

# A smaller NO<sub>x</sub> footprint

Nitrogen oxide (NO<sub>x</sub>) emissions contribute to the formation of acid rain and urban smog. Being highly noxious, they are strictly regulated by environmental agencies. Therefore, cement plants are required to reduce such emissions in their combustion processes through process optimisation and other measures.

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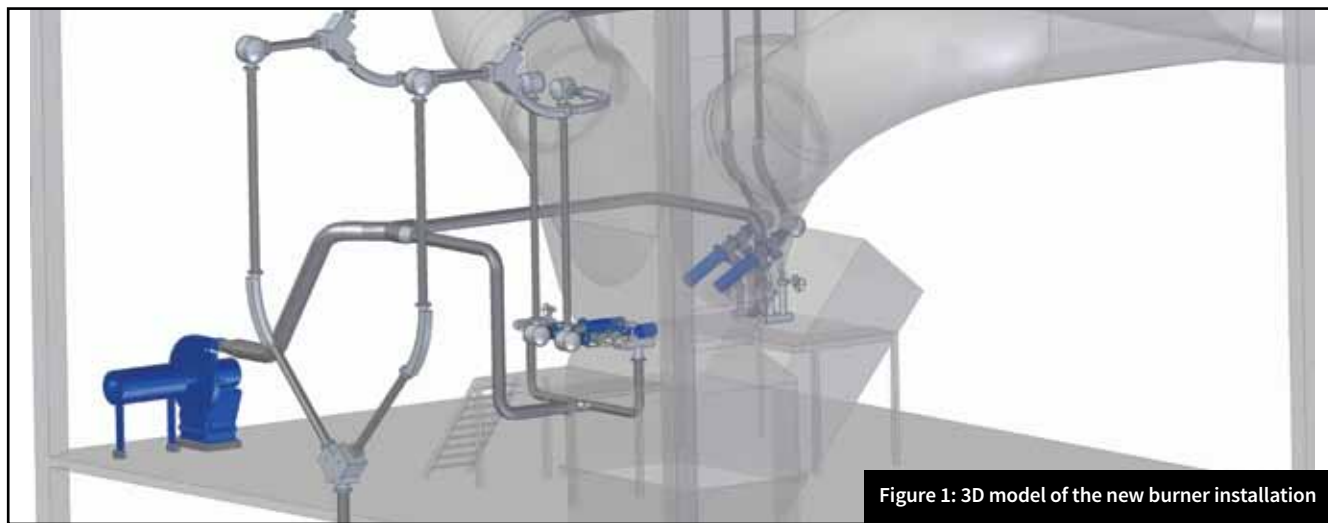


Figure 1: 3D model of the new burner installation

Nitrogen oxides (NO<sub>x</sub>) are generated in almost all combustion processes. Depending on the emissions by its cement plants and the local legislation, the company may have to invest in expensive mitigation solutions or face the payment of fines and a possible production stop. To be competitive and comply with local regulations, cement manufacturers implement innovative solutions to minimise NO<sub>x</sub> emissions, either through the treatment of exhaust gases or through the optimisation of the combustion process. Furthermore, it is not only a matter of mitigating NO<sub>x</sub> emissions but also of maintaining operational efficiency at a viable cost.

Brazil-based combustion specialist Dynamis has been investigating, in close cooperation with cement plants, process optimisation and low-NO<sub>x</sub> combustion systems to help reduce NO<sub>x</sub> emissions. Commercial computational fluid dynamics (CFD) codes as well as in-house developed models and software are used to better understand the process.

## NO<sub>x</sub> formation and destruction

Three main mechanisms govern NO<sub>x</sub>

generation inside a clinker kiln:

- **Thermal mechanism** – in which N<sub>2</sub> from air reacts with oxygen, producing NO<sub>x</sub>.
- **Fuel mechanism** – in which the fuel molecule that contains nitrogen breaks into NO, HCN and NH<sub>3</sub>. The last two react with O<sub>2</sub>, generating NO<sub>x</sub>.
- **Prompt mechanism** – in which fast reactions occur between nitrogen, oxygen and hydrocarbon radicals (CH<sub>i</sub>), producing NO<sub>x</sub>.

After the two main NO<sub>x</sub> formation mechanisms (thermal and fuel) have been closely analysed, the third mechanism (prompt) may also be taken into account. This is because the prompt mechanism is only important in some specific cases, such as the burning of gaseous fuels or lower-temperature combustion processes.

There are two main mechanisms for NO<sub>x</sub> destruction in process optimisation (excluding selective non-catalytic reduction or SNCR). One pathway to decrease NO<sub>x</sub> formation involves the addition of NO-reducing agents (mostly HCN, NH<sub>3</sub>, H<sub>2</sub>, CO and char). Another common approach, called “reburning”, consists of adding simple hydrocarbon

fuels with little or no amount of nitrogen (mostly CH<sub>4</sub>, natural gas, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>). Both techniques require low oxygen atmospheres.

The thermal mechanism occurs more intensely above 1100 °C and the NO<sub>x</sub> destruction reactions have significant rates above 900 °C. Depending on the gas

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**Table 1: emissions of a typical heat capacity distribution (60% calciner + 40% main burner)**

Indicator	Kiln inlet	Stack
Actual NO <sub>x</sub> (ppm)	1000	500
O <sub>2</sub> (%)	4	6
Corrected NO <sub>x</sub> – 10% O <sub>2</sub> (mg/Nm <sup>3</sup> )	1000	800
Gas flow (Nm <sup>3</sup> /kg of clinker)	0.58	1.8
NO <sub>x</sub> emission (mg/kg of clinker)	576	1440

composition, HCN and NH<sub>3</sub> molecules can begin to react with O<sub>2</sub> to form NO<sub>x</sub> above 1000 °C, reducing the net destruction of NO<sub>x</sub>, even increasing the emissions in some cases.

In a cement line, low-NO<sub>x</sub> techniques such as staged combustion and low-NO<sub>x</sub> burners can be applied to some extent without the need for additional operating costs. However, when the system does not allow sufficient NO<sub>x</sub> reduction to comply with local regulations, a more expensive solution must be used.

The lowering of NO<sub>x</sub> emissions requires a deep understanding of NO<sub>x</sub> formation/destruction processes, since the fine analysis of the dominant mechanisms will determine which is the best solution strategy. NO<sub>x</sub> control mechanisms can vary from operational stability (thus reducing the thermal load of the kiln) to changes in the combustion system, or even installation of SNCR systems (using urea or ammonia solutions) with high operating costs.

Combustion staging (regardless of the fuel) not only avoids NO<sub>x</sub> formation, but can also create an environment that may reduce the NO<sub>x</sub> present in the kiln exhaust gases. Hydrogen, simple hydrocarbons, intermediary forms of fuel-bound nitrogen (HCN and NH<sub>3</sub>), and to some extent even carbon monoxide (CO), are NO<sub>x</sub>-reducing agents, which, depending on the concentration and temperature, are more or less important for NO<sub>x</sub> emission reduction.

### NO<sub>x</sub> in cement lines

Clinker production presents some interesting challenges in reducing NO<sub>x</sub> emissions due to the high temperature involved and its direct impact on product quality. The kiln system – the rotary kiln and preheater tower calciner (if installed) – is the most important source of NO<sub>x</sub> emissions at a cement plant. Because of the success of modern kilns with preheater towers equipped with calciners, this article

will focus mainly on this configuration.

The clinkerisation of raw materials requires high temperatures (up to 2200 °C near the flame) inside the kiln and the fuel encounters a stream of hot secondary air. Meanwhile, the combustion that takes

place in the calciner is very different from the one inside the kiln: average temperatures are lower, the fuel can burn for a longer period and often there is a mixture of fuel and raw meal particles to avoid localised high-temperature zones.

While one might think that the kiln is the only major NO<sub>x</sub> source in the cement line, a closer look at the usual NO<sub>x</sub> emission rates from the kiln inlet and stack leads to the conclusion that the calciner is also a significant NO<sub>x</sub> producer. As Table 1 shows, even though the concentration of NO<sub>x</sub> is lower on the stack, the specific output of NO<sub>x</sub> is higher on the stack than on the kiln inlet. In this example, the NO<sub>x</sub> emission from the kiln is 576mg/kg of clinker and the total emission from the

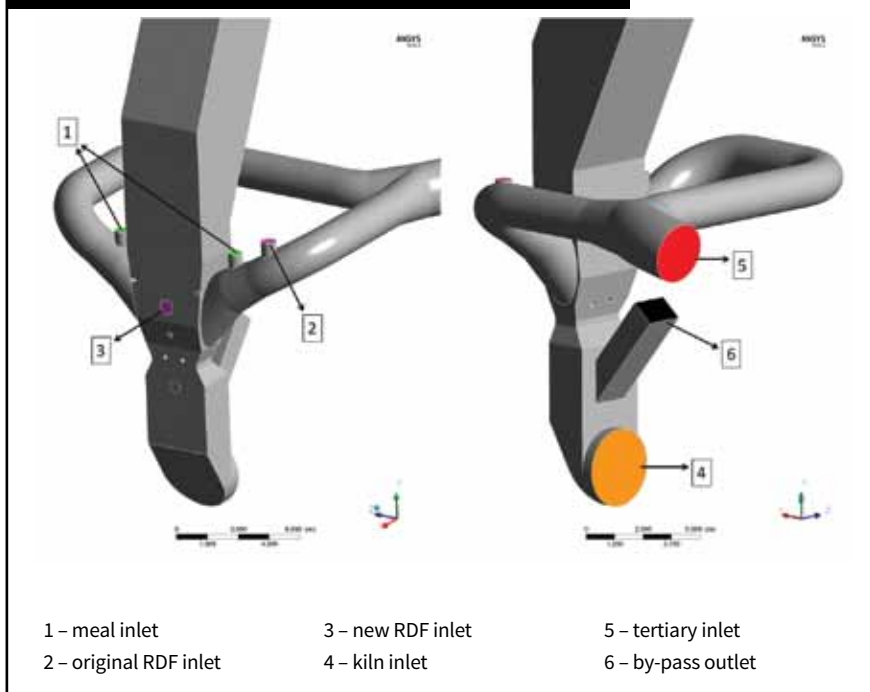
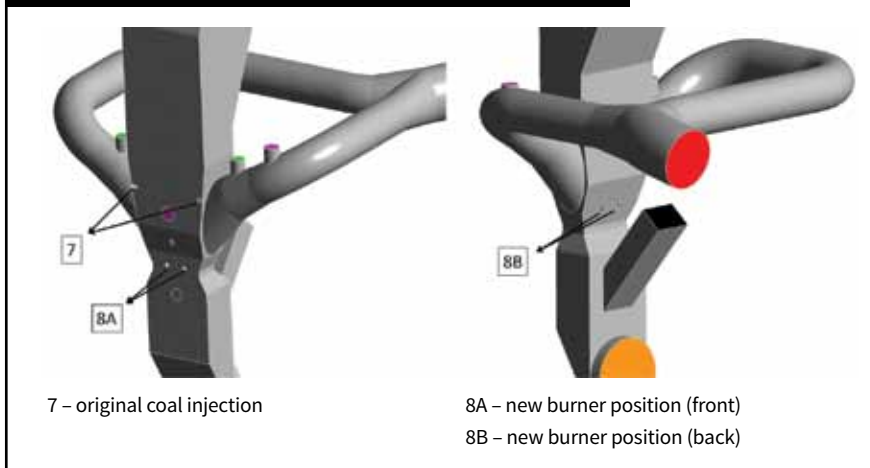
**Figure 2: geometry of the calciner – meal and RDF inlets (left side), kiln and tertiary inlets (right side)****Figure 3: geometry of the calciner – coal original inlets (left side), coal new inlets (left and right side)**

Figure 4: temperature and oxygen profiles across the original calciner

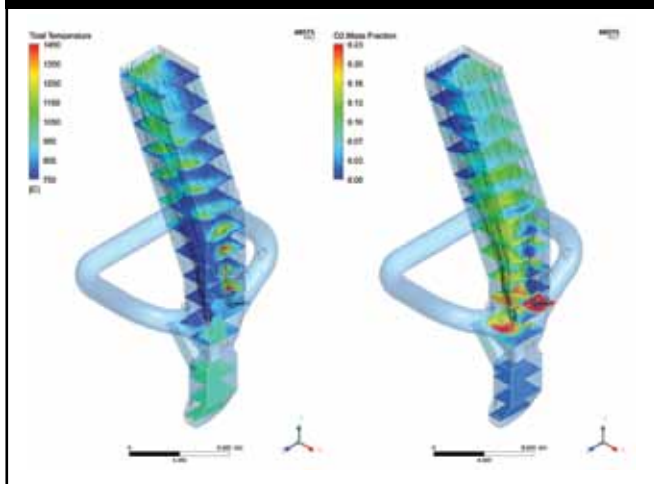
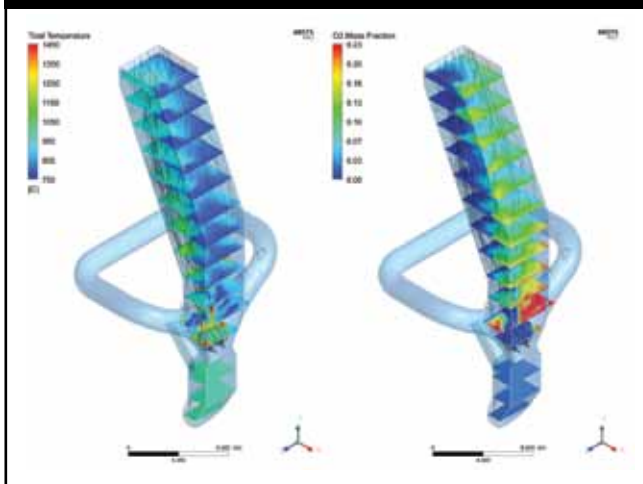


Figure 5: temperature and oxygen profiles across the modified calciner



preheater is 1440mg/kg of clinker, resulting in a net production of roughly 860mg/kg of clinker at the calciner. Although these numbers only illustrate one case, the calciner is not to be neglected when addressing NO<sub>x</sub> emissions.

A closer examination of the kiln burning conditions reveals that there is a restriction on the amount of hot secondary air that enters the flame core, creating a hot under-stoichiometric zone, limiting the formation of NO<sub>x</sub> at the flame core (due to the lack of oxygen) and promoting an internal reduction of NO<sub>x</sub>. Though the standard calciner presents a more uniform fuel-air mixture and temperature, it may contain a few hotspots.

On an in-line calciner (ILC) the fuel injection is often localised close to the tertiary air inlet. The fuel stream must meet tertiary air and meal streams in the best possible mixture condition to result in an uniform temperature profile. The use of adequate burners in the calciner can solve the previously-mentioned mixture and uniformisation issue.

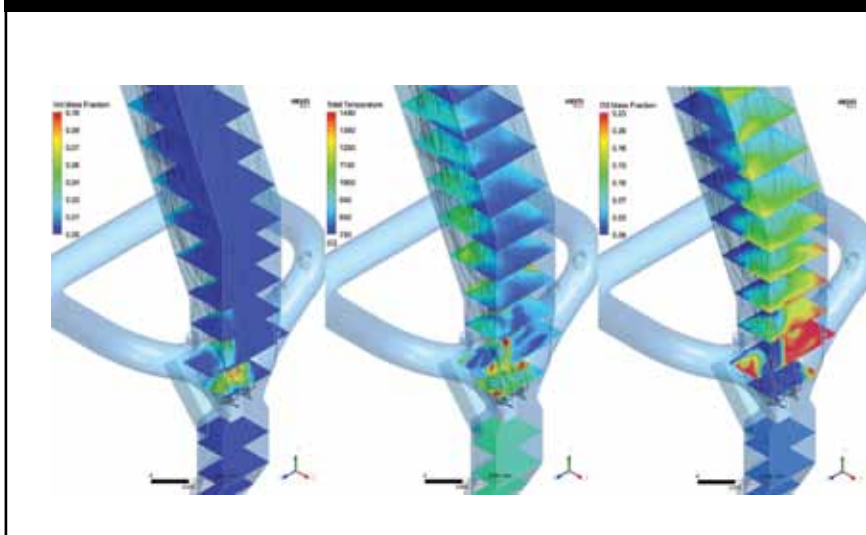
On separate-line calciners (SLCs) the fuel is injected in the centre (through a calciner burner) and tertiary air enters tangentially on the combustion chamber. This configuration allows for a hot zone to be created (near the flame), much like the conditions found in the kiln.

One of the most common strategies to reduce NO<sub>x</sub> is fuel staging. This is effective for two reasons:

1. the peak flame temperatures are reduced, which lessens NO<sub>x</sub> emissions
2. the fuel-rich mixture in the primary flame zone also reduces NO<sub>x</sub>.

Considering only the rotary kiln, when looking at clinker quality, a high peak of temperature is often desirable to allow

Figure 6: volatile concentration vs temperature and oxygen profiles for the new geometry



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smaller C<sub>3</sub>S crystals to be formed. On the other hand, the NO<sub>x</sub> reduction through process modifications often requires a worsening of the optimal combustion conditions (eg, lower excess air, lower secondary air entrainment, smaller temperature peaks). This indicates that, even using the latest-generation low-NO<sub>x</sub> burners, there will be some process limitations to the NO<sub>x</sub> levels that can be reached in the kiln. Inside the calciner there is a greater margin to decrease NO<sub>x</sub>

formation and increase NO<sub>x</sub> destruction, because in this case the limiting factor is the quality of combustion and not the quality of the product.

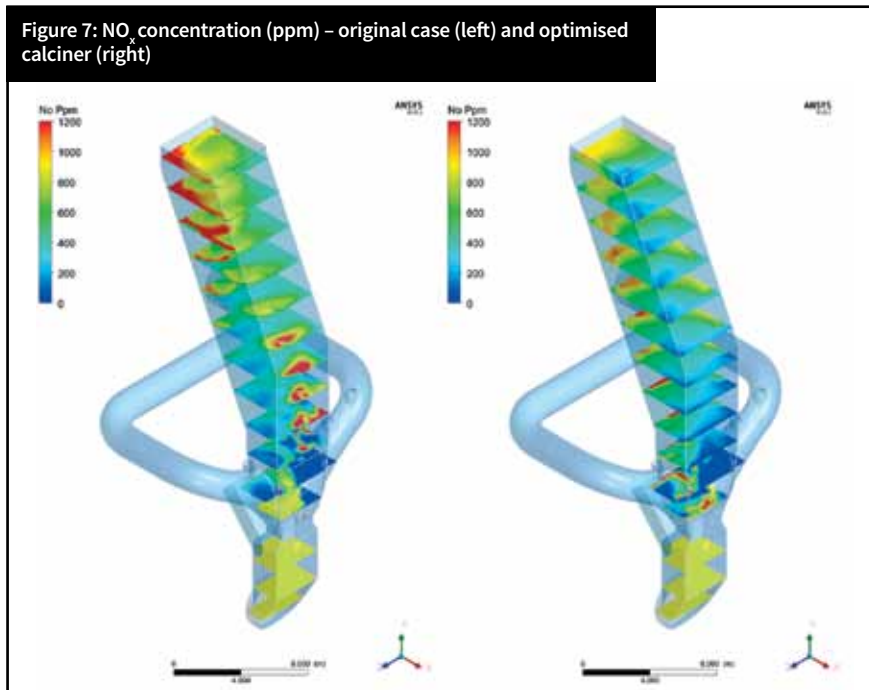
In the calciner most of the difficulty in establishing conditions that prevent the formation of NO<sub>x</sub> relates to achieving the complete combustion of the fuel used.

### Models and tools

Dynamis used CFD to model and analyse in detail the combustion reactions inside rotary kilns and calciners. Understanding what happens in the different stages of each system is key to better deciding which technique (and where) should be used.

For CFD simulations, Dynamis uses Fluent and CFX, developed by Ansys – one of the main global computer-aided engineering (CAE) software suppliers. The NO<sub>x</sub> modelling requires complex iterations between gas phases and solids (fuel and/or raw meal) to determine





how local conditions can influence NO<sub>x</sub> emissions. Correctly modelling the calcination of raw meal is very important, as it is a highly endothermic reaction that has a considerable impact on the local temperature profile. As seen in different calciner simulations, the lack of homogeneity in the mixture of fuel, air, gas and meal streams makes the thermal mechanism of NO<sub>x</sub> formation as important as the fuel mechanism.

In addition, calibrating the models (HCN/NH<sub>3</sub>/NO formation according to the fuel used) has a direct impact on the simulation, and requires extensive knowledge and site measurements. Analytical models and software developed

by Dynamis were also used in conjunction with CFD to improve the accuracy of the simulations.

### NO<sub>x</sub> reduction at a cement plant

At the start of 2017 Dynamis was hired by an international cement company to supply a new secondary combustion system, aimed at reducing NO<sub>x</sub> emissions by 25 per cent. Site measurements indicated a concentration of 782ppm of NO<sub>x</sub> at the preheater tower outlet at five per cent O<sub>2</sub>.

The main calciner fuel was pulverised coal, which was originally injected from two  $\phi$ 200mm ducts positioned in the front side of the calciner. The calciner also used RDF, fed through two meal inlets.

Hot air was entering the system through the tertiary inlet and flue gases from the kiln. All the inlets and outlets are shown in Figure 2 and Figure 3. A CFD analysis of the case showed that with the original geometry, the fuel was injected on a region with high O<sub>2</sub> availability and poor reactant distribution, leading to temperature peaks that favoured NO<sub>x</sub> formation across the calciner.

Dynamis proposed a new geometry for the coal injection through four new burners: two placed at the front side of the calciner and two at the back side, as depicted in Figure 3.

This modification, combined with a repositioning of the RDF injection predicted:

- combustion staging, starting the burning process in a fuel-rich region, generating less fuel NO<sub>x</sub> and reducing some of the NO<sub>x</sub> from the kiln gases
- improved mixing of fuel particles and flue gases from the kiln before the tertiary air inlet
- improved uniformity of reactants and temperature (reducing the hotspots).

All these changes in flow and chemical reaction behaviour contributed to a reduction of the NO<sub>x</sub> concentration in the flue gas. Figure 5 and Figure 6 illustrate how it was possible to create a strongly-reducing atmosphere with high volatiles, CO and temperature zone with the new burner configuration near the calciner throat. In this zone the conditions were favourable to reduce the NO<sub>x</sub> contained in the kiln gases.

In addition, there was an improved mixing of fuel and flue gases before the tertiary air inlet and hotspots were minimised. Figure 7 contains CFD predictions for NO<sub>x</sub> concentration (in ppm) inside the calciner for both original and final geometries. A reduction of 25.6 per cent in NO<sub>x</sub> concentration was calculated at the outlet surface.

Since the coal was to be introduced in a low-O<sub>2</sub> environment, Dynamis used its new D-C burners to help promote complete mixing of the fuel and gases, enhance combustion and achieve the expected results.

These modifications were introduced in December 2017 and yielded the expected results. The NO<sub>x</sub> at the preheater outlet fell from ~1100mg/Nm<sup>3</sup> to ~780mg/Nm<sup>3</sup> (at 10 per cent O<sub>2</sub>), as predicted by the CFD, enabling the cement plant to reduce its NO<sub>x</sub> footprint. The quality of combustion was also enhanced, as CO concentration measurements indicated. ■

