glass WORLDWIDE

Sweeping changes for emissions control and monitoring

The combination of Linde's COROX LowNO$_x$ technology with oxyfuel hotspot burners is said to optimise process and NO$_x$ reduction efficiency. Rainer Mieth and Stephen Harrison discuss the latest developments in emissions control in the EU.

According to European Environmental Agency figures, in 2008 estimated emissions vented into the ambient air by the European glass manufacturing industry included 10,500 tonnes of NO$_x$, 80,000 tonnes of SO_2, 22 million tonnes of CO_2 and 6500 tonnes of dust.

Industrial emissions, including those emanating from the high temperature and energy-intensive glass manufacturing process, can have major environmental and health risks for society. To combat these risks, the European Parliament developed the Industrial Emission Directive 2010/75/EU (IED). The directive has the objective of standardising maximum emission levels across a broad range of combustion-based industries throughout the EU. It will have oversight for the licensing, operation, monitoring and decommissioning of industrial plants to prevent and reduce pollution to the air and water. Beyond that, the IED describes how measuring and monitoring should take place and is driven and enabled by an increase in the use of 'best available techniques' (BAT). The BAT approach is aimed at identifying and applying the best technology available worldwide, applying it as cost-effectively as possible on an industrial scale, to reduce emissions and achieve a high level of environmental protection. The BREF documents which outline BAT will herald lower Emission Limit Values (ELV) for industries and set the standards to obtain better consistency and quality of implementation across the EU member states.

For the transition of the IED into national law in relation to glass manufacturing, EU member states had four years from the publication of the Best Available Technique (BAT) conclusions on 8 March 2012. The corresponding authority in the member state has to review and if necessary, update all permit conditions and ensure that glass manufacturing plants comply with those conditions. The implementation period must be met by all EU member states and must be verified in formal reporting by 2016/2017. The European Commission's IED will mean a considerable change for glass manufactures in terms of what is required of them from an emissions reduction and monitoring viewpoint.

INDUSTRY IMPACT

For glass melting furnace operations and many other natural gas combustion industries, much of the impact will be focused on three pollutants: SO_2, NO$_x$ and CO. Since SO_2 and CO emissions are more manageable for glass manufacturers - for example, through post-combustion for CO and chalk additives in the filter for SO_2 - it is the NO$_x$ emissions that really pose the challenge.

Current NO$_x$ emissions from glass furnaces are typically between 1200-1500 mg/Nm³ NO$_x$. The IED defines significantly reduced new emission limit values - 800 mg/Nm³ NO$_x$ for existing furnaces and 500 mg/Nm³ for new furnaces, measured in 8% residual oxygen on an hourly average.

COPING WITH THE CHALLENGE

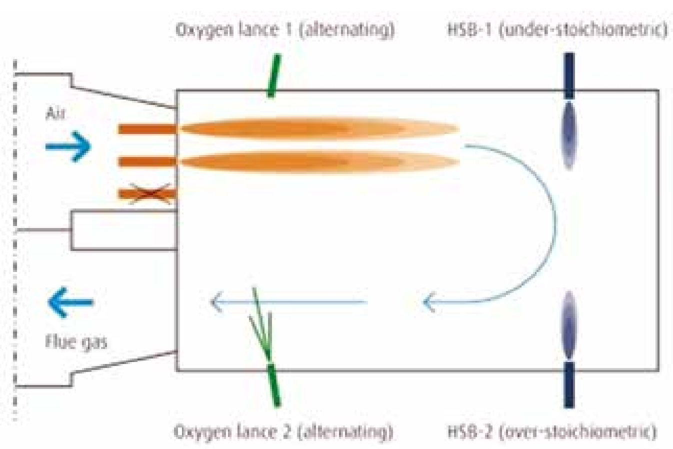
There are three mechanisms for NO$_x$ creation during combustion: 'Thermal NO$_x$', 'fuel NO$_x$' and 'prompt NO$_x$'. Thermal NO$_x$ is created by high temperatures (T>1400°C; Zeldovich principle), fuel NO$_x$ by nitrogen contained in the fuel, reacting with the oxidisers and prompt NO$_x$ by CH radicals during combustion.

To reduce NO$_x$, the BREF notes recommend primary control measures that seek to generate unfavourable conditions for NO$_x$ formation. These primary techniques can be combustion modifications, special furnace design, electric melting and oxyfuel melting. With regard to combustion modifications, there are several BATs outlined, including a reduction of the air/fuel ratio, reduced combustion air temperature, staged combustion, employing flue gas recirculation, the installation of low NO$_x$ burners and adjusting fuel selection.

Industrial gases and gas application technologies can play a significant role in helping reduce combustion pollution including NO$_x$. In general, employing greater levels of oxygen substantially increases the thermal efficiency of a furnace, as radiant heat transfer of furnace gases produced by oxyfuel combustion is significantly more efficient than those of air fuel. In the combustion process, nitrogen can essentially be regarded as ballast, with this ballast acting as a negative influence as it neither takes part in, nor helps combustion.

One such gas technology to considerably reduce NO$_x$ emissions is Linde's COROX LowNO$_x$ for recuperative and regenerative end port furnaces. The novel part is that this technology combines several BATs of the combustion modification part, such as reduction in air fuel ratio, staged combustion of both air and fuel, flue gas recirculation and the use of low NO$_x$ burners.

The process involves injecting additional oxygen through high pressure lances to create a more intense, directional flue gas recirculation effect within the furnace. As a result, the main air/gas burner system produces a diluted, staged combustion process. The fuel dilution leads to a more homogenous flame and a reduced flame temperature. As the flame temperature has a direct impact on thermal NO$_x$ levels, this lowers emissions significantly. >



Top view of an end port glass furnace, showing the COROX LowNO$_x$ solution for NO$_x$ reduction.

A lower flame temperature also reduces the concentration of hydrocarbon radicals in the furnace, thereby limiting prompt NO_x formation. In addition, an improved heat transfer rate shortens the window during which thermal NO_x can form.

Combining COROX $LowNO_x$ technology with oxyfuel hotspot burners optimises its process and NO_x reduction efficiency. Operating the furnace under these conditions, with staged combustion leading to a lower flame temperature and more homogeneous energy distribution, reduces energy consumption by approximately 3%-5%. Alternatively, melting capacity can be increased by 5%-8%, while still complying with the EU NO_x legislation.

Large combustion furnaces with a typical lifetime of 10-12 years and in some cases, up to 20 years or more, represent a large capital commitment. Often major changes in melting technologies are implemented if they coincide with furnace rebuilds. However, COROX $LowNO_x$ can be easily added to existing facilities during a furnace lifetime with minimal space requirements.

EMISSIONS MONITORING

The BREF documents which outline BAT will herald lower Emissions Limit Values (ELVs) that will necessitate investment in more advanced pollution control measures.

Float glass production facilities are often obliged to monitor and control their emissions profile, in order to manage the associated gaseous environmental pollutants such as CO_2, NO_x and SO_2. Therefore, typical stages in flue gas clean-up from the burner are $DeNO_x$ and desulphurisation via an SO_2 scrubber, occasionally with carbon dioxide knock down, before gas is emitted to the atmosphere. In some technologies, as emissions gases flow through the $DeNO_x$ unit, ammonia is added to the flue gas to reduce the NO_x back to their molecular nitrogen, while in the SO_2 stripper, various chemicals absorb the SO_2, changing it from a gaseous form into a liquid form, where it can be handled and treated more efficiently.

Ammonia can be added to the $DeNO_x$ unit because it contains a large amount of hydrogen that is able to reduce the NO_x to react with the oxygen in nitric oxide and convert nitric oxide back to nitrogen, which is regarded as a safe gas to emit. Often included under the banner of a speciality gas, ammonia is supplied in bulk deliveries to major float glass facilities, or in drums and cylinders to smaller scale, R&D and pilot glass production facilities.

Essential to monitoring the different clean-up operations are process control gas mixtures containing, in this application, oxides of nitrogen or SO_2. Frequent calibration is needed with very accurate and precise specialty gases mixtures. These mixtures calibrate the continuous emissions monitoring (CEM) instrumentation in the process train, measuring the flue gas as it comes through all the process steps and eventually goes up the smoke stack. In general, non-dispersive infrared sensor (NDIR) sensors or Fourier transform infrared gas analysers (FTIR) are used for these measurements, both of which require a broad range of calibration gas mixtures, typically mixtures of nitric oxide in nitrogen, or mixtures of SO_2 in nitrogen at relatively low concentrations, sometimes in parts per million.

The role of specialty gases will be critical to ensuring compliance with Directive 2010/75/EU as they are essential for calibration of the emissions measuring instruments – and are precisely prepared for each glass manufacturer to meet their emission monitoring needs.

In some cases where CEM systems are installed, the composition and quality of these gases and calibration mixtures will be independently regulated and controlled by external auditors and is likely to be regulated through accredited schemes for measurement such as ISO17025.

WHERE NEXT?

The introduction of the IED is a major development in emissions control in the EU and it begs the question: "What will the next major development in this arena look like?"

Some speculate that the focus in the EU may extend at some future date towards a closer focus on oxides of nitrogen, as nitric oxide, nitrous oxide and nitrogen dioxide each plays a different role in terms of the pollution they cause to the ambient air.

NH_3 is also very likely to come into the measurement species, because it is added to a lot of combustion off-gas processing operations that use selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) technology to reduce NO_x emissions. Precise measurement and control of NH_3 will ensure it is added in optimum quantities so that NO_x emissions are minimised, while not overdosing the NH_3 to the extent that it is emitted as a pollutant in its own right or is being used in wasteful quantities, with related cost implications.

It is also now becoming common practice to measure ammonia 'slip' after the catalytic reaction at around 5ppm ammonia. However, the accurate measurement of ammonia using on-line instrumentation in such a hot, wet emissions stream is a real technological challenge. The issues are not related to the instrumentation, or the availability of high quality specialty gases calibration mixtures but lie in the problems of sample conditioning and delivery. In fact, to enable the high precision measurement of ammonia in legislated environmental applications, Linde Gas became the first laboratory in Germany to offer ISO17025 accredited calibration gas mixtures in this range of ammonia concentrations in July 2014. As an alternative to on-line ammonia measurement in the flue gas, some proxy measures are also used. For example, ammonia salts can be measured in fly ash samples. However, due to the intermittent sampling and batch analysis technique, this is a relatively slow feedback process control loop.

Besides that, the IED will stretch this scope a bit further and there are already plans to introduce medium combustion plant legislation that will fill a gap not yet addressed by the IED, to focus on slightly smaller combustion operations related to small-scale heating and power generation. Ultimately, it is possible that within the next decade, the impact of EU emissions legislation will impact any operation burning material on an industrial scale.

In many combustion operations, speciation between SO_2 and sulphur trioxide (SO_3) will also come into focus. Distinction between SO_2 and SO_3 becomes vital if the flue gas processing will subsequently involve electrostatic precipitation because the SO_3 can have a very detrimental impact on this process.

FUTURE CHALLENGES

As international emissions legislation becomes more sophisticated, it is propelling the specialty gases and instrumentation sectors into completely different levels of technology, beyond traditional solutions where a calibration gas mixture could simply be hooked up to an analyser. A good example is analysis of the SO_3 molecule, whose half life is too short to allow for the production of a calibration gas standard. This calls for the mixture to be produced on site, using generator technology.

Advancements in emissions legislation will therefore continue to challenge gas companies like Linde Gas to be able to supply products that underpin its requirements. Legislators also need to ensure through BAT and BREF documents that the technology actually exists, or can be applied cost-effectively to any new legislative requirements. ■

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