Danger and Detection of Hydrogen Sulphide Gas in Oil and Gas Exploration and Production

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A rig worker smells rotten eggs near the well head, rubs his itchy eyes as he investigates the frosty pipe connections. After a few moments, he believes all is fine as he no longer smells the tell-tale hydrogen sulphide odour. In this scenario, we can only hope the worker recognises the danger and quickly leaves the site. Oil fields, especially mature ones, can produce hydrogen sulphide gas – deadly at relatively low concentrations. On average, a person takes 12 breaths per minute, so if a hydrogen sulphide (H_2S) gas release occurs, a person might have a very few seconds to reach safety. Crucial to safety, effective hydrogen sulphide gas detection is the topic of this article.

Deadliness of H_2S

Although H_2S is a flammable gas, its toxicity is so high that its flammable level is not reached before it begins to harm people.

People can recognise even trace amounts of H_2S in the parts per billion range, well below the danger level, by a distinctive odour of rotten eggs. Although the odour threshold of H_2S is very low, continued exposure above 30ppm results in an individual losing the ability to smell it; it paralyses the olfactory nerve. The rule here is that; a) If you can smell it, it may be harmful and b) If you can no longer smell it, it may still be present and dangerous.

According to the UK Health and Safety Executive, the acceptable concentration limit for exposure to H_2S is 5 ppm for an 8-hour period. The maximum peak exposure is 10 ppm for 15 minutes. In the US the levels are higher at 20 ppm for an 8-hour period and 50 ppm for 10 minutes according to the Occupational Safety & Health Administration (U.S.Department of Labor). As sensor technology has improved over the years, these levels have been driven down by the health and safety departments in many countries.

H_2S can cause instant death in very high concentrations while relatively short-term exposure to 500-1000ppm can be life-threatening and cause serious harm. Repeated exposure to lower concentrations can cause conjunctivitis, photophobia, corneal bullae, tearing, pain and blurred vision.

Considering the isolation of drilling locations and the length of time for first-aid to be applied, quick detection of the gas and personnel retreat from the hazardous area is imperative. The distance to the nearest hospital may simply prohibit consideration of receiving treatment in time.

Danger of H_2S on Rigs

Sour gas (or methane containing hydrogen sulphide, H_2S) exists in many industrial applications including chemical and oil and gas exploration and production. Specific to oil and gas production, these are some potential hazard areas:

- On HVAC air vents of accommodation buildings and personnel areas
- Driller stand, the shale shaker, and the bell nipple
- Mud return line receiver tank
- Crude oil storage tanks, pipes, flanges, and valves
- Remote well sites at the well heads, the storage tanks, and flare stacks
- In enclosed analyser buildings

Of course, there are many other potential risk areas across oil and gas production and refining as well as many other industries, especially waste water. In each situation, there should be a review of drawings to analyse the probable sources of leaks. In addition, remember that H_2S is heavier than air and will sink to the lowest lying area.

It should also be understood that the specific and changing local environment to each detector can have a significant impact on the sensor detecting gas and providing the necessary protection. Both wind speed and direction along with changing humidity and temperature can all affect decisions on a detector's placement and its ongoing effectiveness.

Issues of Climatic Challenges with Sensor Performance in Hot and Cold Climates

As more and more of the world is opened up to exploration, the areas that companies are exploiting are becoming more challenging. Desert conditions with massive variations in both temperature and humidity along with the arctic conditions found especially in Russia and Alaska are stern challenges for designers and manufacturers of toxic gas detectors. In any case, the established technologies must always be questioned to see if the industry can provide more applicable detectors and other field devices.

When it comes to toxic gas, it should also be remembered that differing climatic conditions have significant effect on the human body, so it would be of benefit to consider a combined effect. A toxic gas detector needs to continue to provide reliable protection as the climate changes through each day and each season.

Sensor Choices

H_2S detectors should be primarily designed to save the lives of workers by warning them of excessive H_2S concentrations in the workplace and initiating emergency procedures and precautions.

The flammability of H_2S is generally not considered in safety applications because the toxic level of the gas is significantly lower. By the time the H_2S level rose to the level of combustion, the toxic air levels would be far exceeded, and people would die. H_2S kills at 1000ppm or 1/40th of the lowest explosive limit (LEL).

Increasingly, the use of personal/disposable portable detectors and hand-held portables, in combination with fixed gas detectors are providing better site-wide safety. Many countries require that every worker should be equipped with a personal device when in potentially hazardous areas.

As manufacturers continue to improve and advance toxic gas detection technologies, it is important to understand how each type of device may be applicable. Electrochemical sensors and metal oxide semiconductor (MOS) sensors have for many years, provided the platform upon which H_2S safety has been built. Now newer technologies are starting to arrive and these should be considered on their merits.

Electrochemical Sensors

Electrochemical cells combine enclosed electrodes and electrolyte. The gas/air diffuses through a permeable membrane into the cell. As the volume of H_2S increases in the air, an oxidation or reduction reaction occurs at one of the electrodes. Small, linear µA current changes occur between the electrodes so that a display/amplifier device may provide a clear indication of gas level.

The low power consumption, allowing for intrinsically safe circuits and their high degree of sensitivity and repeatability make this type of sensor popular in a wide variety of applications. Electrochemical sensors are all cross sensitive to other specific species of gas and this should always be considered, although this is not usually problematic in most applications, particularly in exploration and production.

As we push further into more extreme and isolated environments, the lack of resilience in high and low temperature and humidity of the electrochemical sensor becomes more important. Some sensors may suffer from evaporation of electrolyte in dry and hot conditions, while the extreme cold will reduce the sensor output and its speed of response. You could normally expect a response to 90% of the concentration (T90) in around 30 seconds in 20°C ambient conditions. At temperatures around and below -20°C a significant reduction in speed of response and final output will be noted and at -40°C output will decrease by as much as 25%.

Routine calibration of electrochemical sensors is required at least every 6 months and often more frequently depending on site conditions. These sensors are not fail-safe and cannot provide fault outputs if the sensor has failed to respond to gas.

Metal oxide Semiconductor (MOS) Detectors

MOS sensors differ fundamentally from electrochemical. In an MOS device there is usually a platinum heater element, an insulation medium and the sensing element; a gas-sensitive resistive film. When H_2S enters the sensor there are measurable changes in electrical conductivity in the resistive film. Again, these can be simply amplified in a transmitter device. MOS sensors have long life and continue to operate in wide temperature ranges, especially in higher temperatures, making them popular in arid or desert conditions.

In general the response time of MOS sensors is much slower than electrochemical devices. It will take an MOS sensor as much as 4 times as long to reach a T90 reading. The standard criticism of MOS technology is that they "fall asleep" if they are not regularly exposed to H_2S test gas. This means a frequent maintenance period, perhaps every 30 days, is required or else there is a risk of the detector being unable to respond to a gas event. This effect has been reduced by some manufacturers in recent years. The maintenance period should still be short as MOS sensors may also suffer from output drift and effects of fluctuating humidity.

As with electrochemical sensors, MOS technology is not fail-safe. It can also be affected by changing oxygen levels.

The next challenges for MOS sensor manufacturers is clearly to improve response times, remove the "falling asleep" issue completely and allow for better performance in extremes of temperature and humidity. Nanotechnology MOS (or NTMOS) has recently emerged which deals with these issues particularly effectively. While the look and sensing principal is similar to a MOS device, NTMOS benefits from an array of hundreds of nanotube sensors each nanometers wide. This means that if a single nanotube sensor fails, there are still hundreds to provide the sensor performance required.

The advances in design mean that NTMOS responds faster than both electrochemical and standard MOS sensors: T50 (the time it takes for the detector to reach 50% of full-scale concentrations) can be as quick as 5 seconds, with T90 under 15. This arises because the internal surface area of each nanotube is many times the surface area of its footprint. The latest designs have also removed the "sleep" function and have both temperature and humidity compensation built in, allowing for application into wide variety of hazards across an enormous number of climatic conditions. Latest testing shows that the technology continues to provide fast responses down to -50°C.

NTMOS hydrogen sulphide gas detector provides fast and accurate response.

Optical Sensing Technology

Optical H_2S detectors use the same basic principal as optical hydrocarbon detectors that have now become a familiar feature on rigs, production and process plant. Light is absorbed by H_2S gas as it passes through the sensor's optical path. The sensor can detect the reduction in received light and correlate it with a gas value. Because the detector uses positive feedback at its zero gas level, this technology is inherently fail safe. Any damage to sensors or emitters is detected as having an impact on the positive feedback. Detectors can therefore perform valuable fault diagnostics. They also perform well in a wide variety of temperature and humidity.

There are two types of optical detectors emerging in the market; point-type and open path.

Like other types of gas-detection technology, the optical point-type gas detectors must be strategically located. In order for an early detection of a gas release they should be designated to a specific target area. Routine inspection is necessary to ensure that the detectors are in working condition and that gas paths have not been blocked.

Open path or line-of-sight (LOS) detectors use separate optical transmitter and receiver pairs located up to 100m apart. The pairs of devices monitor the air within the beam of light between them. Like point type devices, any volume of the H_2S gas passing through the beam will provide a reading. It is not possible to determine the ppm level of any given gas cloud with this technology. The detectors use a parts-per-million meter (ppm.M) range, because there is no specific volume being measured. A reading of 5ppm.M could mean that there is a 1m wide cloud of 5ppm gas or a 5m wide cloud of 1ppm gas. It is also important to understand the limitations of their application. Inherent to the design, they may not detect across an area where human beings are working due to the requirement to keep the line between transmitter and receiver clear. They are well suited to gas migration detection and like optical point H_2S detectors, the open-path versions are relatively new to the market.

Climatic Considerations

Throughout this article, there are references to the challenging environments facing manufacturers of H_2S detectors. As oil and gas fields in less problematic locations near the end of their lives, we will increasingly see a move to less hospitable corners of the planet and safety devices need to have the versatility and continued performance in these locations.

MOS sensors tend to have a longer life and can operate in dry and hot conditions but lack the stability where major changes in humidity occur. Electrochemical sensors have repeatable performance and longer maintenance periods but suffer degradation in dry or extremely cold conditions.

The latest advances in technology have greatly advanced the performance of MOS sensors. NTMOS sensors can now provide reliable and fast response in extreme conditions. At the same time, optical sensors, with their fail-safe capability may push the standards of safety higher.

Summary

Day-to-day performance is important throughout each season. Users of H_2S detectors need to understand what conditions detectors will be exposed to and select the best available technology so as to provide the highest degree of safety for personnel. Common modes of failure should be avoided where possible. As new technologies emerge and are proven, it will be possible to combine point devices and open-path, providing layers of safety supporting a higher site standard.

There is an ISA performance standard (ISA 92.0.01, Part I) for H_2S detectors and this should be looked for as a minimum requirement for plant safety today. Performance approval on all gas detectors, whether for H_2S or hydrocarbons is an increasing and warranted trend. Third party testing provides users with a higher degree of assurance in performance and gives manufactures a higher degree of integrity.

World-wide, H_2S detection is becoming increasingly important as are safety systems as a whole. Ensure that you understand what performance you should expect before finally selecting your device.

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