CONSIDER HAZARDS OF CO_2 AND H_2S FOR CCS

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ABSTRACT

CO_2 Capture and Storage (CCS) is receiving significant interest as a result of the federal tax credit program known as Section 45Q. Some streams considered for CCS have both CO_2 and H_2S. Hazards of H_2S are widely known, because significant resources have been expended over decades to publicize those hazards and reduce risks. The hazards of CO_2 appear to be less well recognized. Rather than being a simple asphyxiant like N_2, CO_2 is a mildly toxic gas that can harm and kill at much lower levels than N_2. This paper reviews the hazards of H_2S and those of CO_2 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 H_2S and CO_2 are present and the CO_2 (not the H_2S) is the predominant concern. CO_2 is also compared with N_2. The paper also reviews the concept that 'the dose makes the poison'. To bring this point home, some literature examples are cited where low doses of H_2S are implicated in lengthening lifespan and where H_2S is used in medicine / medical research at low levels.

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Introduction

Some process facilities may produce or use gas streams consisting primarily of carbon dioxide (CO_2) with a low concentration of hydrogen sulfide (H_2S). Examples may be found in CO_2-flood enhanced oil recovery (EOR), natural gas treatment, biogas treatment, and agricultural manufacturing among others. Recently enacted regulations have provided financial incentives for recovering or sequestering CO_2 waste streams rather than venting them to the atmosphere. These financial incentives could result in the installation of more processes that handle high-CO_2 content gas streams.

US Federal tax regulations (45Q) provide tax credits for qualified projects which result in CO_2 emission reductions, and many other countries throughout the world provide for credits and/or penalties which encourage CO_2 emissions reductions. Carbon capture and sequestration (CCS) [also referred to as carbon capture, use, and sequestration (CCUS)] refer to the recovery of CO_2 and its storage underground or conversion to useful products. Some CO_2 capture schemes may be economically practical because of the 45Q incentives.

In many industries that produce or handle a CO_2-rich gas stream, H_2S may also be present, and the potential always exists for an accidental or intentional release of a gas during processing or transmission. The health effects and dangers of H_2S are well known in the oil, gas, and refining industries, but those of CO_2 may not be adequately appreciated. CO_2 is a mildly toxic gas and not just a simple asphyxiant like nitrogen. In gases in which CO_2 is the chief component, with H_2S present at much lower concentration, CO_2 can be more hazardous than the H_2S. In such cases, because of its strong odor, the presence of H_2S may actually allow easier detection of the CO_2 danger.

This paper provides some background information on CO_2 and H_2S mixtures and reviews the hazards of H_2S and those of CO_2 and compares the effects on humans of the two gases. Th goal is to educate the audience to think of CO_2 i) as a mildly toxic gas and not just an asphyxiant and ii) to recognize conditions where it can represent the more significant hazard, even if some H_2S is also present.

CO_2 and H_2S Mixtures, 45Q, and CCS

According to the US Congressional Research Service [1], 45Q tax credits in 2026 of \$50 per metric ton (MT) of CO_2 may be obtained for geological sequestration, \$35/MT for sequestration by EOR, and \$35/MT for making other qualified uses of the CO_2. (The "Build Back Better Act" legislation currently being considered by the US Congress could increase this credit to as high as \$80/MT.) To qualify, the CO_2 captured must have a stream that would have normally been released to the atmosphere; this qualification would exclude, for example, CO_2 originally withdrawn from natural reservoirs and then injected for EOR. Minimum or maximum capture requirements and production amounts may also limit qualification for the credits.

Many other governments throughout the world are implementing their own systems of making CCS economically feasible, or at least making it financially or legally unavoidable. One approach is for the government to tax and/or limit (cap) the CO_2 emissions of industries, which could result in CCS being essential for some operations at some point in the future. Such schemes may also include so-called "cap and trade" with companies which practice CCS selling emissions allowance at market prices to companies that do not, with the government regulations regarding emission taxation rates and emission caps essentially driving the market.

Streams that are highest in CO_2 concentration are considered most amenable to CCS, and this has resulted in some industries that produce high-CO_2 byproduct gas streams – such as fermentation industries – participating in CCS relatively early. The recovery of high concentration CO_2 vent streams may be, in many cases, economically justified without the benefit of tax credits, depending upon the market value of the purified CO_2 products.

An important part of the recovery of CO_2 streams regardless of whether it is for a product, EOR injection, or injection for sequestration, is compression. High pressure and high gas density are usually required to inject the CO_2-rich gas. Gas streams that contain high concentrations of lighter components (nitrogen, methane, oxygen, hydrogen, etc.) in addition to CO_2 are more difficult and expensive to compress than high concentration CO_2 streams, which may result in the need to separate the light components from the CO_2 prior to compression. Gas streams with a CO_2 concentration of at least about 90% are typically favored for direct compression and injection [2], although higher purities may be required for many cases, such as transport in a shared pipeline. H_2S is sometimes present with CO_2 in gas streams and the separation of these two gases from each other can be difficult since they have roughly similar physical properties. When considering compression of CO_2 for injection, there may be no process reason to separate the H_2S from it, although it may be done for other reasons, such as safety or regulations.

Natural gas processing using amine or physical solvents may produce a CO_2 and/or H_2S-rich acid gas stream. Other industries that may also produce CO_2 streams that may contain some H_2S include (but are not limited to):

- Geothermal: Non-condensable gas (NCG) residual after steam condensation
- Fermentation: Vent gas from alcohol production from biomasses
- Oil Refining: Vent gas from various refining processes such as hydrotreating
- Landfill gas and biogas: Byproduct gas from purification processes

Only CO_2 streams which would otherwise be vented are eligible for the tax incentive in the US. If, for example, a company operates an amine plant that creates a

CO_2 acid gas that is normally vented to the atmosphere, it may be possible to qualify for the tax credit by injecting that acid gas stream into a qualified well (additional limitations may apply). Disposal of a CO_2-rich gas stream by injection sequestration requires that a suitable location be available for an injection well, which may not often be the case. Transport of the CO_2 via pipeline may be required to reach an appropriate injection well. Furthermore, the use of CO_2 for EOR is practiced in limited regions, so selling a CO_2 stream into that market is limited by location.

During any unit operations in which a CO_2-rich gas stream is treated, compressed, or transported, mixes of CO_2 and H_2S may be present. The release of gas from these processing steps must be considered, and appreciation of the hazards of all of the components of the gas mixture must be considered, not just H_2S.

Toxicity of Hydrogen Sulfide

In sufficient concentration, H_2S is an intensely hazardous, toxic compound [3]. It is a colorless, flammable gas that can be identified in relatively low concentrations by a characteristic rotten egg odor. H_2S 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. H_2S is produced when bacteria break down sulfur-containing proteins and is thus a component of decomposing biological materials. In addition, H_2S is also produced from man-made operations and processes such as petroleum refineries, food processing plants, tanneries, municipal sewers, sewage treatment plants, landfills, swine/livestock containment and manure-handling operations, fermentation, and pulp and paper mills.

H_2S has a very low odor threshold, with its smell being easily detected by most people in the range of 0.0005 to 0.3 ppmv [4]. At concentrations (up to about 30 ppmv), the gas has a rotten egg smell [5]. Above 30 ppmv, the gas is stated to have a sickeningly sweet odor [5]. However, concentrations in the range of 100-150 ppmv can cause a loss of smell known as olfactory fatigue or paralysis [5]. Because of this, it is not advisable to depend on the sense of smell to detect dangerous levels of H_2S [6].

Once H_2S is released as a gas, it remains in the atmosphere for an average of eighteen hours, after which it changes to sulfur dioxide (SO_2) and sulfuric acid [4]. 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.

H_2S is classified as a chemical asphyxiant, similar to carbon monoxide (CO) and cyanide gases. It interferes with nerve cell function, paralyzing them, including olfactory nerves and those necessary for breathing. Table 1 shows the typical exposure symptoms of H_2S. While H_2S is considered toxic, adverse health effects are only observed when it is present at or above a minimum level. Most irreversible health outcomes, including death, have occurred due to overexposure to H_2S in confined areas.

The above focuses primarily on the negative health effects of H_2S exposure, and rightfully so as the gas industry typically considers H_2S primarily as a hazard to be avoided. However, as the saying by Paracelsus, the father of Toxicology, goes 'the dose makes the poison' [7]; that is, a chemical that causes harm at one level is often essential to life at another level. For example, an Internet search on "H_2S longevity" will turn up a number of articles regarding the health benefits of H_2S. H_2S is endogenously generated in humans and is becoming recognized as a gaseous transmitter that mediates physiology and disease [8]. Further, exogenous exposure to H_2S (e.g., breathing it) at low enough concentrations may also have health benefits [9]; H_2S has been shown to be involved in physiological processes associated with aging, and some experimentation focuses on the potential of H_2S in increasing the lifespan of some micro-organisms. In addition, H_2S is used in certain cases as a medical treatment, for example, with heart attack victims [10].

Table 1. Symptoms from Low to High Concentrations of H_2S

Exposure Level	Concentration	Symptom
Low	0-10 ppmv (0 – 0.001 vol%)	Irritation of the eyes, nose, and throat
Moderate	50-200 ppmv (0.005 – 0.02 vol%)	Coughing Hoarseness Shortness of breath Pneumonia Loss of smell (>100 ppmv)
High	200-500 ppmv (0.02 – 0.05 vol%)	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) [4]
Very High	>2,000 ppmv (> 0.2 vol%)	Coma and death after single breath [11] Known as "knockdown effect" with immediate immobilization and unconsciousness possibly from disruption of oxidative metabolism in brain

Toxicity of Carbon Dioxide

CO_2 is a slightly toxic, odorless and colorless gas. It is typically found in air at around 400 ppmv while exhaled air may contain as much as 40,000 ppmv (4%). Table 2 shows the general effects of CO_2 over different ranges of exposure.

Biochemically-produced CO_2 in the body is eliminated via mass transfer from the blood through the lungs into breathed air. Increased partial pressure of CO_2 in the air results in a reduction in the efficiency of the lung's ability to decrease the CO_2 content in the blood, thus allowing CO_2 to accumulate in the body. At lower concentrations, CO_2 affects the respiratory system and central nervous system, and too much CO_2 also acts as a simple asphyxiant by reducing the amount of oxygen available for respiration [7].

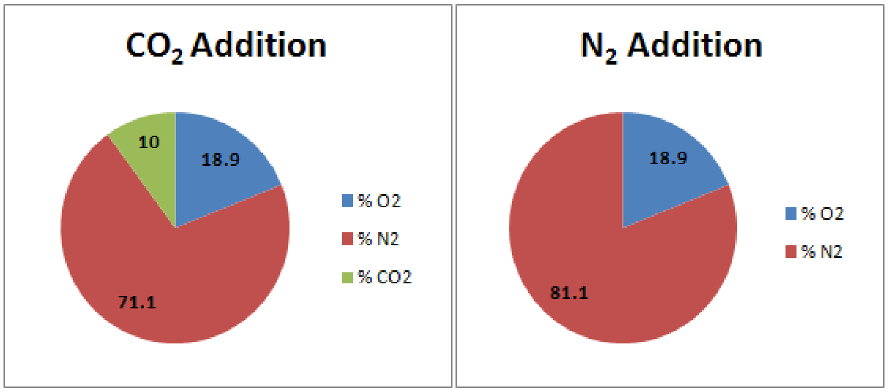
Unlike CO_2, nitrogen (N_2) does not get distributed throughout the body to cause an adverse health effect; rather, N_2 acts simply by displacing oxygen from the air and, thereby, decreasing the amount of oxygen available for respiration. Thus, CO_2 is dangerous at a much lower level than some other simple asphyxiants like N_2.

Table 2. Symptoms from Low to High Concentrations of CO_2

Exposure Level	Concentration	Symptom
Low	20,000 to 30,000 ppmv (2-3 vol%)	Shortness of breath, deep breathing [12]
Medium	50,000 ppmv 75,000 ppmv (5-7.5 vol%)	Breathing becomes heavy, sweating, headache, dizziness, breathlessness, increased heart rate, loss of mental abilities, drowsiness [12]
High	100,000 ppmv (10 vol%)	Respiratory difficulty, loss of consciousness [12]
Very High	300,000 ppmv (30 vol%)	Coma, convulsions, death [13]

N_2 is discussed above because it is a common potential simple asphyxiant in industrial settings. The following example illustrates the differences between CO_2 and N_2. Consider a hypothetical example where 90 parts of atmospheric air (normally 21% O_2 and 79% N_2) are mixed with 10 parts of either pure CO_2 or N_2. The resulting mixture compositions are shown in Figure 1.

Figure 1. Mixture Compositions with 90 Parts Air and 10 Parts CO_2 or N_2



The resulting mixture of air with 10% CO_2 can cause unconsciousness, and eventually death if the exposure is long enough due to the high CO_2 concentration (Table 1). On the other hand, the mixture of air with 10% added N_2, although it reduces the concentration of oxygen to 18.9%, which is below the level at which OSHA considers air to be oxygen deficient (19.5%) [14], is not likely to cause irreversible health effects.

The effect of oxygen availability in the air on humans is primarily a function of the partial pressure of the oxygen, not just concentration. The partial pressure of oxygen in an 18.9% mixture of oxygen in N_2 at sea level is:

0.189 * 14.7 psia = 2.78 psi

This oxygen partial pressure is nearly the same as that present in undiluted air at an elevation of roughly 2,900 ft – the approximate elevation of the Midland, Texas area:

0.21 * 13.22 psia = 2.78 psi

Healthy people who are acclimated to sea level are not significantly affected by traveling to a 2,900 ft elevation region, which illustrates that the effect of the addition of 10 parts of N_2 to air is not consequential, whereas the addition of 10 parts of CO_2 to air can result in severe health effects or even death.

Incidences of H_2S causing death of workers are well-known in the gas industry and has led to a high level of awareness of and training for the hazards of H_2S. Exposure to high concentrations of CO_2 gas has also had tragic results. Deaths of miners due to "choke damp" (CO_2) are well documented. Natural CO_2 eruptions from beneath have also occurred, with one event in 1986 at Lake Nyos in Cameroon costing over 1700 lives [15]. Just recently in October 2021, four men in Italy were killed by CO_2 exposure in a cellar in which grapes were fermenting for wine making [16]. One man collapsed, and in a similar fashion to some H_2S-related fatalities in industry, three other men attempted to rescue the first man and in turn also succumbed. Also very recently (November 2021), one worker was killed and three injured at a nuclear power plant in Spain due to CO_2 poisoning resulting from a leak in a fire suppression system [17].

The large number of incidences of CO_2 poisoning seem to imply that the hazards of CO_2 are not taken as seriously as some other more toxic gases such as H_2S. However, for situations where a bulk-CO_2 gas is present it can clearly represent a significant potential hazard to workers and should be treated accordingly.

Exposure Limits for Hydrogen Sulfide and Carbon Dioxide

Table 3 provides a summary of occupational exposure limits for H_2S and CO_2. 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 H_2S [18] **and CO_2** [19]

Compound	TLV and PEL	STEL	IDLH
H_2S	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 H_2S and CO_2 are purposefully established below levels at which adverse and irreversible health effects would be seen following 30 minutes of exposure. The IDLH for H_2S 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.

For CO_2, 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 CO_2, signs of intoxication become more pronounced. A person may sustain exposure to 70,000 to 100,000 ppmv CO_2 for about 5 minutes [19] and signs of intoxication become intense with very labored breathing, visual impairment, headache, ringing in the ears, and potentially impaired judgment.

Table 4 shows an example of how a gas stream containing initial concentrations of H_2S of 2000 ppmv and of CO_2 of 98% by volume would change assuming a uniform dispersion in air of the gas mixture. As shown in the table, when the IDLH of H_2S (100 ppmv) is reached, the CO_2 content is still above the IDLH level of 40,000 ppmv. Even more dramatic are the 5-minute exposure levels; when the H_2S exposure level is at the 5-minute limit of 800 ppmv [18], the CO_2 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 CO_2 in this gas stream, the danger as a result of the CO_2 is higher than the danger posed by the H_2S.

This analysis can also be extended to examine the exposure limits for other gases that might be expected to be present in CO_2 as well, for example CO and SO_2. For CO, the reported IDLH is 1200 ppmv, so a similar analysis starting with a CO_2 source that contained approximate 2.4 percent CO by volume would, after being mixed uniformly with enough air to dilute the CO_2 to 40,000 ppmv, be at or above the IDLH for CO_2 while still being below the IDLH for CO. SO_2 has a reported IDLH of 100 ppmv, the same as H_2S. The same analysis for CO_2 streams containing 2000 ppmv of SO_2 would show the same results for SO_2 as for H_2S with regard to the IDLH in Table 4.

Table 4. Exposure Limits Example: Dispersion of a 98 vol% CO_2, 2,000 ppmv H_2S Gas Mixture.

Dispersion in Air	CO_2 ppmv	H_2S ppmv	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_2S 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_2S 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

A release of a process gas can occur at any point in a process system or transfer pipeline. Although many processes may contain a high CO_2 content gas stream, common operations include compression, amine units, and dehydration. Pipelines are commonly used to transport CO_2 to sequestration or to EOR injection wells. 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. CO_2 Dehydration Unit and CO_2 Pipeline.

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 H_2S (which has an odor at very low concentrations) may actually provide an early indicator of a CO_2 release that would otherwise go undetected, sort of like an odorant in a domestic natural gas supply. (Note: Although H_2S may provide an early indicator of a release in certain situations, it should not be relied upon, because H_2S 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 H_2S and CO_2 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 CO_2 pipelines and harmful levels of CO_2 can accumulate in these areas, regardless of the presence of H_2S. The presence of H_2S 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 H_2S may provide a warning that a release has occurred and prevent a person from entering the area where potentially dangerous levels of CO_2 or H_2S may be present. The use of direct reading gas detection instrumentation and other protective measures should be required before entering confined spaces such as manholes, tanks, pits, vessels, and other areas that could contain a buildup of these gases.

Potential Synergistic Effects of Concurrent Exposure

Since the mechanisms of action for CO_2 and H_2S 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.

Large-scale swine production is another industry where CO_2 and H_2S may both be generated in enclosed spaces. Anaerobic digestion of manure results in the generation of H_2S, CO_2, and other gases, and human and animal fatalities have occurred in confined spaces where manure is present [20]. Ventilation and monitoring of H_2S and CO_2 concentrations in the air in confined spaces is usually practiced. However, as discussed in the literature synergist effects have not been noted [21], so for situations like this where H_2S and CO_2 are both present in the air and are measured, the occupational exposure limits for each component are not changed from that of the pure component.

Conclusions

Based on the general qualitative analysis of exposure to both H_2S and CO_2 discussed above, it appears that there is no increased risk from the presence of H_2S at low levels (e.g., up to perhaps 2000 ppmv or higher) in bulk CO_2 gas. In fact, in these types of gas streams, the potential exposure to high concentrations of CO_2 in the event of a release is very likely more dangerous than the lower concentration of the more toxic H_2S. (Similar conclusions can be drawn for other gases, such as CO and SO_2, discussed above.) At high concentrations, CO_2 may accumulate in the body which is different than some other asphyxiants (i.e., nitrogen), so it is important to recognize the difference between CO_2 and other common asphyxiants. In some cases, the H_2S in the gas may serve as a warning for the more hazardous CO_2 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.

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