PYRO-PROGRESSING

Norbert Streit and Marc Feiss, KHD, discuss pyro-processing technologies for the control and reduction of NO_x emissions.

The control and reduction of emissions, especially NO_x emissions, has gained greater impetus in recent years. Stricter regulations, even in countries outside of Europe, the US or other regions that already have extensive environmental-protecting governance, raised the demand for systems or methods that enable impactful emission abatement. Until today, optimised kiln burners, staged combustion calciners, and SNCR- as well as SCR-systems are the prevalent solutions available to satisfy set emission limits. Unfortunately, almost none of these solutions are able to meet today's (and certainly not future) emission regulations on their own. The combination of the aforementioned equipment can be successful, but comes with unwanted complexity, or in the case of SNCR or SCR, even with extra operational costs.

To achieve an improved abatement efficiency, KHD developed Pyroredox® – a gasifying reactor that is installed between the kiln inlet chamber and the calciner. The system features a modular design that allows installations in new and existing kiln lines. The first two units sold were realised in China and are retrofits of existing kiln lines.

After one year of operation, a significant abatement of NO_x emissions was sustainably achieved. Due to the fact that China forced the most significant regulation tightening of all major cement-producing countries, Pyroredox was combined with an SNCR system in both projects to satisfy the extremely low emission limits of 30 mg/Nm³ NO_x and 8 mg/Nm³ NH_3 (ammonia slippage is also strictly limited in China and the limit even includes the amount of ammonia that comes from the raw material).

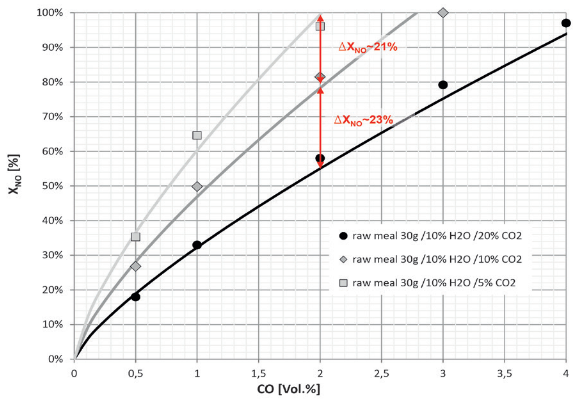

Figure 1. NO conversion vs. CO concentration depending on various CO_2 concentrations.

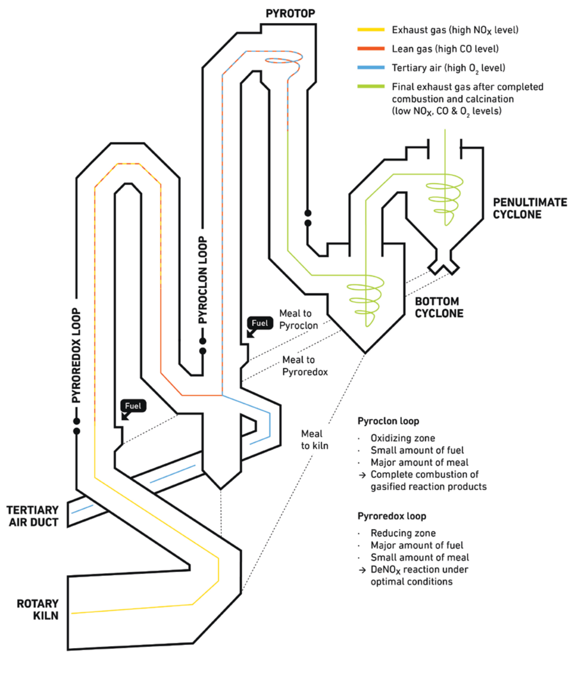

Figure 2. Functional principle of Pyroredox.

Pyroredox limits the NO_x and NH_3 emissions, without a negative impact on production capacity, power demand or fuel consumption, and only a moderate injection of ammonia remains necessary for the SNCR system.

In this article, the various steps of the development of Pyroredox, including the experimental setup, the first commissioning, and the first long-term experience of two installations and their continuous operation, will be elaborated on.

Laboratory results from test setup

In the early stage of product development, it was necessary to verify and quantify the influence of the different parameters known from KHD's own research, as well as existing literature. Initially, an experimental setup was installed in the company's technical centre. This allowed a detailed and systematic examination of the achievable NO_x abatement in controlled conditions.

During these extensive tests, influences and interactions of CO, CO_2, H_2O and kiln dust were evaluated, and resulted in the following conclusions:

- The concentration of CO has the strongest influence on the abatement rate of NO. A reduced NO conversion at higher partial pressure of CO, as found by Ono et al. (1978) cannot be observed.
- The concentration of CO_2 in the kiln gas also has a strong influence on NO conversion rate. In the presence of CO, a decreased CO_2 partial pressure is promoting the NO conversion significantly (Figure 1).
- Kiln dust has a catalytic effect on the conversion of NO with CO. Consequently, a certain amount is essential for efficient NO abatement with CO.
- Water has an inhibiting effect on the abatement of NO with CO.

Final design criteria for the gasifying reactor

The conversion from the experimental study to a real application is based on the conclusion that the most efficient reduction of NO can be achieved with a high CO concentration, lowest possible partial pressure of CO_2 and a sufficient amount of kiln dust acting as a catalyst. The abatement-inhibiting influence of water can only be reduced slightly as the water content in the rotary kiln exhaust gases is primarily dependent on the type and composition of the kiln fuel.

To achieve best possible reduction premises, Pyroredox makes use of the Boudoard reaction. Due to the lack of oxygen, CO_2 emitted from the rotary kiln is reduced with carbon from the calciner fuel to create abundant CO in the gasifying reactor. Because this is an endothermal reaction, the temperature can be managed by adjusting the oxygen content, the kiln inlet and the amount of fuel that is directly fed to Pyroredox. The meal feeding to the first zone on the other hand is limited to a necessary minimum. It will only enable a sufficient catalytic effect. At this stage, it is essential to avoid high amounts of CO_2, which would be released by the meal calcination process.

In the subsequent stages, the NO_x from the rotary kiln is efficiently reduced under optimised conditions. Moreover, the conversion from fuel N to NO_x can also be reduced due to the lack of available oxygen. At the end of the Pyroredox loop, the exhaust gases are then merged with tertiary air (Figure 2). Here, the CO reacts exothermally with the oxygen from tertiary air to form CO_2. The heat created by this exothermal reaction is used for the calcination of meal in the downstream calciner.

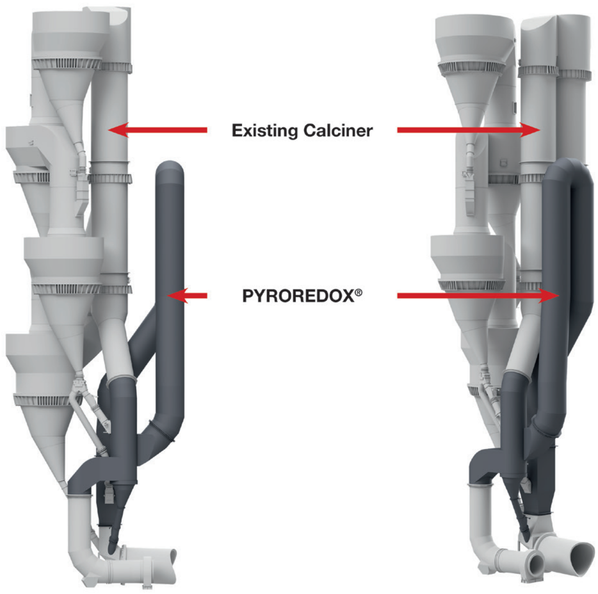

Figure 3. Pyroredox arrangement.

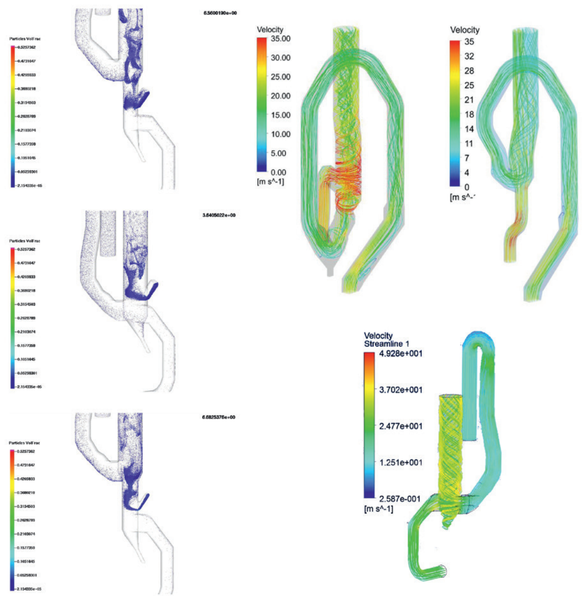

Figure 4. Pyroredox CFD analysis.

Overcoming limitations

State-of-the-art equipment for the primary reduction of NO_x emissions, like KHD's Low NO_x AF calciner, offer a good NO reduction potential. However, there is a drawback; a stable cement process requires a compromise between NO_x conversion and other operational parameters. This compromise naturally limits the NO reduction potential. The Pyroredox system subdivides the traditional calciner into two separate reactors – one purely for NO_x conversion and the other primarily for the calcination. As a result, all previously existing limitations can be overcome and the potential of each parameter promoting the NO conversion rate in a cement kiln can be improved.

Very early in the product development phase, it became clear that Pyroredox should be a largely independent module (Figure 3) to allow retrofits in existing kiln lines, regardless of the original equipment supplier. Additionally, the extra module enables sufficient retention time to be flexible with different fuel types and their reactivity. As a result, all typical calciner fuels, including various alternative fuels, can be used in the system.

Since the core calcination section is not directly connected to the kiln inlet like a conventional calciner, the connection geometry of Pyroredox and the tertiary air duct in the design phase is vital. First of all, it is necessary that combustion residues and kiln dust can still be lifted into the calciner section safely. Secondly, the lean gas from the Pyroredox and tertiary air flow must not create turbulences to ensure that meal is not able to drop into the conical connection section.

To achieve an ideal design, it was necessary to determine the most favourable geometry in terms of gas and material flow properties. Consequently, various single- and multi-phase CFD analyses were performed (Figure 4).

To achieve standalone (no combination with other existing reducing measures) NO_x abatement levels below 200 mg/Nm^3, the operation of Pyroredox has the following requirements:

- 2 – 5% oxygen at kiln inlet.

- Between 60% and 100% calciner fuel is fed to Pyroredox.
- Between 0% and 10% of meal from the penultimate cyclone stage is fed to Pyroredox.

First installations

Since today's cement market is predominantly focused on upgrades and retrofits, the first realised Pyroredox projects were modifications of existing kiln lines.

Figure 5. Pyrodredox installations at Weihui plant (left) and Xindeng plant (right).

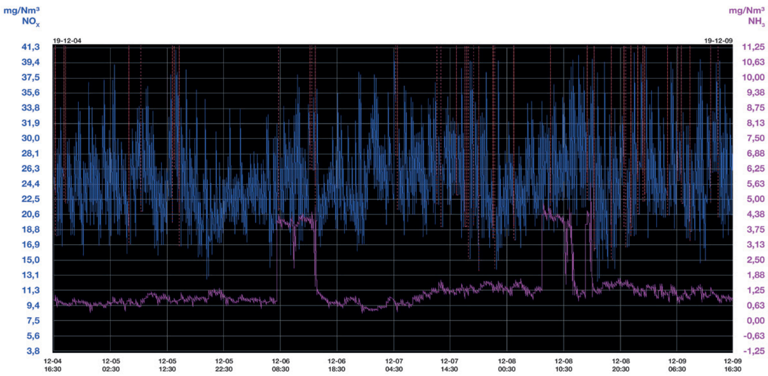

Figure 6. NO_x and NH_3 emission graph from Pyroredox operation.

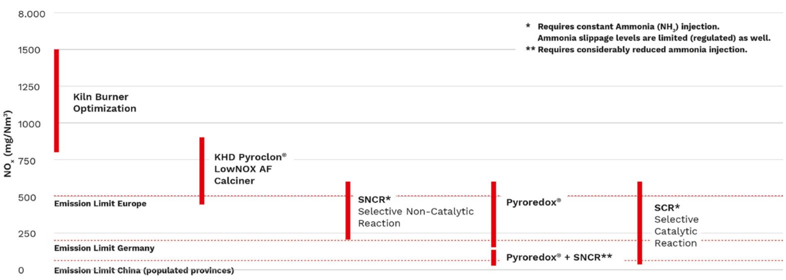

Figure 7. NO_x reducing solutions and achievable levels.

As mentioned, the permitted emission levels in China were drastically reduced in the last few years. This resulted in extreme pressure on cement manufacturers to invest in NO_x abatement measures. Therefore, in mid-2018 China's Tianrui Group decided upon a Pyroredox upgrade of two of their existing kiln lines (Figure 5.)

Both kiln lines with in-line calciner were originally delivered by SINOMA/TCDRI. Thanks to the modular principle behind Pyroredox, the integration into the existing structure was realisable with manageable effort. The total installation and commissioning time for both projects was just seven months. Moreover, almost all of the erection work of Pyroredox can be performed during normal operation of the kiln line. In most upgrade cases, around four weeks are necessary to connect the new equipment to the existing calciner system. At both Tianrui group projects, the final connection and commissioning of Pyroredox was conducted during the regular maintenance shutdown in winter.

Operational results

The final commissioning for both plants was done in January and February 2019. Due to constantly increasing air pollution, the authorities in the Henan province further reduced the emissions limits for industrial plants. Both units had to deal with limits of 100 mg, respectively 50 mg NO_x/Nm^3 of operation. To satisfy these levels and to have the permission to continue production, Pyroredox had to be combined with the existing SNCR system, as the selective non-catalytic reaction system could not achieve and maintain such low emission levels.

With the addition of Pyroredox it was possible to meet the emission limits; when operating both solutions collectively, the NO_x emissions were reduced by 66% and the reagent consumption of the SNCR system could be lowered by 78%. Moreover, both plants still achieved and maintained the production capacity they had before the modification. Additionally, fuel consumption and power demand also remained unaffected by the Pyroredox installation. After the first weeks of continuous and stable operation, a slight capacity increase was reported from the Weihui plant.

With the extensive use of CFD analysis during the initial product development phase, Pyroredox could be designed with a low flow resistivity, which has more than compensated for the increased pressure drop that is a normal result of extra installed equipment. Moreover, the addition of Pyroredox increased the overall calciner volume and led to an improvement of the fuel burnout.

Looking back on one year of constant and stable operation since mid February 2019, both modification projects are considered successes by Tianrui Group and KHD. For both production units it is possible to satisfy all emission limits requested by local authorities. Even the current level of just 30 mg NO_x/Nm^3 can be safely met. This enables Tianrui Group to keep their production up and running even in times when other cement plants had to shut down their clinker production due to high air pollution levels a long time ago. Thanks to the reduced ammonia requirement in both plants, the permitted ammonia emission limit (ammonia slippage) of 8 mg NH_3/Nm^3 can be met.

Figure 7 depicts the NO_x and NH_3 emissions during an uninterrupted production period of five days (120 h) at Xindeng plant in December 2019. The average NO_x emission was 25 mg/Nm^3 and NH_3 emissions were approximately 1 mg/Nm^3 during compound operation (raw mill on) and 4.5 mg/Nm^3 during direct operation (raw mill off).

Figure 8. Visualisation retrofit project, China.

Outlook

The modular concept and the option to combine it with other NO_x reducing technologies means that Pyroredox is able to offer a comparable emission reduction potential like SCR systems (Figure 7), with potentially lower costs in terms of investment as well as operational costs.

The client's expectations during the first two projects were satisfied as Pyroredox enabled Tianrui Group the sustainable compliance with NO_x and ammonia emission limits without a negative impact on production capacity, power consumption or fuel demand. The Tianrui Group and KHD decided to continue the upgrade process of Tianrui's production lines. To this date, a total of five contracts have been signed, including an upgrade of the 12 000 tpd flagship plant, Xingyang. The erection phase at the Xingyang plant has already concluded, and the commissioning is scheduled for the first quarter of 2020.

Additional projects involving Pyroredox are already in negotiation or erection in China, South Korea, Turkey and India. The next project to be finished outside of China is a newly built clinkerisation unit in India, with a Pyroredox gasifying reactor. The commissioning of this project is also scheduled for the first quarter of 2020. ■

About the authors

Marc Feiss has been working in KHD's thermal process department since 2006 and is responsible for the development and design of new technologies for the thermal cement process.

Norbert Streit has been with KHD for almost 30 years and currently fills the position of 'Director of Process Innovation'. He predominantly works on energy-efficient solutions for the use of secondary fuels and raw materials as well as for emission abatement.