

NO_x emission from the hot blast system: formation, effects and the possibilities for its reduction

The environmental footprint of the production of iron and steel is well known by the industry and in general large improvements have been made in this field over the past decades [1]. However, in many places iron and steel companies are still a significant source of water and air pollution. With growing concern from local societies over harmful emissions and the tightening of environmental regulations the need for mitigation remains high and important. One of the emissions that often gains attention from the ironmaking industry is the group of nitrous oxides, or NO_x. This pollutant is formed within many combustion processes, but one of its main sources and points of concern in the iron and steel industry is the hot blast system. This is not only due to its negative impact on the environment, but also because of its influence on the occurrence of inter-crystalline stress corrosion.

This article is intended to give an overview of the formation of NO_x and the available methods to predict it, explaining the need for its mitigation, as well as providing certain directions to reduce its formation.

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CONSEQUENCES

There are two main reasons why NO_x is considered an undesirable reaction product. First the environmental impacts and second, and especially relevant for Hot Blast Systems, is the role NO_x plays in the occurrence of inter-crystalline stress corrosion (ICSC) on the inside of the steel shell of the stoves.

ENVIRONMENTAL IMPACT

The environmental effects of NO_x have been a field of investigation for decades and are well documented [2]. One of the most important negative effects of NO_x is the role it plays in the formation of smog, which presents a severe human health hazard in industrial and densely populated areas. It is for this reason that many countries have imposed strict emission limits for NO_x over many decades. Additional effects of anthropogenic NO_x emissions are related to fine dust generation (PM2.5) and disturbances in ecosystem biodiversity arising from eutrophication (an excess of nutrients).

INTER-CRYSTALLINE STRESS CORROSION

Another phenomenon, and one especially notorious for the iron and steel industry, is the influence of NO_x on the occurrence of ICSC. This type of corrosion is observed mainly in and around the welds in the dome area of the stoves. Although the theory and implications of ICSC in hot blast stoves has been studied extensively since the

early 1970s, there are still regular incidents including full ruptures and explosions of the domes.

Countermeasures to mitigate the risks are known and generally implemented for new, or repaired stoves [3], [4], [5]. Examples include:

- **Material selection:** more resistant steel grades should be used to avoid ICSC.
- **Shell design:** avoid, or minimize areas of high stress within the stove shell, especially around the dome structure.
- **Welding procedures:** the welding of the shell must be executed using procedures focused on creating stress free welds.
- **Coating:** whereby the inside of the shell is coated to prevent the chemical attack.

Although the above-mentioned design methods greatly reduce the chances of ICSC, it cannot be completely avoided and may still form over time. Therefore, it is important to implement proper inspection and maintenance programs which emphasize the particular aspects of ICSC. Moreover, as many stove shells more than 30 years old are still in use today, the issue of ICSC remains a challenge for many blast furnace maintenance crews.

The fact that ICSC cannot be fully eliminated in the hot blast system is due to the formation of NO_x in the combustion process. Environmental solutions exist to remove NO_x as an end-of-pipe technology, but this will not

help to reduce the ICSC related problems. For that reason, the reduction of NO_x must be accomplished within the combustion process itself.

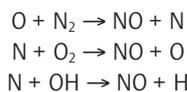
NO_x FORMATION

The term NO_x is used to represent a group of several nitrogen oxide species. Of these various species, it is primarily NO and NO₂ that are of importance with respect to anthropogenic pollution and therefore regulations are focused on these two variants [6]. More precisely, almost all of the NO_x associated with industrial activity is emitted as NO, which is then partly converted into NO₂ in the atmosphere. Atmospheric reactions between the different forms of NO_x and other gasses, make up a complex network of reactions linking the conversion and generation of nitrogen oxides, ozone, nitric acids and more in our atmosphere and soil [7].

This article focuses on the formation, prediction and reduction of the NO_x formed in the hot blast stoves, where there are three important reaction mechanisms. These mechanisms are responsible for the generation of nitric oxide, NO, within the combustion process [8]. The NO produced by one of these mechanisms is referred to as: thermal NO_x, prompt NO_x, or fuel NO_x. The formation of NO_x takes place during the gas phase, via all three mechanisms. During the blast phase however, the high temperature and large concentrations of N₂ and O₂ inside the stove also lead to the formation of NO_x via the thermal route. The focus of this article will be on combustion generated NO_x, as this is the main overall contributor and it can be influenced.

THERMAL NO_x

Thermal NO_x formation is generated by the reaction of molecular nitrogen (N₂) with oxygen radicals (O). This reaction mechanism was first described by the Russian scientist Zeldovich in 1939 and is shown in Equation 1.



Eq 1 Thermal NO_x formation

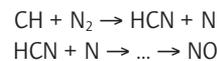
The rate determining step in this mechanism is the breakage of the very strong triple bond of molecular nitrogen. For this reason, thermal NO_x formation is highly temperature dependent. The typical relationship between NO_x formation and temperature shows that only low levels of NO_x are formed at low temperature, but that above a certain temperature threshold NO_x formation increases exponentially with the temperature.

This exponential increase of NO_x formation with temperature is generally accepted in the literature, but

the temperature at which thermal NO_x formation starts is not fully clear. Literature and operational data values range from 1,200 to 1,500°C as the take-off point for the exponential increase. This wide range can be explained by the fact that thermal NO_x formation also depends on residence time, N₂ concentration and O₂ concentration. In addition, in many practical stove applications the NO_x concentration is influenced by the presence of nitrogen compounds in enrichment fuels. These enrichment fuels are used to increase the flame temperature.

PROMPT NO_x

Prompt NO_x (Equation 2) is formed by the oxidation of molecular nitrogen from the air in the presence of hydrocarbon radicals (eg, CH), the latter being produced in the flame fronts.



Eq 2 Formation of prompt NO_x

This reaction has a relatively low activation temperature and will occur very fast under practically all common combustion conditions, if carbon containing fuels are present. Prompt NO_x is sometimes also referred to as Fenimore NO_x. Usually, the contribution of prompt NO_x is relatively minor compared with thermal NO_x for high temperature applications, like hot blast systems.

FUEL NO_x

Several fuels contain nitrogen components that can be converted into NO_x, for example HCN and NH₃. The amount of fuel NO_x in the waste gas is directly related to the prevalence of nitrogen components in the fuel. Fuel NO_x formation takes place at lower temperatures than thermal NO_x formation, because the activation energy to form the required nitrogen radicals is lower. However, fuel NO_x formation also increases with increasing temperature as more fuel radicals are formed. In addition, in hot blast stoves the flame temperature is often increased by fuel enrichment with coke oven gas, thus also increasing the amount of fuel bound nitrogen components.

At low concentrations of fuel bound nitrogen, a sharp increase in NO_x emissions can be seen. At higher concentrations there is still an increase in NO_x emission, but it starts to level off. The reason for this is that the higher the concentration of fuel bound nitrogen, the lower the amount that will be converted into NO_x. For fuels containing 2%wt nitrogen the conversion is 20-40%, while for fuels with only 0.2%wt nitrogen the conversion can be as high as 80-90% [9]. For the combustion gasses in hot blast stoves the amount of nitrogen containing compounds is far below the 0.2%wt and therefore >

virtually full conversion to NO_x can be expected in hot blast systems. The conversion of fuel bound nitrogen also depends on the equivalence ratio. The higher the equivalence ratio, the lower the excess air and the less fuel bound nitrogen is converted into NO_x. However, the excess air quantity in general cannot be decreased, because of the subsequent increase in CO emissions which are also limited by emission standards.

AVOIDING HIGH NO_x EMISSIONS

For the Hot Blast System, it is important to reduce NO_x as much as possible for two reasons, first to comply with the relevant environmental standards and second to reduce the risk of inter-crystalline stress corrosion at the internal steel shell. While the prior goal could be achieved by applying post-treatment, or end-of-pipe methods to treat the flue gas, the latter issue is not tackled in that way. Besides which, there are no known examples where de-NO_x installations have been installed to eliminate emissions from a hot blast system, which would require a significant investment and increase in operational costs. Efforts to reduce NO_x formation are focused around two areas: combustion operation and stove design.

The combustion process can be tuned in several ways to lower the production of NO_x. A strategy which is generally adopted for industrial combustion is to lower the flame temperature. This has a direct impact on thermal NO_x formation. However, for a stove this approach does not readily apply. The incentive for most blast furnace operators is to operate at maximum hot blast temperatures, which in turn require maximum dome temperatures and thus flame temperatures. One possibility using this strategy is to reduce the difference between the dome temperature and the target hot blast temperature. Typically, a difference of approximately 150°C is applied, for example a dome temperature of 1,400°C and a hot blast temperature of 1,250°C. Using a smaller temperature difference, for example 80°C, will result in a lower flame temperature requirement and thus lower NO_x. A consequence of it is that the checker column in the stove needs to be larger, for a given hot blast capacity. For plants where Coke Oven Gas is being used to enrich the stove combustion gas, the effect of a lower flame temperature is twofold, the Thermal NO_x will be lower, but also the amount of Fuel NO_x will be reduced. When less Coke Oven Gas is used this leaves the options of either reducing and avoiding hot spots, or reducing the nitrogen input in the fuel.

Combustion in the stove burner chamber is not a very homogenous phenomenon. The combustion air and combustion gas enter the stove as separate flows and make first contact within, or just above the burner. Further mixing is achieved along the combustion chamber itself. Therefore, the amount of oxygen available for the fuel to burn is not

equally distributed and some areas will have higher fuel-to-air ratios than others. Some places in the flame will see air which was pre-heated within the lower sections of the flame. This leads to a much higher local flame temperature than would be the case when the initial air and gas temperatures are used to calculate the flame temperature.

The extent to which the gas and air are mixed depends greatly on the burner design, especially the burner crown. It is therefore important that during the initial design stage of a new, or upgraded, burner sufficient effort is made to determine the geometry to provide good mixing over the required range of burner duties and gas compositions. For such evaluations it is essential to employ CFD analyses, or elaborate laboratory tests. The first method being the more flexible and economical.

QUANTIFYING AND REPORTING NO_x EMISSIONS

It is important to note that for the reporting of NO_x emissions several conventions are applied [10]. NO_x emission limits are usually given at a 3%vol oxygen concentration. This means that the NO_x concentration at the actual oxygen concentration in the flue gas needs to be recalculated using a correction factor (Equation 3).

$$\text{Correction Factor} = \frac{21 - 3}{21 - \% O_2 \text{ in flue gas}}$$

Eq 3 Correction factor

Emitted NO oxidizes to NO₂ in the atmosphere and so the NO concentration is commonly converted to NO₂ according to Equation 4.

$$C_{NO_2} (NO \text{ part}) = C_{NO} \cdot \frac{M_{NO}}{M_{NO_2}}$$

Eq 4 Conversion of NO concentration to NO₂

This concentration is then added to the NO₂ concentration and the total is referred to as NO_x expressed as NO₂ (Equation 5).

$$C_{NO_x \text{ total}} = C_{NO} \cdot \frac{M_{NO}}{M_{NO_2}} + C_{NO_2}$$

Eq 5 Total NO_x concentration

The concentrations are stated in mg/Nm₃, with MNO = 30g/mole and MNO₂ = 46g/mole. The units of measurements for NO_x are often either ppm or mg/Nm³. Conversion between the two is straightforward, using the normal molar volume of gas (22.4Nm³/mol) and the molar mass of NO_x (as NO₂). So, 100mg/Nm³ equals 100 x 22.4/46 = 49ppm.

PREDICTION METHODS

To evaluate the opportunity for reducing NO_x formation, it is necessary to have reliable estimation methods. At Danieli Corus there are currently two complementary simulation tools in use for this purpose, each focusing on different aspects of the NO_x reduction possibilities. These two methods can broadly be divided into a one-dimensional (1D) simulation, or a three-dimensional (3D) Computational Fluid Dynamics (CFD) simulation. The 1D simulation model used is based on the open source Cantera software [11], which in turn relies heavily on the well-established GRI3.0 reaction mechanism database [12]. This type of modelling can be used to quickly estimate the theoretical impact of changes to fuel composition and combustion process settings, including residence time dependencies.

Examples of cases that are often evaluated for stove systems using 1D modelling will be discussed later, but include the effect of the air/gas ratio, pre-heat temperature and usage of enrichment gas. The 1D model developed by Danieli Corus is based on the following assumptions and simplifications:

- Kinetics and thermodynamics are based on the GRI3.0 Reaction Mechanism dataset, implemented using Cantera.
- There is complete mixing of all reactants before the flame.
- The residence times in the combustion chamber and checker column are considered.
- There are no temperature loss in the combustion chamber.
- here is linear cooling of the waste gas along the checker column, from the adiabatic flame temperature down a specified final waste gas temperature at the stove outlet (Figures 1 & 2).

1D simulations cannot be used where a more thorough analysis of the combustion process in a stove is required, which considers the mixing and flow patterns within the combustion chamber. For this type of evaluation, a sophisticated 3D CFD model is prepared and simulation runs are performed. Such CFD analyses are employed for the following reasons:

- When the geometrical influence of the burner and overall stove design needs to be optimized with respect to emissions, which is the case in many rebuild and greenfield projects.
- To find the proper mixture of gas for existing hot blast stoves, which ensures lower NO_x and CO emissions.

In addition to the valuable information that it provides on NO_x and CO emissions, the 3D simulation simultaneously provides insights into the temperature distribution within the stove. This is done by using Ansys Fluent software to

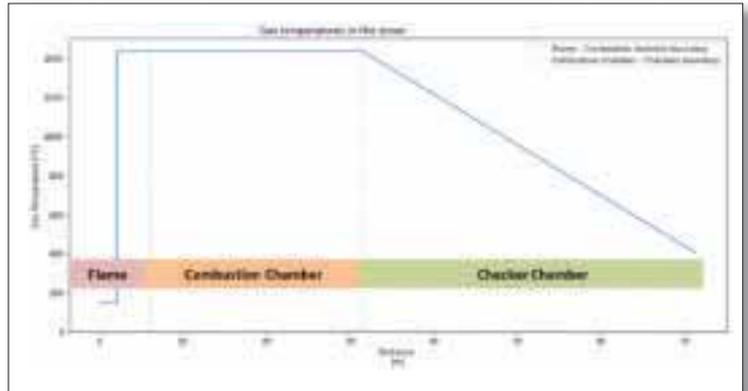


Fig 1 Gas temperature profile for an example 1D NO_x simulation

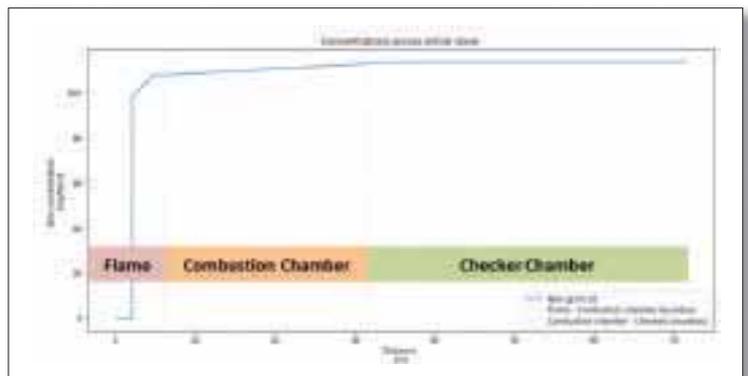


Fig 2 NO_x concentration profile, considering residence times within the combustion chamber and checker column.

analyze the 3D geometry models, including reaction kinetics [13]. Two case studies are presented to highlight the type of information and investigations that can be achieved by either of the two above-mentioned approaches.

CASE STUDY: 1D SIMULATION

For a European steel plant, several scenarios were evaluated to determine the effect of certain measures on the theoretical NO_x emissions from the stoves. The gas compositions used for the calculations are shown in Table 1.

A summary of the cases and calculated NO_x outputs are presented in Table 2. In all the cases except case 6, the combustion air was pre-heated to 200°C. The reactions in the checker column were modelled using a linear cooling profile of the gas temperature from the adiabatic flame temperature towards a final waste gas temperature of 400°C.

Based on the 1D simulations it was observed from cases 1, 1B and 1C that the contribution of the fuel bound NO_x is very significant. The HCN in the blast furnace gas BFG has a large impact, as this corresponds to the largest volume. Replacing coke oven gas by natural gas has only >

	Blast furnace gas/ %vol	Coke oven gas/ %vol	Natural gas/ %vol	BOS gas/ %vol
Carbon Monoxide [CO]	25.2	6.7	0.0	64.0
Carbon Dioxide [CO ₂]	24.0	1.2	1.1	16.9
Oxygen [O ₂]	0.0	0.2	0.1	0.6
Hydrogen [H ₂]	5.3	59.8	0.0	1.6
Methane [CH ₄]	–	23.4	90.3	0.0
Ethane [C ₂ H ₆]	–	0.5	4.1	0.0
Propane [C ₃ H ₈]	–	1.0	0.6	0.0
Butane [C ₄ H ₁₀]	–	1.0	0.6	0.0
Hydrogen Cyanide [HCN]	0.00640	0.02810	–	0.00000
Ammonia [NH ₃]	0.00000	0.00800	–	0.00000
Nitrogen [N ₂]	41.4	4.6	1.6	15.2
Water vapour [H ₂ O]	4.2	1.7	1.7	1.7

Table 1 Gas composition used for 1D simulations

Case ID	Case description	Flame temp / °C	NO_x at outlet / mg/ Nm₃ dry @3% oxygen
1	COG enrichment	1437	115
1B	COG enrichment – No HCN in BF gas	1437	49
1C	COG enrichment – No HCN and NH ₃ in BF gas and COG	1437	27
1D	COG enrichment – 50% HCN removal in BF gas	1437	82
2	Natural gas enrichment	1448	102
4	BOS gas enrichment	1444	96
5	Oxygen enrichment	1448	118
6	No Air pre-heating	1421	121
7	Hot blast temperature lowered to 1,210°C	1396	98
8	Parallel operation (lower dome temperature)	1386	97
9	30% excess air + COG	1431	129
10	Pre-heat BF gas to 100°C, air to 200°C (COG enrichment)	1435	109

Table 2 Cases simulated with 1D combustion model

a limited effect on overall NO_x formation, as can be seen in case 2. It is expected that the fuel bound NO_x contribution will not be affected significantly by the nature of the mixing within the combustion chamber. In other words, it will not become much higher, or lower, when mixing effects are taken into consideration. In fact, improper mixing is more likely to reduce fuel NO_x due to residual HCN in the waste gas when the local combustion temperature is not high enough. This is because HCN conversion requires high temperatures, and poor mixing may result in areas where such high temperatures are not reached.

Thermal and prompt NO_x contributions will be affected by mixing, as local hot spots, corresponding to an increase in thermal NO_x, or pseudo-staged combustion, where thermal NO_x formation is lowered, may be present. Measures to improve mixing alone will most likely not result in significant NO_x reductions at the stack. The flame temperatures within the range of study, from 1,400 to 1,450°C, thermal NO_x alone will most likely not exceed the emission limit of 100mg/Nm³.

In this study we concluded that the reduction, or elimination of HCN in blast furnace gas will have the largest effect on reducing NO_x emissions. Improving the removal HCN from blast furnace gas in a wet gas cleaning system will be rewarded by lower NO_x emission. After that, a further reduction is possible by replacing coke oven gas with natural gas. However, as most NO_x that originates from the coke oven gas is fuel NO_x, this will be emitted somewhere else at the plant, for example the power plant, or heating furnaces, so there is only a limited effect on the total NO_x loading on the local environment.

CASE STUDY: 3D CFD SIMULATION

A second case study is here presented to highlight the benefits of CFD simulations when optimizing the design of a burner for NO_x and CO emissions. This study was aimed at determining the effect of replacing an existing stove burner with a new design during a major repair project. For this comparison the gas and air major compositions and flowrates were kept constant for both burner geometries. Figure 3 shows the

main differences in the burner design, where red indicates the combustion gas and blue the combustion air. This new burner has been designed by Danieli Corus with a strong emphasis on the reduction of emissions and an improved temperature distribution over the checker work.

The gas composition used for the calculations is shown in *Table 3*. The gas temperature at the inlet is 40°C. The combustion air is 20°C, with a relative humidity of 70%.

As can be observed in *Figure 4* the new design results in an improved mixing of air and gas close to the burner crown, creating a more homogeneous gas temperature before it reaches the top of the checkers. Also, the resulting average temperature of the gas is higher. In other words, fewer hot and cold areas are present in the gas flow when it enters the checker column. The important consequence of this is that the dome temperature that can be achieved with the same gas composition and heating value, will be higher when the new burner design is used.

The fact that mixing of air and gas is more complete with the new burner is also clearly observed from the calculated CO concentrations, as shown in *Figure 5*. As the amount of CO is directly related to the presence of non-combusted gas, a lower value means more complete combustion. The effect is twofold, first more chemical energy is converted into sensible heat for storage in the checkers and second, emissions of CO are significantly reduced.

The difference in NO_x emission between the two burner designs is negligible for the given operating conditions (*Figure 6*). This can be explained by the fact that the flame temperature is relatively low, at less than 1,400°C, which means that thermal NO_x formation does not play a major role. Most of the NO_x in this case study comes from the fuel components (HCN and NH₃) and prompt. This also shown by the data in *Table 4*.

When considering the results in *Figure 4*, it can be concluded that due to the higher average gas temperature achieved by the new burner design for equal gas compositions, the amount of coke oven gas can be reduced by keeping the dome temperature equal to the original operating set-points. Lowering the concentration of coke oven gas will also reduce the concentration of fuel-NO_x.

This particular case study, although greatly summarized in this article, shows the potential for using dedicated CFD modelling for the intelligent design of stove burners, to reduce environmental emissions and at the same time increase the fuel efficiency of the hot blast system.

CONCLUSIONS

The hot blast system is a major source of NO_x emissions at most blast furnace plants around the world. A reduction in the formation of NO_x is important to comply with tightening environmental guidelines, as well as to limit the risk of inter-crystalline stress corrosion of the stove shell. In recent decades ▶

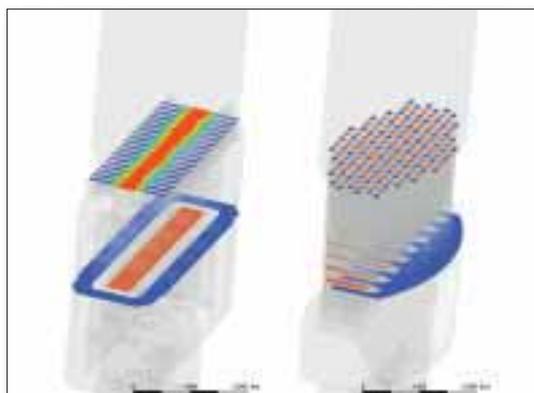


Fig 3 Existing burner (L) and improved burner (R)

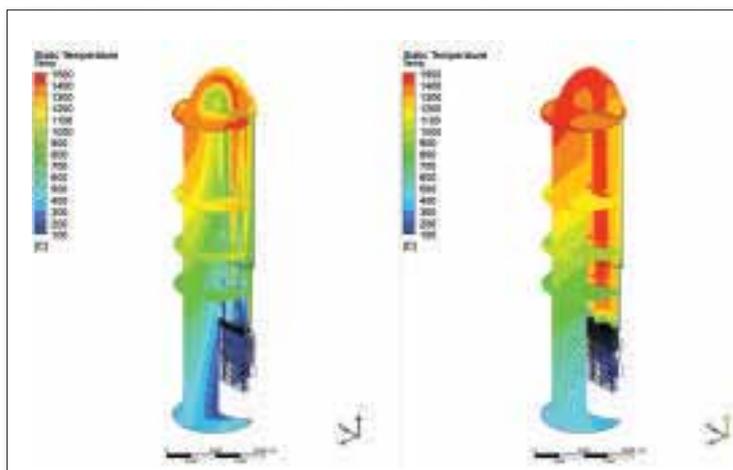


Fig 4 Temperature profiles for old (L) and new (R) burner designs

Gas type	Mixed gas / %vol
Carbon Monoxide [CO]	20.1
Carbon Dioxide [CO ₂]	18.2
Oxygen [O ₂]	0
Hydrogen [H ₂]	9
Methane [CH ₄]	1.5
Ethane [C ₂ H ₆]	0.1
Propane [C ₃ H ₈]	0
Butane [C ₄ H ₁₀]	0
Hydrogen Cyanide [HCN]	0.008
Ammonia [NH ₃]	0.00006
Nitrogen [N ₂]	44.6
Water Vapour [H ₂ O]	6.5

Table 3 Gas composition used in CFD simulations

Formation route	Old burner / %	New design/ %
Thermal NO _x	0.5	1.4
Prompt NO _x	5.0	0.4
Fuel NO _x	94.5	98.1

Table 4 Relative formation routes of NO_x for the two burner designs

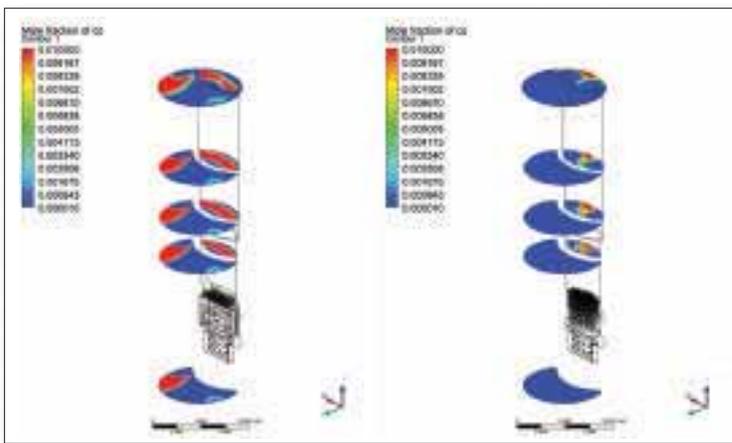


Fig 5 CO concentration for the old (L) and new (R) burner design

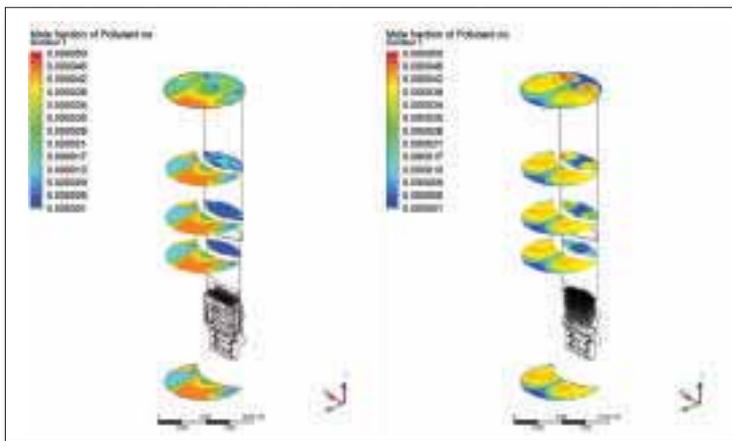


Fig 6 NO concentrations for the old (L) and new (R) burner design

the formation mechanisms for NO_x have been studied and a good understanding of the underlying principles has been established with academia, as well as the industry. However, today most operating hot blast systems struggle to meet the emission limits set by the authorities. Therefore, it is important to keep improving on both the operational side of the systems, as well as to use the sparse opportunities during revamps to replace burners with designs that are known to reduce the emissions of NO_x and CO.

The effects of changes in the combustion process, gas compositions or temperatures can be estimated very well using 1D combustion models. To evaluate the effect of burner geometry and gas flow patterns it is necessary to use more sophisticated, combustion oriented, computational fluid dynamic models, in three dimensions. **MS**

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