OPPORTUNITY NO_x

Helmut Hoppe, VDZ, gives an overview of the development of NO_x reduction technologies.

For every cement producer, NO_x abatement is a long-term environmental issue. More than 30 years ago, first tests with the selective non-catalytic reduction (SNCR) process were carried out, and almost 20 years ago selective catalytic reduction (SCR) technology was introduced for the first time in the cement industry. In the following years, extensive demonstration projects were undertaken to further develop this abatement technology. Today, cement plants have to meet ambitious emission limit values, which have already resulted in the installation of the first multi-component abatement technologies.

Increasing efforts

In the course of the 1980s, NO_x emissions became one of the most important environmental issues for the cement industry. It was foreseeable that future NO_x emission limit values could not be met with the traditional process optimisation measures, and that secondary measures for NO_x reduction would have to be applied at cement kilns.

Against this background, VDZ started extensive trials with different kiln systems to investigate the application of the SNCR process.[1] The promising results from these tests led to two SNCR demonstration projects at the beginning of the 1990s, which were funded by the German Federal Ministry for the Environment.[2] In an additional demonstration project, staged combustion in a precalciner was also investigated as a NO_x reduction measure. The main objective of the projects was to find out if the new NO_x emission limit value of 0.80 g/m^3 (for existing kilns), which was stipulated at that time in the German clean air regulations, could be met by the application of the above mentioned technologies. In the following years, the SNCR process was developed into a state-of-the-art technology and has been installed at many cement kilns worldwide.

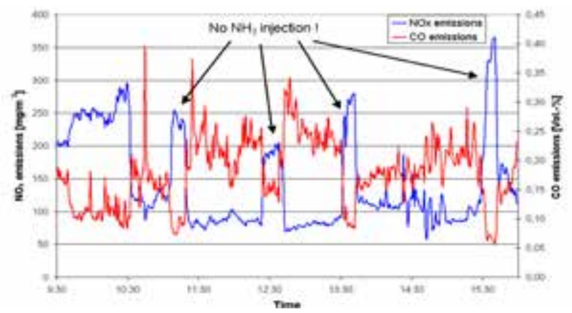

Figure 1. NO_x and CO emissions from a precalciner kiln with and without NH_3 injection (SNCR).

Figure 2. A high-dust SCR plant in the Solnhofen cement plant after recently conducted modifications. Source: Solnhofer Portland-Zementwerke.

BAT process

By the end of the 1990s, a new integrated approach for environmental protection was pursued on a European level, aimed at the protection of the environment as a whole, and the prevention and control of pollution into air, water, and soil from different activities. To fulfil these objectives, the associated IPPC Directive required the use of best available techniques (BAT).[3] This was to be achieved by an exchange of information between the member states and the industries. The results were to be published in the form of comprehensive BAT Reference Documents (BREFs) for each of the industry sectors. The cement industry was one of the first industrial sectors for which a BREF document was elaborated.[4] The reduction of NO_x emissions was an important issue and was discussed controversially between the representatives of the member states and of the industry. Nevertheless, the following techniques were classified as BATs for NO_x reduction:

- Primary measures.
  - Flame cooling.
  - Low-NO_x burners.
- Staged combustion.
- SNCR.

A so-called BAT emission level associated with the application of the above mentioned techniques was considered to be in the range of 200 mg – 500 mg of NO_x/m^3 (expressed as NO_2, based on a daily average basis).

Further development

The specifications in the BREF document were a big challenge for the cement industry. It was not clear whether the available NO_x reduction measures would be able to achieve the BAT emission level of between 200 mg/m^3 and 500 mg/m^3. At the same time, the environmental requirements for cement plants were tightened in many countries, due to the increasing use of alternative fuels. This also resulted in stricter NO_x emission limit values. Against this background, many different activities were started in the following years to improve the performance of different NO_x abatement techniques, or even to investigate their applicability at cement kilns.[5] Numerous trials were carried out to optimise the existing SNCR plants and to reduce the so-called NH_3 slip: the emissions of unreacted reducing agent ammonia (NH_3). In particular, when the reducing agent was injected overstochiometrically or the temperature was too low, the NH_3 slip increased significantly.

Although there was not yet an NH_3 emission limit value in the German clean air regulations, it was likely that future environmental permits would also include an emission limit value for NH_3. In this connection, the so-called high-efficiency SNCR process was developed, which aims at an optimised injection of the reducing agent.[6,7] To achieve this, most technology providers use different injection lances in different layers, with single lance control and online monitoring systems of gas temperatures and gas distribution to follow all process fluctuations.

Furthermore, the application of the SNCR process at precalciner kilns was not investigated sufficiently at this time. However, operational trials in the following years showed that precalciners offer good conditions for the SNCR process, as there is a sufficient residence time for the reduction reactions in the appropriate temperature window. As a result, high NO_x reduction rates could be achieved, accompanied only by very low NH_3 emissions (Figure 1).

In addition, the SCR process, which was state-of-the-art in the power sector and for municipal incinerators, had only been tested at cement kilns in small-scale pilot trials.[8,9] As a result, the SCR process was not yet considered as BAT in the first BREF document, but apart from this there were opinions attributing an associated emission level of between 100 mg and 200 mg of NO_x/m^3 to this technique. As there was an obvious need for full-scale trials, the first SCR plant (high-dust version, see Figure 2) was erected and tested in a cement plant in southern Germany.[10] Soon after this, another SCR plant was installed in the Monselice plant in Italy.[11]

Later, two demonstration projects (one high dust SCR, one tail-end SCR), with funding from the KfW Development Bank, were undertaken in German cement plants. Both projects were accompanied by extensive measuring programmes that were carried out by VDZ (Figure 3).

The results showed that NO_x emission levels below 200 mg/m^3 with very low NH_3 slip could be achieved. Furthermore, it was also shown that organic compounds could be reduced. After the successful optimisation of dust cleaning (high dust SCR), the duration of the catalyst layers seemed to be satisfactory, meaning that the operational costs could be kept at a reasonable level. The results have been summarised in extensive reports.[12,13]

Revisions and legislative requirements

BAT is a dynamic concept, as emission abatement technologies are continually developing and new technologies might also be introduced in different industrial sectors. Therefore, a review of the cement BREF was started in 2009, resulting in an updated document with modified specifications regarding NO_x reduction.[14] In this version, the SCR process was also classified as BAT, but was subject to “appropriate catalyst and process development". Furthermore, the BAT-associated emission level for NO_x was modified to less than between 200 mg/m^3 and 450 mg/m^3 for preheater kilns (with a higher range for Lepol and long rotary kilns).

At about the same time (in 2010), the European Directive on Industrial Emissions (IED) was adopted,[15] which also includes the former IPPC Directive. In annex VI, part four of the directive, emission limit values for cement plants co-incinerating waste were defined. This was namely a NO_x emission limit value of 500 mg/m^3 with a 10% O_2 daily average (Table 1).

In Germany, the IED was implemented on a national level in the Ordinance on Waste Incineration and Co-Incineration (17th BImSchV)[16], but with a further tightening for the NO_x emission limit values (between 200 mg/m^3 and 400 mg/m^3) and an additional limit value for NH_3 (Table 1).

Table 1. NO_x and NH_3 emission limit value for cement plants in Europe and Germany.

Component	Emission limit value in mg/m^3, 10% O_2	
	Europe	Germany
NO_x (as NO_2)	500*	200*/400**
NH_3	/	30*/60**
*daily average **half-hourly average		

Figure 3. VDZ measurements at different levels of the SCR reactor in the Rohrdorf works.

Figure 4. New IKN precalciner kiln in the Burglengenfeld plant in southern Germany Source: HeidelbergCement.

The German cement industry

SNCR and SCR technologies are both BAT and each can be applied to reach the emission limits. For many German cement plants, it has been a big challenge to meet the emission limit value for NH_3 – especially during direct operation (raw mill 'off') of the kiln line. This resulted in the development that more German cement plants have already installed a SCR plant and others have started to plan and apply the SCR process. Today, there are 40 cement kilns in operation and SCR plants are already in operation at 10 of them. Another 10 are in the planning or construction phase. In several other cases, the final decision about future NO_x abatement technology is still pending. Different equipment suppliers have been commissioned, e.g. CemCat, Scheuch, GEA/Lurgi, Yara, CTP (Austria), Boldrocchi, and FLSmidth.

In addition, there are currently 10 precalciner kilns in Germany. One new precalciner kiln was commissioned in 2018 (Figure 4) and another will be put into operation at the beginning of 2019. These kilns apply the SNCR process combined with staged combustion in the precalciner and will meet the ambitious NO_x and NH_3 emission limits of the German 17th BImSchV with this technology. Additionally, there are ongoing activities to optimise existing SNCR plants at preheater kilns, but they will most likely need a specific exemption for the NH_3 emission limit value in the mode of direct operation (raw mill 'off').

Multicomponent abatement technologies

In addition to the further development of standard SCR technologies (high dust, tail-end), other emission abatement technologies have emerged that can reduce not only NO_x and NH_3 emissions, but also other flue gas components. The DeCONO$_x$ process, invented by the Austrian equipment supplier, Scheuch, is a combination of a tail-end SCR and a thermal post-combustion of organic pollutants and CO.

First experiences with this technology have been gained in the Kirchdorf cement plant in Austria[17], but in the meantime there are also two plants in operation in the German cement industry (Figure 5).

Other catalytic NO_x reduction technologies like the AUTONOX process and the CATAFLEX process with catalytic filter bags are also being investigated in the cement industry and will become more important in the coming years.

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Figure 5. DeCONO$_x$ plant in the Allmendingen cement plant.
Source: SCHWENK Zement.

However, it can be expected that the SNCR process will remain the preferred NO_x abatement technology in many countries worldwide – for both economic and ecological reasons.

Conclusion

Over the past 30 years, extensive experience has been gained within VDZ regarding the application of NO_x abatement measures at cement kilns. Due to the constantly increasing environmental demands and the lowering of NO_x emission limit values, so-called secondary measures for NO_x reduction (SNCR, SCR) have been introduced in the cement industry. VDZ has carried out many measurements in connection with the demonstration projects and has also conducted its own research projects on different NO_x reduction technologies. The future European and national environmental legislation will be the decisive factor, if multi-component abatement technologies are to become increasingly important. ■

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