NO$_X$OUT®

Operation Experience with Non-Catalytic NO_X-Reduction in Small and Medium Size Combustion Plants

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FUEL TECH

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Introduction

The NO_xOUT-process is a SNCR process which provides an economical solution for meeting the requirements for NO_x-reduction from fossil fuel and waste fuel combustion sources. The NO_xOUT-process uses urea based chemicals as primary reduction agent and has been applied in a variety of commercial applications using coal, fuel oil, wood, waste, sludge or other fuels.

In this paper the principals of the NO_xOUT-process will be briefly described. Results and experiences will be illustrated with several case studies.

Principals of the NOxOUT process

The NO_xOUT-process removes nitrogen oxides (NO_x) by injecting an aqueous solution of special chemicals into the flue gas stream of a combustor. The overall post-combustion reaction for reducing NO_x with urea is

$$NH_2CONH_2 + 2NO + 1/2\,O_2 \rightarrow 2N_2 + CO_2 + 2H_2O.$$

The reaction products are nitrogen (N_2), water (H_2O) and carbon dioxide (CO_2), which are all natural components of the atmosphere. Within the temperature window (fig.1), the NO_x versus temperature curve consists of three zones: left side, right side and plateau.

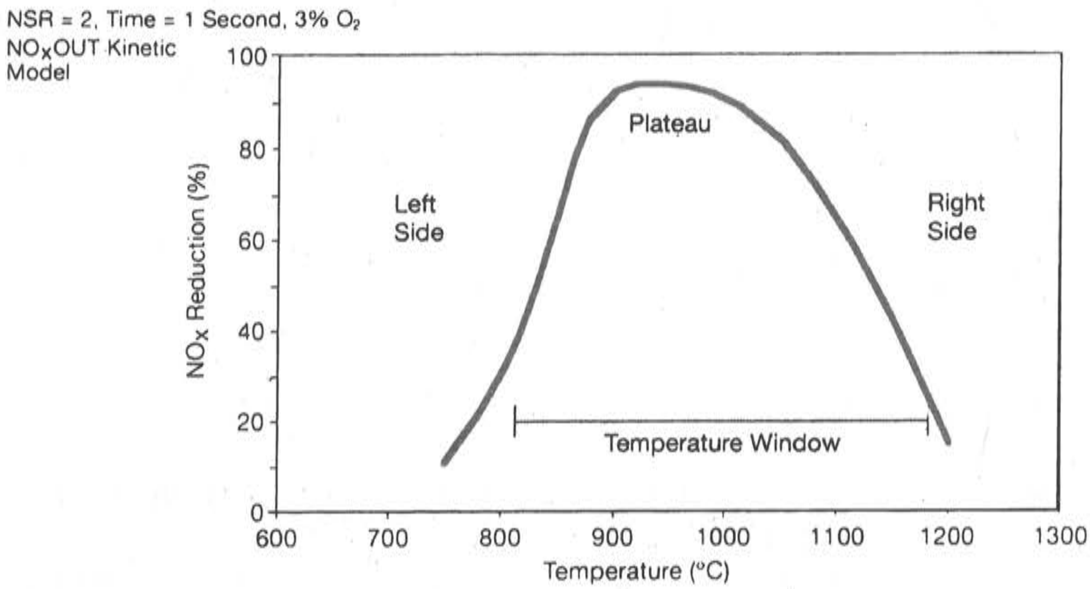


Fig. 1: NO_x-Reduction as a Function of Temperature

At temperatures lower than this window, reductions are negligible and ammonia slip is high. At the left side of the curve, NO_x-reduction increases with increasing temperature; ammonia slip is still significant.

At the plateau, reaction rates are optimum for NO_x-reduction; ammonia slip is decreasing. A temperature variation in this zone has only a small effect on NO_x-reduction.

A further increase in temperature beyond the plateau zone to the right side decreases reduction and also decreases ammonia slip to negligible amounts. At temperatures beyond the right side, NO_x increases above the baseline value.

To minimize the ammonia slip operation at the right side is recommended although the reduction is less than the maximum.

In order to assure high NO_x-reduction also at different loads, the NO_xOUT-process uses specialty chemicals, which shift or expand the temperature window so that an injection at different temperatures becomes possible (fig. 2). Also, injection at different levels allows to follow the optimal temperature window as load varies.

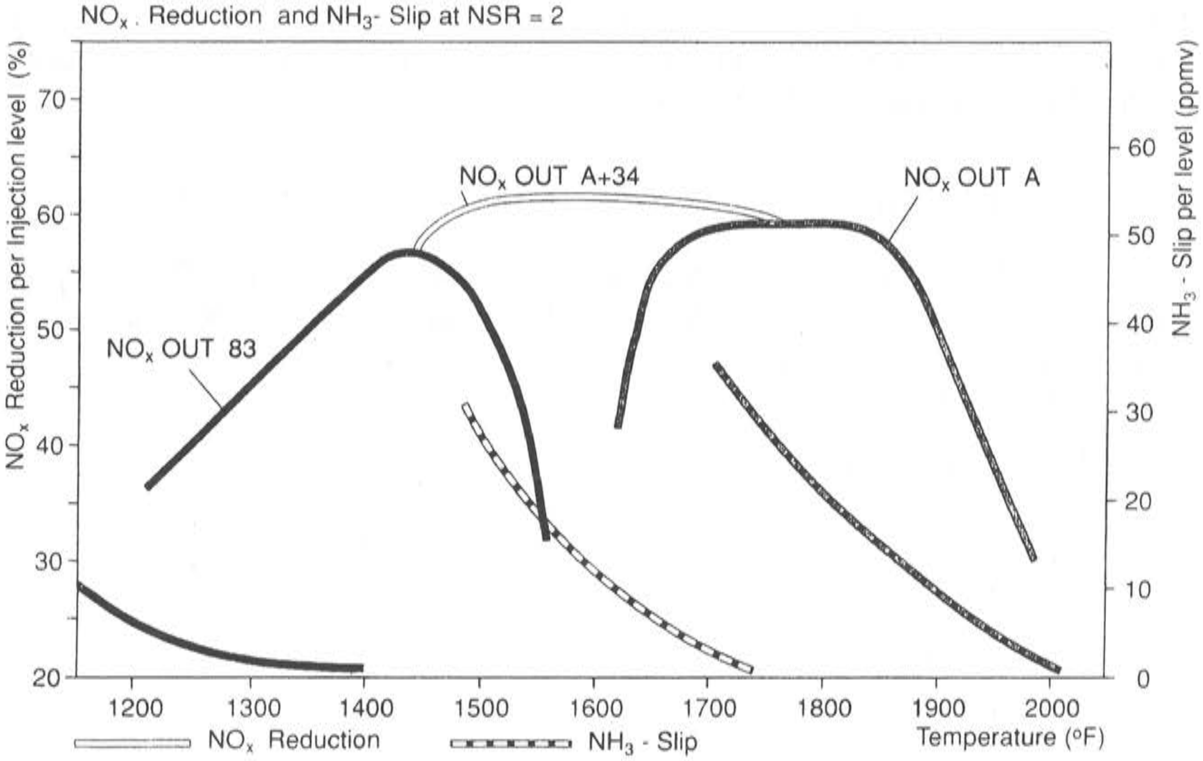


Fig. 2: Performance of NO_xOUT Chemicals

An independent German research institute has determined the NO_xOUT chemicals to be environmentally safe; their use does not result in addition harmful emissions listed in "TA-Luft". The handling of the chemicals is very simple. For storage, only conventional non-pressurized tanks with an overflow basin are required.

The NO_xOUT-process consists of the following four steps:

1. Distribution and mixing of the liquid droplets within the flue gas stream.
2. Evaporation of the water in which the reduction chemicals are diluted.
3. Decomposition of the reduction chemicals to form the active NH_2-radical.
4. Gas phase reaction between NH_2 and NO_x.

In order to achieve optimum results the design of the injection system is equally important as the selection and mixing of the reduction chemicals. A simplified, but typical flow diagram for a NO_x-reduction of approx. 50% can be seen in fig. 3.

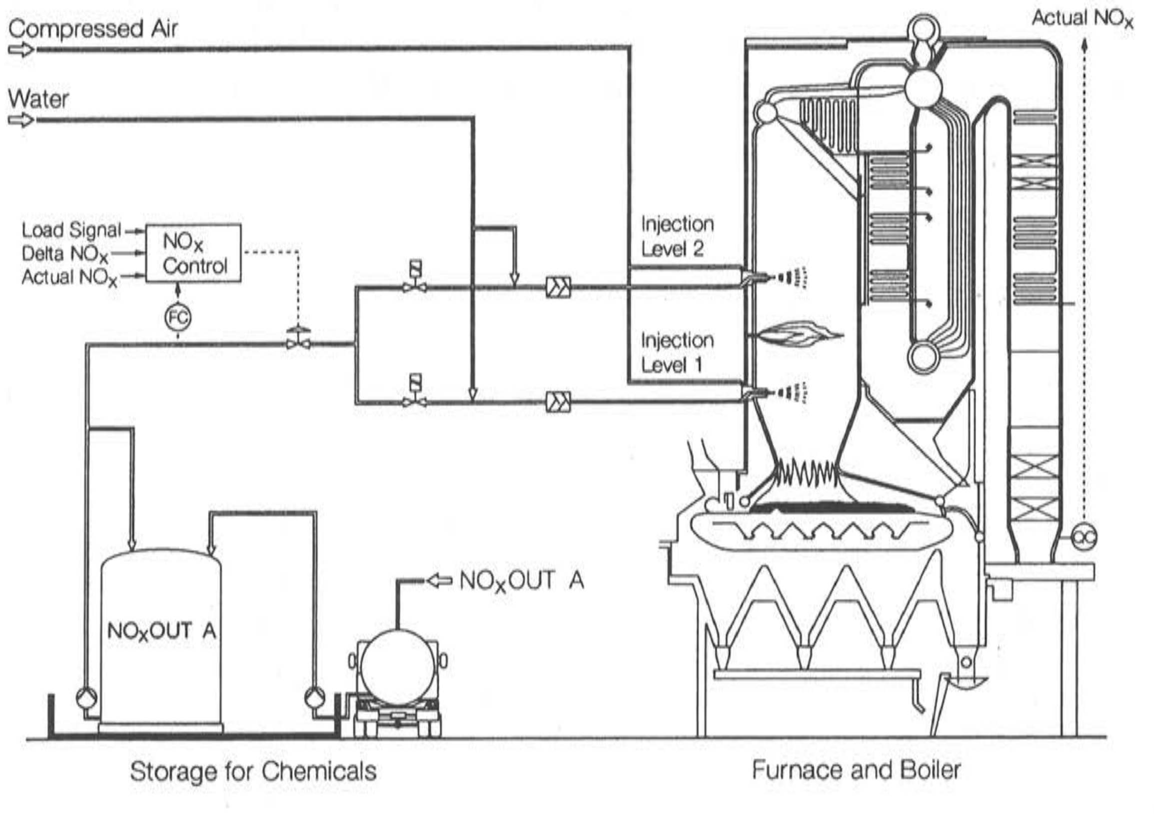


Fig. 3: Process Flow Diagram - District Heating Plant Strakonice

Operation Experience

Municipal Waste Incinerators

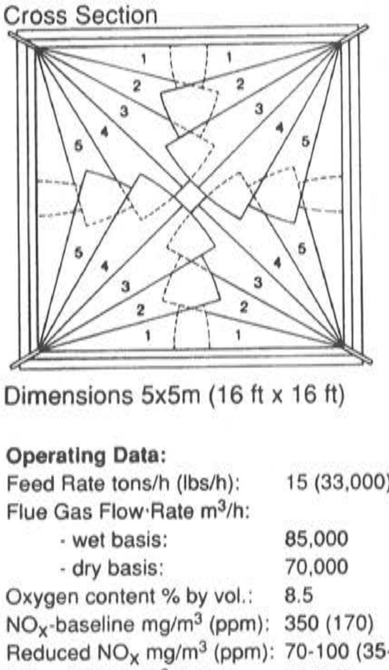
At the end of 1989 a demonstration of the NO_xOUT-process has been performed at one of the four lines of the municipal solid waste incineration plant in Frankfurt. Each line has a capacity of 15 t/h of municipal solid waste. The flue gas volume per boiler is 97.000 m^3/h, whereas the NO_x-emissions at the time of the demonstration varied between 370 and 420 mg/Nm^3, dry as NO_2 (all NO_x-numbers mentioned in the following are expressed as NO_2).

The objective of the demonstration was to prove that the NO_XOUT-process is suitable to achieve NO_X-values of less than 100 mg/m³ with a minimal ammonia slip at continuous operation. The system had to follow all typical operation conditions of the municipal waste incinerator such as

- changing flue gas quantity
- changing flue gas temperature at the injection level
- uneven distribution of NO_X in the flue gas.

At the NO_X-baseline of 400 mg/m³ which is relatively low compared to other combustion systems the average NO_X-reduction per injection level is approximately 50%. Because a reduction of more than 75% was required three injection levels were installed in the furnace walls above the grate where the temperature was appropriate for the process. As reduction chemicals the urea based NO_XOUT A and for low temperatures NO_XOUT 83 were used (fig. 4).

Cross Section



Dimensions 5x5m (16 ft x 16 ft)

Operating Data:

Feed Rate tons/h (lbs/h):	15 (33,000)
Flue Gas Flow·Rate m³/h:	
- wet basis:	85,000
- dry basis:	70,000
Oxygen content % by vol.:	8.5
NO_X-baseline mg/m³ (ppm):	350 (170)
Reduced NO_X mg/m³ (ppm):	70-100 (35-49)
NH_3 - Slip mg/m³ (ppm):	12 (16)
NO_XOUT A-kg/h (lbs/h):	100 (220)
NO_XOUT 83-kg/h (lbs/h):	20 (44)

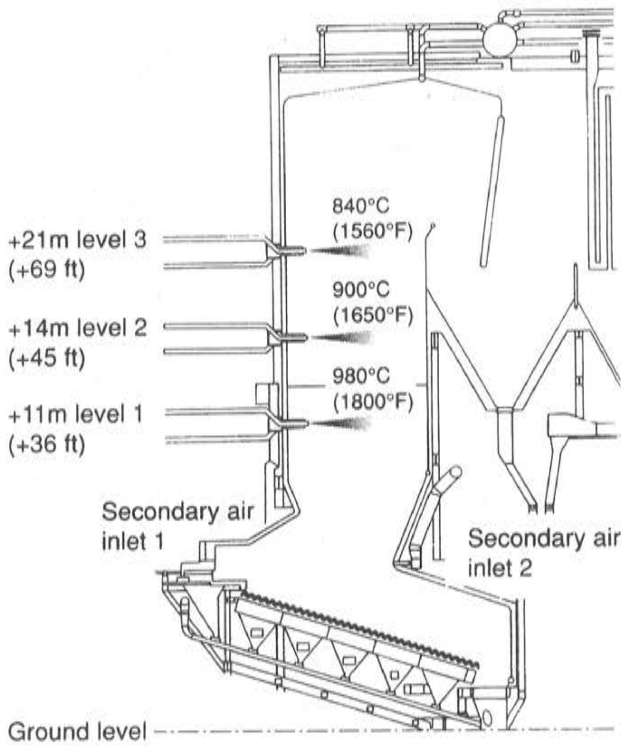


Fig. 4: Municipal Solid Waste Incinerator Frankfurt

Beside the required NO_x-level of less than 100 mg/m³ a low ammonia slip was of great importance. As expected the ammonia slip increased with the NO_x-reduction (fig. 5). At a NO_x-level of 100 mg/m³ the ammonia slip could be controlled at 10 mg/m³ and at 70 mg/m³ at 15 mg/m³.

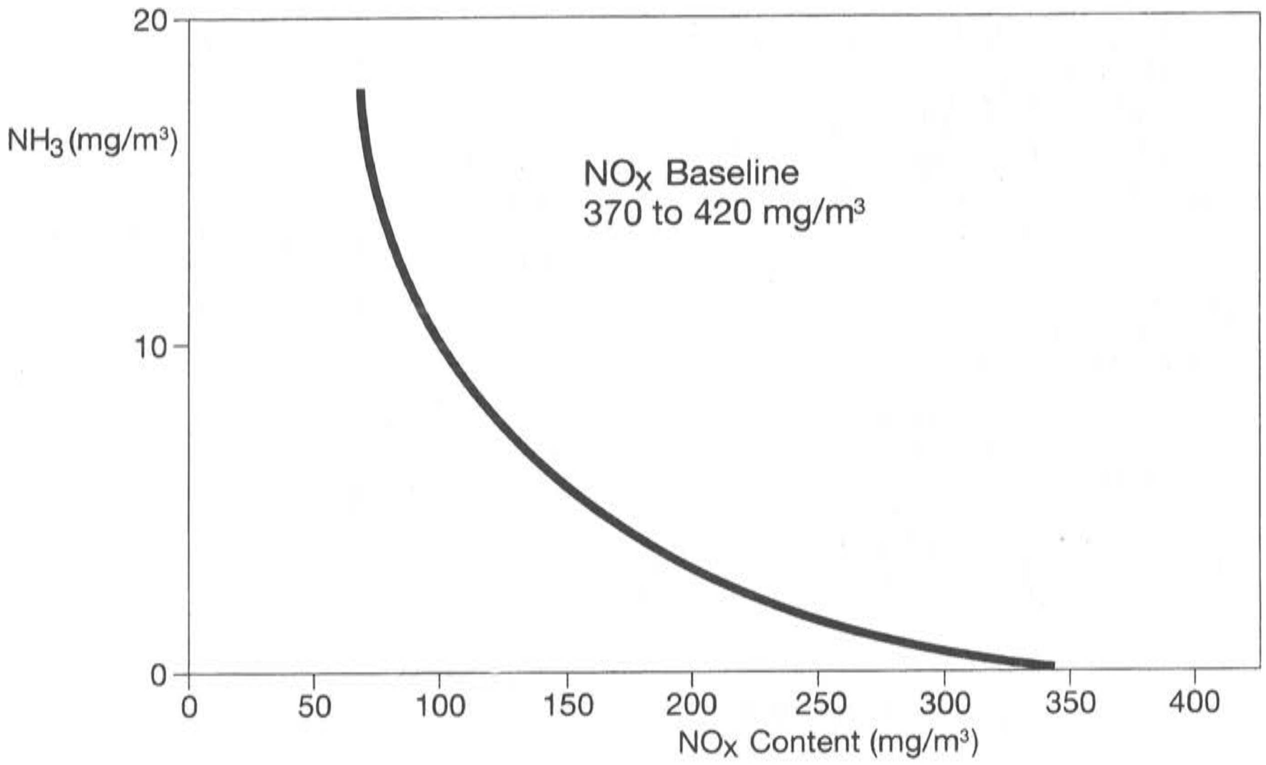
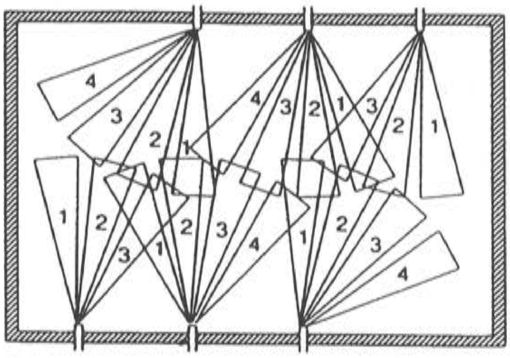


Fig. 5: Ammonia Slip in Relation to NO_x-Content in Clean Gas at Municipal Waste Incinerators

Based on these results the city of Frankfurt decided to equip all four lines with the NO_xOUT-system. The commercial plant is being commissioned now and expected to be handed over to the customer in the middle of 1995.

In the meantime more than four years of experience of continuous operation have been gained with a NO_xOUT-plant at the two incinerators for municipal waste at RZR Herten in Germany. The process was designed to comply with the German regulations (17. BImSchV) which permits a maximum NO_x-level of 200 mg/m³. Since the maximum NO_x-baseline did not exceed 380 mg/m³ only one injection level with the reductant NO_xOUT A was sufficient. The results and the principle of injection can be seen on figure 6. The NO_xOUT-plant worked very reliably since the first day of operation and did not affect the performance of the incinerator. The costs for reduction chemicals for this plant were less than 1.-- DM per metric ton of municipal waste.

Cross Section



Dimensions 7,8x5,25m (25,5x17 ft)

Operating Data:

Feed Rate tons/h (lbs/h):	20 (44,000)	
Flue Gas Flow Rate m^3/h:		
- wet basis:	115,000	
- dry basis:	100,000	
Oxygen content % by vol.:	7.0	
NO_x-baseline mg/m^3:	320	
	Operating	**Demonstration**
Reduced NO_x mg/m^3 (ppm):	180 (88)	120 (58)
NH_3 - Slip mg/m^3 (ppm):	2 (2.6)	7 (9)
NO_xOUT A-kg/h (lbs/h):	45 (100)	70 (154)

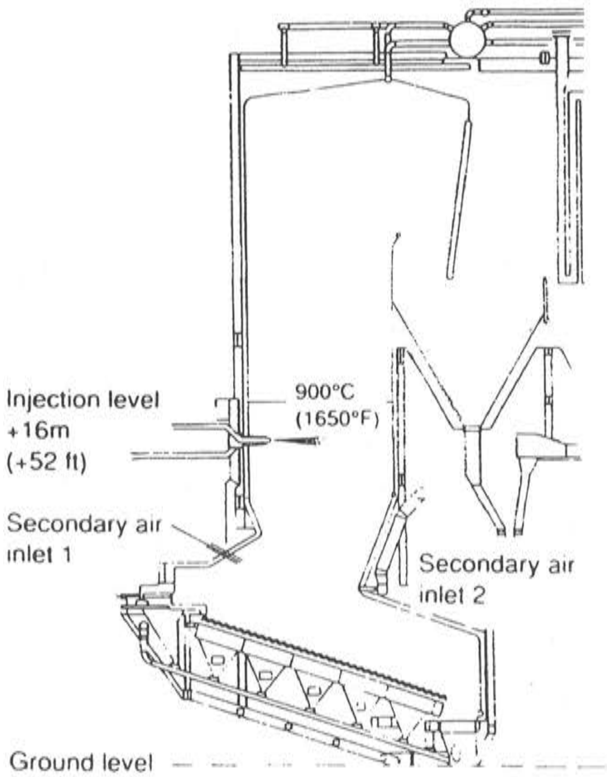


Fig. 6: Results and Principle of Injection - RZR Herten

The results of the four lines of the municipal waste incineration plant in Hamm which are in operation since early 1994 as well as those of the long term test in Bremen during 1994 are comparable to the ones in Herten.

In all of the above mentioned applications the ammonia-slip could be controlled at levels around 5 mg/m^3 and the typical odour of ammonia could neither be smelled in the plant itself nor in the by-product of the flue gas cleaning process. This process in Herten consists of a two stage wet scrubber with lime slurry and a spray dryer. In Frankfurt, Bremen and Hamm semi-dry-systems are installed.

Brown Coal Fired Boilers

In December 1991, Nalco Fuel Tech received the contract for the delivery, installation and commissioning of the NO_xOUT system for boiler No. 1 at the District Heating Plant of Strakonice, Czech Republic (fig 7).

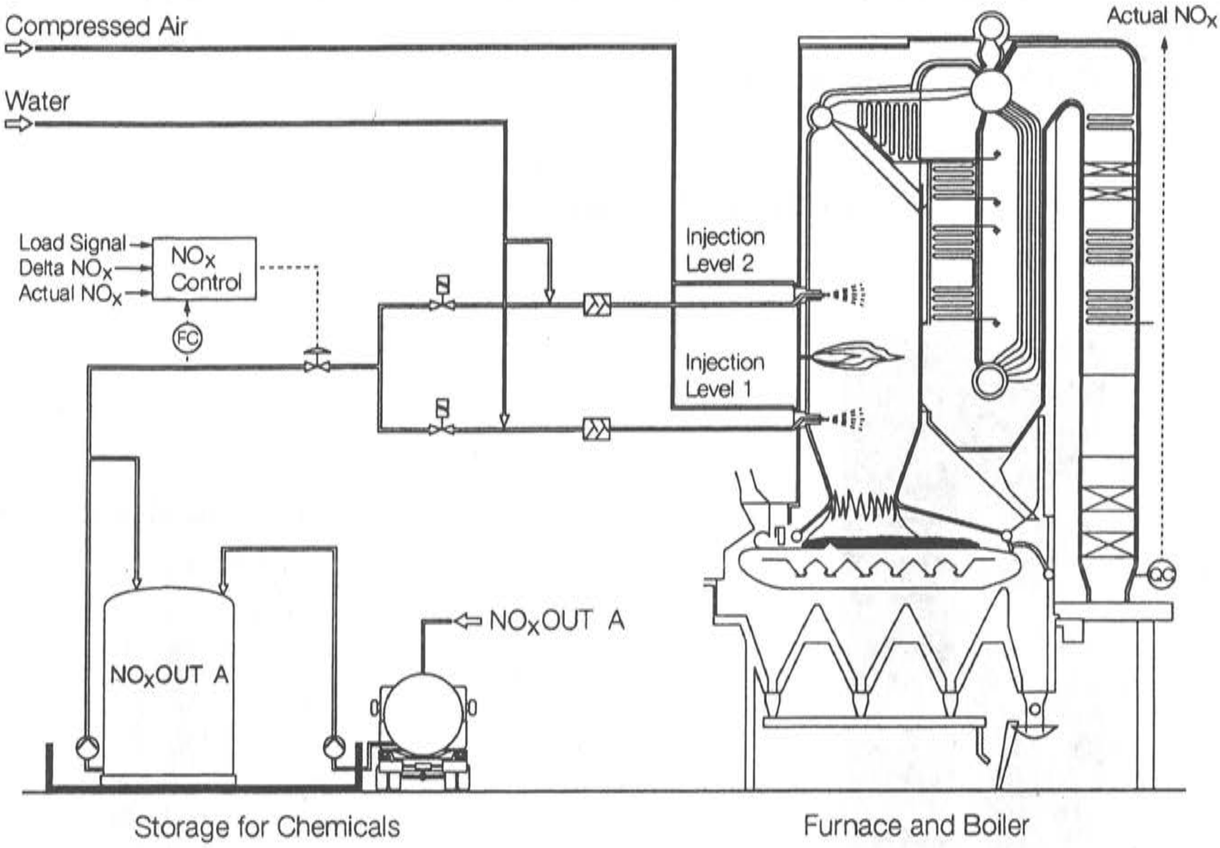


Fig. 7: District Heating Plant Strakonice

The system has to comply with the following criteria:

- NO_x-reduction of more than 50%
- low investment cost
- low space requirements
- short shut-down-time of the boiler
- no decrease of the boiler capacity.

The installation started in August 1992. The first installation of the injection lances could be done without shut-down of the boiler. The necessary injection ports were mounted during a planned boiler service shut down.

In December 1992 the NO_xOUT-system was commissioned and is in operation since then.

Before designing the NO_xOUT plant, flue gas temperatures were measured at different boiler loads in order to define the optimal position for the injectors. Furthermore, NO_x, CO and O_2 were measured for confirmation respectively completion of the previously given flue gas data.

In addition to the temperature measurements the process conditions such as flue gas temperatures and flow fields at different loads were evaluated using computer aided fluid dynamics (CFD) modeling techniques (fig. 8).

Side Sectional Temperature Profile - 30 t/h Steam

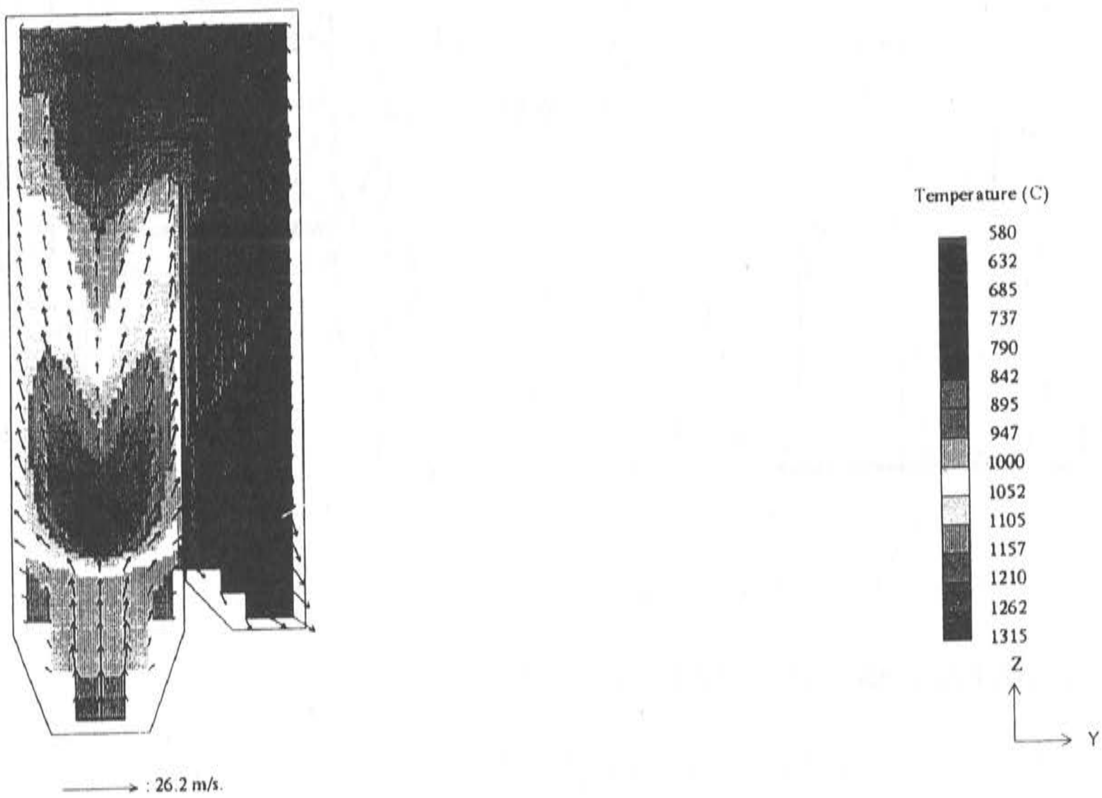


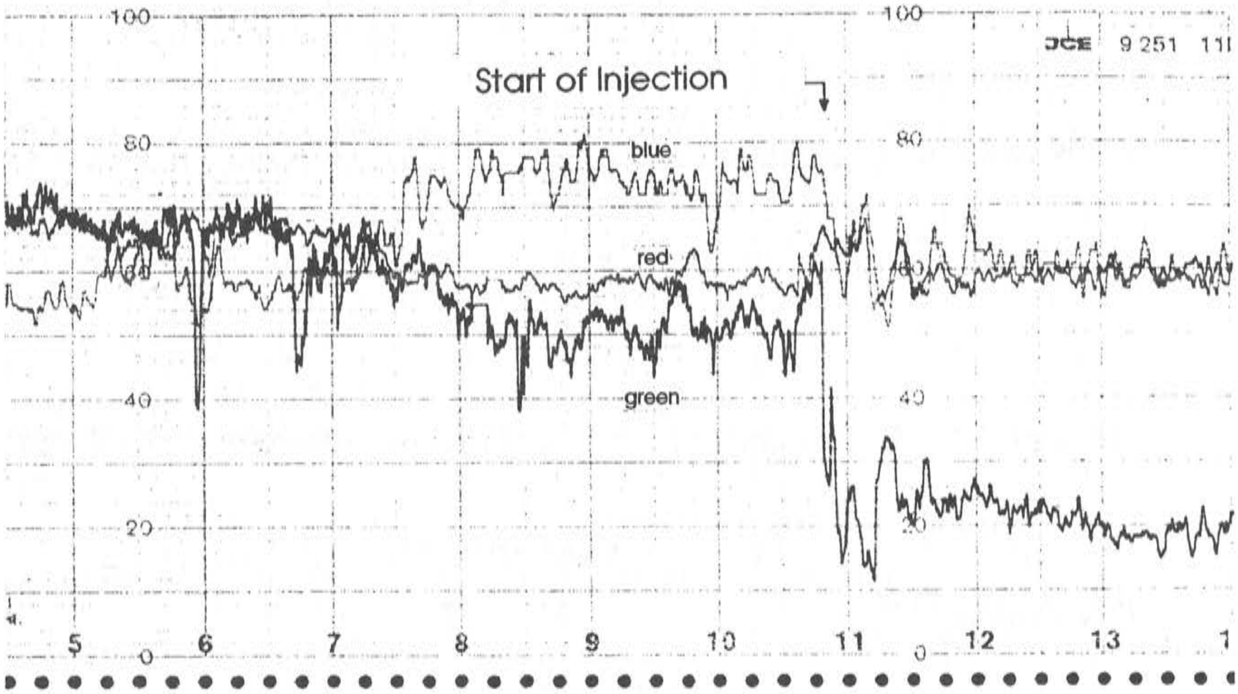
Fig. 8: Results of Computer Aided Fluid Dynamics Modeling

As the final design basis the process performance was analyzed using a chemical kinetic computer model. It showed that the low cost reduction agent NO_xOUT A can be used over the whole load range of the boiler.

After a short period of optimization and adjustment of the automatic control system the guaranteed NO_x-reduction of 50% could be maintained or exceeded over the whole load range. The consumption of NO_xOUT A was always below the guaranteed values.

The ammonia slip in the flue gas after the boiler varied between 2 - 5 mg/Nm^3. Negative influences on components downstream of the boiler like deposits of ammonia salts on heating surfaces could not be noticed until today.

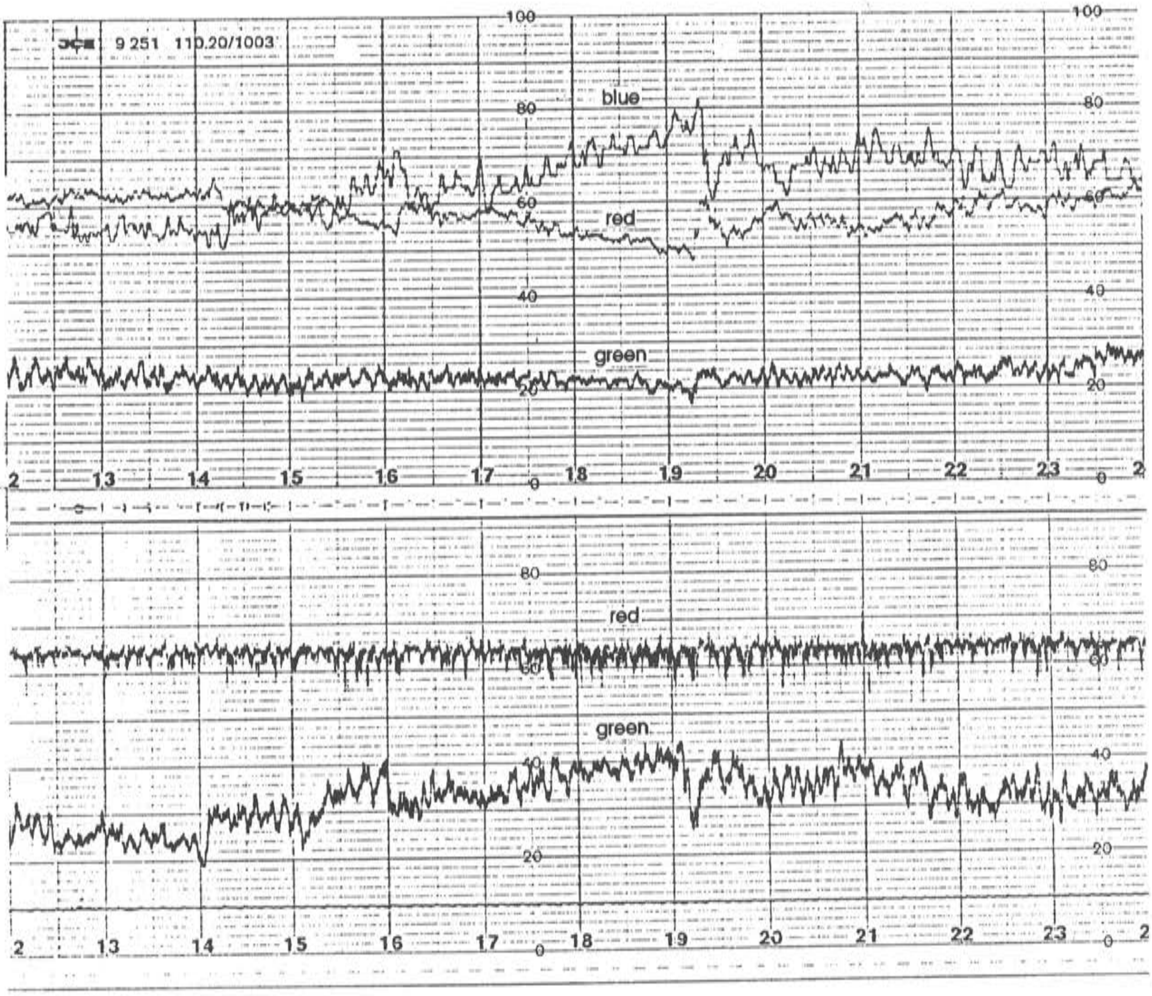
On the diagram (fig. 9) the measured NO_x-value in the flue gas can be seen with and without injection. It is clearly visible how the NO_x-value decreases immediately after injection of NO_xOUT A.



Blue:	Boiler load:	0 - 50 t/h steam
Red:	O2:	0 - 21 %
Green:	NOx:	0 - 1000 mg/Nm³

Fig. 9: Registration of Measurements

Fig. 10 shows a constant NO_x-value at varying boiler loads. It also shows that the consumption of NO_xOUT A varies with changing boiler loads. The water consumption, however, remains constant independent of the boiler load.



Blue:	Boiler load:	0 - 50 t/h steam
Red:	O2:	0 - 21 %
Green:	NOx:	0 - 1000 mg/Nm³
Red:	Water:	0 - 1200 kg/h
Green:	NOxOUT A:	0 - 300 kg/h

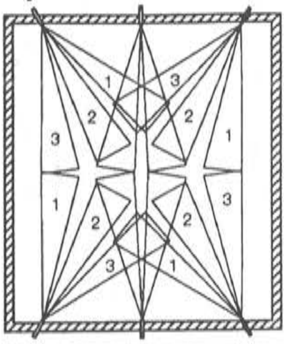
Fig. 10: Registration of Measurements

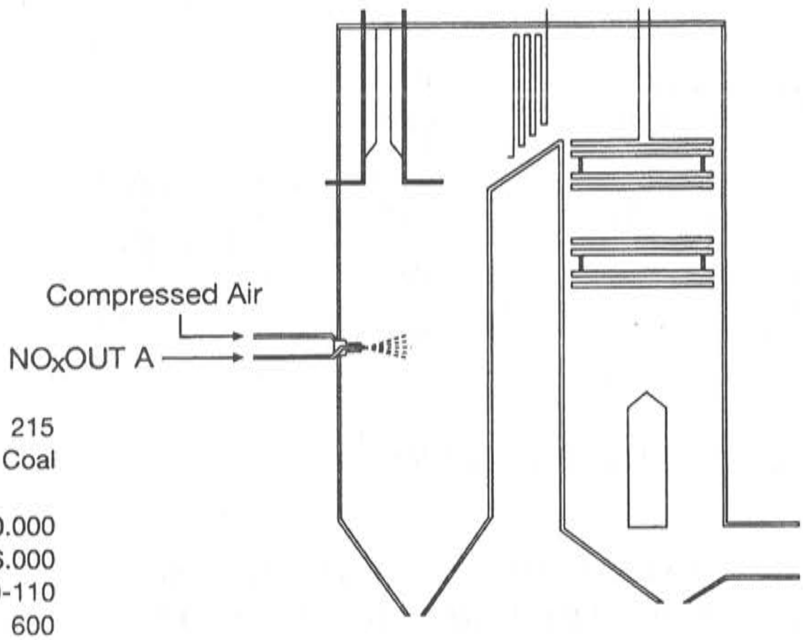
After several months of operation major problems with the NO_xOUT-system did not occur. It still works with the first set of injectors. In May 1994 an identical system for the second boiler was put into service.

Hard Coal Fired Boilers

Fig. 11 shows the operation results which have been obtained with a hard coal fired boiler with a steam capacity of 215 t/h of the District Heating Plant Vitkovice in Ostrava. This plant was the first $DeNO_x$ plant in the Czech Republic and has been put into operation in summer 1992. The guaranteed NO_x-reduction from 600 to 300 mg/m³ has been obtained immediately after start-up with a remarkable low NH_3-slip of approx. 3 mg/m³. Major operation problems have not been reported until today.

Injection Level +16,3 m





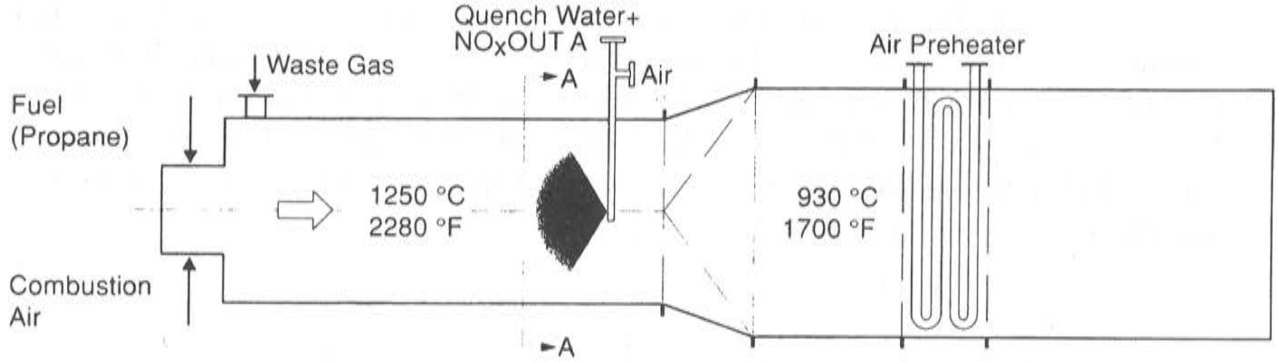
Operating Data:

Steam Capacity (t/h):	215
Fuel:	Hard Coal
Flue Gas Flow Rate (m³/h)	
wet basis:	170.000
dry basis:	156.000
Load Range (%):	40-110
NO_x-Baseline (mg/m³):	600
Reduced NO_x (mg/m³):	250
NH_3 -Slip (mg/m³):	3
Reductant Chemicals	
NO_xOUT A (kg/h):	‹350

Fig. 11: District Heating Plant Vitkovice

Thermal Incinerators

This application shows that the size of the droplets is of importance for the NO_x-reduction. The waste gas of a soil decontamination plant is heated up in a thermal incinerator in order to decompose dioxins and furans (fig. 12). The flue gas quantity is between 7.000 and 10.000 m³/h.



Operating Data:

Flue Gas Flow Rate, m^3/h:	7000 to 10000		
Flue Gas Temperature, °C (°F):	approx. 1250(2280)		
	Case 1	**Case 2**	**Case 3**
NO_x - baseline, mg/m^3 (ppm):	1200(585)	1400(682)	2200(1071)
Reduced NO_x, mg/m^3 (ppm):	480(234)	550(268)	800(390)
NH_3 - Slip, mg/m^3 (ppm):	16(21)	20(26)	22(29)
Reductant Chemical:	NO_xOUT A		
Injection System:	1 Injector with 16 nozzles		

View
A - A

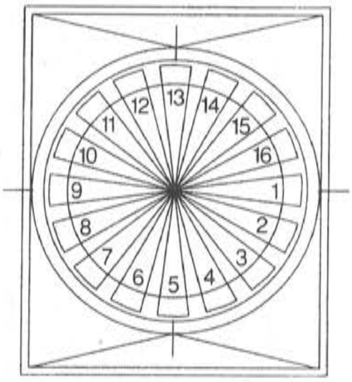


Fig. 12: Thermal Incinerator

During the commissioning phase the NO_x-baseline increased up to 2.300 mg/m³ whereas the only location for the injection which permits sufficient time for the reaction is in the cylindrical duct between the injection and the aircooler.

The flue gas temperature in this area was with approximately 1.250° C outside the temperature window where urea or ammonia are effective so that cooling down of the flue gases normally would be necessary.

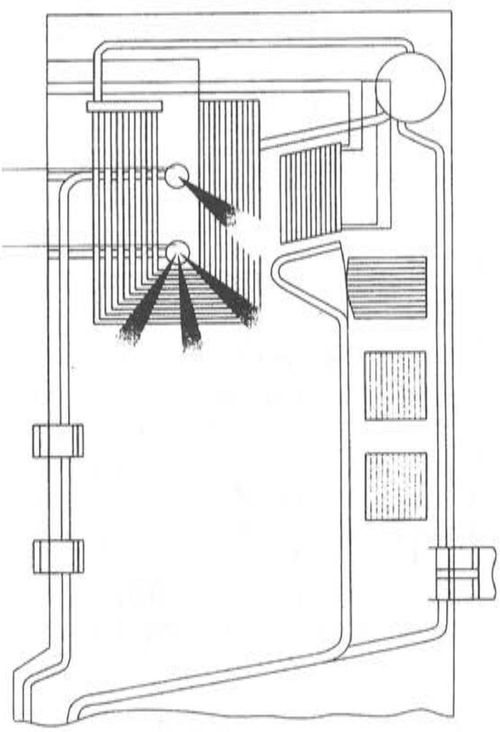
With the NO_xOUT-process the optimal place and temperature for the reaction can be defined in advance with the size of the droplets and the quantity of water. This is one of the major advantages of NO_xOUT-chemicals compared with ammonia or ammonia water. The decomposition of NO_xOUT-chemicals to NH_2-species can only start after the dilution water is evaporated, whereas ammonia immediately evaporates, when the dilution water is being heated up. In this particular case it would react outside the temperature window and increase NO_x instead of reducing it.

The results which have been obtained with the NO_xOUT-process are remarkably good and are with 65% NO_x-reduction similar to lab results in flame tubes with ideal conditions.

Heavy Oil Fired Boilers

In the District Heating Plant Linz nine boilers are operating with different flue gas quantities and compositions. At the beginning of 1990 trials were conducted with the NO_xOUT-process in order to prove that the expected NO_X-regulations of max. 200 mg/m³ could be met.

For the trials the heavy oil fired boiler No. 2 with a steam capacity of 100 t/h was selected (fig. 13). This boiler has the worst preconditions for the application of the NO_xOUT-process of all nine boilers and it was assumed that if the requested NO_X-reduction could be achieved with this boiler it could be easily reached with all other boilers as well.



Operating Data:

Flue Gas Flow Rate, m³/h:	93.700
Load Range %:	50-100
Oxygen content, % by vol:	3
NO_X -baseline, mg/m³ [ppm]:	500-600 (250-300)
Reduced NO_X, mg/m³ [ppm]:	<200 (100)
NH_3-Slip, mg/m³ [ppm]:	<15 (20)

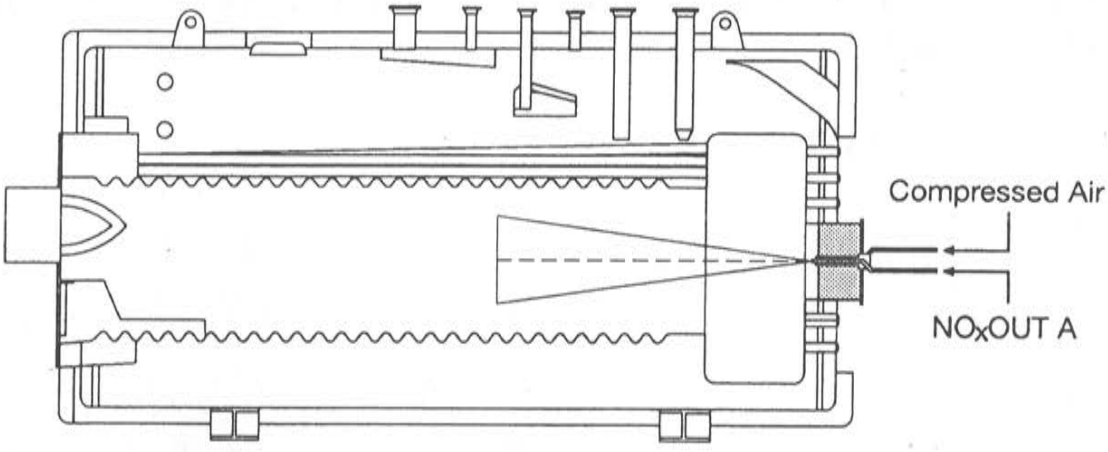
Reductant Chemicals: NO_xOUT A + 34
NO_xOUT 83
Injection System: Watercooled Injectors

Fig. 13: Oil Fired Boiler - ESG, Linz

The flue gas quantity at full load was 93.700 m³/h. The NO_X-concentration varied between 500 to 600 mg/m³ depending on the Nitrogen-content in the fuel oil and boiler load and should be reduced to max. 200 mg/m³. The temperature range which offered the best conditions for all loads was within the superheater. This required that the chemicals had to be injected between the superheater coils which have only approx. 600 mm space between each other.

For injection water cooled in-furnace-lances were specially designed and manufactured. The nozzles were arranged in such a way that they sprayed into the middle of the spaces between the heater coils. The working length of the lances was more than three meters. The demonstration showed that with two injection levels a NO_X-concentration of 200 mg/m³ with a max. NH_3-slip of 15 mg/m³ could be achieved. This corresponds with a NO_X-reduction of 65 - 70%.

Lots of experiences have been gained with heavy fuel fired package boilers with a capacity of 5 - 50 MW_{th} (fig. 14). The NO_x-baseline of these boilers typically varies between 600 to 750 mg/m³ and has to be reduced to 450 mg/m³ according to the German regulations (TA-Luft). Although there is no ammonia limit set by regulations a max. ammonia-slip of 20 mg/m³ could be maintained in general so that secondary problems downstream the boiler did not occur under all operating conditions.



Operating Data:

Flue Gas Flow Rate (m³/h)	9.600
Fuel:	Heavy Oil
Load Range (%):	25-100
NO_x-Baseline (mg/m³):	780
Reduced NO_x(mg/m³):	‹450
NH_3-Slip (mg/m³):	‹30
Reductant Chemical:	NO_xOUT A
Injection System:	Wall Injector

Fig. 14: Fire Tube Boiler

These package boilers of which to date approx. 50 are in operation generally have to supply the heat resp. the steam as required from the consumers in different industrial applications. Therefore load ranges often vary between 25 to 100%. In order to keep the investment cost low a compact standard module has been developed. For these small applications continuous measuring of NO_x is not required.

The NO_x-quantity is a function of the boiler load resp. the fuel oil quantity. Therefore for the dosing of the chemicals the load signal is sufficient. Because of the wide range the varying of the reduction chemical is not sufficient to achieve optimal NO_x-reduction. In order to follow the temperature window and the changing of flue gas velocity the droplet sizes also have to be varied. This is being done with varying of the water quantity which usually is kept constant at larger boilers.

The ammonia content in the by-product is considerable higher and can be explained by the lower exit temperature at the flue gas cleaning of approximately 140° C. As expected the ammonia captured in the by-product is increasing with the ammonia slip. If the MSW plants are being operated according to the German regulations (200 mg/m³) the ammonia-slip can be controlled at levels of approx. 5 mg/m³. At these levels the ammonia in the by-product did not exceed 100 mg/kg.

At levels of approx. 130 mg/kg the by-product can be disposed. Higher ammonia levels should not cause a major problem because of the high pH-value the ammonia evaporates immediately when the product gets into contact with water. This causes of course the typical ammonia smell but also simplifies the treatment of the product if required. With ammonia contaminated by-products also can be blended with non-contaminated products, so that the ammonia content of the mixture can be kept below the acceptable limits.

If wet scrubbing systems are installed practically all ammonia of the flue gas is captured in the waste water which may require an additional ammonia stripper. In Germany the limit is 10 mg/kg if the water is being released into the rivers.

Summary

In many different applications it has been proven that the desired NO_x-level can be achieved with the NO_xOUT-process.

The results of these plants indicate that the reliability of a boiler practically is not being influenced by the operation of the NO_xOUT-system. Regarding the economy the NO_xOUT-process is less costly than the SCR-process with only a few exceptions where high quantities of NO_x have to be removed and/or ammonia slip is of concern.

Beside the low investment cost which are approx. 10 - 20% of a comparable SCR-system this SNCR-process provides a number of advantages to the owner of combustion plants. The process is applicable to standard industrial boilers, refinery process heaters, power- and heating plants, regardless of the fuel used. The ammonia-slip is lower than in other SNCR systems and generally does not cause any problems.

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