Eradicating NO_x

Matteo Giavazzi and Luca Maiocchi, Boldrocchi, discuss how redesigning the components of deNO_x systems helps futher reduce emissions.

Introduction

Many cement plants around the world have had to incorporate deNO_x technologies to limit emissions of nitrogen oxides (NO, NO_2, or NO_x) mainly from clinker production kilns. Now, and going forward, an increasing number of cement plants will have to upgrade their deNO_x technologies to comply with increasingly strict emissions regulations.

As of this year, Germany is leading the way with NO_x limits at 200 mg/Nm^3. Several countries, especially in Europe, but also in North America and Australia, are expected to follow suit. Other methods of deNO_x, including selective non-catalytic reduction (SNCR), can rarely achieve such limits. SNCR is often only able to attain between 350 and 400 mg/Nm^3 at best. The stricter legislation means many cement plants will have to add selective catalytic reduction (SCR) systems to their production lines.

Boldrocchi has decades of experience in deNO_x technologies. The first clients were mainly waste-to-energy and biomass plants, as well as incinerators, as these plants were regulated long ago, due to elevated NO_x emissions.

Given the need for increasingly high-performance deNO_x technologies, Boldrocchi has invested significantly in its R&D, with the goal of being able to offer highly effective and efficient systems that will respect emissions legislation for decades to come. The decision to develop specific in-house expertise with SCR was made to oversee the quality of the engineering and manufacturing, as well as to reduce costs to customers by removing middlemen.

Boldrocchi's focus has been a scientific approach to the detailed design of the SCR system: analysing all the individual components and carefully designing optimal systems. Testing was done with in-house computational fluid dynamics (CFD) simulations and calculations, and results were validated in customer's plants. This article describes the individual components that Boldrocchi analyses and why those analyses are so important.

NO_x causes

Nitrogen oxides (NO_x) are polluting compounds emitted into the atmosphere as result of high-temperature combustion processes. They contribute to the formation of smog and acid rain, as well as the tropospheric ozone. In cement production, they are formed in the following two ways in the clinker production kiln:

- Thermal NO_x is caused when N_2 and O_2 react within the combustion air at the main burner (over 1300°C/2372°F).
- Fuel NO_x, which is mainly created at the auxiliary burner, is caused when the N_2 present in the fuel oxidises.

NO_x: effects on humans

NO_x is toxic, mainly to the respiratory system, as it reacts with ammonia, moisture, and other compounds, forming small particles that penetrate deep into sensitive parts of the lungs. It causes, or worsens, respiratory diseases and may aggravate heart disease, leading to premature death.

NO_x reduction

Primary methods for the reduction of NO_x exist (low NO_x burners, keeping the burning process stable, etc.), but these are rarely sufficient. Secondary methods must come into play. There are two best available technologies (BAT): SNCR and SCR. SCR uses a catalyst to increase the NO_x removal efficiency, which allows the process to occur at lower temperatures.

Selective non-catalytic reduction (SNCR)

- Efficiency: 30 – 65%, depending on the reagent, its quantity, and the temperature.
- Principle: selective (only NO and NO_2 take part in the reaction); non-catalytic (the reaction takes place without a catalyst); reduction (NO and NO_2 are transformed into N_2).
- Ideal temperature range: 900 – 1050°C (1652 – 1922°F) depending on the reagent.
- Reducing agents include ammonia NH_3 aqueous solution (<25 % w/w for safety prescriptions, <19% in US) and urea CH_4N_2O water solution (33% or 45% w/w) to avoid crystallisation (temperature is a key factor here, as 33% urea in water crystalises at -10°C/14°F; 45% urea in water crystalises at 0°C/32°F).

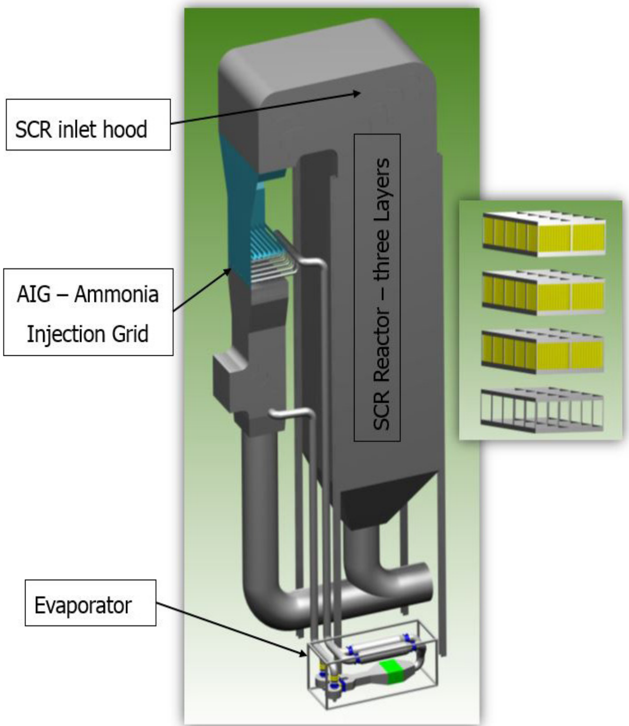

Figure 1. Components analysed in the SCR system.

Selective catalytic reduction (SCR)

- Efficiency: 70 – 95 %, depending on the reagent and its quantity, the specific volume and chemistry of the catalyst, and the temperature.
- Principle: injection of reagent and catalyst to form N_2 and water.
- Temperature allowances: 165 – 600°C (329° – 1112°F).
- Reagents include ammonia (NH_3) (injected as liquid or vapour) and urea solution (liquid or vapour). Boldrocchi has experience using both urea and ammonia and has found that pre-evaporating the ammonia increases efficiency.
- Catalysts include the extrusion of a mixture of carrier material (ceramic) and active components (TiO_2/V_2O_5, WO_3 and Fe_2O_3/Cr_2O_3, Al_2O_3).

Possible operational problems include the following:

- Catalyst plugging, depending on the dust content in the flue gas.
- Catalyst poisoning, mainly due to high sulfur concentrations in the flue gas.

High-dust SCR solution

To solve these problems, Boldrocchi has developed a SCR process with a high-dust configuration in which blowers provide heated air for continuous cleaning. Particular attention is given to the operating temperature to avoid catalyst poisoning and/or obstruction, due to ammonium sulfate formation on the catalyst surface.

Boldrocchi is installing a high-dust SCR system downstream of a cement kiln with the goal of reducing NO_x to a maximum of 180 mg/Nm³. The reduction will take place in the dust-laden exhaust gas, directly after the kiln and preheater tower. The high-dust option was the optimum choice due to the following:

- The temperature window in the flue gas after the preheater tower was suitable.
- Lower complexity and lower investment costs compared to the tail-end.

The kiln:

- Capacity: 2400 tpd.
- Run time: 24 hours/day; average 330 days/year.
- Fuels: lignite, used tyres, fluff, and liquid fuels, such as solvents.

Expected performance:

- NO_x: 180 mg/Nm³ at 10% O_2 daily average value.
- NO_x: 360 mg/Nm³ at 10% O_2 half-hour average value.

With the following ammonia slip values:

- 20 mg/Nm³ at 10% O_2 daily average value.
- 40 mg/Nm³ at 10% O_2 half-hour average value.

Tail-end SCR solution

When a tail-end solution is chosen, more attention must be paid to the sulfur content, as the operation temperature is usually below the ammonium bisulfate (ABS) dew point. This implies a potential risk of ABS condensation on the catalyst surface, reducing its performance.

Boldrocchi has installed many tail-end systems. One of the most relevant projects was a mid-range dust application in a cement plant in China. A complete system was supplied using urea as a reagent (which is transformed into ammonia once evaporated). The contract included the urea preparation, gasification, injection, and reaction in a catalyst reactor.

The solution was designed based on the following process parameters: SO_2 up to 1000 mg/Nm³ and dust up to 400 mg/Nm³. The system successfully reduced NO_x from 1200 mg/Nm³ to 200 mg/Nm³. This abatement level was achieved by installing a pneumatic cleaning system to mitigate dust, instigating stringent temperature control to avoid ABS formation.

Detailed design

In order to achieve such high NO_x abatement levels, while containing ammonia slip, the entire SCR system must be optimally designed. There are a number of considerations and the information in this article proves that analysing the effectiveness of each component results in both improved abatement levels and reagent savings.

Among its results, the company engineered a SCR system working at a mere 160°C/320°F with 60 mg/Nm³ in residual emissions: a successful emission reduction at one of the lowest temperatures in the world. The components analysed are shown in Figure 1.

CFD modelling description

In order to analyse each component, an optimal use of CFD modelling must be undertaken. Once engineering calculations are complete and the design of the system theorised, CFD modelling is a tool that, by numerical resolution of fluid dynamics equations, intends to predict fluid behaviour (velocity and pressure fields, thermal exchange, mass exchange, and chemical reactions).

Whereas many use CFD by simply entering input and output values, Boldrocchi analysed the algorithms to thoroughly understand CFD

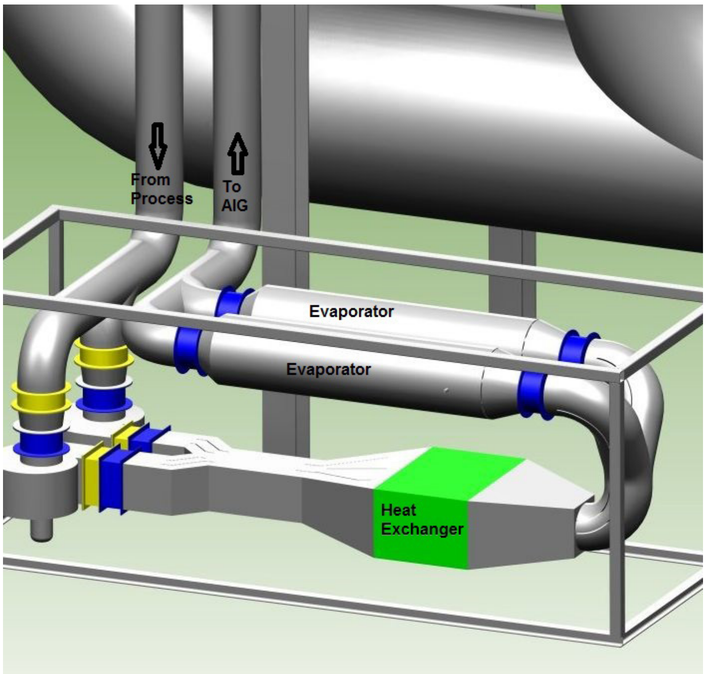

Figure 2. Geometry of evaporator.

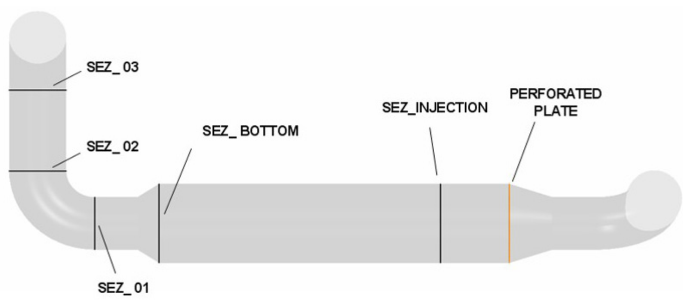

Figure 3. Reference sections of evaporator.

Table 1. Operative conditions of evaporator.

Evaporator name	Sprayed liquid	Amount of injected liquid
Analysis 1	Aqueous ammonia 25%	24.07 kg/hour (53 lb/hour) (normal case)
Analysis 2	Aqueous ammonia 25%	56.93 kg/hour (125.5 lb/hour) (maximum case)

Table 2. Residual liquid on control sections.

	Section name	Residual liquid
Analysis 1	sez_bottom	0.052% of injected
	sez_01	0.000% of injected
	sez_02	0.000% of injected
	sez_03	0.000% of injected
Analysis 2	sez_bottom	1.709% of injected
	sez_01	0.363% of injected
	sez_02	0.002% of injected
	sez_03	0.000% of injected

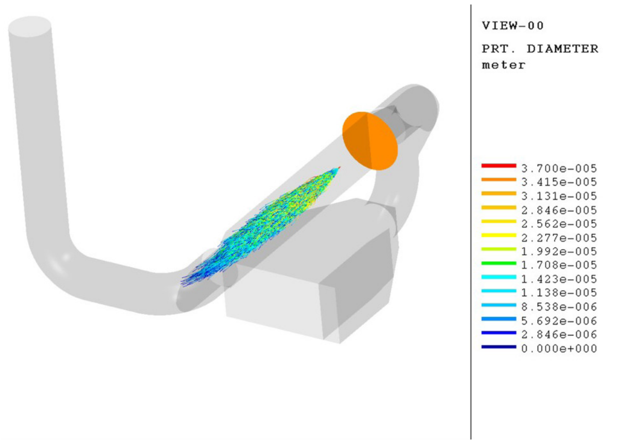

Figure 4. Reagent atomisation.

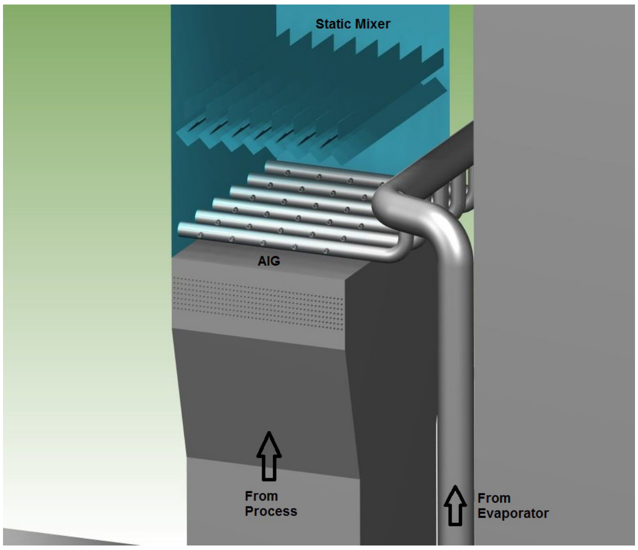

Figure 5. Geometry of ammonia injection grid.

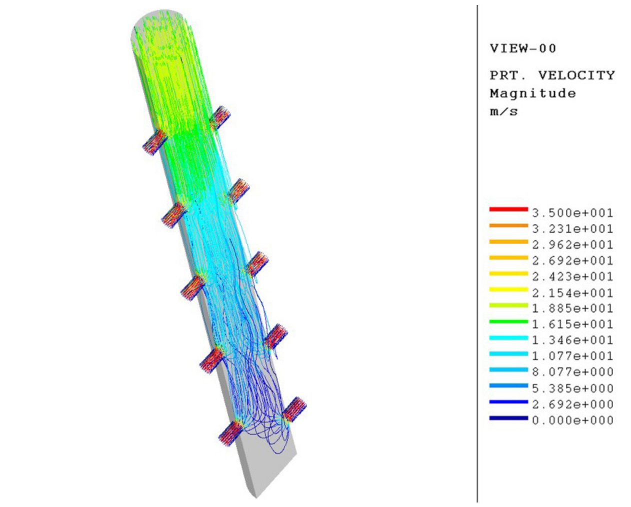

Figure 6. Geometry of ammonia injection grid (detail).

modelling, its calculations, and implications. The partial differential equations used, which govern the convection processes of the fluids, come from the general principles of conservation formulated for open systems.

The energy equation governing temperature distribution is based on the first principle of thermodynamics, while the Navier-Stokes continuity equation, along with equations governing velocity distribution, are based respectively on the principle of mass conservation and the momentum conservation principles. The numerical solution strategies of the equations refer to the laminar flow regime: specific turbulent thermal stresses and flows are evaluated by means of more or less sophisticated models.

A turbulent model is crucial, due to both the types of issues associated with applying SCR to a process and the desired results, as it increases accuracy. Applying a turbulence model to the study of fluid dynamics results in bringing the intrinsically transient oscillations of turbulent phenomena into the typical times of engineering observation and mediating them on appropriate temporal scales.

The most robust turbulence model in this type of application, the K-epsilon (k-e), calculates turbulent thermal and kinematic diffusivity by algebraic expressions in which turbulent kinetic energy is present, as well as turbulent kinetic energy dissipation. This model is implemented in most thermos-fluid dynamic codes that can handle turbulent flows. Of all time-based models, it represents the best compromise between accuracy of results and computational stability.

In order to assess the uniformity of the gas at the inlet of the catalyst layer, the parameters to be analysed are the velocity distribution (which also directly influences the temperature distribution) and the distribution of the molar ratio between NH_3 and NO_X.

The parameters used for the analysis of these processes is the coefficient of variation:

$$Cv = \frac{\sigma}{\overline{x}} 100\%$$

Where:

$$\sigma = \sqrt{\frac{1}{(n-1)} \sum_{i=1}^{n} (x_i - \overline{x})^2} \qquad \overline{x} = \frac{1}{n} \sum_{i=1}^{n} x_i$$

Table 3. **Performance of ammonia injection grid.**

Normal velocity at nozzle outlet (m/sec.)	Tangential velocity at nozzle outlet (m/sec.)	Deviation angle from normal direction ALPHA (°)	Normalised standard deviation of gas flow through
34.1	-0.03	-0.07	4.04%

are respectively the variance and average of the values of the parameter measured on a matrix of n values.

Analysing each system component

Ammonia evaporation system

As Boldrocchi's studies have concluded that pre-evaporating the NH_3 ammonia increases efficiency, it was necessary to design an evaporation device that would ensure optimal evaporation, avoiding any reagent loss and feeding the ammonia injection grid most effectively. If not completely evaporated, NH_3 can accumulate on the walls of the reactor causing unwanted consequences: the ammonia will be lost, requiring more ammonia to be added in order to ensure the appropriate reaction. The NH_3 will solidify and form a crust inside the reactor, causing it to clog, forcing maintenance.

Good reagent atomisation (Figure 4) is also essential for optimal evaporation, as the size of the reagent droplets is directly proportional to the success of the reaction. Boldrocchi opts for two-phase nozzles, which ensure a proper droplet size distribution with an average drop diameter of about 20 μm and a maximum drop diameter under 40 μm.

Ammonia injection grid

The idea was to select nozzles of the appropriate size, calculating the ideal distance between the nozzles, the number of nozzles required, and the speed of the injected air and flue gas, in order to obtain an optimal ammonia distribution without increasing the pressure drop of the grid.

The pollutant/reagent mix was also perfected to feed a completely uniform mixed gas to the surface of the catalyst. The goal is to ensure that all the catalyst is used optimally and not to waste volume the client has paid for.

To calculate these aspects, several CFD models were completed. The final solution offered minimal tangential velocity at the nozzle outlet and a normalised standard deviation of the gas flow of less than 5% through all nozzles.

SCR reactor inlet hood and body

Imposing particularly stringent design constraints on the fluid dynamics of the reactor, including the inlet, hood, and

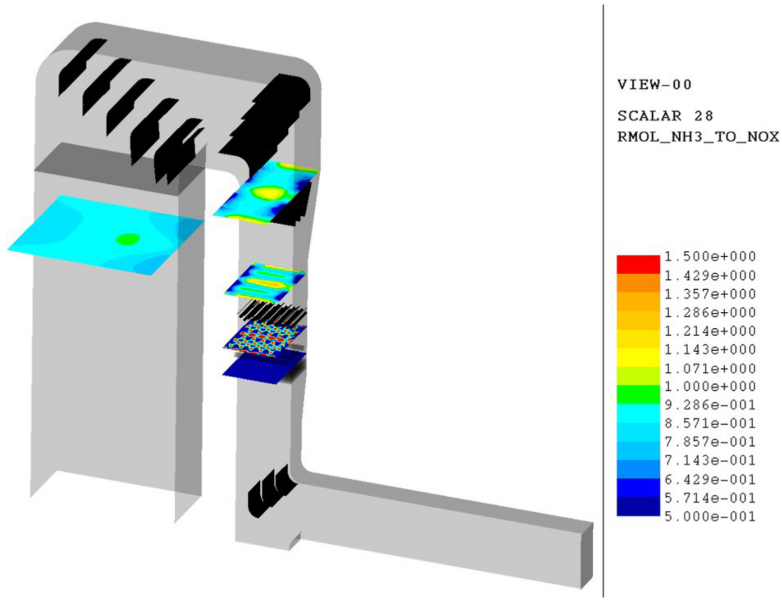

Figure 7. Performance of tail-end SCR.

Table 4. **Performance of tail-end SCR.**

	Normal case	Maximum case
Speed: normalised standard devistion on reference section	8.81%	8.80%
Molar ratio NH_3/NO_X: normalised standard deviation on reference section	5.58%	5.57%

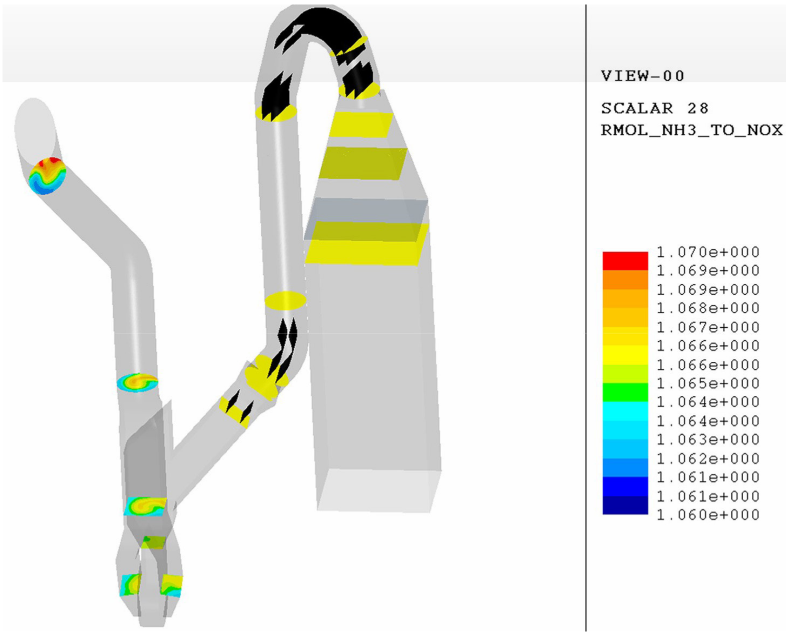

Figure 8. Performance of high-dust SCR.

Table 5. **Performance of high dust SCR.**

	Actual value
Speed: normalised standard devistion on reference section	9.6%
Molar ratio NH_3/NO_X: normalised standard deviation on reference section	<1%

body, offers significant performance enhancement. The uniformity and conditions of the flue gas and how it was affected by the fluid dynamics of the reactor were therefore assessed. This took into account the mixing efficiency between the main stream of gas coming from the kiln and the secondary flow of ammonia vapour from the evaporator.

Indeed, the maldistribution degree of the flue gas and the molar ratio of NH_3/NO_x is correlated with the loss in terms of the useful volume of the catalyst. The higher the maldistribution within the reactor, the less efficient the NO_x reduction.

For both tail-end and high-dust systems, the optimal hood design was studied, as it was found to be an influencial part of the fluid dynamics of the configurations. The deflectors and perforated plates inside the reactor, used as aids, were calculated in terms of their design, placement, number, and size, with the goal of optimising the reaction.

Conclusion

SCR systems from various companies may look the same at a glance, but the secret to a superior solution is in the details. Engineers may like to joke that CFD stands for 'colours for directors', but it is clear that, if used properly, the results can differ substantially. Although CFD modelling is often used by simply inputting numbers, Boldrocchi has concluded that, if used to its full potential, understanding the mathematical calculations and using the correct equations, the implications can make a significant difference in the performance of the system.

In order to achieve high NO_x abatement levels, while containing ammonia slip, shown in the case studies and tables, it is imperative that the entire SCR system be optimally designed.

About the authors

Matteo Giavazzi is responsible for technology development and project coordination in the Air Pollution Control Division of Boldrocchi Group. He started his career in the automotive industry with FCA environmental research team; afterwards he focused on the manufacturing industry. Over the last 20 years, he has held varying roles in environmental process engineering for industrial plants. He is a specialist in air quality, pollution prevention, and environmental problems analysis, with particular reference to air pollution from industrial sources.

Luca Maiocchi is the Director of the Air Pollution Control Division of Boldrocchi Group. He started his career 25 years ago in the environmental field with particular dedication to engineering activities and innovative solutions in the air quality field. Maiocchi is President of Boldocchi France, the oldest branch of Boldrocchi Group, and President of Boldrocchi Egypt.