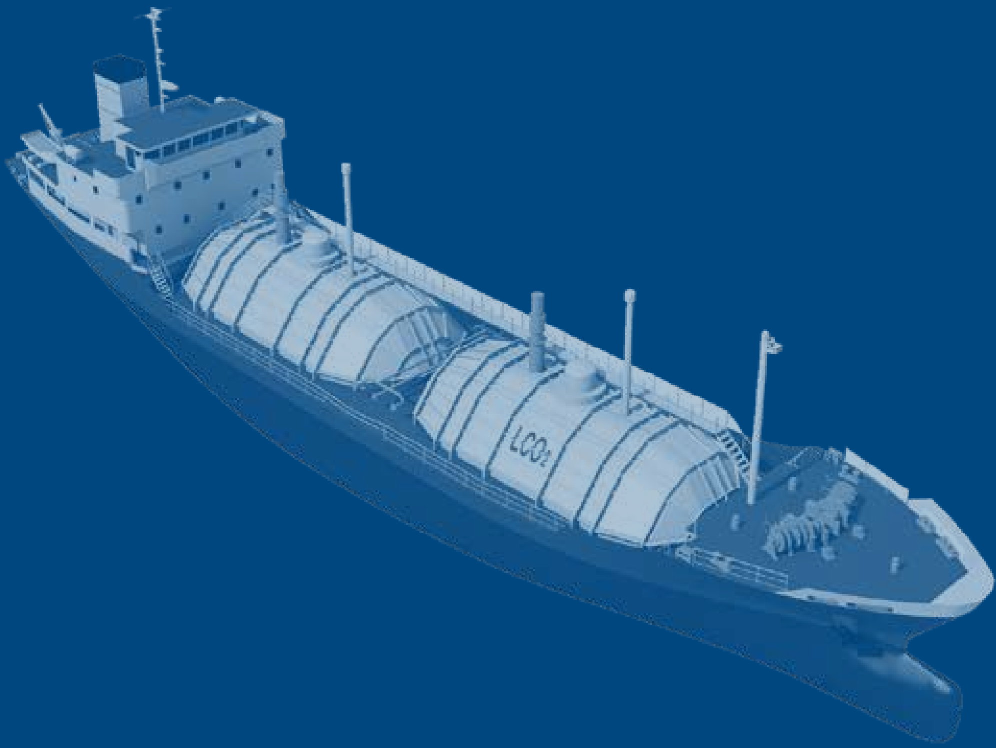

SIGTTO

Society of International Gas Tanker & Terminal Operators Ltd

Carbon Dioxide Cargo on Gas Carriers

First Edition

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The Society of International Gas Tanker and Terminal Operators (SIGTTO) *is a non-profit making organisation dedicated to protecting and promoting the mutual interests of its members in matters related to the safe and reliable operation of gas tankers and terminals within a sound environment. The Society was founded in 1979 and was granted consultative status at the International Maritime Organization in November 1983.*

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Introduction and Scope

1. Introduction and Scope

1.1 Introduction

This document assesses the suitability of current practice for the transportation of liquefied carbon dioxide (LCO_2) on board gas carriers. This safety-focused review considers current liquefied gas regulations such as the IGC Code,[1] and industry best practice, along with the unique properties of CO_2.

The main hazards of liquefied gas cargoes typically carried by gas carriers are related to the flammability and toxicity of the cargo. The industry is familiar with the safety of products such as liquefied natural gas (LNG), liquefied petroleum gas (LPG) and ammonia. LCO_2 is not flammable or highly toxic, but it does present unique properties due to its thermodynamic properties and the effects of possible impurities in the cargo.

It is practical to adopt a risk-based approach to identify the unique hazards of CO_2 and then select the most efficient barriers for safety and environmental protection. Using existing safety measures that are primarily designed for flammable cargoes may not be effective and could hide some dangers.

This review is limited by the current information available for the emerging trade of CO_2 shipping. Once the liquefied gas industry has greater experience, additional information will become available.

[1] IMO – International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk

1.2 Scope

This document provides guidance for organisations that are involved in the design and operation of CO_2 carriers and terminals. This document reviews specific hazards and safety issues of CO_2, it does not provide specific information for ship or terminal design.

The level of technical detail assumes that the reader is familiar with the design and operation of liquefied gas carriers. Not all concepts are simplified or explained at an introductory level.

2

Considerations for CO_2

2. Considerations for CO_2

2.1 Safety Philosophy

Some of the unique properties of LCO_2 are different to the typical liquefied gases that are transported as a cargo on gas carriers. This is relevant as the existing design philosophy of gas carriers is primarily influenced by the flammability and acute toxicity of typical cargoes. There are some features of the IGC Code that are not applicable to CO_2, such as exclusion of ignition sources and firefighting measures. However, there are additional considerations for CO_2 cargo due to its characteristics, particularly in relation to its thermodynamic properties and potential impurities.

Figure 1 shows typical concerns for a flammable gas with consequences that are not applicable to CO_2 crossed out.

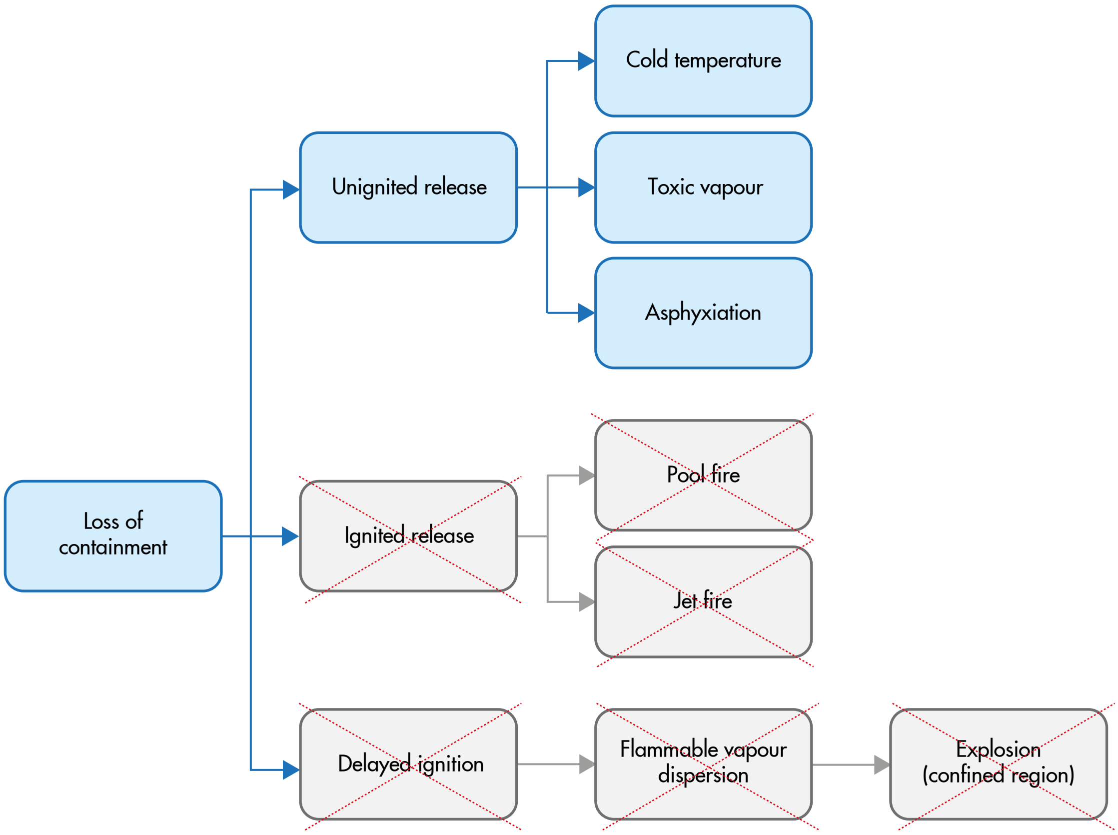


Figure 1: Loss of containment consequences

To consider the carriage of CO_2 it is useful to understand the reasoning behind the philosophy of the current IGC Code, which is primarily based on the hazards of flammable products with added measures for the hazards of chemical gases, which are largely based on the IBC Code.[2] The shipping industry uses prescriptive rules that make it challenging to adapt quickly to the hazards of new products. Modifying prescriptive rules typically involves working back from the current requirement to the original hazard to understand the intent of the risk mitigation measure. Once it is understood, then the regulations can be modified to maintain a similar safety level for new products.

[2] IMO – International Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk

To help with the considerations for CO_2 cargoes, this document will first identify the key properties of CO_2 and consider the hazards alongside the other products that are commonly carried by gas carriers today.

The main hazard is the principal issue that drives the design philosophy of an asset. The main hazard of CO_2 is toxicity, followed by other properties that need to be addressed:

- Asphyxiant
- liquefied gas under pressure
- low temperature
- triple point
- additional hazards from possible impurities.

2.2 Toxicity

CO_2 is designated as a toxic product by many countries and a few examples of exposure limits are shown in Table 1.

Source	Threshold limit value (ppm)	Short term exposure limit (ppm)
HSE (UK)[3]	5,000 (8 hours)	15,000 (15 minutes)
OSHA (US)[4]	5,000 (8 hours)	–
NIOSH (US)[5]	5,000 (10 hours)	30,000 (15 minutes)
ACGIH (US)[6]	5,000 (8 hours)	30,000 (15 minutes)
Directives 91/322/EEC[7] and 2000/39/EC[8] (EU)	5,000 (8 hours)	–
MHLW (Japan)[9]	5,000 (8 hours), 40 hours/week	–
GBZ2.1-2019 (China)[10]	5,000 (8 hours)	9,000 (15 minutes)

Table 1: CO_2 exposure limits (concentrations in volume)

CO_2 is denser than air and may concentrate in low lying areas if there is a leak. This makes it an asphyxiation concern[11] for enclosed spaces and low lying areas as it can accumulate. It is also a concern if CO_2 is allowed to accumulate at low concentrations in other occupied spaces.

More current research indicates that exposure to CO_2 may cause longer term chronic effects. It is not a challenge to design and monitor for low concentration levels of CO_2 on a gas carrier, as current industry

[3] Health and Safety Executive (HSE) – EH40/2005 – Workplace exposure limits
[4] Occupational Safety and Health Administration (OSHA) – Permissible Exposure Limits
[5] National Institute for Occupational Safety and Health (NIOSH) – Recommended Exposure Limits
[6] American Conference of Governmental Industrial Hygienists (ACGIH) – Threshold Limit Values and Biological Exposure Indices
[7] European Agency for Safety and Health at Work – Commission Directive 91/322/EEC – establishing indicative limit values for occupational exposure
[8] European Agency for Safety and Health at Work – Commission Directive 2000/39/EC – indicative occupational exposure limit values
[9] Ministry of Health, Labour and Welfare – Ordinance on Health Standards in the Office
[10] GBZ2.1-2019 – Occupational exposure limits for hazardous agents in the workplace. Part 1: Chemical hazardous agents
[11] hse.gov.uk/carboncapture/carbondioxide.htm

practice is based on managing much lower levels of toxic and flammable gases. The comparison of the threshold limit value (TLV) of CO_2 with a few typical toxic and flammable cargoes covered by the IGC Code is shown in Table 2.

Product name	Threshold limit value ACGIH (ppm)	Lower flammable limit (%vol. in air)	Main hazard
CO_2	**5000**	**N.A.**	**Toxic**
Ammonia	25	15	Toxic
Butadiene	2	2	Toxic
Ethylene oxide	1	3	Toxic
Propylene oxide	2	2.3	Toxic
Vinyl chloride	1	3.6	Toxic
Methane	No data	4.4	Flammable
Ethane	No data	3	Flammable
Butane	No data	1.86	Flammable
Propane	No data	2.1	Flammable

Table 2: TLV and LFL of some liquefied gases

The toxicity of CO_2 is the main hazard,[12] and the design of a gas carrier should take this into account. It is useful to understand the difference of the acute and chronic toxic effects of CO_2 on humans, relative to other gases such as ammonia and vinyl chloride when assessing risk. Risk is defined as the product of probability and consequence. Exposure to low levels of ammonia or vinyl chloride are of more consequence than similar concentrations of exposure to CO_2.

To help place the TLV numbers listed in Table 2 into perspective, the typical composition of human breath is shown in Table 3. Note that the amount of CO_2 in exhaled air is around 4% (40,000 ppm), higher than its TLV and short term exposure limit (STEL).

Gas	Atmospheric air %	Exhaled air %	Change %
Nitrogen (N_2)	79	79	0
Oxygen (O_2)	21	16	-5
Carbon dioxide (CO_2)	0.04	4	+3.96
Water vapour	Variable	Saturated or 1%	–

Table 3: Typical composition of human breath

This information is helpful to understand that at low levels of CO_2 the concern is about the long-term exposure. The design should be based on ensuring a healthy work environment for personnel and the exposure should not exceed the TLV. Larger percentages of CO_2 in the air present the additional hazard of asphyxiation.

[12] HSE – Assessment of the major hazard potential of carbon dioxide (CO_2)

2.3 Asphyxiant

Any gas that is present in sufficient quantities to lower oxygen levels will act as an asphyxiant. Some gases are dangerous at much lower levels and the design philosophy is to control them below that. It is important to understand the main hazard of a specific cargo in order to determine the ship design.

For example, ammonia is toxic and has an immediately dangerous to life or health (IDLH) value of 300 ppm and a TLV of 25 ppm. Ammonia detection is typically set at 25 ppm. Butane is flammable, with a lower flammable limit (LFL) of 1.86% and detection is typically set at 30% of the LFL.

If a cargo is designated as toxic, then the design measures may be more stringent than if it is a simple asphyxiant. An example of a design measure for a toxic gas can be seen in the design of gas detection systems. To monitor the hazard of CO_2, gas detection should be designed to detect low levels of CO_2 rather than to detect a reduction in oxygen levels.

CO_2 is a colourless, odourless gas that is denser than air, so it can settle into low lying areas undetected. Complacency can also be an issue as CO_2 is a common gas found on ships and is used for fire extinguishing. Design and training standards should consider the human factor and try to mitigate the chronic and acute effects of CO_2 exposure.

2.4 CO_2 Under Pressure

CO_2 under pressure is a hazard that designers need to manage. CO_2 as a liquid and gas under pressure presents a similar hazard to other liquefied gases from explosive decompression and the force of high-pressure leaks.

Loss of containment can lead to injuries and fatalities due to dry ice formation, solid and cold liquid ejection, and the toxic effects of CO_2. Loss of containment can also lead to structural damage due to embrittlement of steel from low temperatures.

The IGC Code, standards and industry best practice provide control measures to ensure the safe transportation of liquefied gas under pressure. Current practice may be quite useful for CO_2 transportation. The formation of dry ice and the subsequent actions to mitigate that event may need to be considered in addition to current control measures as this is unique to CO_2.

2.5 CO_2 Triple Point

The triple point is the temperature and pressure at which solid, liquid and vapour phases of a substance can coexist in equilibrium. The triple point of CO_2 is at a temperature and pressure that can impact its transportation as a liquefied gas.

Table 4 shows the saturation temperature and triple point of a few common liquefied gases carried on gas carriers. This type of information may vary depending on the source, so the data in Table 4 is provided for information only. The triple point pressure is not a concern for typical liquefied gases as it is below ambient pressure. For CO_2 this is a concern as it can only exist as a solid or vapour at atmospheric pressure as shown in Figure 2.

This means that if LCO_2 is released at a pressure lower than 517 kPa, it will become a mixture of solid and vapour. This also means that LCO_2 cannot be carried in atmospheric pressure cargo tanks.

Product	Saturation temperature at ambient pressure	Triple point	
	Temperature (°C)	Temperature (°C)	Pressure (kPa) abs
Carbon dioxide (Pure)	-78.5 (dry ice)	-56.6	517
Ammonia	-33	-77.75	6.060
Butadiene	-10	-109.0	*No data*
Ethylene oxide	0	-112.5	*No data*
Propylene oxide	10	-111.93	*No data*
Vinyl chloride	-20	-153.84	*No data*
Methane	-163	-182.47	11.7
Butane	-11	-138.6	7×10^{-4}
Propane	-40	-188.15	1.685×10^{-7}
Ethane	-90	-182	1.1×10^{-3}

Table 4: Saturation temperature, triple point temperature and pressure of common liquefied gases

Most liquefied gases transported at sea can be carried near their boiling point in atmospheric pressure tanks. Some liquefied gases can also be carried at ambient temperature in pressurised tanks.

Possible temperature conditions for LCO_2 transportation are between its triple point (-56°C) and critical point (31.1°C), as shown in Figure 2. There are also practical measures that need to be taken to ensure that CO_2 liquid or vapour does not become a solid during cargo operations. The scope of the IGC Code is liquefied gases so the carriage of cargoes at the supercritical stage is not covered.

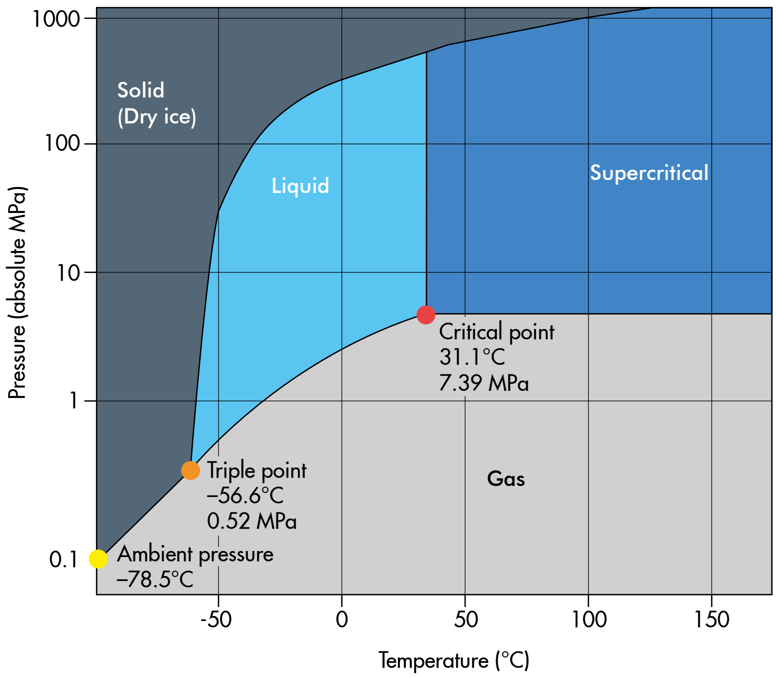


Figure 2: Phase diagram of pure CO_2

2.6 Impurities

The presence of impurities can affect the standard properties of CO_2. This additional risk should be considered in the design stage and the information should be available to the operators.

Certain impurities can cause a significant increase in the density of the fluid which can impact equipment sizing and the operating envelope of the ship and onshore plant as it may need to be designed for a range of different fluid compositions. For hydraulic modelling the selection of an appropriate *equation of state* to model the fluid is important, based upon the expected range of fluid compositions. It is important that the expected range of fluid compositions is established early on in the design phase.

Impurities in LCO_2 may be different depending on the fuel used by the emitter and the carbon capture technology. Pure CO_2 is not assumed to be corrosive but in the presence of impurities, such as water, carbonic acid may form and can cause corrosion. Other impurities in the CO_2 stream can be sources of corrosion and should be carefully considered.

For general information, the following table shows a food grade and captured grade of CO_2 specification.

Component	Northern Lights[13] (ppm mol)	EIGA food grade[14] (ppm v/v)
Carbon Dioxide (CO_2)	Not specified	99.9% min.
Ammonia (NH_3)	≤10	2.5 max.
Argon (Ar)	Not specified	Not specified
Carbon monoxide (CO)	≤100	10 max.
Glycol	Not specified	Not specified
Hydrocarbons	Not specified	50 max. of which 20 max non-methane hydrocarbons
Hydrogen (H_2)	≤50	Not specified
Hydrogen sulphide (H_2S)	≤9	0.1 max. (total sulphur as S)
Methane	Not specified	50 max. of which 20 max non-methane hydrocarbons
Nitric oxide/nitrogen dioxide (NOx)	≤10	2.5 max. each
Nitrogen (N_2)	Not specified	Not specified
Oxygen (O_2)	≤10	30 max.
Sulphur oxides (SOx)	≤10	0.1 max. (total sulphur as S)
Water (H_2O)	≤30	20 max.
Amine	≤10	Not specified
Formaldehyde	≤20	Not specified
Acetaldehyde	≤20	Not specified
Mercury	≤0.03	Not specified
Cadmium, Thallium	Sum ≤0.03	Not specified

Table 5: Typical CO_2 compositions

[13] Northern Lights 2022 specifications

[14] European Industrial Gases Association (EIGA) AISBL – Doc 70/17 – Carbon Dioxide Food and Beverages Grade, Source Qualification, Quality Standards and Verification

The impurities mentioned in CO_2 liquid are typically at low levels and measured in ppm. This will be lower still when the CO_2 liquid has vapourised and is present in the air below 5000 ppm.

Impurities can affect the physical properties of CO_2, such as the triple point, bubble point and phase behaviour. This should be taken into account when designing systems to allow for sufficient margins.

3

Regulations and Industry Guidance

3. Regulations and Industry Guidance

Industry guidance is often provided in addition to regulations and standards and is based on experience and knowledge from industry. This approach means that industry guidance may not cover novel concepts that are not proven or with which the industry has little experience. This chapter reviews current liquefied gas carrier regulations and relevant industry guidance and provides suggestions on what may be considered for CO_2 shipping.

3.1 IGC Code and SOLAS

Gas carriers have to be constructed and certified to the IGC Code to be able to trade freely between countries. Although the IGC Code does not have many requirements based on specific properties of CO_2 cargoes, the basic principles are suitable as the code is based on more hazardous liquefied gases that are flammable or toxic.

Tables 6 and 7 provide suggestions to be considered in relation to CO_2 cargoes and the IGC Code. This takes into account that CO_2 is not flammable and is relatively much lower in toxicity compared to other toxic cargoes listed in IGC Code Chapter 19. Key considerations for CO_2 cargoes are the presence of impurities and the importance of maintaining a safe operation range.

IGC Code Chapter	Application for CO_2	Remarks
1 – General	Applicable	–
2 – Ship survival capability and location of cargo tanks	Applicable	–
3 – Ship arrangements	Applicable	**3.1.2 and 3.1.3** – A single gastight bulkhead A-0 class may be sufficient **3.2.5** – A-60 Class may not be required **3.2.6** – Air inlet and outlet capable of being operated from inside the space **3.3.1** – May not require explosion prevention. Consider SOLAS II-2/9.2.3 for fire protection **3.8.2** – Bow cargo transfer may be allowed **3.3.4** – Bulkhead may not be required **3.6** – Airlocks may not be required
4 – Cargo containment	Applicable	–
5 – Process pressure vessels and liquids, vapour and pressure piping systems	Applicable	**5.7.4** – May not be required
6 – Materials of construction and quality control	Applicable	–
7 – Cargo pressure/temperature control	Applicable	If a flammable or more toxic refrigerant is used within the reliquefaction plant then this should be highlighted in the risk assessment
8 – Vent systems for cargo containment	Applicable	–

9 – Cargo containment system atmosphere control	Significant Exclusions	**9** – May not require inert gas. Dry air may be required to prevent condensation in cargo tanks and piping **9.3** – Dry air to prevent condensation in space
10 – Electrical installations	Significant Exclusions	**10.2.6** – Should be applied
11 – Fire protection and extinction	Significant Exclusions	**11** – May not require fire protection and extinction from cargo. May be able to use SOLAS requirements for general cargo vessels
12 – Artificial ventilation in the cargo area	Applicable	**12.1.1** – Required **12.1.7** – May not require explosion prevention **12.1.9** – May not apply
13 – Instrumentation and automation systems	Applicable	**13.6.5; 13.6.6** – Should be applied
14 – Personnel protection	Applicable	**14.3.2.4; 14.4.3** – May not apply **14.4.2; 14.4.4** – Should be applied
15 – Filling limits for cargo tanks	Applicable	–
16 – Use of cargo as fuel	Not applicable	**16** – Cargo cannot be used as fuel. Other type of fuel used will require additional measures and may require reinstating requirements for other chapters
17 – Special requirements	Applicable	–
18 – Operating requirements	Applicable	**18.10.3.2** – May not be required
19 – Summary of minimum requirements	Applicable	Recommended changes are given in Table 7. Reclaimed quality does not require a separate column and can be captured in the text of the IGC Code

Table 6: Suggestions for the application and improvement of the IGC Code

a	b	c	d	e	f	g	h	i
Product name		Ship type	Independent tank type C required	Control of vapour space within cargo tanks	Vapour detection	Gauging		Special requirements
Carbon dioxide ~~(high purity)~~		3G	–	–	~~A~~ T	~~R~~ C		14.4.2, 14.4.4 17.21, 17.22
~~Carbon dioxide (Reclaimed quality)~~		~~3G~~	–	–	~~A~~	~~R~~		~~17.22~~

Table 7: Suggested changes to IGC Code summary of minimum requirements[15]

[15] Based on summary of minimum requirements in IGC Code Chapter 19

Gas carriers are typically fitted with totally enclosed lifeboats with self-contained air support systems with sufficient air capacity for the personnel in the lifeboat and the engines. This SOLAS[16] requirement is expected to be applicable to CO_2 carriers as well due to the toxicity of the cargo and the effect of CO_2 on the lifeboat engines.

3.2 Industry Guidance

Limited industry guidance is written specifically for CO_2 as a cargo, and what is written for other gas carriers cannot simply be applied to CO_2 without review. From a practical perspective, the documents introduced in this section are considered to be useful. When applying the recommendations in these documents, care should be taken to consider the specific properties of CO_2 that are not addressed.

3.2.1 Manifolds

Recommendations for Liquefied Gas Carrier Manifolds[17] specifies the size and arrangement of cargo and bunker manifolds. This is used by loading arm manufacturers and terminal designers when designing terminals. The standardisation of the manifold layout at the early stages of LCO_2 shipping can lead to efficient operations.

3.2.2 Marine loading arms

Manufacturers design loading arms to ensure that they do not exceed the loads specified in *Recommendations for Liquefied Gas Carrier Manifolds.* Designs should consider the density of CO_2 as it is heavier than other liquefied gas cargoes.

The guidance in *Design and Construction Specification for Marine Loading Arms*[18] can be useful for CO_2, along with the following considerations:

- The material should be suitable for possible impurities and the minimum temperature that can be reached in an emergency, ie stainless steel is recommended due to dry ice
- credible scenarios should be reviewed to determine if emergency release is necessary
- if an emergency release system (ERS) is fitted, then it should be designed to release under pressure
- the swivel joint should be designed to resist damage from dry ice if there is a leak.

3.2.3 Emergency shutdown systems

The purpose of SIGTTO's recommendations in *ESD Systems*[19] is to reduce risk in process systems. This will help to minimise the consequences of an incident. CO_2 carriers should follow the recommendations in *ESD Systems*, with the exception of sections on gas burning in the engine room, liquid sensor in vent mast and firefighting triggers.

The design of ESD and relief systems is of particular importance for CO_2 as transient pressure changes (surge pressures) caused by activation of an ESD system could cause phase changes in the pipelines with the potential for solidification. This is less of a concern for LNG and LPG but a terminal ESD system for a CO_2 carrier may need to be designed and configured differently compared to other liquefaction terminals to ensure a narrower operating pressure envelope.

[16] IMO – The International Convention for the Safety of Life at Sea – Ch.III Reg. 31.1.6

[17] SIGTTO – Recommendations for Liquefied Gas Carrier Manifolds

[18] OCIMF – Design and Construction Specification for Marine Loading Arms

[19] SIGTTO – ESD Systems

3.2.4 Mooring

Mooring Equipment Guidelines (MEG)[20] provides a standardised approach for gas carriers and terminal moorings and should be suitable for CO_2 carriers and terminals. This document is suitable for transient mooring operations where the ship is expected to leave when the wind and current criteria are exceeded. This document may not be suitable for exposed locations or for installations that are expected to stay on station during adverse weather conditions. It is not recommended to extrapolate MEG beyond the weather criteria specified in it.

3.2.5 Alarm management, human-machine interface and cargo control room

SIGTTO recommendations for alarm management,[21] human-machine interface (HMI)[22] and cargo control rooms (CCRs)[23] provide good design practice for gas carrier CCRs and alarm systems. The guidance in these documents may be useful for CO_2 carriers.

3.2.6 Cargo sampling

Liquified Petroleum Gas Sampling Procedures[24] recommends closed loop sampling systems for toxic liquefied gas cargoes. The principles of this design may be useful for CO_2 sampling.

The sampling container will need to be pressurised to a suitable pressure prior to taking a liquid sample. The procedure should ensure that there is no trapped liquid between the sampling valves.

3.2.7 ISO 27913

ISO 27913[25] provides requirements and recommendations on certain aspects of pipelines intended for CO_2 transportation. While existing pipeline standards cover many of the issues related to design and construction, this standard provides supplementary information that is specific to CO_2.

Although it does not directly cover transportation of CO_2 via ship, the information in ISO 27913 can serve as a useful reference for designers of marine CO_2 transportation systems. The document covers aspects of quality assurance and health, safety and environmental aspects specific to CO_2 transportation and monitoring.

[20] OCIMF – Mooring Equipment Guidelines

[21] SIGTTO – Recommendations for Management of Cargo Alarm Systems

[22] SIGTTO – Recommendations for Cargo Control Room HMI

[23] SIGTTO – Recommendations for Designing Cargo Control Rooms

[24] SIGTTO – Liquified Petroleum Gas Sampling Procedures

[25] ISO – 27913 – Carbon dioxide capture, transportation and geological storage – Pipeline transportation systems

4

Design Considerations

4. Design Considerations

In addition to regulations, standards and industry guidance, designing for hazardous cargo is guided by a risk-based approach. The purpose of cargo system design is to ensure effective safety and efficient operations. This chapter provides guidance on specific considerations for the carriage of CO_2 as a cargo.

4.1 Design Philosophy

CO_2 should be carried at a pressure and temperature that is suitable for carriage at sea. This should take into account the nature of ship operations, with crew rotation at regular intervals, and the practical training and experience that can be achieved. The challenges of maintenance at sea compared to shore-based facilities should be considered including access to spare parts and service crew.

The nature of ship operations and human factors considerations should guide designers on the level of complexity and automation that can be introduced in the design. This should also guide designers on active barriers or passive barriers to achieve an inherently safe design. Adequate safety margins should be adopted at the early stages of large-scale CO_2 transportation and over time more experience may lead to more efficient designs.

For hazardous products, the philosophy of design is that no single failure should lead to a major event. Design should consider adequate safety margins, operating procedures, maintenance and training to support the design. For CO_2 carriage, the design should minimise the probability of a significant event occurring such as uncontrolled depressurisation resulting in the formation of dry ice in tanks and pipelines. If dry ice forms in a tank or pipeline, the design and operation procedures should ensure that this situation does not escalate.

As CO_2 cargoes may be derived as the byproduct of combustion, care should be taken to understand the effect of any impurities that may be present. The cargo may be output of different emitters, that use different fuel and carbon capture technologies, which can lead to impurities. Consideration should be given to the possible accumulation of these impurities in parts of the cargo system and any reaction with moisture or other materials that may be reasonably expected in the cargo system.

4.2 Carriage Temperature and Pressure

There are multiple temperature and pressure combination options for transportation of liquefied CO_2. The carriage temperature and pressure should be sufficiently distant from the triple point of CO_2 to avoid the solidification of CO_2. All credible scenarios that can arise due to crew error or equipment malfunction should be identified in a hazard and operability (HAZOP) study. This should ensure that scenarios, such as a cargo tank relief valve lifting or a wrong pumping operation, do not lead to solidification of CO_2.

The selection of carriage temperature and pressure should not result in undue pressure on the ship's crew to maintain complex systems at a high level of precision to ensure safety. Due consideration should be made to human factors in determining the safety margin for the conditions of carriage.

4.3 Material Selection

The IGC Code provides requirements for material selection for piping and cargo tanks. The selection of materials used for CO_2 carriage should also consider possible corrosion due to impurities such as water, sulphur oxides, nitrous oxides and hydrogen sulphide. The assumptions used for the types and amount of impurities that guides the selection of materials should be clearly stated in the ship's documentation for reference by the ship staff.

Material selection should also consider the probability of solidification of CO_2 to dry ice, which can cause the temperature drop to -78.5°C. A structured assessment should be carried out to identify the possible failure modes and probability of dry ice formation. This can then guide the material selection.

For non-metallic materials, such as seals and lubricants, materials used should be compatible with LCO_2 and any identified impurities.

4.4 Cargo Tank

Considering the physical properties, ie pressure and temperature of CO_2, the practical cargo tank containment option available in the current IGC Code may be a Type C tank.

Although unlikely, the entire cargo may turn into a solid if the pressure in the cargo tank is lost due to an uncontrolled situation. This is typically considered to be a low probability event due to the failure modes that require this to happen. The design should still consider this possibility in the risk assessment and incorporate suitable control measures to reduce the risk to acceptable levels.

An example of loss of pressure could arise due to the shearing-off of a cargo tank relief valve due to an impact from a crane lifting operation. This could be mitigated by carrying out a *dropped object study* that can lead to design features that limit the crane operation area.

Mitigation measures for the formation of solids in the cargo tank should be identified and clear instructions should be available on the ship to prevent escalation. Dry ice may also form during cargo transfer operations if the pressure in the cargo tank is not maintained, or there is low pressure in the piping systems. Additional equipment such as vaporisers, compressors or variable frequency drive pumps may be considered as design features.

4.5 Cargo Piping

Sufficient equipment, indicators and permanent piping connections should be provided to permit the crew to pressurise all necessary piping and equipment before transferring liquid. Systems should also be provided to minimise the release of CO_2 to the atmosphere during depressurisation. Making piping and equipment liquid free before depressurisation can help to prevent dry ice formation.

Some types of valves may not be compatible with LCO_2 as they can trap a small amount of liquid in the valve body when closing. This will expand and the resulting pressure may exert a force that damages or ruptures the valve. To avoid liquid lock, solid CO_2 blockage or damage, cavity-free valves are recommended for cargo liquid piping. See *Recommendations for Valves on Liquefied Gas Carriers*[26] for more information on valve types and testing standards.

Cargo piping design should take into account the possibility of dry ice formation when there is a rapid change in liquid velocity. Such a change may occur at the apex of a marine loading arm for example. Suitable pipeline diameter transition and flow control should be considered.

For cargo transfer operations, SIGTTO's *Guidelines for the Alleviation of Excessive Surge Pressures on ESD for Liquefied Gas Transfers Systems*[27] can be used but additional considerations due to the type of cargo and impurities should be considered.

[26] SIGTTO – Recommendations for Valves on Liquefied Gas Carriers

[27] SIGTTO – Guidelines for the Alleviation of Excessive Surge Pressures on ESD for Liquefied Gas Transfer Systems

4.6 Gas Detection

A permanently installed gas detection system is required by IGC Code Section 13.6, *Gas detection*, and this should be set to detect CO_2. The alarm setpoint should be guided by the relevant administration or at 5000 ppm. There should be a suitable number of detector heads located at a low level, taking into account the density of CO_2. Gas detection should also be provided in the accommodation area to check for the presence of abnormal levels of CO_2 into the living quarters.

At least two portable detectors should be provided with the capability to detect CO_2 in both percentage and ppm ranges. Sufficient personal detectors capable of detecting CO_2 in ppm should be provided to ship staff.

4.7 Pressure Relief

Type C cargo tanks on a gas carrier may be fitted with relief valves capable of two phase flow and liquid piping is typically protected by relief valves. When a relief valve discharges CO_2 vapour or liquid to atmospheric pressure there is a possibility of dry ice formation. This is of particular concern when the discharge medium is liquid CO_2.

Safety relief valves are critical systems that should function under emergency conditions. The design should not be a conditional system, for example a relief system that requires external backpressure to work properly.

Design considerations for relief systems may need to depart from the traditional approach taken on gas carriers due to the natural properties of CO_2. Relief systems should not lead to a vent mast and should relieve directly to a safe position using the shortest pipe run possible. The outlet of the relief pipe should not have a mesh cover as this may get blocked by dry ice.

The relief valve outlet should be oriented in such a manner so not to directly impinge on personnel. The areas around the relief outlet may be designated as off limits and fenced off in the design. This fencing approach has been used for explosion lids for hold spaces containing Type A cargo tanks on some LPG carriers.

The loss of pressure from a cargo tank is a major event that the design should prevent. If a relief valve lifts and does not reseat, ship staff may be unable to approach the area and work due to the special arrangement of relief pipework and CO_2 cloud. Consideration may be given to providing remote operation for the isolation valve[28] fitted to the cargo tank pressure relief valve to prevent the cargo from solidifying. Such a system will have a mechanical interlock system to be used in an emergency only.

4.8 Interface with the Terminal

The hazard of a major release of CO_2 from tanks or piping should be assessed to determine the hazardous area dimensions. The UK HSE[29] study provides some guidance on pure CO_2 releases in different conditions, including pressure, temperature, wind speed and rupture size.

In addition to CO_2, the hazards of other gases used should be checked if alternative fuels such as ammonia or hydrogen are present on the ship or terminal as these may present a significant hazard.

[28] See IGC Code Section 8.2.9

[29] HSE – Assessment of the major hazard potential of carbon dioxide (CO_2)

5

Operational Considerations

5. Operational Considerations

This chapter reviews operational considerations that are based on current practice for liquefied gas and may have specific benefit for CO_2 transportation.

5.1 Cargo Information

The design of a gas carrier is based on the properties of the cargoes it can carry, which are listed in the ship's certificate of fitness. The assumptions for the design are based on an understanding of the cargo properties which may be in a specific range, ie temperature, pressure and amount of impurities. CO_2 carriers are expected to be designed for a specific range of cargo temperature, pressure and set limits for impurities. IGC Code Section 18.3, *Cargo information*, stipulates information that should be provided to the ship.

The critical information on the physical and chemical properties of the CO_2 cargo should be provided to all relevant stakeholders, this includes the ship, terminals and Receivers. Traditionally the responsibility for analysing the cargo and providing the cargo information is that of the Shipper. This task is not typically carried out on the ship as they do not have the equipment or the expertise to analyse the physical and chemical properties.

For cargoes such as LPG and LNG, there are conversion tables available (ie ASTM tables) that may be used to standardise the cargo calculation process. For liquefied CO_2 these standard conversion tables are generally not available so this information is required to be provided to the ship. As this may vary with the presence of impurities, the properties of CO_2 liquid and vapour, such as density, and triple point should be tabulated against temperature for a practical range.

IGC Code Section 18.4, *Suitability for carriage*, highlights the requirement to ensure that the cargo carried is suitable for the ship and that the mixing of cargoes should not result in dangerous situations. As CO_2 may be derived as the byproduct of combustion, care should be taken to understand the impurities and any possible reactions with previous CO_2 cargo or coolant that the ship carried.

5.2 Cargo Operations

The IGC Code Section 18.2, *Cargo operations manuals*, stipulates a minimum list of information that should be provided to the ship so that the personnel can operate the ship safely. For CO_2 carriage, additional information should be provided due to the physical and chemical properties of the cargo that affect cargo operations in a unique manner.

For example, personnel should be provided sufficient information to understand that LCO_2 cannot remain as a liquid at ambient pressure. Before LCO_2 is introduced into a pipeline or tank, it has to be pressurised with vapour to the correct pressure to prevent reaching minimum design temperature or dry ice formation.

Pressurisation

Due to the nature of LCO_2, the ship may require design features to pressurise and depressurise cargo piping and cargo tanks. Design features may include a vaporiser, compressors, suitable connections for piping and pressure indication devices with alarms.

The design features should cover operations such as cargo transfer, manifold disconnection and all aspects of cargo operation. The information on this design feature and the practical operational guidance should be provided to the ship staff in the operations manual.

Water vapour

The amount of water vapour that may be present in cargo tanks and piping is controlled depending on the cargo carried. For CO_2 the amount of water content should be reduced to a level that does not cause concern. This may arise due to the reaction with the cargo or any impurities present.

The information surrounding the concerns relating to water content should be provided to the ship in addition to the practical measures on how to control it for that specific ship design.

Depending on the design, there may be restrictions on the water content in the atmosphere of the hold space that surrounds the cargo tanks. This may be to prevent damage to any insulation and help minimise corrosion.

5.3 Training and Experience

Structured classroom training should be carried out to educate the crew on the specific hazards of CO_2 operations. Training should cover safety, contingency planning and all routine operations. The training programme should be similar to *LPG Shipping Suggested Competency Standards*.[30]

Basic training courses should contain but not limited to:

- Properties and hazards of CO_2
- risk mitigation principles for CO_2 carriage
- CO_2 operations guidance
- emergency response and contingency planning for CO_2 cargo
- dry ice formation and management
- concern regarding impurities and mitigation measures.

The experience of the crew that operate gas carriers is guided by industry requirements. This is a practical approach to take for CO_2 carriers as management of the personnel's knowledge and experience is key to safe operations.

Due to the nature of CO_2 operations and the novel design and equipment, consideration should be given to providing equipment-specific training and to carrying out simulator training for cargo operations.

5.4 Emergency Release System

Emergency release systems may be fitted to the transfer equipment used for CO_2 cargo operations. The activation of the system may result in the release of CO_2 without warning. The area around the ship's manifold and terminal transfer equipment can be hazardous and should not be routinely entered during cargo operations when the system is under pressure. See *Recommendations for Liquefied Gas Carrier Manifolds,* Section 6.6, *Access during Cargo Transfer.*

[30] SIGTTO – LPG Shipping Suggested Competency Standards

5.5 Cargo Transfer

Pressure management is a key consideration for LCO_2 ship-to-shore and ship-to-ship transfer operations. Structured operation procedures can assist in managing the pressure difference for cargo transfer, manifold connection and disconnection.

CO_2 piping should always be under pressure, to prevent dry ice forming, prior to introduction of LCO_2. After the connection is made between the ship and terminal, the pressure in the ship and shore piping should be equalised at a suitable pressure before liquid CO_2 is introduced. On completion of cargo transfer, all liquid should be drained before the manifold connection is depressurised.

Liquid CO_2 should be drained to the ship or shore tank and not released to the atmosphere. Once the connection is liquid free, then the section can be depressurised and disconnected. Suitable piping arrangements and equipment may be required for the ship and terminal to drain the liquid back to the tanks by pressurising the manifold connection safely. This should be achieved without opening the main manifold valves.

5.6 Solid CO_2 in Containment

The property of LCO_2 is that it can only exist as a solid or vapour at atmospheric pressure. If there is loss of pressure in the piping or cargo tank then there is a chance that solid CO_2 will form. Solid CO_2 has a greater density than LCO_2 and if it forms in the tank it has the tendency to accumulate at the bottom of the tank.

The danger is that if solid CO_2 forms and an attempt is made to pressurise or heat up the tank to mitigate this issue, the combination of low temperature and higher pressure may exceed the design limits of the containment.

The ship is typically not designed to operate with solid CO_2 and this situation should be handled with caution. The system designer should provide clear step-by-step information on what steps to take in the event of solid CO_2 formation in tanks and piping. This critical information should also form part of regular drill and training exercises for the ship crew.

Annexes

Annex 1 – Glossary of Terms and Abbreviations

ACGIH American Conference of Governmental Industrial Hygienists

ASTM American Society for Testing and Materials

C Celsius

CCR Cargo Control Room

CO Carbon Monoxide

CO_2 Carbon Dioxide

EIGA European Industrial Gases Association

ERS Emergency Release System

ESD Emergency Shutdown

EU European Union

H_2S Hydrogen Sulphide

HAZOP Hazard and Operability

HMI Human-Machine Interface

HSE Health and Safety Executive (UK)

IDLH Immediately Dangerous to Life or Health

IMO International Maritime Organization

kPa Kilopascal

LCO_2 Liquefied Carbon Dioxide

LFL Lower Flammable Limit

LNG Liquefied Natural Gas

LPG Liquefied Petroleum Gas

MHLW Ministry of Health, Labour and Welfare (Japan)

N_2 Nitrogen

NIOSH National Institute for Occupational Safety and Health (US)

O_2 Oxygen

OCIMF Oil Companies International Marine Forum

OSHA Occupational Safety and Health Administration (US)

ppm Parts Per Million

SO_2 Sulphur Dioxide

SOLAS The International Convention for the Safety of Life at Sea

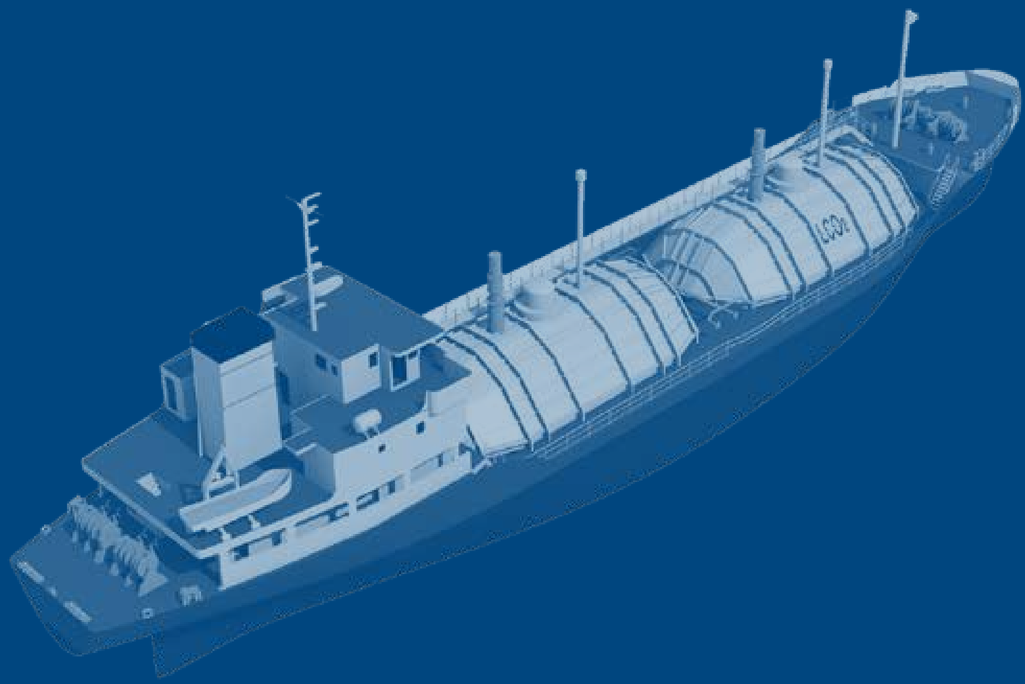
STEL Short Term Exposure Limit

TLV Threshold Limit Value

US United States

Annex 2 – Reference List

- IMO – International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk (IGC Code)
- IMO – International Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk (IBC Code)
- United Kingdom HSE – EH40/2005 – Workplace exposure limits
- United States OSHA – Permissible Exposure Limits
- United States NIOSH – Recommended Exposure Limits
- ACGIH – Threshold Limit Values and Biological Exposure Indices
- European Agency for Safety and Health at Work – Commission Directive 91/322/EEC – establishing indicative limit values for occupational exposure
- European Agency for Safety and Health at Work – Commission Directive 2000/39/EC – indicative occupational exposure limit values
- Japan MHLW – Ordinance on Health Standards in the Office
- China GBZ2.1-2019 – Occupational exposure limits for hazardous agents in the workplace. Part 1: Chemical hazardous agents
- hse.gov.uk/carboncapture/carbondioxide.htm
- HSE – Assessment of the major hazard potential of carbon dioxide (CO_2)
- Northern Lights 2022 specifications
- EIGA AISBL – Doc 70/17 – Carbon Dioxide Food and Beverages Grade, Source Qualification, Quality Standards and Verification
- IMO – The International Convention for the Safety of Life at Sea – Chapter III Reg. 31.1.6
- SIGTTO – Recommendations for Liquefied Gas Carrier Manifolds
- OCIMF – Design and Construction Specification for Marine Loading Arms
- SIGTTO – ESD Systems
- OCIMF – Mooring Equipment Guidelines
- SIGTTO – Recommendations for Management of Cargo Alarm Systems
- SIGTTO – Recommendations for Cargo Control Room HMI
- SIGTTO – Recommendations for Designing Cargo Control Rooms
- SIGTTO – Liquified Petroleum Gas Sampling Procedures
- ISO – 27913 – Carbon dioxide capture, transportation and geological storage – Pipeline transportation systems
- SIGTTO – Recommendations for Valves on Liquefied Gas Carriers
- SIGTTO – Guidelines for the Alleviation of Excessive Surge Pressures on ESD for Liquefied Gas Transfer Systems
- United Kingdom HSE – Assessment of the major hazard potential of carbon dioxide (CO_2)
- SIGTTO – LPG Shipping Suggested Competency Standards



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