Introduction to Hydrogen Sulfide Management

An Online Continuing Education Course for Engineers

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Headlines

The incidents below most likely appeared in a local newspaper or nightly newscast segment in the locations they occurred. Provided by OSHA, these fatal incidents demonstrate the importance of not only understanding H_2S, but managing it with solutions created by Professional Engineers.

A 49-year old sanitation worker died when rescuing a co-worker from an underground sewer vault when he was overcome with hydrogen sulfide gas.

Workers died clearing debris from an underground sewer pipe. Both were overwhelmed by hydrogen sulfide gas. They were 19 and 25 years old.

Workers who entered a 27-foot deep pit in a marshy area died after being overcome by hydrogen sulfide.

Two workers died at an oil field water injection plant while replacing a water transfer pump. Hydrogen sulfide was released when a clamp was removed.

A 25-year old waste hauling service worker died after collapsing in an underground manure waste pit. The pit had a square access opening fitted with a removable stainless steel cover. The pit was not equipped with any type of ventilation system or gas monitoring equipment.

Four workers died in an underground lift station that collected leachate from a landfill. One worker entered to replace a sump pump and was overcome by hydrogen sulfide gas. A second, then third, and finally fourth worker entered to attempt rescue. All were overcome and died in the permit-required confined space. A permit entry system had not been established.

Too often, headlines like these provide a reality check for what our true purpose is as Professional Engineers. Having a focus on what can go wrong from real events points our moral compasses in the right direction, sharpens our design skills, and ensures we leave no stone unturned when assessing the consequences, frequency, and risk of a design. Our client-company may be our employer; however, our duty is to protect the public and the environment by providing safe management, maintenance, mitigation, and design practices.

Section 1: What are the OSHA Standards for Managing H_2S?

Because this course is not intended to be a review of readily available information from OSHA, the student is encouraged to read the provided sources from the OSHA.GOV. The following are provided to demonstrate a few of the regulations involved with managing H_2S. The general industry and maritime regulations are not all-inclusive for each discipline. Mining regulations, agricultural and other regulatory laws must be followed to provide a safe working environment for managing H_2S. Most regulations drive engineering controls in some manner. As Professional Engineers, our ingenuity and inventive spirit change the industry.

Additionally, OSHA and other state regulatory agencies present the minimum requirements. Responsible companies do what it takes to keep workers safe, even going above the minimum requirements. The American Conference of Governmental Industrial Hygienists (ACGIH) recommends exposure limits much more restrictive than that recommended by OSHA. These differences in regulation are demonstrated later in this course. For a complete and comprehensive listing of all applicable OSHA regulations around Hydrogen Sulfide, visit WWW.OSHA.GOV.

General Industry (29 CFR 1910)	
Subpart G – Occupational Health and Environmental Control	1910.94, Ventilation
Subpart H – Hazardous Materials	1910.119, Process safety management of highly hazardous chemicals
Subpart I – Personal Protective Equipment	1910.134, Respiratory protection
	1910.146, Permit-required confined spaces
Subpart J – General Environmental Controls	1910.1000, Air contaminants
Subpart Z – Toxic and Hazardous Substances	1910.1200, Hazard communication
	1910.1450, Occupational exposure to hazardous chemicals in laboratories

Maritime (29 CFR 1915, 1917, 1918, 1926)	
1915 Subpart B – Confined and Enclosed Spaces and Other Dangerous Atmospheres in Shipyard Employment	1915.12, Precautions and the order of testing before entering confined and enclosed spaces and other dangerous atmospheres
1915 Subpart Z – Toxic and Hazardous Substances	1915.1000, Air contaminants
1917 Subpart A – General Provisions	1917.1, Scope and applicability
1917 Subpart D – Specialized Terminals	1917.73, Terminal facilities handling menhaden and similar species of fish
1918 Subpart A – General Provisions	1918.1, Scope and application
	1918.94(f), Ventilation and atmospheric conditions. Employees shall not enter the hold when the hydrogen sulfide level exceeds 20 ppm ceiling or when the oxygen content is less than 19.5 percent, except in emergencies.
1918 Subpart I – General Working Conditions	1918.94, Catch of menhaden and similar species of fish
1926 Subpart D – Occupational Health and Environmental Controls	1926.55, Gases, vapors, fumes, dusts, and mists
1926 Subpart S – Underground Construction, Caissons, Cofferdams, and Compressed Air	1926.800, Underground construction

OSHA QUICK CARD™

Hydrogen Sulfide (H_2S)

Hydrogen sulfide is a colorless, flammable, extremely hazardous gas with a "rotten egg" smell. It occurs naturally in crude petroleum and natural gas, and can be produced by the breakdown of organic matter and human/animal wastes (e.g., sewage). It is heavier than air and can collect in low-lying and enclosed, poorly ventilated areas such as basements, manholes, sewer lines and underground telephone/electrical vaults.

Detection by Smell

- Can be smelled at low levels, but with continuous low-level exposure or at higher concentrations you lose your ability to smell the gas even though it is still present.
  - At high concentrations – your ability to smell the gas can be lost instantly.
- **DO NOT depend on your sense of smell for indicating the continuing presence of this gas or for warning of hazardous concentrations.**

Health Effects

Health effects vary with how long, and at what level, you are exposed. Asthmatics may be at greater risk.

- **Low concentrations** – irritation of eyes, nose, throat, or respiratory system; effects can be delayed.
- **Moderate concentrations** – more severe eye and respiratory effects, headache, dizziness, nausea, coughing, vomiting and difficulty breathing.
- **High concentrations** – shock, convulsions, unable to breathe, coma, death; effects can be extremely rapid (within a few breaths).

Before Entering Areas with Possible Hydrogen Sulfide

- The air needs to be tested for the presence and concentration of hydrogen sulfide by a qualified person using test equipment. This individual also determines if fire/explosion precautions are necessary.
- If gas is present, the space should be ventilated.
- If the gas cannot be removed, use appropriate respiratory protection and any other necessary personal protective equipment (PPE), rescue and communication equipment. Atmospheres containing high concentrations (greater than 100 ppm) are considered immediately dangerous to life and health (IDLH) and a self-contained breathing apparatus (SCBA) is required.

For more complete information:

OSHA Occupational Safety and Health Administration
U.S. Department of Labor
www.osha.gov (800) 321-OSHA

OSHA 3300-10N-05

Section 2: What are the characteristics of H_2S?

Hydrogen Sulfide (H_2S) is a toxic and explosive gas that, in certain conditions, is produced both industrially and naturally. Any place there is decaying organic matter like swamps, marshes, landfills, sewer lines, containment basins, sewage tanks, H_2S will form. Hot springs, volcanoes, thermal vents, caverns, caves, and underground mines can also produce H_2S gasses.

Industrial or manmade sources: H_2S is a byproduct of oil & gas production, petroleum and chemical manufacturing, paper mills, coke and coal-burning plants, wastewater plants on land or marine, and in agricultural facilities, manure pits, and tanks. It can also result from the accidental mixing of acids-strong base chemicals with organics. When organics are breaking down, H_2S can develop in areas and systems that typically would not have H_2S present. This type of source generator of H_2S is the most dangerous because you may not be expecting it.

There have been several fatalities over the last few decades on farms that collect and utilize manure. The manure is recovered and later used to spray on fields. In some cases, it is allowed to decompose, and the gas is collected. The gas can be used to generate electricity or as heating fuel.

Because lethal levels of H_2S are uncommon on farms, unsuspecting farmers were exposed to H_2S without knowing. In many instances, family members trying to rescue them also perished. Although uncommon, it devastates the farm, family, and community with a sudden unexpected loss.

The author had a personal experience with H_2S in an area in which it was not expected. During maintenance work at a plant, a vacuum truck was ordered to pull runoff from a pit next to a crude unit. The pit had a large horizontal drum that was anchored on foundations above its opening. Drainage from the unit was directed through concrete channels to the pit. Normally, only rainwater drained into the pit. The pit was routinely tested for the presence of hydrocarbon, and this determined which treatment area the material would be delivered to. No oil meant going straight to the secondary treatment plant. The presence of hydrocarbon sent it through primary treatment first to remove any hydrocarbons. All previous pit vacuum truck removals had never produced H_2S gasses. However, on this day, several people were exposed, but there were no fatalities.

Unknown to the crew and vacuum truck driver, organics in a sludge layer from the maintenance work in the unit had built up in the bottom of the pit. Cleaning agents being used to remove hydrocarbon in the unit were also routed to the concrete pit. The combined materials had set in the basin for several days. When the vacuum hose was dropped into the water and hit the bottom, it boiled and bubbled briefly. The entrained H_2S broke free from the sludge and water molecules, clinging one to another, and surfaced. Fortunately, the vacuum driver's personal alarm went off along with a couple of other workers, and everyone backed away, moving crosswind and upwind from the pit.

After reporting the incident, Operators returned in fresh air and tested the area, and little or no H_2S was detected. The personal monitor of the vacuum driver had registered IDLH levels of 100ppm. The monitor only registered to a level of 100ppm or IDLH, so no one really knows how high the concentration was at the pit, but it did reach 100 ppm or over. In this situation, people were surprised to find fatal levels of H_2S. This course will provide as many situational examples and mitigations as possible to arm the Professional Engineer, so learning is transferrable.

H_2S Properties & Human Response Characteristics

Hydrogen Sulfide is measured in concentration levels known as ppms (parts per million). The table below is a common sourced table available from OSHA standard information. This table provides exposure concentration and the human response. What is not shown in this overview is that in concentrations of 300ppm and higher, you may not notice the presence. In other words, the rotten egg odor most people attribute to the potential presence of H_2S is not always an indicator.

H_2S is often referred to in the industry as sour gas because of this odor. Between an initial exposure of 1 ppm to 30 ppm, the odor will intensify. Once at concentrations of 30 ppm or with prolonged exposure at this level, your sense of smell decreases due to olfactory fatigue.

As H_2S concentrations increase, the olfactory nerves in your nose become de-sensitized, and you lose your ability to smell. What this means is you won't realize the silent killer as concentration levels and exposure times increase, resulting in fatal irreversible effects. Therefore, many known areas where H_2S may be present still require personal alarm monitors (PAM). PAM's alarm at 10 – 20 ppm normally allowing a person time to respond and escape pending the levels are not extreme. In extreme exposures, even a PAM may not alert you in time to escape.

The table below lists the important properties of H_2S that can be found in any safety data sheet (SDS) and regulatory standards for permissible exposure limits (PEL). Hydrogen Sulfide is a chemical compound composed of two hydrogen atoms and one sulfur atom. It is extremely dangerous and must be managed with the utmost care.

Molecular weight = 34 kg/kmole	Solubility in water = 4.67 m^3/m^3
Gas density = 1.93 kg/m^3	TLV value = 20 … 50 ppm STEL (OSHA) PEL = 1… … (ACGIH)
Specific Gravity = … = 1)	
Chart information … American Confere… Governmental I… Hygienists (ACGIH© …	

The TLV stands for Th… the concentration of gas is considered to be dang… s very low: 1 ppm on a Time Weighted Averag… osure Limit (STEL) is only 5 ppm. This means … for 15 minutes is over the ACGIH limit or cont… our work shift.

Many companies have se… r even 20 ppm. Even though OSHA recognize… y will be held by the alarm limits established i… not what the OSHA limit is. What this means is if … say, 5 ppm, anything you have to manage this limit not followed is s… scrutiny by OSHA.