

When is CO₂ more hazardous than H₂S

Data shows potential harmful effects to workers due to acid gas exposure

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Many different types of facilities produce or use streams containing a high carbon dioxide (CO₂) content (98+%) with low hydrogen sulfide (H₂S) concentrations, e.g., a few parts per million by volume (ppmv) to a few volume percent (vol%). Examples include CO₂-flood enhanced oil recovery, pre-combustion carbon capture (from fossil fuel-fired power plants and industrial facilities) and sequestration, natural gas conditioning, and agricultural manufacturing, among others. In all of these industries, the potential for a release in a processing step or during transmission through a pipeline exists.

The health effects and dangers of H₂S are well known, but those of CO₂ are not as commonly understood. It is uncertain if industry realizes that CO₂ is a mildly toxic gas and not just a simple asphyxiant like nitrogen. Because CO₂ itself is toxic at higher concentrations, the high-purity CO₂ streams can actually be more hazardous than the H₂S and they are the subject of discussion in this article. In such cases, the presence of H₂S may actually allow easier detection of the CO₂ danger.

This article reviews the hazards of H₂S and CO₂ and compares the effects from these acid gases on humans. Concentration levels corresponding to the immediately dangerous to life and health (IDLH) levels of the two gases are used to illustrate conditions where both H₂S and CO₂ are present, and the CO₂ (not the H₂S) is the predominant concern. A goal is to educate readers to think of CO₂ as a mildly toxic gas and not just an asphyxiant, and to recognize conditions where it can represent the more significant hazard, even if small concentrations of H₂S are also present.

Toxicity of H₂S. Hydrogen sulfide is an intensely hazardous, toxic compound.¹ It is a colorless, flammable gas that can be identified in relatively low concentrations by a characteristic rotten egg odor. This acid gas is naturally occurring and is in the gases from volcanoes, sulfur springs, undersea vents, swamps and stagnant bodies of water and in crude petroleum and natural gas. Hydrogen sulfide is produced when bacteria break down sulfur-containing proteins, and it is a component of decomposing materials. In addition, H₂S is also produced from man-made operations and processes such as petroleum refineries, food processing plants, tanneries, municipal sewers, sewage treatment plants, landfills, swine containment and manure-handling operations, and pulp and paper mills.

Hydrogen sulfide has a very low odor threshold, with its smell being easily detected by most people in the range of 0.0005

ppmv to 0.3 ppmv.² As the gas becomes more concentrated, the odor increases with a strong rotten egg smell identifiable up to 30 ppmv. From about 30 ppmv to 100 ppmv, the gas is stated to have a sickeningly sweet odor. However, at concentrations above 100 ppmv, a person's ability to detect the gas decreases due to a rapid temporary paralysis of the olfactory nerves in the nose that leads to a *loss of the sense of smell*. This means that the gas can be present in the environment at extremely high concentrations with no noticeable odor. This unusual property of H₂S makes it very dangerous to depend solely on the sense of smell as a warning sign of the gas.³

Once H₂S is released as a gas, it remains in the atmosphere for an average of 18 hours, after which it changes to sulfur dioxide and sulfuric acid.² It is water-soluble and, therefore, it may partition to surface water or adsorb onto moist soil, plant foliage, or other organic material where it loses much of its toxic properties.

Hydrogen sulfide is classified as a chemical asphyxiant, similar to carbon monoxide (CO) and cyanide gases. It interferes with

TABLE 1. Symptoms from low to high concentrations of H₂S

Exposure level	Concentration, ppmv	Symptom
Low	0–10	Irritation of the eyes, nose, and throat
Moderate	50–200	Coughing Hoarseness Shortness of breath Pneumonia Loss of smell (> 100 ppmv)
High	200–500	Changes in respiratory tissue (200–400 ppmv per laboratory animals) Rapid respiratory distress and failure (acute exposure at > 500 ppmv for 1 to 4 hours) ²
Very high	> 2,000	Coma and death after single breath ⁴ Known as "knockdown effect" with immediate immobilization and unconsciousness, possibly from disruption of oxidative metabolism in the brain

nerve cell function, putting certain nerves to sleep, including olfactory (as discussed previously) and the ones necessary for breathing. Table 1 shows the typical exposure symptoms of H₂S.

It is important to note that while most chemicals are toxic, exposure has to occur (at a level that is considered toxic) before adverse health effects are observed. Most, if not all, of the irreversible health outcomes including death have occurred due to overexposure to H₂S in confined areas.

Toxicity of CO₂. Carbon dioxide is a slightly toxic, odorless and colorless gas. It is typically found in air at around 360 ppmv (0.036 vol%) while exhaled air may contain as much as 40,000 ppmv (4 vol%). Table 2 shows the general affects of CO₂ over different ranges of exposure.

At lower concentrations, CO₂ affects the respiratory system and central nervous system. Too much CO₂ also acts as a simple asphyxiant by reducing the amount of oxygen available for respiration.⁶ At higher concentrations, too, the ability to eliminate CO₂ decreases and it can accumulate in the body. In this way, CO₂ differs from some other asphyxiants, such as nitrogen (N₂). Unlike CO₂, N₂ does not get distributed throughout the body to cause an adverse health effect; rather, N₂ acts simply by displacing oxygen from the air and, thereby, decreasing the amount of oxygen available for respiration. **Result:** CO₂ is dangerous at a much lower level than some other asphyxiants, such as N₂.

Nitrogen is discussed here because it is a common potential asphyxiant in industrial settings. The following example illustrates the differences between CO₂ and N₂. Consider a hypothetical example where 90 parts of atmospheric air (normally 21% O₂ and 79% N₂) are mixed with 10 parts of either pure CO₂ or N₂. The resulting mixture compositions are shown in Fig. 1.

As shown in Fig. 1, the resulting mixture with CO₂ addition contains 18.9% O₂, 71.1% N₂, and 10% CO₂. As discussed previously, such a mixture could potentially kill a person. Conversely, the mixture with N₂ contains 18.9% O₂ and 81.1% N₂; while this mixture is lower in oxygen than normal air and below the recommended O₂ % for workers, it is not likely to cause irreversible health effects. The effect of going from a 21% oxygen atmosphere to an 18.9% oxygen atmosphere is similar to going from sea level to about 3,000 ft in elevation (roughly the elevation of Midland,

TABLE 2. Symptoms from low to high concentrations of CO₂

Exposure level	Concentration, ppmv	Symptom
Low	20,000 to 30,000	Shortness of breath, deep breathing
Medium	50,000 75,000	Breathing becomes heavy, sweating, pulse quickens Headaches, dizziness, restlessness, breathlessness, increased heart rate and blood pressure, visual distortion
High	100,000	Impaired hearing, nausea, vomiting, loss of consciousness
Very high	300,000	Coma, convulsions, death ⁵

TABLE 3. Exposure limits for H₂S and CO₂⁷

Compound	TLV and PEL, ppmv	STEL, ppmv	IDLH, ppmv
H ₂ S	10	15	100
CO ₂	5,000	30,000	40,000

Texas), as far as the oxygen partial pressure is concerned. Most people who are acclimated to sea level would have no trouble going to 3,000 ft in elevation.

In summary, mixing 10 parts CO₂ with 90 parts air can possibly cause a person breathing the mixture to die if exposed long enough. In contrast, mixing 10% N₂ with air probably has little effect on a person. Clearly, it is very important to recognize that CO₂ is not the same simple asphyxiant as N₂.

Occupational exposure limits for H₂S and CO₂. Table 3 provides a summary of occupational exposure limits for H₂S and CO₂. Occupational exposure limits are typically designed to protect health and to provide for the safety of employees for up to a 40-hour work week, over a working lifetime. The threshold limit value (TLV) was developed by the American Conference of Governmental Industrial Hygienists (ACGIH) while the permissible exposure limit (PEL) is an enforceable standard developed by the Occupational Safety and Health Administration (OSHA). The short-term exposure limit (STEL) was developed by ACGIH and represents a 15-minute time-weighted average exposure that should not be exceeded at any time during the workday. The IDLH value was developed by the National Institute for Occupational Safety and Health (NIOSH) to provide a level at which a worker could escape without injury or irreversible health effects.

IDLH values are conservatively established by NIOSH to give a worker approximately 30 minutes to evacuate an area. The IDLH for both H₂S and CO₂ are purposefully established below levels at which adverse and irreversible health effects would be seen following 30 minutes of exposure. The IDLH for H₂S was developed based on human data (and supplemented with information from laboratory animals) that showed that between 170 ppmv and 300 ppmv, a person can be exposed for one hour without serious health effects and that 400 ppmv to 700 ppmv can be dangerous if exposure is greater than 30 minutes. A person can be exposed to H₂S at 800 ppmv for approximately 5 minutes before unconsciousness occurs, while exposure at 1,000 ppmv or greater can cause immediate respiratory arrest, unconsciousness and possibly death.

For CO₂, a person can sustain exposure to the IDLH of 40,000 ppmv for 30 minutes with minimal signs of intoxication (e.g., changes in breathing rate, headache and fatigue). At 30 minutes of exposure to 50,000 ppmv CO₂, signs of intoxication become more pronounced. A person can sustain exposure to 70,000 ppmv to 100,000 ppmv CO₂ for about 5 minutes and signs of intoxication become intense with very labored breathing, visual impairment, headache, ringing in the ears and potentially impaired judgment. Air containing CO₂ at a concentration

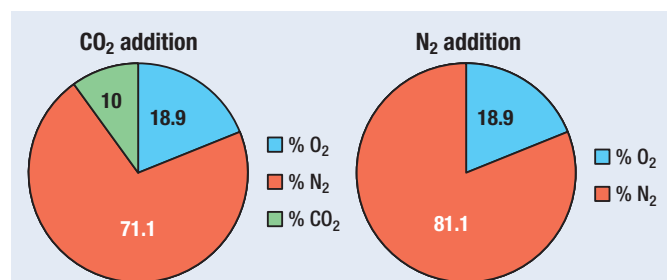


FIG. 1 Mixture compositions with 90 parts air and 10 parts CO₂ or N₂.

greater than 100,000 ppmv (i.e., 10 vol%) can produce extreme discomfort and, as indicated above, can be life-threatening.

Table 4 shows an example of how a gas stream containing initial concentrations of H₂S of 2,000 ppmv and of CO₂ of 98 vol% would change assuming a uniform dispersion in air for both compounds. As shown in the table, when the IDLH of H₂S (100 ppmv) is reached, the CO₂ content is still above the IDLH level of 40,000 ppmv. Even more dramatic are the 5-minute exposure levels; when the H₂S exposure level is at the 5-minute limit of 800 ppmv, the CO₂ concentration is at 392,000 ppmv, which is far above the level a person can survive for 5 minutes. Thus, given the much higher percentage of the CO₂ in this gas stream, the danger from CO₂ is higher than the danger posed by H₂S.

Potential exposure scenarios to H₂S and CO₂. In actuality, it is difficult to determine the likelihood of a release and the potential concentration a person may encounter following a release. A release could occur at any point in the processing unit or transfer pipeline depending on the source of the stream (see Fig. 2). Atmospheric conditions, such as the wind or physical location of the release (low lying area), can greatly affect the dispersion rate and exposure concentrations of the two compounds. Some potential exposure scenarios are discussed here.

If there is wind, a small release (i.e., not a catastrophic event) would most likely disperse relatively quickly. Under this scenario, a person downwind (unless they were within close proximity to the release) would probably not be exposed to a harmful concentration of either compound. In fact, the presence of H₂S (which has an odor at very low concentrations) may actually provide an early indicator of a CO₂ release that would otherwise go undetected. Although H₂S may provide an early indicator of a release in certain situations, this should not be relied upon because H₂S deadens the sense of smell at higher concentrations. Exposure should be kept to a minimum by applying sufficient engineering controls and safe work practices. Appropriate monitoring and personal protective equipment should always be used.

Because both compounds are heavier than air (the specific gravity for H₂S and CO₂ is 1.192 and 1.52, respectively), the most likely place to encounter harmful levels of either compound

would be in a low-lying area or depression. This is currently an issue for CO₂ pipelines in which harmful levels of CO₂ can accumulate in these areas, regardless of the presence of H₂S. The presence of H₂S increases concerns due to its more insidious toxicity (i.e., it can render a person incapable of escape at sufficiently high concentrations). However, levels above the IDLH could occur in a confined space or depression for either compound. As indicated earlier, the presence of H₂S may provide a warning that a release has occurred and prevent a person from entering the area where potentially dangerous levels of CO₂ or H₂S may be present. **Note:** The use of direct reading gas detection instrumentation and other protective measures should be required before entering confined spaces such as manholes, tanks, pits and vessels that could contain a buildup of these gases.

Potential synergistic effects of concurrent exposure.

Since the mechanisms of action for CO₂ and H₂S are very different, it is unlikely that exposure to both compounds will be worse than exposure to only one compound. Most occupational exposure limits are based on exposure to single compounds, even though it is recognized that multiple compounds may be encountered, and Environmental Protection Agency only considers compounds additive if they affect the same target organ or act by the same mechanism. Moreover, industries such as swine production, where both CO₂ and H₂S are measured in the air, do not adjust occupational exposure limits for added worker safety nor have synergist effects (i.e., effects that are worse when in combination than when exposure is to a single compound) been noted for industries where exposure to both compounds occur.⁸

TABLE 4. Occupational limits example (high-purity CO₂ gas with low H₂S)

Dispersion	CO ₂ , ppmv	H ₂ S, ppmv	Occupational exposure limit
Initial concentration, %	980,000	2,000	
10	882,000	1,800	
20	784,000	1,600	
30	686,000	1,400	
40	588,000	1,200	
50	490,000	1,000	
60	392,000	800	5-minute H ₂ S exposure (800 ppmv)
70	294,000	600	
80	196,000	400	
90	98,000	200	5-minute CO ₂ exposure (100,000 to 70,000 ppmv)
95	49,000	100	H ₂ S IDLH (100 ppmv)
95.9	40,000	82	CO ₂ IDLH (40,000 ppmv)
100	0	0	



FIG. 2A Example sources of high-purity CO₂ and low H₂S streams—CO₂ dehydration unit.



FIG. 2B Example sources of high-purity CO₂ and low H₂S streams—CO₂ piping.

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Evaluation of risk. Based on the general qualitative analysis of exposure to both H₂S and CO₂ discussed here, it appears that there is no increased risk from the presence of H₂S at low levels (e.g., up to perhaps 2,000 ppmv or higher) in high-purity CO₂ gas. In fact, in these types of gas streams, the potential exposure to high CO₂ concentrations during a release event could be as dangerous, or more dangerous, than exposure to lower concentrations of the more toxic H₂S. At high concentrations, CO₂ may accumulate in the body, which is different than some other asphyxiants (i.e., N₂). It is most important to recognize the difference between CO₂ and other common asphyxiants. In some cases, the H₂S in the gas may serve as a warning for the more hazardous CO₂ environment. Dispersion modeling for specific release scenarios should be conducted to better understand possible exposure limits and impacts on human health for both compounds. Appropriate safety precautions should be implemented including monitoring (both fixed and personal detection systems) and training on chemical hazards, personal protection equipment and safety rescue procedures. **HP**

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