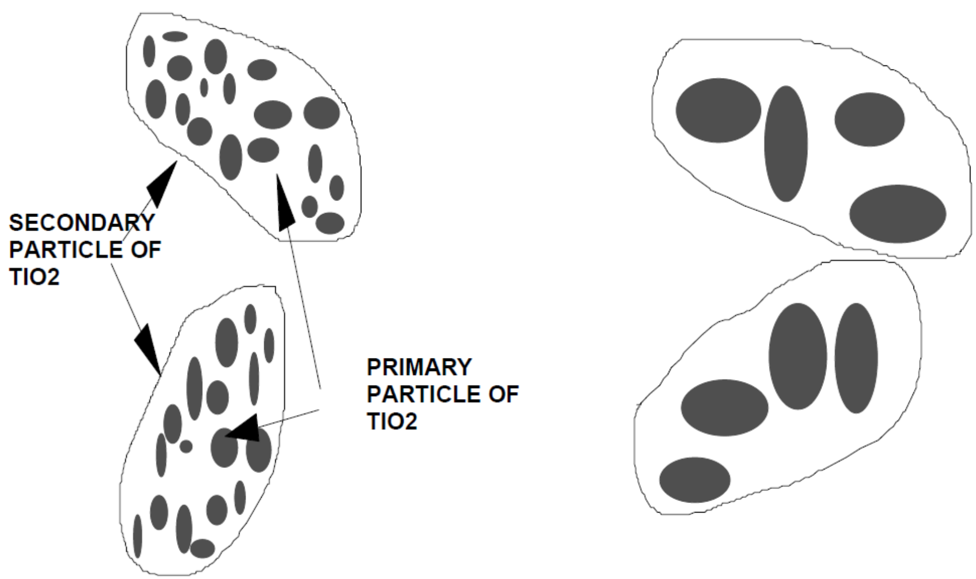
- increasing intervention of unwanted reactions (direct oxidation of ammonia to NO and N_2) with efficiency loss
- potential damage to catalyst by sintering effects

lower T

- high interest for locating catalyst downstream heat recovery and pretreatment systems (cool and clean gas)
- secondary undesired reactions
  $2\ NH_3 + 4\ NO_2 + H_2O \rightarrow NH_4NO_2 + NH_4NO_3$ (ammonium nitrate can cause explosion risk)
  $2NH_3 + SO_3 + H_2O \rightarrow (NH_4)_2SO_4$ (solid salts deposit formations)
- activity reductions by pore blocking
- the minimum operating temperature in SCR DeNOx is determined by the dew point of ammonium salts (ammonium chloride, NH_4Cl, ammonium bisulphate, NH_4HSO_4, ammonium sulphite, $(NH_4)_2SO_3$, and ammonium nitrate, $(NH_4)_2NO_3$). In most cases NH_4HSO_4 has the highest dew point but in waste incineration units with HCl concentrations of several hundred ppm NH_4Cl condensation determines the minimum temperature.

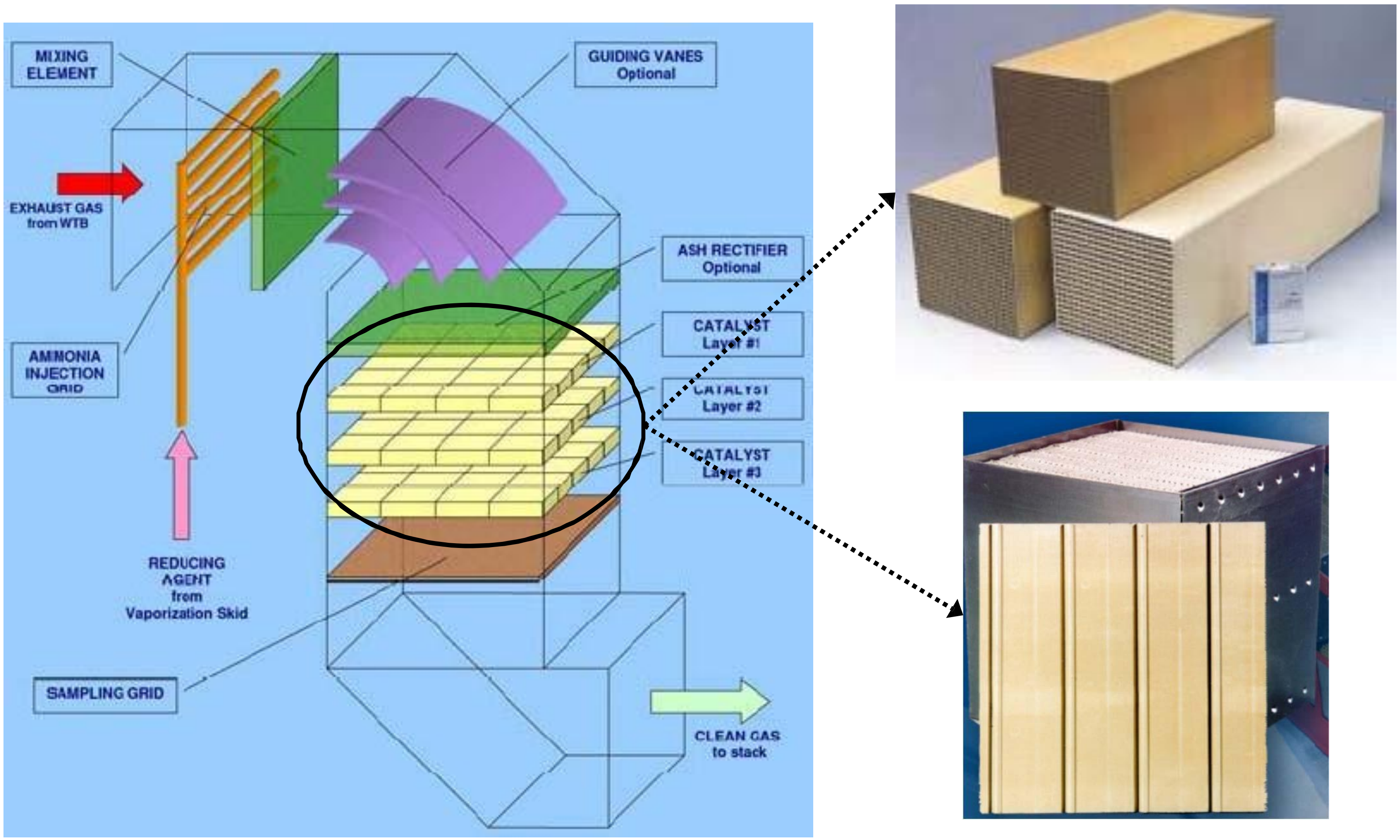
SCR process characteristics: Thermal sintering

Thermal sintering is the growth of primary catalyst particle resulting in a **reduction of catalyst surface area**, which reduces catalyst performance. Figure illustrates this mechanism. Thermal stability is maximized with the corporation of Tungsten in the catalyst formulation. As a result, sintering is negligible at normal SCR operating temperatures.

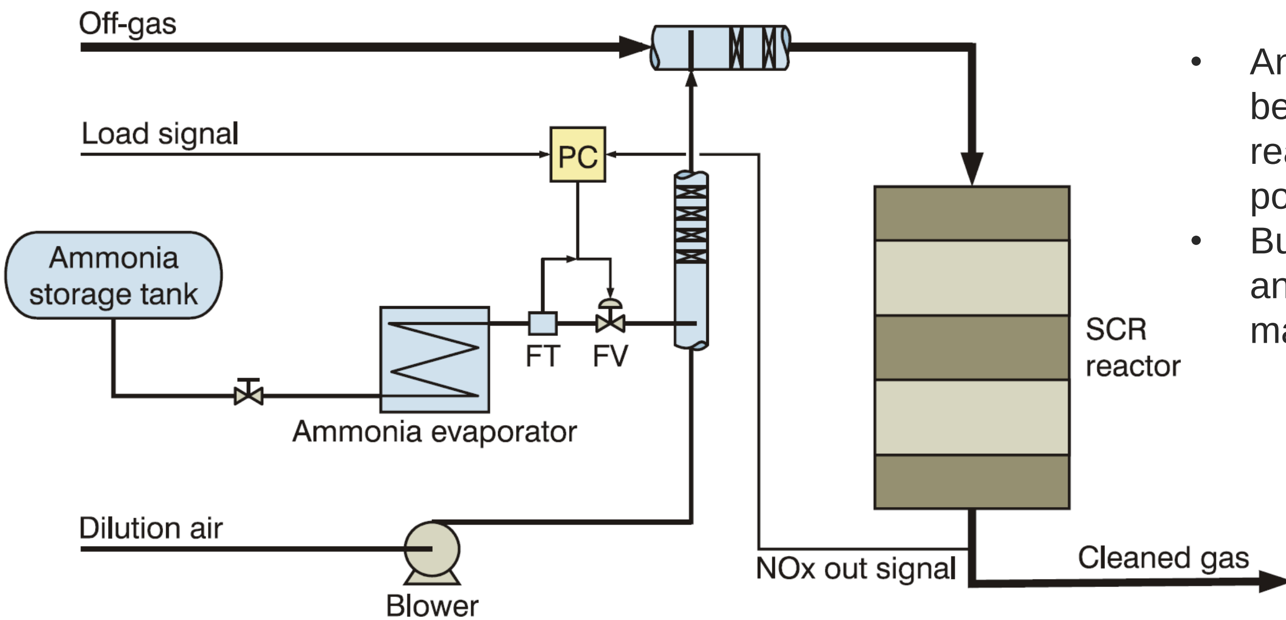


FRESH CATALYST HEAT SINTERED CATALYST

SCR system configuration



SCR system configuration



- Anhydrous ammonia appears to be the most cost-effective reagent, especially for larger power plants
- But anhydrous ammonia is toxic and is regulated as a hazardous material.

The anhydrous ammonia (it contains no water) is stored in the storage tank at ambient temperature and at the corresponding vapour pressure (approx. 10.5 bar or 103 atm at 25°C ambient temperature). From the storage tank the liquid ammonia flows by its vapour pressure to the evaporator, which can be heated by hot water, steam or electricity. A controlled flow of evaporated ammonia is then passed to the NH3/dilution air mixer, where the ammonia is diluted with air supplied by the dilution air blower before injection into the hot flue gas stream.

The ammonia vapour is diluted with air to about 6 vol -% in order to **eliminate the risk of ammonia ignition** when injected into the hot flue gas. The upper and lower explosion limits for diluted ammonia vapour are **15 vol% and 28 vol%** respectively. Secondly, the dilution with air **improves the mixing of the ammonia vapour and the flue gas**.

A static mixing element is located in the flue gas duct before the inlet of the reactor to ensure a homogeneous mixing of the flue gas and the diluted ammonia vapour. It is important to obtain a homogeneous mixing in order to attain a high efficiency of the SCR process and minimise the NH3 slip (unused NH3) from the SCR reactor. A gas distributor plate at the inlet of the SCR reactor is designed to provide a uniform distribution of the gas mixture over the entire cross section of the reactor.

As the homogeneous mixture of flue gas and ammonia vapour passes through the channels of the catalyst, the nitrogen oxides are converted through the catalytic reactions.

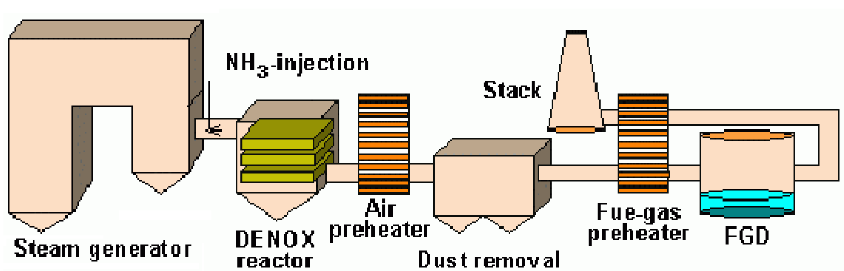
Choosing the correct reagent

Reagent cost is one of the most significant component in the economics of an SNCR or SCR system.

Some key points to take into account when choosing reagent (anhydrous ammonia, aqueous ammonia, and urea) can be summarized as follows:

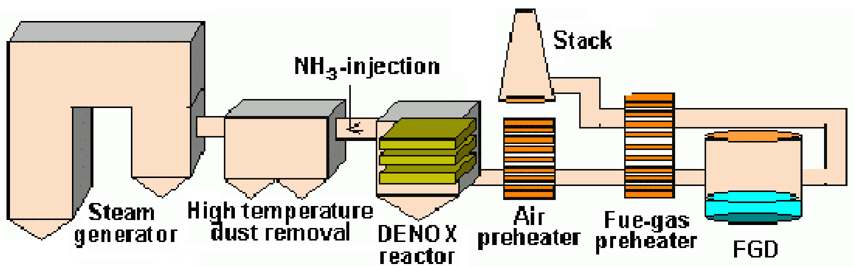
- What will be your estimated annual consumption of NOx control reagent?
- Can ammonia be delivered easily to your location?
- What competences exist in your plant for chemical handling?
- Can storage and handling training be made available?
- Will the storage be located close to a populated area or in an area where there is a high level of activity?
- What are the local and national regulations to consider when handling these chemicals?

SCR system configuration for power plants: location of catalyst reactor



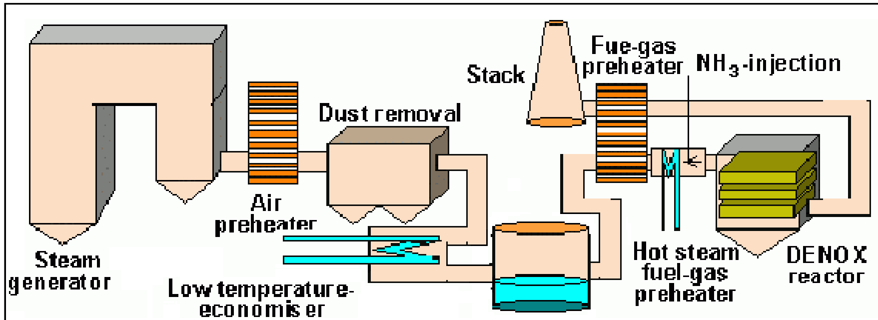
High dust: catalyst reactor located downstream boiler → hot flue gas, high particulate/SO_2 content

- High temperature
- High particulate concentration
- High SO_2 concentration



Low dust: catalyst reactor located downstream high T particulate removal → hot flue gas, low particulate content, high SO_2 content.

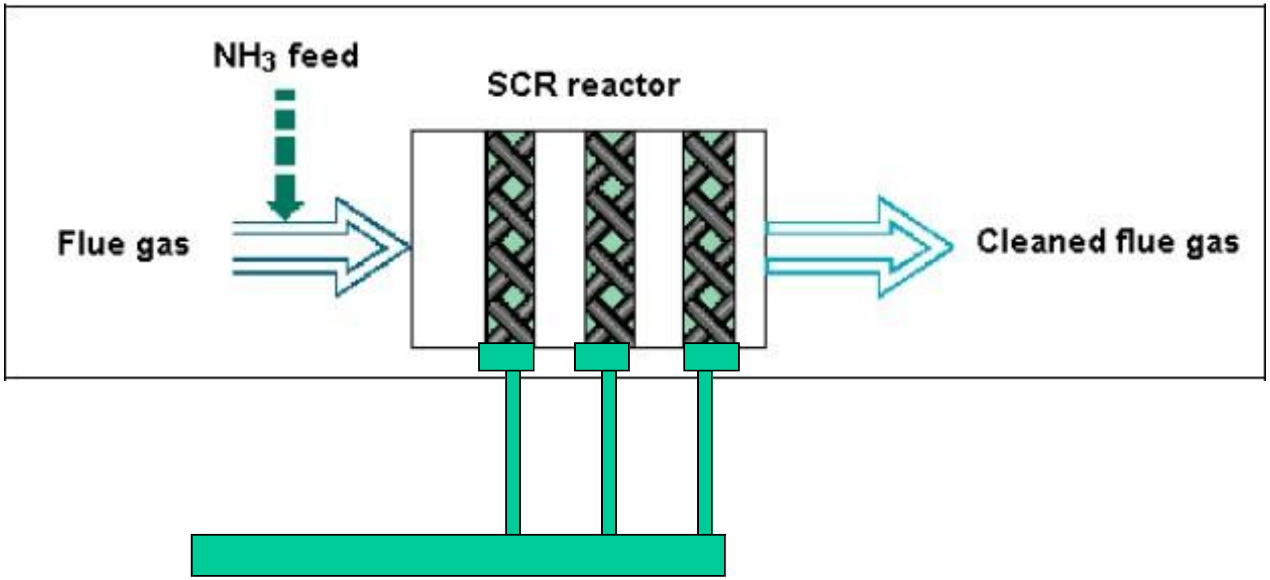
- High temperature
- Low particulate concentration
- High SO_2 concentration



Tail end: catalyst reactor located downstream particulates/SO_2 removal → cool and clean flue gas, need to reheat (heat recovery efficiency loss, auxiliary fuel)

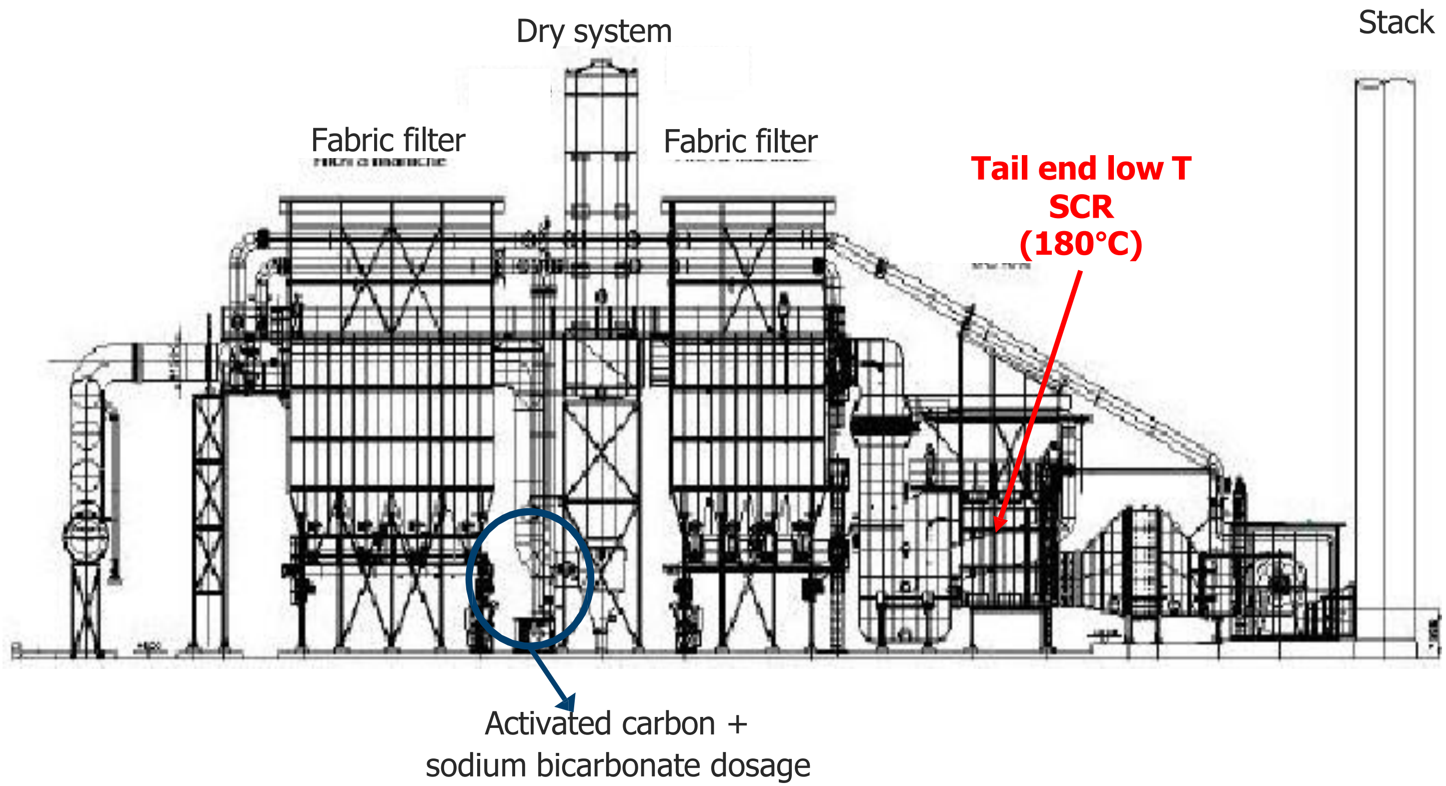
- Low temperature
- Low particulate concentration
- Low SO_2 concentration

SCR system configuration for power plants: cleaning options



Air/steam injection, ultrasonic

SCR system configuration: Low T SCR for waste to energy plants



SCR process main features

- NO_x average conversion efficiencies in the range 80-95%
- lower reactant dosage with respect to SNCR systems
- reduced ammonia slip
- BAT for most combustion applications
- very low N_2O (nitrous oxide) emissions
- simultaneous reductions of trace organics (significance for dioxins in waste to energy plants)
- high capital (catalyst) and operating costs (auxiliary fuel for reheating)

Example: SCR

A power plant operates with 800 ppm NO_X in the flue gas. The flue gas flow rate is 150000 m^3/h at 300°C and 1 atm. An SCR system is being designed for 75% removal of NOx. Calculate the stechiometric amount of ammonia required in kg/day.

R= 8.20573E-05 m^3 atm K^{-1} mol^{-1}

MW NO= 30.01 g/mole

MW NO_2= 46,01 g/mol

MW NH_3 =17.031 g/mole

SNCR and SCR comparison

Secondary measure	General NO_X reduction rate	Other performance parameters		Remarks
		Parameter	Value	
Selective catalytic reduction (SCR)	80 – 95 %	Operating temperature	350 – 450 °C (high-dust) 170 – 300 °C (tail-end) 280 – 510 °C (gas tubines) 200 – 510 °C (diesel engines)	• the ammonia slip increases with increasing NH_3/NO_X ratio, which may cause problems, e.g. with a too high ammonia content in the fly ash. This is a problem which can be solved by using a larger catalyst volume and/or by improving the mixing of NH_3 and NO_X in the flue-gas • incomplete reaction of NH_3 with NO_X may result in the formation of ammonium sulphates, which are deposited on downstream facilities such as the catalyst and air preheater, increased amounts of NH_3 in flue-gas desulphurisation waste waters, the air heater cleaning water, and increased NH_3 concentration in the fly ash. This incomplete reaction only occurs in the very unlikely case of catastrophic failures of the whole SCR system • the life of the catalyst has been 6 – 10 years for coal combustion, 8 – 12 years for oil combustion and more than 10 years for gas combustion • catalyst lifetime of 40000 to 80000 operating hours can be reached by periodical washing.
		Reducing agent	Ammonia, urea	
		NH_3/NO_X ratio	0.8 – 1.0	
		NH_3-slip	<5 mg Nm^3	
		Availability	>98 %	
		SO_2/SO_3-conversion rate with catalyst	1.0 – 1.5 % (tail end)	
		gyConsumption as % of electric capacity	0.5 % for all applications	
		Pressure drop at the catalyst	4 – 10 (10^2 Pa)	
Selective non-catalytic reduction (SNCR)	30 – 50 %	Operating temperature	850 – 1050 °C	• though some manufacturers report a NO_X reduction level of over 80 %, the common view is that SNCR processes are, in general, capable of 30 – 50 % reduction as an average covering different operational conditions. Further NO_X reductions can be obtained on specific boilers where the conditions are good, as well as lower values where the conditions are bad, sometimes on existing plants [33, Ciemat, 2000]. • SNCR cannot be used on gas turbines because of the residence time and temperature window required • incomplete reaction of NH_3 with NO_X may result in the formation of ammonium sulphates, which are deposited on downstream facilities such as the air preheater, increased amounts of NH_3 in flue-gas desulphurisation waste waters, the air heater cleaning water, and increased NH_3 concentration in the fly ash • SNCR cannot be used for gas turbines or engines.
		Reducing agent	Ammonia, urea	
		NH_3/NO_X ratio	1.5 – 2.5	
		Availability	>97 %	
		NH_3 slip	<10 mg Nm^3	
		Energy consumption as % of electric capacity	0.1 – 0.3 %	
		Residence time within temperature range	0.2 – 0.5 sec	