

Potentials and Limitations with respect to NO_x-Reduction of Coke Plants

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Abstract: During combustion processes within heat flues of conventional coke ovens substantial amounts of nitrogen oxides (NO_x) are generated mainly as a function of local flame temperature and excess air coefficient. Within the last decades growing public awareness of the need to protect the environment has been reflected in a number of national statutes specifying rigorously the limits for atmospheric pollutants and hazardous substances like NO_x. However, most recent publications propose to reduce the existing limits even further in special areas down to 150 mg/Nm³, possibly leading to uneconomic plant concepts and operating temperatures in the future. To be in compliance with those new limitations is one of the key challenges facing companies active in the design and construction of coke ovens. For that reason, the paper presented investigates on the potentials and limitations of various primary and secondary measures, available to reduce NO_x-emissions, as well as on alternative plant concepts. In addition, TKIS has decided to validate and broaden the design criteria for heat flues with an in-depth theoretical investigation of the process using a complex flow and staged combustion model based on a finite volume analysis in order to achieve an optimized design of gas, air and flue gas cross sections regarding minimized NO_x-formation. The three-dimensional, transient flow model allows key influencing quantities on NO_x-formation and the main process parameters, such as maximum allowable heat flue temperature, local excess air coefficient as well as optimum vertical position of binder air stage and turning point, to be predicted. Thus, the model enables the limits of application for this coking technology to be worked out with respect to the compliance of new limits on nitrogen oxide of approx. 150 mg/Nm³.

Key words: NO_x-emission of coke ovens, primary reduction methods, secondary reduction measure, heat flue design, combustion and flow simulation

1 Introduction

Growing public awareness of the need to protect the environment has been reflected in a number of national statutes specifying the limits for atmospheric pollutants and hazardous substances. Of particular importance for coke oven plants are emissions of nitrogen oxides (NO_x).

While the national standards limit the admissible NO_x-emissions at present between 150 and 245 ppm, conditioned by 5-7% oxygen content in the waste gas, reissued editions stipulate limits of less than 75 ppm in „special areas“, even for coke oven gas heating [1]. To be in compliance with those new limitations is one of the key challenges facing companies active in the design and construction of coke ovens.

In all combustion processes nitrogen oxide is formed from the nitrogen of air and fuel. In total, there are four NO_x-formation mechanisms known. While the prompt, the NO₂- as well as the N₂O-formation are negligible or system-immanent, i.e. that are not influenced by design or operation, one has to keep the focus on reducing thermal and fuel NO_x-emission proportions. Owing to the high preheating temperatures of gas and air used for combustion and corresponding high flame temperatures, coke oven batteries produce pollution in form of thermal NO_x, mainly.

Because thermal nitrogen oxide-pollution shares are affected by oven and process design, a reduction of emission has to benefit first from the po-

tential offered by primary reduction measures summarized within the subsequent sheet.

Fig.1 shows the main process parameters, influencing the thermal NO-formation during combustion. In a rough approximation the relevance of particular influencing factors on NO-formation reduces from item 1 to 6. Because they stipulate the NO-formation mechanisms the main influences represent the type of gas chosen for combustion, the heat flue temperature and the local excess air coefficient in the flame [2].

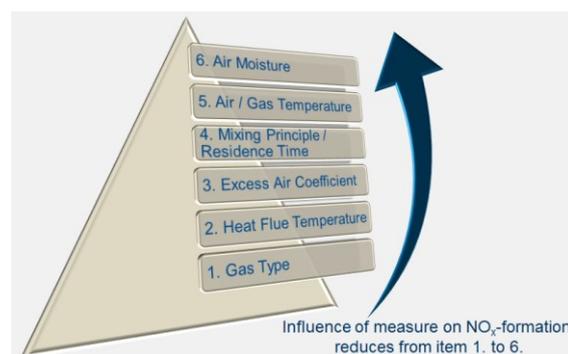


Fig. 1: Main parameters influencing the thermal NO-formation

2 Primary NO_x-reduction measures applicable in conventional coke ovens

The NO_x-concentration for coke oven gas (COG)-combustion is much higher than for the combustion of natural gas (NG) or lean gas (LG). As a basic formula we derive, that under the

same conditions a total substitution of COG by methane would reduce the level of nitrogen oxides down to approx. 50%. This is initially caused by fuel nitrogen components within the coke oven gas like ammonia and hydrogen cyanide reacting to nitrogen oxides immediately within the flame zone. In addition, components within the coke oven gas like benzene, hydrogen, ethylene and ethane are characterized by high combustion temperatures stimulating the thermal NO_x-formation, moreover.

A typical COG contains a methane content of approx. 22-27%. Because the total substitution of COG is often not practicable, to reduce the NO_x-formation one should consider at least the increase of the methane content within the COG by external addition upstream of the batteries.

In case the gas type is fixed, one has to concentrate next on reducing local flame temperatures playing the key role on thermal NO_x-reduction. The local flame temperature in turn depends specifically on air and gas preheating- as well as on oven temperature. The reduction of avg. heat flue temperature is a key instrument for coke oven operators to meet the stringent new requirements placed by the national legislators on NO_x-emissions. The essential factor is the exponential dependence of NO-formation on combustion temperature.

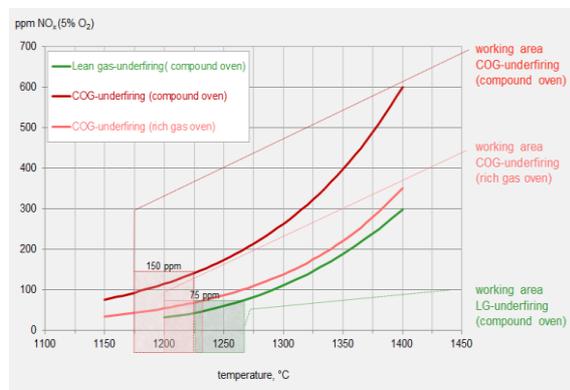


Fig. 2 Practical experience regarding NO_x-pollution as a function of avg. heat flue temperatures

Fig. 2 illustrates some practical experience for three typical modes of operation and oven designs. Normally, a typical coke oven plant is designed both for LG- and COG-application (compound oven). However, its heating adjustment is optimized for LG-mode because of its 95%-usage within a year.

In case of COG-heating, temperatures of approx. 1250°C are established to fall certainly below 150 ppm of nitrogen oxides (oxygen condition 5%). We conclude from Fig. 2, that a plant has to run at uneconomic low temperatures of less than

1150°C in order to meet a potential new limit of less than 75 ppm.

However, so-called rich gas coke oven batteries show a more flexible working area because they are designed and optimized for COG-heating, exclusively. These ovens can even operate up to temperatures of approx. 1230°C in order to keep the lowered limit.

In case of LG-heating there are no uneconomic effects regarding operating temperatures with respect to the new limit, as long as a maximum temperature of 1270°C is kept.

Fig. 3 shows alternative plant concepts for the production of approx. two million tons of coke per year, ensuring low NO_x-emission levels at the same.

Example #1 is prepared for a plant consisting of 140 compound coke oven batteries and demonstrates low NO_x-emissions at the stack of less than 110 ppm. Without changing the typical dual-use design of a compound oven and taking advantage of other effective primary NO_x-reduction measures discussed further below, one of two batteries operates with COG, while the other one is fueled by LG. Both batteries are running at different temperature levels and with different gross coking times.

Example #2 demonstrates an unconventional proposal how to meet a lowered limit of 75 ppm NO_x in the future. While one battery with 70 ovens is exclusively designed as a so-called rich gas oven and optimized for COG- the other one is intended for LG-heating, solely. That means both batteries are operating always with different gas types and temperature levels. This unique combination ensures not only very low NO_x-emissions at the stack, but has the potential to save engineering and refractory investment costs, additionally.

Because the batteries are running with different gross coking times, both solutions proposed require individual sets of machines.

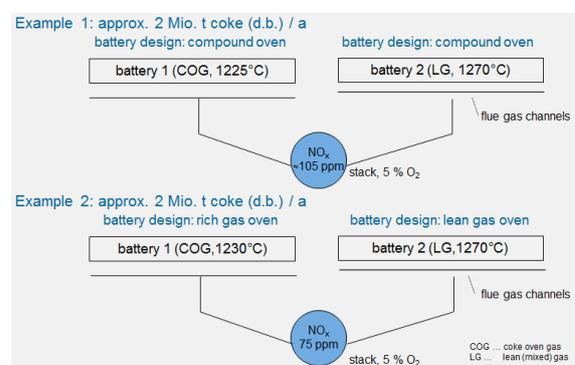


Fig. 3 Alternative plant concepts

Influencing the flame temperature may be additionally realized by the installation of:

- cooling bodies within heat flues
- high emission coatings sprayed on the inner heat flue surface
- water injection / increase of humidity of combustion air

Those measures have a potential to reduce the NO_x-level by approx. 42%, resp. 5-24% and 20%.

Besides temperature reduction there are two other effective primary measures guaranteeing low formation of nitrogen oxide:

- partial combustion by of air staging
- internal flue gas recirculation

The principal mechanisms of both NO_x-reduction methods are independent of one another (fig. 4).

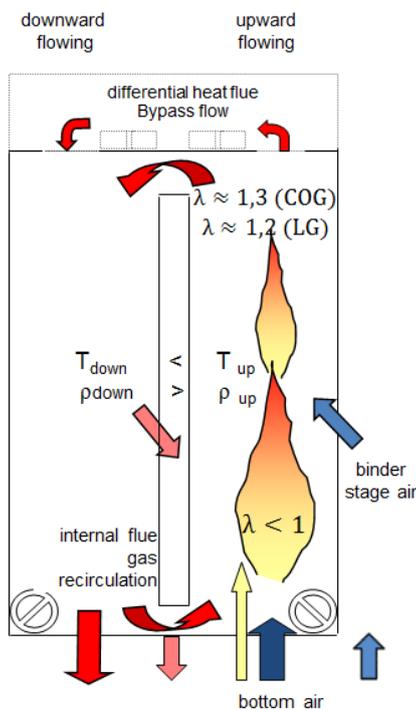


Fig. 4 Combination of air staging and internal flue gas recirculation

The internal flue gas recirculation between two flow-carrying twin flues is caused by the pressure difference between them. The effect is triggered by two components, both leading to flue gas circulation independently:

- the gas- and air-injection impulse near the inlets, and
- the temperature respectively density difference between upward and downward flowing heat flues.

The flue gas amount recirculated is conversely proportional to the flue gas amount formed in the upward flowing heat flue. Depending on rate,

flue gas recirculation reduces the flame front by 100 to 200°C. For COG-heating we see a high circulation rate of flue gas of approx. 35 to 45 %. For LG, a circulation rate of just 15 to 20 % was observed.

Partial combustion brings about a reduction in NO_x-emissions via three different mechanisms as there are:

- the reduction of nitrogen and oxygen concentrations,
- the reduction of nitrogen oxides in regions of sub-stoichiometric combustion,
- the reduction of the maximum flame peak temperature of the upper stage by flue gas from the bottom stage.

The designed ratio between the partial air flow entering at heat flue bottom and the second air flow, entering via stage openings in the binder wall is set with 60 to 40 %.

In order to keep the NO_x-formation at a low level the plant operation has to control the oxygen content of waste gas resp. the optimum excess air coefficient at $\lambda=1,2$ (LG) and $\lambda=1,3$ (COG).

The by-pass channel on top of the heat flue provides an option to influence the heating of the upper parts of the coal charge and on the temperature of the gas collecting space in order to reduce graphite deposits.

The combination of flue gas recirculation and air staging demonstrates a potential for declining of NO_x-emission by approx. 55 to 80 %. The State-of-the-Art-design of TKIS-heat flues (COMBIFLAME[®]) combines these most effective primary NO_x-reduction measures available.

A modified flue gas recirculation method comprises the external recirculation of relative cold flue gas shares, exhausted via fans out of the flue gas channel near stack bottom and its re-supply to the combustion process within the heat flues.

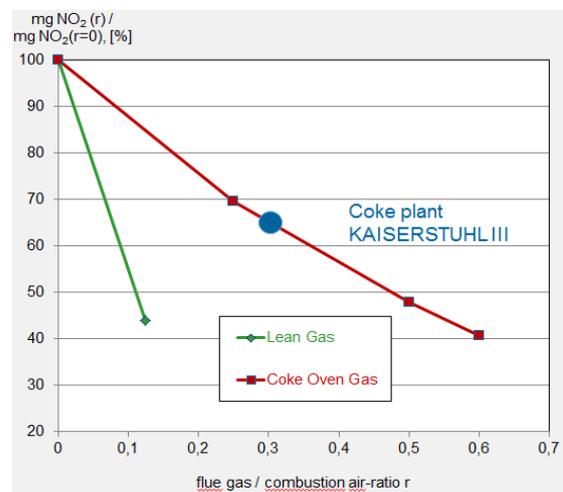


Fig. 5 NO_x-reduction potential by external flue gas recirculation

There are two versions of installation. Version #1 is basing on injection of exhausted external flue gas amounts into corbel area channels below proper heat flue soles. In that case, such external flue gas flows would by-pass the regenerator cells below the corbel area. For that reason, they are not pre-heated.

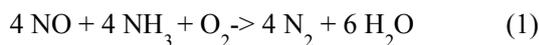
Version #2 is basing on the ad-mixing of flue gas, exhausted externally in the same way, into the combustion air streams upstream of the waste gas boxes. In contrary to version #1, the mixture will flow through the regenerators where it is heated up. That second version requires extended flow cross sections within the refractory structure, however.

Both versions are connected with additional equipment like pipework, control elements and fans to be installed furthermore. The method described leads to NO_x-reduction rates of around 35% (fig. 5) and was successfully tested during commissioning of German coke plant KAI-SERSTUHL III.

3 Secondary NO_x-reduction measures

A significant reduction of nitrogen oxides of up to 90 % can be achieved, alternatively, by selective catalytic reduction of nitrogen compounds (SCR-denitration) using addition of reducing agents into cold flue gas flows downstream of coke oven batteries.

In the SCR-process the nitrogen oxide of flue-gas is catalytically reduced by ammonia to nitrogen and water (eq.1), whereby vanadium pentoxide or tungsten oxide on a titanium oxide carrier are often used as catalysts:



Other possible catalysts are iron oxide, platinum or zeolite. Both natural gas and hydrogen/carbon monoxide-mixture-based reductants provide a useful alternative.

Moreover, those methods are combined with high CAPEX- and OPEX-costs, reducing economic and process efficiency, significantly. The operating temperatures are usually within a range of 250 to 400°C. Such high temperatures decrease the energy recovery in the regenerators of the coke ovens or require additional heating of the waste gas.

Furthermore, cross-media effects result in an increase in ammonia consumption. Moreover, the handling, storage and disposal of toxic agents/catalyst like ammonia compounds, dust and heavy metals is not unproblematic in itself. Special attention should be paid to the deactivation of the catalyst, the accumulation of the explosive

ammonium nitrate, the ammonia slip and the formation of corrosive sulfur trioxide.

The method is connected with additional equipment like pipework, tanks, stack, control elements and ID-fan to be installed downstream of coke ovens.

With regard to SCR-application in coke oven plants there is not much experience in sustainability and benefit. In total, three installations within steel and gas works in Japan are known worldwide. These installations were in operation between 1976 and 1992.

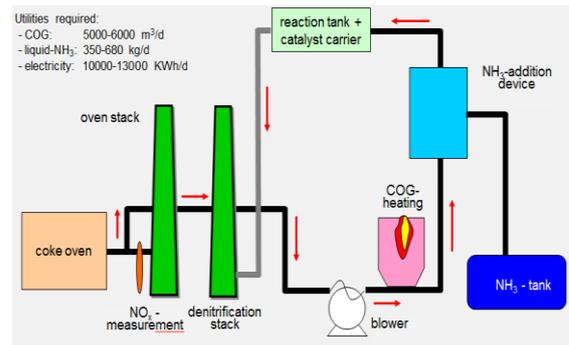


Fig. 6 Schematic SCR-denitration of waste gas

Fig. 6 illustrates a SCR-denitration plant installed in the eighties. The flue gas of the coke ovens was evacuated by a blower out of the waste gas channel in front of a stack. Further downstream within a by-pass it was heated up to 250°C by COG-combustion. After heating up ammonia was added to the flue gas flow. When the mixed gases were passing the reaction tank containing catalysts inside, the mixed gases were made to denitrify, in addition to de-dust. The catalysts were made from aluminum oxide carrier pellet. The catalysts had to be renewed every third month. The figure gives in addition an overview with regard to the utilities used.

The input level of nitrogen oxides in front of the reaction tank was between 290 and 390 ppm, the output level was approx. 30 to 90 ppm, corresponding to a denitrification ratio of approx. 75 to 90%. The dedusting-ratio was about 70%.

4 Fluid mechanical validation and optimization of heat flue oven design

In order to restrict the NO_x-formation as best as possible using most effective primary measures presented, TKIS has decided to validate and broaden the design criteria for heat flues with an in-depth theoretical investigation of the transient flow processes by developing a complex flow and staged combustion model.

The simulation model is based on a finite volume analysis describing the geometry and processes

within a heat flue of a coke oven with a height of 7,634 m (hot) using $2,3 \cdot 10^6$ net elements (fig 7).

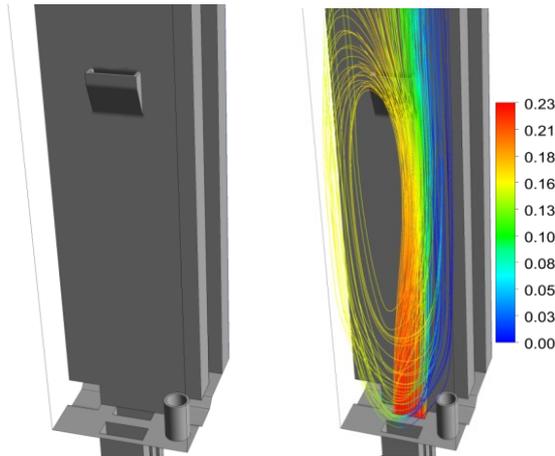


Fig. 7 Lower part of heat flue geometry networked (left) and vertical distribution of mass fraction of oxygen calculated by 3D-simulation model (right)

This enabled the mixing and combustion process to be observed through graphical animation in vertical and horizontal direction and led to an evolutionary improvement in understanding of mixing and combustion laws as well as of location of main thermal NO_x -formation within the heat flue (fig. 8).

In particular, the focus of design validation was set on determination of optimized positions and cross sections of all media inlets, channels and adjusting bricks, as for instance:

- position & cross section of air/gas inlets,
- design of binder air stages
- cross section of heat flue
- cross section of circulation ports, and
- position of COG-nozzle.

The flow model allows key influencing quantities on NO_x -formation and the main process parameters, such as local excess air coefficient and maximum allowable heat flue temperature, to be predicted by verifying subsequent process parameters at the same time, like:

- bottom/stage-ratio of combustion air
- gas composition
- battery working ratio
- air humidity

Thus, the model enabled the limits of application for this coking technology to be worked out with respect to the compliance of new limits on nitrogen oxide of approx. 150 mg/Nm^3 and uniform temperature distribution.

Moreover, using the simulation model we attach special importance on correct location of vertical position of binder air stage and turning point with

respect to low temperature of gas collecting space in the coking chamber above the charge.

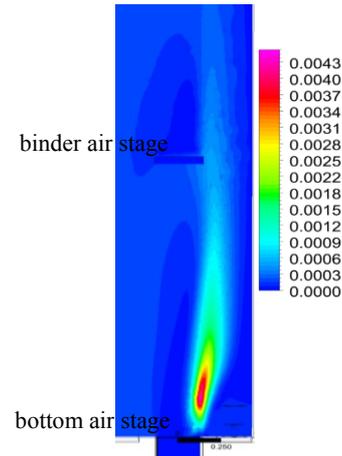


Fig. 8 Vertical distribution of mole fraction of nitrogen oxides calculated by 3D-simulation model

4 Conclusions

(1) Increase of methane content within COG reduces the NO_x -formation, effectively.

(2) When combined with internal flue gas recirculation, the reducing of average heat flue temperature and oxygen content of flue gas at the same time decrease thermal NO_x -formation, significantly by approx. 80% for COG-heating.

(3) Future limitations on maximum plant NO_x -emission (COG-heating with $\ll 150 \text{ ppm NO}_x$) would have met by TKIS considering alternative plant and design concepts, additionally.

(4) NO_x -emissions from coke oven batteries are preferably minimized by process-integrated primary measures, but end-of-pipe techniques such as a SCR-denitrification plant within the flue gas treatment may also be applied. Due to economic reasons TKIS is focused at first on taking advantage and full potential offered by well-known primary NO_x -reduction methods, before considering a secondary SCR-installation.

(5) TKIS performs in-depth theoretical investigation thus generating NO_x -optimized heat flue design and process standards by process simulations using a 3D-flow and combustion model.

(6) The State-of-the-Art-design of TKIS-heat flue (COMBIFLAME[®]) combines the most effective primary NO_x -reduction measures available.

References:

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