SPECIALTY GAS ZONE

Process gases

Leading the search for sustainable alternatives

By Stephen B. Harrison

Throughout this year **gas**world has covered 'Helium Shortage 3.0' with reports of price increases of up to 100%. Such price volatility is a real incentive to search for sustainable alternatives! For some helium applications, such as leak testing and as a chromatography carrier gas, hydrogen can be used as a substitute for helium. Unlike helium, which is a finite resource on Earth linked to natural gas reserves, hydrogen can be produced from water and is therefore a sustainable option for future decades.

For some other applications, such as superconducting magnets in hospital MRI scanners, helium is hard to substitute because no other gas has the right mix of physical properties. There are many examples where sustainable alternative products have been found and a few applications where the hunt is still in progress. In many cases, process gases are leading the way to sustainable solutions.

Leak testing with safe, sustainable hydrogen gas mixtures

Pressure systems that are to be filled with a gas or liquid are generally tested for leaks as part of the manufacturing and quality control process.

In some heavy-duty applications a bubble test using soapy water is suitable. In other cases, a 'drop-test' is used. Here, the system is charged with a gas such as nitrogen and then observed over a set period to see if the pressure is maintained or 'drops'. If the system contains a toxic or flammable gas, the leak testing may be conducted using a portable electronic gas detection device fitted with an appropriate chemical sensor.

For more delicate testing requirements, the use of helium as a tracer gas to detect leaks has been the default choice for many decades because it is inert, easily detected using gas sniffers, and is present at very low concentrations in the background air.

> "The refrigerant gas suppliers have been hard at work to develop lower GWP alternatives..."

Helium has often been used for leak testing as a pure gas or in a process gas mixture of 10% helium in a balance of nitrogen. However, in recent years hydrogen has begun to displace helium for this application because it offers significant cost savings and, as a tiny molecule like helium, is equally good at finding the thinnest cracks and pin-holes to leak through. A mixture of 5% hydrogen in nitrogen is non-flammable but contains enough tracer gas to enable the smallest of leaks to be detected. This process gas mixture therefore combines good economics with safety and is a sustainable substitute for helium.

SF_6 and electrical switch-gear

Sulfur hexafluoride (SF_6) is a process gas with an extremely potent Global Warming Potential (GWP) of 23,900. When compared to the refrigerant gases that the EU fluorinated greenhouse gases (F-Gas) regulations are designed to phase out, this molecule is a monster!

To put the GWP of SF_6 into context, the next phase down for F-Gases will be on 1st January 2020, when the maximum allowable GWP for virgin refrigerant molecules placed on the market in Europe will be reduced to 2,500 – almost one tenth of the GWP that SF_6 has.

With its high GWP in mind, SF_6 was included in the 1997 Kyoto Protocol. For the power transmission industry, this means that companies must operate and maintain SF_6 switchgear in a responsible manner, for example managing switchgear on a closed cycle to avoid deliberate gas release to the atmosphere and monitoring emissions during operation.

In Europe, the F-Gas regulations banned the use of SF_6 in magnesium dye casting over the period from 2014 to 2017. The molecule has also been prohibited for the application of filling vehicle tyres. However, due to its essential use in medium and high voltage switch-gear insulation, there are, at present, no phase down commitments for SF_6 in the same way that there are for high GWP refrigerants. So, for now, this process gas has a reprieve, but it may soon be replaced with a more sustainable alternative.

For example, extensive product development and field testing has taken place to identify alternative molecules such as fluoroketones and fluoronitriles with a high efficacy and low GWP.

The quest for sustainable cold

As already noted, the next step-down in the F-Gas regulations will take place on 1st January 2020 and will impact several refrigerants, with R404A at a GWP of 3,922 being the most commonly used gas affected.

Fabrizio Codella, Refrigerants Marketing & Product Specialist at Rivoira Refrigerant Gases, commented that "the refrigerant gas suppliers have been hard at work to develop lower GWP alternatives."

"Honeywell have introduced Solstice N40 (R448A) with a GWP of 1,390 and Chemours are in the race with their Opteon XP40 (R449A), which has a very similar GWP at 1,397. These are both non-flammable blends of several refrigerant molecules such as R32, R125 and R134a. They also contain R1234yf which is a modern Hydro-Fluoro-Olefin (HFO) molecule, with a GWP of only 4. It has made tremendous inroads as the preferred automotive air conditioning gas in Europe since the →

F-Gas regulations specified that the refrigerant used in automotive air conditioning systems must have a GWP of less than 150 from 1st January 2017," he explained.

In addition to modern fluorinated compounds with low a GWP, anhydrous ammonia (R717), high purity propane (R290) and pure carbon dioxide (R744) are emerging as economic and environmentally sustainable refrigerant gases for some types of system. The quest for sustainable cold is opening doors to new applications and creating growth opportunities for these traditional process gases.

Fighting fires with eco-friendly process gases

Halons are another example of fluorinated hydrocarbons that have GWP values in the thousands. Furthermore, they have a high ozone depletion potential (ODP), which was also a problem associated with early generation CFC and HCFC refrigerants.

On the other hand, halons have been used in many safety-critical fire-fighting applications in aeroplanes, data centres, ships and process control rooms in offshore oil and gas installations for decades. These are applications where there is an instant need to protect people using a highly effective fire suppressant, or where water and foam systems would cause unacceptable damage to valuable or safety-critical electronic equipment.

Inert process gas mixtures containing argon, carbon dioxide and nitrogen, or simply carbon dioxide and nitrogen have sub-zero GWP and no ODP and have emerged as sustainable alternatives to halons in some of these applications. They are especially popular in data-centre protection and offshore oil and gas applications.

In many cases, these process gas mixtures comprise of argon in the range 40-50%, carbon dioxide in the range 0-10%, and a balance of nitrogen. In the event of a fire, the gas mixture is automatically released from a bank of 10 or more large high-pressure steel cylinders. It mixes with air in the room to create an environment of approximately 65-70% nitrogen, 12-13% oxygen, 15-20% argon and 0-4% carbon dioxide. The resultant gas mixture will rapidly extinguish the fire and simultaneously provide a short-term breathable atmosphere to allow safe evacuation.

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Finding ozone-friendly fumigants

Methyl bromide (MB) is a recognised fumigant and an important tool for the control of insects and other pests. It is regarded as an essential enabler of world trade and most of the world's busiest container ports are bases for world-class fumigation companies who are familiar with the use of this process gas. However, MB is also a potent ozone-depleting gas.

As a result of these simultaneously beneficial and environmentally sensitive properties, the use of MB is controlled through two Multilateral Agreements – the Montreal Protocol on Substances that Deplete the Ozone Layer, and the International Plant Protection Convention. Three applications of methyl bromide are exempted from phase-out under the control measures: use as a chemical feedstock, uses that the Parties to the Montreal Protocol deem 'critical' and its use as a fumigant for quarantine and pre-shipment (QPS) purposes.

BOC Australia is active in the fumigant process gas market with products such as Agrigas. Chris Dolman, Business Manager – Analytical and Pharmaceuticals, says that, "methyl bromide is relied upon for imports and exports internationally with many commodities fumigated each year to ensure that pests of concern are not spread globally. Replacements for MB require changes to National Biosecurity protocols which influence international trade agreements, which is difficult. So, MB will remain a key biosecurity tool to support global trade until countries can agree on suitable alternatives."

The most common material to be fumigated using MB is wood: either as logs or wood used in packaging and transportation, such as pallets. MB can prevent the spread of plant pests such as the wood-boring longicorn beetle larva or pine wood nematodes (*pictured page 56-57*) which could have devastating economic and environmental consequences if introduced to new locations. Food and soil are the other main products treated with QPS fumigation.

When we consider other process gases, there are instances where more sustainable alternatives to MB can be used for QPS fumigation applications. For example, an inert mixture of nitrogen and CO_2, similar to the process gas mixtures that are used in fire-fighting, could be applicable for cut flowers, cereals, furniture and machinery. This gas mixture has zero ODP and a GWP of less than 1.

Learning from the medical sector, ethylene oxide (EO) which is used to sterilise surgical items and equipment such as bandages, gloves, scalpels, scissors and tweezers may be suitable to fumigate nuts, furs and furniture. EO has a GWP of 1, identical to CO_2 and is not classified as an ozone depleting substance. These are the hallmarks of a process gas that could lead us towards a more sustainable future.