7 Nitrogen oxides

7.1 General

Acid deposition is due to the emission of primarily three substances namely SO_2 (sulphur dioxide), NO_x (nitrogen oxides) en NH_3 (ammonia). The natural emission of these substances is widely spread out and provides no problems. The unnatural emission is less homogeneously distributed and therefore will provide problems.
SO_2 and NO_x are combustion emissions; the emission of NH_3 originates amongst others from intensive cattle farming.

Acid rain

Acid rain is caused by the emission of this acid deposition, with as consequence:

- Affecting forests
- Acidification of lime poor lakes, with consequence, fish mortality
- Acidification of fens through which vegetation changes
- Decrease of the agriculture / crop yield
- Deterioration of monuments and buildings
- Deterioration of archives
- Degradation through corrosion of all sorts of materials and installations

Traffic

Over 62% of the NO_x released at incineration, comes from road traffic. Approximately 30% is accounted by combustion installations. The remaining 8% is released during various chemical processes.

7.1.1 NO_x forming

NO_x is the sum of mainly nitrogen monoxide NO (>95%) and to a lesser degree of nitrogen dioxide NO_2 (<5%), which originates from the oxidation of nitrogen during the incineration process. The nitrogen is supplied with the incineration air which consists of nitrogen of 78% volume. This nitrogen is present during incineration, in and around the flame but does not play a role in the incineration. The combustion air oxygen, 21% volume, is almost completely used up during incineration. However, because excess air is used for fuelling during incineration, a large quantity of oxygen is left in the flue gases. During incineration, mainly NO is formed while NO_2 is largely formed after incineration at a low temperature in the then formed flue gases.

7.1.2 Yellow / brown flue gases NO_2

NO is an invisible gas, while NO_2 is a yellow / brown coloured gas that is visible in small concentrations. This typical colour becomes visible when the NO_2 emissions in the chimney exceed the 75 ppm.
This yellow colour is an indication for the NO_2 quantity but is not representative for the total NO_x emission, as mentioned before.
Although NO_2 is very poisonous and dangerous for public health (MAC-value < 1 ppm), the adverse effect is the enormous corrosion it can cause by acidification of the environment.

7.2 Background

To meet the emission requirements of nitrogen oxides, further treatment of the flue gases is necessary. NO_x is an important acidifying component. In addition, it is known as greenhouse gas.
Of the element nitrogen (N_2), several oxides exist. The best known which play a part in incineration processes are nitrogen monoxide (NO) and nitrogen dioxide (NO_2). They are usually indicated together with the formula NO_x.
NO_x stands for NO and NO_2.

There are several mechanisms for NOx formation.

- Oxidation of nitrogen compounds from fuel. Here, mainly NO is formed. The NO_x which is formed this way is called fuel NO_x.
- Direct oxidation of molecular nitrogen from the air during incineration. This is referred to as thermal NO_x. This is a strong endothermic (requires a lot of energy) and temperature dependent reaction and takes place mainly at temperatures higher than 600 degrees Celsius. A higher temperature leads to an increased NO_x formation.
- Prompt NO_x
  Is formed just like thermal NO_x from nitrogen molecules in the incineration air, except that the only difference is the nitrogen first reacts with the hydrocarbons from the fuel, after which a further conversion to nitrogen oxides occurs.

Furthermore, small quantities of the following oxides are formed:

- Nitrogen monoxide (N_2O, laughing gas)
- N_2O_3, N_2O_4 en N_2O_5.

Radicals

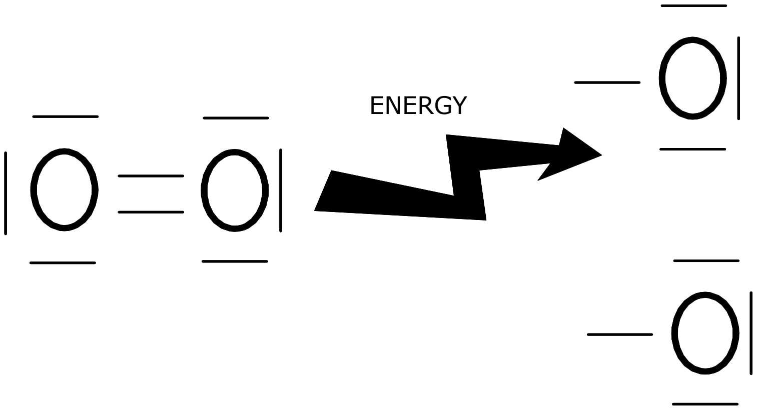
With the formation of any ‘type’ of nitric oxide the temperature plays a key role. With extreme energy supply so-called radicals can originate from molecules.

Radicals are reactive particles which have one electron too many or are one proton short, which makes them react with other molecules very quickly.

$N_2 + O_{isn} \rightarrow NO + N_{isn}$
$N_{isn} + O_2 \rightarrow NO + O_{isn}$

O_{isn} are radicals formed during incineration.

Oxygen strives, like any other gas, for the inert gas configuration where eight electrons are present in the outer shell. This creates a mutual double bond such as in illustration 1. When a large amount of energy is supplied to the molecule, the bond is broken and a radical emerges.



Together, the oxygen atoms have 8 electrons in the outer shell, inert gas configuration

Formed oxygen radicals

Illustration 1. Decomposition of oxygen molecules into radicals.

Inert gas configuration These oxygen radicals easily combine because of the strive to an inert gas configuration, where eventually the NO_x originates according to the given reaction equations, see chart 1. How and where the NO_x forming occurs and where it depends, is also projected on the next page, which also indicate which chemical reactions take place.

The decomposition of the oxygen molecules at temperatures higher than 600 °C with various notations indicated. Thus we have:

$O_2 \rightarrow O_{isn} + O_{isn}$
$O_2 \rightarrow O_{isw} + O_{isw}$
$O_2 \rightarrow O\bullet + O\bullet$
$O_2 \rightarrow$ 2 Oxygen radicals

O_{isn} stands for "in statu nascendi". O_{isw} is the Dutch version and stands for "in staat van wording" which means: "in state of being"

Nitrogen oxide		**Place of forming**	**Reaction**	**Main influence factor NO_x forming**
NO	Thermal	Flame Pre reaction zone	a. From the incineration air: $O_{isw}+N_2 \rightarrow NO+N_{isw}$ $N_{isw}+O_2 \rightarrow NO+O_{isw}$	Concentration of oxygen radicals. This depends again on the incineration temperature and time. At temperatures > 600 ºC
	Fuel		b. from the fuel: $N_{isw}+OH^- \rightarrow NO+H_{isw}$	Here, nitrogen is present in the fuel in bound form.
	Prompt	Flame	$CN+H_2 \rightarrow HCN^*+H_{isw}$ $CN+H_2O \rightarrow HCN^*+OH^-$ $CN+N_2 \rightarrow HCN^*+N_{isw}$	Quantity formed oxygen radicals during incineration. Excess air.
	Fuel	Flame	Reaction with CN-components (see above) and other unknown components	Rapid cooling of the incineration gases by e.g. a gas turbine
NO_2		Flame	$NO+HO_2 \rightarrow NO_2+OH^-$	Temperatures lower than 650 ºC. oxygen concentration and time
		Flue gas channel and chimney	$2NO+O_2 \rightarrow 2NO_2$	Oxygen concentration, brightness (sun), Pollution and time.
		Atmosphere	NO_2 + Light $\rightarrow NO+O_{isw}$ $NO+O_3 \rightarrow NO_2+O_2$	
	* produces NO_x			

Chart 1. Formation of nitrogen oxides NO & NO_2.

After cooling and being in contact with air, the NO is slowly converted into NO_2.
The contribution of the nitrogen oxide formation via this reaction in the process of waste incineration is expected to be minor. The nitrogen oxides are mainly formed out of the already present nitrogen compounds that by degradation are made available in a more accessible form to oxygen, the fuel NO_x. When the furnace energetic conditions are prevailing there is about two kilograms of nitrogen oxides formed from a tonne of waste. So this means with a consumption of 6000 Nm^3 incineration air per ton waste, a concentration of approximately 350 mg NO_x per Nm^3 flue gas. This concentration is quite common in the un-purified flue gases of waste incineration installations.

The nitrogen oxides contribute to the acidification of the environment.

Ozone

In the atmosphere, nitrogen oxides can be converted into detrimental acid substances that are the cause of “acid rain”.
Nitrogen monoxide in the atmosphere is first converted with ozone into NO_2:

$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$

Then through various reactions the NO_2 is converted into nitric acid:

$4NO_2(g) + 2H_2O(l) + O_2(g) \rightarrow 4H^+(aq) + 4NO^-_3(aq)$

Nitric acid

This nitric acid (HNO_3) comes into contact with water vapour in the air, which is condensing and comes down as precipitation.
The originated “acid precipitation” is a threat for forests, crops, surface-, and groundwater.
We must assume that if the emission of acidifying substances in the Netherlands would stop, the quantity of acid rain would decrease by only 25 %. The rest of the pollution drifts over from other countries.
Conversely of course it would also mean that measures on our side would decrease the “acid rain” in our neighbouring countries because 75% of the emitted NO_x from the Netherlands blows over to our neighbouring countries.
Because of the fact that the combustion temperatures with domestic waste incineration don’t normally exceed 1100 ºC, the NO_x formation is limited. Normally the concentration in the flue gases with domestic waste is not more than 250 mg/Nm^3.
To illustrate: per ton waste, approximately 2 kg NO_x is formed.

Summarising we can say that the NO_x formation depends on a number of parameters, namely:

- The flame temperature
- The air factor
- The shape of the flame
- The heat load of the furnace hearth
- Temperature of the incineration air
- The geometry of the furnace hearth
- Residing time

The most important cause however is the flame temperature. On illustration 2, you can see the influence of this. Also schematically shown, is how the various types of NO_x relate.

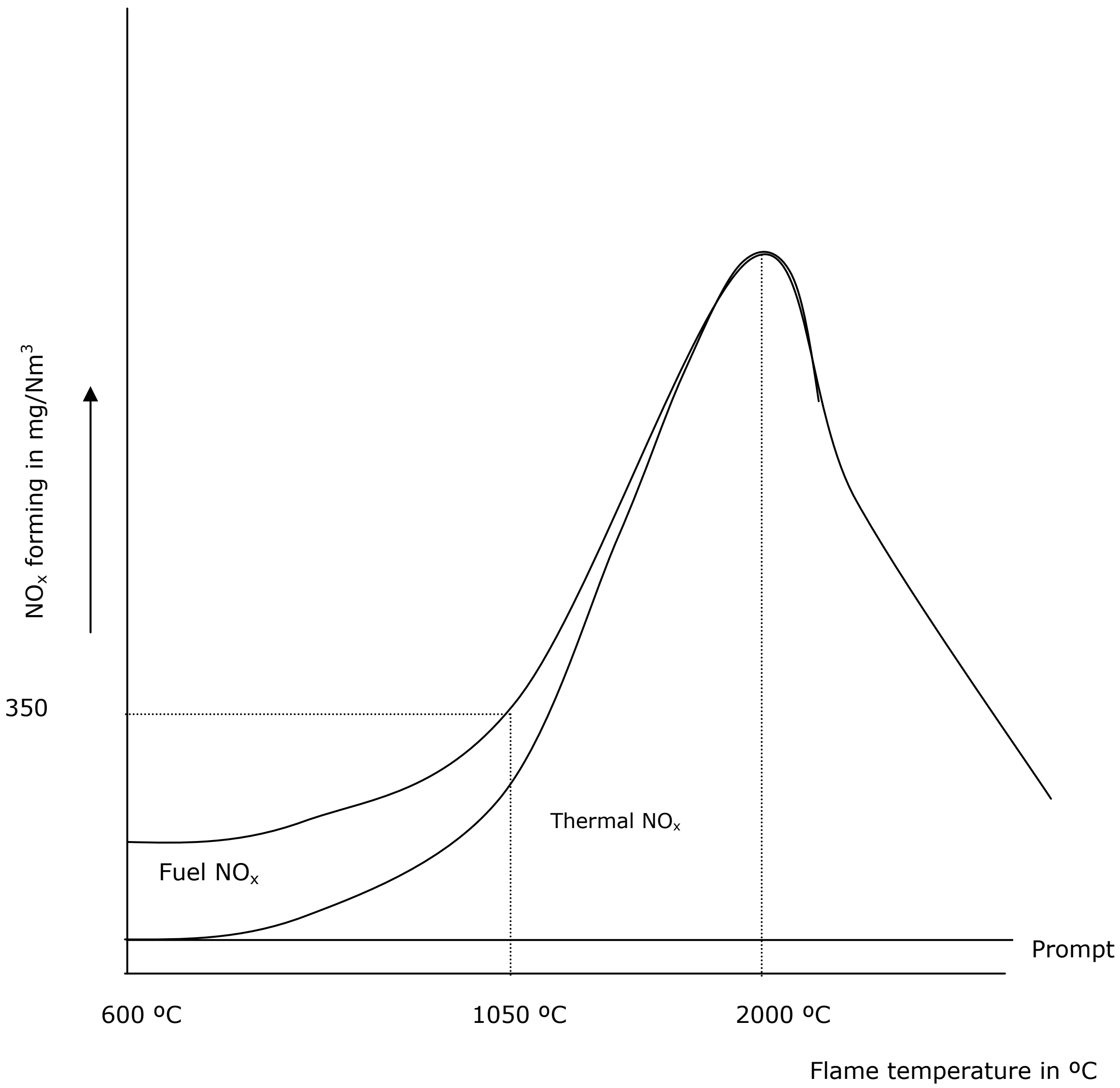


Illustration 2. NO$_x$ formation in a waste burning plant as a function of the flame temperature.

The graph shows that with increasing flame temperature NO$_x$ production increases. We can now ask how we can reduce the flame temperature.
Therefore a small theoretical explanation is required.

According to the DIN 1942 standard applies to the energy input to the boiler:

$$Q_{to} = \dot{m}_b \cdot H_o + \dot{m}_b \cdot c_b \cdot (t_b - t_r) + \dot{m}_b \cdot \lambda \cdot M_{ltheoretically} \cdot c_l \cdot (t_l - t_r) + P_{circ.pump}$$

Now, if we put the circulation pump aside, after all we have natural circulation, then this applies:

$$Q_{to} = \dot{m}_b \cdot H_o + \dot{m}_b \cdot c_b \cdot (t_b - t_r) + \dot{m}_b \cdot \lambda \cdot M_{ltheoretically} \cdot c_l \cdot (t_l - t_r)$$

The DIN Norm 1942 always calculates with the following values:

Specific heat air	c_l	=	1.005 kJ/(kg·K)
Specific heat flue	c_g	=	1.0 kJ/(kg·K)
Guide temperature	t_r	=	25 °C
Specific heat fly ash	$c_{fly\ ash}$	=	0.84 kJ/(kg·K)
Specific heat slag	c_{slag}	=	1 kJ/(kg·K)

We assume the following:

Mass waste that is incinerated	m_b	= 25 ton/hour
Lower calorific value waste	H_0	= 10,000 kJ/kg
Theoretical air quantity	$M_{ltheoretically}$	= 3.5 kg/kg waste
Specific heat waste	c_b	= 2 kJ/kg
Mass fly ash	$m_{fly\ ash}$	= 3 %
Temperature fly ash	T_{flame}	= Flame temperature
Mass slag	m_{slag}	= 25 %
Temperature slag	t_{slag}	= 500 ºC
Air temperature	t_l	= 30 ºC
Temperature of the waste	t_b	= 50 ºC

Now we can say that the added energy to the furnace must be equal to the one that leaves the furnace.
So, the supplied heat is the sum of the heat in the flue gases, that of the heat in the slag and of the heat in the fly ash.

Or:

$$Q_{to} = Q_{fluegas} + Q_{slag} + Q_{flyash}$$

First we assume an air factor of 1,5.

Entered:

$$Q_{to} = \frac{25000}{3600} \cdot 10000 + \frac{25000}{3600} \cdot 2 \cdot (50 - 25) + \frac{25000}{3600} \cdot 1.5 \cdot 3.5 \cdot 1.005 \cdot (30 - 25)$$

$$Q_{to} = 69974.8 \text{ kW}$$

The mass flue gas becomes:

$$\dot{m}_g = (\dot{m}_b - \dot{m}_{slag}) + (\dot{m}_b \cdot \lambda \cdot M_{ltheor})$$

$$\dot{m}_g = (\frac{25000}{3600} - 0.25 \cdot \frac{25000}{3600}) + (\frac{25000}{3600} \cdot 1.5 \cdot 3.5)$$

$$\dot{m}_g = 41.66 \text{ kg/s}$$

The heat in the flue gases:

$$Q_{fluegas} = \dot{m}_g \cdot c_g \cdot T_{flame}$$

$$Q_{fluegas} = 41.66 \cdot 1.2 \cdot T_{flame}$$

c_g above 1000 ºC amounts to 1.2 kJ/(kg·K)

The heat with the slag:

$$Q_{slag} = \dot{m}_{slag} \cdot c_{slag} \cdot t_{slag}$$

$$Q_{slag} = 0.25 \cdot \frac{25000}{3600} \cdot 1.0 \cdot 500$$

$$Q_{slag} = 868 \text{ kW}$$

The heat with the fly ash:

$$Q_{flyash} = \dot{m}_{flyash} \cdot c_{flyash} \cdot T_{flame}$$

$$Q_{flyash} = 0.03 \cdot \frac{25000}{3600} \cdot 0.84 \cdot T_{flame}$$

All together in succession:

$$Q_{to} = Q_{fluegas} + Q_{slag} + Q_{flyash}$$

$$69974.8 = 41.66 \cdot 1.2 \cdot T_{flame} + 868 + 0.03 \cdot \frac{25000}{3600} \cdot 0.84 \cdot T_{flame}$$

$$69974.8 = 49.992 \cdot T_{flame} + 868 + 0.175 \cdot T_{flame}$$

$$T_{flame} = 1377 \text{ ºC}$$

Suppose, the air factor now becomes 1.2:

$$Q_{to} = \frac{25000}{3600} \cdot 10000 + \frac{25000}{3600} \cdot 2 \cdot (50 - 25) + \frac{25000}{3600} \cdot 1.2 \cdot 3.5 \cdot 1.005 \cdot (30 - 25)$$

$$Q_{to} = 69938.2 \text{ kW}$$

The heat in the flue gas becomes now:

$$\dot{m}_g = (\frac{25000}{3600} - 0.25 \cdot \frac{25000}{3600}) + (\frac{25000}{3600} \cdot 1.2 \cdot 3{,}5)$$

$$\dot{m}_g = 29.16 \text{ kg/s}$$

$$Q_{fluegas} = 29.16 \cdot 1.2 \cdot T_{flame}$$

The heat in the slag and the fly ash remains the same, so now follows:

$$69938.2 = 29.16 \cdot 1.2 \cdot T_{flame} + 868 + 0{,}03 \cdot \frac{25000}{3600} \cdot 0.84 \cdot T_{flame}$$

$$T_{flame} = 1964\ ^{o}\mathrm{C}$$

This is only meant as an example, however it is demonstrated that with a decreased air factor, the flame temperature initially increases. However, if the air factor, *prior to burning,* becomes lower than 1, the flame temperature reduces due to lack of oxygen.

Pay attention: This calculation applies to an adiabatic burning in a furnace with refractory fire proofing as walls and a downstream boiler. In a downstream boiler, approximately 10 to 15 % of the contributed energy is removed from the furnace hearth, due of flame radiation to the furnace walls, so this is accompanied by a temperature reduction.

7.3 Reducing the flame temperature

In principal, the temperature of the flame can be reduced in three ways, namely:

- Increase of the air factor.
- Drastic decrease of the air factor before incineration, thus, the primary air factor.
- Flue gas recirculation.

7.3.1 Increasing the air intake factor

This is not recommended. As a result the mass flow of flue gases increases, with the result that the chimney loss increases and the boiler efficiency decreases.

7.3.2 Reducing the air intake factor prior to burning

One option is reducing the quantity of primary air, in other words, a deprived oxygen environment is created. Consequence of this is that the flame temperature decreases due to less heat production from the carbon. An annoying side effect is that we create CO formation.
This CO must be converted with the secondary air into CO_2.
Pay attention! The total air factor must remain constant; after all one is bound to a minimum of 6 volume % oxygen in the stack.

7.3.3 Flue gas recirculation

Here one uses flue gas which is branched off downstream of the ESP. Then we mix the flue gas with primary or secondary air. Here we also create a deprived oxygen environment.

7.4 Carbon monoxide

CO originates inside the furnace due to incomplete burning of waste. There are several reasons for this incomplete conversion; namely, too low combustion temperature locally, or a too low furnace hearth temperature in general and a (local) shortage of oxygen on the grate or in the burn out zone.
High CO formation usually occurs with slightly out dated incinerators with non-optimal furnace geometry. Therefore mixing the combustion gases with oxygen is deficient and the combustion process will not be completed.
To obtain the emission values for CO, only primary measures will have an effect.
Too low combustion temperatures, even locally, can for a good portion be prevented by:

a. Good air mixing under and above the grate.
b. Good arrangement of the grate.
c. Injecting secondary combustion air in the right place and under the right circumstances.
d. Application of primary air heating.

One can say that heating of primary air increases the average hearth temperature as such that the conversion of CO into CO_2 will occur more complete and quicker. In addition, the probability of the presence of cold airflows in the hearth is significantly reduced.
With existing installations the hearth geometry can only be optimized to a limited extent. When building new facilities, the opportunities for optimization of the furnace geometry will be present particularly in the design stage. By means of flow research will then be shown that an optimal hearth shape is obtained. Sidewall cooling also has an effect on the CO percentage. Although sidewall cooling is favourable with respect to reducing the quantity of slag which deposits itself, on the other side however, one brings in cold air which then produces cold CO.
Now, chemically speaking, there is no difference between cold and warm CO, only the way it originates is different.

7.4.1 Cold CO

This originates with sufficient oxygen and too low combustion temperature.

7.4.2 Warm CO

This originates with sufficient combustion temperatures but a lack of oxygen.

7.5 The SNCR-system

This is a process, where ammonia or urea is sprayed into the flue gas flow as a reaction agent, to reduce the nitrogen oxides (NO_x) to molecular nitrogen and vapour. Nowadays they experiment with injecting various derivatives of ammonia (for example organic amines) into the hearth to expand the temperature window. Animal manure contains ammonia and organic compounds and in principal after processing, it can be a good replacement of an ammonia solution.

Reduction

The reduction takes place in a temperature range of 850 - 950 °C and is subject to the following reactions:

$4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O$
$6\ NO_2 + 8\ NH_3 \rightarrow 7\ N_2 + 12\ H_2O$

The mechanism of this reaction is based on nitrification/nitration, which is a specific reaction of NO_x. As a by-product a small quantity of nitrous oxide N_2O "laughing gas" can arise.

The reaction above is also called the over all reaction. The actual reaction takes place in stages these are as follows:

$4\ NH_3 + 6\ O_2 \rightarrow 4\ NH_2 + 4\ OH$
$NH_3 + OH \rightarrow NH_2 + H_2O$
$NH_2 + NO \rightarrow N_2 + H_2O$

If the temperature falls below 850 °C, then less NH_2 radicals will be formed. Because there are less NH_2 radicals formed, less nitrogen oxides are converted into molecular nitrogen and vapour. The result is that the ammonia concentration in the flue gases increases.

In a SNCR-DeNO$_{x,}$ the reaction above takes place in a relatively closely defined temperature range of approximately 850-950 °C. At higher temperatures the injected NH_3 is converted ("burned") into NO_x.

At temperatures above 1000 °C, the equation is:

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

Reaction speed

At lower temperatures the reaction speed of the DeNO$_x$–reaction decreases as such that the effect is lost. Only by application of a catalyst are lower reaction temperatures possible (SCR-systems). To achieve sufficient effect, application of excess NH_3 is required in the indicated temperature range.

Ammonia

In general the ammonia or urea is injected into the furnace in the form of a 25% solution. To cover a large surface area sprinkler nozzles are built in on the left and the right side of the furnace / boiler.
The feed tank for the 25% ammonia is designed pressure free.
An adjustable dosage pump pumps the ammonia to a steam injector, through which the steam- NH_3-mixture is added.
There can only be a high degree of NO_x separation achieved when the quantity of NH_3 is added above the stoichiometric value. The largest part of the NH_3 surplus ends up in a scrubber as molecular ammonia, where it is washed. In the acid scrubber water the ammonia converts directly into NH_4^+.

Aerosols

A portion of the quench water which is pumped into the circuit is continuously extracted and carried back into the ammonia recovery. The rest of the ammonia which is already in the flue gases combines itself to ammonia sulphate $(NH_4)_2SO_4$. These compounds occur as fine aerosols. On illustrations 3 and 4, the SNCR-system is schematically projected. The system with urea is not applied in waste burning plants; however, urea injection is applied in smaller biomass plants.

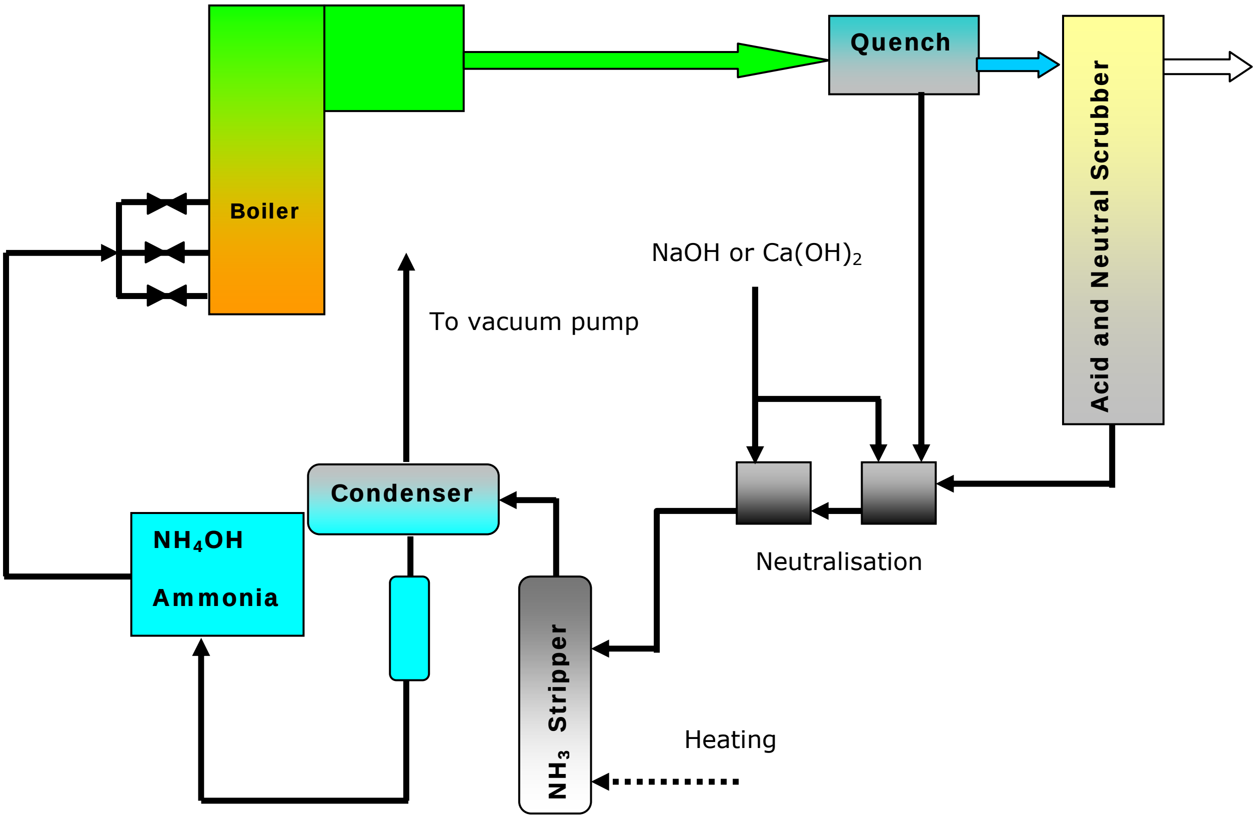


Illustration 3. SNCR system with ammonia.

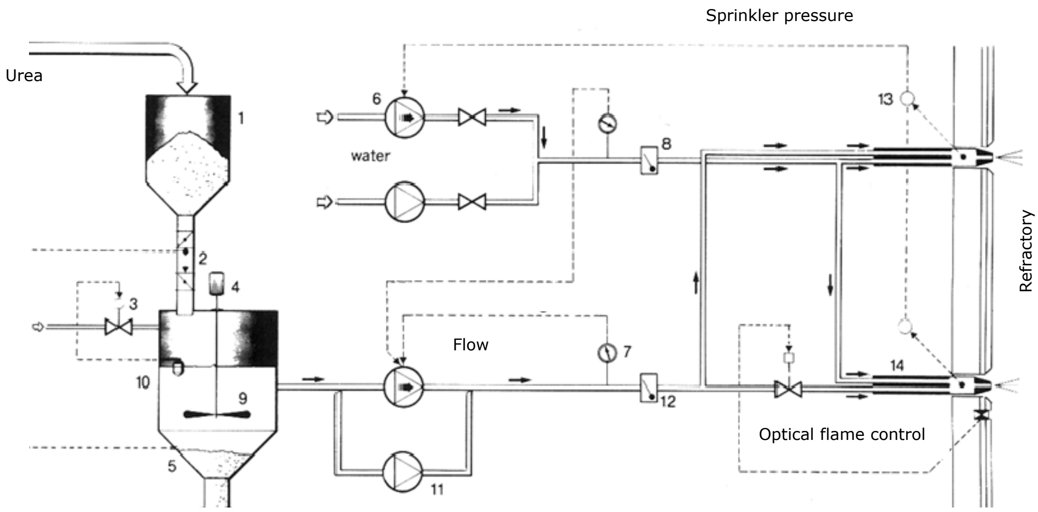


Illustration 4. Schedule SNCR system with Urea.

1. Urea
2. Sluice
3. Water supply
4. Mixer
5. Level gauge
6. Pump
7. Quantity measurement
8. Check valves
9. Mixer
10. Mixing vessel
11. Pump
12. Check valves
13. Pressure measurement
14. Sprinkler nozzles

Urea

If Urea is used instead of Ammonia, then the following equation applies:

Urea = $CO(NH_2)_2$ or also CH_4N_2O

$CO(NH_2)_2 + 2NO + O_{isn} \rightarrow 2N_2 + CO_2 + 2H_2O$

The above reaction equation is purely illustrative, in reality, the urea is thermally cracked in the furnace where amongst others NH_3 is formed. The formed ammonia NH_3 reacts further according:

$4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O$
$6\ NO_2 + 8\ NH_3 \rightarrow 7\ N_2 + 12\ H_2O$

Urea is blown in at temperatures between 850 en 950 °C.
In addition this applies:
At temperatures above 1000 °C the equation is:

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

Comparison chart Ammonia:

Advantage	Disadvantage
Only N_2 and H_2O-forming. Little space required. Catalyst not necessary unless injected into fire. Low investment.	High NH_3 consumption. Formation of $(NH_4)_2\ SO_4$. Efficiency ± 70 %. Chance of NH_3 leakage.

Temperature

850 °C

For correct operation of the SNCR it is important that one works in a narrow temperature window (optimal at approximately 850 °C), see illustration 5.

This requires an accurate dosage at the various spray levels, where injection of ammonia takes place. By adding additives the lowest operation temperature can be decreased to nearly 700 °C. Applicable additives include multiple alcohols and ammonia compounds.

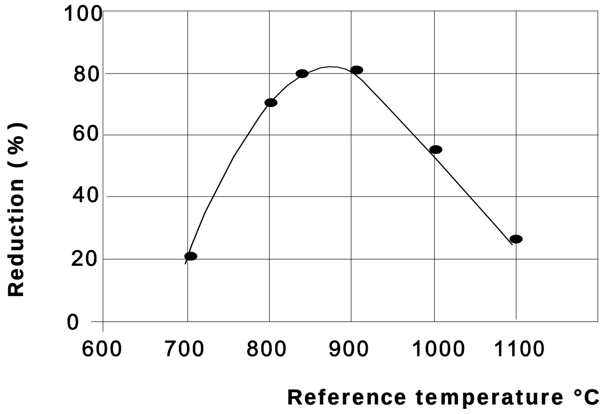


Illustration 5. Temperature window SNCR.

Consumption ammonia

To reach a good efficiency, a large excess of ammonia will have to be applied (a stoichiometric ratio of approximately 2 to 4 for a removal of 80%). This excess will be retrieved on the fly ash and in the salt/fly ash mixture (in a semi-dry method) or in the wastewater (wet scrubbing). A consequence is that the application possibilities of the fly ash can decrease (odour problems).

The wastewater will have to be treated: in principle, the ammonia will be stripped and can then be recycled.

Laughing gas

Application of urea instead of ammonia is not desirable, because recirculation is not possible and laughing gas can be formed.

Salt deposits

Ammonia salts

In applying the necessary excess of ammonia there is a risk that in the cold section of the boiler salt deposition will occur. In addition (very fine) aerosols of ammonia salts originate that are difficult to remove from the flue gases and that possibly require an additional treatment stage in the RGR.

An SNCR can only meet the values of BVA if a significant excess of ammonia, with the above mentioned risks will be applied. The advantage of SNCR is that no extra components have to be added to the RGR.

SNCR is very sensitive to variations of the boiler temperature, including variations in the calorific value and composition of the waste. A good mixture of the waste and a constant combustion is necessary.

7.5.1 Ammonia recovery in SNCR

Because a significant amount of ammonia is supplied in surplus, which among others is intercepted in the scrubbers, this can result in a high ammonia load of effluent water. It is therefore necessary to recover the ammonia from the quench reservoir.

Ion form

For recovery of the ammonia, this must be first brought back from the produced ion form (NH_4^+) into the molecular soluble form (NH_3). For this purpose, the pH value of the quench water is increased up to approximately 10 – 10,5 by means of lime milk, $Ca(OH)_2$, or through help of sodium hydroxide, NaOH. The relationship between free ammonia, temperature of the stripper water and the pH of the water in the stripper is projected on illustration 5.1.

In a so-called stripper column the ammonia is dissipated with steam. The ammonia steam mixture is cooled down to a temperature of 20 - 30 °C by an air-or water-cooled condenser and is supplied to the reservoir of the column in liquid form. The main product flows through a condenser and is supplied to the ammonia injection.

The security of the entire installation is executed as such, that no dangerous operational situations can occur in case of any operation malfunctions.

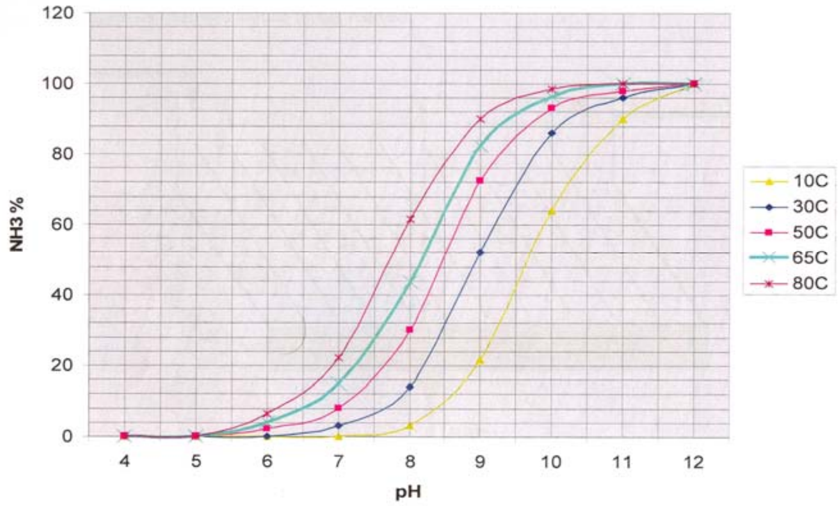


Illustration 5.1. The quantity free ammonia in the stripper water as function of the pH and the water temperature.

7.5.2 Flue gas temperature and enthalpy

In the SNCR system ammonia is transported in the direction of the boiler through help of water or steam. If this happens with steam, then a relatively large quantity of steam is required, the flue gas volume can increase even up to 5 %.

"Cold" steam

Because there is relatively "cold" steam used; the flue gas temperature on the spot of injection will decrease, after all the steam must be warmed up. As a result, there will be less radiation heat available in the boiler and in the flue gases, because there is more vapour present in the flue gases they leave the boiler with the same temperature, however the heat content is increased. In short, the enthalpy of the flue gas when leaving the boiler increases when an SNCR is used while the flue gas temperature remains unchanged.
This is graphically projected on illustrations 6 and 7.

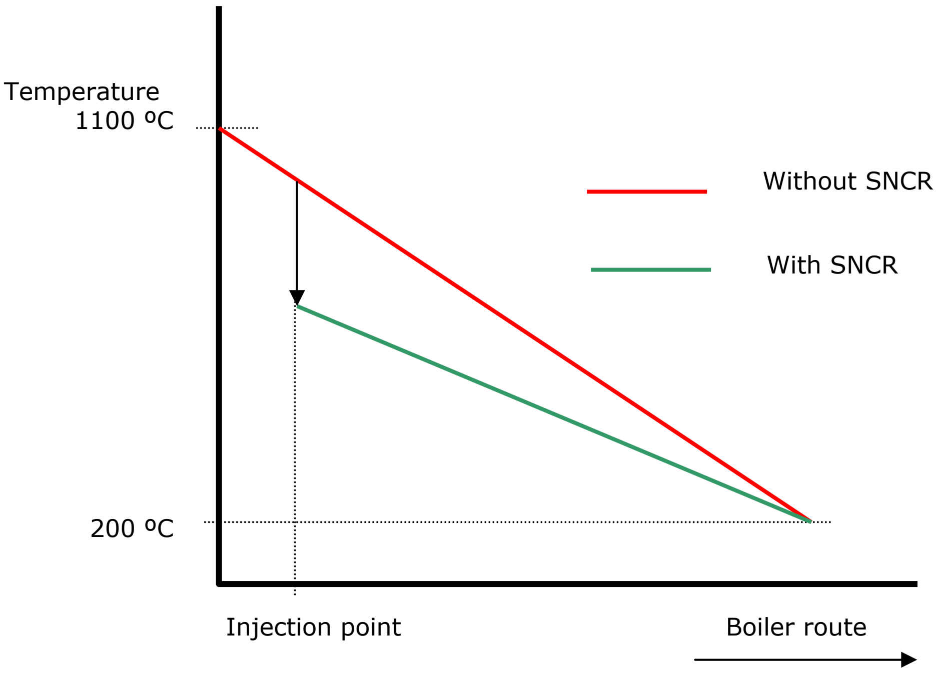


Illustration 6. The influence of the SNCR on the flue gas temperature.

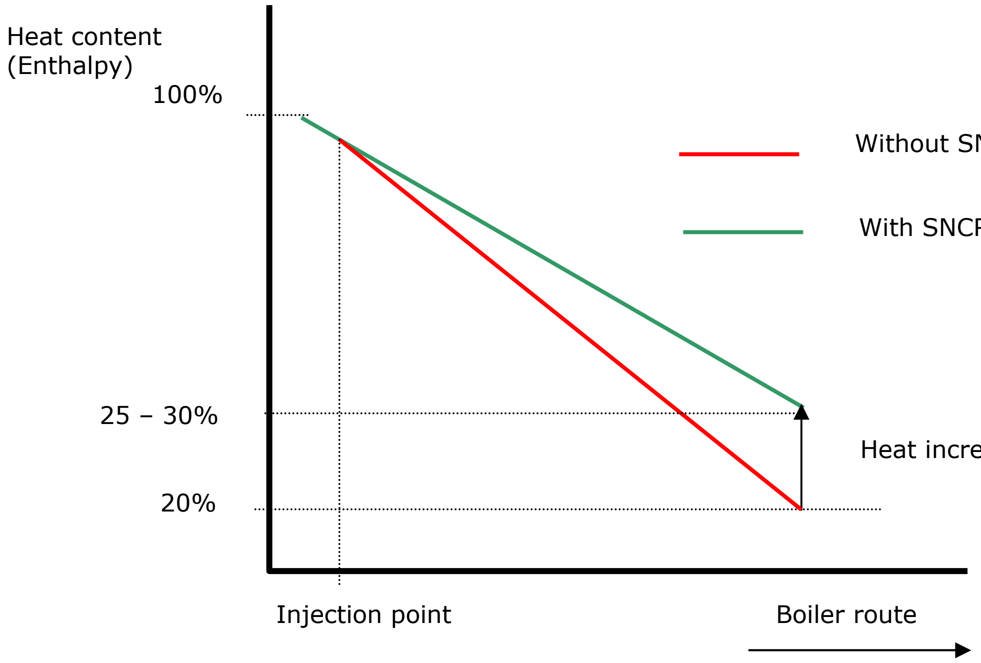


Illustration 7. The influence of the SNCR on the enthalpy of the flue gas.

In summary, in an SNCR installation where the carrier is steam we can observe the following:

- The flame temperature at the injection point decreases.
- Flue gas temperature when exiting boiler remains the same.
- The enthalpy of the flue gases when exiting boiler increases.
- Boiler efficiency decreases.

The four latter points are also known as the term: deteriorated isobaric cooling.

7.6 The SCR system

The SCR-method is a catalytic method which operates at a temperature of between 200 en 350 °C. The NO_x is converted into molecular nitrogen and vapour in the catalyst, following the same reactions as with non-selective reduction. The catalyst decreases the activating energy (energy barrier) by temporary exchange of atoms with the reacting molecules (active complex) but does not change in the chemical sense. Experiments are done at temperatures of approximately 180 °C, the findings are satisfactory. The situation of the SCR-system in the flue gas purification system is important for the function of the catalyst. This can be 'poisoned' or blocked, by dust, SO_x and particularly arsenic, to the effect that it will not operate "correctly" anymore for the conversion of NO_x and the life span deteriorates considerably. In general, the catalyst consists of metal oxides like vanadium pent oxide V_2O_5, titanium dioxide (TiO_2), or tungsten trioxide (WO_3) and has an average life span of approximately nine years.

Position of the catalyst

High, low, tail

The catalyst can be deployed in various positions in the system. When the SCR is built in the boiler, prior to the economiser and ESP, where the flue gas has the required temperature of 300 - 400 °C, we speak of "high dust" SCR. The catalyst can also be placed downstream of a high temperature ESP, prior to the economiser (temperature up to 260 °C, depending on the ESP): "low dust" SCR.
Finally, the catalyst can be situated as last component in the FGP, where the flue gas is stripped of all polluting components (with exception to NO_x): "tail end" SCR, see illustration 8.

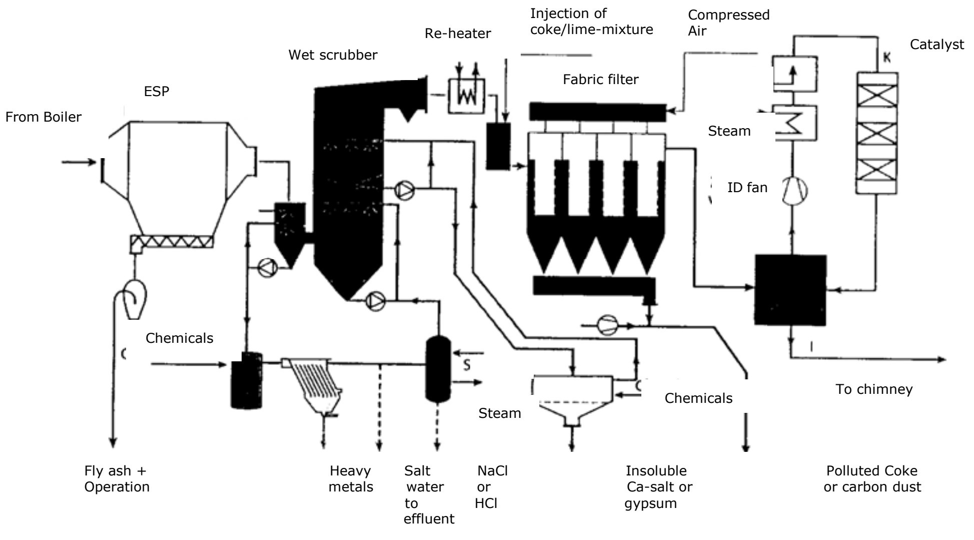


Illustration 8. Complete installation with SCR system.

Substance content

In a waste burning plant application of a "high dust" SCR is not possible because of the high dust content, combined with a high concentration of futile components. Because of this, activity will decrease quickly. "Low dust" SCR however, is applicable and also has the advantage that re-heating of the flue gas is not necessary.

Catalyst

"Tail-end" SCR is generally applied for the removal of NO_x from flue gases at various industries. The advantage of this is that the flue gas is already highly purified and the risk of contaminating the catalyst is low. Moreover, a catalyst with smaller distance between the plates is chosen (larger specific surface area) due to the very low residue content and the risk of salt deposits (especially NH_4HSO_4) is significantly smaller so that a lower operating temperature is possible.

In SCR, the reactions are as follows:
The temperature varies from 180 °C - 300 °C, depending on the catalyst used.

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$
$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$$

It should be noted that the catalyst could be contaminated with Arsenic and SO_2. If this happens, the life span of the catalyst reduces drastically, which entails large costs.

Temperature

In general, an SCR is operated at a temperature of 300 up to 350 °C. At lower temperatures, the reaction speed will be significantly lower and another type of catalyst will have to be applied and / or a larger resistance time will be required. The risk of a lower temperature is that the formation of SO_3 increases and more salt deposition can occur. With a "low dust" SCR the temperature cannot be reduced lower than approximately 260 °C.
With a "tail end" this problem is less present (see above) so that a further temperature decrease (to approximately 180 °C) can be implemented and the re-heating of the flue gases can take place in an energetically favourable manner. There is still few practice data known of SCR's at such low temperatures. The development of LTSCR however is progressing very quickly and is promising. At AVR Rozenburg, an LTSCR is in use.

Number of layers

The number of layers catalyst stipulates to an important degree the pressure loss on the SCR. With "tail end" SCR's, operating at 300 up to 350 °C, 2 to 4 layers are applied with a total pressure loss of approximately 2 kPa. Due to the decrease in activity of the catalyst, a reserve capacity needs to be built in. There is often a space reserved for an extra layer, which will be introduced after a period of time.
If the flue gases contain (almost) no more substance, a packed bed can be applied. The advantage of a packed bed is that the specific surface is significantly larger and the reactor becomes smaller and simpler. In relation to the risk of dust contamination, packed beds are not yet applied.

Dioxins

The possibility exists to apply SCR for dioxin removal:
It appears that dioxins (and other high hydrocarbons) are oxidised on the catalyst.
With such an SCR, one or more layers are added in which oxidation of organic hydrocarbons occurs. Of importance is the temperature at which the SCR is conducted. For a sufficient removal of dioxins, it seems that a high temperature (up to 400 °C) is necessary. It is shown that hardly any adsorption of dioxins occurs on the catalyst.
However, the reaction mechanisms which occur with the formation / decomposition of dioxins are not very clear yet. In addition, the influence on this of various substances (like ammonia) is insufficiently known. Originally, it was assumed that ammonia was impeding the oxidation. Meanwhile, however, the ammonia has shown no inhibitory effect.

Consumption ammonia

The ammonia consumption, this means the ratio used NH_3/NO_x, determine to an important degree the efficiency of the SCR. However, ammonia slip is undesired. In a "low dust" SCR, the ammonia that slips through will be retrieved in the wet scrubber and/or on the fly ash. Also with a "tail end" SCR, the ratio NH_3/NO_x cannot be increased too much, this to keep the residual concentration of ammonia in the flue gases to a minimum. The government maintains a requirement of maximum 5 mg ammonia per kg flue gas.

The method of re-heating

Re-heating

The necessary re-heating with a "tail end" SCR usually takes place through help of gas burners. This has a significant impact on the total energy consumption. Application of process heat can serve as an alternative; however, this option also contributes to its own energy consumption.
By applying a precisely dimensioned SCR, it is possible to meet the requirements of BVA for NO_x. Load variations, as well as flue gas quantities as NO_x-concentrations hardly have influence on the proper implementation.

Plate heat exchanger

Natural gas burner

The flue gases (t > 85 °C) that come out of the scrubber respectively suction fan, are heated by a plate heat exchanger and a natural gas burner to the required operational temperature to approximately 300 °C.
The plate heat exchanger operates according to the cross-/ back flow principle. The cold flue gases that come out of the scrubber are heated up to approximately 260 °C in the plate heat exchanger by the warm purified flue gases. The flue gases are brought on to the necessary catalyst operation temperature through help of the natural gas burner. After the heating (natural gas burner), the NH_3-injection is introduced. The reduction agent (NH_4OH) is injected in the flue gas channel and is homogeneously mixed via a mixing system (delta wing).
Subsequently, the flue gases reach the SCR-reactor, which is equipped with catalytic converters, which reduce nitrogen oxides and dioxin degradation occurs. The purified flue gases then return to the heat exchanger and are cooled to a temperature of 200 °C, and then led into the chimney.
The plate heat exchanger consists of an impermeable gas plate heat exchanger in a modular construction and functions according to the cross-/ back flow principle.

The heat exchanger consists of two stages. The lower heat exchange stage (cold side) is fabricated acid resistant (Alloy 59). This section is at the acid dew point. The second heat exchanger stage consists of normal steel (St. 12.03).
The plate heat exchanger operates without an external energy source. Upstream and downstream of the inlet respectively outlet of the plate heat exchanger, on the hot and the cold side, temperature gauges are installed.
With these operational measurement points, the company staff can monitor the warming up of the $DeNO_x$ installation. Decrease of the flue gas entry temperature down to below the design temperature (t = 85 °C) leads to the acid dew point shifting to the unprotected range of the plate heat exchanger.

Differential pressure The differential pressure gauge over the plate heat exchanger is to check if the pressure loss increases at the purified gas side due of deposits. The raw gas side of the plate heat exchanger is monitored with help of the differential pressure gauge.
When the pressure loss decreases at the plate heat exchanger by 30%, then the plate heat exchanger can be cleaned when the installation is in standstill.
Then it is also possible to clean the heating surfaces.

Natural gas burner

The flue gases recuperated from the pre-heater in the plate heat exchanger can be heated with a natural gas burner to the required operation temperature of the catalysts. The natural gas burner can be designed as a channel surface burner and can be connected to the flue gas line upstream of the NH_4OH-injection.
The natural gas burner consists of:
- Air storage with gas burner element
- Ignition burner
- Redundantly executed combustion fan
- Compound regulator
- Burner control

The natural gas burner is adjusted in accordance with the flue gas temperature for the catalyst. In accordance with the established temperature of the temperature regulator (normal operational temperature 300 °C), the quantity of fuel and air is adjusted by means of the compound regulator.

NH_4OH-quantity regulation

Lances The NH_4OH-injection often consists of lances with a sprinkler for two substances (NH_4OH/compressed air).
The NH_4OH-sprinklers are implemented between the natural gas burner and the catalyst in the flue gas channel. Via a static mixing system (Delta wing) the NH_4OH which is injected with atomized air is distributed into the flue gas in accordance with the required homogeneous.

Via the control valve, in accordance with the NO_x disposal rate, flue gas volume flow, the NH_4OH that is introduced into the flue gas is injected as atomizer medium with help of compressed air. The injected quantity of NH_4OH is registered at the measuring point and indicated on the central switchboard.
With the manual control valves and the local flow meters it is possible to correct both sprinklers.
Both the NH_4OH-line and the atomizer air injector pipe are closed off through help of the quick closing valves isolating the flue gas line when stagnation or breakdown occurs.

7.6.1 Catalyst deactivation

Principally a difference is made between reversible and irreversible deactivation.

Deactivation through condensation of ammonium salts:

The system NH_3 - SO_3 - H_2O displays complex thermodynamic behaviour. In the gas phase, 3 substances are coexistent.

In a stoichiometric or over-stoichiometric ratio
NH_3 / SO_3 originate with condensation ammonium sulphate.

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

An under-stoichiometric ratio of NH_3 / SO_3 leads to a temperature drop below the condensation temperature of formation of ammonium hydrogen sulphate.

$NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4$

Condensed ammonium salts reduce the active surface of the catalyst and therefore reduce the separation capacity of the catalyst; this is the so-called reversible deactivation.

Deactivation by contaminating with alkali metal salts:

Dust-like deposits on the catalyst contain Sodium and Potassium. Through condensation of vapour in the pores of the catalyst during standstill of the installation, the alkali metal salts are dissolved and deactivate the active centres; this is the so-called irreversible deactivation.

7.6.2 NO_x-reduction through means of active carbon (ACCR)

With this method, the NO_x is removed by allowing the flue gases to pass through an active carbon filter. Because the active carbon acts as a catalyst, this method is known as the low temperature SCR method. Upstream of the filter NH_3 must be dosed to make the conversion of NO_x into N_2 possible. Because the active carbon from the catalyst (SAK) works absorbing for the other residue pollutions that are present in the flue gases, the filter will quickly loose its affectivity when no measures are taken. An option is to place the active carbon filter (HOK) upstream of the SAK-filter. The HOK-filter must then remove the residue pollutions from the flue gases so that the SAK-filter has a very low consumption of active carbon. Because of the very low velocity of the flue gas flow inside the filter, the placement space that this installation requires will be very large. One can calculate with a filter capacity of 360 m^3_0 per hour for each m^2 filter surface. Research indicates however that the feasibility of BVA for NO_x with ACCR is questionable. Besides, ACCR gives a substantial increase of the CO-degree in the flue gases, especially at higher temperatures. This increase can even amount to 20 up to 30 mg/m^3_0, which makes the requirement from the BVA (maximum 50 mg/m^3_0 CO) difficult to achieve.

Desorbed

This system works well at temperatures up to 70 °C, when the temperature becomes 95 °C or higher, then the NO_x is desorbed by the active carbon.

7.6.3 SCR for gas engines

In waste incineration plants gas engines are increasingly used for emergency power. In some systems, the flue gases are fed directly into the flue gas purification, this for example if the engines are applied for the combustion of biogas. If these engines only run on natural gas they can be fabricated with their own SCR reactor, which is visable on illustration 9. The operation is the same as the already discussed SCR system.

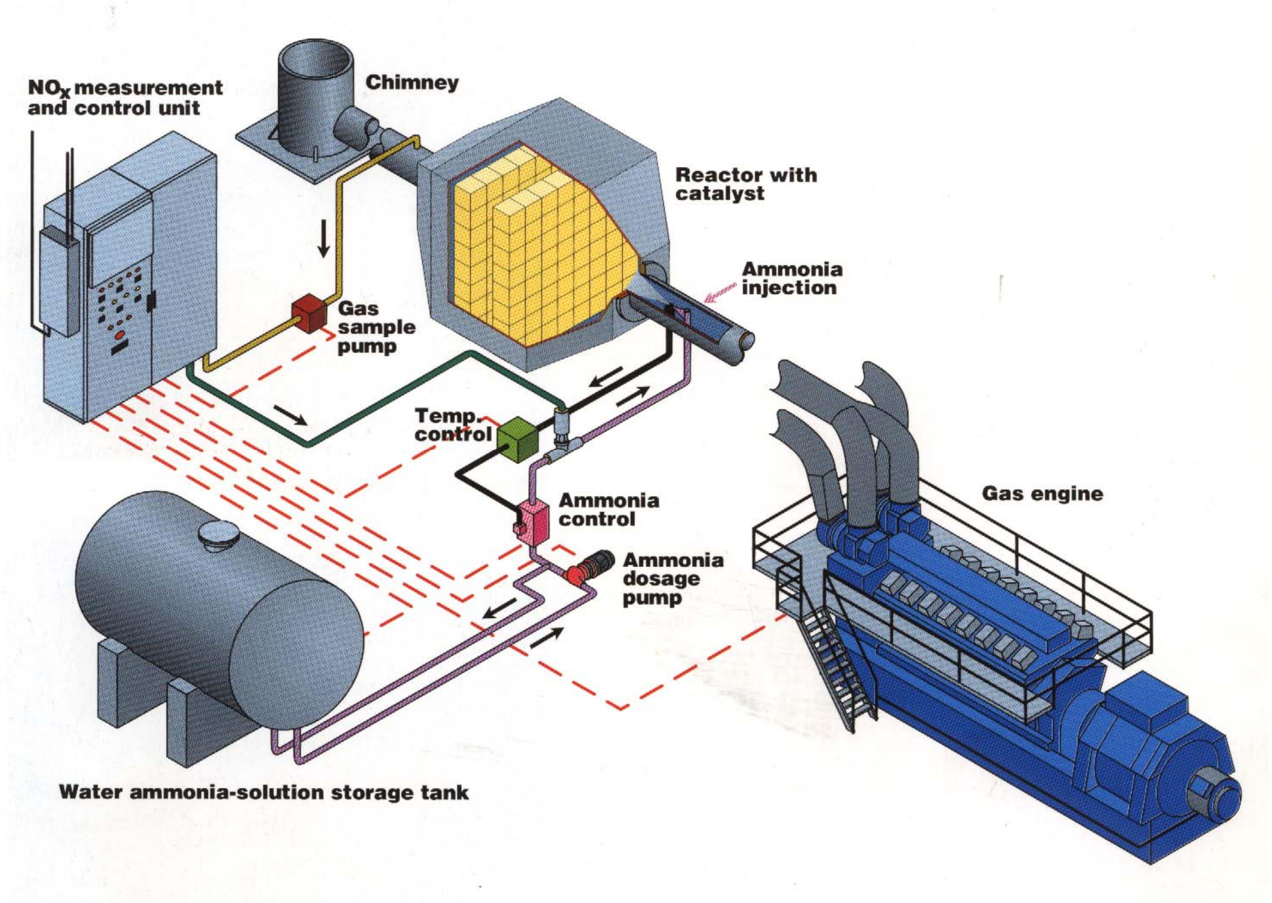


Illustration 9. SCR reduction in gas engines. Source Wärtsila Netherlands.

7.7 Ammonia (NH_3)

7.7.1 What is ammonia

When under pressure ammonia is a gas condensed to liquid with a stinging odour. When dissolved in water considerable heat development originates. Ammonia reacts violently with oxidants and acids.

7.7.2 Physical qualities

Colour: colourless (liquid as well as gaseous)

Smell: tingling en suffocating
Smell limit 15 to 30 mg/Nm^3

Density of the gas: 0,597 compared to air at 0,1013 MPa en 0 ºC

Density and specific volume of liquid ammonia		
0 °C	**Density kg/m^3**	**Specific volume m^3/kg**
- 30	677.7	0.0014747
- 20	665.0	0.0015037
- 10	652.0	0.0015338
0	638.6	0.0015660
10	624.7	0.0016008
20	610.3	0.0016386
30	595.2	0.0016800
40	579.5	0.0017257
50	562.9	0.0017766

Triple point:	-77.74 ºC	0.0607 bar	(0.00607 MPa)
Critical point:	132.4 ºC	114.8 bar	(11.48 MPa)
Boiling point:	-33.4 ºC	1.013 bar	(0.1013 MPa)

Triple point (melting point):
That value of temperature and pressure where a solid substance, gas and liquid can coexist simultaneously in mutual balance.

Under normal terms of use, between triple and critical temperatures and pressures, ammonia occurs as gas, liquid or as a gas/liquid mixture.
Ammonia only becomes a solid below the triple point. Under normal atmospheric conditions 1.013 bar (0.1013 MPa) and 15 ºC ammonia is gaseous and much lighter than air.

Vapour pressure:
Vapour pressure is the pressure on which the vapour is in balance with the liquid under a certain temperature.
The pressure which liquid ammonia is stored in a pressure vessel depends on the temperature in which it is located.
In very severe cold this pressure could reach a value that would be too low to use in the process.