

WHEN CO₂ IS MORE HAZARDOUS THAN H₂S

Kenneth E. McIntush, P.E. (Presenter)

Joseph E. Lundeen

Kevin S. Fisher, P.E.

Carrie Ann M. Beitler

Trimeric Corporation

P.O. Box 826

Buda, TX 78610

512 295-8118

ken.mcintush@trimeric.com

joe.lundeen@trimeric.com

kevin.fisher@trimeric.com

carrie.beitler@trimeric.com

Kirby Tyndall, Ph.D., DABT
Pastor, Behling, & Wheeler LLC
2201 Double Creek Drive, Suite 4004
Round Rock, TX 78664
512 671-3434

kirby.tyndall@pbwllc.com

Brimstone Sulfur Symposium
September 2011
Vail, Colorado

WHEN CO₂ IS MORE HAZARDOUS THAN H₂S

*Kenneth E. McIntush, P.E., Joseph E. Lundeen, Kevin S. Fisher, P.E., and Carrie Ann M. Beitler (Trimeric Corporation)
Kirby Tyndall, Ph.D., DABT (Pastor, Behling, & Wheeler LLC)*

Introduction

There are a number of types of facilities that 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 [%]). Examples include CO₂-flood enhanced oil recovery (EOR), 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 often well known, but those of CO₂ are not as commonly understood. It is not clear 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, CO₂ can actually be more hazardous than the H₂S in the high purity CO₂ streams considered in this paper. In such cases, the presence of H₂S may actually allow easier detection of the CO₂ danger.

This paper reviews the hazards of H₂S and those of CO₂ and compares the effects on humans of the two gases. 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 the audience 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 Hydrogen Sulfide

Hydrogen sulfide is an intensely hazardous, toxic compound¹. It is a colorless, flammable gas that can be identified in relatively low concentrations by a characteristic rotten egg odor. Hydrogen sulfide 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. Hydrogen sulfide 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 to 0.3 ppmv². As the gas becomes more

concentrated, the odor increases with a strong rotten egg smell identifiable up to 30 ppmv. From about 30 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 hydrogen sulfide makes it very dangerous to depend solely on the sense of smell as a warning sign of the gas³.

Once hydrogen sulfide is released as a gas, it remains in the atmosphere for an average of eighteen hours, after which it changes to sulfur dioxide and sulfuric acid². 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 and cyanide gases. It interferes with nerve cell function, putting certain nerves to sleep, including olfactory (as discussed above) and the ones necessary for breathing. Table 1 shows the typical exposure symptoms of hydrogen sulfide.

Table 1. Symptoms from Low to High Concentrations of H₂S

Exposure Level	Concentration	Symptom
Low	0-10 ppmv	Irritation of the eyes, nose, and throat
Moderate	50-200 ppmv	Coughing Hoarseness Shortness of breath Pneumonia Loss of smell (>100 ppmv)
High	200-500 ppmv	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	>2000 ppmv	Coma and death after single breath ⁴ Known as "knockdown effect" with immediate immobilization and unconsciousness possibly from disruption of oxidative metabolism in brain

With that said, 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, irreversible health outcomes including death have occurred due to overexposure to hydrogen sulfide in confined areas.

Toxicity of Carbon Dioxide

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

Table 2. Symptoms from Low to High Concentrations of CO₂

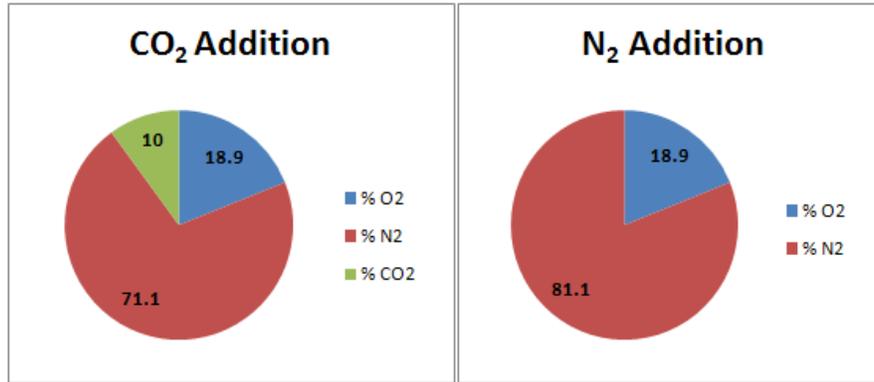
Exposure Level	Concentration	Symptom
Low	20,000 to 30,000 ppmv	Shortness of breath, deep breathing
Medium	50,000 ppmv 75,000 ppmv	Breathing becomes heavy, sweating, pulse quickens Headaches, dizziness, restlessness, breathlessness, increased heart rate and blood pressure, visual distortion
High	100,000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

At lower concentrations, carbon dioxide affects the respiratory system and central nervous system, and too much carbon dioxide also acts as a simple asphyxiant by reducing the amount of oxygen available for respiration⁶. At higher concentrations too, the ability to eliminate carbon dioxide decreases and it can accumulate in the body. In this way, CO₂ differs than some other asphyxiants, such as nitrogen (N₂). Unlike CO₂, nitrogen does not get distributed throughout the body to cause an adverse health effect; rather, nitrogen acts simply by displacing oxygen from the air and, thereby, decreasing the amount of oxygen available for respiration. Thus, CO₂ is dangerous at a much lower level than some other asphyxiants, such as nitrogen.

Nitrogen is discussed above because it is a common potential asphyxiant in industrial settings. The following example illustrates the differences between CO₂ and nitrogen. 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 Figure 1 below.

As shown in Figure 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. On the other hand, 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, this mixture 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 3000 ft in elevation (roughly the elevation of Midland, Texas), as far as the oxygen partial pressure is concerned. Most people who are acclimated to sea level would have no trouble going to 3000 ft elevation.

Figure 1. Mixture Compositions with 90 Parts Air and 10 Parts CO₂ or N₂



In summary, mixing 10 parts CO₂ with 90 parts air can possibly cause a person breathing the mixture to die if exposed long enough. On the other hand, 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 nitrogen.

Occupational Exposure Limits for Hydrogen Sulfide and Carbon Dioxide

Table 3 provides a summary of occupational exposure limits for hydrogen sulfide and carbon dioxide. 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) is 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.

Table 3. Exposure Limits for Hydrogen Sulfide and Carbon Dioxide⁷

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

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 hydrogen sulfide was developed based on human data (and supplemented with information from laboratory animals) that showed that between 170 and 300 ppmv, a person can be exposed for one hour without serious health effects and that 400 to 700 ppmv can be dangerous if

exposure is greater than 30 minutes. A person can be exposed to hydrogen sulfide 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 carbon dioxide, 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 carbon dioxide, signs of intoxication become more pronounced. A person can sustain exposure to 70,000 to 100,000 ppmv carbon dioxide 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 carbon dioxide at a concentration greater than 100,000 ppmv (i.e., 10 volume %) 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 hydrogen sulfide of 2000 ppmv and of carbon dioxide of 98% by volume 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 carbon dioxide in this gas stream, the danger as a result of the CO₂ is higher than the danger posed by the H₂S.

Table 4. Occupational Limits Example (High Purity CO₂ Gas with Low H₂S)

Dispersion	CO₂ ppmv	H₂S 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	

Potential Exposure Scenarios to Hydrogen Sulfide and Carbon Dioxide

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 Figure 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 below.

Figure 2. Example Sources of High Purity CO₂ and Low H₂S Streams (CO₂ Dehydration Unit and CO₂ Piping)



If there is wind, a small release (i.e., not a catastrophic event) would most likely disperse relatively quickly. Under this type of 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 hydrogen sulfide (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, it should not be relied upon, because H₂S deadens the sense of smell at higher concentrations. Exposure should be kept to a minimum by employing 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 hydrogen sulfide and carbon dioxide 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 carbon dioxide pipelines and harmful levels of carbon dioxide can accumulate in these areas, regardless of the presence of hydrogen sulfide. The presence of hydrogen sulfide increases concern 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 above, though, the presence of hydrogen sulfide may provide a warning that a release has occurred and prevent a person from entering the area where potentially dangerous levels of carbon dioxide or hydrogen sulfide may be present. (Please note that 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 to Hydrogen Sulfide and Carbon Dioxide

Since the mechanisms of action for carbon dioxide and hydrogen sulfide 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 (EPA) 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 carbon dioxide and hydrogen sulfide 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 occur⁸.

Conclusions

Based on the general qualitative analysis of exposure to both hydrogen sulfide and carbon dioxide discussed above, it appears that there is no increased risk from the presence of hydrogen sulfide at low levels (e.g., up to perhaps 2000 ppmv or higher) in high purity CO₂ gas. In fact, in these types of gas streams, the potential exposure to high concentrations of carbon dioxide in the event of a release could be as dangerous or more dangerous than the lower concentration of the more toxic hydrogen sulfide. At high concentrations, CO₂ may accumulate in the body which is different than some other asphyxiants (i.e., nitrogen), so it is 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 then be implemented including monitoring (both fixed and personal detection systems) and training on chemical hazards, personal protection equipment, and safety rescue procedures.

References

- 1) United States Environmental Protection Agency (EPA), 2010. *Integrated Risk Information System (IRIS)*. Profile for Hydrogen Sulfide (CASRN 7783-06-4). On-line database. <http://www.epa.gov/iris/subst/0061.htm> . August.
- 2) Hydrogen Sulfide Fact Sheet. August 2004. SafetyDirectory.com; http://www.safetydirectory.com/hazardous_substances/hydrogen_sulfide/fact_sheet.htm

- 3) Agency for Toxic Substances and Disease Registry (ATSDR), 2004. *Draft Toxicological Profiles for Hydrogen Sulfide*. United States Department of Health and Human Services. Public Health Service. September.
- 4) Gossel, T.A. and J.D. Bricker, 1994. *Principles of Clinical Toxicology, Third Edition*. Raven Press: New York, NY.
- 5) Goodman Gilman, A., L.S. Goodman, T.W. Rall, and R. Murad, 1985. *The Pharmacological Basis of Therapeutics, Seventh Edition*. MacMillan Publishing Company: New York, NY.
- 6) Klaassen, C.D., 2008. *Cassarett and Doull's Toxicology – The Basic Science of Poisons, Seventh Edition*. M^cGraw-Hill Publishing Company: New York, NY.
- 7) National Institute for Occupational Safety and Health, 2004. *NIOSH Pocket Guide to Chemical Hazards*. US Department of Health and Human Services. Public Health Service. Centers for Disease Control and Prevention. February.
- 8) Lemay, S., Chenard, L., and R. MacDonald, 2002. *Indoor Air Quality in Pig Buildings: Why Is It Important And How Is It Managed?* London Swine Conference – Conquering the Challenges 11-12 April.