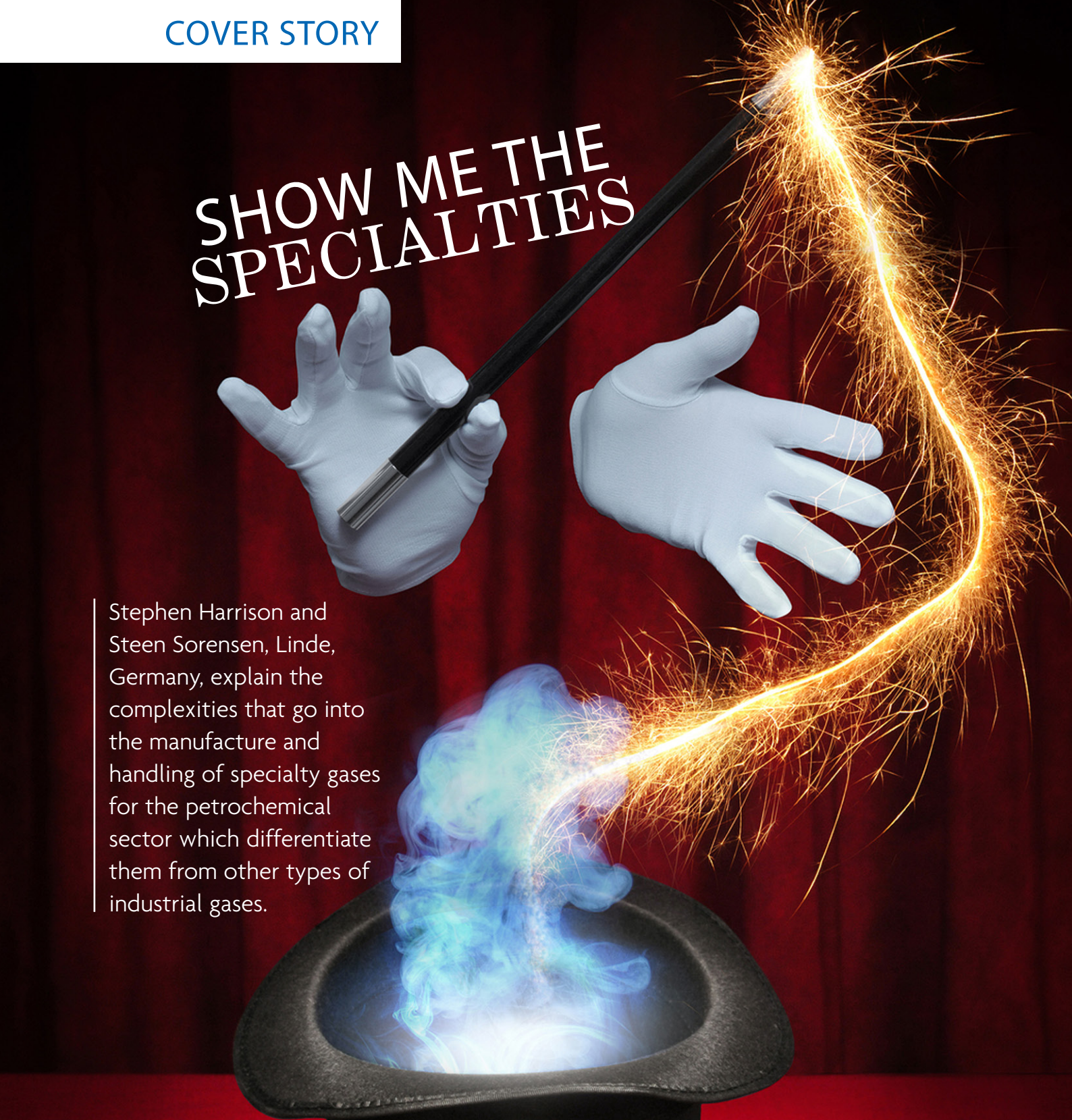
SHOW ME THE SPECIALTIES



Stephen Harrison and Steen Sorensen, Linde, Germany, explain the complexities that go into the manufacture and handling of specialty gases for the petrochemical sector which differentiate them from other types of industrial gases.

Advanced industrial processes in the petrochemical sector continue to demand specialty gases with ever higher levels of purity and more precise accuracies. An increasing number of specifications for these gases now go down to parts per billion (ppb) and sometimes even to parts per trillion (ppt). Gas supply companies have to ensure that the specialty gas supplied is the one that best corresponds to the application it will be used for in this industry.

The characteristics of these exotic, non-standard specialty gases, in comparison with standard industrial and medical gases, divide the gas supply market into specific segments. Within the pure specialty grades, purity can reach up to 99.99999% (7.0). Higher purity means fewer and lower levels of the impurities that cause problems with high tech production processes or instrumentation and analytical measurement.

This high level of purity, compared to the same gas at an industrial or medical purity, is one of the differentiators that make a specialty gas 'special'. Oxygen, for example, is a common medical gas and its purity must be suitable for people to breathe. Oxygen is also used in industrial applications, for instance, when it is mixed with acetylene to create a flame to weld and cut metal. In this application, the purity level of the oxygen need only be sufficient to create a flame. Oxygen is also used in speciality gas applications, such as laboratory instrumentation, but the purity of oxygen required in this laboratory gas application is much higher.

Figure 1. There are often more than 1000 gas cylinders of different types on a large petrochemical site at any given time.

Another characteristic of specialty gases in comparison to medical or industrial gases is the complexity of the product. While a gas mixture for a welding application could comprise a mixture of argon and carbon dioxide to weld steel, and a gas mixture used in a medical application could harness a mixture of nitrous oxide and oxygen for anaesthesia, speciality gas mixtures are far more complex. Instead of two or three different chemicals in the mix, there could be a combination of 20 or 30 chemicals. In addition, instead of blending these chemicals to a tolerance of, for example, plus or minus 5%, the end user might require the component to be blended at an accuracy of plus or minus 1%.

Refinery and petrochemical processing calibration mixtures can range from a simple 2.5% methane/air mixture, to much more complex mixtures of 20 or more hydrocarbon components. Most calibration mixtures are stored outside the analyser stations, and with winter temperatures often dropping to -15 °C or lower, gas mixtures must be specially formulated to avoid the condensation of some heavy mixture components. Additionally, environmental mixtures need to comply with requirements for continuous emission monitoring systems (CEMS).

With any gas mixture used for calibration purposes, the most important requirement is that it must accurately and repeatedly report values of the relevant instrument being calibrated. Calibration should be precise and must be proved to be so. Many gas mixtures used to conduct environmental monitoring are required by national environmental authorities to be accredited. Accreditation is therefore an important factor in the production of specialty gases, proving to petrochemical plant operators that the gas mixture has been prepared to the required quality.

Specialty gas plants and filling stations should achieve certification as producers under ISO 9001, often with selected facilities independently accredited to programmes such as ISO 17025:2005 as testing and/or calibrating laboratories and ISO Guide 34 that provides the highest level of quality assurance. Companies such as Linde Gases can confidently state that methods used to certify its accredited calibration gas mixtures are accurate, consistent, documented and validated.

Scale of supply is another major differentiator between specialty gases and industrial and medical gases. The quantities in which specialty gases are requested by end users are frequently much smaller than the other gases. How much of the gas will be used and how many customers will want this particular product also influences scale of supply.

Some of the most common industrial gases are supplied to customers through pipelines in quantities of tpd, or in bulk format by 20 – 30 t road tankers, where the liquefied gas is supplied to customer facilities and vapourised on site to yield the gas required. This is a cost effective way to buy high quantities of standard industrial or medical gases. In contrast, specialty gases are typically supplied in cylinders containing approximately 10 m^3 of the gas or in small portable cylinders that only contain one cubic metre of the product.

There are often more than 1000 gas cylinders of different types on a large petrochemical site at any given time, while an air separation unit (ASU) supplies tonnage scale nitrogen or oxygen requirements. Bulk storage tanks also contain liquefied gases for intermediate volume supply requirements.

Specialty gas production

In many cases, specialty gases and mixtures are unique 'one off' products developed for a specific customer application and they require a great deal more product engineering compared to the standard industrial or medical gas products. For this reason, they are not always 'off the shelf' items and can even take several weeks to produce in the most complex of cases.

Where a raw material of the required purity cannot be sourced, the gas producer must buy the highest purity available and introduce additional purification processes in house to achieve an end product of a sufficiently high purity.

Finally, the level of quality control associated with specialty gas production is far higher than with industrial and medical gases. Sophisticated laboratory instrumentation is used to analyse and verify the constitution of many products and customers are then provided with a certificate declaring the analytical results.

As many as 200 different multi component gas mixtures are often required at a large refinery complex. These are all 'made to order' and therefore require fairly lengthy production, certification and delivery lead times in comparison to the standard 'off the shelf' industrial gases range. To facilitate timely repeat ordering of these complex gas mixtures, plant instrument tag numbers can be used to allow personnel to reference exactly where the mixtures are deployed in the different sections of the plant.

Packaging is an issue on its own. Since these gases are generally required in small quantities, they are typically supplied in cylinders, and extreme care must be taken when introducing the specialty gas into the cylinder. The materials of construction for these cylinders are also very important in maintaining the integrity of product. While steel cylinders can be used for most industrial and medical gases, and some specialty gases, specialty gas products often require aluminium alloy cylinders, which are more compatible with the purities and chemicals associated with specialty gases. The valves on top of the cylinders must ensure that the contents remain inside and contaminants from the atmosphere remain outside. Specialist

Figure 2. Thousands of tpd of the most common industrial gases are supplied to customers through pipelines, or in bulk format by 20 – 30 t road tankers.

materials, such as stainless steel or a very high grade brass, are therefore also needed for valve construction.

Packaging of specialty gas mixtures is also a challenging task because the tolerance, or accuracy, of the component percentages must be maintained. Often these highly accurate mixtures are needed to calibrate a measurement and gas producers must utilise highly sophisticated filling equipment and processes to ensure the products' integrity. Speciality gas cylinders have to be heated, evacuated and purged to expel any traces of moisture or other impurities before the product is introduced, creating yet another production step that is not necessarily required for the majority of industrial and medical gases.

Refinery process safety is supported by the supply of calibration gas mixtures used to calibrate sensors that detect explosive environments. These sensors would detect the buildup of an explosive gas, such as ethylene, and trigger an alarm to implement corrective action if the buildup reached a critical level. These sensors require frequent calibration with highly accurate calibration gas mixtures to ensure they function correctly.

Maintenance and efficiency

The most practical way to reduce emissions from a refinery is to ensure that the processes operate optimally. This requires each unit to operate at maximum productivity levels, so that less energy is required and fewer waste gases are emitted. To achieve this, plant personnel use process control analysers, which also require frequent calibration, to obtain accurate and reliable readings. These devices continuously consume high purity gases in order to function and require occasional calibration with high precision gas mixtures.

Regular maintenance of refinery process equipment is a vital intervention at longstanding facilities. In addition to safety, maintenance is targeted at maintaining optimal performance of plant equipment and at minimising operating costs, for example periodic descaling of heat exchangers using large quantities of acidic gases such as hydrogen chloride.

Additionally, the efficiency of a refinery's refrigeration system relies to a large extent on optimum heat exchange. The refrigeration plant requires refrigerant gases and also oil to lubricate its moving parts and, over the course of this operation, oil inevitably leaks into the refrigerant over time and this contamination of the refrigerant gas compromises the plant's efficient function. Linde has installed patented technology in at least one of its primary refinery customer sites: a self contained, compact and portable high speed decontamination unit which purifies the refrigerant, separates out the oil, removes moisture, non-condensables and any other potentially damaging particulates and then returns the refrigerant gas to the system. All of this is done during refrigerant plant operation, to avoid the cost of process shut down.

Specialty gas distribution equipment

Protecting the integrity of gas throughout the supply chain, from manufacture to end user, is an ongoing challenge to gas suppliers, requiring intense focus on the safety and integrity of gas equipment. Many of the gases supplied are corrosive, toxic, flammable or high purity, all of which require a complex infrastructure of high precision regulators, valves and piping to ensure their safe supply. This equipment ages with use, particularly the moving parts, and can deteriorate over time, owing to the harsh nature of the gases passing through it, requiring regular inspection and maintenance activities to prevent incidents and accidents.

Complex petrochemical processing and instrumentation demand products of the highest quality to maintain peak performance. Distribution systems for specialty gases must meet increasing demands for optimal standards of performance, new analysing methods and production refinements. Impurities occurring in just a few ppm can have serious consequences to end users in application. The demands made on regulators and valves in these environments are extremely high and components must be capable of handling high and low pressures, large and small flows and must also be suitable for high purity inert gases, as well as reactive, flammable, corrosive or toxic gases.

These often low concentration components in specialty gases are easily compromised by a reaction with contaminant gases in the atmosphere. In response Linde continues to develop increasingly high tech containers, valves, regulators and supply systems, constructed from new generation materials, to ensure that gas products remain pure and uncontaminated throughout their life cycle and mitigate risks to the environment or human health, protecting all parties from the high cost of integrity failure. At critical moments, quality of the gas is only as good as the gas distribution system itself.

As dangerous substances can be constituents in specialty gas mixtures, personal safety and environmental protection are primary concerns. Gas distribution systems must meet stringent requirements to protect the health and safety of the people who work with them.

Optimum gas handling equipment functionality is critical and must be equal to the sophisticated gas being handled. This encompasses factors such as pressure reducing regulators and purge functionalities. Materials of construction are once again critical to the integrity of the distribution system, particularly where speciality gases contain corrosive components. Joints, seals, moving parts and fittings in regulators and valves must be absolutely tight and impermeable; much more so than for the equipment used to supply industrial and medical gases.

In these applications, the term 'helium leak tightness' is often used to determine leak potential, referring to how much helium will leak out within one second under certain circumstances from the inside of the system to the outside. Typically, with industrial and medical equipment, 1 cm^3 helium could leak within an hour from a component. On the other end of the scale, specialty gas distribution systems might display far lower leak rates, capable of maintaining their integrity up to and even far beyond 30 years for the loss of 1 cm^3 of helium.

To avoid any reaction between the specialty gas product and the material of construction of the distribution system, sophisticated materials such as stainless steel or Hastelloy® can be utilised to construct the system components, owing to their excellent anticorrosive characteristics and their first rate sealing qualities once welded. These components must also be impermeable, both in terms of gas leaking out of the system and atmospheric gases infiltrating into the system. The sum of the leaks is critical and all connections, components, piping and tubing must be as tight as possible. Bar stock and forged components are favoured for specialty gas applications, rather than the cast componentry suitable for industrial and medical gas distribution systems, which does not provide sufficiently tight housings required for specialty gases.

In these specialty gases distribution systems, connections between the gas cylinder, the gas distribution system and the application are generally comprised of polytetrafluoroethylene (PTFE) hoses or thin walled, flexible stainless steel hoses, because rubber hosing, which is often used for industrial gases, is slightly porous. In addition, compression fittings and orbital welds are used to ensure uncontaminated and unyielding joins. Where very low ppm or particularly corrosive mixtures are being supplied, metal gaskets are also favoured above rubber or plastic alternatives.

Another factor is the internal roughness of the distribution system and this must be very smooth to ensure contaminants such as oxygen and water cannot attach to the rough surface during the purging process. Stainless steel tubing is less rough internally and is therefore preferred over copper. It is imperative that no impurities remain in the system when a new installation is commissioned or when a cylinder is changed out. For this reason, extreme care must be taken when making or breaking a connection in an existing specialty gas pipeline to conduct maintenance or change out a cylinder connected to the gas distribution system. In these instances, technicians are effectively opening up a closed system to the atmosphere.

When this kind of activity is associated with an industrial gas distribution system, new tubing can simply be soldered or welded in. Pressure testing can then be undertaken using water or compressed air. Medical gas distribution systems are more complicated and require particular care to ensure the correct gas has been returned to the system.

But before specialty gas distribution systems can be brought back on stream, several precautionary processes are necessary. These systems should not remain open more than necessary and, during maintenance or building operations, all open ends must be properly sealed to ensure that no contaminants enter the system from the atmosphere.

High purity argon is generally used as a shielding gas during welding of stainless steel pipework for specialty gases applications to ensure that the joints are smooth and non porous. Furthermore, the gas used to pressure test the system after any welding activity must be of a similar quality to the product the system is being used for. Purging with a lower quality gas could introduce moisture and other impurities into the system that can be difficult or impossible to remove afterwards. Other tests prior to bringing a specialty gases piping installation online might include vacuum testing and helium leak testing, depending on the sophistication of the system and the customer's requirements for the process gas.

Once maintenance activities have been completed, gas pipes and process units are generally flushed through with nitrogen to purge them of any atmospheric air and moisture, which could pose a safety risk related to an explosive chemical reaction when a flammable gas, such as ethylene, reenters the process.