Figure 1. Portable gas detectors, like Linde's G-TECTA, monitor and warn of the existence of toxic or combustible gases as well as oxygen deficiency.

Safety in a cylinder

Stephen Harrison, Linde Gases Division, Germany, focuses on identifying hazards and mitigating risks when dealing with industrial gases.

Although critical for the operation of refineries and petrochemical plants, industrial gases can be associated with a spectrum of possible hazards and need to be treated with respect. This involves assessing and controlling the relevant risks. Safe handling of gases is vital, as risks range from minor injury at one end of the scale, to potentially more serious damage to health and even (on rare occasions) death. Effective product stewardship is therefore required to uphold safety levels at such facilities. A holistic approach to product responsibility is required; one that involves identifying the possible hazards and evaluating the risks that may stem from a product throughout all stages of its lifecycle. The risk potential is assessed in relation to employees, neighbouring facilities and the environment. The aim is then to avoid or reduce these risks as far as possible.

Figure 2. Industrial gases are vital for the operation of refineries, but are associated with a spectrum of hazards, so need to be treated with respect.

Figure 3. PPE is non-negotiable when handling cyrogenic or corrosive gases and heavy cylinders.

Physical and health hazards

One of the main hazards when handling gases is toxicity. Examples of gases that fall under this hazard category include carbon monoxide or some of the gases that contain sulfur, such as hydrogen sulfide or carbonyl sulfide. These are commonly produced in refinery operations, especially with recent trends that are seeing increased desulfurisation taking place in refineries as oil companies are forced to tap into a lower quality of crude. Any leakage of these gases potentially creates a significant safety issue.

Another leading hazard in a refinery is the flammability of gases; and with flammability comes the more severe implication of explosion. Flammable gases present in a refinery include hydrogen and any of the hydrocarbons being processed in the plant, such as LPG, LNG and the volatile petroleum derivatives. These gases generally only pose a flammability hazard when mixed with air or other oxidants, creating a combustible atmosphere that might be ignited by flames, sparks, hot surfaces, electrostatic energy or other ignition sources.

Asphyxiation is a further primary hazard in refineries and petrochemical plants. Asphyxiation occurs where there is a lack of oxygen and it only takes two deep breaths in an atmosphere that excludes oxygen (for instance where air has been displaced by pure nitrogen) to cause an individual to collapse instantly into unconsciousness. If they continue to inhale the nitrogen while unconscious, death will follow very rapidly. Asphyxiation is often referred to as 'the silent killer', as there is seldom any warning that these inert gases are present in such a large volume. With these inert gases, there are no warning odours and often an absence of visible vapour clouds.

Oxygen deficiency can occur as a result of an excess of nitrogen, which might perhaps be used intentionally in a refinery for the purpose of enhancing safety. For example, nitrogen can be used to blanket a flammable atmosphere, or as an initial step to purge a storage vessel that previously contained a flammable gas, to allow welders to subsequently work in the vessel after a second purge with breathable air. In these cases of confined space entry, it is imperative to have a robust work permit system in place to ensure the atmosphere in the confined space is safe before entering. The entry permit procedure should include confirmation of ventilation, gas monitoring equipment, availability of rescue equipment and a safety guard on duty just outside of the confined space.

Conversely, the other safety issue associated with oxygen is if too much of it is present. If oxygen levels exceed 23% during oxygen enrichment, combustion procedures that are very familiar are altered. For example, in a normal air atmosphere, a welding flame would burn at a controllable rate, but where there is too much oxygen present, flames unexpectedly burn with a much larger flame.

Oxygen enrichment could be caused by a leak of oxygen, which is often used in large quantities on refineries in many applications, including contemporary desulfurisation processes. The potential for a major leakage is small, but it must be considered as a potential hazard.

The next safety issue is corrosive gases, which are generally also toxic, and have the potential to cause rashes, long term skin damage and also burn respiratory tissue on contact, with potentially fatal consequences. Gases in this category include ammonia and the hydrogen chloride used on plants for descaling piping and process equipment. These scale deposits are sometimes flushed with gases such as hydrogen chloride, which are acidic and capable of efficiently returning process equipment to its original state, thereby improving its performance.

These potentially hazardous gases are intentionally handled in plants for maintenance purposes or produced as byproducts. Providing they remain within the system, there is no threat. However, these gases are aggressive, particularly in combination with high moisture content, and have the potential, over time, to dissolve pipe work and create holes from which they and other gases can escape.

A niche category of hazards is radiation. Some instrumentation and level control devices harness radioactive sources for optimal function. For example, a radioactive float can be used to measure the liquid levels. The rare gas isotope krypton 85 might also be present in some refineries. Although radiation is an uncommon hazard in refineries and petrochemical plants, plant personnel should have a good understanding of the associated risks where radioactive materials are being processed.

Figure 4. Through its internet based ACCURA tracking service, Linde helps gas users take control of their cylinder inventories.

Then there is the element of hazard related to pressure. Many cylinder gases are stored under pressures up to 300 bar. This represents high energy and the hazard therefore relates to a sudden release of pressure. This release could harm personnel and cause damage to assets, especially if the cylinder itself is projected at a high velocity due to the sudden release of the pressure energy.

Providing gas cylinders are used as instructed and stored in well ventilated areas and at normal temperatures, there is rarely an incident. However, if these cylinders are placed in direct and intense sunlight they begin to heat up and the pressure of the gas inside starts to increase. This does not pose a problem for most gas products, because the cylinder is designed to withstand this pressure build up. However, with liquefied gas such as LPG, the contents begin to vaporise when the cylinder is heated and a leak could occur due to overpressurisation.

Additionally, if cylinders are exposed to extreme heat sources such as a fire, pressure can build up to a point where it will rupture the cylinder and explode, releasing the considerable stored energy in the cylinder in a dramatic fashion: essentially a phenomenal explosion with potentially very severe consequences.

Gas cylinders are designed to safely contain their contents up to 1.5 times the normal working pressure, but a fire near any cylinders could overcome this safe limit and have severe consequences for personnel, as well as fire fighting teams. These teams need to be aware of the hazard in order to be able to make the right decisions in an emergency situation.

Moving on from cylinders, liquid nitrogen is an example of a gas that is often supplied to and stored in the refinery as a cryogenic liquid. It is generally used as a purge gas to blanket the top of a storage vessel for enhanced safety. Although nitrogen is used in this application to mitigate another hazard, it brings its own hazards to the site. Under normal storage conditions, liquid nitrogen exists at the extremely low temperature of -196 °C. If a leakage occurs, liquid nitrogen can cause skin and tissue damage, known as 'cold burns'.

Appropriate personal protective equipment (PPE) is non-negotiable when handling cryogenic or corrosive gases and heavy gas cylinders. Complete chemical body suits are used to protect personnel entering atmospheres that contain high levels of toxic gases or where the presence of these gases is suspected. Linde provides a wide range of PPE and breathable air for personnel who wear chemical body suits, supplied in a cylinder or through a piping system into the suit.

Chemical hazards

Dissolved acetylene gas is used in a refinery for welding and cutting metal and for a variety of maintenance operations. The gas is supplied to refineries in a cylinder containing the acetylene, which is dissolved in a solvent and supported in a porous mass.

Cylinders containing dissolved acetylene are particularly sensitive to heat sources, meaning that heat exposure could take place unknown to plant personnel. Such an insidious kind of reaction might propagate from a small beginning, with no one aware that it has begun. Hours later the cylinder can explode for no apparent reason. Therefore, on occasions where the cylinder is suspected to have been exposed to a heat source, such as a nearby fire or excessive sunlight, best practice is for the cylinder to be cooled down for at least 24 hours before being handled. Following this, a complete inspection has to be carried out before using the cylinder again. Additionally, immediate advice should be sought from the gas supplier if such a situation is suspected.

Material handling hazards

There are also several safety issues associated with the transport and handling of gases. For instance, many gases are supplied to the plant in large, heavy cylinders that can weigh up to 70 kg and the simple act of manual handling could involve health hazards to plant personnel.

The risk of injury associated with handling heavy gas cylinders can often be mitigated by placing cylinders in a covered but open walled outside storage area, close to where the cylinders are delivered, and piping the gas indoors to where it is needed in the plant or laboratory. A central external storage area also helps to address the risks associated with potential gas leaks through suitable ventilation and can minimise cylinder delivery vehicle movements. As part of its HiQ® specialty gases and equipment product range, Linde designs, installs and maintains central gas supply systems to safely supply potentially dangerous gases from these central cylinder stores to multiple local work areas.

Another hazard is the movement of gas delivery vehicles on site. Gas cylinder delivery trucks and bulk liquid tankers can drive to each gas storage area to minimise potential handling risks. Yet their presence on site can pose a potential safety hazard to personnel walking around in the area. Occasionally, there is a lack of emphasis placed on these basic, everyday physical and material handling risks. This is because attention is sometimes diverted to the potentially more severe hazards of toxicity or explosion.

Mitigation

To mitigate the safety risks, plant personnel should ideally ensure that leaks from pipe work and equipment never occur by continuously testing for the presence of leaks. This precaution also applies before new plant facilities are commissioned.

Leak detection is a key way to mitigate many safety risks related to gases. Gases used for leak detection are often pure helium or a mix of helium in nitrogen. Linde Gas is able to help with these gases, providing, for example, cylinders containing a mixture of 10% helium in nitrogen. Helium is a very small molecule and quickly draws attention to the presence of a leak. It is also ideal for leak testing because it can be selectively detected using a helium 'sniffer', which is a simple gas chromatograph. Helium is not normally present in the atmosphere in large quantities, so if the sniffer detects it, it is a conclusive indication of a leak.

However, equipment vibrates and ages through prolonged use. Cracks can appear, flanges can loosen and corrosion occurs. Over time long term deterioration is inevitable, even if successful leak tests in the build phase have been conducted. Plant personnel therefore need to detect gas leaks on a continuous basis, using sensors and detectors placed around the refinery that are primed to detect very specific kinds of gas leaks.

Gas detectors are used to monitor for and warn of the existence of specific toxic or combustible gases and oxygen deficiency or enrichment hazards. Typical measurement levels will be in the low ppm levels for toxic gas. Combustible gases are measured in percent levels related to the lower explosive limit (LEL) and oxygen deficiency//enrichment level of oxygen (in percent), around the target of 21%.

Gas detection monitoring devices can be classified in three ways. A fixed system refers to a stationary monitoring system permanently installed in the workplace. The detecting sensor may be hard wired, or use wireless signals to a central reporting station. Most will come with an auditory alarm system. The type of sensor used is defined by the system and the gas/gases to be detected. Fixed gas detection can be used indoors, as well as having outdoor use as a perimeter monitor with chemical manufacturing and petrochemical sites.

Gas detectors are quite specific in what they search for. One detector may be deployed to identify oxygen, either to flag enrichment or a deficiency. Another might be primed to detect a flammable gas leak, such as methane, or a toxic gas like sulfur dioxide. Knowing which gases are being handled in a particular plant, the gas detection system can be tailored to detect specific leaks. If the equipment needs to be portable, four sensors are commonly built into one device to detect the typical risks. These devices are utilised when personnel walk through different areas where a variety of gases may be used.

Area monitoring detection offers the benefits of a multi gas fixed system in a transportable unit. These units are designed for team protection or area surveillance for short term work where fixed gas systems are not suitable.

Portable gas detection refers to gas detectors that are carried or worn by the plant employee as part of their PPE. Typically battery operated, portable monitors are used for toxic or combustible gas detection, as well as for oxygen deficiency/enrichment monitoring in confined spaces. Linde's G-TECTA™ portable gas detection range offers simple one button operation and can be used and tested by field engineers through to manufacturing operatives. This ensures reliable and high quality gas readings and an immediate warning indication if there are any issues with the functionality of the sensor. G-TECTA is certified to global standards and is suitable for use in potentially explosive environments as well as safe areas.

The efficacy of the human nose as an extremely reliable gas detector is notable: certain toxic gases have a distinctive scent. For example, hydrogen sulfide smells like rotten eggs, while the pungent odour of ammonia can also be detected by smell. Crucially however, many gases have no odour and make their detection by the human nose impossible. In addition to Linde's G-TECTA gas detection range, Linde supplies a full range of test mixtures and calibration gases to ensure the optimal function of gas detectors critical in potentially life threatening circumstances.

A simple but effective way to mitigate gas risks on site is to keep personnel fully informed of hazards through safety data sheets and proper product labelling. This information is critical to conducting risk assessments relating to handling and usage. Training is another option: Linde provides gas safety courses, seminars and workshops for gas users.

Yet another mitigation tool is inventory management. The more cylinders on site, the more chemicals present and the more opportunity for cylinder valve leakages. By storing only what is needed, the probability of a potentially hazardous leak is reduced as well as the potential severity of the consequences. Through its internet based ACCURA® cylinder tracking service, Linde can help gas users take complete control of their cylinder inventories including movement history, batch expiry dates and custom warnings. Additionally, for bulk gas supplies, Linde's remote SECCURA® service will monitor gas levels and manifold pressures, in addition to organising replacement of cylinders and bundles by trained Linde drivers, further mitigating potential incidents.