DET NORSKE VERITAS

Mapping of potential HSE issues related to large-scale capture, transport and storage of CO$_2$

Petroleumstilsynet

DNV Report no: 2008-1993

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Summary:

Det Norske Veritas (DNV) was commissioned by the Petroleum Safety Authority Norway (PSA), to identify and detail the key health, safety and environmental (HSE) issues and concerns related to industry-scale capture, transport and injection (excluding storage) of CO$_2$. The potential hazards of CO$_2$ handling for CCS purpose have been identified by reviewing publicly available knowledge and industrial experience. Based on this review and workshop discussions with relevant stakeholders from industry and regulators, the identified HSE concerns have been assessed with respect to the gap in current knowledge and experience.

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CONCLUSIVE SUMMARY

Det Norske Veritas (DNV) was commissioned by the Petroleum Safety Authority Norway (PSA), to identify and detail the key health, safety and environmental (HSE) issues and concerns related to industry-scale capture, transport and injection (excluding storage) of CO_2 based on available experience and knowledge. The driver for this project has been to ensure that HSE regulation in Norway of the emerging carbon capture and storage (CCS) industry will be conducted on a robust understanding of the potential hazards, issues and concerns.

Throughout the world there are high hopes that CCS can contribute significantly to mitigate global warming by controlling the CO_2 emissions from hydrocarbon fuelled power stations and other significant CO_2 producers. However, to do so CCS has to be deployed on a global scale. CCS projects will require dense phase CO_2 (i.e. liquid or supercritical CO_2) to be handled and this introduces a number of 'new' hazard management issues that require to be addressed.

The potential hazards of CO_2 handling for CCS purpose have been identified by reviewing publicly available knowledge and industrial experience. Based on this review a workshop was held with relevant stakeholders from industry and regulators, where the relevance and management of issues identified were discussed and assessed.

Most of the HSE issues identified were related to phase characteristics when dense phase CO_2 is depressurized, either through a planned operation or by an accidental release. The categories of hazards that have been identified can be divided broadly into three groups:

- CO_2 pipeline issues (external and internal corrosion, hydrate formation, overstress due to free span, pipeline fracture propagation);

- Material issues (CO_2 solvent properties and material compatibility, elastomers);

- Operation and engineering challenges (solids formation, system depressurization (both controlled and accidental), low temperatures, vessel ruptures/failures, rapid phase transition, cold CO_2 BLEVEs).

Provided that CO_2, when handled in the volumes required for CCS, is recognised as a potential Major Accident Hazard (MAH), then existing MAH risk management strategies should enable MAH risk to be managed down to an acceptable level. In addition, provided the boundaries of applicability are known and respected codes, standards, good practices, experience and knowledge from other existing industries can be applied in the relatively immature CCS industry. The challenge faced by the CCS industry and Regulators is knowing where these boundaries lie.

It is not anticipated that any of the identified hazards and HSE areas of concern will represent a show-stopper to the deployment of CCS, as long as the risks are assessed and managed properly.

Still, there are gaps in knowledge and experience for certain issues that should be further investigated in order to be closed and enable a better understanding for safe design and operation across the CCS value chain. In particular, the lack of validated consequence models for dense phase CO_2 could result in delays in CCS projects due to permitting difficulties, or considerable

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costs for the CCS developer due to an overly-conservative approach being taken, and is therefore recommended for further development work. Furthermore, there is a lack of knowledge on the impact of impurities in the CO_2 stream, both with respect to corrosion and the impact on phase change parameters that should be further investigated.

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LIST OF ABBREVIATIONS

BLEVE	Boiling Liquid Expanding Vapour Explosion
CAP	Chilled Ammonia Process
CCS	Carbon Capture and Storage
CFD	Computational fluid dynamics
CHIP	UK Health and Safety Commission's Chemicals (Hazard Information and Packaging for Supply) Regulations 2002
COSHH	Control of Substances Hazardous to Health
DEG	Diethylene Glycol
DOT	Department of Transportation
DTL	Dangerous Toxic Loads
EOR	Enhanced Oil Recovery
EPA	US Environmental Protection Agency
GHS	Globally Harmonised System
HC	Hydrocarbon
HEM	Homogenous equilibrium method
HSE	1) Health, Safety and Environment 2) UK Health and Safety Executive
IGCC	Integrated Gasification Combined Cycle
LTEL	Long Term Exposure Limit
MAH	Major Accident Hazards
MEA	Monoethanolamine
OEL	Occupational exposure limit
OPS	Office of Pipeline Safety
PHMSA	Pipelines and Hazardous Materials Safety Administration
Ppm	Parts per million
Ppmv	Part per million by volum
SLOD	Significant Likelihood Of Death
SLOT	Specified Level Of Toxicity

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STEL	Short Term Exposure Limit
STP	Standard temperature and pressure (0°C and 1.013 bara)
TEG	Triethylene glycol
TWA	Time Weighted Average
v/v	Ratio of volumes

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1   INTRODUCTION

The Petroleum Safety Authority of Norway (PSA) has commissioned DNV to undertake a study with the objective of identifying the potential health, safety and environmental risks associated with large-scale deployment of Carbon Capture, transport and Storage (CCS).

1.1   Background

CCS can contribute significantly to cut global CO_2 emissions and thereby mitigate increased CO_2 concentration in the atmosphere. For CCS to have such effect it is necessary to implement thousands of large scale CCS projects world-wide over the coming decades. This will require a joint and dedicated effort from industry, regulators, authorities, and inter-governmental policymakers.

The dominant HSE concern for large scale CCS has so far tended to be potential leak (seepage) from geological storage sites, both slow and rapid. However, gradually there is also a growing concern among regulators and other stakeholders that there could be other significant HSE issues which require their attention and development of procedures for adequate risk management. When humans and animals are exposed to elevated concentrations of CO_2 (i.e. >5% v/v in air) it has a potentially significant toxicological impact ranging, depending on concentration and exposure duration, from muscle tremors, headaches and hyperventilation, to unconsciousness, coma and death. The large quantities of CO_2 associated with CCS projects (e.g. 10s to 100s of thousands of tonnes pipeline inventory) creates the potential for hazardous accidental releases of CO_2, which if released in populated areas, could be a significant threat to people.

In addition to the toxicological harm issues it is known that there are other gaps in knowledge about the criticality of issues such as the adequacy of engineering practice for CO_2 management. Moreover, it is well known that lack of substantial operational experience in a novel process, technology or scale generally leads to significant difficulties in accurately identifying the hazards. There is relatively little experience worldwide in managing the risks associated with the large-scale CO_2 quantities likely to be handled at a CCS facility, compared with hydrocarbon handling. CCS projects will be major undertakings that will involve new technology, technology significantly scaled up from well proven practice (factor 10 to 100), as well as technology expected to function reliably over unprecedented time scales (100s to 1000s of years).

1.2   Scope of Work

The project aims to identify and detail the key health, safety and environmental issues and concerns related to industry-scale capture, transport and storage of CO_2 based on available experience and knowledge. Where gaps in knowledge are identified, the potential impact on CCS implementation will be examined and, where appropriate, recommendations will be proposed on how best to fill the critical gaps. The scope of work can be summarized as follows:

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- Identify health, safety and environment issues relevant to CCS deployment;

- Examine the criticality of issues and risks identified;

- Assess the adequacy of existing risk management measures, such as design codes and recommended practices;

- Identify areas requiring further work and recommend how to address these areas; and

- Produce a document that will be made publicly available that provides a firm basis for moving forward.

1.3 Project Boundaries and Limitations

This study focuses on large-scale handling of CO$_2$ from capture via transport to the point of injection into sub-surface geological formations. Thus, leak of CO$_2$ after injection is not considered. A schematic drawing is shown in Figure 1-1.
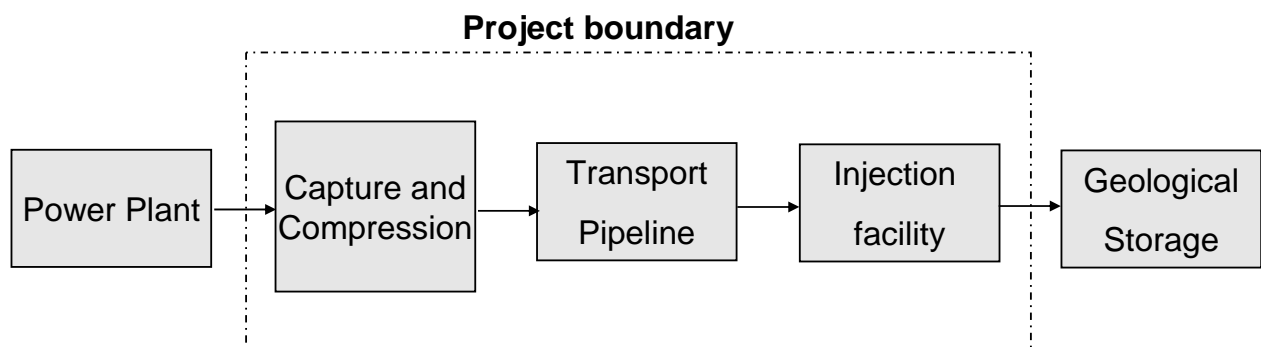
Figure 1-1: Schematic drawing of CCS value chain and boundary of the study

Plausible HSE issues related to CCS technologies could besides CO$_2$ itself also include new hazards introduced by large scale use of hydrogen in pre-combustion capture and use of oxygen in oxy-fuel capture. Moreover, a range of organic amines, methanol, propylene carbonate and methyl-2- pyrrolidone are commonly used in CO$_2$ capture processes. It is, however, beyond the scope of the current project to assess HSE issues related to large-scale deployment of these industrial chemicals associated with CCS.

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1.4   Report Rationale and Structure

The work has been organized in three phases, where the initial phase was a comprehensive review of available relevant knowledge, experience and industry practices to identify all significant HSE issues related to CCS deployment in design, operation and decommissioning. An initial draft report containing the preliminary findings (based on Chapters 2 to 9 of the current report) was issued to a selected number of stakeholders from industry, regulators and competent authorities and other competent scientific communities as input for a workshop session.

Furthermore, a hazard identification and assessment workshop was arranged to discuss the relevance of the identified HSE issues for CO$_2$ handling and rank them according to their criticality. The findings and discussions of the workshop are found in Chapter 10. Chapter 11 contains a discussion of how the identified issues of concern can be managed.
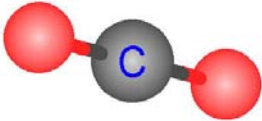
Finally, in Chapter 12, conclusions and recommendations on which actions and investigations that should be undertaken for closing the knowledge gaps that have been identified are delineated.

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2 CO₂ PROPERTIES AND BEHAVIOUR

2.1 Chemical and Physical Properties

Carbon dioxide is a colourless, odourless gas. At standard temperature and pressure (STP), the density of carbon dioxide is approximately 1.98 kg/m³, about 1.5 times that of air. The CO_2 molecule is composed of two oxygen atoms covalently bonded to a single carbon atom. It has no electrical dipole. As it is fully oxidized, it is not very reactive and, in particular, not flammable. Some key properties of CO_2 are listed in Table 2-1.

Table 2-1: Properties of carbon dioxide /1/

Molecular formula and shape	CO₂
	O=C=O
Molar mass	44.01 g/mol
Density	Gas: 1.98 kg/m³ (STP[1]) Liquid: 955 kg/m³ (0°C, 70 bar) Solid: 1562 kg/m³ (at freezing point) Critical density: 467 kg/m³ (at critical point)
Critical point (see Chapter 2.3.1)	31.03°C, 73.9 bara
Triple point (see Chapter 2.3.1)	-56.6°C, 5.18 bara
Aqueous Solubility of CO₂	1.45 g/L at 25°C, 100kPa
Acidity	$H_2CO_3 \leftrightarrow HCO_3^- + H^+$, pK$_a$=6.35 $HCO_3^- \leftrightarrow CO_3^{2-} + H^+$, pK$_a$=10.25

[1]STP refers to Standard Temperature and Pressure defined at 0°C and 1.013 bara

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2.2 Natural existence of CO_2

Carbon dioxide plays a vital role in the earth's environment. It is a constituent in the atmosphere and, as such, is a necessary ingredient in the life cycle of animals and plants. In animal metabolism, oxygen from the atmosphere reacts with sugars in the body to produce energy, with the by-product of this being CO_2. In the reverse reaction, in plant metabolism, carbon dioxide from the air is absorbed by the leaves of the plant. Using energy from light, carbon dioxide reacts with water in the presence of enzymes to produce sugar. This reaction is known as the photosynthesis.

In addition to being a component of the atmosphere, carbon dioxide also dissolves in the water of the oceans and lakes. At room temperature, the solubility of carbon dioxide is about 90 cm^3 of CO_2 per 100 ml of water. In aqueous solution, carbon dioxide, *CO_2 (aq),* exists in many forms. First, the gaseous *CO_2 (g)* dissolves.

$$CO_2(g) \leftrightarrow CO_2(aq) \tag{1}$$

Then, equilibrium is established between the dissolved CO_2 and H_2CO_3, carbonic acid /2/ .

$$CO_2(aq) + H_2O(l) \leftrightarrow H_2CO_3(aq) \tag{2}$$

Only about 1% of the dissolved CO_2 exists as H_2CO_3, as carbonic acid is a weak acid which dissociates in two steps.

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \tag{3}$$
$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \tag{4}$$

There are large amounts of carbon normally in the ocean—about 50 times the amount in the atmosphere. The balance between animal and plant life cycles as affected by the solubility of carbon dioxide in the earth's water results in the carbon dioxide content in the atmosphere of about 380 ppmv (i.e. 0.038% by volume) /3/.

When inhaled at concentrations much higher than usual atmospheric levels, it can produce a sour taste in the mouth and a stinging sensation in the nose and throat. These effects result from the gas dissolving in the mucous membranes and saliva, forming a weak solution of carbonic acid. Inhaling concentrations in air above 5,000 ppm (0.5%) is considered hazardous over an extended period (e.g. > 8hrs), and inhaling concentrations above about 100,000 ppm (10%) is immediately dangerous to humans. A thorough assessment of human response to CO_2 is found in Chapter 6.

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2.3 Thermodynamics of CO_2

2.3.1 State of Aggregation

CO_2 can exist as a gas, liquid, solid or a supercritical fluid, as shown in the phase diagram in Figure 2-1**.**
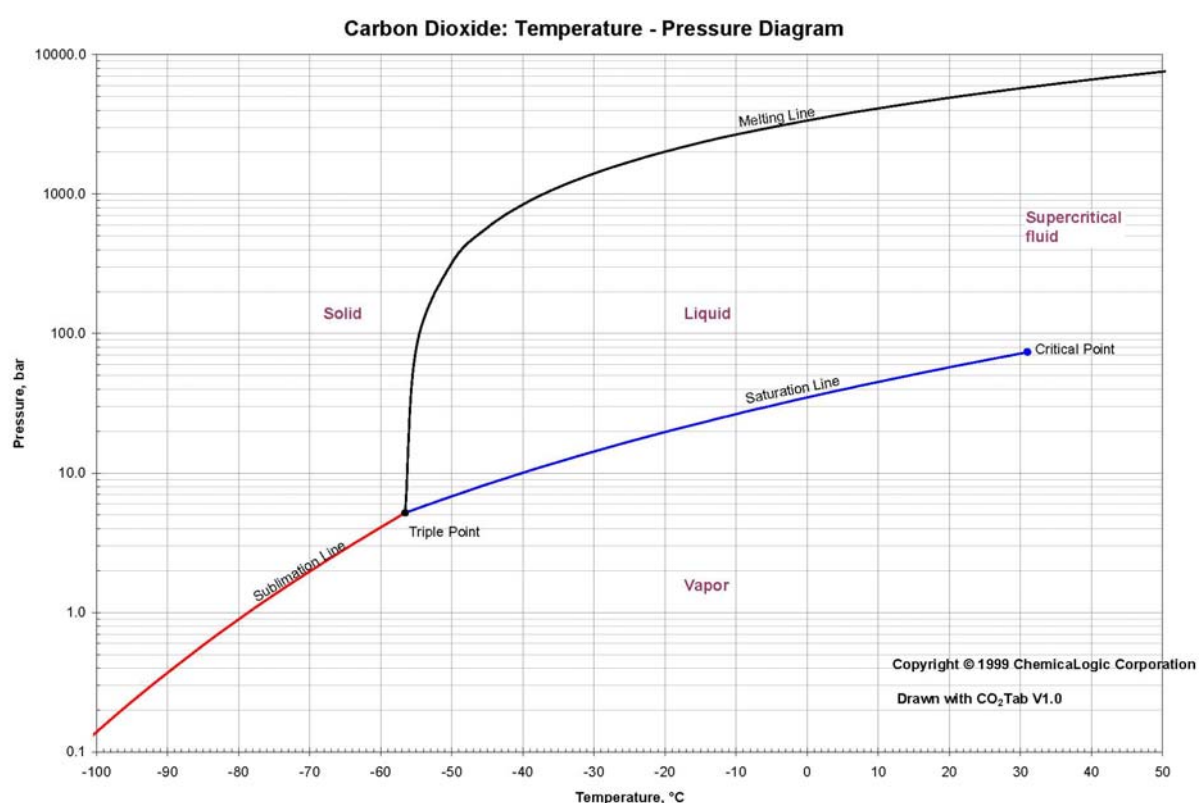
Figure 2-1: Phase diagram of CO_2 /4/

At normal atmospheric pressure and temperature, the stable carbon dioxide phase is gas. The triple point (pressure 5.18 bara., temperature -56.7°C) is defined as the temperature and pressure where three phases (gas, liquid and solid) can co-exist in thermodynamic equilibrium. Another interesting feature is the solid-vapour phase boundary (sublimation line). Physically, this boundary implies that the gas and solid can co-exist and transform back and forth without the presence of liquid as an intermediate phase. The phase change of solid CO_2 changing into vapour is called sublimation.

Above the critical point (pressure 73.9 bara, temperature 31.1°C) the liquid and gas phase cannot exist as separate phases. In this region, known as the supercritical phase, CO_2 possesses the

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viscosity similar to that of a gas and the density closer to that of a liquid. In addition, CO_2, particularly supercritical CO_2, has excellent solvent properties.

CO_2 captured from flue gas streams for the purpose of permanent storage in geological formations is likely to be transported in a supercritical or dense phase state. For economic and technical reasons it is likely CO_2 will be handled close to or above its critical pressure where many of its properties are similar to that of a liquid. The expression *dense phase CO₂* is often used as a collective term for describing supercritical or liquid phase CO_2.

The temperature and pressure effect on the density is illustrated in Figure 2-2, which show that the temperature dependency is much more pronounced at lower pressures. Moreover, the density is most sensitive to temperature changes near the critical point.
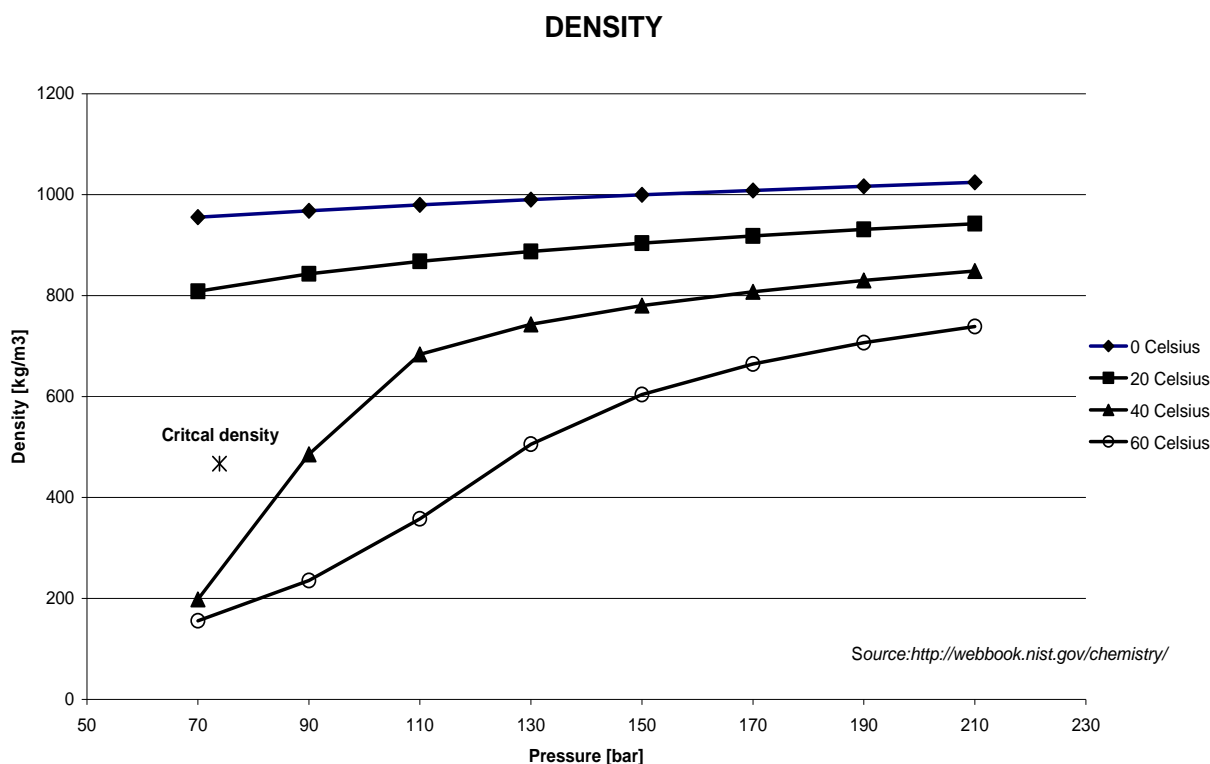
Figure 2-2: Density of pure CO_2 /1/

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2.3.2 CO₂ Phase Changes

A phase diagram, as shown in Figure 2-1, is common way to represent the various phases of a substance and the conditions under which each phase exists. However, it tells us little regarding how the change of state for CO_2 occur during transient action; instead, the CO_2 pressure-enthalpy (P-h), shown in Figure 2-3, or temperature-entropy (T-s) diagrams provide insight to the phase changes.
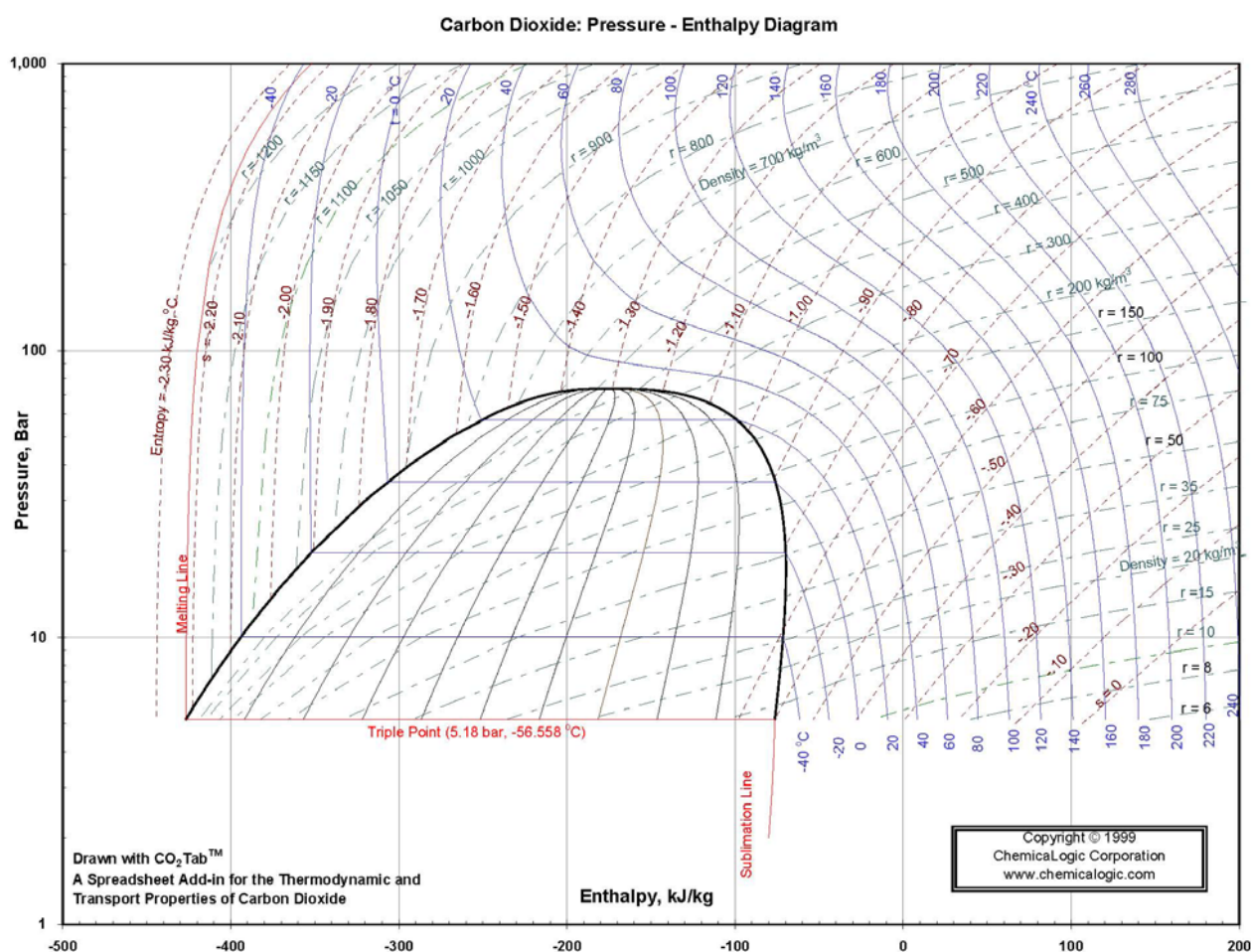
Figure 2-3: CO_2 Pressure-Enthalpy diagram

P-h and T-s diagrams can be used to examine phase changes, energy transfers, and density, pressure and temperature changes during depressurization, for example, for a leak of CO_2 from a vessel or a pipeline.

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In order to understand and interpret such a diagram some basic thermodynamic theory and terms must be established.

The adiabatic (no heat exchanged) expansion of a gas may be carried out in number of ways. The change in temperature experienced by the gas during expansion depends on the initial and final pressure, but also on the manner in which the expansion is carried out.

<u>Isenthalpic expansion</u>: expansion which takes place without any change in enthalpy. In a free expansion, the gas does no work and absorbs no heat, so the internal energy is conserved. Expanded in this manner, the temperature of an ideal gas would remain constant, but the temperature of a *real gas* may either increase or decrease, depending on the initial temperature and pressure. This is called the Joule-Thomson effect. Temperature change of either sign can occur during the Joule-Thomson process. Each real gas has a Joule–Thomson inversion temperature above which expansion at constant enthalpy causes the temperature to rise, and below which such expansion causes cooling. For CO_2 the inversion temperature, at atmospheric pressure, is 1500 K (ref. Perry's Chemical Engineering Handbook), which means that the gas cools by isenthalpic expansion for conditions relevant for CO_2 in CCS applications.

<u>Isentropic expansion.</u> If the expansion process is reversible, meaning that the gas is in thermodynamic equilibrium at all times, it is called an isentropic expansion. In this scenario, the gas does positive work during the expansion, and its temperature decreases. Here, the temperature drop will be greater than for the case of isenthalpic expansion.

The way depressurising a dense phase CO_2 system is performed, is important with respect to solids CO_2 formation and cooling effects, which is further elaborated in Chapter 8.2.4.

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3 MERCHANT CO₂; SOURCES, RECOVERY AND INDUSTRIAL USAGE

The carbon dioxide business is traditionally thought of as the recovery and distribution of liquid carbon dioxide, since this is the product most commonly bought and sold. Liquid carbon dioxide is usually recovered as a gaseous by-product of industrial operations such as hydrogen production by steam reforming of natural gas or the production of ethanol by fermentation. The gaseous carbon dioxide is liquefied for sale as a merchant product because liquid carbon dioxide can be transported more economically than gaseous CO₂. Liquid carbon dioxide reaches end users through a network of highway tankers, re-supply depots and railcars. As a result, the carbon dioxide business is highly regional. A key difference between the carbon dioxide sold in merchant market and that of CO₂ for CCS is the purity requirements. However, several properties of CO₂ as a chemical compound in terms of application area are relevant for CCS. The subsequent sections reviews the most common sources of CO₂, and some important recovery processes and, finally, reviews the applications of CO₂.

3.1 Sources

Sources of carbon dioxide for commercial carbon dioxide recovery plants are /5/:

- Synthetic ammonia and hydrogen plants in which methane (or other hydrocarbons) are converted to carbon dioxide and hydrogen ($CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$);
- Flue gases resulting from the combustion of carbonaceous fuels;
- Fermentation in which a sugar such as dextrose is converted to ethyl alcohol and carbon dioxide ($C_6H_{12}O_6 \leftrightarrow 2C_2H_5OH + 2CO_2$);
- Lime-kiln operation in which carbonates are thermally decomposed($CaCO_3 \leftrightarrow CaO + CO_2$);
- Sodium phosphate manufacture ($2Na_2CO_3 + 2H_3PO_4 \leftrightarrow 2Na_3PO_4 + 3CO_2 + 3H_2O$); and
- Natural gas wells containing high percentages of carbon dioxide.

The most relevant and significant sources for commercial CO₂ production /5/ /6/ are described in the next subsections.

Ammonia and hydrogen plants
More carbon dioxide is generated and recovered from ammonia and hydrogen plants as of today than from any other source. Both plants produce hydrogen and carbon dioxide from the reaction between hydrocarbons and steam. In the case of hydrogen plants, the hydrogen is recovered as a pure gas. For ammonia plants the hydrogen is produced in the presence of air, controlled to give the volume ratio between hydrogen and nitrogen required to synthesize ammonia. In order to produce either product it is necessary to remove the carbon dioxide. A substantial amount of the carbon dioxide recovered from ammonia plants is used for urea production.

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Fermentation
Large quantities of carbon dioxide are present in gases given off in the fermentation of organic substances such as molasses, corn, wheat, and potatoes in the production of beer, distilled beverages, and industrial alcohol.

Natural gas wells
Natural gas, containing high percentages of carbon dioxide, has been found in a number of locations including New Mexico, Colorado, Utah, and Washington. Several small plants have been in operation for a number of years producing commercial solid and liquid carbon dioxide from these sources. Several large CO$_2$ plants are in operation using natural gas wells as a source of CO$_2$.

Combustion of carbonaceous fuels
Flue gases have long been an important source of CO$_2$ for the merchant CO$_2$ market, especially in remote locations where by-product CO$_2$ sources are unavailable. Fuel is combusted to produce flue gas, and CO$_2$ is then extracted from the flue gas using a solvent, as sufficient heat is available from the combustion process to support the heat required for the CO$_2$ capture.

3.2   Recovery and Purification

There are a number of methods of recovering carbon dioxide from industrial, flue or natural gases, such as:
- Purisol process;
- Rectisol process;
- Sulfinol process;
- Potassium carbonate process;
- Sodium carbonate process; and
- Girbotol Amine Process

The potassium carbonate and ethanolamine processes are most common. In all these processes the CO$_2$ containing gases are passed countercurrent to a solution that removes the carbon dioxide by absorption, and retains it until it is desorbed in separate stripper unit. All of these processes are in commercial use and the most suitable choice for a given application depends on individual conditions (pressure, temperature and composition). Water could be used as the absorbing medium, but this is uncommon because of the relatively low solubility of carbon dioxide in water at normally encountered pressures. The higher solubility in the alkali carbonate and ethanolamine solutions is the result of a chemical combination of the carbon dioxide with the absorbing medium.

Although carbon dioxide produced and recovered by the methods outlined above has a high purity, it may contain traces of hydrogen sulfide and sulfur dioxide, which cause a slight odor or taste. The fermentation gas recovery processes include a purification stage, but carbon dioxide recovered by other methods must be further purified before it is acceptable for beverage, dry ice, or other uses. The most commonly used purification methods are treatments with potassium permanganate, potassium dichromate or active carbon.

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Liquefaction and solidification

Carbon dioxide may be liquefied at any temperature between its triple point (-56.4°C) and its critical point (32°C), as shown in Figure 2-1, by compressing it to the corresponding liquefaction pressure, and removing the heat of condensation. Two liquefaction process routes are commonly used /5/:

- In the first, the carbon dioxide is liquefied near the critical temperature; water is used for cooling. This process requires compression of the carbon dioxide gas to pressures of about 76 bar. The gas from the final compression stage is cooled to about 32°C and then filtered to remove water and entrained lubricating oil. The filtered CO_2 gas is then liquefied in a water-cooled condenser.

- The second liquefaction process is carried out at temperatures from -12°C to 23°C, with liquefaction pressures of about 16–24 bar. The compressed gas is pre-cooled to 4°C to 27°C, water and entrained oil are separated, and the gas is then dehydrated in an activated alumina, bauxite, or silica gel drier, and flows to a refrigerant-cooled condenser. The liquid is then distilled in a stripper column to remove non-combustible impurities.

Solid carbon dioxide is produced in blocks by hydraulic presses. Dry ice is about 1.7 times as dense as water ice, causing dry ice to sink in water, whereas its net refrigerating effect on a weight basis is twice that of water ice. Liquid CO_2 from a supply tank is fed to the press chamber through an automatic feed valve. The pressure in the press is maintained slightly above the triple point. The pressure is reduced and the evolved CO_2 vapour is returned to a recycle system. When the pressure falls below the triple point, the liquid CO_2 solidifies to form dry ice. Also, liquid carbon dioxide from a cylinder may be converted to "snow" by allowing the liquid to expand to atmospheric pressure. This simple process is used only where very small amounts of solid carbon dioxide are required because less than one-half of the liquid is recovered as solid.

Although liquid carbon dioxide may be stored without loss in tanks and cylinders, dry ice undergoes continuous loss in storage because of sublimation. This loss can be minimized by keeping the dry ice in insulated boxes or bins. Special insulated rail cars and trucks are used for hauling dry-ice blocks. Most plants produce the material at the time it is sold to avoid storage losses and rehandling costs.

3.3 Usage

Carbon dioxide is used by the food industry, the oil industry, and the chemical industry. A large portion of the CO_2 recovered is used at or near the location where it is generated as an ingredient in a further processing step. In this case, the gaseous form is most often used. Low temperature liquid and solid carbon dioxide are used for refrigeration. Where the producer and the consumer are distant, carbon dioxide may be liquefied to reduce transportation cost and re-vaporized at the point of consumption.

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Dry ice
Refrigeration of foodstuffs, especially ice cream, meat products, and frozen foods, is the principal use for solid carbon dioxide. In addition, dry ice is used for the following applications:

- Dry ice pellets are used to replace sandblasting when removing paint from surfaces. It aids in reducing the cost of disposal and cleanup.
- Dry ice is mixed with moulded substances that must be kept cold. For example, dry ice is mixed with moulded rubber articles in a tumbling drum to chill them sufficiently so that the thin flash or rind becomes brittle and breaks off.
- Dry ice is used to chill aluminum rivets. These harden rapidly at room temperature, but remain soft if kept cold with dry ice.
- It has found numerous uses in laboratories, hospitals, and airplanes as a convenient and readily available low temperature coolant.

Liquid carbon dioxide
The rapid increase in the use of liquid carbon dioxide is the result of new applications as well as improved facilities for transporting, storing, and handling liquid carbon dioxide. Liquid CO_2 can be stored without loss as long as pressure is maintained and temperature is controlled and is easily measured or weighed. Some application areas are listed below:

- Liquid (and also solid) carbon dioxide is used for quick freezing, surface freezing, chilling and refrigeration in the transport of foods. In cryogenic tunnel and spiral freezers, high pressure liquid CO_2 is injected through nozzles that convert it to a mixture of CO_2 gas and dry ice "snow" that covers the surface of the food product. As it sublimates (goes directly from solid to gas states) refrigeration is transferred to the product.
- Liquid carbon dioxide has been used for many years in the Long-Airdox blasting system for mining coal. A steel cartridge containing liquid carbon dioxide is placed in a hole drilled in the coal seam. A heating mixture in the cartridge is ignited electrically. This vaporizes the carbon dioxide, causing the pressure to increase enough to burst a steel rupture disk and release the carbon dioxide, which shatters the coal. The cartridge is then recovered and reused.
- Liquid carbon dioxide is used as a source of power in certain applications. The vapour pressure of liquid carbon dioxide may be used for operating remote signalling devices, spray painting, and gas-operated firearms. Carbon dioxide in small cylinders is also used for inflating life rafts and jackets.
- Fire-extinguishing equipment, ranging from hand-type extinguishers to permanent installations in warehouses, chemical plants, ships, and airplanes, uses liquid carbon dioxide. In addition to its snuffing action liquid carbon dioxide exerts a pronounced cooling effect helpful in fire extinguishing. It may be used on all types of fires and leaves no residue.
- Carbon dioxide is sometimes added to irrigation water, in the same manner as fertilizer ammonia, in hard water regions. Carbon dioxide is also used with other gases in treating respiratory problems and in anesthesia.

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Gaseous carbon dioxide

In addition to being a chemical reagent and in chemical synthesis, e.g. methanol and urea production, gaseous CO_2 has the following application areas:

- Carbon dioxide gas is used to carbonate soft drinks, beers and wine and to prevent fungal and bacterial growth.
- Carbon dioxide gas under pressure is introduced into rubber and plastic mixes, and on pressure release a foamed product is produced.
- Carbon dioxide and inert gas mixtures rich in carbon dioxide are used to purge and fill industrial equipment to prevent the formation of explosive gas mixtures.
- The addition of small amounts of carbon dioxide to the atmosphere in greenhouses greatly improves the growth rate of vegetables and flowers.
- Carbon dioxide is used on a large scale as a shield gas in metal inert gas (MIG) welding, where the gas protects the weld puddle against oxidation by the surrounding air.
- Carbon dioxide gas is used to immobilize animals prior to slaughtering them. In addition to providing a humane slaughtering technique, this results in better quality meat. The CO_2 increases the animal's blood pressure, thereby increasing blood recovery.
- Used as a propellant in aerosol cans, it replaces more environmentally troublesome alternatives.
- As a weak acid (in aqueous solution) carbon dioxide neutralizes excess caustic in textile manufacturing operations. It does not injure fabrics and is easy to use. Carbon dioxide is also used for neutralizing alkaline wastewaters, treating skins in tanning operations, and carbonating treated water to prevent scaling.
- A common type of industrial gas laser is the carbon dioxide laser.
- CO_2 is often used as coolant in gas cooled nuclear reactors.

Supercritical CO_2

Supercritical carbon dioxide refers to carbon dioxide that is in a fluid state while also being at or above both its critical temperature and pressure, where it can diffuse through solids like a gas, and dissolve materials like a liquid. Examples of the most common applications areas are:

- Supercritical carbon dioxide is gaining popularity for de-caffeinate coffee. Supercritical CO_2 is forced through the green coffee beans and then they are sprayed with water at high pressure to remove the caffeine. The caffeine can then be isolated for resale (e.g. to the pharmaceutical industry or to beverage manufacturers) by passing the water through activated charcoal filters or by distillation, crystallization or reverse osmosis.
- Supercritical CO_2 extraction coupled with a fractional separation technique is used by producers of flavors and fragrances to separate and purify volatile flavor and fragrances concentrates.
- Supercritical carbon dioxide can be used in dry cleaning of clothes, as a substitute for conventional solvents.
- Supercritical carbon dioxide is used to enhance oil recovery (EOR) in mature oil fields. When CO_2 is pumped into an oil well, it is partially dissolved into the oil, rendering it less viscous, allowing the oil to be extracted more easily from the bedrock. Considerably more oil can be extracted through this process (for more on EOR; see Section 3.4).

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3.4 CO$_2$ Enhanced Oil Recovery (EOR)

Enhanced Oil Recovery (EOR) is a generic term for techniques for increasing the amount of oil that can be extracted from an oil field. Gas injection is the most commonly used EOR technique. Oil displacement by CO$_2$ injection relies on the phase behaviour of CO$_2$ and crude oil mixtures that are strongly dependent on reservoir temperature, pressure and crude oil composition. These mechanisms range from oil swelling and viscosity reduction for injection of immiscible fluids (at low pressures) to completely miscible displacement in high-pressure applications. In these applications, more than half and up to two-thirds of the injected CO$_2$ returns with the produced oil and is usually re-injected into the reservoir to minimize operating costs. The remainder is trapped in the oil reservoir by various means.

CO$_2$ enhanced oil recovery (CO$_2$-EOR) is currently or has recently been employed in 4 countries: USA, Canada, Turkey and Trinidad & Tobago. Of the 74 active projects, 70 are in the USA; in 1998 these were producing some 196,000 barrels of oil per day. To supply these CO$_2$-EOR projects there are already existing long distance CO$_2$ pipelines. The oldest long-distance CO$_2$ pipeline in the United States is the 225 kilometer Canyon Reef Carriers Pipeline (in Texas), which began service in 1972 for EOR in regional oil fields /10/. Other large CO$_2$ pipelines constructed since then, mostly in the Western United States, have expanded the CO$_2$ pipeline network for EOR. Currently, there are some 2400 km of large CO$_2$ pipelines in operation, most of which are in the USA /8/.

An example of a well known CO$_2$-EOR project is the Weyburn Oil Field in southern Saskatchewan, Canada. The CO$_2$ is produced from a coal gasification facility located at Beulah, North Dakota. CO$_2$ purity is in the order of 96%, with traces of H$_2$S, hydrocarbons and nitrogen in the stream. The CO$_2$ is compressed to approximately 152 bar and fed into a 330 km pipeline terminating at Weyburn field. There is no additional pumping required along the pipeline. The CO$_2$ is delivered in supercritical condition at 150 bar. The project is expected to inject a net 18 million ton CO$_2$ and recover an additional 130 million barrels of oil, extending the life of the oil field by 25 years /7/.

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3.5 Merchant CO_2 Market

In 1998, 35 million tonnes of gaseous carbon dioxide was consumed. Liquid carbon dioxide consumption was 6.6 million tonnes /5/.

About 51% of the carbon dioxide consumed in the United States is used in the food industry. It is generally purchased in liquid form but may be used in any form. It is generally used for food freezing or chilling. Numerous patents on applications and equipment for these applications have been received. Approximately 18% of carbon dioxide output is used for beverage carbonation. About 10% of the carbon dioxide produced is for chemical manufacturing. Sold as a liquid, it is used as a raw material, for inerting and pressurizing, and for cooling. Other applications include metal working (4%) and oil and gas recovery (6%).

More recent figures on total volume CO_2 consumed and the volumes of each segment in the CO_2 merchant market are difficult to obtain due to the fact that those CO_2 volumes are in most cases confidential.

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3.6 Production Installations

Some of the largest installations for recovery of CO_2, operated today or with recent operational experience, for various sources to produce merchant CO_2 are listed in Table 3-1.

Table 3-1: Commercial post-combustion capture plants /11/ /12/

Operator	Location	Capacity (tons/day CO_2)	Fuel Source	CO_2 Use	Technology	Status
Carbon Dioxide Technology	Lubbock, TX	1200	Gas boiler	EOR	Dow MEA	Shut
North American Chemical Co.	Trona, CA	800	Coal boiler	Carbonation of brine (soda ash)	Kerr-McGee MEA	Operational since 1978
Mitchell Energy	Bridgeport, TX	493	Gas heaters, engines, turbine	EOR	Inhibited MEA	Shut
Indian Farmers Fertilizer Co	India	2x450	Steam reformer flue gases	Urea	Mitsubishi Heavy Industry, KS-1	Operational since 2007
Northeast Energy Associates	Bellingham, MA	320	Gas turbines	PURPA (food-grade)	Fluor Daniel	Shut
Soda Ash Botswana	Sua Pan,	300	Coal boiler	Carbonation of brine (soda ash)	Kerr-McGee MEA	Operational since 1991
Applied Energy Systems	Poteau, OK	200	Coil boiler (fluidized bed)	PURPA (food-grade)	Kerr-McGee MEA	Operational since 1991
Sumitomo Chemicals	Chiba, Japan	165	Gas boilers plus oil/coal boiler	Food-grade	Fluor Daniel	Operational since 1994
Petronas Fertilizer	Malaysia	160	NH_3 plant reformer exhaust	Urea	Mitsubishi Heavy Industry, KS-1	Operational since 1999
Indo Gulf Fertilizer Co.	India	150	NH_3 plant reformer exhaust	Urea	Dow MEA	Operational since ~1988
N-ReN Southwest	Carlsbad, NM	104	Gas boiler plus NH_3 reformer exhaust	EOR	Retrofit to Dow MEA	Shut
Prosint	Rio de Janeiro, Brazil	90	Gas boiler	Food-grade	Fluor Daniel	Operational since 1997
Liquid Air Australia	Australia	2 x 60	Gas boiler	Food-grade	Dow MEA	Operational since ~1985

The list is not presented as a complete review; however, it is indicative of the order of magnitude of CO_2 capture volumes experienced for several plants world-wide to date. In contrast, installations in an order of magnitude larger are expected for CCS (see discussions in Chapter 5).

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4 INCIDENTS INVOLVING CO_2

This chapter presents some reported incidents related to CO_2 showing the potential harmful effects on humans.

4.1 Fire Extinguisher Systems

Carbon dioxide is the most commonly used "inert" gas extinguishing agent, followed by nitrogen. On a volume basis, carbon dioxide is approximately twice as effective as nitrogen (e.g. for ethanol fires, the minimum required volume ratios of carbon dioxide and nitrogen to air are 0.48 and 0.86, respectively). However, because carbon dioxide is 1.57 times heavier than nitrogen (44 and 28 molecular weight, respectively) for a given volume, the two gases have nearly equivalent effectiveness on a weight basis. Carbon dioxide fire extinguishing systems are useful in protecting against fire hazards when an inert, electrically nonconductive, three-dimensional gas is essential or desirable and where clean up from the agent must be minimal.

A comprehensive review of carbon dioxide incidents related to use in fire protection was undertaken by the US Environmental Protection Agency (EPA) /13/, which reviewed governmental, military, public, and private document archives. The findings are summarized as follows:

- From 1975 to 2000, a total of 51 carbon dioxide incident records were located that reported a total of 72 deaths and 145 injuries resulting from accidents involving the discharge of carbon dioxide from fire extinguishing systems.

- Prior to 1975, a total of 11 incident records were located that reported a total of 47 deaths and 7 injuries involving carbon dioxide. Twenty of the 47 deaths occurred in England prior to 1963; however, the cause of these deaths is unknown.

The review indicates that the majority of reported incidents occurred during maintenance on or around the carbon dioxide fire protection system. In many of the situations where carbon dioxide exposure led to death or injury during maintenance operations, the discharge resulted from personnel inadvertently touching, hitting, or depressing a component of the system. In some cases, personnel did not adhere to the precautionary measures prescribed. In other cases, the safety measures were followed, but other accidental discharge mechanisms occurred. Also, some references point to the phenomenon of CO_2 BLEVE (Boiling Liquid Expanding Vapour Explosion) as a potential cause for some reported incidents. This phenomenon is described in more detail in Chapter 8.3.2.

More recently (August 2008), a lacquer-making plant in Moenchengladbach in Germany /14/ had a fire break out in an area where wooden pallets were stored causing the carbon dioxide extinguishing system to discharge, extinguishing the fire and putting the building into alarm, automatically closing all the exterior doors while the CO_2 discharged into the building. Because of a mechanical flaw, one of the fire doors failed to seal properly and the CO_2-enriched atmosphere began leaking out into the surrounding area. Ambient external conditions were warm

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and still (i.e. no wind) at the time of the incident and as the CO_2-enriched atmosphere escaped from the building it accumulated in the vicinity to the extend that an engine of a response vehicle suddenly stopped running and three firefighters collapsed. These firefighters were outside at the time and, probably due to their lack of understanding of the hazards, were not wearing breathing apparatus. The incident resulted in a reported 107 respiratory injuries with three needing to be revived by rescuers. Of the casualties, 19 people were transported to hospital.

4.2 Pipeline Incidents

In the US, the Secretary of Transportation has primary authority to regulate interstate CO_2 pipeline safety under the Hazardous Liquid Pipeline Act. Under the act, the Department of Transportation (DOT) regulates the design, construction, operation and maintenance, and spill response planning for CO_2 pipelines. The DOT administers pipeline regulations through the Office of Pipeline Safety (OPS) within the Pipelines and Hazardous Materials Safety Administration (PHMSA). Although CO_2 is listed as a Class 2.2 (non-flammable gas) hazardous material under DOT regulations the agency applies nearly the same safety requirements to CO_2 pipelines as it does to pipelines carrying hazardous liquids such as crude oil, gasoline, and anhydrous ammonia /15/.

Statistics on pipeline incidents can be found at the Office of Pipeline Safety (OPS) within the U.S. Department of Transportation, Pipeline and Hazardous Materials Safety Administration /16/, and is summarized below:

- In the period 1986-2001: **11** incidents related to pipeline transport of CO_2 are reported with one fatality and two injuries. According to the statistic log, the fatality was associated with welding work and not as a direct consequence of pipeline operation. 9 of the incidents were related to the pipeline (all onshore), whereas the remaining two were located at the pumping station.

- In the period 2002- 2008: **18** incidents related to pipeline transport of CO_2 are reported with no fatalities and injuries. 9 of these incidents were solely related to the onshore pipeline itself, whereas the remaining where related to incidents at pump/meter station, terminal/tank farm piping and equipment, including sumps.

The failure modes of all the 29 reported incidents from 1986-2008 are grouped and presented in Figure 4-1.

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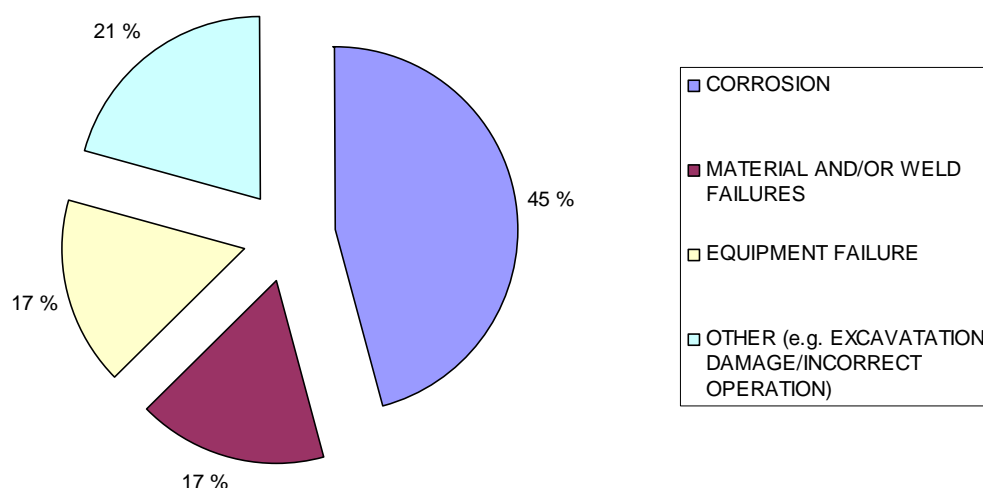
Figure 4-1: Grouping of reported failure modes for CO$_2$ pipeline systems

By contrast to the above statistics, there were 5,610 accidents causing 107 fatalities and 520 injuries related to natural gas and hazardous liquids (excluding CO$_2$) pipelines during the period 1986-2006. Reported data for natural gas pipelines in the US showed the principal causes of pipeline accidents were outside force (35%), corrosion (32%), other (17%), weld and pipe failures (13%) and operator error (3%). The category ''outside force'' includes ''human error'' accidents principally as a result of third party damage by contractors, farmers and utility workers. The ''other'' category includes incidents such as vandalism, train derailment and improper operation of manual valves /8/.

A mile-by-mile comparison is made by Gale and Davidson /8/, and according to their study CO$_2$ pipelines have a frequency of incident of 0.32 per 1000 km per year, whereas for natural gas and hazardous liquids pipelines have a frequency of 0.17 and 0.82, respectively.

Table 4-1: Statistics of pipeline incident in the USA /8/

	Natural gas transmission (1986–2001)	Hazardous liquids (1986–2001)	CO$_2$ (1990–2001)
No. of incidents	1287	3035	10
No. of injuries	217	249	0
No. of fatalities	58	36	0
No. incidents per 1000 km pipeline per year	0.17	0.82	0.33

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As seen from the numbers in Table 4-1, the frequency of incidents in CO_2 pipelines between 1990 and 2001 was higher than that of natural gas pipelines, but caution must be taken in drawing any conclusions because of the low sample number. Nonetheless, as the number of CO_2 pipelines expands to support CCS, analysts suggest that "statistically, the number of incidents involving CO_2 should be similar to those for natural gas transmission /9/.

Other issues related to the differences in physical properties of the pipeline itself, (e.g. pipeline diameters and inventory volumes) should be taken into account when assessing the risks of future CO_2 pipelines and comparing it to statistics for other gases or liquids. Moreover, features that need to be considered when evaluating and comparing the different incident data for natural gas and hazardous liquids pipelines are:

- CO_2 pipelines account for less than 1% of total natural gas and hazardous liquids pipelines; and
- CO_2 pipelines currently run primarily through remote areas

4.3 Natural Outgassing of CO_2

Lake Nyos is one of only three lakes in the world known to be saturated with carbon dioxide - the others are Lake Monoun, also in Cameroon about 100 km away, and Lake Kivu in Rwanda. A magma chamber beneath the region is an abundant source of carbon dioxide, which seeps up through the lake bed, charging the waters of Lake Nyos with an estimated 90 million tonnes of CO_2.

Lake Nyos is thermally stratified, with layers of warm, less dense water near the surface floating on the colder, denser water layers near the lake's bottom. Over long periods, carbon dioxide gas seeping into the cold water at the lake's bottom is dissolved in great amounts.

Most of the time, the lake is stable and the CO_2 remains in solution in the lower layers. However, over time the water becomes supersaturated, and if an event such as an earthquake or volcanic eruption occurs, large amounts of CO_2 may suddenly come out of solution.

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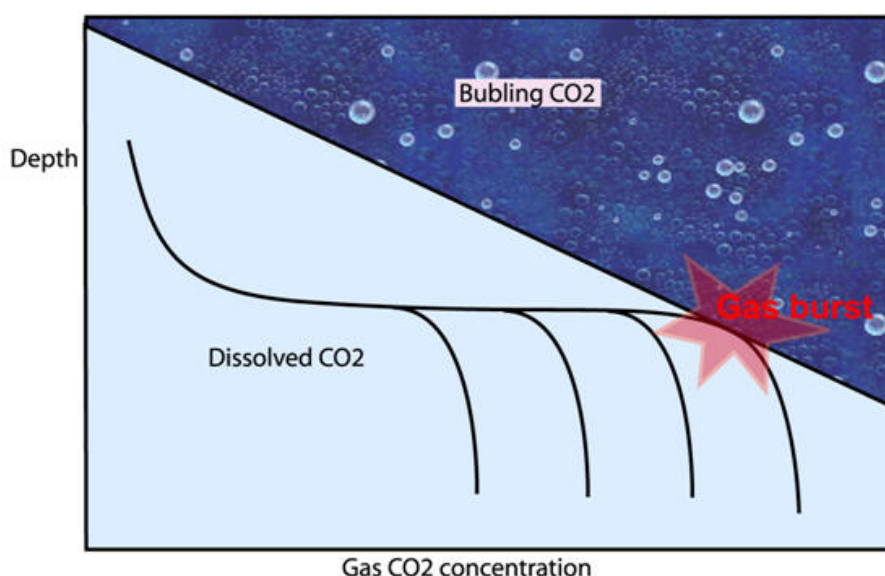
Figure 4-2: CO_2 saturation profile /17/

On August 21, 1986, a limnic eruption occurred at Lake Nyos which triggered the sudden release of about 1.6 million tonnes of CO_2. The gas spilled over the northern lip of the lake into a valley, resulting in the death of some 1,700 people within 20 km of the lake, mostly rural villagers, as well as 3,500 livestock. Worst affected villages were Cha, Nyos, and Subum. About 4,000 inhabitants fled the area, and many of these developed respiratory problems, lesions, and paralysis as a result of the gases.

Prior to the Lake Nyos a similar incidents with sudden outgassing of CO_2 occurred at Lake Monoun in 1984, killing 37 local residents.

The scale of these disasters led to much study on how a recurrence could be prevented. Estimates of the rate of carbon dioxide entering the lake suggested that outgassings could occur every 10-30 years. Several researchers independently proposed the installation of degassing columns from rafts in the lake /17/. The principle is simple: a pump lifts water from the bottom of the lake, heavily saturated with CO_2, until the loss of pressure begins releasing the gas from the diphasic fluid and thus makes the process self-powered.

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5 CARBON CAPTURE, TRANSPORT AND STORAGE (CCS)

5.1 Introduction to CCS

Power production and other uses of fossil-fuelled energy will, in the future, be the largest sources of greenhouse gas emissions. The carbon capture and storage option could be one of the bridging technologies that will help the world to come closer to a cleaner energy future. Large-scale deployment of CCS technologies will help allow global energy demands to be met whilst substantially reducing anthropogenic CO_2 emissions. With a potential to provide up to 55% of the mitigation efforts needed to keep climate change consequences at an acceptable level, CCS will be a key technology in the near to mid-term future /18/. In order to reach widespread commercialization of CCS it is crucial to demonstrate the concept in large-scale projects, reduce cost, build infrastructures for transportation of CO_2, establish a legal framework and gain acceptance by the public.

5.2 CO_2 Capture

Carbon capture is today technically feasible. However, it still remains to provide large-scale capture technology for fossil fuel power generation that is economically and environmentally feasible. The three main technology options (a principal sketch of the different options is shown in Figure 5-1) that are considered for CO_2 capture from power plants are:

- Post-combustion capture
- Pre-combustion capture
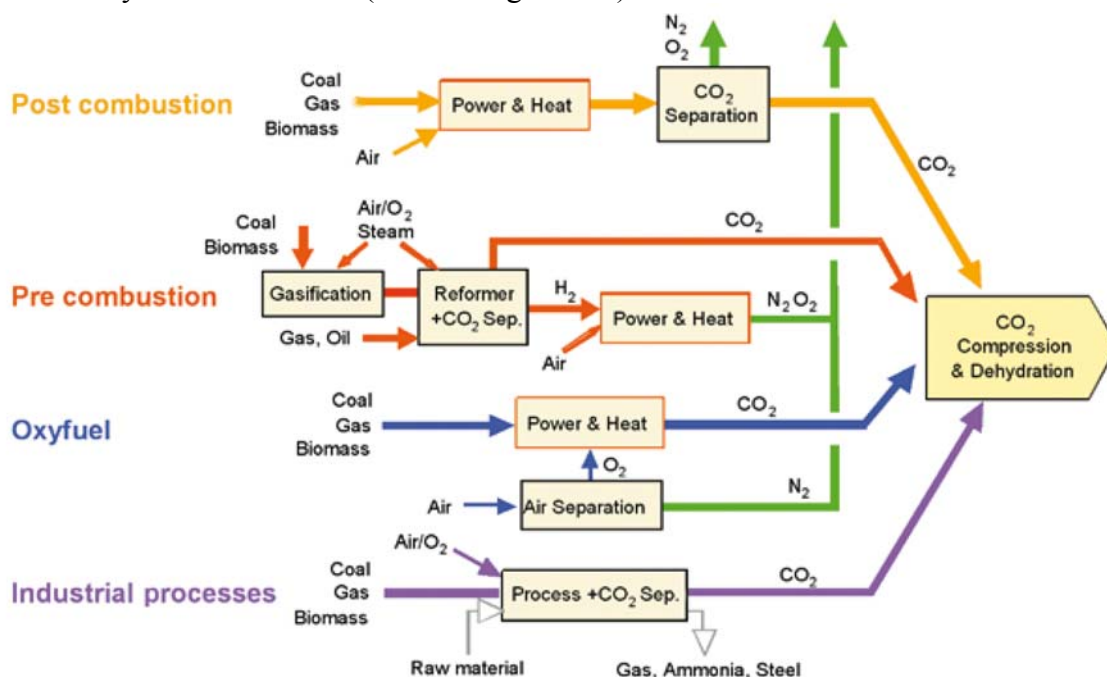- Oxy-fuel combustion (or Denitrogenation)

Figure 5-1: Overview of CO_2 capture processes and systems /18/

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In **post-combustion capture**, the CO_2 is removed from the power plant flue gas. Chemical absorption uses organic and inorganic aqueous solutions to attach the carbon dioxide and form weakly bonded intermediate compounds. Organic amines are able to react with carbon dioxide forming water soluble compounds from streams with low CO_2 partial pressure. Monoethanolamine (MEA) is currently the most used solvent. Inorganic solvents include potassium carbonate, sodium carbonate and aqueous ammonia. Soluble carbonate compound react with carbon dioxide to form bicarbonate. The latter, when heated, releases CO_2 regenerating the initial carbonate. There are two available systems using ammonia, the ammonia-based wet scrubbing and the chilled ammonia process (CAP), which are operated similarly to amine systems. In principle, ammonia and its derivatives react with CO_2 by a range of mechanisms. For instance, ammonium carbonate, water and CO_2 react and form ammonium bicarbonate.

A simplified process flow diagram for a typical post combustion capture plant based on amine absorption is shown in Figure 5-2. The CO_2 reacts with the amine in the absorber and is later separated from the amine solution in the stripper, dried, compressed, and transported to the storage site. For flue gases with a low partial pressure, a large amount of energy is needed to regenerate the solvent. Improved solvents and optimized processes are currently being developed. However, alternative methods for separating CO_2 from flue gases are also evolving.
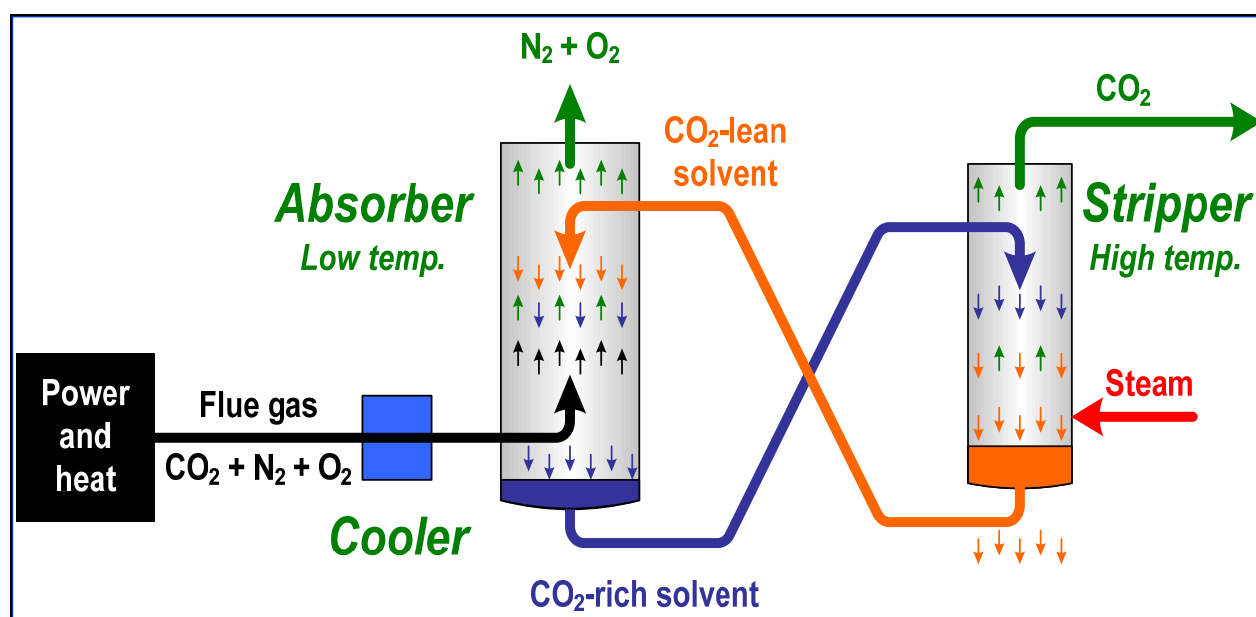
Figure 5-2: Example of a process flow diagram for a post combustion capture plant.

It should also be noted that CO_2 capture with the use of amines might have some critical issues related to emissions to air. The amine used for CO_2 capture will vary and have different possibilities of degradation and chemical reactions after the flue gas is emitted. The different amines will also probably need different additives to prevent corrosion and degradation. The knowledge of emissions to air and effects of CO_2 capture with the use of amines are limited, however, it is beyond the scope of this study to investigate the potential HSE issues related use of amine (for further reading, e.g. the NILU report /19/ could be consulted).

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Pre-combustion capture is a technique where the CO$_2$ is captured before burning the fuel in a combustor. It is commercial available for several applications, such as hydrogen, ammonia, or synthetic gas production. The technique consists basically of reforming/conversion of a fossil fuel (natural gas, oil, or coal) with subsequent steps for CO$_2$ separation and H$_2$ to produce a H$_2$-rich gas. The main technological challenge within this concept to make it economically feasible is to develop gas turbines that reliably can burn fuel with a H$_2$ content of more than about 60% /20/. Because of the world-wide interest in the hydrogen economy, a lot of R&D effort is currently put into this field.

In the **oxy-fuel** concept, the fuel is combusted using almost pure oxygen at near stoichiometric conditions. This creates a flue gas consisting mainly of CO$_2$ and H$_2$O (and small amounts of SO$_x$ and NO$_x$). A portion of the CO$_2$ in the flue gas is recycled in order to control the combustion temperature. Oxy-fuel combustion has been used within the metal and glass manufacturing industries for some time, but has so far not been applied to full-scale conventional steam boilers. The main challenges within this concept are the new combustion environment in the burner and the high energy demand of the air separation unit.

The three processes briefly described above, are today considered as the main technology options for CO$_2$ capture. However, considerable R&D efforts are ongoing within these three options that combine capture technologies that often are considered to be connected within the concepts, as well as within novel concepts. It might therefore be wise to discuss the terminology for CO$_2$ capture technologies that is not tied up in these three main capture routes.

5.3 Compression of CO$_2$

To avoid corrosion of carbon steel in pipelines and hydrate formation in the CO$_2$ stream, no free water can be present in the pipeline. Water removal will therefore normally be required upstream of the pipeline inlet. The drying requirements may vary from a water content of 50 ppm to 600 ppm. However, <u>theoretical</u> calculations show that the limit for free water precipitation at supercritical, dense, conditions in the pipeline average is 1300 ppm /22/.

Waters solubility in CO$_2$ is mainly dependent on the temperature and pressure. And this characteristic can be utilized in the drying process. A typical compression process includes compressors with inter coolers and knock out drums between each compression stage in order to reduce the gas temperature and to knock out free water.

The inlet pressure of a CO$_2$ pipeline is usually determined by the delivery pressure at the storage site, given by the geological reservoir pressure, and the pressure drop in the pipeline. Pressure booster stations can, if required, be placed along the pipeline to compensate for pressure drop or other operational or safety influences. The most energy efficient phase to transport CO$_2$ in pipelines is in dense phase condition. It is important to keep the pressure high enough to maintain dense phase within the operational temperature envelope.

Typical delivery pressure for storage in a deep saline aquifer is about 70-100 bar, while for EOR purposes the pressure will be higher. To meet such pressures an inlet pressure from 150 – 300

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bars, depending on transport solution and reservoir pressure, is suitable /23/. A typical compression train of CO_2 with intermediate cooling and water scrubbing, is shown in Figure 5-3. Please note that the number of stages might of a compression train can vary from project to project.
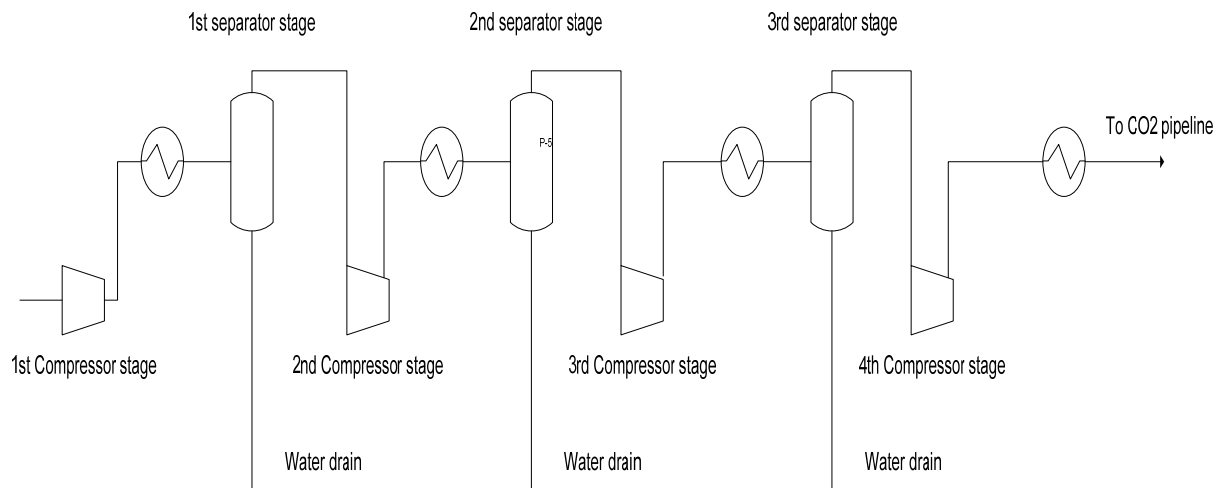
Figure 5-3: Four stage compression train

By using coolers with seawater at 9 ºC as a cooling medium, the water content can be reduced to approximately 600 ppm, only by compression, intermediate cooling and scrubbing for dehydration. However if air at 20 ºC is the only available cooling media, the theoretical achievable water content in CO_2 is approximately 1600 ppm /22/. To further reduce the water content, from 600 or 1600 ppm, the following techniques can be utilized for water removal in a CO_2 stream:

- Adsorption using e.g. molecular sieves

- Adsorption with TEG or DEG as an absorber medium

The size and cost of these water dryers is highly dependent on the water requirement, and a uniform requirement should be established. In Table 5-1 a selected set of CO_2 requirements is shown.

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Table 5-1: Different proposed CO_2 specifications /66/

Compound	Specification (Kinder Morgan)	Specification (Ecofys)	Specification (Dynamis)	
CO_2	Min. 95%	Min. 95%	Min 95,5 %	
N_2	Max 4%	Max 4%	Max 4 %	(combined all non cond. gases)
CH_4	Max 5 %	Max 4%	Max 4 % Max 2 %	(Aquifer) (EOR)
H_2O	257 ppm wt	Max 500 ppm	Max 500 ppm	
O_2	10 ppm wt	Max 4 vol %	Max 4 % Min 100 - 1000 ppm	(Aquifer, combined all non cond. gases) (EOR)
SOx	-	-	Max 100 ppm	
NO	-	-	Max 100 ppm	
H_2S	10-200 ppm	-	Max 200 ppm	
H_2	-	Max 4 %	Max 4 %	(combined all non cond. gases)
Ar	-	Max 4 %	Max 4 %	(combined all non cond. gases)
CO	-	-	Max 2000 ppm	
Glycol	Max $4*10^{-5}$ l/m^3	-	-	
Temperature	Max 50 ºC	Max 30 ºC		

5.4 Transport of CO_2

Transport of CO_2 by pipeline or ship will be necessary if large volumes of captured CO_2 are to be stored in geological formations that are not adjacent to the capture location. For a number of countries, including Norway, the preferred storage locations will be offshore, necessitating offshore pipelines between the capture and storage facilities.

The quantities that need to be transported will change from project to project, but it is likely that it will be between 1-3 million tonnes per annum, per capture plant. The CO_2 volumes are directly correlated to the power plants size, efficiency and the capture plants capture rate.

To benefit the economy of scale in transportation and storage, it is likely that a CO_2 pipeline network will emerge in the future. It is then possible that pipelines transporting much higher volumes will be installed.

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Table 5-2: Examples of some existing long CO_2 pipelines /66/

Name of pipeline	Operator	Length (km)	Diameter (in)	Capacity (MT/yr)	Country
NEJD Pipeline	Denbury Resources	295	20		USA
Cortez Pipeline	Kinder Morgan	808	30	19,3	USA
Bravo Pipeline	BP	350	20	7,3	USA
Transpetco Bravo Pipeline	Transpetco	193	12,75	3,3	USA
Sheep mountain part 1	BP	296	20	6,3	USA
Sheep Mountain part 2	BP	360	24	9,2	USA
Central Basin Pipeline	Kinder Morgan	-	26 and 16	11,5	USA
Este Pipeline	Exxon Mobil	191	12 and 14	4,8	USA
West Texas Pipeline	Trinity	204	8 to 12	1,9	USA
SACROC Pipeline		354	16	4,2	USA
Weyburn Pipeline	Dakota Gasification Company	330	12 to 14	4,6	USA
Canyon Reef Carriers	Kinder Morgan	225	16	4,6	USA
Bati Raman	Turkish Petroleum	90		1,1	Turkey
Snøhvit	StatoilHydro	153	8	0,7	Norway

5.4.1 Onshore Pipelines

CO_2 pipelines have been in use since the early 1970s for transporting CO_2 for Enhanced Oil Recovery (EOR) purposes and are a well-established technology. The largest existing CO_2 pipeline is the 808 km long Cortez pipeline from Cortez in Colorado to Denver City in Texas. The pipeline delivers about 20 million tonnes of CO_2 per year to the CO_2 hub in Denver. North America has approximately 3000 km of CO_2 pipelines and is transporting approximately 45 million tonnes carbon dioxide annually /21/. All of these are designed for dense/supercritical phase transport of CO_2, and are onshore pipelines.

5.4.2 Offshore Pipelines

The oil and gas industry has considerable experience with offshore pipeline transport of natural gas; however, CO_2 as a fluid has properties and behaviour that differ from natural gas. Therefore one needs to be careful when applying experience from the oil and gas industry to a CO_2 pipeline. The only existing offshore pipeline for transporting CO_2 is the Snøhvit pipeline which started operation in May 2008 (ref. Table 5-2). Processing natural gas into LNG requires a complete absence of CO_2 due to likely dry ice formation in LNG equipment. CO_2 is thus separated from gas stream with amine separation in the processing plant at Melkøya, and transported to the Tubåen reservoir with a sub-sea pipeline for injection. Total extracted and injected volume is designed to be 0.7 mill tons CO_2/year. The pipeline design pressure is 240 bars and its design temperature from –23 to +35 ºC. Due to the possible low temperatures in the artic climate, hydrate formation has been regarded as the dimensioning requirement for the water content,

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rather than corrosion. If water is present, hydrate challenges are expected before corrosion will be a problem.

Moreover, Statoil have injected and stored CO_2 in the Sleipner field since 1996. The storage site is the Utsira formation aquifer 240 km south west of Stavanger, Norway. Injected volume has been approx. 1 mill. tonnes CO_2/year. The purpose of the injection is to store CO_2, and is not EOR related. The source for the CO_2 is a natural gas stream from the Sleipner West Field, containing 9 mole % CO_2. CO_2 is extracted in order for the natural gas stream to the meet export quality specifications, with a maximum CO_2 level of 2 and 5 mole %. CO_2 injection at Sleipner differs from industry practice because the CO_2 is wet and contaminated with methane. CO_2 is stripped from the well stream with amine separation and injected directly from the platform with no horizontal pipe sections.

The relatively short timeline in capture projects that is planned across Europe makes it necessary to gain more knowledge about CO_2 transport in an offshore pipeline.

5.5 Effect of Impurities

The captured CO_2 stream may contain impurities which would have practical impacts on CO_2 transport and storage systems and also potential health, safety and environmental impacts. The types and concentrations of impurities depend on the type of capture process, as shown in Table 5-3, and detailed plant design. The major impurities in CO_2 are well known but there is little published information on the fate of any trace impurities in the feed gas such as heavy metals.

CO_2 from post-combustion solvent scrubbing processes normally contains low concentrations of impurities. Many of the existing post-combustion capture plants produce high purity CO_2 for use in the food industry.

CO_2 from pre-combustion physical solvent scrubbing processes typically contains about 1-2% H_2 and CO and traces of H_2S and other sulphur compounds. Integrated Gasification Combined Cycles (IGCC) plants with pre-combustion capture can be designed to produce a combined stream of CO_2 and sulphur compounds, to reduce costs and avoid the production of solid sulphur.

The CO_2-rich gas from oxy-fuel processes contains oxygen, nitrogen, argon, sulphur and nitrogen oxides and various other trace impurities. This gas will normally be compressed and fed to a cryogenic purification process to reduce the impurities concentrations to the levels required to avoid two-phase flow conditions in the transportation pipelines. A 99.99% purity could be produced by including distillation in the cryogenic separation unit. Alternatively, the sulphur and nitrogen oxides could be left in the CO_2 fed to storage in circumstances where that is environmentally acceptable as described above for pre-combustion capture and when the total amount of all impurities left in the CO_2 is low enough to avoid two-phase flow conditions in transportation pipelines /18/.

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Table 5-3: Concentrations of impurities in dried CO_2, % by volume /18/

Impurity Capture process	SO$_2$	NO	H$_2$S	H$_2$	CO	CH$_4$	N$_2$/Ar/O$_2$	Total
Coal fired plant								
Post-combustion capture	<0.01	<0.01	0.00	0.00	0.00	0.00	0.01	0.01
Pre-combustion	0.00	0.00	0.01-0.6	0.8-2.0	0.03-0.4	0.01	0.03-0.6	2.1-2.7
Oxy-fuel	0.5	0.01	0.00	0.00	0.00	0.00	3.70	4.20
Gas fired plant								
Post-combustion	<0.01	<0.01	0.00	0.00	0.00	0.00	0.01	0.00
Pre-combustion	0.00	0.00	<0.01	1.00	0.04	2.00	1.30	4.40
Oxy-fuel	<0.01	<0.01	0.00	0.00	0.00	0.00	4.10	4.10

Impurities affect the design of equipment like pumps and compressors. For example, if the suction pressure is lower than the vapour pressure, unwanted cavitations will occur in the pump. The compression strategy will also be affected by impurities. For example one can choose to pressurize the CO_2 by compression and condense the CO_2 to liquid prior to further pressurization by pump. The pressure at which CO_2 can be liquefied will be set by available cooling water temperature. When impurities are present the vapour pressure will be higher. Thus at a given cooling water temperature higher compression pressure (power) will be needed to liquefy the CO_2. In addition higher pipeline operating pressures will be needed to maintain dense phase /66/.

In addition to the compounds listed in Table 5-3, there might be carry-over of small concentrations of amine from the capture plant (for post- and pre-combustion) that might influence the internal corrosion rate in the pipeline (see Chapter 8.1.2).

Reference to part of this report which may lead to
misinterpretation is not permissible
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6 HUMAN IMPACT TO INHALED CO_2

6.1 Introduction

In humans, CO_2 is a normal component of blood gases at low concentrations, however, at high inhalation levels it is lethal. Humans are very sensitive to changes in CO_2 concentrations. In addition to the hazard of asphyxiation due to released CO_2 displacing oxygen in the air, the inhalation of elevated concentrations of CO_2 can increase the acidity of the blood triggering adverse effects on the respiratory, cardiovascular and central nervous systems. Depending on the CO_2 concentration inhaled and exposure duration, toxicological symptoms in humans range from headaches, increased respiratory and heart rate, dizziness, muscle twitching, confusion, unconsciousness, coma and death /13/ /24/.

Breathing air with a CO_2 concentration of around 5% will within a few minutes cause headache, dizziness, increased blood pressure and uncomfortable and difficult breathing (dyspnea). At CO_2 concentrations greater than 17%, loss of controlled and purposeful activity, unconsciousness, convulsions, coma, and death occur within 1 minute of initial inhalation.

The dangers of breathing in elevated concentrations of CO_2 are well known to people such as divers, submariners, anaesthetists and astronauts. But outside these specialist communities knowledge about the impact of breathing elevated concentrations of CO_2 is generally low. Concentrated CO_2 inventories may be present, for example as part of a fire suppression system, but the potential for persons to be exposed to CO_2 inhalation are usually localised and the associated safety risks can be effectively managed through localised hazard management measures.

With the advent of CCS, where pipeline systems are likely to have inventories of dense phase CO_2 in the order of 10s if not 100s of thousands of tonnes, the potential for widespread population exposure to air with hazardous concentrations of CO_2 will exist.

To effectively manage the risks associated with handling large quantities of CO_2, a full understanding of the impact CO_2 has on the human body is required. This section provides details of this.

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6.2   Human Respiratory System

The function of the respiratory system in humans is, first, to supply oxygen to the tissues and, second, to remove the metabolism produced CO_2. Air in the lungs is a mixture of inhaled air, water vapour from the respiratory passageways, and CO_2 excreted from the blood. In normal conditions the air in the lungs is a mixture of nitrogen ($\approx 75\%$), oxygen ($\approx 14\%$), CO_2 ($\approx 5\%$) and water vapour ($\approx 6\%$) /25/. Figure 6-1 presents a simple representation of the respiratory and circulatory systems showing the flow of blood and the transfer of CO_2 and O_2 within the lungs.
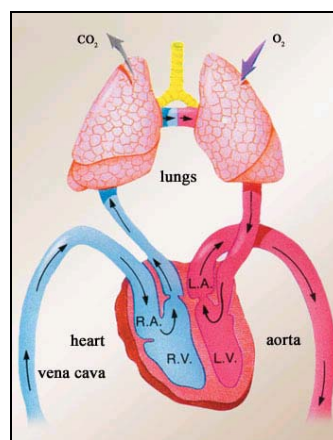

Figure 6-1: Human respiratory and circulatory systems

The air in the lungs is continually replaced with the breathing action with the oxygen being transferred to the blood and CO_2 diffusing out of the blood into the lungs. At rest, the average sized adult produces approximately 200ml of CO_2 per minute which is removed from the body through breathing /26/. The transport of oxygen from the lungs to the tissue cell requires three different events (1) diffusion of oxygen from the lungs into the blood, (2) transport of the blood through the arteries to the tissue capillaries, and (3) diffusion of oxygen from the capillaries to the tissue cell. The difference in partial pressures of the oxygen from the lungs to the cells results in the diffusion of the oxygen firstly to the blood and then to the cells.

When oxygen defuses from the lungs into the blood a small proportion of it becomes dissolved in the fluids of the plasma and red cells, but approximately 60 times that much combines immediately with the haemoglobin of the red blood cells and is carried in this combination to the tissue capillaries. Without the haemoglobin, the amount of oxygen that could be carried to the tissues would be only a fraction of that required to maintain life. As blood flows through the capillaries, 27% of the oxygen is usually removed from the haemoglobin however this percentage can rise to 75% when the demand from the cells increases. Therefore, haemoglobin acts as an oxygen buffer to automatically maintain cell oxygen levels without the need for an increase in blood flow.

Only about 5% of the CO_2 is transported in the blood in the dissolved state. About 95% of it diffuses from the plasma into the red cell where it undergoes two chemical reactions. First, CO_2 reacts with water to form carbonic acid which immediately reacts with the acid-base buffers of the cells and becomes mainly bicarbonate ions. This reaction prevents the acidity of the cell from

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becoming too great. Second, a few percent of the total CO_2 entering the red cell combines directly with the haemoglobin but not at the same point on the haemoglobin molecule as the reaction between oxygen and haemoglobin. Therefore, haemoglobin can combine with both CO_2 and oxygen at the same time. The CO_2 haemoglobin reaction occurs relatively slowly so that this method of CO_2 transport is much less important than transport in the form of bicarbonate ions.

It should be noted that CO_2's combination with haemoglobin is unlike the way carbon monoxide (CO) combines with haemoglobin which does so at the same point as the oxygen and in an almost identical way. CO also has an affinity to bind with haemoglobin that is approximately 210 times more than that of oxygen and therefore relatively low concentrations of CO in the air will result in a large proportion of the haemoglobin being unavailable for oxygen transport (e.g. 0.1% CO results in a 50% reduction in oxygen carrying haemoglobin and 0.2% CO will remove nearly all the haemoglobin available for oxygen transport). CO is termed a chemical asphyxiant as it is capable of starving the cells of the body of oxygen by preventing the oxygen from being transported around the body in the blood.

6.3 Response to Elevated CO_2 Concentrations

6.3.1 Overview

CO_2 is a colourless gas which, when inhaled can produce a sour taste in the mouth and a stinging sensation in the nose and throat. These effects result from the gas dissolving in the mucous membranes and saliva, forming a weak solution of carbonic acid. It is normally present in the atmosphere at a concentration of around 0.04% /27/. It is also a natural end product of human and animal metabolism. As a result, CO_2 dramatically influences the function of major vital processes, including control of breathing, blood vessel dilation or constriction (particularly in certain brain tissues), and body fluid acidity levels (i.e. pH levels).

Human respiration is controlled by the respiratory centre of the brain which keeps the basic rhythm of respiration continuous. The depth of respiration varies significantly in response to the need of the tissues for oxygen and the need to rid the tissues of CO_2. One of the most powerful stimuli known to affect the respiratory centre is CO_2.

The respiratory system acts as a physiologic buffer system /28/. It is controlled by a typical feedback mechanism where the respiratory centre responds directly to alterations in blood pH (i.e. changes in blood H+ concentrations for example as a result of increased CO_2 levels), and the lung ventilation rate in turn can regulate H+ concentration. When blood H+ concentrations rise above normal levels, lung ventilation is stimulated to reduce the concentration of CO_2 in the blood. When the H+ concentration falls toward normal level the stimulus for increased lung ventilation rate is removed and breathing returns to normal levels.

Greatly elevated CO_2 concentrations can lead to abnormal acidity of the blood (respiratory acidosis) if the capacity of the blood buffering system is exceeded. Apart from increasing the ventilation rate, the human body has no other significant means for controlling CO_2 concentration in the blood and body fluids.

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Hypercapnia is a condition where there is too much CO_2 in the blood. Hypercapnia is generally caused by inadequate lung ventilation (hypoventilation), lung disease, or diminished consciousness but it may also be caused by exposure to environments containing abnormally high concentrations of CO_2, or by re-breathing exhaled breath.

Symptoms of early hypercapnia include flushed skin, full pulse, irregular heart beat, muscle twitches, hand flaps, and possibly a raised blood pressure. In severe hypercapnia, symptoms progress to disorientation, panic attacks, hyperventilation, convulsions, unconsciousness, and death.

When elevated CO_2 levels are breathed in from the surrounding atmosphere the body's automatic response of increasing the depth and frequency of breathing will exacerbate the hazard.

There has been considerable research and experiments conducted to understand the body's response to elevated CO_2 concentrations. Specialist communities such as the medical profession, submariners, astronauts and pilots have all undertaken extensive and detailed work to gain a full understanding of the subject area.

Sources for information on CO_2 and the effect it has on humans can be found in the EPA's "Carbon Dioxide as a Fire Suppressant: Examining the Risks" report /13/, the National Research Council's "Spacecraft Maximum Allowable Concentrations for Selected Airborne Contaminants" report /29/and the NIOSH publication "criteria for a recommended standard … occupational exposure to CO_2" /30/.

Further details of the acute health effects associated with CO_2 are provided in Section 6.3.2 and in Section 6.3.3 the potentially beneficial effect of CO_2 at low exposure concentrations is discussed.

6.3.2   Acute Health Effects from High CO_2 Concentrations

CO_2 acts as both a stimulant and depressant on the central nervous system. Immediately after exposure to elevated CO_2 levels, the ventilation rate, total volume of air inhaled and exhaled during ventilation, CO_2 partial pressure in the lungs, and acidity of the blood are elevated. References for the details provided in this section can be found in the EPA report /13/.

Acute exposure to 1% and 1.5% CO_2 is tolerated quite comfortably with very little noticeable respiratory stimulation occurs until the inspired CO_2 concentration exceeds about 2%. After several hours' exposure to atmospheres containing 2% CO_2, headache and difficult breathing can occur with mild exertion.

A concentration of 3% CO_2 results in a measurable increase in ventilation rate and volume. CO_2 at this level also cause headaches, diffuse sweating, and difficult breathing at complete rest after an exposure period of several hours.

Exposure to 4 to 5% CO_2 for 15 to 30 minutes can produce headache and dizziness, increased blood pressure, and can produce uncomfortable breathing within a few minutes. Mental depression can occur following several hours of exposure to 5% CO_2.

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Exposure to a concentration of 6% CO$_2$ can produce hearing and visual disturbances within 1 to 2 minutes. Headache and difficult breathing can also result during exposure to 6% CO$_2$ in air after around 15 minutes.

Exposure to 7 to 10% CO$_2$ can produce unconsciousness or near unconsciousness within a few minutes. Other symptoms associated with the inhalation of CO$_2$ in this range include headache, increased heart rate, shortness of breath, dizziness, sweating, rapid breathing, mental depression, shaking, and visual and hearing dysfunction following exposure periods of as little as 1.5 minutes.

Exposure to concentrations in the range of 10% to 15% CO$_2$ will lead to dizziness, drowsiness, severe muscle twitching, and unconsciousness within a minute to several minutes.

Exposure of humans to CO$_2$ concentrations ranging from 17% to 30% will quickly (i.e. within one minute) result in loss of controlled and purposeful activity, unconsciousness, coma, convulsions, and death.

As previously noted, inhaling a concentration of CO$_2$ above 3% results in a measurable increase in ventilation rate and volume. If inhaled CO$_2$ concentration is increased above 3%, respiratory stimulation then increases sharply until inspired CO$_2$ concentrations of about 10% are reached. Between 10% and 30% inspired CO$_2$, the rate of increase in respiratory rate and volume reduces per unit of rise in inspired CO$_2$ until inhalation of 30% CO$_2$ in oxygen is reached at which point ventilation suddenly declines, and convulsions occur.

CO$_2$ also affects the body's circulatory system. If the concentration of CO$_2$ in the inspired air increases, the body will compensate by increasing the respiratory depth and rate with an accompanying increase in cardiac output. If the CO$_2$ in the breathing atmosphere continues to increase, the increases in cardiac and respiratory rates cannot effectively compensate (i.e. eliminate CO$_2$) and CO$_2$ will accumulate in the blood and other body tissues. A short-term exposure of 17 - 32 minutes in humans to 1% - 2% CO$_2$ has been shown to cause a slight increase in blood pressure. A 15 - 30 minute exposure to 5% - 7% CO$_2$ caused increases in blood pressure and blood flow to the brain (cerebral blood flow) and a decrease in blood flow resistance in the brain (cerebrovascular resistance) but no change in cardiac output.

The acute health effects that are seen following exposure to high concentrations of CO$_2$ are presented in Table 6-1.

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Table 6-1: Acute health effects of high concentrations of CO_2

CO_2 Concentration in Air (% v/v)	Exposure	Effects on Humans
17 – 30	Within 1 minute	Loss of controlled and purposeful activity, unconsciousness, convulsions, coma, death
>10 – 15	1 minute to several minutes	Dizziness, drowsiness, severe muscle twitching, unconsciousness
7 – 10	Few minutes	Unconsciousness, near unconsciousness
	1.5 minutes to 1 hour	Headache, increased heart rate, shortness of breath, dizziness, sweating, rapid breathing
6	1 – 2 minutes	Hearing and visual disturbances
	≤ 16 minutes	Headache, difficult breathing (dyspnea)
	Several hours	Tremors
4 – 5	Within a few minutes	Headache, dizziness, increased blood pressure, uncomfortable breathing
3	1 hour	Mild headache, sweating, and difficult breathing at rest
2	Several hours	Headache, difficult breathing upon mild exertion

6.3.3 Health Effects from Low CO_2 Concentrations

In the previous section, the acute health effects of high concentrations of CO_2 are detailed. In this section, the beneficial health effects of exposure to slightly elevated CO_2 concentrations in certain situations are discussed. References for the details provided in this section can be found in the EPA report /13/.

CO_2 is useful for counteracting the effects of oxygen deficiency /31/. In the presence of low oxygen, CO_2 is beneficial because it exerts a blood vessel dilating effect (vasodilator effect) on the blood vessels in the brain (cerebral blood vessels) /32/. Dilation of brain's blood vessels may account for the severe headache also produced by CO_2 inhalation.

Other beneficial effects of CO_2 in the presence of low oxygen include the fact that it increases the ventilation of the lungs, and it shifts the hemoglobin dissociation curve so that with a given oxygen saturation more oxygen is delivered to the tissues.

Uptake of oxygen into the bloodstream in low oxygen environments can therefore be enhanced by the presence of CO_2 but only within a narrow concentration range and in controlled conditions.

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6.3.4 Asphyxiation from Elevated CO_2 Concentrations

There is general alignment within the reference material that CO_2 concentrations greater than around 5% in respiratory air poses a threat to humans through hypercapnia and not primarily through its ability to asphyxiate by displacing oxygen from the atmosphere (e.g. like nitrogen) or from preventing the efficient transfer of oxygen via the blood (e.g. like carbon monoxide).

At normal atmospheric conditions air has, by volume, around 78% nitrogen, 21% oxygen, 1% argon and 0.04% CO_2. A release of CO_2 would increase the level of CO_2 in the air and in doing so decrease proportionately the other air components. In this situation, asphyxiation would occur when the level of oxygen in the air decreases significantly. The effects of asphyxiation are described by the British Cryogenics Council /33/ as presented in Table 6-2.

Table 6-2: Asphyxiation stages

Asphyxiation Stage	Oxygen Concentration (%v/v) Effects
1st	21 to 14% : Increased pulse and breathing rate with disturbed muscular coordination
2nd	14 to 10%: Faulty judgement, rapid fatigue and insensitivity to pain
3rd	10 to 6% : Nausea and vomiting, collapse and permanent brain damage
4th	Less than 6% : Convulsions, breathing stopped and death

The approximate relationship between decreasing oxygen concentration with the increase in CO_2 concentration, for example following a significant CO_2 leak, is shown in Figure 6-2.
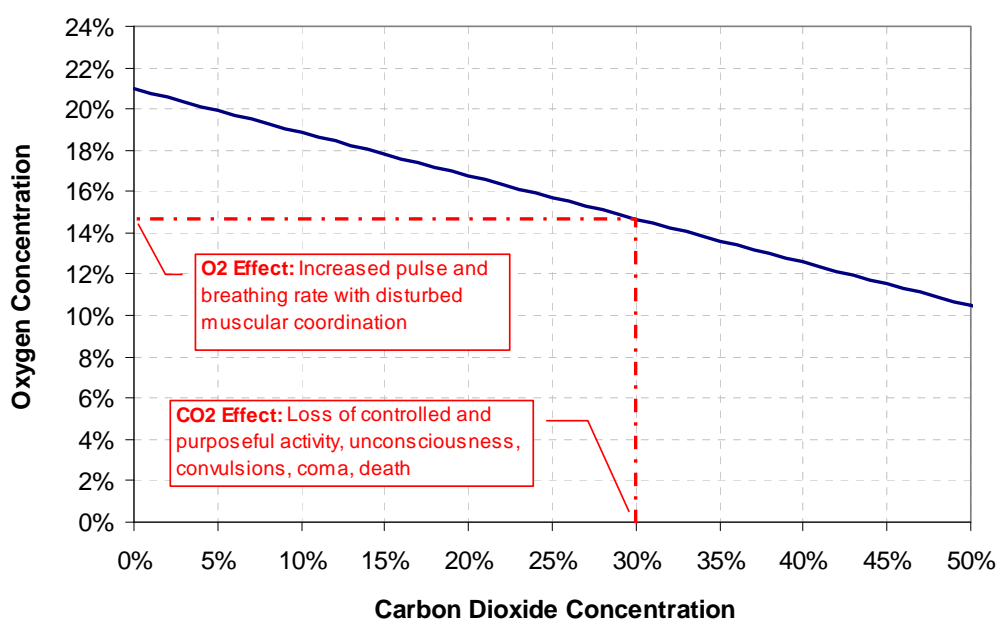
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Figure 6-2: Relationship between O_2 and CO_2 in air

The figure illustrates that when CO_2 is at 30%, the oxygen level will have been reduced to just under 15% and whereas a person breathing in this air composition would be mildly effected by the reduced O_2 (Table 6-2) they would be in a life-threatening situation as a result of the CO_2 (Table 6-1)

CO_2, like nitrogen, will displace oxygen but unlike nitrogen which does not have a neurological impact on humans, people would be at severe threat from increasing CO_2 concentrations well before they were from the reducing oxygen concentrations. Further supporting discussion on this subject can be found in a UK Health and Safety Executive Toxic Substances Bulletin /34/.

6.4   Occupational Exposure Limits

An occupational exposure limit (OEL) is an upper limit on the acceptable concentration of a hazardous substance in workplace air for a particular material or class of materials. It is typically set by competent national authorities and enforced by legislation to protect occupational safety and health. It can be a tool in risk assessment and in the management of activities involving handling of dangerous substances.

Regulatory and other recognised bodies around the world have published OELs and in some countries OELs have legal status. For example in the UK, OELs have legal status under the Control of Substances Hazardous to Health (COSHH) Regulations, and they are listed in the Health and Safety Executive (HSE) publication EH40, which is updated annually. UK employers must compare OELs in the list with exposure levels measured at work, to ensure that exposure is being controlled.

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In Norway, the Arbeidstilsynet (Central Labour Inspectorate) issues OELs. The Inspection has established a working group with representatives from the employers, employees and direction of the inspection. There are also values for Time Weighted Average (TWA), Short Term Exposure Limit (STEL) and Ceiling. There is also notation for issues such as carcinogenicity. The standards are recommendations and they are not legally binding until they are used by the labour inspection in orders or instructions for companies. The list is reviewed yearly.

It should be noted that just because a substance does not have an OEL does not mean that it is non hazardous.

All OELs assume that the exposed persons are healthy adult workers, although in some cases the OELs should also protect "sensitive subgroups". Normally, exposure limits are not valid for pregnant women and nursing mothers or other sensitive people, and specific action should be taken where necessary to protect these groups.

The most common limit values are air limit values defining the maximum "admissible" or "acceptable" concentration of a hazardous substance in the workplace air. This concentration varies from substance to substance according to issues such as the substances' physico-chemical characteristics.

The average exposure time in OEL lists is normally 8 hours per day (often referred to as TWA-8h or Time-Weighted Average - 8h). The OELs are usually defined under the assumption that a worker can be exposed to a substance for a working life of 40 years with 200 working days per year.

Even if the daily working time is longer than 8 hours, the daily dose based on the 8-hours-day cannot be exceeded. The limit of the OEL must be lower. For example, if there is a limit of 100 ppm for 8 hours, it must normally be reduced to 80 ppm for a 10-hours-day and to 67 ppm for a 12-hours working day.

Some substances have a ceiling value that should not be exceeded at any time to ensure protection against both acute effects, such as throat irritation, and chronic, long-term effects. For others, peak concentrations are determined. In these cases, one substance has two limit values. In addition to the "normal" 8-hours OEL there is a highest acceptable short-term or peak concentration limit, sometimes also referred to as a short-term exposure limit or STEL. These short-term OELs are intended to protect workers during brief exposure to substances. These exposure limits are often for 15 minutes and referred to as Short-Term Exposure Limits - 15 minutes (STEL - 15m) /35/.

As previously mentioned, OELs vary around the world and further details can be found from the International Occupational Safety and Health Information Centre website /39/. Table 6-3 contains details of some of the published CO_2 exposure limits for humans along with other reference criteria that are considered relevant when considering the management of personnel exposure and the management of emergencies.

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Table 6-3: Published exposure limits

Exposure Time	% CO_2	Comment	Reference
10 hours	0.50%	Time weighted average	NIOSH (US)
8 hours	0.50%	Time weighted average	OSHA (US)
8 hours	0.50%	Occupational Long Term Exposure Limit (LTEL)	COSHH HSE (UK)
60 mins	4%	Emergency Exposure Level for submarine operations	USA Navy
	2.5%	Emergency Exposure Level for submarine operations	National (US) Research Council
	5%	Suggested Long Term Survivability Exposure Limit	HSE (UK)
	2%	Maximum exposure limit	Compressed Gas Association 1990
20 mins	3%	Maximum exposure limit	Compressed Gas Association 1990
15 mins	1.5%	Occupational Short Term Exposure Limit (STEL)	COSHH HSE (UK)
	3%	Short Term Exposure Limit (STEL)	Federal occupational safety and health regulations (US)
10 mins	4%	Maximum exposure limit	Compressed Gas Association 1990
7 mins	5%	Maximum exposure limit	Compressed Gas Association 1990
5 mins	5%	Suggested Short Term Exposure Limit (STEL)	HSE (UK)
	6%	Maximum exposure limit	Compressed Gas Association 1990
3 mins	7%	Maximum exposure limit	Compressed Gas Association 1990
1 min	15%	Exposure limit	NORSOK (Norway)
<1 min	4%	Maximum Occupational Exposure Limit	Federal occupational safety and health regulations (US)

In most regions of the world companies have a legal and/or corporate duty to ensure that as far as reasonably practicable people are not exposed to CO_2 concentrations greater than the accepted exposure limits of the region or the company, which ever is more stringent.

6.5   MAH Risk Assessment Impairment Criteria

Major Accident Hazards (MAH) are generally considered to be those hazards that could pose significant harm to one or more of the following categories: a large number of people; the environment; a facility or infrastructure; or a company's reputation. They can be categorised as high consequence, low frequency events as opposed to occupation type hazards (e.g. slips, trips and falls) which are generally significantly lower consequence but more frequent events.

Examples of MAH events include the events at Bhopal, Flixborough, Seveso, Piper Alpha and Mexico City.

In some regions of the world (e.g. UK) there is a legal duty to demonstrate effective management of MAH risks down to an acceptable level.

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A major release of CO_2 has MAH potential. It is a substance that if it is released in sufficient quantity has the potential to cause harm to a large number of people (as well as other impacts). The natural up-welling of CO_2 within the Cameroon Lakes of Monoun (1984) and Nyos (1986), where the number of resulting fatalities were around 40 and 1700, respectively, illustrates the potential threat to human life when a large quantity of CO_2 is released (or escapes) into the atmosphere.

Dense phase CO_2 pipelines will contain tens and sometimes hundreds of thousands of tonnes of CO_2 which, if containment is lost, could foreseeably create a CO_2-rich cloud that could potentially threaten large geographical areas. The MAH risks associated with large scale CO_2 handling must therefore be robustly assessed in CCS projects.

The assessment of MAHs must be both suitable and sufficient, meaning, it must be based on sound understanding, use appropriate techniques and tools, have a breath and depth proportionate to the possible magnitude of the risk, and provide a basis for demonstrating that the risks associated with the hazards are being managed effectively. An essential part of any risk assessment is the impairment criteria used to assess the potential consequences of the hazardous scenarios examined. For example in a fire risk assessment, the recommended thermal radiation flux criteria for immediate fatalities to all personnel local to a fire is 35 kW/m^2 /36/ /37/.

It should be noted that MAH impairment criteria are criteria required for undertaking a numeric risk quantification exercise and do not have a direct relationship with, or impact on, industry-accepted occupational exposure limits (e.g. the LTELs and STELs as presented in Table 6-3). MAH impairment criteria are used purely to enable an estimate to be made of the risks (in terms of potential fatality numbers) associated with the various MAHs that are identified within a facility or operation so as to enable effective MAH risk management. It is accepted practice to base MAH impairment criteria on the 50% mortality criteria (i.e. LC_{50} or LD_{50}) /37/.

The UK's Health and Safety Executive (HSE) has developed Dangerous Toxic Loads (DTLs) relating to levels of harm substances pose to people. The DTL describes the exposure conditions, in terms of airborne concentration and duration of exposure, which would produce a particular level of harm in the general population. Two DTLs are defined by the HSE /37/ these being the Specified Level Of Toxicity (SLOT) and the Significant Likelihood Of Death (SLOD).

In general terms, exposure to the SLOT level would result in many people with serious injury requiring prolonged treatment and exposure to the SLOD level would result in many people dying.

The harm level expressed by a given substance in the air is influenced by two factors, the concentration in the air (c) and the duration of exposure (t). A functional relationship between c and t has been developed by the HSE, such that the end product of this relationship is a constant called the Toxic Load.

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For CO_2, the following expressions have been defined for the SLOT DTL and SLOD DTL:

SLOT DTL: $1.5 \times 10^{40} = c^8 . t$

SLOD DTL: $1.5 \times 10^{41} = c^8 . t$

The above expressed graphically as shown in Figure 6-3.
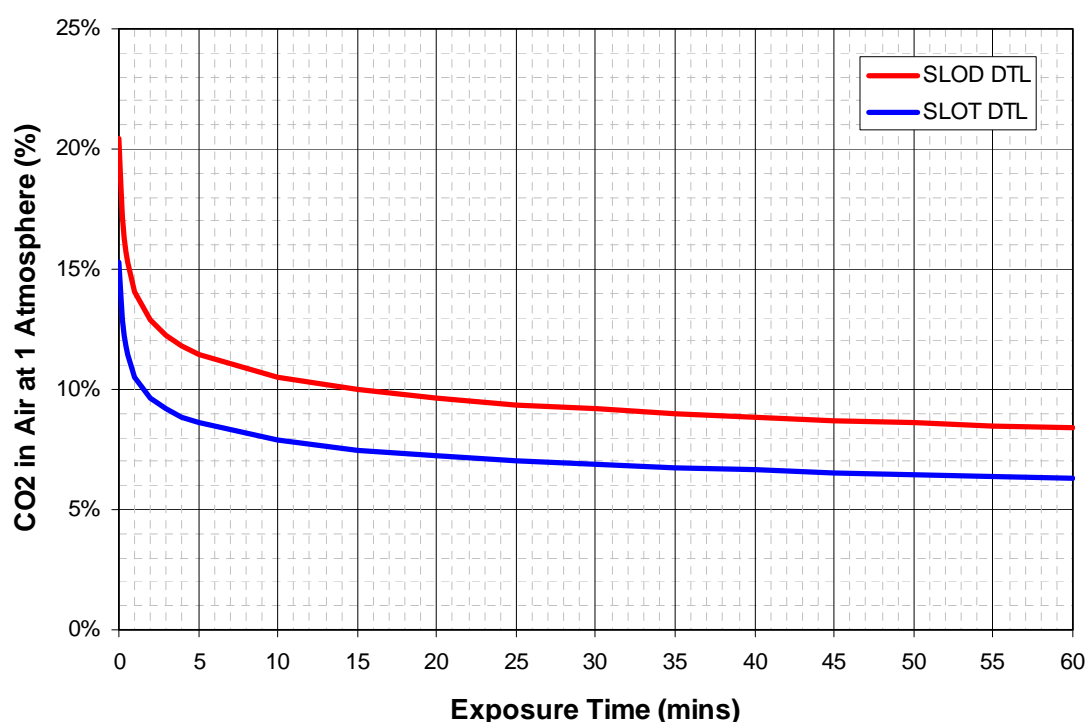
SLOT DTL = Specified Level Of Toxicity Dangerous Toxic Load
SLOD DTL = Significant Likelihood Of Death Dangerous Toxic Load

Figure 6-3: HSE SLOT and SLOD curves for CO_2

When undertaking a MAH risk assessment, assessors are required to provide estimates of the extent (i.e. hazard ranges and widths) and severity (i.e. how many people are affected, including the potential numbers of fatalities) of the consequences of each identified major accident hazard. For an evenly distributed population, the number of fatalities resulting from a harmful substance release may be approximated by estimating the number of people inside the concentration contour leading to the mortality of 50% (LC_{50}) of an exposed population which is equivalent to the defined SLOD DTL. This approximation results from the assumption that those people inside the SLOD contour who do not die (due to factors such as physiology, fitness levels, etc) will be balanced by an approximately equal number outside the SLOD contour who do die (again, due to factors such as physiology, state of health etc.)

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In addition, the number of people injured (serious and minor) by the release may be approximated by the number people estimated to be between the SLOD and SLOT DTL contours (i.e. the SLOT DTL contour is taken as a pragmatic limit for injuries).

6.6 Hazardous Substance Solutions

Supercritical CO$_2$ is a highly efficient solvent but when it undergoes a significant pressure reduction, for example during a leak, it changes to a gaseous state with virtually no solvent capability. This characteristic of CO$_2$ introduces the potential for any compounds or elements that are in solution within the CO$_2$ inventory being precipitated out at the point of pressure drop. The concentrated release of any hazardous substance held in solution could then result in harmful human exposure or environmental damage.

6.7 Hazardous Substance Mixtures

It is very unlikely that CO$_2$ streams will be 100% pure CO$_2$, some other substances will either be mixed and/or in solution with it (see Section 6.6). Substances such as hydrocarbons, hydrogen sulphide (H$_2$S) and carbon monoxide (CO) as well as various other impurities may well be present. To determine the potential harm that the CO$_2$ mixture could pose on people exposed to it, a study of the mixture should be undertaken.

Prior to considering the combined effects of a mixture, individual impairment criteria need to be developed for the relevant harmful components. To ensure a level of consistency, it is important to base these criteria on levels where each of the harmful concentrations results in similar physical effects to personnel. The impairment criteria need to be based, where possible on industry recognised data sources such as:

- HSE COSHH Levels / Workplace Exposure Levels /38/
- International Workplace Exposure Levels /39/

For CO$_2$, criteria based on the work described in the previous sections can be used.

When two or more harmful substances are mixed, the resulting harm level may be less than, equal to, or greater than, the sum of the individual substances, depending on whether the harmful effects are additive, synergistic, antagonistic, lead to potentiation or inhibition or remain independent.

These effects are defined below for two harmful components a & b:

Additive / Addition i.e. combined effect is equal to the sum.
$$a = 2, b = 2 \quad a + b = 4$$

Synergistic / Synergism i.e. combined effect is greater than the sum.
$$a = 2, b = 2 \quad a + b > 4$$

Antagonistic / Antagonism i.e. combined effect is less than the sum.
$$a = 2, b = 2 \quad a + b < 4$$

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Potentiation i.e. a non harmful component plus a harmful component increases the harm effect of the harmful component.

$$a = 0, b = 2 \quad a + b > 2$$

Inhibitive / Inhibition i.e. exposure to a non harmful component decreases the harm effect of another

$$a = 0, b = 2 \quad a + b < 2$$

Independent i.e. the harmful components affect different organs

$$a = 2, b = 2 \quad a + b = 2$$

The additive approach is often used by Occupational hygienists, but is considered to have two significant issues:

- It has only been demonstrated in animals (for acute effects).
- The approach is only considered valid if the harmful agents considered bring about the same end point, attack the same organ, or have similar mode of action.

Despite this, the approach is considered conservative /40/.

6.8 Cryogenic Impact

The venting of dense phase CO$_2$ to atmosphere whether through a vent or leak will result in a phase change as the CO$_2$ depressurises through the release aperture with vapour and, depending on the inventory temperature, solid CO$_2$ being formed. Where the inventory temperature is below the critical point temperature the rapid expansion combined with the phase change will result in a very high velocity, very low temperature, two phase flow. Anyone caught in the extremely cold jet of gas and entrained -78°C solids will suffer cryogenic burns and potentially, impact injuries. Inhalation of such a cold atmosphere would also cause severe internal injuries.

6.9 International Classification of CO$_2$

Hazard Classification is the process for assessing the dangers from substances and mixtures and then ensuring that appropriate labelling is used so as to minimise the dangers. Across the world, countries and regions have adopted different Hazard Classification protocols and this has led to challenges when substances are transported between countries and regions.

In the UK, the Health and Safety Commission's Chemicals (Hazard Information and Packaging for Supply) Regulations 2002 (CHIP) underpin Great Britain's chemical management framework /38/. CHIP implements the Dangerous Substances Directive, the Dangerous Preparations Directive, and the Directive on Safety Data Sheets. These Directives, through CHIP, place a number of duties on chemical suppliers. They include ensuring that dangerous substances and preparations ("chemicals") are correctly classified (a process which identifies all hazards to human health and/or the environment), labelled accordingly, and safely and appropriately

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packaged. A further duty requires suppliers who are supplying dangerous chemicals for use at work to provide a safety data sheet.

Since 1990, activities have been underway at the international level to establish a Globally Harmonised System (GHS) for classification and labelling of chemicals and mixtures in order to eliminate existing barriers to trade. The GHS is intended to become a 'practical and coherent standard' for chemical hazard communication within the transport chain, at the workplace and for consumers with potentially significant impact on the chemical safety legislation of all countries.

For a substance or mixture under consideration, decision logic is used to assess whether it satisfies the defined GHS criteria and therefore is "Classified" or is "Not Classified".

CO_2 is a substance that is "Not Classified" within the GHS and other systems.

That said, a substance or mixture that is "Not Classified" may still have hazardous properties albeit at a quantity, concentration, dose or other characteristic that is outside the threshold limits defined in the classification criteria. As detailed in Section 6.3, CO_2 at elevated concentrations is known to have toxicological effects on the human body, but this apparent disparity is rational as discussed below.

Within the GHS Acute Toxicity criteria, any substance that has a median lethal concentration (LC_{50}) of less than 5000 parts per million (ppm) (0.5% v/v in air) is Classified within one of the five defined Hazard Categories. A substance with a LC_{50} concentration greater than 5000 ppm is defined as "Not Classified".

As noted in Section 6.5 and presented in Figure 6-3, the HSE's SLOD DTL (LC_{50}) curve is well above a concentration of 5%. It can therefore been concluded that CO_2 is correctly classified as a "Not Classified" substance as its harmful levels are at least one order of magnitude lower than that required to categorise it as a Classified Acute Toxicity substance.

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7 ENVIRONMENTAL IMPACT

CO_2 may affect the flora and fauna with which it comes into contact, from microbes in the deep subsurface near injection point to plants and animals in shallower soils and at the surface. The effect of elevated CO_2 concentrations would depend on several factors, for example, for terrestrial ecosystems the type and density of vegetation; the exposure to other environmental stresses; the prevailing environmental conditions like wind speed and rainfall, the presence of low-lying areas; and the density of nearby animal populations. This section will coarsely discuss impact on onshore and offshore environment given CO_2 exposures. Two recent reports, the IPCC Special Report on Carbon Capture and Storage /18/ and the OSPAR report "Effects on the marine environment of ocean acidification resulting from elevated levels of CO_2 in the atmosphere" /41/ give a good and detailed overview of observations and results from research within the field. For further details around the effect on onshore and marine environment these two reports, and other references mentioned, should be consulted. The discussion will focus on possible effects given CO_2 exposure in general. Scenario descriptions and corresponding probabilities is not a part of this chapter, and long term effects from CO_2 exposure are not elaborated in the discussion since releases from capturing; transport and injection presumably are of a short-term character.

7.1 Onshore Environment

According to IPCC /18/ the effect of CO_2 on subsurface microbial populations is not well studied. A low-pH, high- CO_2 environment may favour some species and harm others. In strongly reducing environments, the injection of CO_2 may stimulate microbial communities that would reduce the CO_2 to CH_4; while in other reservoirs, CO_2 injection could cause a short-term stimulation of Fe(III)-reducing communities /42/. From an operational perspective, creation of biofilms may reduce the effective permeability of the formation.

Leaks from, for example, buried pipeline or from injection of CO_2 can also find its way to the surface. While elevated CO_2 concentrations in ambient air will enhance plant growth and photosynthesis, the negative effect from the high CO_2 levels in the soil will probably be higher. CO_2 fluxes large enough to significantly increase concentrations in the free air will typically be associated with much higher CO_2 concentrations in soils /18/. The main characteristic of long-term elevated CO_2 zones at the surface is the lack of vegetation. New CO_2 releases into vegetated areas cause noticeable die-off. In those areas where significant impacts to vegetation have occurred, CO_2 makes up about 20–95% of the soil gas, whereas normal soil gas usually contains about 0.2–4% CO_2. Carbon dioxide concentrations above 5% may be dangerous for vegetation and as concentration approach 20%, CO_2 becomes phytotoxic (IPCC, 2005). Carbon dioxide can cause death of plants through 'root anoxia', together with low oxygen concentration /43/ /44/. One example of plant die-off happened in Mammoth Mountain in California, USA. In 1989, a series of small earthquakes occurred near Mammoth Mountain. A year later, 4 ha of pine trees were discovered to be losing their needles and by 1997, the area of dead and dying trees had expanded to 40 hectare /45/. Soil CO_2 levels above 10–20% inhibit root development and decrease water and nutrient uptake; soil oil-gas testing at Mammoth Mountain in 1994 discovered soil gas readings of up to 95% CO_2 by volume. Total CO_2 flux in the affected areas averaged about 530 t day^{-1} in 1996. Measurements in 2001 showed soil CO_2 levels of 15–90%, with flux rates at the largest affected area (Horseshoe Lake) averaging 90–100 t CO_2 day^{-1} /46/ /47/. A

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study of the impact of elevated CO$_2$ on soils found there was a lower pH and higher moisture content in summer. Wells in the high CO$_2$ area showed higher levels of silicon, aluminum, magnesium and iron.

According to IPCC /18/ there is no evidence of any terrestrial impact from current CO$_2$ storage projects. Examples of possible impacts from CO$_2$ leakage can therefore be found from volcanic activity, however it is important to mention that these leakages represent a poor analogue to leakages from, for example, CO$_2$ storage sites. For instance, the CO$_2$ leakage from the plant die-off example in Mammoth Mountain was in the order of a 0.2%/year leak from a storage site of 100Mt CO$_2$. This corresponds to a fraction retained of 13.5% over 1000 years, thus this is not representative for a typical storage site.

CO$_2$ leaks might impose a risk to groundwater. Dissolved CO$_2$ forms carbonic acid that can change the pH in the solution causing mobilization of (toxic) metals, sulphate or chloride. A change in pH could also give the water an odd odour, colour or taste. In the worst case, contamination might reach dangerous levels, excluding the use of groundwater for drinking or irrigation. In addition to the change of pH, the injection of CO$_2$ causes changes in pore-fluid pressure. These changes can lead to displacement of brines, which again can lead to migration into shallower drinking water formations. In the worst case infiltration of saline water into groundwater or into the shallow subsurface could impact wildlife habitat, restrict or eliminate agricultural use of land and pollute surface waters /18/ .

Animals exposed to high CO$_2$ concentrations will experience the same effects as described for humans in Chapter 6 and are caused by hypercapnia (elevated levels of CO$_2$ in the bloodstream) and asphyxiation leading to respiratory distress, narcosis and mortality. The extent of effect from the elevated CO$_2$ concentration will vary between species due to difference in, for example, in behaviour and body size.

7.2   Offshore Environment

Several studies have been carried out in order to identify the effect of CO$_2$ on marine environment and many of them are related to effects from CO$_2$ ocean storage. As mentioned in the introduction, this section describes possible effects given exposure of elevated CO$_2$ concentrations and the findings and conclusions are therefore relevant also for activities that can lead to discharge of CO$_2$ in the ocean that possibly can lead to the same concentrations. However, some of the effects are related to long term CO$_2$ exposure (as can be the situation with ocean storage) and such effects are not included in this section as the CO$_2$ exposure from the activities included in the scope is of limited duration, as a significant leak from a pipeline is likely to be discovered and remediated within a short period of time after a failure.

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7.2.1 Sensitivity towards CO_2 Effects

The sensitivity towards CO_2 exposure is dependant on how stable the surrounding environment is and how the organisms have adapted to the surroundings. It will also vary from species to species.

According to IPCC /18/ physiochemical factors in the deep sea vary little over time and this has through evolutionary selection probably eliminated organisms apt to handle environmental perturbation. As a result, deep-sea organisms may be more sensitive to environmental disturbance than their shallow water cousins /48/.

Deep-sea ecosystems may take a long time to recover from disturbances that reduce population size. Because of the energy-limited environment of the deep sea organisms have adapted by limiting investment in reproduction, thus most deep-sea species produce few offspring. Due to their low metabolic rates, deep-sea species tend to grow slowly and have much longer lifespans than organisms in the upper layer of the ocean. This means that populations of deep-sea species will be greatly affected by the loss of individual larvae. Upon disturbance, recolonization and community recovery in the deep ocean follows similar patterns to those in shallow waters, but on much longer time scales. In contrast to organisms living in the deep sea (and also in sea in general) species living in marine sediments, especially in the intertidal zone, are regularly exposed to changing CO_2 concentrations and thus may be better adapted to high and variable CO_2 concentrations.

Fish may be able to avoid contact to high CO_2 exposure because they possess highly sensitive CO_2 receptors that could be involved in behavioural responses to elevated CO_2 levels /49/. In addition, compared to squid or other invertebrates, fish appear to be less sensitive to added CO_2, probably due to their lower metabolic rate, presence of red blood cells to carry oxygen, existence of a venous oxygen reserve, tighter epithelia, and more efficient acid-base regulation /18/. However, not all animals avoid low pH and high concentrations of CO_2; they may actively swim into CO_2-rich regions that carry the odour of potential food.

Direct effects of dissolved CO_2 on diving marine air breathers (mammals, turtles) can likely be excluded since they possess higher pCO_2 values in their body fluids than water breathers and gas exchange is minimized during diving. They may nonetheless be indirectly affected through potential CO_2 effects on the food chain.

7.2.2 Changes in Chemical Composition and Physiological Effects

CO_2 dissolved into water changes the chemical composition of the sea water in several ways:

- CO_2 dissolves into water causing a reduction in the pH of the water, through the formation of carbonic acid /51/
$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^- + H^+$$

- There will be a decline in carbonate ion (CO_3^{2-}) concentrations as they react with increased concentrations of CO_2 /41/
$$CO_2 + CO_3^{2-} + H_2O \rightarrow 2HCO_3^-$$

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- Increase the partial pressure of CO_2 (pCO2)

Each of these ways will have an effect on marine environment. Typically, tolerance limits to CO_2 have been characterized by changes in ocean pH or pCO_2 /51/ /52/. However, changes in molecular CO_2, carbonate, and bicarbonate concentrations in ambient water and body fluids may each have specific effects on marine organisms /53/. In water breathers like fish or invertebrates the acute effect of CO_2 accumulation is more severe than that of the reduction in pH or carbonate-ion concentrations. As an example, fish larvae are more sensitive to low pH and high CO_2 than low pH and low CO_2 /18/. Reduced pH, not directly involving CO_2 may also have an impact on marine environment. Studies on effect on aquatic organisms from lowered pH have mainly focused on freshwater organisms /54/. Observed consequences of lowered water pH (at constant pCO_2) include changes in productivity in algae and heterotrophic micro-organisms, changes in biological calcification/ decalcification processes, and metabolic impacts on zooplankton species, ocean bottom species, and fish /18/. Low pH conditions will generally increase the proportion of biologically available free metals /55/ /56/.An increased availability of free forms of metals is of the greatest toxicological significance /57/. It is difficult to say to what extent these effects will impact the environment given the relatively short term CO_2 exposure which is the focus in this report.

Cold blooded water breathing animals will suffer of hypercapnia in the same way as organisms in onshore environment when surrounded by high concentration of CO_2. Mainly through diffusion across respiratory surfaces CO_2 will accumulate in the body and will be responsible for most of the effects observed in animals (reviewed by Pörtner and Reipschläger /53/, Seibel and Walsh /50/, Ishimatsu *et.al.* /58/, /59 and Pörtner *et.al.,* /60/, /61/).

Anasthesia and narcotic effects due to CO_2 uptake and accumulation has been observed in deep-sea animals close to hydrothermal vents or experimental CO_2 exposure. Among invertebrates, this type of CO_2 sensitivity may be highest in highly complex, high performance organisms like squid, e.g. blue-blooded squid which do not possess red blood cells (reviewed by Pörtner *et.al.,* /60/). Acute CO_2 exposure causes acidification of the blood, will hamper oxygen uptake and binding at the gills and reduce the amount of oxygen carried in the blood and at high concentration could cause death /18/. At high CO_2 concentrations animals can asphyxiate because the blood cannot transport enough oxygen to support metabolic functions. Model calculations predict acute lethal effects with a rise in pCO_2 by 6500 ppm and a 0.25 unit drop in pH. Acute CO_2 sensitivity varies between squid species. Tests on shallow water fish have shown short-term limits of adult fish at a pCO_2 of about 50000 to 70000 ppm, in other words a relatively high tolerance to added CO_2. European eel has even higher tolerance up to 104000 ppm (Ishimatsu et.al. /58/, Pörtner et.al. /60/). With mean lethal CO_2 levels of 13000 to 28000 ppm, juveniles are more sensitive to acute CO_2 stress than adults. In all of the cases, the immediate cause of death appears to be entry of CO_2 into the organism, and not primarily some other pH-mediated effect.

A water column release scenario could cause acute effects in areas where pCO_2 plumes reach significantly above 5000 ppm of atmospheric pressure (for the most sensitive squid) or above 13000 or 40000 ppm for juvenile or adult fish, respectively. For long time exposure one can expect effects on marine fauna in areas where pCO_2 are more than 400-450 ppm or associated moderate pH changes by about 0.1-0.3 units /18/. The effects are expected primarily in marine invertebrates /61/ and possibly, unicellular organisms.

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The table below is taken from IPCC /18/ and gives a summary of physiological and ecological processes affected by CO_2 based on numerous reference studies. The table do not differentiate between negative and positive effects and does not give any indication of the criticality of the effects. Some of the effects are related to more long term exposure while others are more related to short term exposure; the table does not distinguish between these to ways of exposure. However, the table gives a good overview of the physiological and ecological processes affected by CO_2.

Table 7-1: Physiological and ecological processes affected by CO_2

Affected processes	Organisms tested
Calcification	• Corals • Calcareous benthos and plankton
Acid-base regulation	• Fish • Sipunculids • Crustaceans
Mortality	• Scallops • Fish • Copepods • Echinoderms/gastropods • Sipunculids
N-metabolism	• Sipunculids
Protein biosynthesis	• Fish • Sipunculids • Crustaceans
Ion homeostasis	• Fish, crustaceans • Sipunculids
Growth	• Crustaceans • Scallops • Mussels • Fish • Echinoderms/gastropods
Reproductive performance	• Echinoderms • Fish • Copepods
Cardio-respiratory functions	• Fish
Photosynthesis	• Phytoplankton*
Growth and calcification	
Ecosystem structure	
Feedback on biogeochemical cycles (elemental stoichiometry C:N:O, DOC exudation)	

* note that listed effects on phytoplankton are not relevant in the deep sea, but may become operative during large-scale mixing of CO_2

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8 DESIGN, OPERATION AND ENGINEERING HAZARDS

8.1 Materials and Pipeline Issues

8.1.1 Material Compatibility

Supercritical CO_2 is used as an industrial solvent possessing a low dielectric constant. Because of its low dielectric constant, it is not corrosive to metallic materials under supercritical condition. However, the solvating ability must be taken into account in the selection of organic materials used for seals, gaskets, internal lining, and other safety or integrity-critical components.

Generally, elastomers do not respond well to exposure to dense phase CO_2 /66/. Problems have been reported with the use of standard Nitrile, Polyethylene, some fluorelastomers, chloroprene and to some extent ethylene-propylene compounds. Swelling of the elastomer is attributed to the solubility/diffusion of the pressurized CO_2 into the bulk material.

With dense phase CO_2 explosive decompression of the elastomer can occur. This phenomenon occurs when system pressure is rapidly decreased and the gases that have permeated or dissolved into the elastomer expand. In a mild case, the elastomer will only show blistering (due to the expansion of the diffused CO_2), but potentially rupture may occur. These issues may be more severe with higher operating pressures and larger pressure differentials. Hence, there is a need for in-depth knowledge of the explosive decompression properties of seal and gasket materials.

8.1.2 Internal Corrosion

CO_2 in combination with free water is well known from the oil and gas industry to form carbonic acid which is highly corrosive to carbon steels /69/. It is, however, presumed that CO_2 corrosion, or sweet corrosion, will not take place unless the moisture concentration is sufficiently high to result in the formation of a condensed aqueous phase. Pure, dry CO_2 is essentially non-corrosive even at supercritical conditions. Carbonic acid can lead to corrosion rates exceeding 10 mm/y, depending on the CO_2 partial pressure, temperature, and the presence of other impurities. A defective dehydration unit within the CO_2 capture facility could lead to sufficient moisture in the CO_2 leading to precipitation of an aqueous phase along the pipeline. If this aqueous phase collects at low points, corrosion could be an immediate issue. In contrast to CO_2 gas, dense phase CO_2 has the ability to store several hundred ppm of water depending on the temperature and other impurity concentrations. However, if the pressure falls, water may precipitate out and create carbonic acid.

No special actions are expected if the pipeline is carrying dense CO_2 with no free water or provided that the pipeline is made of corrosion resistant material. However, for pipeline material in 13%Cr steel, there may be restriction with respect to the operational temperature in the combination with a high partial pressure of CO_2 /68/.

Aqueous CO_2 corrosion has been studied extensively and forms a serious problem for pipeline operations where the chosen material is carbon steel. For longer pipelines, carbon steel is about the only economically feasible material choice for dense phase transport of CO_2, balancing material cost with the mechanical strength needed to withstand the internal high pressures and the external loads.

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Major studies have been conducted regarding CO$_2$ corrosion in oil and gas pipelines for hydrocarbons containing several mole% CO$_2$. However, very little experimental work has been carried out regarding CO$_2$ corrosion in pipelines at the high partial pressures encountered when transporting high purity CO$_2$ /66/ /67/.

The major concerns and uncertainties that remain to be investigated for a better understanding of corrosion issues in transporting dense CO$_2$ can be summarized as follows:

- <u>Modelling of corrosion rates</u> Understanding the phase behaviour and chemical speciation in CO$_2$ is an important component of modelling corrosion. At present few models exist to enable accurate speciation in dense CO$_2$ containing moisture and other impurities. Several CO$_2$ dependent chemical, electrochemical and mass transport processes occur simultaneously. These are depending on a variety of parameters, including CO$_2$ partial pressure, chemical speciation, and temperature. All this will have to be accounted for in the models. At high partial pressures the existing models tend to significantly overestimate the corrosion rates because of lack of accurate speciation information. Recent modelling using OLI Systems Analyzer models has shown some promise, but needs further data to engender higher confidence in the predicted results.

- <u>Presence of impurities</u>. Furthermore, carry-over of small concentrations of amine, gaseous impurities such as SO$_2$ and NO$_2$, have been shown to significantly affect corrosion rates in the condensed phase /67/. The presence of O$_2$, H$_2$S, SO$_2$ and NO$_x$ all have an influence towards higher corrosion rates, whereas amine carry-over may decrease corrosion rates. The mechanism of CO$_2$ corrosion in the presence of impurities is not entirely understood.

Drying of CO$_2$ to water concentrations below the dew point for operating conditions is thus regarded as effective corrosion prevention. The technology for drying of CO$_2$ is well known and can be applied at reasonable cost. Control of sweet corrosion is therefore regarded as a fully feasible for transport of CO$_2$ from a capture site to a storage site as part of a CCS solution. There might be situations where some water drop-out from CO$_2$ is unavoidable. There could be accidental situations which lead to wet CO$_2$ in the pipeline, such as accidental injection of wet CO$_2$ from the CO$_2$ capture plant or induction of seawater in a situation where internal overpressure is not maintained /70/.

Frequent pipeline inspections are likely to be needed to ensure internal corrosion is being effectively managed and is within acceptable limits. Moisture management and record keeping will be vital to maintain safe operations.

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8.1.3   Pipeline Fracture Propagation

Fracture propagation and arrest in high pressure pipelines has been the subject of study for many years but there is only limited experience with CO_2 pipelines. Propagating fractures initiate at sites where an initial flaw, most often the result of corrosion or mechanical damage (e.g. digger impact or anchor impact if pipeline is subsea), has exceeded the critical length or crack tip opening displacement.

There are two fracture failure mechanisms, namely, brittle and ductile, and both can result in pipelines unzipping very rapidly along a considerable distance (e.g. hundreds or thousands of meters).

In brittle failures the crack propagation is close to the speed of sound in the metal (400+ m/s) which will be faster than the speed the depressurization front can travel along the pipeline. In other words, the crack tip is ahead of the depressurization front caused by the releasing fluid and therefore it continues until there is a transition in the pipeline (e.g. a block valve) that changes the properties of the toughness of the material.

Avoidance of a propagating brittle fracture in a pipeline is by ensuring that the pipeline material toughness is sufficiently high at the lowest material temperature that could realistically occur to prevent a brittle facture. One aspect of a dense phase CO_2 release is the potential for very cold temperatures that may (depending on inventory conditions) occur at the release point due to the Joule-Thomson effect and the formation of solid CO_2 at -78˚C. The toughness of CMn steels will decrease as the temperature decreases.

In ductile failures, it is a race between the crack propagation velocity and the speed at which the pipeline depressurizes through the growing rupture. The crack will continue to propagate with a speed that is much slower than for a brittle fracture until decompression causes the hoop stress in the pipe to fall below the arrest level (i.e. the forces in the pipe from the internal pressure drops to below the fracture toughness of the pipeline). Due to the phase change that occurs at the release point of a CO_2 pipeline, the depressurization may be relatively slow therefore indicating that the distance a ductile failure may run before it arrests may be significant.

The ductile fracture arrest properties at a given temperature and pressure depend on the wall thickness and the material properties, particularly fracture arrest toughness. Ductile propagating fractures are controlled by:

- Ensuring the pipe has sufficient fracture toughness to tolerate material flaws without fracturing.

- Ensuring the pipe has sufficient toughness to absorb sufficient energy to arrest a ductile failure should one start to run. If the base material of the pipeline has insufficient toughness then the addition of fracture arrestors can be added at appropriate distances apart.

In the US, crack arrestors are used on a number of CO_2 pipelines with spacing between arrestors ranging from over 3km to 300m. Crack arrestors are normally rings of metal, tightly bonded to

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the outer surface of the pipeline. They function as a local increase of the wall thickness. In addition, on segmented lines the housings of the inline block valves can double as fracture arrestors /66/.

Should a pipeline propagating fracture occur, the contents of a pipeline can be released within a very short period, and, depending on the pipeline contents and location, this leading to a potentially catastrophic consequence.

Further work is required to fully understand CO_2 pipelines in relation to propagating failures. In particular further knowledge on transient behaviour of the CO_2 inventory during a release as well as validating the equations of state of dense phase CO_2 with impurities is required. Guidance on fracture arrestors and their spacing is also required which aligns with risk-based hazard management.

8.1.4 Free-span Stress

Re-using existing pipeline systems that has been in service for natural gas (typical density ~50 - 300kg/m³) for dense phase CO_2 (~1000 kg/m³) will cause a significant increase in weight that have to be reviewed to ensure the areas of free-span are acceptable. The change to CO_2 would also affect the dynamic response of spans.

8.2 Operation and Engineering

8.2.1 Solids Formation

Thermodynamic theory, as described in Section 2.3 determines that CO_2 when released to the atmosphere will be released either as a pure vapour or as a two phase mixture of solid phase CO_2 and vapour phase CO_2 (i.e. liquid phase CO_2 cannot exist at atmospheric pressure).

The Temperature/Entropy (T-s) diagram for CO_2 is useful for understanding of the post-release condition of CO_2, which again is dependent on the upstream release point and the thermodynamic path. Figure 8-1 illustrates the CO_2 T-s diagram, where three different initial conditions (denoted A, B and C) are highlighted. An isenthalpic approach (see Section 2.3) is assumed as basic assumption for establishing the post-release condition, which is marked as A*, B*and C* at the line of constant pressure of 1 bar.

From Figure 8-1 it can be seen that for the starting condition represented by the point C, an expansion along the constant enthalpy line would result in the supercritical CO_2 cooling into the vapour phase (point C*). Hence, the path of expansion does not end in the region of solid and vapour and no solids are expected to form upon release for the given initial conditions.

For the initial conditions A and B, it can be seen that the lines of constant enthalpy enter into the liquid+vapour region and then into the solid+vapour region (points A* and B*), and therefore solid CO_2 will be formed. The relative proportion of solid versus vapour can be estimated from

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where the constant enthalpy line intersects with the 1 bar line using the Lever Rule. For example, if the intersection point is close to the vapour line (i.e. right end of the horizontal 1 bar line) there would be virtually no solid CO_2 present, however, if the intersection point was approximately half way along the 1 bar line then the masses of solid and vapour would be approximately the same. For the illustrative example in Figure 8-1, the A* post-release point will have the larger portion of solids in the mixture compared to B*.
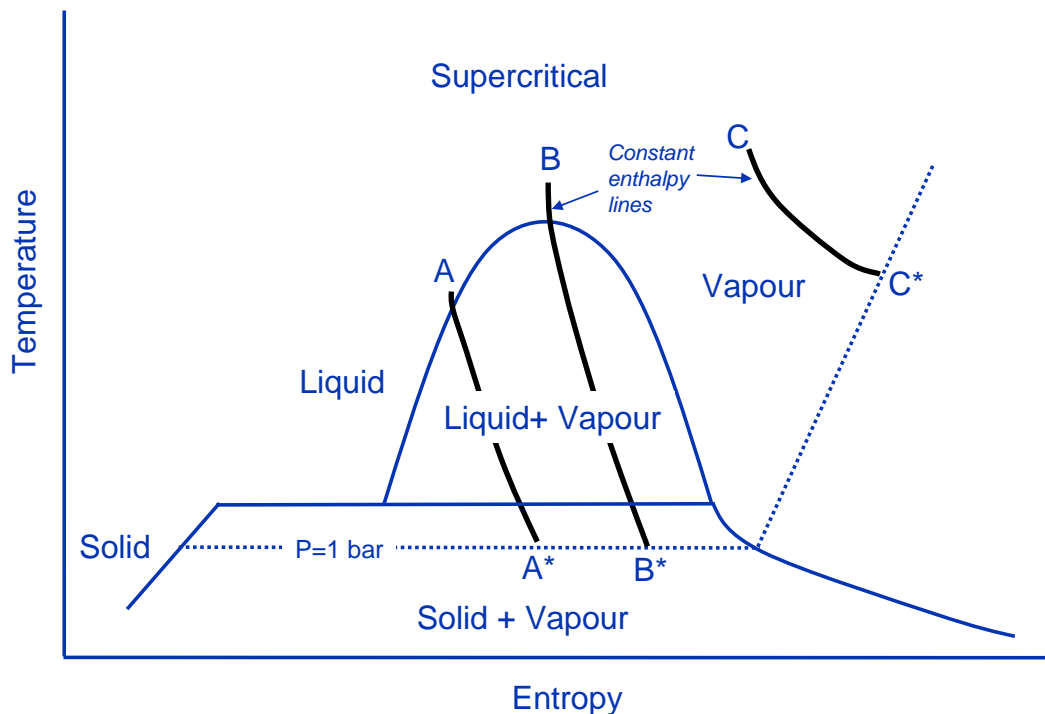
Figure 8-1: Thermodynamic path of CO_2 release

A leak that results in formation of solid CO_2, during the process delineated above, will have the following potential hazards associated to it:

- If solid CO_2 accumulates or is in contact with critical instruments, electrical systems and the structure of facilities this could potentially cause failure of the contacted system due to the cooling from solids (at temperature -78°C) and be a major threat to the structural and functional integrity of nearby plant.

- Large quantities of solid CO_2 may collect in the vicinity of release points and spread some distance over adjacent plant and equipment. As these deposits warm up, carbon dioxide gas will be produced as the solids changes directly into a gas. The localised high concentration of CO_2 that this produces represents a significant hazard to personnel. It is extremely important to ensure that the design and maintenance of gas monitoring and alarm systems are appropriate for the very low temperatures that may be present in the vicinity of CO_2 releases. Cryogenic burns and impact injuries from extremely cold jet of gas and entrained projectiles are serious hazards to personnel /71/.

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- Supercritical CO_2 is a highly efficient solvent in its supercritical state, and when it undergoes significant pressure reduction it moves from its supercritical state with super solvent properties, to a gaseous state with virtually no solvent capability. Any toxic substance (the solute) held in 'solution' will therefore 'precipitate' out, if a leak occurred, and there would therefore be a 'toxic' contamination effect in the area of the leak /72/.

- Impurities, such as particulates, present in the captured CO_2 stream could combine with the solids formed to produce particles of a much greater abrasive capability than solid CO_2 alone. This would enhance the erosion effects on process pipework and vessels adjacent to the leak which could lead to further damage to equipment and hence risk to people. The use of pellets of solid carbon dioxide for heavy-duty surface scouring and supercritical CO_2 for erosion cutting reflect the potential for high-pressure releases to cause serious harm to nearby structures, instruments or personnel /73/.

8.2.2 Low Temperatures

As described in the Human Impact section (Section 6) the venting of dense phase CO_2 to atmosphere will result in a phase change as the CO_2 depressurises through the release aperture with both vapour and potentially solid CO_2 being formed. The rapid expansion combined with the phase change, if not properly controlled, will result in a very high velocity, and potentially low temperature ($\approx$ -78˚C), two phase flow that would create a local area hazard to instruments, electrical systems and the structure of facilities. Cryogenic embrittlement of structural steelwork caused by extremely cold gas jets could be a threat to the integrity of safety-critical equipment or structures.

8.2.3 Flow Assurance; Hydrate Formation

In case free water is present in the pipeline, CO_2 hydrate may form. The consequence of hydrate formation may be localized reduced hydraulic diameter of the pipeline, hence reduced transport capacity. In worst case hydrate formation may cause blockage of the pipeline. In CO_2 gas phase, given the appropriate combination of pressure and temperature, CO_2 hydrate may form. However, it is not evident whether CO_2 hydrates will form under dense phase conditions, even with free water present. If the pipeline for some reason needs to be depressurised during shut-in to below the critical pressure, the gaseous CO_2 is able to contain less water than the dense phase (i.e. if the water content is too high) water may drop out. Combined with the possible hydrate condition (pressure and temperature), hydrates may form. In conventional hydrocarbon gas pipelines, hydrate formation may be remediated by depressurising the pipeline, causing hydrate dissociation. Knowledge on the hydrate formation/dissociation envelope for CO_2 at varying pressure and temperature is essential for selecting the appropriate hydrate prevention and remediation strategy. The hydrate formation/dissociation properties for dense phase CO_2 are not fully understood, and availability of appropriate hydrate inhibitors for CO_2 are not clear.

There is a degree of uncertainty as to whether free water in dense phase CO_2 will form hydrates before carbonic acid, but there will be a dependency on the CO_2 pressure, temperature and, not the least, the water content. If the pressure is high, there is a higher risk for hydrate formation. If the pressure is low, there is a higher likelihood for corrosion.

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8.2.4   System Depressurisation

CCS CO$_2$ systems will require to be depressurised for operational reasons and potentially as part of a hazard management strategy sometime during the lifecycle of the systems. In addition to situations where a controlled depressurization is undertaken, unplanned or inadvertent depressurization of dense phase CO$_2$ inventories is also reasonably foreseeable (e.g. a loss of containment event occurs).

Depressurisation of a dense phase CO$_2$ inventory, be it a large compressor or pump or pipeline, can, if not carefully controlled, result in large amounts (potentially tonnes), of solid CO$_2$ being deposited at the low points within the system. At atmospheric pressure these solids will be at -78°C and therefore there is potential for metallurgical damage. Also, if the solid CO$_2$ is then warmed rapidly, say by the reintroduction of dense phase CO$_2$, there is a likelihood of system over-pressurisation due to the rapid increase in volume as the solid sublimes into the vapour phase.

Depressurising a dense phase CO$_2$ system in a manner that prevents significant solid CO$_2$ formation within the system and excessive material cooling can be achieved by careful control of the depressurisation rate.

When a dense phase CO$_2$ inventory is vented to atmosphere the pressure in the inventory will quickly drop, along with an associated temperature decrease, until the remaining inventory becomes a two-phase liquid-vapour mixture. The pressure and temperature of the mixture will then continue to decrease, at a rate dictated by release rate and energy transfer between liquid/vapour and across the containment boundary, until the internal and external pressures reach equilibrium (i.e. atmospheric pressure).

If the depressurisation rate is relatively slow or the venting locations are at low points, all the liquid CO$_2$ will either be vented and/or allowed to evaporate into vapour before the pressure falls below the CO$_2$ triple point pressure of 5.18 bar. If this happens then only vapour will remain in the system when the pressure drops below the triple point pressure and no solid CO$_2$ will be formed in the system. If however liquid CO$_2$ is present when the pressure drops below the triple point, a large proportion of this liquid will freeze into solid CO$_2$ and be deposited within the system.

For pipelines in particular it is likely that the solid CO$_2$ deposits will form plugs, effectively subdividing the volume. These plugs may cause operational difficulties and/or safety issues that need to be considered.

It is therefore essential if solid CO$_2$ is to be avoided in a dense phase CO$_2$ system during a controlled depressurisation to ensure that there is no liquid CO$_2$ remaining in the system before the pressure drops to below 5.18 bar. In practice this can be achieved by vent system design and/or controlling the venting rate (e.g. inserting holds in the depressurization operation to allow the system to warm up and allow the liquid CO$_2$ to vaporize before allowing the pressure to go below the critical point. Following an inappropriate depressurisation of pipeline or vessel that

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leads to solid CO_2 build up inside system, the re-introduction of the liquid CO_2 stream before the solid CO_2 has full sublimed to vapour could lead to over pressurisation of the containment envelope and loss of containment (also referred to as rapid phase transition).

Should a leak occur in a dense phase CO_2 system there will be less opportunity to control the depressurization rate as discussed above. Although counter intuitive, it may be beneficial to continue to flow CO_2 into the leaking system whilst at the same time restricting or halting the down stream flow so as to maintain or at least control inventory pressure until a remedial measure can be implement to stop the leak or minimise the inventory prior to depressurization (e.g. using pigs).

As it is reasonably foreseeable for a significant leak to occur in a dense phase CO_2 system, the challenges associated with an uncontrolled depressurisation must be fully considered within in the design phase.

Land based pipelines in the USA are often segmented by block valves. The pipeline can then be isolated in shorter sections should there be a leak or need to depressurisation part of the line. The use of block valves, their spacing and depressurization arrangements will require careful consideration as part of the operation and hazard management of the pipeline.

For offshore pipelines it is unlikely that the pipeline length will be subdivided by multiple valves. There may be a hazard management requirement to install valves at strategic locations such as where the pipeline makes landfall or close to an offshore platform but for the majority of the pipeline there will be no segregation valves. In addition, depressurized of a subsea pipeline will likely only be possible at one or both ends unless subsea venting is developed.

Another potential issue for subsea pipelines during a rapid depressurization is the potential for ice formation on the external surface of the pipeline due to the CO_2 phase change cooling discussed above. It is conceivable (until proven otherwise) that a thick layer of ice to form along a considerable length of the pipeline, particularly at low points, and for this to create buoyancy issues.

The preceding discussion highlights the issues within a dense phase CO_2 system when it is depressurized but there are also challenges associated with designing the depressurization system itself (i.e. the vent system). This system must be able to handle the extreme colds and solid CO_2 formation that it will be exposed to and also the release point must be designed and located such that people and other sensitive receptors are not exposed to harmful concentrations of CO_2 during all reasonably foreseeable ambient conditions. Particular consideration must be taken when releasing virtually pure CO_2 in still weather conditions, especially if there is a temperature inversion, since the cold CO_2 being released will slump on the ground (or sea) surface with minimal dispersion. Because venting is a design activity (as compared to an accidental release) the operator of the vent must be able to show that people will not be exposed to harmful levels of CO_2. The long term and short term exposure limits discussed in Section 6.4 will form part of the demonstration that the vent system is appropriate.

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In summary, handling large inventories of dense phase CO_2 creates considerable challenges due to the issues highlighted above and in particular due to the phase characteristics when dense phase CO_2 is depressurized either through a planned operation or by an accidental release /66/.

8.3 Failure of Pressurized CO₂ Systems

8.3.1 Failure of CO₂ Vessels

A vessel can fail for a number of reasons. It can be damaged by impact from an object, thus causing a crack to develop and grow, either as a result of internal pressure, vessel material brittleness, or both. Thus, the container may rupture completely after impact. Weakening the containment envelope beyond the point at which it can withstand internal pressure can also cause large cracks, or even cause the container to separate into two or more pieces. Weakening can result from corrosion, internal overheating, manufacturing defects, overheating causing overpressure and failure of the relief valve to operate.

Clayton and Griffin /62/ did an extensive research for information of CO_2 vessels that had ruptured. They concluded that the overall safety record of carbon steel CO_2 vessels and process equipment had been good. However, they did uncover a number of failures that had occurred, and these are reported in Figure 8-2.

Table 1   Reported and Possible CO₂ Vessel Ruptures

Location/Equipment	Steel*	Size	Fatalities	Year	Comments & Opinion
U.S. Supplier (12)	?	?	?	1946 (?)	Vessel went to dry ice and ruptured when refilled with liquid CO₂.
Sweden (10)	?	25 ton	?	1960	Rupture of 25 ton CO₂ tank causing extensive property damage.
Repcelak, Hungary, CO₂ purifying storage vessels at a purification plant (14). Total of 4 tanks ruptured.	C	24 ton	9	1969	Process vessels made of ordinary carbon steel. High stresses from fabrication. Water contamination from purification caused freezing. Overstress from fabrication, overpressure, or impact caused the rupture.
U.S. Cylinder Supplier (12)	?	--	0	1960's(?)	Portable CO₂ cylinder filled twice by mistake. Heated up and ruptured.
Milano, Italy. Candia Cy (10)	?	50 ton	3	?	Ruptured 4 weeks after installation.
Solano, NM (reported in newspaper as ammonia) Ice Plant (15).	?	?	0 or 1	1974	No documentation of details. Partial information in Reference 10.
Germany. Rail Car (10)	TTStE36	23 ton	1	1976	Rigid pull assembly connected to C-Mn steel.
Mexico City (12)	?	?	?	Mid 1970's	No information available.
Spain. CO₂ road tanker (10)	?	?	?	?	CO₂ road tanker collided with bridge and exploded.
Dublin, Ireland Brewery process vessel (4)	C	15 ton	0	1986	Combination of high stress and material lacking adequate fracture toughness.
Worms Germany CO₂ storage (8)	F	30 ton	3	1988	Overpressure from overheating and frozen relief valve.

*F means fine grain low temperature C-Mn steel. C means coarse grain carbon steel.

Figure 8-2: Reported and possible CO_2 vessel ruptures (Clayton and Griffin /62/)

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One of the most catastrophic examples was the explosion of a tank of CO_2 at a plant in Worms, Germany in 1988 /62/ (Figure 8-3 shows two pictures of the accident site). A tank of 30 tonne capacity was shattered into a number of pieces and only 20% of the tank was present in the original premises after the explosion. Most of the tank was propelled 300 metres into the Rhine. There were three fatalities and a further eight casualties.
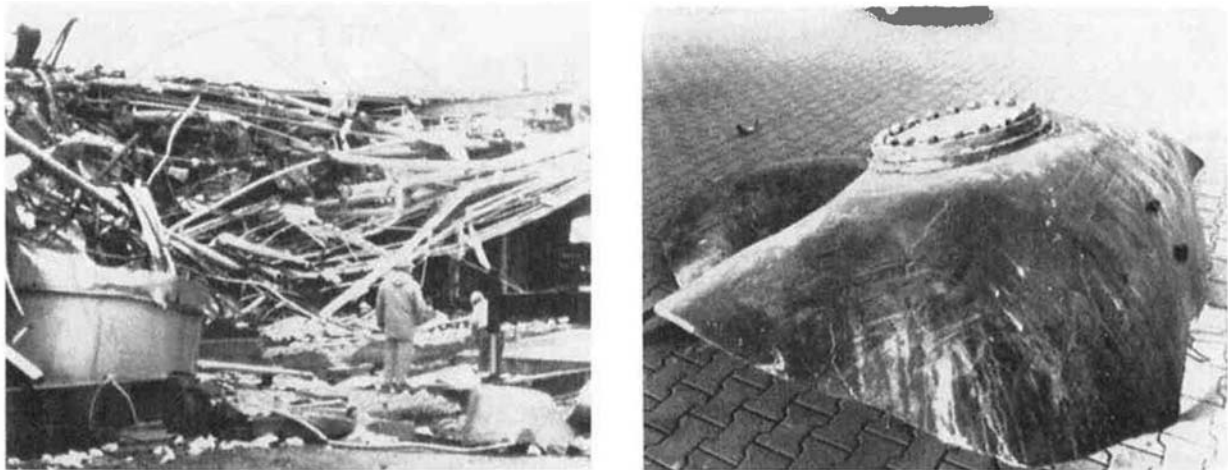
Figure 8-3: Plant area and head of CO_2 tank after failure /62/ (Worms, 1988)

In a CO_2 vessel failure incident, damage can occur from several sources: the cold liquid released can freeze people, fragments can be thrown with tremendous force, parts of the vessel with CO_2 still expanding can act as a rocket. It is also discussed /62/ that shock waves can form from a short time formation of superheated liquid to a spinodal state, followed by a homogenous nucleation, known as a Boiling Liquid Expanding Vapour Explosion (BLEVE). Initial catastrophic failure of the vessel must occur for a BLEVE. This could be:

- Mechanical damage caused, for example, by corrosion or collision;
- Overfilling and no relief valve;
- Overheating with an inoperative relief valve;
- Mechanical failure;
- Exposure to fire

The Worms investigation concluded that the vessel failed catastrophically, most likely due to overpressure from overheating and an inoperative relief vale. Based on the damages, number of fragments and the distances these were spread out from the plant area, fatalities and injuries it was speculated that the failure caused a cold CO_2 BLEVE.

Reference to part of this report which may lead to
misinterpretation is not permissible
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8.3.2 CO$_2$ BLEVE

Boiling Liquid Expanding Vapour Explosion (BLEVE) is a very unusual but extremely catastrophic event that can occur when a vessel containing liquid above its normal boiling point fails. If the vessel is ruptured, the sudden drop in pressure inside the container causes violent boiling of the liquid, which rapidly liberates large amounts of vapour in the process.

In the general literature on BLEVE, a majority of publications discuss hydrocarbon (LPG, propane) tank explosions. The key safety issues in such incidents are the ignition and combustion of the flammable content when this is vaporized, creating severe damage due to shock waves and burning. Usually, this situation arises due to a fire near the tank or due to an ignition source that starts an explosion of the escaped gas/vapour cloud.

The concept of a 'cold' BLEVE a subject that has attracted minimal focus and the few publications that report accidents with CO$_2$ storage tanks generally do not mention BLEVE effects. However, there have been some reported BLEVEs with carbon dioxide, mostly involving fire extinguishers. In addition to the Worms incidents, a CO$_2$ storage vessel failure in Hungary in 1969 was believed to cause a BLEVE to occur.

8.3.3 CO$_2$ BLEVE Principles

A very sudden depressurisation of a pressurised liquid such as CO$_2$ creates a superheated liquid phase that suddenly vaporizes in an explosive manner. This may give a transient overpressure peak inside the vessel, which again may lead to a powerful burst of the whole vessel, with total loss of content, a resulting blast wave and risk of flying fragments. A number of theories have been suggested to explain these phenomena, but according to Pettersen /65/ no fully reliable method can predict BLEVE.

The most frequent cited theory is presented in a paper by Reid and Kim /63/, which shows that a very spectacular physical event must occur under certain circumstances, and this is likely to be the explanation of BLEVEs. A simplified explanation of this theory /64/ can be given with the aid of the figure below, which is a diagram of the relationship between the pressure in a substance and the volume it occupies as a liquid, gas and fluid.
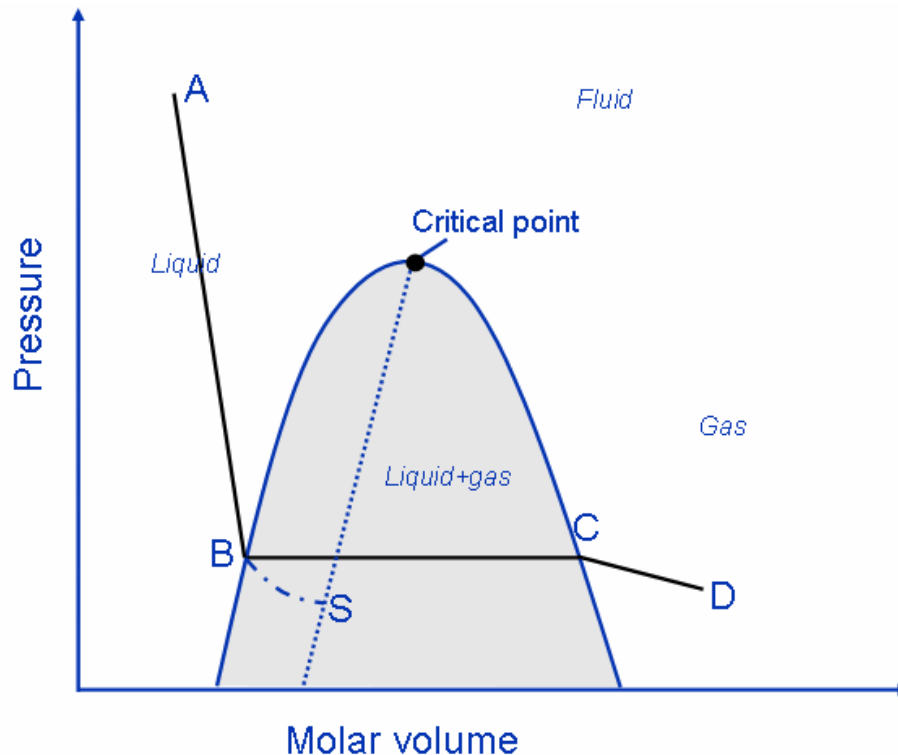
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Figure 8-4: Decompression path

The continuous line ABCD shows the behaviour of the substance undergoing depressurisation at a constant temperature and at thermodynamic equilibrium. In the section AB, the substance is a liquid and as the volume it occupies is expanded the pressure falls dramatically. The pressure falls to the vapour pressure of the liquid at the particular temperature at B. The liquid then starts to evaporate to become a liquid-gas mixture, and the pressure stays constant at the vapour pressure. Eventually it reaches C, where the liquid has been completely converted to gas. The pressure then drops as it is expanded further.

However, if the pressure falls suddenly, due to a failure in the container, the substance can become an unstable liquid along the path BS (dashed line). Along the path BS the substance is metastable and can at any time boil to return to the equilibrium horizontal line BC. Although such an event can be very violent it is not thought to be a BLEVE. Typically violent boiling will occur before the point S is reached and a BLEVE will not occur.

However, in the unlikely event that the point S is reached a special and catastrophic situation arises. S is known as a spinodal point and the slope of the line at this point is zero (i.e. $(\partial p/\partial V)_T = 0$). The dashed line connects these points at different temperatures and is known as the spinodal curve, which ends at the critical point. The special nature of situations represented by points along this curve are that large density fluctuations can occur because of the insensitivity of pressure to volume.

Once the spinodal curve is reached, separation into liquid and gas must occur. The density variations develop spontaneously into liquid and gas regions. This occurs homogeneously throughout the whole liquid. The rise in pressure on to the vapour pressure line BC is not large

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but it happens at great speed, homogeneously and at time scale of molecular motion. The shock to the containing vessel is huge and a disastrous BLEVE happens.

8.3.4   BLEVE Zones

An important reason for considering the possible occurrence of BLEVE with CO$_2$ is the paper by Kim and Reid /63/, which pointed to this possibility. The authors applied a thermodynamic model based on the spinodal fluid state, which represents the limit-of-stability for the liquid phase during expansion.

For a BLEVE to occur, the substance has to find itself on the spinodal curve between 1 bar and the critical point where the curve ends. When a catastrophic failure occurs there is not time for heat to pass into the system and so the path during failure is adiabatic. In thermodynamic terms the entropy of the system is constant during failure and the conditions for BLEVE to occur means that the initial entropy has to be higher that the entropy of the intersection of the spinodal curve and the 1 bar isobar, shown in Figure 8-5. As a result, a region of initial conditions that could give a spinodal state can be identified, as shown in Figure 8-6.

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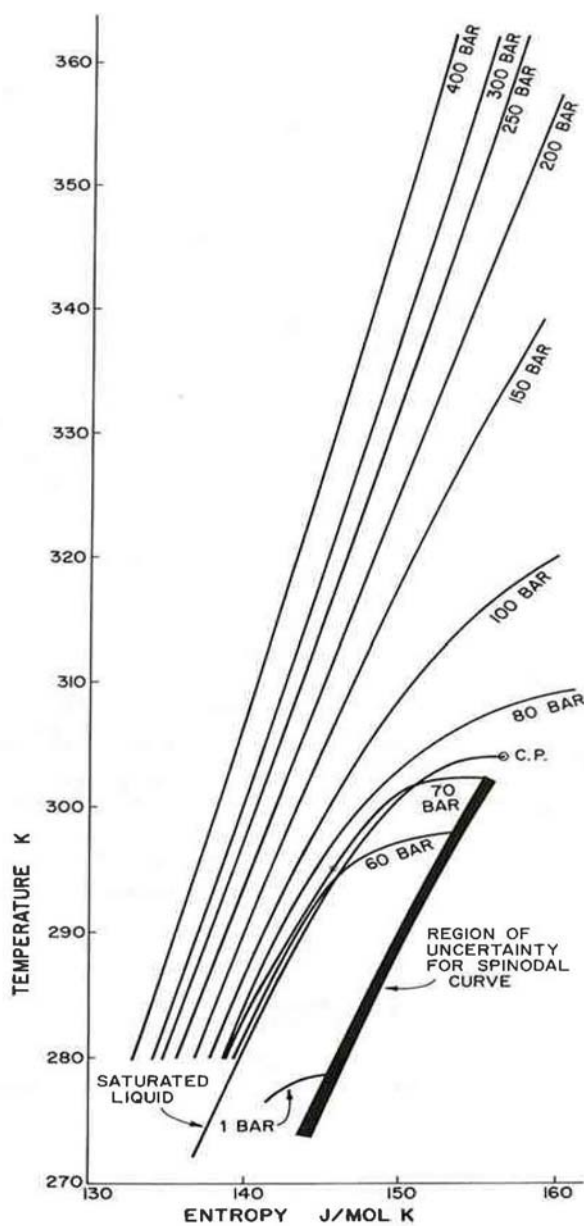
Figure 8-5: T-S diagram for CO_2 showing superheated liquid region /63/

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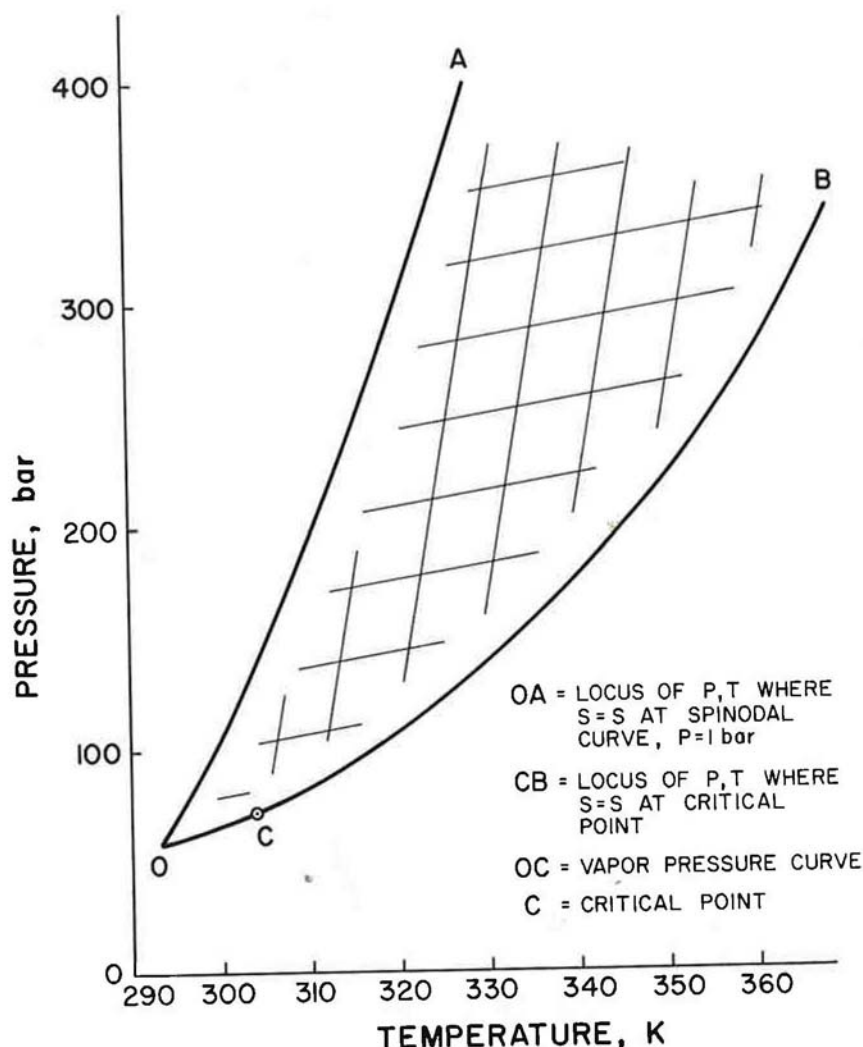
Figure 8-6: Domain which could lead to a spinodal state upon rapid, isentropic depressurization /63/.

In Figure 8-6, the curve marked OA represents the P-T states with a value of entropy equal to the estimated entropy on the spinodal curve at 1 bar. The CB curve contains the locus of P, T states with entropy equal to that of the critical point. Branch OC represents the saturated liquid state. According to Kim and Reid /63/, any initial P, T state within the marked region could (theoretically) attain a spinodal state by isentropic depressurization, and should therefore be avoided. Note that the region in Figure 8-6 is calculated based on pure CO₂, and should be re-calculated for mixtures of CO₂ with varying concentrations, and evaluated from a case to case basis.

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Although the phenomena could occur in theory, Kim and Reid /63/ performed some simple experiments with saturated liquid and supercritical CO$_2$ with depressurization that did not lead to any explosions. Reasons for disagreement between theory and experiments was speculated to be associated with factors like vapour bubbles on the wall of the vessel and shock waves or disturbances from the mechanism that ruptured the burst disk of the test vessel. The presence of vapour bubbles before depressurization may have given heterogeneous nucleation instead of the homogeneous nucleation required for a BLEVE.

Also, Pettersen /65/ performed an experimental study aimed at clarifying the possible occurrence of BLEVE in CO$_2$ systems. A test vessel was built and instrumented in order to measure transient pressures during initial depressurisation, and to record possible subsequent overpressure peak(s). The study concluded that none of the experiments, which were conducted over a wide range of initial conditions, showed signs of BLEVE, which would be characterized by a sudden re-pressurisation to a level significantly above the initial pressure.

It is evident from the experimental trials described above that a BLEVE is unlikely, even under the conditions that theoretically predicted as critical. However, because of the severity of BLEVE explosions, it should not presently be discounted as not being reasonably foreseeable. Further research is required in this area to examine, firstly the robustness of the theory and secondly that of the experimental programmes that sought to prove it. If it is found that the theory has substance and the experiments were incomplete, inconclusive or flawed, further experiments should be completed.

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9 MODELLING OF CO_2 RELEASES

9.1 Introduction

This chapter provides guidance on the approaches required for release modelling of CO_2 in carbon capture and storage (CCS) projects from a health and safety perspective. The section was developed with significant input from modellers *MMI Engineering Ltd.*

The principal concerns of this section are how to model the release and subsequent dispersion of CO_2 as an aid to understanding the hazards which may be presented by operational, emergency and accidental releases. The consequence of such releases are generally presented in the form of contours or iso-surfaces of CO_2 concentration at values which relate to differing levels of harm to exposed persons. Harm criteria range from 'occupational' long and short term exposure limits, through to fatality thresholds. In general it is desirable for predictive models to be conservative, but not overly so, since highly conservative models can unduly impose constraints on a facility design. Equally, predictive models should not lead to key aspects of a potential hazard being overlooked. Ultimately, as with all hazard modelling, the competent selection and use of the appropriate tools and techniques is critical.

Modelling for CO_2 consequence analysis typically takes place in two stages. In the first stage the release rate from a given inventory or scenario is calculated. In the second, the dispersion of the released CO_2 is calculated. It can be noted that some hazard modelling packages may carry out both stages without the need for the user to transfer data, or even being aware of that this procedure takes place.

The level of complexity or difficulty associated with each of these tasks depends on the particular scenario. For release rate calculation, the thermodynamic state of the inventory is a key parameter in determining this. This is also true for dispersion, where additional parameters which need to be considered in choosing a methodology include whether or not surrounding buildings need to accounted for and the length scales of interest.

For example, if the requirement is to calculate low concentration level contours from a warm, vertical, low speed gaseous release into a moderate wind with no influence from surrounding buildings, then a simple Gaussian plume model may suffice. In practice it has been found that this type of scenario is very rare in CCS projects where the effect of the high density of the gas cannot usually be neglected.

On the other hand, for the release of a very cold gas and its interaction with the topsides of an offshore platform in a low wind, such a model would be entirely inappropriate and a computational fluid dynamics (CFD) model would be needed. Cases intermediate between these two extremes should be treated individually, and in many cases it may be most appropriate to use a more sophisticated integral modelling tool such as that within DNV's PHAST code. In some cases, such as the release of CO_2 from a liquid inventory a high proportion of solids can be produced. In these cases, off the shelf codes may not be able to handle the physics so that either special procedures must be carried out (examples are given later) or a particular code version obtained.

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There are numerous reasons for modelling to be carried out. Three possibilities include:

- Due to a shutdown or problem at the site at one end of a pipeline, blowdown of the pipeline and/or plant through a stack may be required at the site. It is then important to understand: can a CO_2 plume touch down inside or outside of the site boundary; at what concentration level; in what wind conditions. It may necessary to modify the vent stack, or its location.

- During accidental releases from pressurised vessels can the gas plume go off-site; at what concentrations; how far.

- Should a leak occur in a dense phase CO_2 pipeline how large could the hazardous area extend; are there any particular topographical features such as valleys or hollows that need special attention; what effect does burying the pipeline have in terms of hazardous distances; are the safety distances on either side of the pipeline adequate; what information should be passed to the local authorities for their emergency response planning.

This chapter aims to give an overview over important modelling issues associate with predictive release modelling of CO_2 and in particular dense phase CO_2 release modelling, whereas more details on modelling approaches are found in Appendix A.

9.2   Typical Scenarios

9.2.1   Planned/Emergency Releases

During planned venting, the CO_2 will often be released in the gaseous phase, perhaps upstream of export compression, though this is not necessarily the case – blowdown of some inventories directly from the liquid state may be required in some circumstances. Usually, the vent will be from a high point such as a stack at an onshore site, or the flare tower on an offshore installation. Planned releases can occur at a variety of temperatures from close to the sublimation temperature up to over 100ºC. Offshore, where the CO_2 may be used for enhanced oil recovery (EOR) the gas may not be pure CO_2, but may contain hydrocarbon components.

Venting can be designed to give either a sub-sonic release or a release which is sonic at the exit. In some cases the venting can occur over a long period of time in which case a steady-state calculation can be carried out. In other cases, though the flow rate may fall over the period during which the venting takes place, the rate at which it falls may be sufficiently small to allow a pseudo-transient calculation to be used. By this it is meant that a number of separate steady-state calculations are carried out, each corresponding to flow rates at fixed points during the transient. For some calculation methods, such as CFD, this technique can substantially reduce the required computing time and should be used when practical.

9.2.2   Accidental releases

Accidental releases can occur from a huge variety of process conditions, including both gaseous and liquid inventories together with the supercritical fluid state. These releases could be above

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water either onshore, or on offshore platforms, sub-sea, below ground or within densely packed and congested plant areas.

Gaseous releases from a hole in a vessel or broken pipe-work are similar to planned releases, though there are notable differences:

- In general they will be sonic releases from pressurised vessels.

- They will generally be close to ground level (in the onshore case), or associated with one of the modules (in offshore cases), rather than from a high stack.

- They may be of short duration and inherently transient if the vessel inventory is small.

- The release can typically be through a narrow crack instead of a round hole.

Releases from vessels with liquid and supercritical CO_2 inventories are significantly more complex. In these cases, as the CO_2 enters the atmosphere it makes a transition from the liquid state to a two-phase gas/solid mixture where the solid fraction depends on the upstream conditions. During this transition the fluid expands in a characteristic "tulip" shape. The solids particles which are formed then, assuming there is sufficient energy available, sublime to a gas.

A second, distinct, class of accidental release is that from a pipeline. Normally, for risk assessment purposes, various leak sizes are considered including a full-bore rupture as this is the worst case in terms of peak flow rate. Again, while the case of a gaseous pipeline is relatively straightforward with analytical expressions in common use, the case of a liquid or supercritical pipeline is significantly more complex to calculate.

For accidental releases which occur under water from sub-sea pipelines and associated plant, the CO_2 must rise to the sea surface before being dispersed. The CO_2 will spread as it rises in the bubble column and the size of the release at the sea surface can be much larger than the area of the hole in the pipeline.

Using the North Sea as an example, at the sea bed the pressure and temperature are around 10 bar and 4°C, respectively. At these conditions, CO_2 is in the gas phase. A pipeline could, however, contain liquid or supercritical CO_2. Hence at a pipeline rupture or fitting failure there could be a very complex region of mixing between the CO_2 (undergoing phase change) and the water. However, it is expected that within a short distance from the release, gaseous bubbles of CO_2 will have formed which then rise through the water forming a bubble column. The evolution of this bubble column must be tracked using some form of model to give the size of the release at the sea surface. Since the initial bubble size (and other conditions at the release) is uncertain, sensitivity studies must, in general, be carried out to account for this.

9.3 CO_2 Modelling

Details on the release rate and dispersion modelling for gaseous and dense phase CO_2 are found in Appendix A.

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9.4 Gaps and Uncertainties

As highlighted in Appendix A, several gaps and uncertainties with respect to CO_2 modelling and experimental validation exist and they are discussed in more detail below.

Pipeline Depressurisation Modelling

Validation of pipeline blowdown models is largely based on a set of experiments carried out at the Isle of Grain on 100m long LPG pipelines with a diameter of 2 or 6 inches /88/. There are additional lab-scale experiments /89/ carried out on various hydrocarbon mixtures, but these are not generally quoted in the numerical papers.

Therefore validation data for pipelines is limited, in part doubtless, due to the cost of carrying out such tests at full scale. The Isle of Grain test data (Ref. /88/) is quoted in essentially every paper on numerical modelling of pipeline blowdown. There is no particular reason to believe that carbon dioxide will behave differently to any other liquefied gas so long as the pressure throughout the pipeline remains above the triple point pressure (5.2 bar). However, it is foreseeable that during a depressurisation event (e.g. due to a leak) the inventory pressure will drop below the triple point pressure.

For long pipelines the pressure may remain above the triple point pressure for a considerable period, however for shorter pipelines or longer durations this may not be the case and solid formation may occur at the ruptured end of the pipeline. Typically, pipeline blowdown codes use cubic equations of state to represent the thermodynamics of the fluid. This method does not have any mechanism to deal with solid formation so that the two-phase region of the pipeline would be implicitly assumed to be a gas/liquid mixture down to atmospheric pressure. It is not clear what effect this will have on flow rate calculations.

Vessel Depressurisation Modelling

Vessel blowdown models have been validated in general using other gases /84/ /85/ /86/. The only obvious issue for CO_2 is solids formation if/when the pressure anywhere in the vessel drops below 5.2 bar. The experiments most often quoted were reported by Haque *et al.* /87/. They carried out a number of experiments on blowdown of vessels. Several vessels were used together with several materials including pure nitrogen, several hydrocarbon mixtures and nitrogen/carbon dioxide mixtures. In the latter case the highest proportion of carbon dioxide was 55% by mole fraction. However, detailed results for these cases were not reported. Other experiments have been carried out for materials such as water, methanol and Freon. Several are listed in Ref /95/.

A set of experiments specifically designed to investigate both the release and subsequent dispersion of CO_2 were carried out by BP who gathered extensive data during their research programme at Spadeadam towards the end of 2007. Four contractors modelled the release and dispersion of CO_2 for several of these experiments as part of a carefully controlled modelling exercise. BP has not released the experimental data into the public domain and has retained control and ownership of the data. Although the four modelling companied involved have had sight of *some* of the data, they do not own this data and cannot disseminate it. Some comparisons between experiment and calculations have been published /82/, but with all scales removed.

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Release rates for carbon dioxide from a supercritical/liquid inventory has also been experimentally investigated by Gebbeken and Eggers /83/ and this has been used to demonstrate that calculating vessel blowdown with the Peng-Robinson equation of state is satisfactory (Ref. /82/).

The validation data available for vessels is therefore also limited and similar comments apply to depressurisation of vessels as apply to pipelines.

Buried Pipeline Releases

A significant leak from a buried CO_2 pipeline would lead to a crater being formed through which the CO_2 will flow. There appears to be great uncertainty around the size and shape of this crater. It is noted that this is not an issue which is specific to CO_2 but is general to all buried pressurised pipelines. The size and shape of the crater is of high importance for CO_2 modelling as it will influence the momentum of the release at ground level. A release with a large proportion of its momentum removed due to leak orientation, crater size and shape would likely lead to low dispersion rates and correspondingly high hazardous distances.

The uncertainty regarding the crater produces an uncertainty regarding the interaction of the crater with the fluid issuing from the pipeline and hence the source term definition. Under such circumstances it is possible to define a worst case, which is that the gas loses all of its momentum and emerges from the ground slowly. This is, however, considered a rather unlikely scenario but could produce extremely severe hazard distances. A jet release appears the more likely scenario but the uncertainty, nonetheless, remains.

As pipelines associated with CCS projects will inevitably contain very substantial inventories, and are expected to make a corresponding contribution to the overall major accident hazard risk from such projects, there appears to be a strong case for further research in this area to substantiate the assumptions used.

Subsea Pipeline Releases

Similar to buried pipeline releases discussed above, the effect water depth has on sea-surface dispersion modelling needs to be investigated to reduce uncertainty. This is also an issue which is not specific to CO_2 but is general to subsea pressurised pipelines. Of particular concern would be ensuring pipeline releases near the sea/land interface and, to a lesser extent, the sea/platform interface can be modelled with an acceptable level of uncertainty since, like buried pipelines the momentum the CO_2 comes to the sea surface will have a significant influence on the hazardous distances predicted

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CO$_2$ Mixtures
Methods for dealing with the thermodynamics of mixtures of several components are well established. In the context of cubic equations of state this is accomplished using so-called "mixing rules" whereby the parameters in the equations of the components are combined to give a new set of parameters for the mixture. There are papers (Refs. /89/ and /90) giving mixing rules specifically for CO$_2$ with hydrocarbons, but is not clear how well validated these rules are or if the rules which are included in commercial process simulators are adequate. In future CCS projects in which enhanced recovery of hydrocarbons is a feature, then it will be necessary to understand in some detail the behaviour of CO$_2$/hydrocarbon mixtures upon release.

Scale-Up
In general, most types of releases have uncertainties related to scale-up as experimental data are typically smaller than the worst case accidental scenarios. There are limited experimental studies of CO$_2$ release and dispersion. The only full-scale study of which the author is aware is the BP dense phase CO2 experimental programme carried out at Spadeadam. The data for this programme is unavailable at present. There are several potential scale-up issues, for example, the solid CO$_2$ particle size may vary depending on hole size, duration of the release, the shape of the initial tulip and phase change may occur further into the vessel or connecting pipe.

It should be noted that even when BP's Spadeadam experimental data is released, further validation experiments are required to fill in the scale up knowledge gaps. The data from Spadeadam experiments will help model validations but were of short duration (i.e. < 2mins), of limited pressure and temperature combinations and had a maximum hole size of 1" diameter. As CCS CO$_2$ pipelines could be larger that 24" diameter and have an isolatable inventory of tens of thousands of tonnes there is a need to understand and be able to confidently model larger and longer duration releases.

Particulates
According to Haque *et al*. /87/ the solubility of nitrogen in solid carbon dioxide is very low so that for a CO$_2$/N$_2$ mixture while the gas at the end of the depressurisation tulip would be a CO$_2$/N$_2$ mixture, the particles would be essentially pure CO$_2$. It is not clear if this would be true for other components (e.g. hydrocarbons or H$_2$S) and it is not certain what the effect on dispersion would be.

Confined Releases
The release of dense phase CO$_2$ into, for example, the confined and congested environment of an offshore platform topsides, may result in the deposition and accumulation of solid CO$_2$ on structures and process equipment. The implications of this, including transient reduction in material fracture toughness, have not yet been fully explored.

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Release Geometry

In an accidental release, the friction through the hole/crack is highly dependent on the shape of the hole/crack. Hence, accurately modelling the mass flow rate, downstream temperature profile and other release characteristics is dependent upon understanding hole/crack geometry influences. The effect of a crack rather than a hole cannot be found by simply adding a discharge factor, as it affects the temperature development through the hole/crack as well.

Uncertainty around release geometry influences could prove to be more of a source uncertainty than there is in the choice between the different release models. Further work in this area is required.

Temperature Envelope

Experience suggests that near-field temperature envelope is more sensitive to modelling assumptions (e.g. initial CO_2 solid particle size) than the CO_2 concentration further downstream from the release. Since the temperature envelope of releases from liquid inventories is becoming a primary concern (especially in congested geometries) this is, perhaps, becoming a more important issue. This leads to corresponding requirements in the modelling methods adopted. The temperature in the near field will also be dependent on the type of release – i.e. through a hole or through a crack.

Visibility

Understanding and being able to predict the visible cloud of a CO_2 release will be valuable in hazard management particularly emergency response planning and in managing public perceptions. A large proportion of the visible cloud from a CO_2 release will be water vapour that has condensed from the air due to cooling from the CO_2 release. Obviously temperature of inventory and CO_2 stream, vapour and solid CO_2 flowrates, and ambient air conditions will all have an impact on the size and characteristics of the visible cloud. Lack of vision can make it difficult for personnel/3rd party inside the cloud to escape.

Further investigation and data could be used to assist educate people as to the actual danger should they see or be caught in a visible cloud being created by a CO_2 release.

Vertical/Angled Releases

For operational and emergency releases the more relevant case is often vertical/angled releases, particularly with a low wind speed. There are some slightly different mechanisms at play with vertical releases so that validation for horizontal releases does not guarantee vertical releases will also be correctly predicted. It should be noted, however, that vertical releases at full scale would be much harder to carry out requiring more stringent bound on acceptable weather conditions and more difficult placement of instrumentation. There could however be operational experience available from the oil and gas industry on cold flaring that would be relevant.

Specific Dispersion Modelling Issues

There may be dispersion modelling issues not yet identified for modelling CO_2 releases which will come to light within the first CCS projects. For example, during a long duration dense phase CO_2 release the cooling of the surrounding area over time may have an impact on the dispersion and/or solid CO_2 fallout and subsequent sublimation.

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10   HAZARD IDENTIFICATION

10.1   Approaches to Hazard Identification and Risk Assessment

Hazard identification is the most important step in the risk management process, since a hazard that is not identified or fully recognised will not be effectively managed. If important hazards are not identified, the total risk picture will be incomplete. Hazard identification is the process of identifying and classifying credible and incredible hazards, by cause, location, method of assessment, consequence, impact or any other grouping, with the objective of specifying failure cases, or starting conditions for events to be ranked with respect to their frequency, consequence and impact.

There are many hazard identification techniques used in other industries and these can and should be applied with little modification for CCS.

Great care should be taken during hazard identification exercise to recognise and compensate for the CCS industry's relative immaturity where few people have relevant hands-on experience and best-practice CCS risk assessments have not been established. This immaturity may lead to hazards not being identified, or hazards that are identified being deemed non-credible due to lack of relevant knowledge. Until experience and knowledge is built up and communicated within the CCS industry, greater focus should be applied to hazard identification (and risk assessment) to compensate for the lack of a track record.

Once the hazards have been identified their risk needs to be assessed so that the risk acceptability can be determined and the appropriateness of risk management measures evaluated. The risk analysis can be broken down into frequency analysis and consequence analysis. In both these areas there is significant uncertainty that requires to be understood and adequately managed.

Without extensive CO_2 pipeline and system experience there is little directly relevant incident statistics for a CCS frequency analysis. That said, there is extensive experience from other pipelines and systems that can, with care, be used. The key is being able to identify where existing historical incident data is relevant and where it may not be, and then using suitable modification factors for the non-relevant data. Generic leak frequency data is usually broken down into, for example for a pipeline:

- Contribution from corrosion (≈30%)
- Contribution from 3rd party (≈42%)
- Contribution from design (≈7%)
- Contribution from incorrect operation (≈13%)
- Contribution from natural hazard (≈8%)

The contribution from 3rd party and natural hazard (≈50%) should be the same for all pipelines regardless of the pipeline contents so should require minimal, if any factoring for CO_2 service. However, it is where the behaviours and properties of CO_2 may differ from the existing 'generic' experience that needs to be incorporated into the frequency analysis.

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The following, for example, needs to be considered, with (conservative) frequency modification factors employed (until directly relevant CO$_2$ experience is established):

- Corrosion – Potential for high corrosion rates due to out of specification contaminants within CO$_2$ stream (e.g. water, H$_2$, O$_2$, H$_2$S, etc.);
- Design – Appropriateness of design codes and standards for CO$_2$ service (e.g. designing for preventing propagating failures, for severe chilling, etc.); and
- Operation – Potential for blocking pipeline with solid CO$_2$ or for over-pressurising pipeline with inappropriate process re-start with solid CO$_2$ present.

With regard to consequence analysis for incidents relating to dense phase CO$_2$ systems, there is uncertainty around the accuracy and applicability of the models currently available. There is little directly relevant accident data and experimental data that can be used to validate models. Therefore, although there is no reason to believe the existing consequence models will be very inaccurate, it will be very difficult to make a robust argument that the risks associated with a CO$_2$ operation are being managed to an acceptable level.

10.2 Description of Workshop and Methods

A draft version of the report, containing the preliminary findings, was issued to a group of selected stakeholders from industry, legislative authorities and other competent scientific communities as input for workshop discussions, which was arranged at the Thon Vika Atrium Conference Centre 10th of November 2008.

The main purpose of the workshop was to discuss the relevance of the identified HSE issues for CO$_2$ handling and the rank them according to their criticality. The approach taken during the workshop was to identify a comprehensive list of potential hazards by using the DNV method of SWIFT ("Structured What IF Technique") analysis.

10.2.1 SWIFT Analysis

The SWIFT method is a flexible and efficient group-based approach to identifying potential hazards and uncertainties /91/. The technique was developed by DNV in collaboration with GE Plastics and has been applied to a wide range of industrial activities from process engineering to heavy lifting operations, and more recently CO$_2$ storage.

Some distinctive features of SWIFT are:

- It is able to identify hazards, evaluate risks in a qualitative sense, and recommend appropriate additional safeguards:

- It uses the expertise of a group with specialist knowledge of the activity under study;

- It follows a procedure that combines brainstorming, structured discussion and checklists;

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- It considers the activity from a top-down perspective starting with systems or operations, rather than individual features, events or processes;

- It maps uncertainty related to the probability and/or consequence of hazards and is conservative in estimating risk.

The session was facilitated by DNV and the discussions were logged in spreadsheet format in real time with the minutes visible to all participants on a projector screen.

The SWIFT technique makes use of checklists to ensure that the exercise is comprehensive in identifying hazards. This is important because the purpose of SWIFT is to generate the input information to the remainder of the risk assessment workshop.

The idea behind using a checklist was to use a list of keywords that could be read through quickly that was specific enough to stimulate ideas amongst the experts in the room.. The checklist that was used is shown in Table 10-1. The keywords originated from the findings of the draft report issued to the participants prior to the workshop.

Table 10-1: Category specific keyword checklists used for SWIFT analysis

Hazard category	Keyword
System, Scale and Usage (size and service life)	- Capture - Pipeline - Terminals - Injection
CO_2 properties and behaviour	- Properties - Impurities
Human Impact	
Environmental Impact	
Engineering and Operational Challenges	- Solids formation - Decompression (accidental) - Decompression (controlled) - Flow assurance
Materials	- Elastomers - Corrosion - Compatibility - Crack propagation
Hazard Phenomena	- CO_2 BLEVE - Others
Modelling Aspects	

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10.3 Criticality of Identified Hazards

The criticality of the identified hazards was assessed by using the principle of a Rapid Risk Ranking (RRR) procedure. This procedure assigns semi-quantitative values of Probability and Consequence to each of the hazards logged, and it is necessary for the experts to have a common understanding of the meaning behind each numerical value. Due to time restrictions the risk assessment was not completed within the workshop session and the log sheet was processed and completed by DNV after the workshop, and feedback and comments to the proposed ranking of concerns was collected by email from the participants.

In a traditional RRR procedure the assigned numerical values of Probability and Consequence of the identified hazards are transformed into semi-quantitative risks in a format suitable for visualisation in a risk matrix, enabling a risk ranking from high, medium to low risk categories. However, this approach was not found easily adaptable for the case of risk assessment of CO$_2$ handling for CCS, due to several reasons:

- The hazards identified were generic in nature and not referring to any specific technology or CCS facility. This relates to the nature of the study, which aims to map all possible HSE issues across the value chain from capture (including post-combustion, pre-combustion and oxy-fuel) to injection, without being too specific in technology;

- It was difficult to establish a common understanding on the frequency classification of a hazard from the workshop session. This was due to the fact that there is not any extensive CO$_2$ pipeline and system experience, and there is little directly relevant incident statistics for a CCS frequency analysis; and

- Also, with regard to consequence analysis for incidents relating to dense phase CO$_2$ systems, mitigation methods should be taken into consideration when determining the risk and these are presently not properly established for all hazards due to the immaturity of CCS. Moreover, there is little directly relevant accident data and experimental data that can be used to validate models.

Therefore, the identified issues of concern and hazards have been classified as knowledge gaps rather than risks, based on the workshop discussions and the feedback collected from the workshop. These gaps refer to *the current lack of knowledge and experience to adequately understand and manage what may cause or significantly influence a CCS major accident hazards (MAH) or be a treat to the deployment of CCS*, and these gasps have been assigned with traffic lights (red/amber/green):

- Red: "not solved without significant R&D/development of guidelines/recommended practices"

- Amber: "will probably be solved based on ongoing activities and initiatives"

- Green: "will be solved by applying regular engineering and existing safeguards and uncertainty reduction measures"

The complete list of identified hazards with cause and consequences are found in Appendix B2, whereas the identified hazards assigned with red and amber traffic lights are listed in Table 10-2.

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Table 10-2: Identified concerns and knowledge gap criticality

Concern Issue/ Hazard	Consequences	Causes	Gap description	Knowledge gap criticality
CCS not publicly acceptable	Potential Show stopper. NIMBY ("Not In My Backyard") and/or others present a professional anti-view that scares the public before the CCS industry and regulators can build an evidence-based case for responsible operations.	Mixed messages. Lack of "education". Failure to present compelling safety case for the pipeline	A consistent and clear communication and education is needed. An active communication with various stakeholders before any specific project is actioned so as to head-off the unsubstantiated claims from anti-focus groups. A comprehensive public consultation documentation that openly presents all aspects (pros and cons) of CCS pipelines should be developed.	●
Placing of pipeline in populated area	Publicly not accepted as risks are not sufficiently communicated. Potential show stopper.	Onshore transportation of CO$_2$ is not accepted.		●
The modelling tools are not sufficient to capture leak/dispersion/ internal source term/process simulation modelling	Insufficient confidence in model results. Risk reduction measures chosen on the basis of inaccurate information. People put at risk should a loss of containment (LOC) occur. Permitting not possible as Regulators are not presented with robust case for safety.	Improper thermodynamic assumptions (Equation of State issue related to presence of impurities)	There is a need for defining good practice and limits for use. Validation of models (from experimental data) is needed. Release and dispersion models require to go through a thorough validation process across the full spectrum of release scenarios (where practicable). Modelling guidance needs to be developed to ensure that validated models are used with appropriate input variables and assumptions.	●
Underground pipeline bursts	Momentum of release is reduced leading to lower dispersion rates and an increased hazardous zone.	External impact from 3rd party action corrosion and possible propagating failure	Validation of models (from experimental data) is needed. Development of guidance for underground release modelling that includes crater size estimates and momentum assumptions.	●

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Material incompatibility	Loss of containment. Loss of life from a major release	Reuse of existing infrastructure with too high level of impurities and water left in the system/pipeline	Need for guidance on managing re-using existing infrastructure. Suitability of all existing components needs to be assessed for re-use with CO$_2$.	●
Crack propagation	Loss of inventory. Loss of the pipeline. Multiple fatalities. Escalation from small to major leak. One major incident might cause public to turn against CCS. High cost.	Corrosion. External damage. Inappropriate re-use of existing infrastructure. Initial defects. Inadequate material specification.	Need to improve understanding propagating failure both in terms of internal pressure decay/loads and material failure mechanism and then convey this improved knowledge in the form of guidance or RP. Provide risk based hazard management guidance.	●
Corrosion	Loss of containment	Presence of free water/oxygen/H$_2$S	The mechanism of CO$_2$ corrosion in the presence of impurities is not entirely understood. At present few models exist to enable accurate speciation in dense CO$_2$ containing moisture and other impurities.	●
High water content entering the pipeline from the compression stage	Free water within the pipeline could lead to hydrate formation. Potentially leading to corrosion, leak and possible rupture. Rupture could pose a threat to a large number of people especially onshore.	Defective dehydration unit within the CO$_2$ capture facility. Incorrect control system settings. Failure of control system to detect out of spec. flow and shutdown before flow enters pipeline.	Need for improved understanding of impact of varying the level of all potential impurities (e.g. H$_2$O, H$_2$S, NOx, SOx, O$_2$, etc.) in CO$_2$ stream. Safety Integrity Level (SIL) system Lack of guidance on approach to be taken to determine appropriate control criteria for water content in CO$_2$ stream. Lack of guidance for effective response to out of specification CO$_2$ stream that leads to potential free water in pipeline.	●

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Out of spec CO_2 entering pipeline (impurities issue; H_2O, SO_2, NOX, H_2S etc) *a) immediately after compression* *b) downstream of compression (cooled)*	Impurities in the CO_2 stream will alter the phase diagram for the mixture, which will impact phase change parameters. Corrosion if free water is formed inadvertently due to change to phase envelopes, dew points, solubility, etc. Transport properties will change. Corrosion leading to leak and rupture could pose a threat to a large number of people. Venting or leakage of CO_2 with H_2S is worse than pure CO_2.	Upstream failure, e.g. dehydration unit/FGD	Lack of guidance on impact and issues relating to possible variations of impurities in the CO_2 stream. Impurities should include contaminants that could pass into the CO_2 during normal operations (e.g. CO, O_2, H_2, H_2S, NOx, SOx, H_2O, etc.) and abnormal upsets (e.g. glycol or amine carryover). The impact of impurities on the triple point of CO_2 is not known.	●
Carry-over from capture plant (glycol/amine)	Could affects corrosion rates. Corrosion leading to leak could pose a threat to a large number of people.	Failure of water wash system and/or failure of coalescing filters to remove surplus solvent from outgoing CO_2		●
Increased O_2 concentration	Increased risk of corrosion that potentially could result in a leak that could lead to harm to people. Risk of having a oxygen/HC mixture if CO_2 is used for EOR applications.	Surplus of oxygen for combustion (i.e. oxy-fuel combustion)/wrong mixing ratio of fuel and O_2		●
Impurities present	Thermodynamic envelope is changed	Upstream failure, e.g. dehydration unit/FGD		●
Not sufficient education/skilled personnel	Human error. Damage to pipeline or systems due to mal-operation or poor design (e.g. damage to steel due to allowing solid CO_2 to form in pipeline). Possible harm to people if damaged system is brought back into service	Lack of skill and training. Wrong decisions. Polymer material damage. HC/scale mindset	Need for education and training to where possible that CCS CO_2 guidance highlights the differences (and similarities) with current experience and practices for HC systems.	●

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Mixing of different CO_2 sources with different spec that do not comply with pipeline spec.	Material compliance issue (corrosion). Liability issue Harm to people if loss of containment event results	Not sufficient guidelines/regulatory framework on CO_2 quality in place.	Lack of guidance on approach to be taken to determine appropriate control criteria for water content in CO_2 stream. Lack of guidance for effective response to out of specification CO_2 stream that leads to potential free water in pipeline.	●
CO_2 is present at high conc. and no detection systems in place	Human exposure to elevated CO_2 cons. causing aspyxiation/hypercapnia	Large leak from equipment/pipeline or an undetected prolonged smaller leak.	Lack of clear guidance for requirement for, specification of, and use of, fixed and portable CO_2 gas detection systems.	●
Lack of commonly accepted harm criteria	Applying wrong acceptance criteria - exposure of dangerous amount of CO_2	State-of-the art knowledge on CO_2 harm criteria not formulated. Inappropriate safe distances and risk reduction measures implemented.	Need to ensure that the acceptance/harm/risk assessment criteria are science-based and standardised across all European States.	●
Failure of downstream process equipment - leads to need to vent the gas in the capture facility from the stack (pure CO_2) Long-term venting at full flow may cause environmental damage in vicinity of vent stack (acidity on foliage?)	Prolonged venting leading to exposure above occupational limit	Presence of impurities. Equipment failure.	Need to ensure that proper design is in place and that all designed venting can be undertaken safely, without harm to people.	●
Decompression/ venting (Insufficient dispersion of CO_2)	CO_2 released through a vent system at high concentration.	Planned maintenance of pipeline or shutdown due to operational issues of upstream equipment		●

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Decompression/ venting (accidental)	Solids deposited (form plugs) at the low points within the system. Metallurgical damage due to low temperatures.	Rupture of pipeline.	Lack of clear guidance and understanding of decompression issues associated with dense phase CO_2 and how best to design for, operate to avoid, and respond to, un-planned decompression in dense phase CO_2 systems.	●
Solids formation	Structural and functional integrity of equipment. Cryogenic burns and impact injuries to humans.	$scCO_2$ depressurized into the two-phase vapour solids region.	Unclear what mechanism to precipitate solids formation is envisaged.	●
Hydrate formation	Appearance of free water and eventually corrosion. Restricted flow/blockage of the pipeline.	Presence of free water	Lack of knowledge and uncertainty as to whether free water in dense phase CO_2 will form hydrates before carbonic acid.	●
Transient pressure and temperature in pipeline	Two phase flow. Stresses to structure. "Water hammer effects" If pipeline failure due to stresses and/or hammer then large-scale threat to people.	Fire. Leak. Warming up of pipeline inventory	Need to understand if hammer effects could occur	●
Rapid Phase Transition	Following inappropriate depressurisation of pipeline or vessel that leads to solid CO_2 build up inside system, the re-introduction of the liquid CO_2 stream before the solid CO_2 has full sublimed to vapour could lead to over pressurisation of the containment envelope and LOC	Rapid sublimation of CO_2 with heat energy from liquid CO_2 stream	Need clear guidance to ensure upset conditions that could lead to solid CO_2 formation are appropriately understood and procedures are in place to prevent over pressurisation due to rapid sublimation of solids.	●
Release of CO_2 in closed space	Significant solids CO2 build-up. Embrittle steelwork	Restricted heat flow to the module	Lack of understanding of dense phase releases into enclosed spaces (e.g. an offshore platform module) .	●
Intelligent pigs not suitable or damaged during operation	Unable to effectively monitor integrity of pipeline. Potential to lead to a leak and threat to people.	Elastomer and lubrication issues	Lack of guidance on most appropriate elasomers and lubricants for use in dense phase CO_2 service	●
Elastomer explosion	Local elastomers damage. Leak from valves, flanges, etc. Local hazard (e.g. in a building or enclosure) due to CO_2 accumulation	Inappropriate choice of elastomers		●

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A water mist/fog is created from a CO$_2$ release	Reduction of visibility may lead to incorrect or inefficient emergency response (especially on an offshore installation). Reduced visibility on a busy road may lead to accidents.	Cooling effect from dense phase CO$_2$ vaporization cause condensation of moisture in air	Need to improve understanding of the relationship between visible cloud and CO$_2$ concentrations at different ambient conditions and release scenarios and then use this in planning emergency response and informing the public.	🟡
Local temperature/icing impact from leak (e.g. flanges)	Material creep/degradation/ Enbrittlement	Exposure to low temperature (thermodynamics of the leak)	Need to investigate issues around thermodynamic cooling in and around a leak point and provided information to designers and hazard management specialists to allow any issues to be addressed.	🟡
CO$_2$ BLEVE	Catastrophic explosion. Missiles/projectiles from CO$_2$ containment	Sudden depressurization of a liquid phase CO$_2$ which results in an instantaneous vaporization which creates an explosive shock that disintegrates the vessel or pipeline	Theoretical basis still not proven. CO$_2$ needs to be in a specific envelope of pressure and temperature. Need of further investigations regarding the possibility of CO$_2$ BLEVE and if required conduct experiments to prove or disprove phenomenon	🟡

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The issues raised from the workshop sessions, listed in Table 10-2, can broadly be divided into the following areas of concern:

- Public Acceptance;
- Modelling of dense phase CO$_2$ releases;
- Behaviour of dense phase CO$_2$, particularly around the thermodynamic changes when dense phase CO$_2$ experiences a reduction in pressure (e.g. leak, venting, throttling, etc.);
- Corrosion due to impurities or contaminants (e.g. H$_2$O, H$_2$, O$_2$, H$_2$S, etc.) either during steady state operation or upset conditions;
- Crack propagation;
- Loss of integrity of elastomers due to CO$_2$ absorption; and
- Changes that CO$_2$ mixtures (e.g. CO$_2$ with HC, H$_2$, CO, H$_2$S, etc.) have on the behaviour and properties of pure CO$_2$.

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11 CCS CO_2 RISK MANAGEMENT AND MITIGATION

11.1 General

Provided that CO_2, when handled in the masses required for CCS, is recognised as a potential Major Accident Hazard (MAH), then existing MAH risk management strategies should enable MAH risk to be managed down to an acceptable level. In addition, provided the boundaries of applicability are known and respected codes, standards, good practices, experience and knowledge from other existing industries can be applied in the relatively immature CCS industry. The challenge faced by the CCS industry and Regulators is knowing where these boundaries lie.

A robust lifecycle risk management strategy that builds on industry best practices (e.g. as described in ISO 17776 and 13702 or as required for NORSOK, and UK COMAH and Safety Case Regulation compliance), should ensure CCS MAH risks are effectively controlled. However, due caution needs to be captured within delivery of the risk management strategy to compensate for the lack of experience and knowledge.

The risk management strategy should be centred upon the concept of inherent safety and the prevention of incidents which could endanger people, the environment or property. This establishes a hierarchy of prevention before control, mitigation, protection and emergency response. The strategy should encourage a balanced approach to risk management by ensuring that the resources provided to manage risks are commensurate with the degree of risk from these hazards and to provide a framework whereby everyone can work effectively together to understand and manage the risks.

One key element of effective management systems is a systematic approach to the identification of hazards and the assessment of the associated risk in order to provide information to aid decision-making on the need to introduce risk-reduction measures. Risk-reduction measures should include those to prevent incidents (i.e. reduce the probability of occurrence), to control incidents (i.e. limit the extent and duration of a hazardous event) and to mitigate the effects (i.e. reduce the consequences). Preventive measures, such as using inherently safer designs and ensuring asset integrity, should be emphasized wherever practicable. Measures to recover from incidents should be provided based on risk assessment and should be developed taking into account possible failures of the control and mitigation measures. Based on the results of the evaluation, detailed health, safety and environmental objectives and functional requirements should be set at appropriate levels. The results of the hazard identification and risk assessment activities and the decisions taken with respect to the need for, and role of, any measures required for risk reduction should be recorded in strategies.

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The following three generic steps are inherent in all hazards identification and risk assessment approaches:

1. <u>Step 1:</u> Identification of the hazard, based upon consideration of factors such as the physical and chemical properties of the fluids being handled, the arrangement of equipment, operating and maintenance procedures and processing conditions. External hazards such as mechanical impact, extreme environmental conditions, etc., also need to be considered at this stage.

2. <u>Step 2:</u> Assessment of the risk arising from the hazards and consideration of its tolerability to personnel, the facility and the environment. This normally involves the identification of initiating events, identification of possible accident sequences, estimation of the probability of occurrence of accident sequences and assessment of the consequences. The acceptability of the estimated risk must then be judged based upon criteria appropriate to the particular situation.

3. <u>Step 3:</u> Elimination or reduction of the risk where this is deemed to be necessary. This involves identifying opportunities to reduce the probability and/or consequence of an accident.

The above steps are not new, what is new is that there is little history of applying them for CCS. Several hazards related to CCS handling of CO_2 were identified and assessed in the previous Chapter 10, without discussing how the risk could be managed in any detail. This chapter presents approaches to risk management during a CCS project.

11.2 Risk Management

Existing risk management approaches should be directly applicable for CCS provided their effectiveness for the particular situation can be demonstrated. CCS, in particular the transport of large quantities of dense phase CO_2, brings new challenges that are not fully understood and it is this gap in knowledge that will undermine the robustness of risk management processes.

The concept of inherently safer design refers to an approach in which hazards are 'designed out' at source. The primary means of prevention are the use of appropriate standards for design and operation, the quality standards applied to design, construction and operation and the optimisation of the pipeline routing and plant layout for safety (as well as for other business drivers).

Due to the relative immaturity of the large scale transportation of dense phase CO_2 (when compared to hydrocarbon carrying pipelines) the appropriateness of standards and best practice guidance has not been established and should therefore be challenged. If necessary, due to an actual or perceived knowledge or experience gap, the following should be undertaken to support available codes, standards, guidelines and experience:

• Taking a first principle, in-depth, approach to systematically examine or establish the theory;
• Undertaking research, experiments and trials to validate theory;
• Over-engineering or over-specifying equipment or systems to increase the safety margins;

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- Front-end loading the inspection, test and maintenance until experience and operating confidence is built up.

Effective management of the structural integrity of the containment system is critical in preventing loss of containment hazards. This will include:

- Demonstrating applicability of design Codes and Standards used;
- Providing evidence of conformity to the design Codes and Standards;
- Determining normal operation and foreseeable extreme criteria;
- Demonstrating suitability of materials used in construction;
- Demonstrating applicability of construction standards used;
- Providing evidence of conformity to the construction standards.

Where it is not practicable to eliminate the hazard by design, prevention measures will need to be achieved in other ways, for example, through design measures, engineering and procedural controls or management systems. Good design is the most effective means of preventing CO_2 releases. This involves addressing issues such as:

- The need to minimise the frequency, rate and quantity of releases by, for example, reducing the number of release points and addressing causes of failure, and limiting the inventory available for release;
- Optimising the pipeline route and the location and layout of any associated systems.

The causes of potential hazardous events should be identified and assessed within the hazard identification and risk assessment processes. The risk assessment should also provide information on the contribution or influence of identified causes to the overall risk profile. For CO_2 pipeline transmission systems the following causes (as a minimum) should be adequately examined and measures put in place to prevent, or if this is not reasonably practicable, minimise the likelihood of occurrence:

- Corrosion;
- External loading (e.g. seismic, subsidence, etc.);
- Internal loading (e.g. bends, two phase slugs, pigs, debris, etc.);
- Impact (e.g. digger, vehicle, plane, ship, anchor, etc.);
- Pressure deviation;
- Temperature deviation;
- Vibration (incl. hammer effect);
- Incorrect equipment;
- Defective equipment;
- Human error;
- 3rd party action or interference.

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Measures to control activities which might lead to a CO$_2$ release should include adequate procedures and arrangements for:

- Control of maintenance activities;
- Control of modification, start-up and shut-down of plant and equipment, and isolation of inventories storage.

Personnel required to implement procedures should be competent to do so, adequately trained, and supervision and information about the hazards should be provided. Human factors issues should be identified and taken into account in the design of procedures and systems.

Normal and safe operating limits should be defined and safeguards (i.e. measures) against excursions from the design conditions put in place. These limits should, as a minimum, define acceptable limits along the pipeline system for:

- Water
- Other impurities (e.g. H$_2$, NOx, SOx, H$_2$S, CO, O$_2$)
- Temperature
- Pressure

The effective management of water and other impurities will be critical for preventing potentially very rapid internal corrosion. The limits set should be based on a sound understanding of the corrosion mechanisms and should consider all reasonably foreseeable mixtures (rather than just the individual substances in isolation) and operating conditions (planned and upset).

The depressurisation of dense phase CO$_2$ in a pipeline or other system may, if not carefully controlled, result in a significant temperature drop of the inventory and containment envelope (e.g. pipeline material). Should the inventory pressure be allowed to drop below the triple point pressure before all the liquid phase CO$_2$ has either vaporised or removed via a low-point drain, solid CO$_2$ will form. Allowing the formation of solid CO$_2$ in a system is not desirable unless the system has been designed for this since:

- Solid CO$_2$ at ambient pressure is -78˚C and this would severely chill the containment envelope possibly leading to:
  - Embrittlement and fracture
  - Damage to linings or coatings
  - Ground freezing with potential ground heave (e.g. buried onshore pipeline)
  - Ice coating (e.g. subsea pipeline);
- Plugs could be created in the pipeline or associated pipework leading to pressure build up in trapped inventories as the solid CO$_2$ sublimes to vapour phase (with a corresponding 500+ fold increase in volume);
- Danger of system over-pressurisation if the system is brought back on stream with dense phase CO$_2$ due to the very rapid sublimation of the solid CO$_2$;
- Time required for the solid CO$_2$ to clear (i.e. sublime to vapour) and the pipework to warm to an acceptable level will likely be very significant.

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The potential for solid CO_2 formation in the pipeline or other system should be fully assessed and the associated hazards and issues carefully managed.

A characteristic of CO_2 at conditions around its critical point is a large change in density with a relatively small change in temperature (see Figure 2-2). The potential for system over-pressurisation of isolated inventories due to, for example, high ambient temperatures or accidental fire loading requires to be assessed.

The control and protection systems incorporated into the design will form an integral part of the risk management process in both preventing hazardous situations from occurring and minimising the impact should an incident occur. The following systems will require to be considered when specifying and designing the CO_2 systems:

- Safety related control and protective systems;
- Process control systems (including back-ups);
- Safety instrumented systems;
- Loss of containment detection systems;
- Alarm systems;
- Automatic shutdown systems;
- Automatic pressure control or let-down systems;

Detection measures should be based on the findings of the risk assessment. Detection measures will vary according to the type of incident to be detected. Automatic detection systems may be used in buildings or other containment area. They may take the form of CO_2 concentration detectors, leak acoustic detectors, open path infrared detectors, thermal detectors (to detect the temperature drop upon dense phase CO_2 depressurization) or process detection (e.g. pressure drop or change in flow). Due to the relative immaturity of CCS experience, detection technology may not have been fully developed and tested. It is therefore important to ensure adequate validation has been conducted before taking credit for a particular detection measure.

Where automatic detection is not possible, it may be appropriate to use vigilant people (e.g. during a non-routine maintenance intervention).

Detection systems should be appropriate for the range of incidents for which they may be needed.

Detection equipment should be appropriately located, taking account of the type of incident, how it may develop, and the capacity of the equipment to respond and to relay the right information for effective control action to take place. For CO_2 detection due cognisance should be taken that CO_2 vapour is denser than air and will tend to sink down, slump and spread out over the ground, follow topographical downward slope, valleys and ditches, and accumulate in low level areas.

Detection measures should be automatic with automatic transmission of information to an appropriate control point, where this is reasonably practicable. Where this is not possible, adequate arrangements should be in place to detect incidents and to instigate control action.

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Detection systems should be able to ensure the timely detection and alerting of appropriate people that a hazardous situation has occurred or is occurring.

Effective contingency arrangements for circumstances when all or part of the detection system is not available because of maintenance or because of damage must be in place. Detection systems need to remain operational during the emergency to the extent necessary to do the job required of them. The potential failure mode of electronic devices when exposed to extreme chilling, as would be the case in the plume a large dense phase CO$_2$ release, needs to be considered.

Appropriate control measures to limit the extent of a hazardous incident need to be put in place. Control measures may comprise structural measures, operational and management procedures, plant and equipment, and their control systems. Control measures include measures to monitor the extent of an emergency for the purpose of exercising managerial command and control. Control measures should take account of, and be influenced by, the risk assessment. Control measures may require to be installed for legal compliance such as pipeline emergency shut-down valves. A risk-based approach should be used for selecting control measures in addition to the regulatory minimum.

Equipment used to control the extent of an emergency should be designed on the principle that it does not fail to danger. Additionally, the design of such equipment should take into account human factors including ergonomic factors with respect to its operation in an emergency. Appropriate measures to control the emergency should include suitably staffed control points which can be used safely for the period necessary to control the emergency.

For the CO$_2$ pipeline system control measures may include:

- Propagating crack arrestors;
- Emergency shutdown (ESD) system;
- Automatic isolation valves;
- Vents and drains;
- Emergency depressurisation (blowdown) system.

For CO$_2$ service, the following should be considered within the design process:

- Elastomers should be selected for the CO$_2$ duty. Dense phase CO$_2$, particularly supercritical CO$_2$, is a low viscosity substance that will penetrate some elastomers and will cause damage to the elastomer should a rapid depressurisation of the system occur;
- Lubrication should be selected for the CO$_2$ duty. Dense phase CO$_2$, particularly supercritical CO$_2$, has excellent solvent properties that will effectively remove the lubricant;
- Should the valve fail to seal completely, the flow through the valve will lead to severe cooling on the downstream side with the potential for considerable solid CO$_2$ build up (at -78°C);
- Re-pressurisation of a system where there is dense phase CO$_2$ on one side of the valve and sub-critical pressure on the other will result in cooling and solid CO$_2$ as previously discussed. Re-pressurisation of systems requires careful consideration;

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- Depressurisation of a dense phase CO$_2$ inventory, be it a large compressor or pump or pipeline, can, if not carefully controlled, result in large amounts (potentially tonnes), of solid CO$_2$ being deposited at the low points within the system. This is discussed further below.
- Bringing back into service systems in which solid CO$_2$ may have been deposited (see previous bullet) to prevent a sudden, potentially catastrophic, pressure rise due to rapid sublimation of the solid CO$_2$ and accompanying volume increase.

Handling large inventories of dense phase CO$_2$ creates considerable challenges due to the issues highlighted above and in particular due to the phase characteristics when dense phase CO$_2$ is depressurized either through a planned operation or by an accidental release. Further discussion on particular aspects of control measures is provided below.

System Depressurization

CCS CO$_2$ systems will require to be depressurised for operational reasons and potentially as part of a hazard management strategy (e.g. emergency blowdown) sometime during the lifecycle of the systems. In addition to situations where a controlled depressurization is undertaken, unplanned or inadvertent depressurization of dense phase CO$_2$ inventories is also reasonably foreseeable (e.g. a loss of containment event occurs).

Depressurising a dense phase CO$_2$ system in a manner that prevents significant solid CO$_2$ formation within the system and excessive material cooling can be achieved by careful control of the depressurisation rate.

When a dense phase CO$_2$ inventory is vented to atmosphere the pressure in the inventory will quickly drop, along with an associated temperature decrease, until the remaining inventory becomes a two-phase liquid-vapour mixture. The pressure and temperature of the mixture will then continue to decrease, at a rate dictated by release rate and energy transfer between liquid/vapour and across the containment boundary, until the internal and external pressures reach equilibrium (i.e. atmospheric pressure).

If the depressurisation rate is relatively slow or the venting locations are at low points, all the liquid CO$_2$ will either be vented and/or allowed to evaporate into vapour before the pressure falls below the CO$_2$ triple point pressure of 5.18 barg. If this happens then only vapour will remain in the system when the pressure drops below the triple point pressure and no solid CO$_2$ will be formed in the system. If however liquid CO$_2$ is present when the pressure drops below the triple point, a large proportion of this liquid will freeze into solid CO$_2$ and be deposited within the system.

It is therefore essential if solid CO$_2$ is to be avoided in a dense phase CO$_2$ system during a controlled depressurisation to ensure that there is no liquid CO$_2$ remaining in the system before the pressure drops to below 5.18 barg. In practice this can be achieved by vent system design and/or controlling the venting rate (e.g. inserting holds in the depressurization operation) to allow the system to warm up and allow the liquid CO$_2$ to vaporize before allowing the pressure to go below the critical point. More discussions on system depressurization are found in Chapter 8.2.4.

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Inventory Segmentation

CCS pipelines will have inventories of tens, if not hundreds of thousands of tonnes of CO_2. Segregating a pipeline inventory into smaller volumes should be considered as part of the risk management process by the use of actuated block valves. Check or non-return valves can also be considered to prevent back-flow. The use of segregation valves, their spacing and depressurization arrangements, and associated required level of performance, will require careful consideration as part of the operation and hazard management of the pipeline system.

On land pipelines, the risk profile along the pipeline will be heavily influenced by the nearby population density, topography and potential leak inventory. Taking a risk-based approach to determining the requirement for segregation valves should help to ensure a balanced solution (e.g. leak inventory reduction versus leak frequency increase versus capital and operational costs, etc.). A risk-based solution would likely have relatively closely spaced block valves where the pipeline passes close to densely populated areas or on either side of a valley, and fewer or no valves where the pipeline crosses sparsely populated countryside.

A key part of determining the benefit obtained from check valves will be the realistic delay between the incident and closure of the valves. If the valves are actuated by a local control system (e.g. triggered by a sudden change in flow or pressure) then a rapid closure time for large leaks could be assumed. Where however, the detection means is vulnerable to failure or delay, this must be taken into account in the risk assessment and control measure strategy.

For offshore pipelines it is unlikely that the pipeline length will be subdivided by multiple valves. There may be a hazard management requirement to install valves at strategic locations such as where the pipeline makes landfall or close to an offshore platform but for the majority of the pipeline there will be no segregation valves. In addition, depressurized of a subsea pipeline will likely only be possible at one or both ends unless subsea venting technology is developed.

Another potential issue for subsea pipelines during a rapid depressurization is the potential for ice formation on the external surface of the pipeline due to the CO_2 phase change cooling discussed above. It is conceivable (until proven otherwise) that a thick layer of ice to form along a considerable length of the pipeline, particularly at low points, and for this to create buoyancy issues.

Vent System

The preceding discussion highlights the issues within a dense phase CO_2 system when it is depressurized, but there are also challenges associated with designing the depressurization system itself (i.e. the vent system). This system must be able to handle the extreme colds and solid CO_2 formation that it will be exposed to and also the release point must be designed and located such that people and other sensitive receptors are not exposed to harmful concentrations of CO_2 during all reasonably foreseeable ambient conditions. Particular consideration must be taken when releasing virtually pure CO_2 in still weather conditions, especially if there is a temperature inversion, since the cold CO_2 being released could slump on the ground (or sea) surface with

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minimal dispersion. Because venting is a design activity (as compared to an accidental release) the operator of the vent must be able to show that people will not be exposed to harmful levels of CO_2. The long term and short term exposure limits discussed in Chapter 6 will form part of the demonstration that the vent system is appropriate.

11.3   Mitigation Measures

As part of an effective risk management plan measures that will mitigate the effects of a CO_2 pipeline incident need to be identified, considered and implemented if reasonably practicable to do so. Equipment provided and action taken should be based on the risk assessment. The roles of different measures should be considered in an integrated way so that the functioning of one measure does not prevent another from meeting its required level of performance.

For the CO_2 pipeline system mitigation measures may include:

- Cold resistant coatings (e.g. on offshore platform steelwork);
- Ventilation control systems;
- Manual response equipment and procedures.

The mitigation measures should:

- Be appropriate for the hazards;
- Provide adequate levels of protection for key locations (e.g. muster points, escape routes, etc.) and emergency systems which may be effected by the incident.

All facility and pipeline operators must prepare adequate emergency plans for dealing with the on-site consequences of possible major accidents and providing assistance with off-site mitigation action. On-site should be taken as operator controlled areas (e.g. power station sites, compression station sites, etc.) whereas off-site are the other areas where the operator does not have management control or direct influence (e.g. pipeline route outside on-site areas).

The emergency plans should be in writing and cover the full range of possible major accidents including the operator's response to reasonably foreseeable low-probability, high-consequence events such as catastrophic pipeline failure.

All potential major accident scenarios should be taken into account when developing the plans.

On-site plan should establish the system for managing information in the event of a major accident. It should ensure that necessary information can be identified and communicated to people on-site and anyone off-site who may have a role to play (e.g. emergency services, local authorities, etc.).

The on-site plan should detail the roles that those who work on the site will have to play in the event of a major accident. It should include the arrangements that are established for assisting with emergency response off-site.

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The on-site plan should describe the arrangements and details for making-safe, restoration and clean-up of the impacted area and local environment after a major accident.

The off-site emergency response plan is usually prepared by a local authority who has responsibility for the pipeline system. The off-site plan details the roles to be carried out by emergency services, local authorities and other external organisations in the event of a major accident. This includes the arrangements established to help with the emergency response on site.

The off-site plan cannot be prepared without obtaining necessary information from the facility or pipeline operator.

During preparation of the emergency response plans (both on-site and off-site) local health authorities should be consulted as they will have to deal with any casualties from an incident.

The on-site plan and the off-site plan must dovetail together to ensure effective and efficient communication of information and provision of mutual assistance.

Due to the relative immaturity of the CCS industry, it is unlikely that external authorities and agencies will be aware of, or fully understand the hazards posed by large CO$_2$ releases. The CO$_2$ pipeline operator therefore has a duty to provide education for the people responsible for the development of the off-site plant as well as the people who have roles to play in the plan, with regard to CO$_2$, its characteristics and its dangers. The following subject areas need to be covered:

- **Response to inhalation of elevated concentrations of CO$_2$**
  CO$_2$ acts as both a stimulant and depressant on the central nervous system. Immediately after exposure to elevated CO$_2$ levels, the ventilation rate, total volume of air inhaled and exhaled during ventilation, CO$_2$ partial pressure in the lungs, and acidity of the blood are elevated.

  Inhalation of elevated CO$_2$ concentrations can produce a sour taste in the mouth and a stinging sensation in the nose and throat from the gas dissolving in the mucous membranes and saliva, forming a weak solution of carbonic acid. It can also lead to abnormal acidity of the blood (respiratory acidosis) if the capacity of the blood buffering system is exceeded. Apart from increasing the ventilation rate, the human body has no other significant means for controlling CO$_2$ concentration in the blood and body fluids.

  Hypercapnia is a condition where there is too much CO$_2$ in the blood. Hypercapnia is generally caused by inadequate lung ventilation (hypoventilation), lung disease, or diminished consciousness but it may also be caused by exposure to environments containing abnormally high concentrations of CO$_2$, or by re-breathing exhaled breath.

  Symptoms of early hypercapnia include flushed skin, full pulse, irregular heart beat, muscle twitches, hand flaps, and possibly a raised blood pressure. In severe hypercapnia, symptoms progress to disorientation, panic attacks, hyperventilation, convulsions, unconsciousness, and death. Further details of the impact CO$_2$ inhalation has on humans can be found in Chapter 6.

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- **CO$_2$ dispersion**
  CO_2 is a heavier-than-air substance which will tend to slump to the ground or sit on the sea surface unless there is sufficient air movement to disperse and dilute it. Low level areas such as valley bottoms, dips in the ground, drains, basements, etc., are probable locations where CO_2 vapour may accumulate following a large CO_2 release. If people cannot move quickly clear of a CO_2 release then moving to an elevated location may be the best alternative.

- **Handling CO$_2$ solids**
  In the close proximity of a dense phase CO_2 release it is likely that solid CO_2 will be deposited. The solid CO_2 or dry ice as it is commonly known, is white in colour and may range from powder deposits to dense consolidated blocks.

  Solid CO_2 is at a temperature of -78°C and if handled without protective gloves could cause severe cold burns to the skin.

  Solid CO_2 will sublime to the vapour phase as it absorbs energy from the surroundings but as heat transfer can be slow, solid CO_2 may remain a considerable time after the CO_2 release has stopped.

  The sublimation of solid CO_2 deposits will create a continual production of vapour phase CO_2 which is heavier than air and in still air conditions can accumulate in low level areas such as dips in the ground, drains, basements, etc., to pose a threat to people returning to the area after an incident.

- **Detecting CO$_2$ accumulations**
  There is no significant inherent human response to CO_2 that could be useful as a detection mechanism, in contrast to other harmful gases. Human response to H_2S by smell occurs at very low (ppm) concentrations, similarly with ammonia and sulphur dioxide. CO_2 is present in the air we breath 0.037% and this may cause problems with instrumented detection because the 'background CO_2' levels are so high. Secondly the cooling effects of a CO_2 leak may have an adverse effect on the accuracy and operability of CO_2 gas detection systems /72/. CO_2 in its normal vapour phase is invisible and detecting hazardous concentrations requires specialist CO_2 detectors. Oxygen detectors could be used as an alternative provided the alarm level is set accordingly. Chapter 6.3 provides a section on asphyxiation that notes that there can be lethal concentrations of CO_2 present whilst oxygen levels are still non-dangerous.

  A CO_2 may create a visible cloud that may spread a considerable distance from the leak point. Close to the leak point the cloud would likely be a mixture of solid CO_2 particles mixed with condensed water ice crystals and condensed water vapour. Further from the leak point the solid CO_2 will have either sublimed into invisible CO_2 vapour or dropped-out onto the ground. The remaining cloud will be condensed water vapour due to the cold CO_2 stream that is condensing the water in the air. As the CO_2 stream warms up due to the

Reference to part of this report which may lead to
misinterpretation is not permissible
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mixing of relatively warm air, the condensed water vapour will progressively get less until the cloud disappears.

The visible cloud represents the extent of the water vapour condensation (not the extent of the elevated CO_2 levels). If the CO_2 inventory stream that is leaking is hot (e.g. a leak from a compressor before an interstage cooler), there will be no visible cloud produced. If the ambient atmosphere is very dry into which a CO_2 release flows, the water vapour cloud will be smaller than on a humid day. The presence of a visible cloud should <u>not</u> be taken to indicate the presence of a CO_2 leak.

The German incident highlighted in Section 4.1 is a good example where the dangers associated with elevated concentrations of CO_2 were not fully understood and because there was no visible cloud (due to the release warming to above the dew point temperature of the water vapour in the air) emergency response personnel inadvertently moved into a life-threatening location.

Risk management measures once identified must be maintained to deliver the defined level of performance that is required. To achieve this there should be a continuous management cycle of:

- Maintaining an understanding of the hazards and risk;
- Identifying the critical risk management measures;
- Defining the minimum level of performance from each critical element;
- Implementing a robust inspection, test and maintenance regime to keep the critical elements performing;
- Having a verification process to provide assurance that the critical elements are actually likely to deliver the defined level of performance; and
- Having a review loop to ensure any changes in the risk profile or its management is identified and fed back into the cycle.

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12   CONCLUSIONS AND RECOMMENDATIONS

12.1   Concluding Remarks

Throughout the world there are high hopes that CCS can contribute significantly to mitigate global warming by controlling the CO_2 emissions from hydrocarbon fuelled power stations and other significant CO_2 producers. However, to do so CCS has to be deployed on a global scale that is 1000 times larger than it is today. Although CO_2 in its gaseous form is a well known substance, conveying dense phase CO_2 with inventories in the order of tens or even hundreds of thousands of tonnes, will require that current design, operations and hazard management knowledge needs to be expanded. Moreover, compared with large scale hydrocarbon handling, there is much less experience worldwide with managing potential risks associated with large scale CO_2 handling.

The EOR industry, predominantly in the US, has been transporting and handled relatively large amount of CO_2 for several decades, and the HSE experience gained from that industry should indeed be utilized in order to ensure that operational HSE concerns are adequately understood in the process of wide-scale deployment of CCS. However, there are some aspects that make a direct transfer of experience and knowledge from EOR to the future CCS industry not straight forward. In particular, the location of future CCS pipeline networks could potentially run in proximity to densely populated areas creating additional challenges which have not been experienced for EOR pipelines located in typically remote areas.

CO_2 is classified as non-flammable and non-toxic substance (category C), and according to the GHS CO_2 is a substance that is currently "Not Classified". That said, a substance or mixture that is "Not Classified" may still have hazardous properties albeit at a quantity, concentration, dose or other characteristic that is outside the threshold limits defined in the classification criteria. CO_2 at elevated concentrations is known to have toxicological effects on the human body. The classification of CO_2 as of today and the implications with respect to safety regimes in design and operation have not been further elaborated in this study, as the scope has been to map the potential hazards.

The potential hazards of CO_2 handling for CCS purpose have been identified by reviewing publicly available knowledge and industrial experience. Subsequent to the review a workshop was held with relevant stakeholders from industry and regulators assessed and discuss the issues identified, their relevance and their management.

Although the study intended to map the value chain of CCS, from capture to injection, most of the hazards has been identified in association with the compression unit and pipeline transport system, where large inventories of dense phase CO_2 is present. For most captures plants, CO_2 is likely to be in its gaseous form at low pressures, however, potential hazards due to, for example, venting (planned or due to upset conditions) should be equally assessed and managed. Most of the HSE issues identified are related to phase characteristics when dense phase CO_2 is depressurized, either through a planned operation or by an accidental release. The categories of hazards that have been identified can be divided broadly into three groups:

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- CO$_2$ pipeline issues (external and internal corrosion, hydrate formation, overstress due to free span, pipeline propagation fracture);

- Material issues (solvent properties an material compatibility, elastomers);

- Operation and engineering challenges (solids formation, system depressurization (both controlled and accidental), low temperatures, vessel ruptures/failures, rapid phase transition, cold CO$_2$ BLEVEs).

It is not anticipated that any of the identified hazards and areas of concern will represent a show-stopper to the deployment of CCS, as long as the risks are assessed and managed properly.

Still, there are gaps in knowledge and experience for certain issues relevant for large-scale handling of CO$_2$ for CCS that must be further investigated in order to be closed and enable a better understanding for safe design and operation across the CCS value chain. The most important gaps identified related to HSE concerns were:

- Modelling of dense phase CO$_2$ releases;
- Behaviour of dense phase CO$_2$, particularly around the thermodynamic changes when dense phase CO$_2$ experiences a reduction in pressure (e.g. leak, venting, throttling, etc.);
- Corrosion due to impurities or contaminants (e.g. H$_2$O, H$_2$, O$_2$, H$_2$S, etc.) either during steady state operation or upset conditions;
- Crack propagation;
- Loss of integrity of elastomers due to CO$_2$ absorption; and
- Changes that CO$_2$ mixtures (e.g. CO$_2$ with HC, H$_2$, CO, H$_2$S, etc.) have on the behaviour and properties of pure CO$_2$.

Moreover, public acceptance remains an important issue, and a consistent and clear communication with various stakeholders is needed. However, this is not a unique aspect to CO$_2$ handling but rather an important issue for CCS throughout the whole value chain.

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12.2   Recommendations for Future Work

In the previous Table 10-2, a summary of the issues of concern that should be given the highest priorities in order to close the identified gaps in knowledge, are listed. However, we recognize that efforts and initiatives are underway or under planning in dealing with several of these issues elsewhere; such as corrosion, crack propagation and material issues. Therefore, we recommend focusing on the gaps not sufficiently covered in initiatives underway or under planning elsewhere. Moreover, the issue of CCS public acceptance is also a topic that has been receiving increased attention recently.

The lack of knowledge on impact and issues relating to possible variations of impurities in the CO$_2$ streams requires more research. Impurities could include contaminants that could pass into the CO$_2$ during normal operations (e.g. CO, O$_2$, H$_2$, H$_2$S, NOx, SOx, H$_2$O, etc.) and abnormal upsets (e.g. glycol or amine carryover). The impact of impurities on the triple point of CO$_2$ is not known and should be further assessed.

The lack of validated consequence models for dense phase CO$_2$ could result in delays in CCS projects due to permitting difficulties, or considerable costs for the CCS developer due to an overly-conservative approach being taken. Areas of dense phase CO$_2$ consequence modelling that require further development work and validation include:

- Modelling within a pipeline and vessels when there is a rapid depressurisation down to atmospheric pressure;
- Modelling of underground releases particularly around modelling the release momentum when the CO$_2$ reaches ground level;
- Modelling of releases into a contained volume (e.g. an offshore module);
- Modelling of subsea releases particularly around predicting the sea surface characteristics;

These modelling aspects are identified as critical gaps, and sufficient efforts, to our knowledge, have not been initiated to close the observed gaps. Therefore, issues listed in Table **12-1** should also be given priority for further assessment.

Another aspect that is particularly relevant in the current development period for CCS is the lack of experience-based codes, standards and best practices. Stakeholder pressure is driving CCS projects forward but without accepted guidance, the projects (and the CCS marketplace) will have significant risk exposures. One of the key aspects for most CCS projects will be determining route options for CO$_2$ transmission, and in particular, what distance of safety should be used on each side of a pipeline. Minimum proximity distances are available for existing pipeline inventories but currently not for dense phase CO$_2$. To assume, for example, that natural gas pipeline safety distances are applicable for CO$_2$ without adequate justification could result, if the safety distances for CO$_2$ subsequently prove to be greater, in significant cost impact to a project and/or a forced acceptance of heightened safety risk levels for people living in the vicinity of CO$_2$ pipelines. It is therefore recommended that once the suitability of consequence models has been established that a pipeline consequence modelling project is conducted with the aim of establishing industry guidance for pipeline planning purposes.

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Table 12-1: Recommendation for future work

Identified Gap	Proposed Activity	Explanatory notes
Models for predicting the conditions within a dense phase CO$_2$ pipeline during a rapid depressurisation have not been validated.	Review and establish appropriate depressurisation theory. Develop and undertake small, medium and, if required, large scale experiments to collect data for theory and model validation. Undertake a set of controlled model validation exercises to assess model/modeller performance and accuracy bounds.	Understanding and being able to accurately model how a dense phase CO$_2$ pipeline will depressurise along its length is of critical important in assessing ductile crack propagation, assessing low temperature impacts to pipeline structure, predicting leak source terms, predicting solid CO$_2$ accumulations and for developing safe operating practices.
There is insufficient data across the full range of release sizes to validate dense phase CO$_2$ release and dispersion models.	Develop a dense phase CO$_2$ release and dispersion model validation programme that extends currently available data across the full range of CCS relevant release cases. Deliver the validation programme. Control the release of the validation data so as to gain confidence in the accuracy of the release and dispersion models being used in CCS consequence analysis.	Understanding the accuracy and uncertainty around release modelling is key to consequence analysis and effective risk management. Currently there are few, if any, release and dispersion models that have been validated across a representative range of dense phase CO$_2$ accidental scenarios. The lack of validation data prevents model validation. Moving forward without validated models, particularly for large scale and long duration dense phase CO$_2$ releases, will introduce a threat to the successful implementation of CCS.

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There is no robust guidance on modelling dense phase CO_2 releases and system depressurisation.	Develop best practice guidance for consequence analysis modelling of dense phase CO_2 systems and releases from such systems.	With the lack of definitive guidance, consequence analysis modellers, even using the same validated models, could arrive at a wide spread of predictions for the same scenario due to how they set variables, make assumptions and otherwise adjust the models. Guidance is required to help modellers model dense phase CO_2, which to many will be a new experience.
There is no substantiated guidance for dispersion modellers for predicting the ground-surface source term from a buried pipeline release.	Create a representative set of buried pipeline leak scenarios. Undertake a set of experiments to collect release and dispersion data from buried pipeline releases. Develop modeller guidance for modelling releases from buried dense phase CO_2 pipelines.	The momentum of a CO_2 plume when it reaches the surface will have a significant influence on the predicted hazardous distances. Assuming that all the momentum has been removed may prove to be overly conservative resulting in extremely large predicted hazardous distances but to move away from this approach requires evidence that currently does not exist.
There is no substantiated guidance for dispersion modellers for predicting the sea-surface source term from a subsea pipeline or riser release.	Create a representative set of subsea pipeline and riser leak scenarios. Undertake a set of experiments to collect release and dispersion data from subsea releases. Develop modeller guidance for modelling releases from subsea dense phase CO_2 pipelines.	The momentum of a CO_2 plume when it reaches the surface will have a significant influence on the predicted hazardous distances. This will be of particular importance for shallow water releases such as near a land/sea or sea/platform interface. Errors predicting the momentum as the CO_2 emerges into the air could result in significant over and under estimation of hazardous distances.
Understanding of Boiling Liquid Evaporating Vapour Explosions (BLEVE)	Undertake further investigation regarding the possibility of CO_2 BLEVE and if required conduct experiments to prove or disprove phenomenon	Theoretical basis still not proven. CO_2 needs to be in a specific envelope of pressure and temperature

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There is a lack of understanding of the impact CO_2 mixtures and impurities will have on modelling of flow, release and depressurisation.	Undertake a study on the effect of impurities and how they alter the phase diagram/impact on phase change parameters. Undertake a set of experiments to collect release and dispersion from different CO_2 mixtures to validate models, form a set of release scenarios.	Impurities could include contaminants that pass into the CO_2 during normal operations (e.g. CO, O_2, H_2, H_2S, NOx, SOx, H_2O, etc.) and abnormal upsets (e.g. glycol or amine carryover)
There is a lack of knowledge regarding solid CO_2 drop-out during a release within a contained space (e.g. an offshore module) or when there are impurities in the CO_2 stream.	Plan and undertake small, medium and if required, large scale dense phase CO_2 releases within a contained space. Plan and undertake experimental releases to investigate how contaminants and particulates in the CO_2 stream alter solid CO_2 production. Record data.	A dense phase CO_2 release unless the inventory is hot, will produce a 2-phase flow of solid and vapour CO_2. A release into the air or open area will likely see the solid CO_2 particles subliming almost immediately to vapour with little fallout and accumulation. A release into a space where boundaries will restrict ambient heat energy may result in limited sublimation and a considerable build up of solid CO_2. At -78 deg C a large accumulation of solid CO_2 could impact the structural integrity of any steel structures that it is in contact with (e.g. offshore platform primary steelwork).

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In addition, activities left out from the scope of work in the original proposal should be investigated, i.e.:

Identified Gap	Proposed Activity	Explanatory notes
Large-scale deployment of industrial chemicals (oxygen, hydrogen, amines)	Map relevant HSE issues, experience and knowledge related to large-scale handling of industrial chemicals.	Future capture plant will introduce handling of industrial chemicals (oxygen for oxyfuel, hydrogen in pre-combustion and amines/ammonia for post-combustion) at scale that would require assessment from a HSE perspective.
Lack of public available experience from operators and knowledge transfer to CCS industry.	Interview experienced operators and other industry actors. Include review of standards and practise applied and experience gained relevant for HSE in CCS projects operated to-date, in particular in the US, Algeria, Norway and UK.	There are several project today operating and transporting large quantities of CO_2 for EOR purpose. In particular, operator experience from the US would provide valuable input when assessing design and operation of a CCS facility.

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APPENDIX A

MODELLING CO$_2$ RELEASES

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A1   Release Rate Modelling

Under most circumstances there is no reason to assume that the flow rate from a gaseous CO_2 inventory release should be calculated in a different manner to other gases (e.g. using the ideal gas and/or Peng-Robinson equations of state, ideal gas law, etc.). There are a number of text-books such as Lees /92/ that provide details of the assumptions and expressions that can be used and there is considerable experience modelling gaseous releases. For gaseous CO_2 the main point to watch is that in an assumed gaseous isentropic expansion the thermodynamic path may terminate in a two-phase region.

With regard to gaseous pipeline inventory releases there are a number of methods available with varying levels of complexity. These range from simple, analytical expressions derived using various assumptions to methods which solve the fluid flow equations directly such as the 'method of characteristics'.

As with gaseous CO_2 releases, in many circumstances there is no reason to assume that the flow rate from a liquid inventory should be calculated in a different manner to other compressed volatile liquids.

For a vessel containing either a sub-cooled liquid or a supercritical fluid with a thermodynamic state to the left side of the saturation dome on a p-h diagram, a typical thermodynamic path from the vessel conditions to the exit plane is shown by case A in Figure A1.1. The reason for the path terminating where it does is that in this position the flow rate is maximised; any further drop in pressure along the isentrop results in a liquid/vapour two-phase state at the exit plane where the density rapidly falls due to the vapour portion.
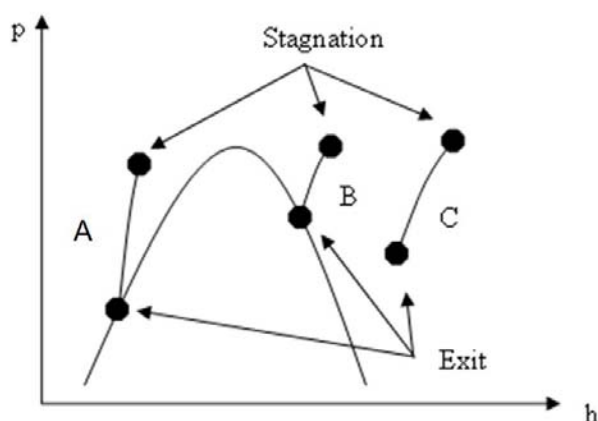

Figure A1.1: Typical thermodynamic paths from vessel (stagnation) to exit plane conditions for three vessel thermodynamic states.

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For path A the flow rate can be calculated reasonably by several methods such as homogenous equilibrium method (HEM) or Omega method /94/. A modified version of the Bernoulli equation using the pressures at the start and end of the path will also give comparable results in many cases. However, it can be noted that for a saturated liquid, where the thermodynamic state lies on the saturation dome (for example the bottom point of line A in Figure A1.1), the "modified" Bernoulli equation is not valid, and indeed as this point is approached it must begin to break down. The normal form of the Bernoulli equation can still be used, but as shown in the example below it is very pessimistic.

In the Omega method /94/ a correlating factor (ω) for compressibility is used with an assumed equation of state. The advantages of the ω-method are that only upstream conditions are required and the process of varying the exit pressure required in the HEM is not needed. In addition, because the thermodynamic data required by the method is less than in the HEM, tabulated data can be used. Also, the method has been extended to allow it, for example, to deal with a release which takes place through a length of pipework.

The various methods described for sub-cooled and supercritical liquids are compared in Figure A1.2 where the upstream temperature is 0°C. This graph show mass flow rate per unit area as a function of pressure, without any discharge coefficient applied. It can be seen that the straightforward application of the Bernoulli equation gives a significantly higher flow rate than the other methods. On the other hand, all three of the other methods are in good agreement. It can be noted that the three methods which are in good agreement here are in agreement for a reason, this being that they are doing essentially the same thing in the particular region of thermodynamic states under consideration well above the saturation dome.

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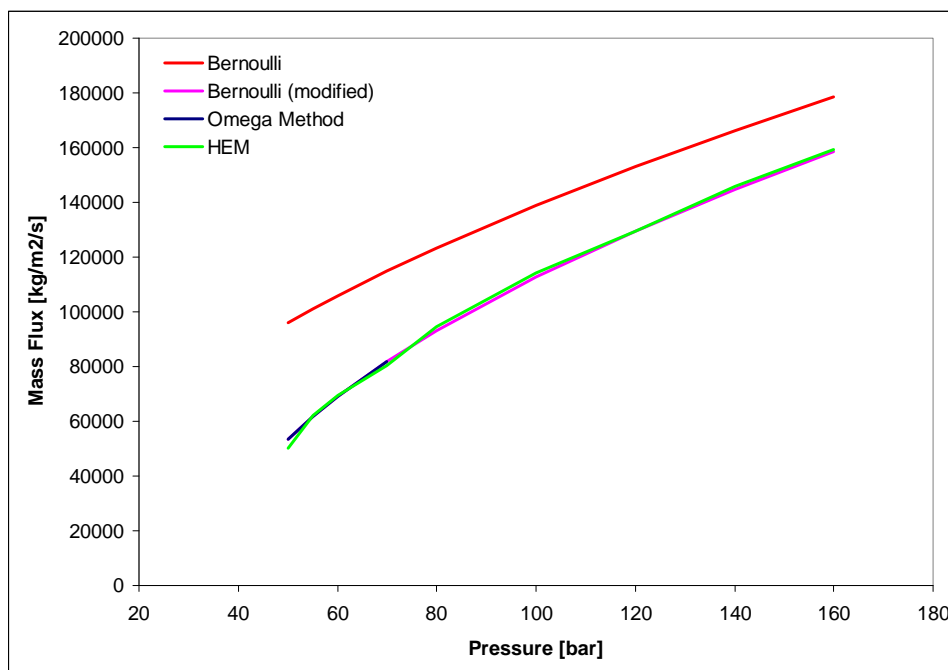
Figure A1.2: Mass flow rate per unit area as a function of pressure for sub-cooled liquid and supercritical inventories. In each case the temperature is 0°C. Flow rates are calculated using the Bernoulli equation, the Bernoulli equation assuming the saturated vapour pressure at the exit, the ω-method and HEM.

Figure A1.3 shows a similar graph for the case of a saturated liquid inventory. In this case it is not possible to use a "modified" form of the Bernoulli equation as this would give a flow rate of zero. The remaining three methods are compared, and again the ω-method and HEM are found to be in good agreement with each other, but the Bernoulli equation is higher by up to a factor of four.

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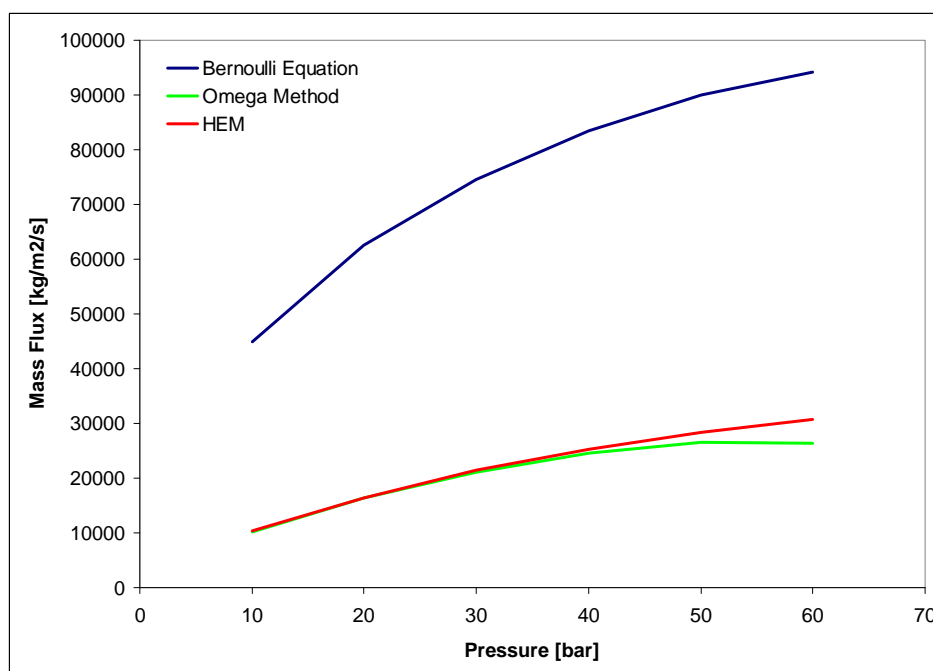Mapping of potential HSE issues related to large-scale
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Figure A1.3: Mass flow rate per unit area as a function of pressure for saturated liquid inventories. Flow rates are calculated using the Bernoulli equation, HEM, and the omega method.

It can be noted that in all of the cases used to populate these graphs, the pressure at the exit plane was calculated to be above the CO_2 sublimation pressure of 5.2 bar. While this is the case the fluid is either liquid, vapour or a two-phase liquid/vapour mixture for which the various models (HEM and ω-method) are valid. If the pressure falls below this then the models become invalid and this is the reason there is considerable uncertainty around modelling dense phase CO_2 releases as it is not clear what the effect of this will be.

It should however be noted that an accidental release can be through a crack rather than a hole – which would affect the thermodynamics – due to the difference in friction through the crack.

The above methods neglect losses and these can be accounted for using a discharge coefficient. There is some uncertainty to the discharge coefficient for the liquid case. For liquid discharge, a value of 0.62 is commonly used /92/, but in the case of CO_2, there is additional physics taking place with flashing at the exit. Cumber /95/ suggests a value of 0.8 for both gaseous and two phase releases. For the releases considered in this section, the flow will generally be a saturated two phase mixture at, or close to, the outlet. Hence, if the thermodynamic state of the fluid within the vessel is a sub-cooled liquid, a two-phase liquid/vapour mixture or a supercritical fluid with entropy below the critical entropy, it is suggested that the discharge coefficient is chosen to be 0.8, while if the fluid within the vessel is a gas or a supercritical fluid with entropy above the critical entropy a value of 0.85 is suggested.

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With regard to liquefied gas pipeline inventory releases, as in the gaseous case, there are a number of methods available with varying levels of complexity. In the case of liquefied gases, the approximate methods have to make substantial assumptions.

A representative example of an approximate model is that of Cumber which is described in two papers /96/ and /97/, the first describes a model for a volatile liquid pipeline (typically used for propane, but also applicable to carbon dioxide so long as the pressure remains above the triple point pressure, 5.2 bar. Below this pressure, solids can be produced in carbon dioxide); the second extends this model to the case of a supercritical fluid.

The overall basis of the method is to take the equation for pressure gradient in the two-phase region and approximate a number of factors as functions of pressure (only) so that it can be integrated. To allow the integration to be carried out, several significant assumptions are necessary including:

1. The pipeline is assumed to be infinitely long.

2. Flow is assumed to be isenthalpic

3. Mass flow rate is assumed to increase linearly from the liquid/two-phase interface to the location of the rupture.

4. Several assumptions relating to the method by which some integrals are estimated, which can be found in the published paper

The model was originally applied to volatile liquid pipelines. The extension to supercritical fluids is described in reference (Ref. /97/). In this paper the fluid considered is ethylene, but the physics is the same with carbon dioxide However, the method is only applicable to a limited range of supercritical states. Practically, the model for supercritical fluids is the same as for a liquid pipeline. The reason for this can be found in the references.

Since the approximate methods are unsuitable for calculating the flow rates from, for example, short lengths of pipeline the "method of characteristics" can be used as for the vapour case. The theory is essentially the same as in the vapour case, but a real gas equation is needed to describe the two-phase thermodynamics. A cubic equation of state such as the Peng-Robinson equation is typically used. Applications to liquefied gases and supercritical conditions are described, for example, in reference (/98/). Finite difference models can also be used in place of the method of characteristics, as described in Refs. /99/ and /100/ .

A2   Dispersion Modelling

Provided below is an overview of dispersion modelling with a particular focus on CO_2.

The main issues that need to be adequately addressed within a carbon dioxide dispersion analysis (whether from a dense-phase or gaseous inventory) are:

- It is denser than air so that it will tend to slump, particularly in low wind speeds and the influence of buildings and topology may be important

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- It is often cold at its release point accentuating its dense nature

- Solid CO_2 may, depending on the upstream inventory conditions, be formed in the expansion region and be carried into the dispersing cloud

- The CO_2 inventory is unlikely to be pure and due account needs to be taken of impurities (e.g. H_2S, CO)

The only significant aspect of a gaseous CO_2 release where care is required is where the thermodynamic path followed enters the two phase region resulting in both vapour and solid phase CO_2 being formed in the expansion region. However, generally, from gaseous inventory releases any solid fraction would be relatively small and would be expected to quickly sublime. Hence, in many cases it is likely that it can be neglected.

There is, however, a particular challenge when modelling dense phase CO_2 releases due to the potential to form significant fraction of solid CO_2 both in the inventory should the pressure drop below the triple point pressure of 5.2bar, and in the expansion region of the release. It is the solid formation aspect of CO_2 that differentiates it from other well known inventories such as liquid propane, LPG, etc. when release modelling is required. It should be noted that in a dense phase CO_2 release where both vapour and solid CO_2 is exited at the release point, once the majority of the solid CO_2 sublimes into vapour, the existing CO_2 dispersion models can be used, as per a gaseous CO_2 release. The difficulty is determining the appropriate source term for the gaseous CO_2 release dispersion modelling that takes into account the influence the solids have in the vapour only modelling.

Some of the aspects described above are shared with other gases. The only truly unique aspect is the solid particles carried by the plume. There are several general methodologies which can be employed for dispersion calculations for carbon dioxide and other gases. Parameters which need to be considered in choosing a methodology include whether or not surrounding plant and/or terrain needs to accounted for, wind speed and direction relative to the release, and length scales of interest. The two broad methodologies which can be employed are integral models and computational fluid dynamics (CFD). These two general classes of technique are described below.

A2.1 Integral Models

Many atmospheric dispersion models for environmental analysis are conducted with Gaussian plume models. The Atmospheric Dispersion Modelling Liaison Committee which is an independent organisation which advises on matters of atmospheric dispersion modelling has developed a simple Gaussian plume model which has been widely used and is often referred to as the R91 model /74/. The R91 model has been extended to include a variety of effects (deposition, coasts, plume rise, buildings) which led to the development of more complex Gaussian models /75/. This provides the basis for commercial codes such as ADMS.

Gaussian plume models have a number of limitations, some of which are that: there is a minimum wind speed for applicability which is generally taken as 1 m/s; zero wind speed cannot be calculated; any vertical component of the wind, which might be generated by upwash or downwash over buildings, structures and terrain, cannot be included; only applicable when

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release source is sufficiently distant from surrounding buildings for airflow at release height to be undisturbed; any momentum in the released plume is accounted for by specifying an "equivalent height" of release; no transient calculations.

Gaussian plume models are not expected to be appropriate for the majority atmospheric dispersion calculations in CCS projects since they will only applicable at concentrations of CO_2 at which the hazard is negligible. A possible exception may be if the CO_2 contains significant quantities of a more toxic material such as H_2S.

There are more advanced integral models available than the simple Gaussian plume models described above, which can deal with heavy gases. These include HGSYSTEM /77/ and PHAST /78/. Under some circumstances these models can deal with the negative buoyancy of CO_2 and the tendency of a plume to slump on the ground. In some cases they can also deal with the transition from a momentum dominated jet, through a slumping gas to a passively dispersing cloud. At least one model (PHAST) can also deal with the formation and subsequent sublimation of CO_2 particles, though *advice must be sought* from the code vendor to ensure that an appropriate code version is being used.

These more advanced integral models still have some disadvantages in regard to carbon dioxide dispersion:
 ▪ they cannot be used with very low wind speeds

 ▪ they cannot deal with cases where the plume interacts with itself, for example where a jet is directed into the wind so that the gas blows back around the jet

 ▪ the effect of interaction with buildings and/or plant cannot be accounted for.

These limitations are particularly pertinent to carbon dioxide dispersion where the most interesting cases tend to encompass one or other of these things. Another limitation of *some* integral model is that they do not include carbon dioxide as one of the materials which can be chosen as a flashing liquid release, so that scenarios cannot be attempted.

The primary advantages of integral models are that they are quick to set up and run, work well in appropriate scenarios and the main codes are well validated and accepted by regulators.

A2.2 CFD Models

Computational fluid dynamics (CFD) overcomes many of the limitations of integral models. CFD codes are based on the solution of mass, momentum and energy conservation equations (Navier-Stokes equations) to provide full 3D flow maps in an identified volume. Additional transport equations can be included to calculate the effects of turbulence and model the transport of different gas species (CO_2, CH_4 etc), pollutants or particulates. Calculated flows may be steady or transient, there are no limiting wind speeds, and momentum of releases and buoyancy are included explicitly. Physical obstructions such as buildings, structures and terrain which modify the flow and subsequent dispersion can be included explicitly in the models. General purpose CFD codes which are available commercially and lend themselves to modification to include models for particle transport etc.

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There are several disadvantages and problems still to overcome with CFD:
- in comparison with integral models the cases are slow to set up and slow to run,
- they typically require specialist staff to run,
- the codes are general purpose and are not specialised to dispersion so that there is more work required by the analyst, setting up source terms and atmospheric profiles, etc,

Moreover, CFD solvers are not designed to deal with the atmospheric boundary layer unless a proper meshing strategy is applied (proper grid size, structured mesh in the height direction and proper mesh checking procedures). Poor quality meshes will typically cause the profiles to change slowly though an empty terrain. Also, only wind and turbulence profiles for stability class D have received significant attention in the CFD literature. Articles on how to model the stable boundary layer using CFD are however available /76/.

There are several commercially available CFD solvers, the primary ones being FLUENT /79/ and ANSYS-CFX /80/ both of which are owned by ANSYS Inc and which will shortly be integrated to form a new code with the best features of each. Alternatively there is an open source code called Open-FOAM /81/ which is receiving increasing attention.

A2.3   Dense Phase CO_2 Releases

This section briefly describes some of the particular aspects of modelling dispersion from dense phase CO_2 releases concentrating on the expansion zone close to the release point. For a release where the vessel inventory is a liquid the fluid state at the exit plane is expected to be a saturated liquid or a liquid/vapour mixture. Beyond the exit the liquid will flash to a vapour and rapidly expand in a "tulip" shape whilst simultaneously cooling such that particles of solid carbon dioxide are formed. These particles will then sublime external to the vessel or pipeline.

For dense phase CO_2 releases this process is expected to be rather complex with three phases present, gas/liquid, liquid/solid and solid/gas phase changes occurring and very steep gradients. In addition, the length and time scales are separated from those of the far-field dispersion, so that, for example, including the detail of the region immediately adjacent to the nozzle in a CFD model for the far field dispersion may not be considered viable.

Hence, a simplified method for dealing with the region immediately adjacent to the release needs to be employed giving a pseudo-source in a similar manner to that employed in the case of an under-expanded sonic jet. One method to fix the parameters of the pseudo-source is based on the work of Fauske and Epstein /101/. The first stage is to find the flow rate and the exit plane conditions, using, for example, HEM as described previously.

Beyond the exit plane, the fluid expands and the resulting jet structure is shown schematically in Figure A2.1, where the jet is divided into two regions: a depressurisation zone and a two-phase entrainment zone. The inlet to a CFD model would normally be taken to be at the end of the depressurisation zone where the pressure in the jet has reduced to atmospheric pressure. The following assumptions would also normally be made:

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- There is no entrainment of air into the jet in the depressurisation zone, due to the pressure being above ambient in this region.

- Friction and heat transfer are neglected in the depressurization zone.

Conservation principles are used to find the jet properties at the end of the depressurisation zone, specifically *conservation of momentum flux*, c*onservation of energy* and c*onservation of mass*.
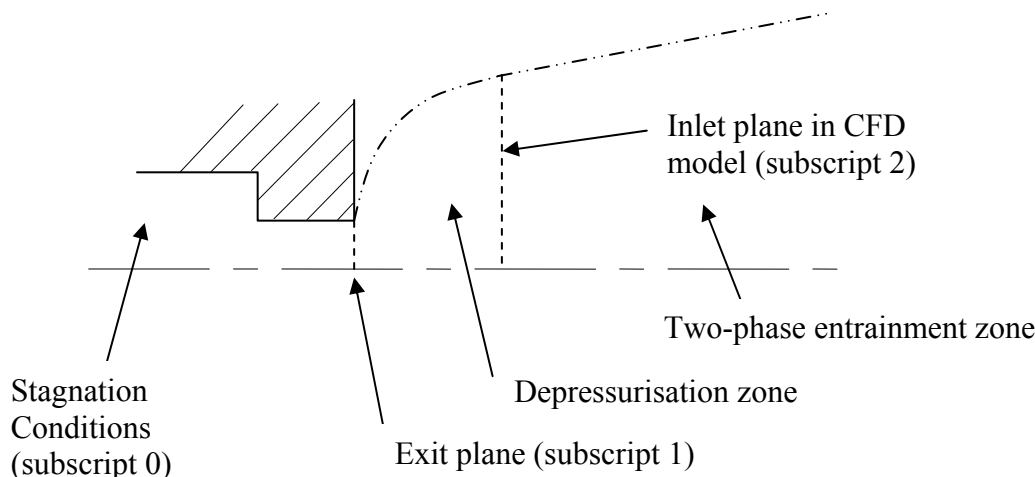
Figure A2.1: Schematic diagram of the jet structure for a flashing liquid.

It should be noted that at the end of the depressurisation zone there is the potential, depending on inventory conditions, for a significant flow of solid CO_2 within the jet in the form of very small particles. How these particles are taken into account as they sublime is important as they could significantly influence the CO_2 dispersion predictions.

Experimental evidence gathered during the BP research programme at Spadeadam, together with the modelling results confirmed that at the high pressures employed there, the particles are very small and, at least for jets into open air where there is effective mixing with the air, there is little fall out of particulates. Whether this observation holds true with a release into a contained volume such as found on offshore installations or compressor houses is doubtful.

It was previously mentioned that modelling the dispersion of CO_2 release, once it is in the gaseous phase is not a problem as there are validated models and considerable experience in this area. However, of the four issues that were highlighted for CO_2 dispersion modelling the following two have a particular relevance for dense phase release modelling:

- It is often cold at its release point accentuating its dense nature – this is particularly true for liquid CO2 releases due to the J-T cooling effect and the quantity of -78˚C solid CO_2 particles entrained in the release flow

Reference to part of this report which may lead to
misinterpretation is not permissible
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- Solid CO_2 may, depending on the gaseous inventory conditions, be formed in the expansion region and be carried into the dispersing cloud – as noted above the quantity of solid CO_2 from a liquid release will be significant

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APPENDIX B

WORKSHOP LOG

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B1   Pre-workshop Questionnaire

Prior to the workshop a simple questionnaire was sent out to the stakeholders that participated in the workshop in order to do an initial mapping of some of their concerns. The intent was to obtain an overview of what are the key HSE hazards, issues, threats and/or risks, with respect to CCS from capture through to injection (excluding storage), they believed was directly relevant to the developing CCS industry, and rank the level of concern from 1 to 10. The table that was sent out is presented in Table B1.1.

Table B1.1: Pre-workshop questionnaire table

Concern	Description	Concern Level (1-10)*

*   1 = Business as normal
          5 = Considerable effort required to move forward
          10 = Potential industry Show-Stopper

The feedback was collected by email and is summarized in Table B1.2.

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Table B1.2: HSE concerns among workshop participants

Concern	Description	Concern Level
1	Lack of an approach which effectively takes care of the complex totality of the whole value chain	10
2	European-wide agreement on methodology for Dispersion Modelling	10
3	Amine	8
4	European-wide agreement on composition for CO$_2$ suitable to be included in a North Sea infrastructure and agreement on the effect of impurities on Critical Point	8
5	Acceptability of locating CO$_2$ transportation systems in proximity to populated areas	8
6	Identification of suitable source terms to enable the modelling of pipeline leaks	7
7	Public perception of CCS in particular CO$_2$ transportation	7
8	Uncertainty in dense phase CO$_2$ releases from pipelines (e.g. dispersion, crater impact etc)	7
9	Decompression energy of CO$_2$ in dense phase => level of toughness in steel material for pipelines, need for crack arrestors. Segmentation as onshore will not be a practical solution offshore.	6
10	Energy consumption	6
11	Understanding dense phase releases from buried pipelines and resulting dispersion characteristics	6
12	CO$_2$ composition requirements - corrosion to pipeline	6
13	Input to quantitative risk analysis => probability and consequence of failure onshore and offshore, distribution model for CO$_2$. Lack of experience data	5
14	Releases of heated water	5
15	Technical feasibility of reusing/converting existing pipelines for CO$_2$ service	5
16	Venting of CO$_2$ (dispersion, solid formation in headers)	5
17	Lack of standards/guidelines for CCS design (e.g. pipelines)	5
18	Training of operators and management to run a CCS chain in a safe matter. New technology in Norway.	4
19	Reuse and an infrastructure of CO$_2$ pipelines are most likely needed. Quality of existing pipelines, control of possible water ingression and impurities from many catch sources.	4
20	Safe (emergency) blow-down arrangement. When required?	4
21	Discharges from the stripper column. General including NOx excluding amine.	4
22	CO$_2$ release hazard. / Release of Amine	4
23	Public acceptance of CCS	4
24	Effect of CO$_2$ release impacting on adjacent structure / hydrocarbon	4

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	pipe work in an offshore module, e.g. cryogenic effects	
25	Blowdown philosophy, risk to hardware (temperature issues, 2-phase flow, ...)	4
26	Simulation of CO_2 flow in pipeline (pressure/temperature) existing tools not optimized for CO_2 pipelines	4
27	Establishment of methods and procedures for venting CO_2 from offshore platforms	3
28	Materials issues (low temperature cracking, elastomers)	3
29	CO_2 pumping and compression	3
30	Blowdown philosophy, risk to personnel in vent area	3
31	Blowdown philosophy, environmental risk	3
32	Requirements to pipeline inner liner - CO_2 effect on liner material - clogging of injection well	3
33	Longitudinal fracture properties for high pressure CO_2 pipelines - need for fracture arrestors	3
34	Establishment of leakage detection systems - based on flow simulation tools not optimized for CO_2 transport	3
35	Effect of CO_2 on seals, gaskets etc	3
36	Availability of tools for internal monitoring (pigging)	3

Note that the above table summarizes all concerns raised in the feedback form, sorted by level of concern, without grouping them into categories; therefore, some issues are found several places in the list with a somewhat different wording and concern level.

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B2 Workshop log sheet

The complete list hazards/issues ("what ifs"), causes and consequences from the workshop are listed below. Moreover traffic lights are assigned indicating the criticality of the present knowledge gap.

Question Category	What-If (hazard/issue/concern)	Consequences	Causes	Gap
System issues (capture plant, pipeline, terminals, injection)				
	High water content entering the pipeline from the compression stage	Free water within the pipeline could lead to hydrate formation. Potentially leading to corrosion, leak and possible rupture. Rupture could pose a threat to a large number of people especially onshore.	Defective dehydration unit within the CO$_2$ capture facility. Incorrect control system settings. Failure of control system to detect out of spec. flow and shutdown before flow enters pipeline.	🟡

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	Out of spec CO₂ entering pipeline (impurities issue; H2O, SO2, NOX, H2S etc) *a) immediately after compression*	Impurities in the CO2 stream will alter the phase diagram for the mixture which will impact phase change parameters. Corrosion if free water is formed inadvertently due to change to phase envelopes, dew points, solubility, etc. Transport properties will change. Corrosion leading to leak and rupture could pose a threat to a large number of people. Venting or leakage of CO₂ with H₂S is worse than pure CO₂.The impact of impurities on the triple point of CO₂ is not known.	Upstream failure, e.g. dehydration unit/FGD	🟡
	Out of spec CO₂ entering pipeline (impurities issue; H2O, SO2, NOX, H2S etc) *b) downstream of compression (cooled)*	as above	Upstream failure, e.g. dehydration unit/FGD	🟡
	Compression surge	Backflow to the capture plant	Compressor failure	🟢
	Out of spec temperature from compression stage	Solubility of impurities affected	Insufficient cooling	🟢
	Water ingress in sub-sea pipeline implies risk to pipeline integrity	Enhanced corrosion. Risk to people if pipe brought back into service and corrosion has lead to pipeline weakening resulting in leak near sea/land interface	Damage to pipeline (external)	🟢
	Carry-over from capture plant (glycol/amine)	Affects corrosion rates. Leak could pose a threat to a large number of people.	Failure of water wash system and/or failure of coalescing filters to remove surplus solvent from outgoing CO₂	🟡
	Not sufficient education/skilled personnel	Human error. Damage to pipeline or systems due to mal-operation or poor design (e.g. damage to steel due to allowing solid CO₂ to form in pipeline). Possible harm to people if damaged system is brought back into service	Lack of skill and training. Wrong decisions. Polymer material damage. HC/scale mindset.	🟡

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	Increased O_2 concentration	Corrosion resulting in a leak that could lead to harm to people. Risk of having a oxygen/HC mixture if CO_2 is used for EOR applications.	Surplus of oxygen for combustion (i.e.oxy-fuel combustion)/wrong mixing ratio of fuel and O_2	🟡
CO_2 Properties and Behaviour				
	Impurities present	Thermodynamic envelope is changed	Upstream failure, e.g. dehydration unit/FGD	🟡
	Mixing of different CO_2 sources with different spec that do not comply with pipeline spec	Material compliance issue (corrosion). Liability issue Harm to people if loss of containment event results	Not sufficient guidelines/regulatory framework on CO_2 quality in place	🟡
	CO_2 is present at high conc. and no detection systems in place	Human exposure to elevated CO_2 cons. causing aspyxiation/hypercapnia	Large leak from equipment/pipeline or a undetected prolonged smaller leak.	🟡
Human Impacts				
	Leakage from a pipeline in a populated area (big leak-rupture)	Multiple fatalities	Large leak from pipeline	🟡
	Leakage from a pipeline in a populated area (small leak)	Danger within local area of the leak	Small leak from pipeline	🟡
	Lack of commonly accepted harm criteria	Applying wrong acceptance criteria - exposure of dangerous amount of CO_2	State-of-the art knowledge on CO_2 harm criteria not formulated. Inappropriate safe distances and risk reduction measures implemented.	🟡
Environmental Impacts				
	Big leak (onshore)	Impact for animals as for humans (see Human Impacts above)	Pipeline failure/loss of containment	🟢

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	Small leak (onshore)	Soil acidification (vegetation damage). Impact on subsurface microbial populations, impact on animals with (part of) habitats under ground.	Small leak from pipeline	🟢
	Big leak (offshore)	Increased pCO2 and decrease in pH. Impact on bottom dwelling organisms, impacts on fish/mammals as given for humans,	Pipeline failure/loss of containment	🟢
	Small leak (offshore)	See Big leak. NB: Deep-sea ecosystems take a long time to recover.	Small leak from pipeline	🟢
	Undetected long term CO$_2$ leakage to sea water	Reduced carbonate ion conc. Damage to coral reef and species that is a part of food chain	Corrosion	🟢
Engineering and operational challenges				
	Failure of downstream process equipment - leads to need to vent the gas in the capture facility from the stack (pure CO2) Long-term venting at full flow may cause environmental damage in vicinity of vent stack (acidity on foliage?)	Prolonged venting leading to exposure above occupational limit	Impurities. Equipment failure	🟡
	Decompression/venting (Insufficient dispersion of CO$_2$)	CO$_2$ released through a vent system at high concentration.	Planned maintenance of pipeline or shutdown due to operational issues of upstream equipment	🟡
	Decompression/venting (accidental)	Solids deposited (form plugs) at the low points within the system. Metallurgical damage due to low temperatures.	Rupture of pipeline	🟡
	Solids formation	Structural and functional integrity of equipment. Cryogenic burns and impact injuries to humans.	scCO2 depressurized into the two-phase vapor solids region	🟡

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	Hydrate formation	Blockage of the pipeline	Presence of free water	🟡
	Transient pressure and temperature in pipeline	Two phase flow. Stresses to structure. "Water hammer effects" If pipeline failure due to stresses and/or hammer then large-scale threat to people.	Fire. Leak. Warming up of pipeline inventory	🟡
	Failure of monitoring system (measurements of water/leakage detection monitoring)	Lack of controlled and safe operation (corrosion issues covered above)	Mechanical/electronically/software etc. failure	🟢
	Release of CO$_2$ in closed space	Significant solids CO$_2$ build-up. Embrittle steelwork	Restricted heat flow to the module	🟡
	Failure of detectors due to low temperature	Lack of controlled and safe operation	Low temperature	🟢
	Suitable internal monitoring tools for pipelines (pigs) not available	Unable to effectively monitor integrity of pipeline. Potential to lead to a leak and threat to people.	Elastomer and lubrication issues	🟡
	A water mist/fog is created from a CO$_2$ release	Reduction of visibility may lead to incorrect or inefficient emergency response (especially on an offshore installation) Reduced visibility on a busy road may lead to accidents.	Cooling effect from dense phase CO$_2$ vaporization cause condensation of moisture in air	🟡
Materials				
	Corrosion	Loss of containment	Presence of free water/oxygen/H$_2$S	🔴
	Local temperature/icing impact from leak (e.g. flanges)	Material creep/degradation/enbrittlement	Exposure to low temperature (thermodynamics of the leak)	🟡
	Crack propagation	Loss of inventory. Loss of your pipeline. Multiple fatalities. Escalation from small to major leak. One major incident might cause public to turn against CCS. High cost	Corrosion. External damage. Inappropriate re-use of existing infrastructure. Initial defects. Inadequate material specification.	🔴

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	Material incompatibility	Loss of containment. Loss of life from a major release	Reuse of existing infrastructure with impurities and water left in the system/pipeline	🔴
	Elastomer explosion	Local elastomers damage Leak from valves, flanges, etc. Local hazard (e.g. in a building or enclosure) due to CO_2 accumulation	Inappropriate choice of elastomers	🟡
	Reactivity of CO_2 to inner lining of pipeline (CO_2 solvent properties)	Collapse of inner pipeline/integrity issue to the well	Non-inert material to CO_2 (and/or impurities present)	🟢
Hazard Phenomena				
	CO2 BLEVE	Catastrophic explosion. Missiles/projectiles from CO_2 containment	Sudden depressurization of a liquid phase CO_2 which results in an instantaneous vaporization which creates an explosive shock that disintegrates the vessel or pipeline	🟡
	External damage to onshore pipeline	Full pipe rupture. Impact on the environment/personnel/animals	Excavation	🟡
	Rapid Phase Transition	Following inappropriate depressurisation of pipeline or vessel that leads to solid CO_2 build up inside system, the re-introduction of the liquid CO_2 stream before the solid CO_2 has full sublimed to vapour could lead to over pressurisation of the containment envelope and LOC	Rapid sublimation of CO_2 with heat energy from liquid CO_2 stream	🟡
	CO_2 storage vessel exposed to a fire	BLEVE/uncontrolled pressure relief Fire extinguished (which is a hazard if fire source is a gas release)	Heating up of vessel, and pressure exceed the design pressure of the vessel	🟢

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	CO_2 cloud formation offshore/onshore	Reduction of visibility. Blockage of emergency/escape routes	Cooling effect from release of dense phase CO_2 and vaporization cause condensation of moisture in air	🟡
Modelling aspects				
	The modelling tools not sufficient to capture leak/dispersion/internal source term/process simulation modelling	Insufficient confidence in model results. Risk reduction measures chosen on the basis of inaccurate information. People put at risk should a LOC occur. Permitting not possible as Regulators are not presented with robust case for safety.	Improper thermodynamic assumptions (Equation of State issue related to presence of impurities)	🔴
	Underground pipeline bursts	Momentum of release is reduced leading to lower dispersion rates and an increased hazardous zone	External impact from 3rd party action corrosion and possible propagating failure	🔴
Public acceptance				
	CCS not publicly acceptable	Show stopper. NIMBY ("Not In My Backyard") and/or others present a professional anti view that scares the public before the CCS industry and regulars can build an evidence-based case for responsible operations.	Mixed messages. Lack of "education". Failure to present compelling safety case for the pipeline	🔴
	Placing of pipeline in populated area	Publicly not accepted as risks are not sufficiently communicated. Show stopper	Onshore transportation of NIMBY	🔴

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