

Carbon Dioxide Major Accident Hazards Awareness

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Commercial carbon capture and sequestration projects will handle very large quantities of carbon dioxide, which will present new challenges and hazards.

Carbon dioxide (CO₂) capture, transportation, injection, and geological storage (CCS) requires the linking and integration of separate process activities to capture CO₂ at an emitter facility, transport it to a designated storage site, and then inject it deep underground for permanent geological storage. The amount of CO₂ handled within a commercial CCS operation may be in the order of thousands of tons per hour, with transportation systems likely to have inventories that are ten times more. CCS operations may range in complexity from relatively simple point-to-point chains with a single capture facility, storage site, and interconnecting pipeline, to multiple capture plants feeding CO₂ into a network of pipelines from which the CO₂ is supplied to multiple storage sites.

Many aspects of CCS have been successfully deployed in various industries; therefore, a wealth of experience is available. The challenge facing the emerging CCS industry is to take existing and new technologies, experience, and practices, ensure their suitability for use in CCS, and then integrate the various links in the CCS chain together to create an efficient, optimized, and safe operation.

A longer version of this article is scheduled to appear in *Process Safety Progress*.

CO₂ has unique properties that must be understood and managed when handling such large quantities in different systems and locations. This article explores the potential hazards posed by large-scale CO₂ releases (including the inhalation effects), and addresses the phase behavior of CO₂ and the potential impact of impurities. Guidance is presented to raise awareness of important CO₂ properties that may lead to or contribute to major accident events.

CO₂ characteristics

CO₂ is a colorless and odorless gas that is about 1.5 times heavier than air (at standard temperature and pressure conditions). Depending on the pressure and temperature of the system, CO₂ can exist as a gas, liquid, solid, or supercritical fluid. Under normal atmospheric pressures, CO₂ can only exist as a gas or solid; it cannot exist as a liquid under atmospheric conditions.

CO₂ is fully oxidized and thus not very reactive nor flammable. Nevertheless, it poses a toxic and asphyxiation hazard. In humans, CO₂ is a normal component of blood gases at low concentrations; however, if inhaled at certain concentrations, it can be lethal. Humans are sensitive to changes in CO₂ concentrations.

In addition to the asphyxiation hazard of CO₂ displacing oxygen in the air, the inhalation of elevated concentrations of CO₂ can increase the acidity of the blood, triggering adverse effects on the respiratory, cardiovascular, and central nervous systems. A CO₂ concentration of around 5% by volume in air may cause headaches, dizziness, increased blood pressure, and difficulty breathing within a few minutes. If concentrations above 17% by volume in air are inhaled, this could cause loss of purposeful activity, unconsciousness, convulsions, coma, and death within one minute. CO₂ does not meet the definition of acutely toxic according to the Global Harmonized System (GHS) (1). However, it may be considered mildly toxic given the aforementioned hazards.

Professionals such as divers, submariners, astronauts, and anesthesiologists know very well the dangers of breathing high concentrations of CO₂ since they need to maintain inhaled gas mixtures within acceptable limits to sustain life.

Human exposure limits are defined by regulators and are typically a function of concentration and exposure time. The U.S. Occupational Safety and Health Administration (OSHA) set an 8-hr exposure limit of CO₂ to 5,000 ppm (0.5% by volume), *i.e.*, permissible exposure limit (PEL) (2). The National Institute for Occupational Safety and Health (NIOSH) established an immediately dangerous to life or health (IDLH) CO₂ concentration of 40,000 ppm (4% by volume) (3). It should be noted that the typical CO₂ concentration outdoors is 300–400 ppm (0.03% to 0.04%), but this can be as high as 600–900 ppm in metropolitan areas (4).

With the development of CCS systems, where pipelines transport large inventories of liquid-phase or supercritical CO₂ (in the order of tens to hundreds of thousands of tons), effective risk management of industrial systems handling large quantities of CO₂ and a public understanding of the impact of CO₂ on the human body is needed.

Past incidents

In the past, CO₂ releases from different types of installations, including pipelines, have caused injuries and fatalities. The following discussions review some CO₂ incidents that highlight the hazards when a large quantity of CO₂ is released.

Sartaria, MS (2020). A 24-in. buried pipeline transporting liquefied CO₂ ruptured near Sartaria, MS. A girth weld failure generated a CO₂ plume that traveled toward surrounding populations. Emergency evacuation protocols were activated and approximately 200 residents were evacuated. There were no fatalities, but 45 people sought medical attention. The pipeline failed on a steep embankment. Heavy rains caused soil subsidence, creating axial strain on the pipeline that resulted in a full-bore rupture girth weld failure. The U.S. Pipeline and Hazardous Materials Safety Administration (PHMSA) investigation reported several contributing factors to the

incident, including not addressing the risks of geohazards in plans and procedures, underestimating the potentially affected areas in the dispersion model, and not notifying local responders about a potential failure of the system (5).

Mönchengladbach, Germany (2008). Approximately 15 tons of CO₂ were accidentally released from a fire extinguishing facility in Mönchengladbach, Germany. The released CO₂ was not contained by the building due to the failure of a door to close, and CO₂ spread outside where the air conditions were very stable with little wind. Although no fatalities were associated with this incident, 107 people were affected (19 of whom were hospitalized). Because CO₂ is invisible, it was difficult for first responders to assess the extent of the hazard.

U.S. Environmental Protection Agency (EPA) database on fire protection systems. CO₂ is one of the most used inert gas extinguishing agents. The EPA performed a comprehensive review of CO₂ incidents related to its use in fire protection (6). From 1975 to 2000, a total of 51 incidents reported 72 deaths and 145 injuries from CO₂ releases from fire extinguishing systems. This study reported that most of the incidents occurred during maintenance on or near the CO₂ fire protection system. It is worth highlighting that the mass of CO₂ to be released by a fire suppression system will depend on the area being covered, but would likely be in the order of tons.

Worms, Germany (1988). In 1988, a 30-m.t. capacity CO₂ tank in Worms, Germany had a catastrophic vessel failure resulting from a cold CO₂ boiling liquid expanding vapor explosion (BLEVE). The tank shattered, and tank fragments were propelled 300 m, resulting in three fatalities and extensive damage (7).

These release incidents show the potential consequences when CO₂ forms a hazardous cloud and is inhaled by people and animals. It should be noted that the consequences typically associated with any type of release are very dependent on the source of the release (including the operating conditions of the system), the inventory released, the arrangement of the surroundings (*e.g.*, surrounding populations), the ground topography, the weather conditions, potential containment by buildings or enclosed spaces, and other factors.

CO₂ storage and transportation conditions

Figure 1 shows that pure CO₂ can exist as vapor, liquid, solid, or supercritical fluid depending on the pressure and temperature (8, 9). At the triple point, the solid, vapor, and liquid phases coexist at equilibrium. Above the critical point, the system will be in supercritical condition. Supercritical CO₂, also referred to as dense-phase CO₂, has a viscosity similar to gas but a density closer to a liquid.

The horizontal line in Figure 1 represents atmospheric conditions at 1 bar (14.5 psi). It is observed that at atmo-

spheric pressure, pure CO₂ can only exist as a vapor or as a solid. And depending on the temperature, it will change phases directly between solid and vapor. At atmospheric pressure, the phase diagram shows that CO₂ cannot exist as a liquid.

For CCS applications, CO₂ is typically transported in pipelines or ships. To avoid two-phase flow within pipelines, CO₂ is transported as a vapor, liquid, or supercritical fluid. In the case of ship transportation, CO₂ is transported in storage tanks at a pressure and temperature on the saturation line; at this condition, the CO₂ inventory is characterized by a liquid with a vapor space on top, both phases in thermodynamic equilibrium. Typical CO₂ transportation conditions are illustrated in Figure 1. One of the main takeaways from the pure CO₂ phase diagram is that the triple point and/or the critical point may be within or near the operating region of typical industrial processes and CO₂ transportation systems.

Depressurization behavior: The phase diagram in Figure 2 shows what occurs when a pipeline or a storage

system containing liquefied CO₂ ruptures (8, 9). Assuming an inventory of liquid CO₂ at 100 bar and 10°C (*i.e.*, Point A), a breach to atmospheric conditions would cause the system to undergo a series of phase transitions represented by the red path from Point A (liquid phase at typical operating conditions) to Point B (vapor phase at ambient pressure).

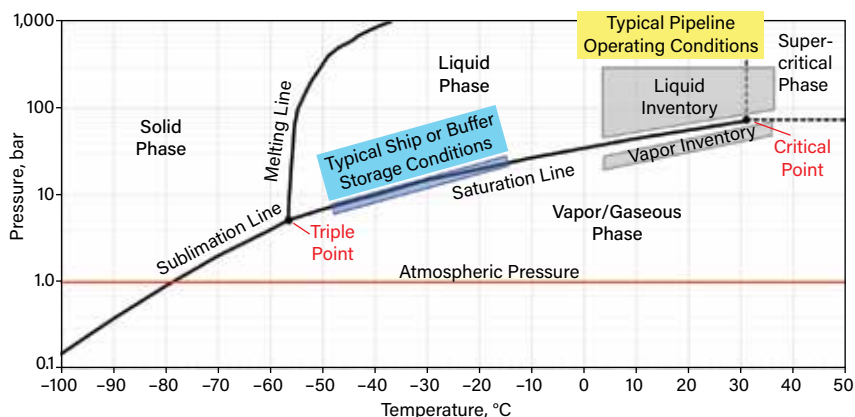
First, the pressure and temperature will decrease until reaching the saturation line. At this point, the phase transition starts and two phases (liquid and vapor) will coexist at equilibrium. The depressurization continues through the saturation line with the vaporization of the liquid.

Below the triple point, the liquid has transitioned into a mixture of vapor and solids, represented by the sublimation line. After reaching atmospheric pressure at 1 bar (14.5 psi), these solids will slowly sublime using the heat of the surroundings until reaching the final condition, corresponding to 100% vapor at ambient pressure and temperature. One of the most important takeaways from Figure 2 is the formation of solid CO₂ (*i.e.*, dry ice) during the depressurization process.

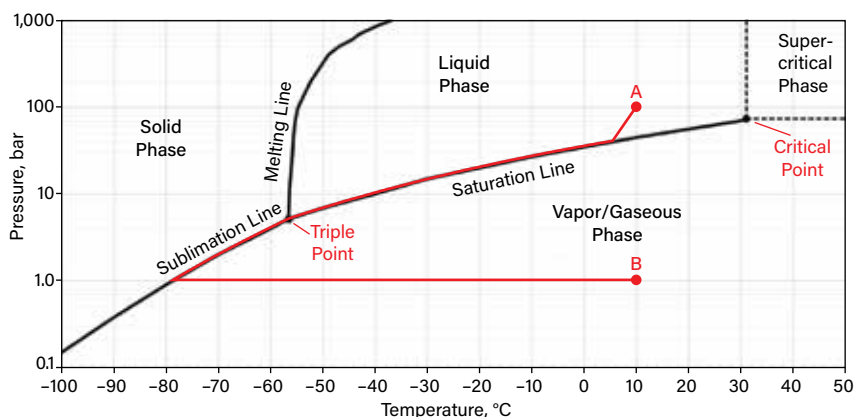
In general, two types of CO₂ releases are associated with typical transport or storage systems: cold CO₂ releases and hot supercritical releases.

A cold release corresponds to the depressurization example in Figure 2, where the initial operating conditions correspond to CO₂ transported or stored as a liquid. Once system rupture occurs, the release behavior is characterized by a white cloud containing a mixture of vapor and solid CO₂. It is important to recall that vapor CO₂ is not visible; therefore, the CO₂ cloud becomes visible due to the condensed water vapor formed by the humidity of the air combined with the cold temperatures upon release (below the dew point of the air). In this type of release, it is very common to observe deposits of solid CO₂ on the ground surrounding the release point; this dry ice slowly transforms into vapor CO₂.

The second main release type, commonly known as hot supercritical release, is typically associated with operating conditions in the supercritical region of the phase diagram, *e.g.*, 150 bar (2,176 psi) and 150°C (302°F). In these releases, the formation of a visible cloud containing condensed water vapor does not occur since the temperature close to the release point is above the dew point



▲ **Figure 1.** This CO₂ phase diagram highlights typical transportation conditions. The red horizontal line represents atmospheric conditions at 1 bar (14.5 psi). Source: Adapted from (8, 9).



▲ **Figure 2.** In this example, Point A represents an inventory of pure CO₂ at 100 bar and 10°C (*i.e.*, liquid-phase CO₂ at typical operating conditions). If a rupture occurs, the CO₂ will undergo a series of phase transitions to depressurize along the red path, eventually reaching Point B (vapor-phase CO₂ at ambient conditions). Source: Adapted from (8, 9).

of the air. The formation of solid CO₂ does not take place during the release event since there is a direct transition from the supercritical to the vapor phase.

It is important to highlight that the CO₂ release behavior varies significantly depending on the initial operating conditions in the system that ruptures. Therefore, it is recommended to use a temperature-entropy diagram to predict the potential release behavior and phase transition (if any) for the specific initial conditions of any industrial system storing or transporting CO₂.

CCS facilities

A CCS chain may consist of some, or possibly all, of the following elements:

- CO₂ capture facilities
- onshore pipeline
- underwater pipeline
- CO₂ carrier ship and (un)loading facilities
- intermediate storage facilities
- injection facilities
- injection and other wells
- storage sites.

Comprehensive and detailed descriptions of the CCS chain are available in the Intergovernmental Panel on Climate Change (IPCC) special report on Carbon Dioxide Capture and Storage (10). The following subsections briefly discuss a few of the special issues and hazards to consider for various CCS facilities.

Capture facilities. The composition of the CO₂ stream is dependent on the source and capture process. The source stream is unlikely to be 100% CO₂ and will contain other components and impurities, such as carbon monoxide (CO), oxygen, water, argon, nitrogen, hydrogen, methane (CH₄), hydrogen sulfide (H₂S), sulfur dioxide (SO₂), and heavy metals. These additional components have their own hazards and design considerations that should be accounted for. If multiple capture facilities are feeding into a common network, then a variety of compositions could potentially exist.

Impurities have several impacts on CO₂ systems. The presence of impurities within the CO₂ stream can change the phase envelope by introducing a two-phase liquid/vapor region and/or significantly raising or lowering the saturation pressure of the mixture. Impurities increase the mixture's critical pressure and generally reduce the critical temperature; however, SO₂ and H₂S impurities cause an increase in critical temperature (11). Impurities vary significantly between CO₂ sources, changing the properties and behavior of the CO₂ stream and potentially impacting the system's mechanical integrity.

Free water in the CO₂ system can cause internal corrosion. The water can combine with CO₂ to form carbonic acid, which is corrosive to carbon steels. Water content in

the CO₂ stream should be controlled to minimize the potential corrosion rate, and a robust inspection program should be implemented.

Pipeline transport. Following capture, the CO₂ will need to be transported to handling or injection facilities. The CO₂ will be transported via pipeline in vapor phase or as a high-density fluid. Corrosion concerns from the stream impurities are relevant for the pipeline integrity given the potential for cross-chemical reactions.

Supercritical CO₂ is an excellent solvent that can break down lubricants. Any impurities within the stream solution will precipitate out at the point of pressure drop with a decline in solubility. For example, any heavy metals will precipitate out at a point of loss of containment and may pose a health or environmental hazard. CO₂ is also highly invasive and can dissolve into some elastomers (e.g., seals), causing damage. Careful consideration when selecting lubricants and materials is necessary to ensure suitability for service.

Propagating pipeline fractures can release a large volume from the pipeline within a short period. The two fracture failure mechanisms — brittle and ductile — should be accounted for in the design. A brittle fracture occurs without (or with very little) plastic deformation of the material prior to failure; examples of pipes that may experience brittle fracture are those that operate at low temperatures or have poor microstructures. A ductile fracture is associated with large plastic deformation of the material prior to failure. Most pipe failures occur in a ductile manner.

Pipeline designs avoid propagating brittle cracks, but the potential low-temperature effects of a CO₂ release should be accounted for in the design. Running ductile fractures must also be evaluated as part of the design, with fracture-arrest requirements (e.g., pipeline toughness, thickness) added as needed (12).

Injection. Injection facilities may need pressure-boosting or reduction systems depending on the nature of the transported CO₂ and the characteristics of the storage/injection site. The design of wells for CO₂ injection will be similar to those used for gas injection into current hydrocarbon fields. The design will still need to account for pressure, temperature conditions, and material selection to limit corrosion.

In the event of a well blowout, the release may contain downhole formation fluids and other components. The potential components in a formation release should be considered during design and hazard analysis.

General considerations. Whether by design or by accident, depressurization of CO₂ can result in temperatures at or below -78°C (-108°F) within systems and/or within any release plume. In addition, significant quantities of solid CO₂ can be formed within systems and/or within the release area, which could add to the low-temperature issue and cause system blockages. Releases within enclosed areas may expe-

rience a rapid temperature drop and significant solid particle formation. The impacts of low-temperature exposure should be accounted for in the system design and operation.

CO₂ density is sensitive to temperature changes, especially close to critical point conditions (*i.e.*, 31°C and 74 bar). This can lead directly to system over-pressurization with a relatively small change in CO₂ temperature. Appropriate design of pressure relief systems should avoid this over-pressurization event.

Hazard management

Commercial CCS projects will handle very large quantities of CO₂. Handling such large inventories of CO₂ is new to many involved with CCS implementation. It is worth highlighting that regulatory frameworks are in place for CO₂ pipeline systems. The hazard potential of CO₂ must be managed along with the other potential hazards. Existing hazard management processes are suitable to manage these hazards if appropriately implemented. Generic approaches are described in International Organization for Standardization (ISO) 31000 (13) and “Guidelines for Risk Based Process Safety” (14). The risk management framework should implement the “Plan-Do-Check-Act” cycle.

Over the past decade, DNV has collaborated on joint industry projects and large-scale testing to understand the potential hazards of CO₂. The company developed the CO2RISKMAN project and guidance as a robust knowledge source for CCS projects to understand CO₂ hazards within the facility hazard management (8). This guidance is not prescriptive but is meant to provide the base informa-

tion for operators to develop suitable hazard management strategies. When designing and operating CCS systems, keep the following guidelines in mind:

- Recognize the CO₂ hazard potential through the application of robust hazard identification techniques and risk management systems.
- CO₂ is a colorless and odorless gas at atmospheric conditions. A CCS CO₂ release will be highly concentrated until dispersed. Before diluted to a concentration below 5% by volume in air, the plume will pose a hazard to people. CO₂ is heavier than air and will accumulate in low areas. Managing the risks associated with hazardous mixture inhalation is well understood in industrial and public settings. This experience can be used to help ensure the safety of CO₂ systems.
- Recognize that CO₂ concentration associated with a release cannot be assessed by only looking at the size of the visible cloud. CO₂ vapor is invisible — the visible cloud that is commonly seen is the condensing water vapor generated by the low temperatures upon release and is not representative of the CO₂ concentration.
- Stream composition with all potential impurities needs to be documented and considered in the design. The CO₂ stream specification should be defined with requirements for purification and drying to limit the potential impurities that promote internal corrosion. System monitoring should be in place to ensure that excursions outside the specification cannot occur.
- Use models for the prediction of release discharge conditions based on the potential stream composition and phase envelopes.

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SAFETY

- Selection of materials is extremely important for seals, flexible hoses, instruments, wire and cable insulators, controls, and other safety-critical components.
- Pipeline designs should account for CO₂-specific issues related to propagating fractures for both brittle and ductile failure mechanisms.
- Understand the thermodynamics of the CO₂ stream, including the effects of impurities, for the design and operation of the CO₂ handling systems. Remember that depressurization can result in low temperatures (*i.e.*, -78°C or -108°F) and solid CO₂ formation.
- Thermal expansion can lead to system over-pressurization; appropriate system pressure relief should be included in the design.
- Liquid-phase CO₂, and especially supercritical CO₂, are highly efficient solvents. During a release, any impurities within the CO₂ stream will be released — either in vapor with the CO₂ plume or deposited in the vicinity of the release point. Addressing the potential hazards associated with the release of CO₂ impurities is important.

As CCS projects are delivered and operational experience grows, the challenges associated with CO₂ will become more familiar to engineers. The industry will mature with recognized codes, standards, and best practices.

In closing

Handling large inventories of CO₂ may be new to many involved with CCS implementation. For effective risk management, members of CCS projects must be aware of the properties and hazards associated with CO₂. The CO2RISK-MAN guidance includes the following key message (8, 9): “There is no reason why the major accident risks from a CO₂ handling system within a carbon dioxide capture, transportation, and geological storage (CCS) operation cannot be low and well within acceptable limits. To achieve this will require the application of existing rigorous hazard management processes combined with an adequate understanding of the properties and behaviors of CO₂.”

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