Hazardous materials:
compressed and flammable gases (UN class 2)

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This is the second in a series of articles dealing with the nine UN classes of hazardous materials. This month we will cover the second class in the UN classification, emergencies involving gases. Instead of providing you with an unnecessary (and particularly boring) chemistry lesson, I will mostly focus on the hazards you and your department might face when responding to a gas emergency and hopefully provide some ideas on how to manage such an incident.

Classification and hazards

According to the United Nations Sub-Committee of Experts on the Transport of Dangerous Goods (UNSCETDG), gases are classified as follows:

- Class 2.1 – Flammable gases
- Class 2.2 – Non-flammable, non-toxic gases
- Class 2.3 – Toxic gases
- Class 2.4 – Substances when in contact with water emit flammable gases

We know that gases are stored in a compressed state in various forms of cylinders, depending on the specific properties of the gas. Should these cylinders be compromised in any way that causes the gas therein to escape into the surrounding atmosphere, it could give rise to a wide range of potential hazards. Pressurised vessels can be a potential source of high energy and can fail if over-pressurised or exposed to heat. A leaking gas cylinder can also cause the expelled gas to disperse into the surrounding atmosphere with relative ease and cause extremely volatile conditions. Odourless gases can disperse over a significant area without being detected. It must never be assumed that built-in safety systems such as

Dealing with a fire impingement on an LPG vessel will require immediate and massive cooling of the entire surface

- pressure relief valves are working perfectly (especially after an accident). A compromised valve might not release as designed, which might give fire fighters a false sense of safety resulting in them being exposed to its risks for too long.

Cylinders are designed to withstand high internal pressures but if they are involved in fires, this pressure will increase exponentially and coupled with the weakening of the cylinder walls, could fail spectacularly resulting in a blast pressure wave, fireball and cylinder fragments flying in all directions at great velocity. All these events could lead to severe damage to structures in its proximity.

With the exception of helium, acetylene, hydrogen, ammonia and methane, gases are denser than air and will therefore accumulate at low levels before dispersing over various distances where they are at risk of finding a possible ignition source. Gases that are lighter than air can accumulate in high spaces such as ceilings unless they are ventilated.

In addition to the inherent dangers of compressed gases and specific hazards of flammable gases, toxic gases could cause harm to whoever it comes into contact with either through inhalation or skin absorption. Escaping cryogenic gases such as liquid oxygen and liquid nitrogen present a thermal burn hazard if released rapidly.

Transport and storage

The storage of gases in South Africa is governed by the Occupational Health and Safety Act, 1993 (Act No 85 of 1993) of the Department of Labour, which regulates the storage of dangerous goods. A series of national standards (such as SANS 10263-2:2008: The warehousing of dangerous goods Part 2: The storage and handling of gas cylinders) cover all aspects governing the safe handling of hazardous gases.

Gas storerooms should be of fire-proof construction and so designed that in the event of fire, the cylinders are easily removable. They should be well ventilated, top and bottom and must never be below ground level. This is due to the properties of most gases, which make them heavier than air.

Any light fittings and electric switches in stores containing acetylene, LP gas or other flammable gases should either be of the flame-proof type or should be placed outside the building lighting the interior through fixed windows.

Oxygen cylinders may be stacked horisontally provided that they are firmly secured at each end to prevent any uncontrolled displacement.

Strict rules exist for the storage of cylinders away from any heat sources such as furnaces, boilers and radiators.

Transportation of gases must take into account the properties of such gases such as transporting cylinders in a vertical position as well as the legal quantities that may be transported on a single load. Generally, all safety mechanisms for the storage of gas must be adhered to when it is transported.

Responding to a gas emergency

As with any hazard risk it is important that you identify any businesses in your area of response that store significant quantities of gas on their premises. Also consider the fact that if your primary response area is a suburban residential area, you could find various types of gases ranging from acetylene to liquid-petroleum-gas (LPG). Your preplanning should indicate safe areas where you might be able to set up master streams for cooling large volume cylinders and approach routes, which will assist in avoiding any explosive risks.

All the information gained from your preplanning exercise must be available to the initial incident commander (IC) en-route to the incident. This information will assist the IC in determining the initial staging points for all units (outside the potential blast zone) and which areas might need to be evacuated. If an area is indeed to be evacuated, close liaison with law enforcement agencies on scene will be necessary. Should it not be possible to evacuate a particular area, the public must be warned of the potential dangers related to the incident and must be advised to stay away from any openings and to occupy structures as far away from the risk as possible.

Personnel tasked with operating in close proximity to the incident site must utilise as much shielding as possible and wear full structural personal protective equipment (PPE) including a flash hood and breathing apparatus if there is a risk of a fire erupting due to a rapid gas release. Eye protection must also be worn.

In the initial (rapid) size-up, the incident commander must try to ascertain if any (and how many) cylinders are involved in the fire, whether they are exposed to direct fire or radiated heat, are any cylinders venting, bulging or leaking and what gases are involved.

In determining your safety zones also consider the size and number of cylinders, what shielding is available and what the effect of a possible blast pressure wave might have. Also consider the possibility of cylinders becoming projectiles and being thrown long distances if not contained inside a building. Other projectiles such as cylinder fragments and glass can cause considerable damage to fire fighters not adequately shielded.

Although the marking of cylinders are well regulated, it is possible that cylinders could be imported into the country with markings that may differ from South African standards and therefore need to be assessed to ensure what you are dealing with. Command should make use of as many sources of information as possible to identify the cylinders involved. This could include the cylinder markings, verification by the owner/operator, any documentation available and any visual signs such as the cylinder connected to an oxygen cylinder or strapped to a welding machine.

Cylinders involved in fires will obviously heat up and thereby cause the pressure inside them to increase. Direct flame impingement onto a cylinder will also weaken its walls. If the maximum safe working pressure is exceeded, the cylinder could fail in a violent manner resulting in the release of a significant amount of energy. Further hazards could prevail depending on the type of gas involved. Cylinders containing oxidants, toxic or flammable gases may lead to further risks manifesting in the surrounding area. Continuous measurement of the ambient atmosphere must continue until it has been declared safe.

When it is discovered that a cylinder is involved in a fire, the incident commander must initiate all efforts to bring the situation on control. This will most likely entail the extinguishment of the fire that is impinging on the cylinder (if possible) and directing water streams to cool the cylinder(s) down. Cylinders that have been involved in a fire for a prolonged or unknown period of time must be handled defensively and the possibility of using monitors must be considered to remove staff out of harm's way.

If a cylinder is burning at the valve group, try to ascertain if the fire is not at the cylinder neck or at the hoses that are connected to the valve group in which case it can be simply turned off. If the fire is at the cylinder neck, it will not be possible to simply turn it off and will have to be cooled off. Cooling off might just be sufficient to bring the internal pressure down to such a point that it can be safely vented to a point where it is safe and under control. Always remember to do this from a defensive position. Remember the golden rule and that is to never extinguish the gas fire with a water stream. With LPG it can happen very easily and therefore great care must be taken not to direct the nozzle directly onto the fire whilst cooling the cylinder down.

Specific hazards

Certain gases such as acetylene, LPG, cryogenics, ammonia and chlorine have unique characteristics that need to be considered if involved in an emergency. We will deal here with some of them.

Acetylene

Acetylene has a unique characteristic to continue to heat itself after the fire has been extinguished (or it has been removed from the heat source). This is because when acetylene is exposed to extreme heat it begins to decompose into its constituent elements of hydrogen and carbon and thereby causes an exothermic reaction. Acetylene cylinders are designed to inhibit decomposition; however, if left unchecked this decomposition could lead to cylinder failure. The other hazards of acetylene are:

- Highly flammable
- Asphyxiation risk in high concentrations
- Low concentrations may have narcotic effects
- When used with oxygen the risk may increase

When responding to an incident involving a single acetylene cylinder, a hazards zone of 200 metres should be established if the cylinder is in the open; if indoors a suitable defensive position should be identified. The cylinder should be cooled for approximately one hour or until it has reached the ambient temperature. Using a thermal imaging camera will be useful here. Once the cooling phase has been completed, the cylinder should be monitored for a further hour with temperature checks done every 15 minutes. Under no circumstances must the cylinder be moved at this time.

Leaking cylinders will increase the possibility of decomposition and should be vented safely with due consideration of the additional risk caused by the escaping product.

When multiple cylinders are involved, the cooling may not be as effective if they are closely stacked. If the incident commander detects that the water streams are not reaching more than 50 percent of the cylinder's surface areas, the cooling time must be increased to a minimum of three hours.

Cylinders in close proximity to a fire may be moved out of harm's way. However, it is important to check their ▸

Old propane gas cylinders

temperature before attempting to move them. A thermal imaging camera or the use of a water spray onto the cylinder will help you to determine that.

When a cylinder has been sufficiently cooled, it may be approached with caution if there is no gas still leaking from it. Moving a still heated cylinder may accelerate the decomposition of the acetylene, which could result in a catastrophic failure. It is therefore important to ensure sufficient time is spent on the cooling process.

Liquefied petroleum gas (LPG)

Certain hydrocarbons exist as a gas at normal atmospheric temperatures but can be liquefied under moderate pressures. These liquids would occupy 250 times less space than they would in their gaseous state and therefore it is commercially more viable to store and transport them in this state. LPG is colourless and odourless and heavier than air, which will result in released gas to accumulate in low-lying areas. In areas where air movement is limited, this gas could form pockets of extremely hazardous environments and react violently to any ignition source. LPG is as a rule odourised enabling detection (by smell) down to one fifth of its lower flammable limit.

Escaping LPG has a major cooling effect on the surrounding air and causes condensation and a freezing of the water vapour, which could present as ice at the area surrounding the leakage. It can also cause severe burns to any unprotected skin it may come into contact with at this point.

LP gas is highly flammable and when pressurised containers are heated without sufficient cooling, a boiling liquid expanding vapour explosion (BLEVE) could occur. This usually happens when a vessel containing LPG suffers flame impingement from an external fire. The contents of the vessel are heated to above their boiling point and the pressure inside the vessel increases. If the flame impingement is towards the part of the vessel still containing liquid, the over-pressure will be transferred to the built-in pressure relief valves (PRV) situated at the top of the construction. The escaping gas will ignite once it is vented and comes into contact with the external fire. The PRV outlets are sufficiently high enough to direct this fire away from the vessel; however, it is also important to direct water streams to the area directly below the PRV without extinguishing its fire.

In the event that the flames impingement reaches the vapour space of the vessel, it could sufficiently weaken the vessel wall to the point that the vessel could rupture violently and propel parts of the vessel over great distances. The vessel could still contain overheated liquids causing a massive fireball. Incident commanders have in the past been misled by the fact that PRVs have not activated and subsequently believed that the vessel had not reached sufficient pressure to set them off. These PRVs may have been damaged due to a rollover accident or some other fault and quite simply failed. Do not rely on the PRV to inform your tactics. BLEVEs may occur several hours into an incident.

Another major hazard event involving LPG is when an escaping gas/air cloud migrates over a considerable distance before reaching an ignition source of some description. The resulting ignition will generate shock waves and a flame front accelerating from a low initial velocity to sonic velocity. This phenomenon is known as an unconfined vapour cloud explosion (UVCE) and differs from a BLEVE in the sense that the escaping gas/air cloud could travel a significant distance before igniting. The fireball caused by an UVCE could also ignite flammable materials in its way causing a number of secondary fires that will have to be dealt with.

Dealing with a fire impingement on an LPG vessel will require immediate and massive cooling of the entire surface with special attention being given to the area of flame contact. Ground monitors are a definite consideration and the strategy of flame-bending ie utilising attack teams to direct the flame away from the vessel, may be implemented. This can also be utilised to get close to the open valve and to turn off the supply of gas feeding the fire. Many hours are spent by both industrial and municipal fire services to perfect this tactic. Operationally, it must only be used when the objectives are clear and when there are enough fire fighters to carry out the task.

When responding to a gas leak that has not ignited, the incident commander should take into account the possible size of the leak, wind strength and direction and possibility of a vapour cloud ignition. All personnel and public located downwind from the leak should be evacuated and all possible ignition sources removed. Also initiate water streams to disperse the vapour clouds to a point below its flammable range. Deploy detectors into the surrounding area to measure the effectiveness of the dispersion operation.

Fire fighting teams should only enter the gas cloud under extreme situations such as rescue or to isolate the leak. In such an event they should all be in full protective gear including flash-hoods and move behind a protective water spray.

Cryogenic liquids

Cryogenic liquids are gases that are liquefied and keep in their liquid state at extremely low temperatures. In their normal state they are gases and must be cooled to well below room temperature before an increase in pressure can convert them into a liquid state. If these liquids are released from their containers they remain extremely cold and also present a highly visible fog cloud.

Cryogenics are broadly divided into the following classifications:

- Inert gases: These gases do not burn or support combustion, they are not able to react chemically to any significant extent. Nitrogen, helium, argon, neon and krypton are examples of inert gases.
- Flammable gases : This category includes nitrogen, methane and liquid natural gas (LNG)
- Oxygen: Many materials that are ‘non-combustible’ can burn fiercely in the presence of liquid oxygen. Organic materials can react explosively with liquid oxygen.

Cryogenics are stored and transported in thermally insulated containers that are specifically designed to withstand rapid changes in temperature and extreme temperature conditions.

Bulk cryogenic containers are stored in specially designed, pressurised cylinders. These cylinders are able to dispense either gas or liquid only or both. The cylinders have valve configurations for filling and decanting, pressure relief valves and a frangible disk as an added protection.

The extreme cold at which cryogenics are stored poses the risk of severe (and extremely painful) thermal burns.

An asphyxiation risk also prevails when the liquids form a gas, which is heavier than air. These gases will accumulate at low levels and although non-toxic, has the ability to displace oxygen. The capacity of liquid-nitrogen to expand from one litre to 659 litres of nitrogen gas underlines the risk of asphyxiation.

Cryogenics such as hydrogen, methane, LNG or carbon monoxide can burn and in large volumes, even explode. Due to its high flammability range, hydrogen is a particularly high risk product.

A high pressure release of liquid oxygen can create an extremely flammable situation if it saturates materials it comes into contact with. Clothing saturated by liquid oxygen can remain a flammability risk for hours.

The enormous pressures generated inside a cryogenic container can lead to a BLEVE if the pressure relief valve configuration is inadequate for any particular reason.

When responding to a cryogenic gas release incident, you must accept that the product that has escaped will absorb enough heat from the atmosphere to boil and form a vapour. This can then be dispersed. Water may, however, react violently with some liquids and therefore it is vital to know what product you are dealing with and what the hazards thereof are.

Finally, never have anyone enter the vapour cloud if they are not wearing the appropriate protective clothing.

Ammonia gas

Ammonia is a corrosive, toxic gas that is lighter than air and although it has a narrow ignition range and will only ignite at high temperatures, is still regarded as a flammable gas. It can, however, ignite if it comes into flame contact in high concentrations. Ammonia has a severe irritating effect on the eyes, nose and throat and skin contact with ammonia can cause burns.

Responding to an unignited ammonia gas leak, the main priorities should be to isolate the leak and use water streams to disperse the escaped product. A safety perimeter of approximately 100 metres should be established before any operations are commenced. People directly affected by the leak might present with severe discomfort brought about by the irritating effect of the gas.

In the event of a fire, the main objective should be to prevent the gas from interacting with surrounding materials and cooling down the container. Again, do not extinguish the fire if it is not possible to isolate the source of the leak. As with virtually all compressed gases the heating of the container will lead to an increase in the internal pressure and could result in an explosion.

Chlorine gas

Mainly used for water purification, sanitation and as a bleaching agent, chlorine is a very reactive pale-green gas two-and-a-half times denser than air. Chlorine is a gas in its natural state but can be cooled and pressurised into a liquid state for storage and transport.

In addition to being toxic when inhaled, chlorine gas is also corrosive to the skin and could cause severe damage to the eyes. Chlorine is not flammable but can react explosively or form explosive compounds with other chemicals such as ammonia.

In the event of a spillage, the first objective should be to plug and control the leak if possible. Do not spray water onto a spillage or leaking cylinder. Due to its relative density, spilled chlorine will accumulate in low lying areas and for that reason any possible areas of contamination must be evacuated and isolated while being monitored with gas detectors until the gas has been sufficiently dispersed.

In a fire situation, all fire suppression activities should be done from a maximum distance or using monitors. Prevent any run-off of fire water from reaching drains or watercourses. The same procedures to prevent overheating and over pressurising cylinders and a possible BLEVE are relevant here.

Conclusion

Responding to compressed and flammable gas emergencies is complex and challenging. You will need to, in most cases, be able to flow large quantities of water over fair distances and also have access to sufficient ground monitors. You will also have a myriad on ‘unknowns’ to deal with ie how long has the cylinder been involved in the fire, what is the condition of the pressure relief valve and where has the escaped gas accumulated. A clear direction must be given by incident command at the very beginning of the incident and followed through until its successful conclusion. Gas emergencies will require you to be alert and demand your respect.