

# Meeting tighter NOx emissions rules

## A low temperature oxidation technology uses ozone to remove very low levels of nitrogen oxide from refinery gases

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**R**equirements for reducing air pollution emissions have been evolving over the past couple of decades and today are an intricate mix of limits, targets and caps. In many parts of the world, industries emitting pollutants must not only comply with rigid emission limits, but also need to provide emissions data to numerous different agencies and bodies in order to comply with disparate legislative formats and reporting systems at regional, national and international level – and legislation is going to get increasingly stringent. The global community is working to improve cooperation between emitting sources, monitoring systems – and the legislation they support – in order to reduce the number of serious pollutants being released into the air, soil and water to help mitigate the negative impacts on human health and adverse affects on the environment in coming years.

In 2007, the EU, acknowledging that existing legislation on industrial pollution was complex, sometimes inconsistent and not far reaching enough, adopted new legislation to strengthen the provisions already in force and reduce further industrial emissions. The new directive aims to improve the uptake and implementation of 'Best Available Technologies' (BAT), which maximise the use of technology in plant design, build and operation in order to drive down emissions. Critically, it also tightens current minimum emission limit values for large combustion plants and introduces minimum provisions on environmental inspections of installations and incentives for the development

and employment of environmentally friendly technologies.

Nitrogen oxides, mainly consisting of nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>), and commonly referred to as NO<sub>x</sub>, is among one of the major criteria pollutants listed under the Clean Air Act by the US Environmental Protection Agency and is also monitored by several other countries, notably China. NO<sub>x</sub> deriving from stationary combustion sources makes a major contribution to total emissions and proper control of NO<sub>x</sub> emissions could result in

### Proper control of NOx emissions could result in significant environmental benefits, especially when combusting oil and coal

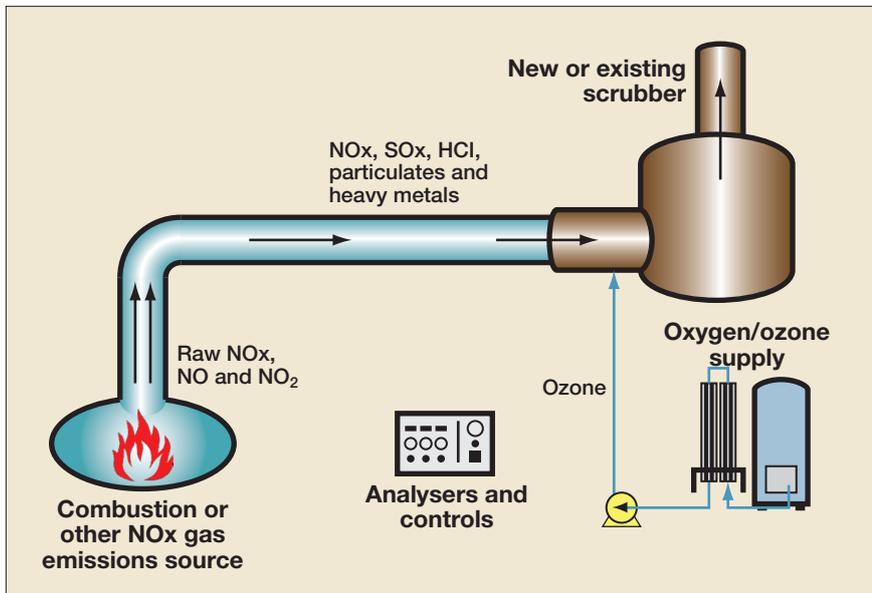
significant environmental benefits, especially when combusting oil and coal.

In most cases, NO<sub>x</sub> is a product of the combustion of fossil fuels or industrial processes and contributes to the formation of smog, acid rain and other health hazards. NO<sub>x</sub> undergoes chemical and photochemical reactions in the atmosphere and reacts with volatile organic compounds (VOCs) in the presence of sunlight to form smog and ground level ozone. The effect is very significant and harmful in

the summer months to children and people with lung diseases such as asthma, causing damage to lung tissue and a reduction in lung function. NO<sub>x</sub> also reacts with ammonia, moisture, and other compounds to form small particles capable of penetrating deeply into sensitive parts of the lungs and causing or worsening respiratory diseases such as emphysema and bronchitis, also aggravating existing heart and lung disease. In addition, NO<sub>x</sub> interacts with oxygen in the atmosphere to produce the atmospheric pollutant low level (or tropospheric) ozone, which impacts on human health. NO<sub>x</sub> emissions also contribute to the formation of damaging acid rain, eutrophication and oxygen depletion degrading water quality and harming wildlife and plant life.

High levels of industrial activity and increasing vehicle emissions have elevated ambient NO<sub>x</sub> and ground level ozone levels in several critical geographies, particularly in the US, Europe and China. In response, environmental authorities are tightening their regulations governing NO<sub>x</sub> emission management and applying sector specific parameters. However, control of NO<sub>x</sub> from each source is a complex process affected by factors that include the amount and distribution of air in the combustion process, temperature, unit load and burner design.

The largest output of NO<sub>x</sub> emissions in stationary sources is from coal fired boilers, especially those in the power generation segment. Other major sources of NO<sub>x</sub> emissions include kilns and furnaces



**Figure 1** The LoTOx process is applied at a controlled temperature zone within the scrubbing system

from the cement, lime, ferrous and non-ferrous metals industries. However, petrochemical processes also produce large amounts of NOx and other airborne pollutants, primarily originating from utility boilers, cogeneration units, process heaters, steam methane reformers, ethylene cracking furnaces and fluid catalytic cracking (FCC) regeneration units. Consequently, the NOx emission levels specified for this sector are among the lowest in industry, highlighting the need for efficient NOx removal.

While some industry sectors claim there is no effective means to remove NOx from their emissions – or rather, no cost effective means to sustain the economic viability of such an operation – there is a spectrum of conventional and more recently introduced technologies available in the market to address this important obligation.

A common approach to controlling NOx emissions is to modify the basic combustion process within the furnace. By using oxygen instead of air in the production process, which removes the nitrogen ballast, energy efficiency is not only increased, but one of the most important benefits is the very significant reduction of both direct and indirect greenhouse gas emissions, including CO<sub>2</sub> and NOx. CO<sub>2</sub> emissions can be reduced by up to 50% and, for NOx, emissions levels

of below 50 mg/MJ can be reached.

However, since emissions vary widely according to changes in temperature and air/fuel mixing, modifications to the combustion process impact not only the emissions, but very frequently also the efficiency and operability of the furnace. This renders NOx control a technically challenging undertaking that calls for understanding of complex issues around combustion chemistry and plant operations, as well as the economic issues related

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to plant fuel consumption and maintenance. NOx reduction by combustion modification is limited, typically in the 30% to 50% range and must be implemented where it is effective and applicable without significant de-rating of the combustion furnace. Alternatively, replacement of the existing combustion equipment can be done but this is obviously capital intensive.

NOx can also be treated

post-combustion and the most commonly specified technique for the removal of high levels of NOx is selective catalytic reduction (SCR), a technology designed to facilitate NOx reduction reactions in an oxidising atmosphere. It is called ‘selective’ because it reduces levels of NOx using ammonia as a reductant within a catalyst system. The reducing agent reacts with NOx to convert the pollutants into nitrogen and water. SCR has been adopted effectively in lowering NOx emissions from gas fired clean flue gas streams. However, in treating dirty gas streams from industrial processes involving kilns, furnaces and combusting coal or oil with SCR possess a risk of the catalyst being compromised by chemical poisons in the flue gas, or blinded by the dust and particulate matter also resident in the flue gas.

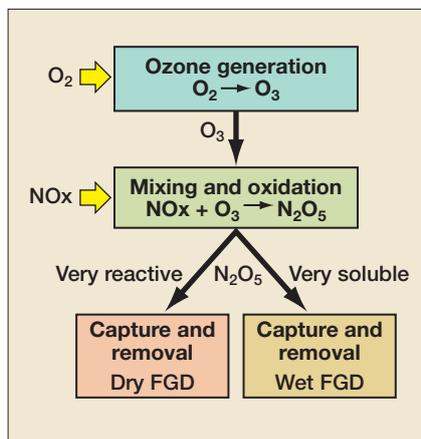
SCR must be integrated into a high temperature region of the process, so if it is not included in the original design of the furnace, later installation will require a major rework of the process. The intermediate technology selective non-catalytic reduction (SNCR) is also applicable in the high temperature regions impacting the process. SNCR does not make use of a catalyst, but requires a highly defined temperature region to provide a reaction with ammonia. This technology is capable of achieving a 50-60% NOx removal.

The effective temperature for reduction in NOx through a SCR catalyst is in the range 200-400°C – and for SNCR to be effective, ammonia injection and reduction need to be in the range of 900-1100°C. Additionally, retrofitting NOx reduction solutions such as SCR or SNCR can often be disruptive to the industrial process and can have negative implications with respect to operations and costs.

Linde’s LoTOx technology, which stands for ‘low temperature oxidation’, has been specifically developed for the control of NOx emissions. LoTOx, which works on ‘dirty’ exhaust gas streams to oxidise and then capture NOx, is a selective, low temperature oxida-

tion technology that uses ozone to oxidise NOx to water soluble and very reactive nitric pentoxide (N<sub>2</sub>O<sub>5</sub>). The process is applied at a controlled temperature zone within the scrubbing system (see **Figure 1**). It does not require additional scrubbers but can leverage those already installed to remove other pollutants such as SOx. Dirty gas means gas with other targeted pollutants, typically particulate matters, SOx and other acid gases. Irrespective of NOx removal, for control of these pollutants, air pollution control devices such as wet and dry scrubbers are required to remove those pollutants. Integrating the LoTOx process within such air pollution control devices is relatively simple and acts as a multi-pollutant removal system.

Inside a wet or dry scrubber, N<sub>2</sub>O<sub>5</sub> forms nitric acid that is subsequently scrubbed by aqueous spray and neutralised by the alkali reagent. The conversion of higher



**Figure 2** LoTOx uses ozone to oxidise NOx to water soluble nitric pentoxide (N<sub>2</sub>O<sub>5</sub>)

oxides of nitrogen into the aqueous phase in the scrubber is rapid and irreversible, allowing an almost complete removal of NOx, in the region of 90-95% – even as high as 98% – from flue gases. The low operating temperature allows stable and consistent control, regardless of variation in flow, load or NOx content, and acid gases or particulates have no adverse effect on the

performance of the process.

LoTOx is a versatile NOx removal process but is ideally suited when the level of removal required is greater than 80% or where stack emissions must be below 20 ppm. The process offers inherent flexibility in NOx removal. In most gases, simply increasing the amount of ozone injection may meet increasingly stringent regulations or limiting tiered NOx emissions.

The benefits of this technology include increased capacity, greater flexibility in the choice of feeds, increased conversion rates and reduced emissions. Since the technology is a post-combustion solution that treats the flue gas at the end of the process, it does not interfere with the process in any way. The system does not utilise a fixed catalyst bed and does not impact system hydraulics, making it robust and reliable, capable of operating without maintenance for periods of two to three years between refinery shutdowns. It is

also able to manage unit upsets without impacting overall reliability and mechanical availability.

The ozone required is produced from oxygen on site in response to the amount of NO<sub>x</sub> present in the flue gas generated by the combustion process and the final NO<sub>x</sub> emission required (see **Figure 2**).

Some 40 LoTOx installations have been commissioned to date – 30 of them in petroleum refineries through Linde's LoTOx licensee for refinery applications, DuPont Belco. Installations are almost equally divided between the US and, notably, China, which is advancing its NO<sub>x</sub> control regulations due to heavy industrialisation and challenging air quality issues. There are two more installations in progress, one in Romania and another in Thailand, indicating stricter environmental regulations on the horizon.

LoTOx is attracting a reputation for being able to bypass some of the problems associated with the dirty flue gases that impact the effective operation of SCR. It is suitable for both new and retrofit applications and is the only post combustion technology of its kind in industry today, set apart by its method of treating flue gases with ozone and the fact that most of the other oxidation and reduction processes take place at high temperatures.

To control costs, LoTOx is frequently recommended in combination with a lower end combustion modification technology to remove a certain level of NO<sub>x</sub>, before it takes out the remaining NO<sub>x</sub> to a low level.

Operating costs derive from the power, oxygen and cooling water associated with ozone generation and each of these costs is directly proportional to the levels of NO<sub>x</sub> being treated. In comparison to the ammonia storage and handling issues associated with SCR or SNCR, LoTOx produces ozone on demand by passing oxygen through a conventional industrial ozone generator, as required and on site. The other operating cost relates to the addition of caustic solution to neutralise the nitric acid produced

by the process of reducing NO<sub>x</sub>. This marginally increases the amount of caustic solution used by the scrubber for removing particulates and sulphur oxides.

A further, unexplored benefit of recent interest is the LoTOx system's ability to reduce mercury emissions as part of a complete multi-pollutant control solution.

More recently, Linde's engineering division has developed a new NO<sub>x</sub> removal technology for use with carbon sequestration and storage, called Liconox.

### **Monitoring, detection and reporting**

Environmental concerns have come a long way since the 1970s, when acid rain caused by sulphur dioxide and nitrogen oxides prompted power stations to install sulphur dioxide scrubbers and SCRs for

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nitrogen oxide reduction and motor vehicles were fitted with catalysers. Emissions measurement was carried out for compliance, resulting in fines for those who overstepped the mark. Today, however, as legislation and action plans grow in number and stringency, the importance of monitoring and quantifying emission pollutants in an accurate and transparent manner is becoming a priority. Day-to-day emissions measurement has serious financial implications and compliance to measurement is absolutely critical. Real-time and on-line reporting systems will be the aim for most large sources.

Frequent sampling may be

required during start-up and upset conditions. Once a record of consistent performance has been established, air emissions from stacks should be visually monitored for opacity at least once every eight hours. Annual emissions monitoring of combustion sources should be carried out for SO<sub>x</sub>, NO<sub>x</sub> and organics, with fuel sulphur content and excess oxygen maintained at acceptable levels during normal operations.

Monitoring data should be analysed and reviewed at regular intervals and compared with the operating standards, so that any necessary corrective actions can be taken in a timely manner. Monitoring records should be kept in an acceptable format for submission to the responsible authorities and relevant parties, as required.

The automation enabled by technological advances favours continuous emission monitoring systems (CEMS), while emission measurement instruments are becoming smaller and less expensive. This has heralded the way for gas phase measurement and gas phase calibration from gas cylinders, with a move away from manual and people-intensive 'wet chemistry' measurement.

Government institutes used to carry out much of the emissions measurement themselves, but have now outsourced this function to a large extent. There is a distinct trend of moving from control to compliance. Metrology has been commercialised and the establishment of primary calibration standards has moved from the government domain into that of the major oil and gas companies. Such a development has been enabled by improved international standards and by global recognition of these standards, such as ISO Guide 34 and the emerging ISO 17025. However, many pockets of local, national and regional requirements are still in place, for instance the GBW standards in China and the US-centric EPA.

### **Technology for monitoring and detection**

With the growing importance and

prioritisation of monitoring and quantifying emissions, accuracy and reliability in measurement calibration is critical. The demand for stable, accurate measurement is the cornerstone of emissions analysis. However, calibration standards for low level reactive mixtures, typically those with levels below 5 ppm, can prove to be unstable over time and can result in incorrect measurements, lost productivity and – with emissions monitoring – potential legislative fines.

To keep pace with increasingly stringent legislative requirements, calibration gas mixtures are now being delivered with state-of-the-art packaging technology so that they even exceed the demanding requirements for consistency and stability – down to part-per-billion levels.

With any gas used for calibration purposes, the most important requirement is that it can accurately and repeatedly report values of the relevant instrument being meas-

ured. In the US, the EPA has defined shelf lives for protocol gases as between six to 36 months – depending on the gas and concentration – and similar shelf life standards exist in the ISO framework for reference materials. Notwithstanding these international protocols, Linde's range of HiQ 60 specialty gas products have an extended five-year shelf life – a significant advance in the supply of calibration gases. Previously, gas suppliers offered product expiration guarantees generally limited to 36 months, with many products available with only 12 or 24 months of shelf life. Gas products with these more limited shelf lives can impact measurement accuracy, as gas stability in terms of consistency and quality can change over time. Where consistency or purity of the gas has been compromised, this can result in expensive system recalibration procedures, additional cylinder changeovers and wasted human resource time.

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