ECOCYL® is Linde's environmentally friendly and portable cylinder for calibration gases.

Stephen Harrison, Linde Gases, Germany, provides an update on emission monitoring and detection.

Emissions EDUCATION

Requirements 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 becoming 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.

What this means for industry is that more pollutants will require monitoring from a greater number of emitting sources; for example, mercury (Hg) is rapidly moving up the agenda in the EU, the US and Asia ahead of the legally binding United Nations EP Global Treaty on Mercury to be implemented in 2013. Advanced systems and methods will be required to measure lower and lower concentrations of pollutants as emission limits tighten. Increased accuracy will become paramount as pollutants such as N_2O, CH_4 and possibly Hg are introduced to trading markets in the EU and US. The change will mean that once a monetary value comes into play, measurement accuracy becomes an economic target as well as an environmental one.

For those industrialised member states, including energy and emissions giant Russia, the Kyoto Protocol has already established legally binding commitments for the reduction of greenhouse gases (GHGs) down to 1990 levels by 2012. The Protocol also established a global carbon trust incorporating market based mechanisms, which can assign concrete financial values to each tonne of GHG emission. Although countries such as Russia still lack longer term energy strategies to enable them to participate fully, the potential to benefit financially from selling surplus emission reduction credits to the EU and other member states internationally, places even greater importance on emissions measurement and evaluation.

In March last year, the US Environmental Protection Agency (EPA) proposed the implementation of the first mandatory national carbon emissions reporting programme to ensure a reduction of carbon dioxide and other GHGs produced by major sources in the US. GHGs, like CO_2, are produced by burning fossil fuels and through industrial and biological processes. Approximately 13 000 facilities, accounting for 85 – 90% of GHGs emitted in the US, would be covered under the proposal. The new reporting requirements will apply to suppliers of fossil fuel and industrial chemicals, as well as large direct emitters of GHGs with emissions equal to, or greater than, 25 000 tpy. The direct emission sources covered under the reporting requirement would include energy intensive sectors such as cement production, metallurgy production and electricity generation, among others. The first annual report will need to be submitted to the EPA for this year in 2011.

This type of initiative is being repeated at various locations worldwide to address climate change head on, in a straightforward manner with immediate financial incentives to drive rapid and economy wide adoption of carbon reduction and market based trading.

In 2005, the EU published its Thematic Strategy on Air Pollution, which set out clear objectives for the reduction of a number of important air pollutants. While industrial emissions have decreased over the past few years, they continue to have a significant impact on the environment and need to be reduced further. The largest industrial installations still account for a considerable share of total emissions of key atmospheric pollutants: 83% for SO_2; 34% for NO_x; 43% for dust and 55% for volatile organic compounds (VOCs). It was soon recognised that EU member states' projected air emissions would greatly exceed the 2020 targets of the Thematic Strategy on Air Pollution unless timely action was taken.

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.

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. Real time and online reporting systems will be the aim for most large sources. As Lisa P. Jackson, Administrator for the EPA stated, 'our efforts to confront climate change must be guided by the best possible information. Through this new reporting, we will have comprehensive and accurate data about the production of GHGs. This is a critical step toward helping us better protect our health and environment.'

Petrochemical sector emissions

The petrochemical industry harnesses a variety of processes that use fossil fuels or petroleum refinery products as feedstock. These raw materials range from crude petroleum, natural gas, refinery gas, natural gas condensate, light tops or naphtha and heavier fractions such as fuel oil.

The hundreds of process units used in the production of petrochemicals are associated with emissions that impact air, land and water. Setting the petrochemical industry apart from other industrial sectors, in terms of emissions, is the wide variety of hydrocarbon compounds, many considered carcinogenic or toxic, potentially emitted by petrochemical plants.

Fugitive air emissions from pumps, valves, flanges, storage tanks, loading and unloading operations and wastewater treatment are of particular concern. Air emissions can include alkenes (such as propylene and ethylene), benzene, butadiene, 1,2-dichloroethane, vinyl chloride, particulates, carbon monoxide, nitrogen oxides, sulfur oxides, as well as a multitude of other VOCs.

Petrochemical units generate wastewater from process operations (such as vapour condensation), cooling tower blow down, and storm water runoff. Process wastewater may contain suspended solids, oil and grease, as well as other active chemical compounds.

Petrochemical plants also generate solid wastes and sludges, some of which may be considered hazardous because of the presence of toxic organics and heavy metals. Spent caustic and other hazardous wastes such as distillation residues, associated with units handling aldehydes, chlorides, amines, as well as other active organic compounds, may be generated in significant quantities.

Mitigations

The Multilateral Investment Guarantee Agency (MIGA), part of the World Bank, outlines a number of general areas where emission improvements are often possible in the petrochemical production process, recommending that site specific emission reduction measures in these areas should be designed into the plant and targeted by plant management.

For instance, air emissions can be reduced by minimising the VOC leakages from valves, pump glands (using mechanical seals), flanges, and other process equipment by following good design practices and equipment maintenance procedures. Mechanical seals can be used where appropriate, while losses from storage tanks, product transfer areas, and other process areas can be minimised by adopting methods such as vapour recovery systems and double seals (for floating roof tanks).

Other broad measures include recovering catalysts and reducing particulate emissions, using low NO_x burners to reduce NO_x emissions and optimising fuel usage. In some case, organics that cannot be recovered can be effectively destroyed by routing them to flares and other combustion devices.

MIGA suggests that pollutants could be eliminated or reduced by using non-chrome based additives in cooling water and by using long life catalysts and regeneration to extend the cycle. Cooling water and treated wastewater can, in some cases, be recycled or reused, while recovery and reuse of solvents and other chemicals is sometimes feasible.

Improved operating procedures also play a key role in reducing the impact of emissions. MIGA suggests segregating process wastewaters from storm water systems, optimising tank and equipment cleaning frequency, preventing solids and oily wastes from entering the drainage system and establishing and maintaining an emergency preparedness and response plan.

Frequent sampling may be required during startup 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 8 hrs. Annual emissions monitoring of combustion sources should be carried out for SO_x, NO_x and organics, with fuel sulfur content and excess oxygen maintained at acceptable levels during normal operations. Leakages should be visually checked every 8 hrs and at least once a week using leak detection equipment.

Liquid effluents should be monitored at least once every 8 hrs for most parameters, except for metals, which should be monitored on at least a monthly basis. Each shipment of solid waste going for disposal should be monitored for toxic content.

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 timeously. Monitoring records should be kept in an acceptable format for submission to the responsible authorities and relevant parties, as required.

Emission monitoring trends

Environmental concerns have come a long way since the 1970s, when acid rain caused by sulfur dioxide and nitrogen oxides prompted power plants to install sulfur dioxide scrubbers and selective catalytic reduction units (SCRs) for nitrogen oxide reduction and motor vehicles were fitted with catalysers.

While these issues remain, global warming, GHGs and CO_2 emissions have become the concerns of the 21st century, bringing with them the requirement to measure emissions at progressively lower levels and with greater accuracy.

Up until quite recently, emissions measurement was carried out for compliance, resulting in fines for those who overstepped the mark. Now, however, day to day emissions measurement has financial implications and compliance to measurement is absolutely critical.

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.

Where government institutes used to carry out a lot of emission measurement themselves, today they have outsourced this function to a large extent. They retain control, however, by checking that industry complies with the standards.

A definite trend moving from control to compliance is evident. Today, metrology has been commercialised and establishment of primary calibration standards has moved out of the government domain into that of the major gas companies. This 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 emissions reduction

Combined with demands to increase energy efficiency and production yield, decrease fuel consumption and also align processes to comply with increasingly environmental regulations, emissions reduction has become one of the most important issues facing the process industries today. As a result, the process industries have seen continued momentum in the uptake of oxyfuel technologies.

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_2 and NO_x. CO_2 emissions can be reduced by up to 50% and, for NO_x emissions, levels of below 50 mg/MJ can be reached.

Originally prompted by rapidly rising fuel prices in the 1970s, methods of using oxygen enrichment was first pioneered in the steel industry, but today Linde continues to explore innovative uses of oxyfuel technology for the refining and petrochemical industries.

Technology for emissions 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 of 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.

In the US, the EPA has defined shelf lives for Protocol gases as between 6 - 36 months, depending on the gas and concentration, and similar shelf life standards exist in the ISO framework for reference materials. Not withstanding these international protocols, the development of what is an extended five year shelf life is a significant leap forward in the supply of calibration gases. Previously, gas suppliers across the market 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.

A further development in emissions monitoring and detection has been the miniaturisation of emissions monitoring devices, which are often dispersed across remote locations throughout a plant. These instruments demand smaller, highly portable gas calibration solutions.