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**MEDITERRANEAN ACTION PLAN (MAP)  
REGIONAL MARINE POLLUTION EMERGENCY RESPONSE CENTRE FOR THE  
MEDITERRANEAN SEA (REMPEC)**

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Thirteenth Meeting of the Focal Points of the Regional  
Marine Pollution Emergency Response Centre  
for the Mediterranean Sea (REMPEC)

REMPEC/WG.45/12/2  
Date: 30 April 2019

Malta, 11-13 June 2019

Original: English

Agenda Item 12

**GUIDE FOR RISKS OF GASEOUS RELEASES RESULTING FROM MARITIME ACCIDENTS**

**Note by the Secretariat**

**SUMMARY**

**Executive Summary:** This document presents the final version of the revised Guide for Risks of Gaseous Releases resulting from Maritime Accidents.

**Action to be taken:** Paragraph 12

**Related documents:** REMPEC/WG.32/11, REMPEC/WG.37/16, REMPEC/WG.41/16,  
REMPEC/WG.43/4, REMPEC/WG.43/9, REMPEC/WG.45/4,  
REMPEC/WG.45/12/1, REMPEC/WG.45/INF.14

**Introduction**

1. The Guide for Risks of Gaseous releases resulting from maritime accidents published by the Regional Marine Pollution Emergency Response Centre for the Mediterranean Sea (REMPEC) prepared in 1996, hereinafter referred to as the Guide, aims to facilitate the implementation of the Protocol concerning Co-operation in Preventing Pollution from Ships and, in Cases of Emergency, Combating Pollution of the Mediterranean Sea ("The Prevention and Emergency Protocol, 2002") by the Contracting Parties to the Convention for the Protection of the Marine Environment and the Coastal Region of the Mediterranean ("the Barcelona Convention") and its Protocols.

2. The Guide provides emergency-planning personnel with informative background on the issues related to releases of gases, and is intended for the response personnel, in particular, for the decision-makers, who have a basic maritime and technical background. The document deals with aspects of the chemistry of gases pertaining to their carriage at sea, container systems for packaged gases, layouts of gas carriers, international regulations governing the transportation of gases by sea, hazardous properties of gases, behaviour of airborne gas releases, and response measures for gas releases.

3. The need for a review of the Guide was acknowledged by the Tenth Meeting of the Focal Points of REMPEC (Malta, 3-5 May 2011), taking into account the recommendation of the Mediterranean Technical Working Group (MTWG) which was requested to identify recommendations, principles and guidelines available through the Regional Information System (RIS) that needed to be developed, revised, updated and/or amended.

4. The Eleventh Meeting of the Focal Points of REMPEC (Attard, Malta, 15-17 June 2015), agreed to include in the programme of work of the MTWG for the biennium 2016/2017 the update of the Guide.

5. Having noted the information provided on the update of the Guide, the Twelfth Meeting of the Focal Points of REMPEC (St. Julian's, Malta, 23-25 May 2017), agreed to:

- .1 **roll over** into the biennium 2018-2019, this task scheduled within the framework of the programme of work of the MTWG for the biennium 2016-2017; and
  - .2 **establish** an OPRC-HNS Correspondence Group under the MTWG to support the process of the update of the Guidelines on Risk of gaseous releases resulting from marine incidents;
6. In December 2017, REMPEC initiated, a revision of the Guide, within the framework of the MTWG, through the established OPRC-HNS Correspondence Group.
7. To provide technical support to the OPRC-HNS Correspondence Group, the Centre of Documentation, Research and Experimentation on Accidental Water Pollution (Cedre), was engaged by the Secretariat of the MTWG to produce an updated version of the Guide considering the following steps:
- .1 **to provide** a detailed and exhaustive overview of developments which occurred since 1996 related to the topics addressed within the Guide;
  - .2 **to identify** parts of the Guide requiring an update and define new parts to be added to reflect the current situation;
  - .3 **to propose** a first draft of the revised Guide including the required amendments of the text, diagrams, photos and other illustrations; and
  - .4 **to amend** the first draft of the revised Guide taking into consideration the comments and amendments provided by REMPEC and the MTWG through OPRC-HNS Correspondence Group.
  - .5 **to propose** brief recommendations on any identified needs to strengthen capacity building and to raise awareness on this matter and **suggest** ways forwards including development of additional material and potential source of funding.
8. Pursuant to the Programme of Work and Budget for 2018-2019 of the Mediterranean Action Plan (MAP) of the United Nations Environment Programme (UNEP); REMPEC organised the Regional Workshop on Response to Spill Incidents involving Hazardous and Noxious Substances (HNS) (MEDEXPOL 2018) (Valletta, Malta, 20-21 June 2018)<sup>1</sup> amongst other to examine and agree upon the draft Guide.
9. Having considered the information provided, the Workshop agreed upon the Draft Guide, as amended, including additional information (e.g. ammonia) and the addition of a general introduction of the scope of the document. The Workshop invited the Secretariat to submit the revised Draft Guide, to the present Meeting, for adoption.
10. To address the output 5 referred to in paragraph 7 of the present document the Workshop concurred with the need to establish, in collaboration with the national competent authorities, a stronger partnership with the private sector, in particular with chemical companies, harbours and salvage companies, with the view to raise the awareness on the risks of gaseous releases and HNS marine pollution and improve knowledge on the operational response to be implemented. In this regard, the Secretariat proposed to explore the required synergies to address this need.
11. The Guide for risks of gaseous releases resulting from maritime accidents reproduced in the Appendix to the present document is the result of the consultation process detailed above.

### **Action Requested by the Workshop**

#### **12. The Meeting is invited to:**

- .1 **take note** of the information provided in the present document; and
- .2 **consider** the proposal laid down in paragraph 10 of the present document.
- .3 **adopt** the Guide for risks of gaseous releases resulting from maritime accidents, which is presented in the Appendix to the document under review.

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<sup>1</sup> REMPEC/WG.45/INF.14

**APPENDIX**

**GUIDE FOR RISKS OF GASEOUS RELEASES RESULTING FROM  
MARITIME ACCIDENTS**





## Guide for Risks of Gaseous releases resulting from Maritime Accidents



**MEDITERRANEAN ACTION PLAN (MAP)  
REGIONAL MARINE POLLUTION EMERGENCY RESPONSE  
CENTRE FOR THE MEDITERRANEAN SEA (REMPEC)**





REGIONAL MARINE POLLUTION EMERGENCY

RESPONSE CENTRE FOR THE MEDITERRANEAN SEA (REMPEC)

MEDITERRANEAN ACTION PLAN

# **Guidelines on Risk of Gaseous releases resulting from Marine Accidents**

**Regional Information System**

[www.rempec.org](http://www.rempec.org)

**June 2018**

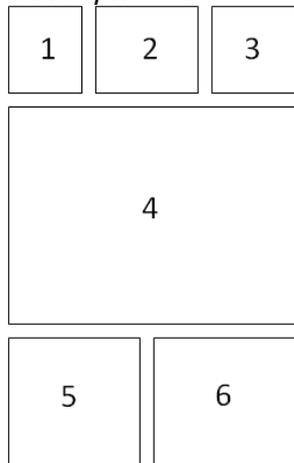
## Note

This document is aimed at facilitating the implementation of the “Protocol concerning Co-operation in Combating Pollution of the Mediterranean Sea by Oil and Other Harmful Substances in Cases of Emergency” of the Barcelona Convention (Emergency Protocol, 1976) and the “Protocol concerning Co-operation in Preventing Pollution from Ships and, in Cases of Emergency, Combating Pollution of the Mediterranean Sea” (Prevention and Emergency Protocol, 2002) by the Contracting Parties of the Barcelona Convention.

These "Guidelines", which are advisory, do not affect in any way already existing or planned national laws and regulations related to matters covered by it. REMPEC assumes no liability whatsoever for any potentially damaging consequences which could result from the interpretation and use of information presented in this document.

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The Guidelines are downloadable from REMPEC’s website ([www.rempec.org](http://www.rempec.org)) in the Section “RIS/Operational Guides and Technical Documents”.

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In addition, gases are also carried in "package" form, which means that they are transported in portable tanks of various sizes, albeit in smaller quantities, on vessels other than specialized gas carriers. The possibility of an accidental release of a gaseous product is therefore not limited to originate only from gaseous cargoes carried in bulk.

In a region intensely used by merchant shipping, irrespective of whether a particular type of ship has an exemplary safety record and therefore might not be perceived as a great risk such as is the case with gas carriers, the possibility of an accident remains. The Mediterranean is no exception and as shown in **Table 1** there have been some maritime related incidents involving gaseous or very volatile cargoes.

The fact that there have been incidents involving this type of cargo indicates that there is a need to address the potential accidental release of such products within the whole context of preparedness for and response to maritime incidents. In order to understand better the way these products might be dispersed once released to the environment, as well as the consequences of such releases and the mitigating measures that might be used, it is necessary to focus not only on the relevant factors that have a direct bearing on such aspects but also to have an appreciation of the basic chemistry of gases as well as a knowledge of the way gases are transported at sea.

<i>Date</i>	<i>Location</i>	<i>Vessel / plant</i>	<i>Substance</i>	<i>Incident Details</i>	<i>Source</i>
24.07.08	Perama shipyard	Friendshipgas	LPG	Explosion and fire. The fire brigade worked for over 4 hours to extinguish the fire and prevent the flames from reaching the neighbouring vessel. 8 crew members were killed.	Cedre
19.01.04	Skikda, Algeria	Gas-liquefaction plant	LNG	Explosion, the blast shook buildings and shattered windows more than a mile away. 27 employees died, 56 injured and cost \$900 million	International Journal of Global Energy Issues
06.01.04	Italy	Panam Serena	Benzene	An explosion happened during the discharging operations (benzene and fuel). Two crew members are missing.	Cedre
30.10.95	Alexandria	Capo Argento	LPG	LPG carrier went aground near the port entrance when sailing for port on charge; vessel was re-floated and entered port for inspection.	Lloyd's
26.03.94	off Ancona	Capo Cervo	Butylene	Collision with a general cargo vessel; bow damage occurred; after inspection, vessel proceeded to Ravenna to discharge cargo.	Hazardous Cargo Bulletin
05.07.93	off Marsa el-Brega	Lulligas	Ammonia	Grounding of vessel on soft bottom; ship to ship transfer of part of cargo followed by re-floating.	Lloyd's
18.05.90	off Brindisi	Golden Star	empty	LPG carrier in collision with MV Brega: both were empty at the time.	Lloyd's
28.04.90	Brindisi	Val Rosandra	Propylene	Fire in compressor room and cargo tank during propylene discharge; no casualties but towed offshore and left to burn; later sunk.	Hazardous Cargo Bulletin
22.10.89	off Taranto	Agip Siracusa	LPG	Vessel in collision with vehicle carrier; serious bow damage to both vessels; gas carrier discharged cargo at Ravenna.	Hazardous Cargo Bulletin
26.02.89	Haifa	Zim Iberia	Ethylene oxide	20 cannisters fell into Haifa harbour whilst unloading; most were retrieved.	Hazardous Cargo Bulletin
15.02.89	Skikda	Tellier	LNG	Vessel broke free during loading in heavy weather; damaging 4 loading arms; small leakage of product and hull damage; repairs to vessel undertaken at Marseille-Fos.	Cedre

16.11.84	Sibenik (Yugoslavia)	Brigitta Montanari	vinyl chloride monomer	The tanker, transporting more than 1,300 tonnes of Vinyl Chloride Monomer (VCM), sank in the Adriatic Sea to a depth of 82 m. Solution chosen was to refloat the wreck and to pump out the cargo.	Cedre
12.10.78	Hyères, France	Gaz East	Butane	Vessel on route from Pylos to Port St. Louis suffered severe list due to error in ballasting; crew abandoned vessel; vessel was towed to sea and sunk by French authorities.	France Focal Point

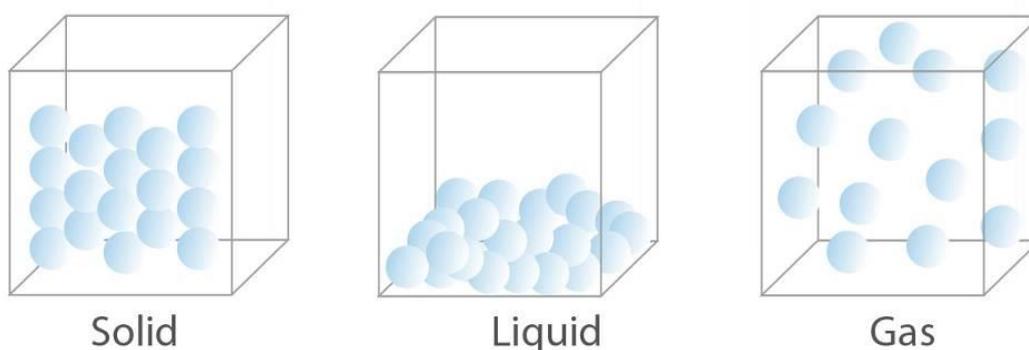
**Table 1. Maritime related incidents involving gaseous or very volatile cargoes in the Mediterranean Sea.**

# CHAPTER 1. An overview of the chemistry and different classification of gases

An appreciation of the complex engineering technology that is involved in the transport of gases in general and more specifically in the sea-borne transport of gases requires a certain understanding of the physical chemistry of gases. Although this is a rather extensive and specialized subject, an examination of certain fundamental chemical principles pertaining to the different physical states of matter with a focus on the gaseous phase, coupled to a brief description of the classification of gases would facilitate such an appreciation.

## 1. State of matter

Most substances can exist in more than one homogeneous physical state: solid, liquid or gas. These states are usually called "phases" i.e. the solid phase, the liquid phase and the gaseous or vapour phase. A substance may have two or even all three phases present simultaneously. The phase in which a particular substance exists can be considered as an expression of the orderly arrangement and distance between the component particles of the substance i.e., when they are orderly arranged and close together, the substance is a solid and as the particles move apart and begin to lose their orderliness, the substance expands becoming a liquid and then a gas. A gas is thus characterized by the disorderly distribution and random arrangement of its particles (see **Figure 2**).



**Figure 2 (Copyright Cedre). Two-dimensional illustration of the different phases of matter.**

## 2. Terminology associated with states of matter – a short overview

Some common terms used in conjunction with the description of the states of matter may seem rather conventional; however it is imperative to consider their meaning and interpretation.

- i) **Heat:** the total amount of "molecular movement" or kinetic energy present in a substance and is measured as a quantity of energy (thermal energy).
- ii) **Temperature:** a measure of the availability of heat and describes the intensity or degree of hotness or coldness measured on a scale (e.g. Celsius, Fahrenheit or

Kelvin Scale); temperature indicates the amount by which the molecules of a substance are vibrating and also indicates the direction of heat flow, since heat always flows from a warm to a cooler body.

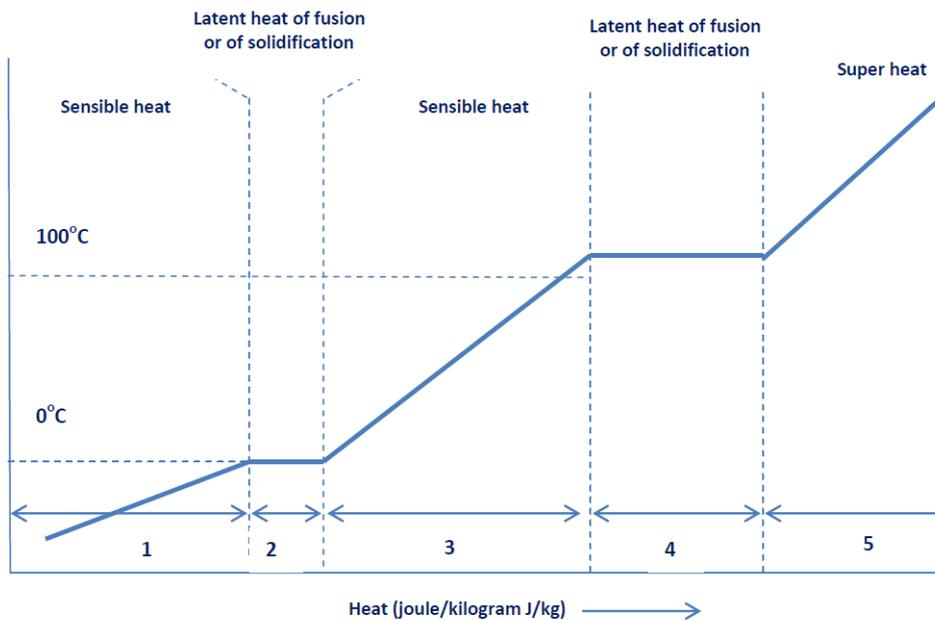
The distinction between heat and temperature can be made clearer by considering the example of a burning match and a small fire in a grain silo which can both be of the same temperature but in the latter case, there will certainly be more heat.

- iii) **Vapour pressure:** the pressure at a particular temperature in the space above a liquid which is exerted by the vapour molecules, as molecules leave the liquid to enter the vapour phase and vice-versa; it is a measure of a liquid's tendency to vaporize; as the temperature changes, so also does the vapour pressure (the higher the temperature, the higher the vapour pressure) and for any particular temperature there is always a fixed value of vapour pressure; solids also exert a vapour pressure, although for most solids, it usually becomes apparent at elevated temperatures.
- iv) **Saturated vapour pressure:** the pressure at a particular temperature when a continuous exchange of molecules between the vapour and the liquid takes place in a confined space but under these conditions the space above the liquid cannot accept any further vapour.
- v) **Boiling point:** a guide to the strength of the cohesive forces of a liquid and is the temperature at which the saturated vapour pressure of a liquid is equal to the pressure above it; the boiling point is a function of the pressure; under spill conditions, the boiling point would be the temperature at which the vapour pressure equals the ambient air pressure.

### 3. Changes of states

When a solid is heated, it melts to form a liquid and on further heating, the liquid evaporates to form a gas. In the solid state, the particles are ordered, less so in a liquid and completely disordered in a gas. The changes of state i.e. melting and evaporation can therefore be considered as disordering processes.

In changing from a solid to a liquid (fusion/melting) or vice-versa (solidification), heat must be given to or given up by the substance respectively. For example, when a solid melts, it requires additional heat to be added so that it will turn into a liquid. The heat involved when a substance changes state is called the latent heat and for a given mass of substance, the latent heat of fusion and solidification are the same. Similarly, when changing from a liquid to a vapour (vaporisation) or vice-versa (condensation/liquefaction), the latent heats are the same, although they are different from the latent heats of fusion or solidification. Using water as an example, the states of aggregation of the different physical phases of matter as a function of the uniform addition of heat are illustrated in the heating curve - **Figure 3**.



**Figure 3. Illustration of the behaviour of water when heated or cooled.**

In terms of particle order-disorder processes, the variations that accompany the changes of states shown in the diagram can be explained as follows:

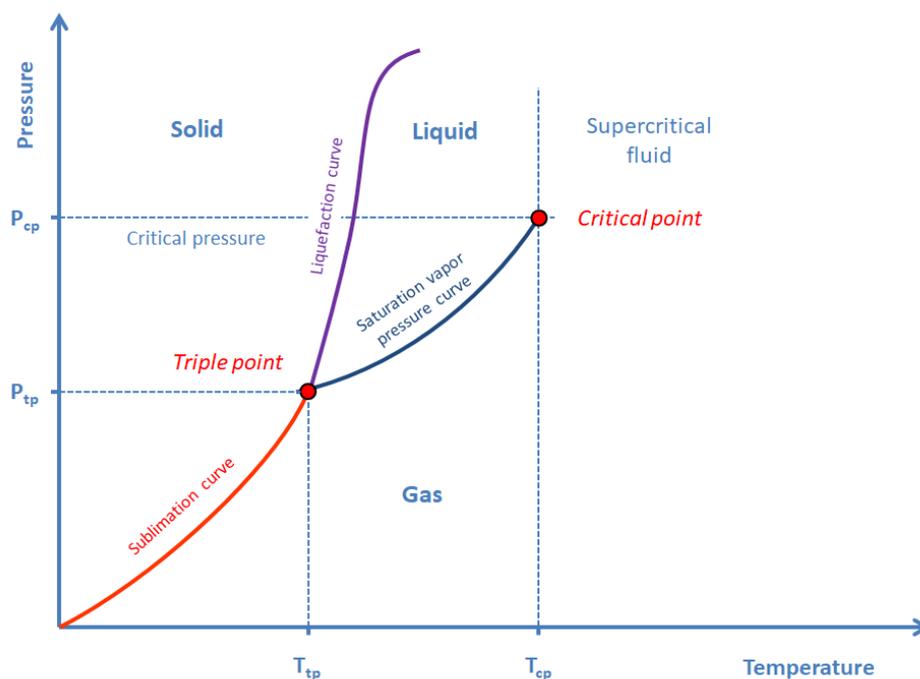
Along the portion (1) of the curve, heat is supplied and the particles in the solid substance i.e. the ice crystal begin to vibrate. As more heat is added, the vibrations become greater but although no change is visible, the particles within the solid become slightly less ordered. The heat added increases the kinetic motion of the particles. Since temperature is a measure of the kinetic energy, the temperature rises along portion (1) of the curve which continues until the melting point is reached at portion (2) of the curve. At the melting point, the vibrations of the particles are so great that any added heat serves to loosen binding forces between neighbouring particles. Consequently along portion (2) of the curve, added heat does not increase the kinetic energy of the particles but goes to increase the potential energy of the particles acting against the attractive forces of the particles. Along portion (2), there is no change in kinetic energy, hence the substance stays at the same temperature, but the amount of liquid increases at the expense of the solid. Thus at 0°C, water and ice co-exist.

When sufficient heat has been added to tear all the particles from the ice crystal, added heat increases the kinetic energy of the particles and the temperature of the liquid rises - portion (3) of the curve. This continues until the boiling point is reached. At the boiling point, added heat is used to overcome the attraction between the particles in the liquid. Along portion (4) of the curve, there is an increase in the potential energy of the particles but no change in their average kinetic energy. Along portion (4) of the curve, liquid converts to gas. Finally, after all the liquid has been converted to gas, added heat raises the kinetic energy of the particles as shown by the rising temperature along portion (5) of the curve.

The curve can also be viewed in the reverse whereby, heat is removed from the substance and in this case the curve is called a "cooling curve". Since the concern is the gaseous state, it is convenient here, against the background of the preceding paragraphs to consider what happens when a gas, in this case water vapour, is cooled. As heat is removed from the water vapour, the temperature begins to drop - portion (5) of the curve. Along this portion of the curve, the kinetic energy of the water vapour particles decreases in order to compensate for the removal of energy. This slowing down proceeds until the attractive forces become dominant and the particles coalesce to form a liquid. In the liquefaction process, particles leave the gas and enter the liquid state - portion (4) of the curve. The importance of

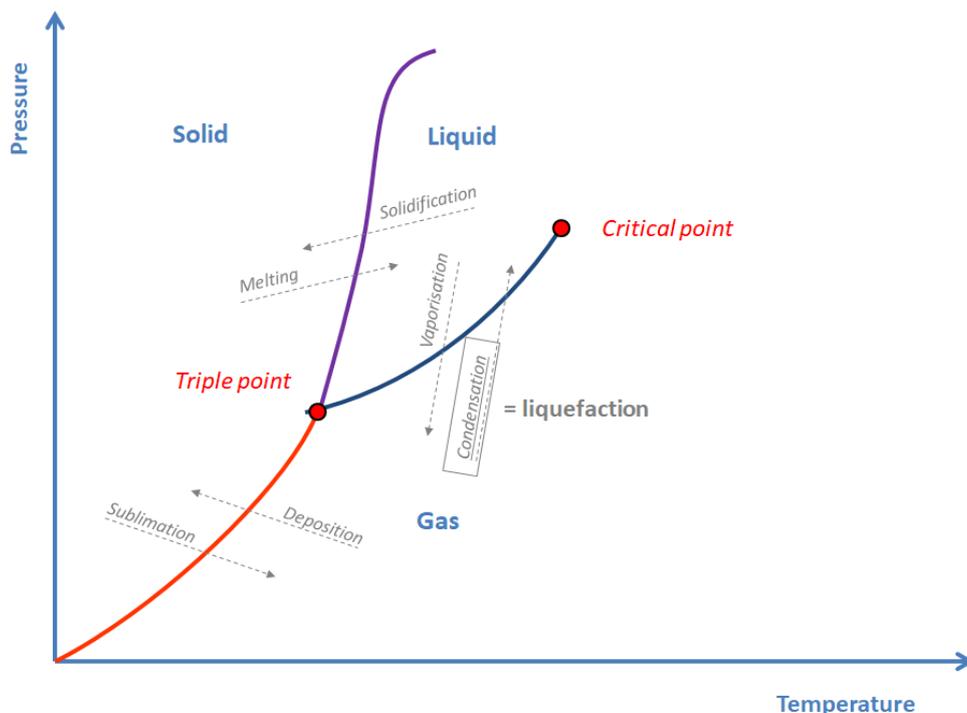
temperature on the phase of a gas is best seen by the example of ethylene oxide which is a gas at 20 °C and a liquid at 10 °C.

In addition to the temperature, the physical state of a particular substance depends on the external pressure so that the changes between solid, liquid and gaseous states are dependent on both temperature and pressure. This relation between solid, liquid and gaseous state as a function of the temperature and pressure can be summarized on a single graph known as a phase diagram. Each substance has its own particular phase diagram which has been worked out from experimental observation and a typical phase diagram for a particular substance would look like that shown in **Figure 4** below. In the diagram, pressure is shown vertically with higher pressures at the top whilst temperature is shown horizontally with higher temperatures to the right. Very briefly, each of the regions correspond to a single (one) phase system. For all values of pressure and temperature falling inside a single phase region, the substance is in the state specified.



**Figure 4 (Copyright Cedre). Phase diagram.**

The line which separates one region from another is an equilibrium line and this represents equilibrium between two phases. If one takes the solid-liquid line, this shows the temperatures and pressures at which the solid and liquid phases exist in equilibrium - the amount changing from solid to liquid being exactly balanced by the amount changing from liquid to solid. The same applies to the line which separates the solid from the vapour phase and the liquid from the vapour phase. Thus, by finding the point on the diagram which represents a particular temperature/pressure combination, the final phase of a substance can be determined. The single point where all three lines on the diagram meet is the "triple point". The triple point represents the only temperature and pressure at which all three phases can be in equilibrium together. Although at any other combination of the temperature and pressure all three phases may exist, they will not be in equilibrium. An additional usefulness of a phase diagram is that it graphically illustrates that a gas can be liquefied and therefore reduced in volume by removal of heat and/or by pressure by pressurizing (compressing) as shown in **Figure 5**.



**Figure 5 (Copyright Cedre). Phase diagram showing how a gas can be liquefied by removal of heat and/or pressurizing.**

#### 4. Interactions between seawater and chemicals

Demineralized water is being used to determine physico-chemical parameters in Safety Data Sheets (SDS). The major difference between seawater and demineralized water is salinity. This difference of chemical composition has a strong influence on solubility values of chemicals. Xie at al. (1997) has shown it can reach a 20-30% decrease for some chemicals. In this cited study, results are shown for a 32 ppt salinity while it is close to 38 ppt in Mediterranean sea. Thus solubility values should be expected to be still slightly less important. Some examples are presented in **Table 2**.

Chemical	Solubility (g.L <sup>-1</sup> )	
	Ethyl acrylate	Ethyl acrylate
Freshwater	17.5	12.8
Seawater (35 ppt)	10.0	9.8

**Table 2. Example of chemicals with solubility determined in freshwater or seawater (Source Cedre).**

## 5. Liquefaction of gases

### 5.1. Physical matters

As shown in **Figure 5**, the most favourable conditions for liquefaction of a gas are high pressure or low temperature or a combination of both. Two counterbalancing factors are involved in the process of liquefaction. These are the intermolecular attractive (intermolecular cohesive) forces which tend to bring the particles together and which increase with higher pressure and the thermal (kinetic) energy of the particles which tends to keep the particles apart and which decreases with lower temperatures.

There is, however, for each gas, a temperature above which the attraction forces are not strong enough to produce liquefaction, however high the pressure. This temperature is called the **critical temperature**. The critical temperature depends on the magnitude of the attractive forces between the particles of a substance. Above the critical temperature, no amount of pressure can produce liquefaction. Above its critical temperature, a gas may be regarded as a "permanent" gas, since it cannot be liquefied. Below the critical temperature, it is appropriately described as a vapour since it can always be liquefied if the pressure is increased sufficiently. Viewed differently, if a substance exists in its gaseous state, below its critical temperature, it is considered a vapour. If a substance exists as a gas above its critical temperature it is called a gas. Thus, for example gaseous water which has a critical temperature of 374 °C will be considered as water vapour if heated above its boiling point of 100 °C but below 374 °C. A gas can be therefore liquefied by keeping the pressure constant and cooling the gas. The minimum pressure to compress a gas to its liquid state at its critical temperature is known as the **critical pressure**.

**Annex I** lists the critical temperatures and pressures of some common gas cargoes.

It is also usually found that substances with high critical temperatures are easy to liquefy and can be liquefied by pressure alone, whilst substances with low critical temperatures need to be cooled before they can be liquefied. Thus, extending this generalization to the cargo listing of **Annex I**, all the cargoes would be below their critical temperature at the normal ambient range of temperatures during sea passage. They can therefore be liquefied by pressure alone and be carried at ambient temperature. For the carriage of methane, or ethane or ethylene as liquids, this is not possible because the critical temperatures are too low and some refrigeration process is required for their carriage (or storage) as a liquid.

### 5.2. Plant liquefaction process

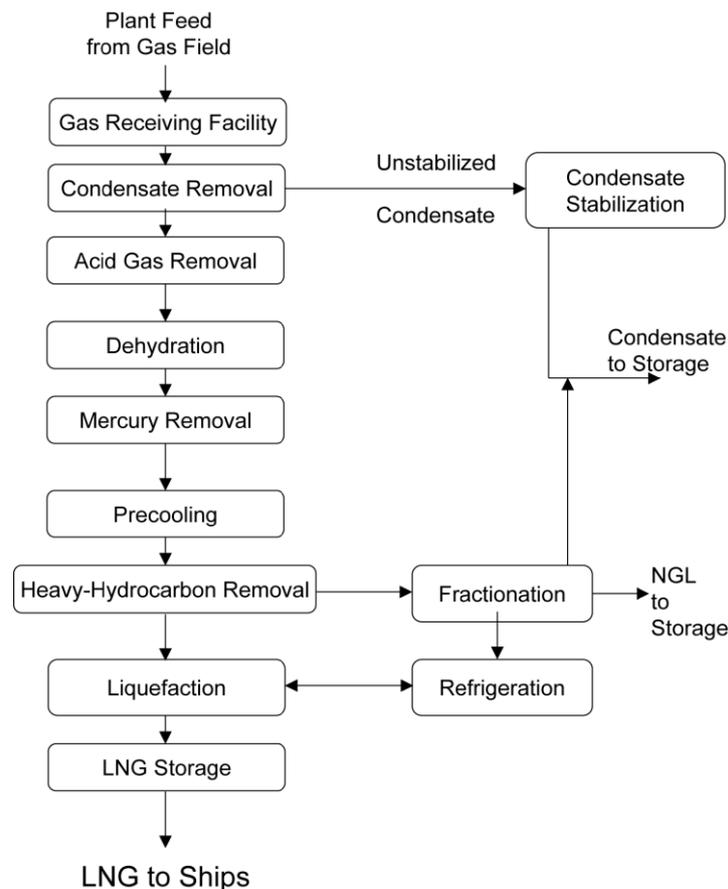
Natural gas is a mixture of many compounds, with methane being the main hydrocarbon constituent. When natural gas is produced from an underground reservoir, it is saturated with water vapor and might contain heavy hydrocarbon compounds as well as non-hydrocarbon impurities.

To fulfil consumer expectations, optimisation economic productivity and respect different standards, raw natural gas must previously undergo different processes before transportation (**Figure 6**).

In general the following processes units are required:

- Condensate removal: raw natural gas feedstock is cooled to lower the gas temperature to below its hydrocarbon dew point at the feedstock pressure.

- Acid removal: carbon dioxide and hydrogen sulphide are both acid gases that present corrosive properties in presence of water and high level of toxicity for the second.
- Dehydration: presence of water is not acceptable due to a risk of accelerated corrosion and potential accumulation in low-points regions of pipelines. Solid hydrates can also plug key elements such as valves or fittings.
- Heavy-Hydrocarbon removal and fractionation: heavy hydrocarbons (C5+) are removed by fractionation before liquefaction. Natural gas is pre-cooled to about -35 °C by propane. Fractionation works based on the different boiling points of the different hydrocarbons in the NGL stream.
- Liquefaction: natural gas goes through successively colder heat exchangers down to its temperature of liquefaction (-162 °C). Transportation at atmospheric pressure in the form of LNG is possible.



**Figure 6.** Key components of a LNG liquefaction plant (Source Petrowiki.org).

## 6. Description and general characteristics of gases

Based on the foregoing, a gas can be described as a formless fluid whose component particles are in constant motion and arranged in a completely disorderly fashion. Unlike a solid which has shape and volume or a liquid which has volume but no shape, a gas has neither shape nor volume. A gas is thus, the most diffused state of matter and like other states of matter is nothing other than matter in a specific homogenous physical state. A

common distinction between a liquid and a gas is that whereas a gas may be reduced in volume, a liquid is relatively incompressible.

General characteristics common to gases are:

- they can be reduced in volume, implying that matter in the gaseous phase is not as compact as in the liquid and solid state;
- they are indefinitely expansible and will always occupy all the volume of any vessel in which they are confined, implying that matter in the gaseous state is in constant motion; this energy due to the motion of the component particles of the gas is called kinetic energy;
- they exert pressure (force) on the interior wall of the vessels in which they are confined implying that gases exert a pressure on all boundaries with which they are in contact.

## **7. Classification of gases**

Gases can be broadly classified according to:

- their hazardous properties;
- their physical properties;
- their usage;
- their chemical composition;
- their behaviour once spilled.

### **7.1. Classification according to hazardous properties**

This category can be further sub-divided into:

- flammable gases: these are gases which will burn in the presence of oxygen and an ignition sources e.g. methane, propane;
- non-flammable gases: these are gases which will not burn in air, however within this sub - category there are those which support combustion, often called oxidizing gases whilst there are those which do not support combustion and are called inert gases e.g. helium, argon;
- toxic gases: gases which will endanger human life on exposure e.g. arsine, phosgene, chlorine;
- reactive gases: gases which will react with other materials or within themselves by a process other than burning at the same time liberating heat which sometimes also results into flaming e.g. fluorine, acetylene, vinyl chloride.

### **7.2. Classification according to physical properties**

This category can be further sub-divided into:

- non-liquefied compressed gases: gases which inside a gas container are at normal temperature and exist in the gaseous state under pressure e.g. argon, helium, air, hydrogen;

- liquefied compressed gases: gases which are liquefied by increasing the pressure and exist in the liquid and gaseous state at equilibrium in the gas container e.g. propane, butane, chlorine;
- cryogenic liquids: liquids made from gases liquefied by cooling to very low temperatures via refrigeration systems and are maintained in their containers at low temperatures at relatively low pressure e.g. LNG, oxygen, hydrogen.

### 7.3. Classification according to usage

This category can be further sub-divided into:

- fuel gases: gases used for burning to produce heat, power or light e.g. LPG, LNG;
- industrial gases: gases used in industrial processes such as welding and cutting, refrigeration e.g. acetylene;
- medical gases: gases used for health care purposes such as anaesthesia and respiratory therapy e.g. nitrous oxide.

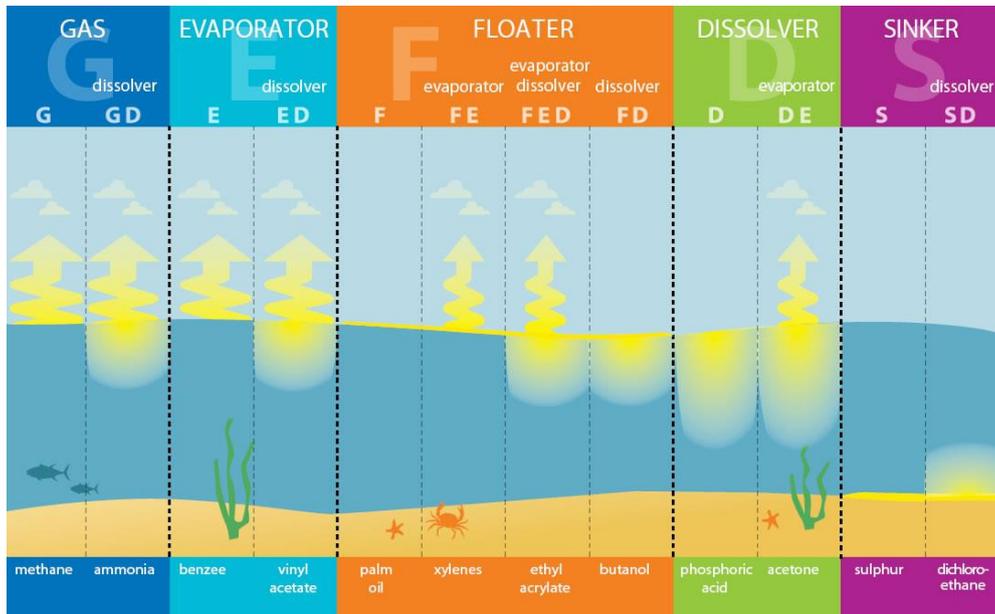
### 7.4. Classification according to their chemical composition

Behind acronyms used should be understood the presence of specific chemicals or characteristics:

- Liquefied Natural Gas (LNG): the major constituent is methane (CH<sub>4</sub>),
- Liquefied Petroleum Gas (LPG): the major constituents are propane (C<sub>3</sub>H<sub>8</sub>) and butane (C<sub>4</sub>H<sub>10</sub>),
- Natural Gas Liquids (NGL): NGL are liquid or liquefied hydrocarbons recovered from natural gas in separation facilities or gas processing plants. Natural gas liquids include ethane, propane, (normal and iso-) butane, (iso) pentane and pentanes plus (sometimes referred to as natural gasoline or plant condensate),
- Compressed Natural Gas (CNG): fuel source that is made from compressing natural gas to less than 1% of its standard atmospheric volume.

### 7.5. Classification according to behaviour in the marine environment once spilled

The behaviour of a substance spilt at sea is the way in which it is altered during the first few hours after coming into contact with water. Predicting this behaviour is one of the most important stages in the development of a response strategy. The Standard European Behaviour Classification (SEBC) determines the theoretical behaviour of a substance according to its physical and chemical properties, and classifies it into one of five main families, as presented in **Figure 7**:



**Figure 7 (Copyright Cedre). Standard European Behaviour Classification. G (Gas), E (Evaporator), F (Floater), D (Dissolver), S (Sinker) and behaviour combinations (e.g. FED for Floater and Evaporator and Dissolver).**

Most of the time, a substance does not have one single behaviour but rather several behaviours due to its nature and environmental processes (wind, waves, current). For example, ethyl acrylate is classified as FED as it floats, evaporates and dissolves. However, the SEBC code has its limits. It is based on experiments conducted in the laboratory on pure products at a temperature of 20 °C in fresh water. These conditions are quite different from those encountered in the case of incidents at sea, and the actual behaviour of the product may be quite different from its theoretical behaviour. Yet the SEBC code remains a valuable tool for use in the elaboration of spill response strategies, although it is important to bear in mind its limitations when using it.

It should be noticed that, depending on the exact location of the source of the gas spilled at sea, the fate of the chemical and its consequences may be very different. For example, in the case of a subsea pipeline rupture and besides breach characteristics and gas transport conditions (nature, state, pressure, flow), chemical processes governing the behaviour of a gas plume in the water column are of high importance and will determine consequences at sea surface in terms of behaviour and associated risks.

For soluble gases, a subsea leakage will favour solubilisation versus evaporation, especially if depth from source of leakage to sea surface is important. For gases mostly insoluble, which represent the major fraction of gases transported by pipelines, such as LNG or LPG, depth and temperature are the main parameters that will influence the fate of gas bubbles in the water column and the impact at sea surface. It should be noticed that for sufficient depths, gas hydrates can be formed and, depending on the release conditions, such phenomenon can modify gas surface flux at sea surface. In all cases involving underwater gas blowouts, prior risk assessments and contingency planning must be conducted before any rescue or clean-up operations.

## CHAPTER 2. Maritime transport structures for gases

Gaseous products are considered hazardous cargoes in that they possess hazards such as corrosively, toxicity and flammability. In addition to the problems of transporting a cargo which is inherently hazardous are the normal difficulties of ensuring the safe transport and handling of cargo at sea and in port areas.

These products can be transported in either of two ways; i) as packaged dangerous goods; ii) in bulk. To this end, an international regulatory framework has been developed whose aim is to put into place safeguards when such products are transported in bulk and in packaged form. The following is a brief description of the way gases can be carried at sea and the international regulations associated with their carriage.

### 1. Gases carried out as dangerous goods

**Packaged dangerous substances** are usually known as **dangerous goods**. Gases carried as dangerous goods are placed in some kind of portable tank. The portable tank is either placed directly on board the vessel or in or on a transport unit which itself is then placed on the vessel.

#### 1.1. Types of portable tanks

Gases are carried in rigid portable tanks. These are portable tanks which will retain their shape when either full or empty, even when compressed at pressures. They come in various sizes and the types of portable tanks used for the carriage of gaseous products include:

- **cylinders** which have a tubular like shape with a circular cross section and a valve (regulator) or valve arrangement at one end of the cylinder; some might have a seal instead of a valve which is meant to be used with equipment having a valve arrangement; most cylinders come with a heat sensitive pressure relief device or plug which prevents internal over pressurization with catastrophic consequences if the cylinder is subjected to intensive heat.

cylinders for carrying gases could be of two types:

- **uninsulated cylinders** are usually made of steel although it is not uncommon to find cylinders made of aluminium or fiberglass with an aluminium outer casing; they have rounded shoulders on top and screw-on caps or cylindrical rings for valve protection; they could range approximately in size up to 0.25 m diameter and 1.5 m height;
- **insulated cylinders** used for cryogenic liquids which consist of a core insulated metal cylinder with an outer protection metal jacket; the area between the cylinder and the jacket is normally under vacuum; the cylinders have a small protection ring at the top to protect the valve and a foot ring for handling; they could range approximately in size up to 0.6 m diameter and 1.5 m height;

Potentially a portable tank might be equipped with a sunshield system.

Illustrations of the various types of cylinders are shown in **Figure 8**.



***Figure 8. Various types of gas cylinders (not to scale).***

- **tube modules or Multiple Element Gas Containers (MEGCs)** which consist of several steel cylinders positioned horizontally which are permanently mounted inside an open box frame with the cylinder valves at one end enclosed in a box-like compartment; an illustration of a tube module is shown in **Figure 9**;



***Figure 9. Example of a tube module.***

- **ton containers** which are cylindrical pressure tanks made of steel approximately 0.9 m diameter and 2 m length; the name "ton container" comes from their capacity to transport one ton of chlorine; the valves are found at one and under a protective cover plate held in place with bolts; two rolling bands around the mid-waist of the cylinder facilitate handling; various aspects of a ton container are found in **Figure 10**;



***Figure 10 (Copyright Cedre). Example of a ton container.***

- **intermodal tank containers** which consist of a tank barrel mounted in a metal supporting framework; the type of framework could be either box (full frame) or beam (end frame); illustrations of the two types of frameworks are shown in **Figure 11**; both types are equipped with corner casting for handling purposes; typically the length of a tank container is 20ft although 40ft tank containers do exist but are rare due to the high gross container weight; the tank barrel is manufactured with a particular product or range of products in mind and is typically made from unlined steel or mild steel with an interior impervious lining; tank containers come equipped with numerous fittings and attachments for filling, discharging, safety and vacuum relief and air-line connection, plus any other requirements dictated by the product(s) to be carried;



***Figure 11. Intermodal tank containers: box type frame (left) and beam type frame (right).***

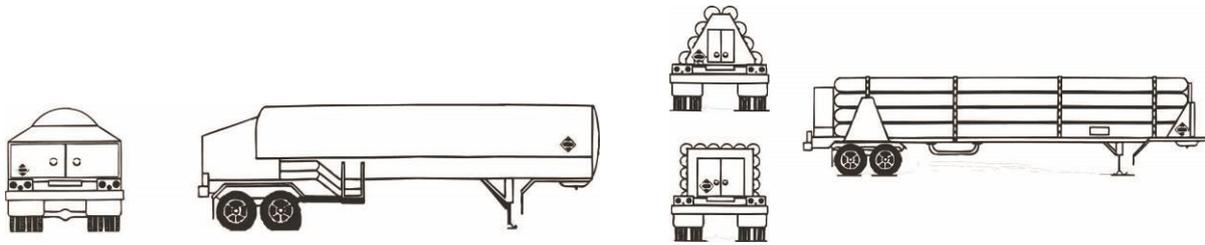
tank containers suitable for the carriage of gaseous products can be of two types:

- **pressure portable tanks** which transport liquefied compressed gases;
- **cryogenic portable tanks**, each consisting of a tank within a tank with insulation between the inner and outer tanks; insulation could consist of expanded polyurethane, polystyrene or mineral wool or a combination of such materials whilst cladding is applied over the insulation; the space between the inner and outer tanks is normally maintained under vacuum;

- **road tank trailers** and vehicles, each consist of a cargo tank that is permanently mounted on a truck or mounted on a trailer which is then drawn by a motor vehicle; a lot of what has already been described for the safety and constructional requirements of intermodal tank containers also applies to road tank trailers and vehicles; road tank trailers and vehicles can be of two types:

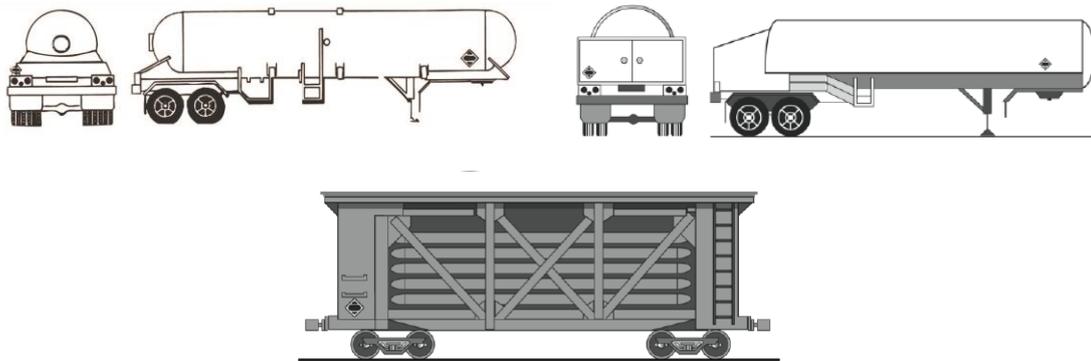
- **pressure cargo tanks** which transport liquefied and compressed gases; they have circular cross sections with rounded ends or heads; these tanks may also carry different substances in separate compartments; separate temperature gauges are found for each compartment;
- **cryogenic cargo tanks** which transport cryogenic liquids; as in the case with all portable tanks carrying cryogenic liquids, this type of cargo tank consists of a tank within a tank with a space between the inner and outer tank held under vacuum and filled with insulation material; each tank has a circular cross-section with dish-like ends;

- **tube trailers (Figure 12)** which resemble tube modules/MECGs but instead are permanently mounted on a trailer;



***Figure 12. Examples of road trailers and vehicles carrying gaseous products.***

- **rail cars** which consist of tank cars that are constructed to transport gases; all of what has been previously described for the safety and construction requirements of portable tanks containers and road tank trailers also applies to rail cars; tank cars are divided into: i) pressure tank cars; ii) cryogenic tank cars; iii) tube cars; illustrations of the different types of rail cars are shown below in **Figure 13**.



***Figure 13. Examples of road trailers and vehicles carrying gaseous products.***

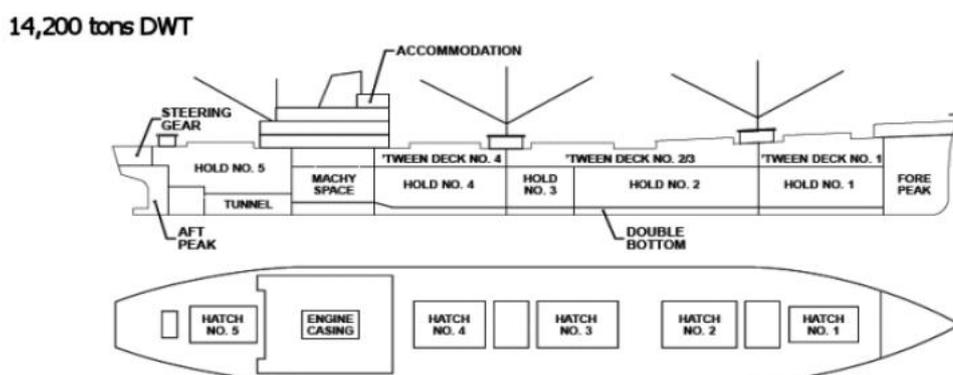
## 1.2. Vessels carrying dangerous goods

Before the development of integrated cargo transportation systems, the availability of modern construction methods for ships and the existence of sophisticated shore handling equipment, the general cargo ship was probably the most common type of merchant vessel which carried packaged dangerous goods. Reflecting the adaptability of the shipbuilding industry, a wide variety of mercantile ships are in existence today which are able to carry such cargo.

Different types of ships can be recognized by certain distinctive features in their general appearance because the design of a ship depends mainly on the work she is set out to do. A breakdown of the more common categories of vessel which can carry dangerous goods including gaseous products are as follows (see **Figure 14**):

- **General cargo ships** (when the vessel operates on a regular service between ports, the term liner is used although some countries employ the term freighter; when the vessel is employed on charter to take cargo from port to port at any time anywhere in the world, the term tramp is used). General cargo ships can be of two types. The first are break bulk carriers which carry dry cargo in small consignment e.g. crates, bags or barrels. These vessels contain dunnage to support and separate cargo in their cargo spaces which tend to be box-shaped. These vessels have four or five holds and one or two tween decks which run practically the full length of the ship, so that the various items carried can be methodically stowed for convenient access at the relevant ports of discharge and the weight of the cargo more easily distributed. The second type are multi-purpose carriers designed to carry a variety of cargoes at the same time. Special systems are available to transport break bulk, refrigerated (frozen) and liquid cargoes.

- **Cellular container ships** which are specialized carriers that carry containers in which could be found packaged dangerous goods. The majority of containers are designed for general dry cargo (box-type) but specialized units can take liquid, powder, or refrigerated cargo. Containers when on deck need to be lashed and secured. The carrying capacity of these ships is specified in TEUs (Twenty-foot Equivalent Units).
- **Ro/ro unit load vessels** where the cargo is moved on and off using trailers normally carrying containers. A common characteristic of these vessels is their intermodal capacity, which means that their cargo can move directly onto the road system. Other vessels which operate on a roll-on/roll-off method are passenger and car ferries.



Break bulk carrier



Container ship

**Figure 14.** Illustrations of some vessels which transport packaged dangerous goods.

### 1.3. International regulations

- **Carriage at sea of gaseous dangerous goods**

Chapter VII of the International Maritime Organization's (IMO) International Convention for the Safety of Life at Sea (SOLAS), 1974, contains requirements covering the carriage of dangerous goods at sea.

Further measures are included in the IMO's International Maritime Dangerous Goods Code\* (IMDG Code) which was first adopted by the IMO Assembly resolution A.81(IV) of 27 September 1965. Although the main concern of chapter VII of SOLAS and the IMDG Code is safety, many substances listed can also cause pollution and in 1987, the IMDG Code was extended to cover pollution aspects. The IMDG Code is in fact used to implement the requirements of Annex III of MARPOL 73/78.

The IMDG Code sets out comprehensive recommendations for the transport of dangerous goods at sea concerning their classification, documentation, marking and labelling, packing and packaging, stowage and segregation, fire prevention and firefighting and other related subjects. The Code is published as a consolidated version in two loose-leaf volumes. Amendments are published regularly to keep pace with the technological developments of cargoes. A third volume contains additional information on subjects such as medical first-aid, safe use of pesticides in ships etc. IMDG code is published every two years with 2 volumes and additional information. Other existing formats can be ordered: for windows (Mac users will need to use a Windows emulator), for web, for intranet, for IMO bookshelf. A focus will be done on details to be given by specific persons in case of emergency situation.

In the Code, substances are grouped together under various class headings. Each class has an introduction giving general information on chemical properties, packing, stowage, segregation, fire-fighting and where appropriate specifications for the carriage of limited quantities. Each substance usually has an individual page (schedule) to itself and the information in each schedule includes the proper chemical (shipping) name and formula, the United Nations identification number, observed human health effects, chemical properties, packing, stowage and where applicable the explosive limits and flash point.

Gases carried as packaged dangerous goods on board ships have varied chemical properties and are transported under different conditions. They may be compressed, liquefied at ambient temperature under high pressure, dissolved under pressure in a solvent which is then absorbed in a porous material, or liquefied by refrigeration. They may be non-flammable, flammable, poisonous, corrosive, support combustion or be a combination of all or some of these. Some of the gases are lighter than air whilst others are heavier. The Code groups gases under Class 2.

For the purposes of stowage and segregation on board ships, Class 2 is further divided according to the hazards presented by gases during transport:

Class 2.1 - Flammable gases

Class 2.2 - Non-flammable gases

Class 2.3 - Poisonous (toxic) gases

To indicate more accurately the hazards presented by gases, the classification required by regulations 2 and 5 of chapter VII of SOLAS 1974, as amended, has to be supplemented by the additional description of the subclass.

*\*Code: Within the context of the IMO, a code contains detailed technical recommendations on a specific aspect of shipping for improving the safety of international maritime trading and the protection of environment.*

- **Fuel Gas or low-flashpoint fuels propulsion**

The IGF Code regulates ships fuelled by gases or other low-flashpoint fuels. This code aims to minimize the risk to the ship, its crew and the environment, having regard to the nature of the fuels involved.

The goal of the Code is to provide criteria for the arrangement and installation of machinery for propulsion and auxiliary purposes, using natural gas as fuel, which will have an equivalent level of integrity in terms of safety, reliability and dependability as that which can be achieved with a new and comparable conventional oil fuelled main and auxiliary machinery.

## 2. Gases products carried in bulk

**Gas carriers** are designed to **carry gases in liquid form in bulk**. The general arrangement of a gas carrier is similar to that of the conventional oil tanker in that the machinery and accommodation are aft whilst the cargo containment is spread over the rest of the ship to forward. However, the cargo containment and its incorporation into the hull of the vessel is very different due to the need to carry gaseous cargo under pressure or refrigerated or under a combination of both. There are thus, many features which are unique to gas carriers due to the basic requirement for pressurizing and cooling gases during transport.

Fundamental to these requirements is the material of construction of the cargo tanks. It is important to realise that tanks designed to carry pressurized substances have to be able to withstand the pressure exerted by the cargo at the highest temperature encountered by the vessel during its voyage.

### 2.1. Types of gas carriers

For tanks which carry bulk cargoes in refrigerated form at below ambient temperature, the design pressure of the tank depends on the degree of refrigeration of the cargo and the material used in the construction of the tanks would need sufficient ductility. If the cargo is refrigerated so that the tank can be operated at atmospheric pressure, there is no need to fulfil the requirements for a pressure tank. In this case, the cargo is said to be "fully refrigerated" and the temperature is maintained at or below the cargo's boiling point at atmospheric pressure. If the cargo is not fully refrigerated, it can still exert a significant vapour pressure and the tanks would need to be designed to take a relatively low temperature and withstand a certain degree of pressure.

Based on the different tank systems, gas carriers can be categorized as follows:

- **fully pressurized vessels:** these are the most basic type of gas carriers and are the simplest of all gas carriers in terms of containment systems and cargo-handling equipment; cargo is carried in pressure tanks designed to withstand working pressure of 15-17 bars (a few ships can accept up to 20 bars); the tanks are normally cylindrical although some ships have spherical tanks or vertically mounted cylinders or a combination of both, ships carry two to six tanks which are arranged below or partly below deck, some might have more tanks; because of their working pressure, the tank weights are high; these vessels tend to be small with cargo capacities rarely exceeding 2000 m<sup>3</sup> ; typical cargoes carried are LPG or ammonia in the shortsea or nearsea trade; an illustration of this type of carrier is shown in **Figure 15**;



Fully Pressurized LPG Carrier 7,000 cbm

**Figure 15.** An example of a fully pressurized LPG carrier.

- **semi-pressurized vessels;** these usually have tapered cylindrical or lobed tanks suitable for carrying cargoes in the temperature range of approximately -33 °C to -50 °C at a pressure range of 4-7 bars; vessels tend to be reasonable large with a cargo carrying capacity of 12,000 m<sup>3</sup>; they usually have four to six cargo tanks arranged in two groups of two or three tanks, each group having a port and starboard tank found below deck and when a third is present, it is found above deck along the centre line; the outer surfaces of the tank are insulated and vapour given off ("boil off") which collects in the head space (ullage) of the tanks is withdrawn via a vapour line to a reliquefaction system which cools, compresses and condenses the vapour which is then returned via a return line to the tanks; typical cargoes carried are LPG and other chemical feedstocks such as ammonia, butadiene, propylene and vinyl chloride; an illustration of this type of carrier is shown in **Figure 16**;



***Figure 16. An example of a semi-pressurized LPG/NH<sub>3</sub> carrier.***

- **fully refrigerated LPG vessels:** these are generally designed to transport large quantities of LPG at atmospheric pressure and at temperatures as low as -47 °C and -55 °C depending on the ethane content of the LPG; they may be equipped to carry ammonia; four different cargo containment design systems have been used in these vessels although the prismatic free-standing unit is the most common type of tank used; because of the low temperature carriage conditions, thermal insulation and reliquefaction equipment are fitted; there are normally between three and six cargo tanks extending almost the full beam of the ship; the cargo capacity is usually 5,000 m<sup>3</sup> to 100,000 m<sup>3</sup> so the ships can be quite large; an illustration of this type of carrier is shown in **Figure 17**;



***Figure 17. An example of a fully refrigerated LPG carrier.***

- **ethylene ships:** these are built for specific trades; the cargo is carried fully refrigerated at  $-104\text{ }^{\circ}\text{C}$  and at about atmospheric pressure; insulation and reliquefaction equipment is fitted; the cargo tanks used are independent; the ships tend to be highly specialized having cargo capacities in the range of  $1,000$  to  $12,000\text{ m}^3$ ; they are often equipped to carry LPG cargoes; an illustration of this type of carrier is shown in **Figure 18**;



**Figure 18.** An example of a semi-pressurized/fully refrigerated ethylene/LPG carrier.

- **LNG ships:** these are built to transport large volumes of LNG and are normally dedicated to a specific project where they will remain for their entire contract life; the cargo is carried fully refrigerated at  $-162\text{ }^{\circ}\text{C}$ , at about atmospheric pressure; insulation is fitted but no reliquefaction equipment is fitted since "boil-off" gas is either vented to the atmosphere or used as propulsion fuel in the boilers; the ships are large having cargo capacities between  $40,000\text{ m}^3$  to  $135,000\text{ m}^3$  with four to six cargo tanks of either the self-supporting or membrane type; an illustration of this type of carrier is shown in **Figure 19**.



**Figure 19 (Copyright Cedre).** Overall view of a LNG carrier (Spherical type on the left, prismatic type on the right).

The two type of structure have some advantages and disadvantages presented in **Table 3**:

Type of tank	Spherical tank	Membrane system
Main advantages	The void space between the hull and tanks is monitored for the presence of methane for leak detection but also serves to provide access to the tank exterior (and hull interior) for inspection and repair, providing a greater sense of integrity. In the event of major damage, individual tanks can be replaced. Due to the separation between the tank and hull, the tanks have a measure of protection in the event of a collision or grounding.	Low main deck profile reduces the windage area and allows topside equipment to be installed.
Main disadvantages	The spherical geometry leads to higher tank heights with increased wind loading.	The membrane system is apparently vulnerable to LNG sloshing induced damage. As the main load-bearing component is the hull itself, it is theoretically possible for the high-impact pressures induced by sloshing to locally damage the insulation or even breach the containment barrier. To mitigate this, the membrane tanks incorporate corner chamfers and most class societies require that the cargo level be either above 70% or below 10%. Not having a void space between the tanks and the hull, inspection, and maintenance are inhibited.

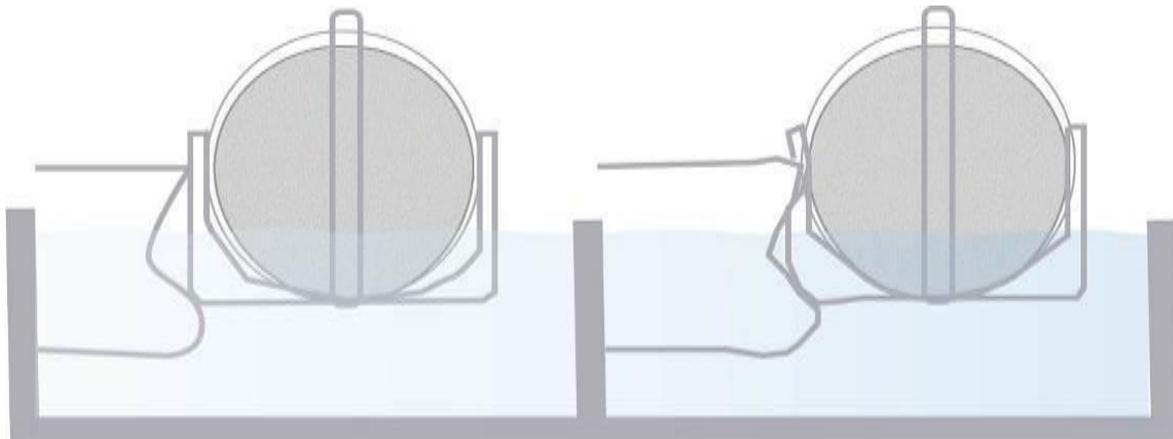
**Table 3. Main advantages and disadvantages of LNG carriers structures.**

## 2.2. International regulations governing the carriage at sea of gaseous products in bulk

For the construction and equipment of vessels transporting gases in bulk, gas carriers must comply with the standards of the various gas codes of IMO i.e. the *Code for Existing Ships Carrying Liquefied Gases in Bulk* for ships built before October 1976; the *Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk* for ships built after October 1976 but before July 1986 and the *International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk*, for ships built after June 1986. The first two codes are known as the IMO Gas Codes whilst the last is known with the short title of the *International Gas Carrier (IGC) Code*. The IGC Code has been incorporated into the 1974 Safety of Life at Sea International Convention (SOLAS) as well as MARPOL 73/78.

Although it is beyond the scope of this short section to examine in details the contents of the Codes, it is worth noting that the object of the codes is to recommend suitable design criteria, construction standards and other safety measures (e.g. fire protection, ventilation) for ships transporting liquefied gases in bulk and certain other substances listed in the Codes so as to minimize, as far as is technologically possible, the risk to the gas ship, to its crew and to the environment.

The possibility of a gas carrier experiencing an incident does exist (see Introduction, **Table 1**). This could lead to cargo tank damage and an uncontrolled release of the product resulting in evaporation and dispersion of the product and in some cases brittle fracture of the ship's hull. One of the basic aims of the Codes is that a ship built to the construction requirements of the Codes should be able to survive the normal effects of flooding following assumed hull damage caused by some external force, to protect the cargo tanks from penetration damage caused by minor incidents such as ramming a jetty, tug or some other hard object and to give a measure of protection to the ship from major damage caused by incidents such as collisions and groundings (see **Figure 20**). To this end, the construction and compartmentation of all gas carriers offer substantial protection of the cargo containment so that penetration damage is not transmitted to the cargo containment system.

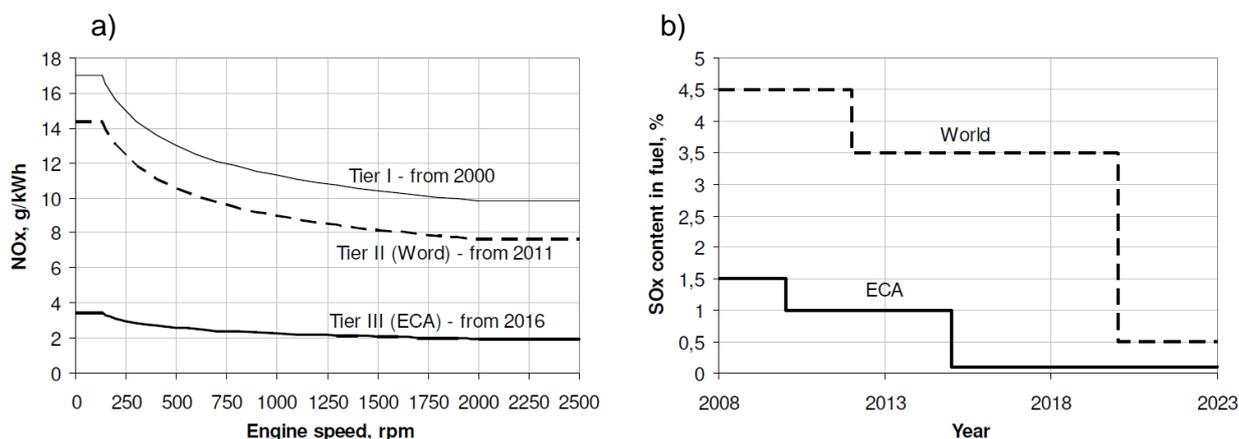


**Figure 20** (Copyright Cedre). One of the objectives of the Codes is to ensure substantial protection against accidental damage.

### 3. Propulsion systems and equipment

#### 3.1. Gas propulsion systems

The IMO introduced Annex VI of the International MARPOL Convention to regulate and to limit the main air pollutants contained in ships' exhaust gas, in particular Nitrous Oxides (NO<sub>x</sub>), Sulphur Oxides (SO<sub>x</sub>) and Particulate Matter (PM). Revision of Annex VI in 2008 established the emissions limit values and the Emissions Control Areas (ECAs) covering waters up to 200 nautical miles from the coast of the US and Canada, the US Caribbean Sea area, the Baltic Sea, the North Sea, and the English Channel where the pollution emission of SO<sub>x</sub> is much more restricted than in other nautical areas. The future extension of the ECA to the Mediterranean Sea as well as to sea coasts along Norway, Mexico, Japan and Singapore is under consideration.



**Figure 21. a) NOx emission and b) SOx content in fuel limits for ships in acc. with MARPOL Annex VI.**

To fulfil these regulatory requirements, a prospective alternative is found in natural gas. LNG bunkering offers several advantages as its gas exhaust contain 25% lower CO<sub>2</sub> and 85% lower NOx emission values than the Marine Diesel Oil or Marine Gas Oil, and it also contains no SOx or PMs. The main features of the type of engine are presented in **Table 4**:

Type of engine		Main features
Gas-Diesel dual fuel		Two types of engines can be found, high-pressure, Diesel cycle type and low-pressure, Otto cycle type. High-pressure engines require the supplying gas pressure to be as high as 250-300 bars while low-pressure engines need 5-7 bars only
Fuel gas systems LNG tank types, integral with the hull structure		Such tanks are non-self-supporting and consist exclusively of a thin layer (membrane) supported through insulation by the adjacent hull structure. Thanks to their adjustability to hull shape, the ship's hull volume fulfilment is very effective and can contain from 100 to 20,000 m <sup>3</sup> . Their Maximum Allowable Working Pressure (MAWP) is normally lower than 0.25 bar g but can increase to 0.7 bar g.
Fuel gas systems LNG tank types, independent of the hull structure	A-type tank	Equipped with a full secondary barrier which is capable of collecting the leaking gas and transferring the gas vapor to a controlled area. Comparable to the membrane tanks (integral), the hull volume fulfilment effectiveness is slightly lower. MAWP 0.25-0.7 bar g.
	B-type tank	Similar design in comparison with A-type tanks the use of model tests, analytical tools and methods of analyses to determine stress levels, fatigue life, and crack propagation characteristics. Therefore, only a partial secondary barrier, in the form of a drip tray to protect the hull structure against low temperatures, is required.
	C-type tank	Considered to be pressure vessels (MAWP > 0.7 bar g). The shape of C-type tanks is often cylindrical and has a presently limited volume (500-600 m <sup>3</sup> ) but capacities up to 2,000 m <sup>3</sup> are under consideration. C-type tanks can equip new ships and also used for upgrading existing ships with fuel gas systems.

**Table 4. Different types of engines and main feature of gas propulsion systems.**

## 3.2. Other equipment onboard

Few other systems are generally present on the carrier and that, in case of incident, could represent a risk for responders or for the environment: electrical equipment, storage facilities of chemicals, etc. Such information could be used for risk assessment.

Among all equipment present onboard, it is deemed important to mention inert gases (e.g. carbon dioxide) systems. They can concern two aspects:

- Inert gas generator: it generates a gas or mixture of gases in such a way that oxygen content of the atmosphere ensures non-flammable conditions, i.e. combustion cannot continue. Such gases can be used for inerting or freeing of cargo tanks, cargo pipes and void spaces. This system can be used during transport or prior to and after a refit or inspection period.

- Fire-extinguishing system with release. Such system is triggered automatically or manually and one should consider risk associated with inerting gas.

For all systems involving inert gas, it is essential to scrupulously respect the established procedures, for both personnel and responders, because the risks of asphyxia and anoxia are reached very rapidly without precursory sign (invisible gas, no odour).

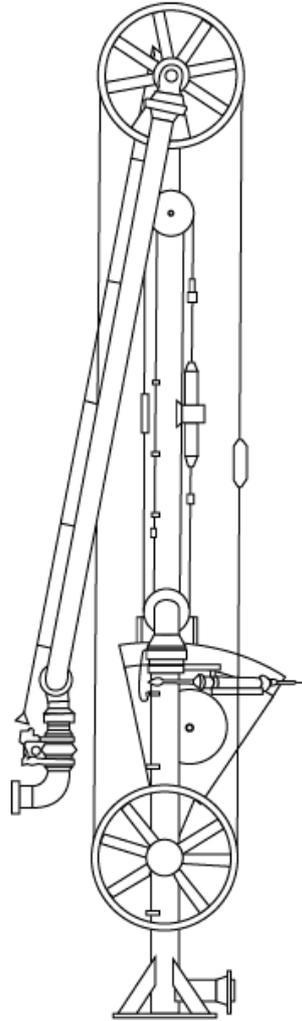
## 4. Loading/unloading operations

### 4.1. Cargo

To load cargo in an efficient and safe manner, some important criteria must be considered in terms of efficiency but also safety.

- Operational concerns

Flow rate of hoses or loading arm can determine the delay to fill cargo and present an economic interest. The dimensions of a hose and its capacity to move or to be supported in a hose cradle have a great importance to load different types and sizes of ships. The main reason for using loading arms is their flexibility accommodating any movement in all directions of the vessel during loading or discharging operations, especially for tidal variation. It should be noticed that two arms can be used, for loading and one for vapour return. Moreover, due to dimensions and safety reasons they are remotely operated with hydraulic systems. An example is shown in **Figure 22**:



***Figure 22. Example of gas carrier loading arm.***

Offloading LNG is a new challenge to be met, with more drastic specifications compared to loading onshore. Different types of structures may be concerned, mainly between floating units such as Floating Production Storage and Offloading (FPSO) or Floating Storage Regasification Unit (FSRU). As the duration of a cargo transfer may last several hours or even tens of hours, offloading system must remain efficient and safe all along cargo transfer operation. To this purpose, structures should be designed to endure harsh environments, e.g. steep waves, and as a result a wider mooring envelop for offloading operations.

Quick Connect/Disconnect Connection (QCDC) facilitates connection between the loading arm with the corresponding vessel manifold. A hydraulic remoted system operated by qualified personnel is a guarantee for an efficient offloading connection.

Different configurations can be used for offloading from a Floating LNG unit (FLNG) to a LNG carrier, such as tandem (**Figure 23**) or side-by-side (**Figure 24**).

Tandem offloading configuration is designed to operate in harsh environment, with the help of a dynamic positioning system. The separation distance between the two vessels allows, both during connection and loading, to continue operations at significant wave heights of up to about 5 meters. In the case of stern-to-bow configuration a dedicated fleet of LNG carrier with bow loading system is required.



**Figure 23 (Copyright Cedre). Tandem LNG offloading system. Reel (orange) holding flexible hoses for transfer operation).**

Despite requirement of relatively calm/mid environment for offloading, side-by-side seems to be the most considered method.



**Figure 24. Side-by-side LNG offloading system.**

- Safety concerns

Rubber or composite hoses can be used for LPG as soon as the material are compatible with the product transferred and in compliance with the local standards. LNG hoses are of special low temperature alloy which has a very good thermal expansion and contraction properties, or preferentially of composite type. The hydraulic system is connected with an Emergency Release System, automatically triggered during the emergency situation to disconnect the loading arm from the ship. Dry break system has a valve on each side of the release point to minimise spillage.

The Emergency Release System (ERS), initiated to disconnect rapidly loading arm from the ship and minimize gas release, can be triggered in the following ways:

- Automatically, when the arm reaches the specified limit; alarms usually sound;
- Manually, from the central control panel ashore;
- Manually, using hydraulic valves in the event of loss of electrical power supply ashore.

Flange generally have swivel joint, one at the top and other at the bottom. The loading arms are equipped with strainers to protect against debris picked up in any piping and the loading arms. Due to a risk of electrical arcing at the manifold during connection and disconnection of the shore hose or loading arm, cargo hose strings and metal arms are fitted with an insulating flange. With flexible hose strings, one length only of non-conducting hose without internal bonding, insertion of such a resistance completely blocks the flow of stray current and the whole system remains earthed, either to the tanker or to the shore. In addition to all these equipment, frequent inspections are performed to test integrity of material, pressure resistance, elongation of hose, electrical continuity and every important element.

In the case of offshore terminals, a steel guide cable is kept under tension during loading operation (red cable in **Figure 23 and 24**) to maintain a proper mooring envelop. However, once emergency disconnection has been activated, the loading arm is automatically retracted to avoid any risk of interference with the manifold and surrounding area.

## 4.2. Loading bunkering fuel

Different modes can be used to deliver LNG fuel, as presented in **Table 5**:

Mode of LNG bunkering	Description	Advantage	Disadvantage
<b>Truck-To-Ship (TTS)</b>	The LNG truck is connected via a flexible hose to the ship present on the quayside.	<ul style="list-style-type: none"> <li>- Good provisional solution as it requires relatively low investment costs</li> <li>- Operational Flexibility, with bunkering possible in different locations within the same port, serving different ships in different conditions (possibility to adjust delivered volumes),</li> <li>- Possibility to adapt to different safety requirements.</li> </ul>	<ul style="list-style-type: none"> <li>- Operation highly dependent on the transfer capacity of the truck (volume and flow),</li> <li>- Small to moderate demand for LNG,</li> <li>- Significant impact on other operations involving passengers and/or cargo,</li> <li>- Limited movement on the quay-side, mostly influenced by the presence of the bunker truck(s),</li> <li>- Exposure to roadside eventual limitations (permitting, physical limitations, traffic related, etc.).</li> </ul>
<b>Ship-To-Ship (STS)</b>	The receiving vessels are fed by another ship, boat or barge, moored alongside on the opposite side to the quay. LNG delivery hose is handled by the bunker.	<ul style="list-style-type: none"> <li>- Ability to use maritime vessels and barges,</li> <li>- Possibility of bunkering in port and at sea,</li> <li>- Possibility of bunkering in the port during loading /unloading,</li> <li>- Interesting option for ships with a short port turnaround time.</li> </ul>	<ul style="list-style-type: none"> <li>- Dependent on vessel traffic,</li> <li>- Dependent on weather conditions,</li> <li>- The need to equip the port of fenders and mooring lines for bunkering,</li> <li>- Limited ability for transshipments and storage, limited by the parameters of the vessel.</li> </ul>
<b>Terminal (port)-to-ship (PTS);</b>	LNG is either bunkered directly from a small storage unit (LNG tank) of LNG fuel, small station, or from an import or export terminal.	<ul style="list-style-type: none"> <li>- Good option for ports with stable, long-term bunkering demand,</li> <li>- Possibility of bunkering at the quay or jetty,</li> <li>- Bunkering using cryogenic wire, or re-loading arm,</li> <li>- The possibility of bunkering other means of transport.</li> </ul>	<ul style="list-style-type: none"> <li>- Time and costs (switch loading arm and cryogenic cables).</li> </ul>

<p><b>ISO container-to-ship</b></p>	<p>Pressurized storage tanks contained within and ISO frame that allows the LNG to be transported through the wider logistical chain.  ISO 20 feet: 20,5m<sup>3</sup>, ISO 40 feet: 43,5m<sup>3</sup>.  NB: ISO containers that are embarked for plug-in, onboard LNG fuelled ships, are not covered as they are covered by the IGF Code.</p>	<p>- Flexible,  - Modularity and convenience of ISO standardized LNG fuel containers.</p>	<p>- If the tank is not in Cold condition, i.e. Boil Off Gas (BOG) temperature &lt;120°C, filling with new LNG will generate excessive BOG.</p>
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***Table 5. Different modes, that can be used to deliver LNG fuel, with corresponding description, advantages and disadvantages.***

## **CHAPTER 3. Risk and response to an accidental gaseous release**

Within the context of a maritime emergency, risk can be defined as a characteristic or action wherein a number of adverse outcomes are possible, yet the particular outcome that will occur and the chain of events leading to the outcome cannot be determined precisely. Thus, In addition to understanding the way gaseous products are carried at sea, the background against which preparing for and responding to an accidental release of a gaseous product takes place, is a consideration of the pattern of events describing hypothetical but credible accident scenarios as well as a hazard evaluation of the product.

### **1. Accident scenarios**

The objectives of such an exercise would be to assist decision-makers involved in preparedness activities appreciate the possible chain of events leading to such releases and the detrimental effects associated with such events as well as the response measures that might be taken. The following summarizes some of these events.

#### **1.1. Packages gaseous dangerous goods**

With packaged gaseous dangerous goods, two scenarios will be described, both of which will assume that the gases released do not take place in circumstances which would change the internal and/or external temperature of the container such as in the case of a fire.

##### **1.1.1. Scenario No. 1 – compressed gases**

Gases which are compressed to high pressure and are contained in a portable tank such as a gas cylinder but which have not been liquefied will vent at high velocity from a puncture or from any other similar small opening. At some stage, the pressure within the portable tank will drop to the external atmospheric pressure and the intense venting will either cease or subside to a rate proportionate with the amount of heat that enters the portable tank from the external surroundings.

##### **1.1.2. Scenario No. 2 – compressed liquefied gases**

Gases carried as compressed liquefied gases would typically be in pressurized portable tanks designed to withstand a certain amount of pressure and what may happen will very much depend on the location of the puncture or damage:

- i. If the puncture occurs in the head space (ullage) above the liquid, the gas will vent at high velocity, possibly creating some liquid droplets in the process; as the temperature increases and reaches the boiling point of the cryogenic liquid, the liquid turns into vapour picking up heat from the surroundings which provides the latent heat needed to change the liquid into vapour (change of state); the portable tank can become quite cold and even frost around the area of the puncture due to this "thermodynamic cooling"; although the velocity of the venting might drop, it may still continue so that eventually no more material remains in the portable tank;

- ii. If the puncture occurs below the liquid, the liquid may jet from the opening due to the pressure in the head space above the liquid which forces the liquid out, large amounts of liquid may flash into vapour due to the warmer temperatures found on the exterior; this might result in the formation of a mist/aerosol (vapour mixed with small liquid droplets); if the cryogenic liquid has the chance to reach a surface, it will have a tendency to form a rapidly evaporating liquid pool and, as in the previous case, pick up heat from the surroundings to evaporate, possibly causing brittle fracture of the material it has come in contact with, if the material is not designed to withstand low temperatures;

## **1.2. Gaseous products in bulk**

With gaseous products carried in bulk, describing accidents scenarios is more complicated than for packaged dangerous goods since any scenario would need to incorporate all aspects of the marine casualty and not treat the cargo containment as an entity separate from the rest of the vessel.

### **1.2.1. Scenario No. 1 – collision**

A high energy collision could lead to cargo tank damage, resulting in an uncontrolled release of the product. The pattern of events following a collision will depend upon on a number of factors:

- type and size of ships;
- speed of colliding vessels;
- locations of the penetrations of hull and cargo containment in relation to water line;
- geometry of rupture;
- pressure of a double side shell;
- presence in the cargo tank;
- angle of impact;

For example, penetrations above the water line in a double-hulled vessel, e.g. a LNG carrier, will subject those parts of the ship's structure which come into contact with the cold cargo to brittle fracture. Contact of the cold cargo liquid with the warmer ship structure will result in rapid vaporization. Any adjacent enclosed space receiving cargo vapour might inhibit further significant leakage due to the resultant build-up of back pressure from the vapour within the space. Assuming there is no propagation of the rupture of the hull to below the water line, liquid cargo may not escape to the sea. Cargo which does escape to the sea may spread, vaporize and dissolve, depending on its properties. A prolonged vapour release from the breached cargo tank might also occur.

Penetrations below the water line will probably result in an initial outflow of cargo until sea water and cargo heads balance, followed by alternating inflow/outflow of water/cargo respectively in the breached tank and eventually all the cargo in the tank would be lost.

A possible consequence of collisions and the associated release of cargo is ignition. A gas carrier or parts of it may be engulfed with gas vapour on impact due to the rapid vaporization of the escaping liquefied gas. If ignition does not occur on impact, the vaporization of cargo released by the impact may still maintain suitable conditions of flammability in the vicinity of the casualty although this threat could be offset for a very short time by the over-rich concentration of gas. In conditions of possible flammability, it is not only the gas carrier which has suffered the impact which is at risk but also the impacting vessel may be a likely source of ignition if the vapour cloud moves in its direction.

### **1.2.2. Scenario No. 2 – grounding**

The double bottom construction found in the majority of gas carriers provides protection in the event of grounding. However grounding could result in build-up of water within certain enclosed spaces. If penetration through the hull leads to a major rupture of the cargo tank, there would be an initial outflow of cargo to the sea until a balance of heads (cargo/water) is achieved. Ice and vapour formation would also take place.

### **1.2.3. Scenario No. 3 – ramming**

This scenario covers situations arising from gas carriers involved in low-energy impacts e.g. striking a structure on the dockside or a fixed navigational aid, e.g. beacon.

It would be accepted that a gas carrier striking a navigational beacon would do so at relatively high speed. On the other hand, the damage that may be sustained by the vessel would probably be superficial and it is unlikely to result in cargo loss directly. However, striking such objects may cause damage to the rudder or propellers resulting in some loss in steering capabilities giving rise to possible grounding or collision possibility.

Berthing incidents are not likely to give rise to loss of integrity of the cargo containment, since the energy of impact is usually too low to result in enough damage to cause tank rupture. However these minor incidents may cause damage to deck pipework and valves which, whilst not causing immediate loss of cargo, could give rise to losses during cargo discharge. Furthermore any leakage of gas may tend to lie around the decks since many of the vapours originating from liquefied cargoes are heavier than air. These may enter doors and other openings near the cargo deck and may be drawn into machinery spaces and air intakes.

### **1.2.4. Scenario No. 4 – fire on board a gas carrier**

Fires in machinery or accommodation spaces are unlikely to spread to the cargo area because of the totally closed and oxygen-free nature of a gas carrier's cargo system.

Fire or explosion in a compressor house, situated as it usually is on deck within the cargo area could result in damage to adjacent tank domes and connecting gas lines and to the ignition of gas which is released at the points of disruption.

### **1.2.5. Scenario No. 5 – spillage resulting from inadvertent disconnection piping failure or tank overflowing**

Unexpected meteorological conditions e.g. high winds or the effect of another vessel passing at excessive speed, by a gas carrier which is secured alongside a berth may put extra strain on the mooring lines and fenders to the extent of damaging or severing the transfer cargo lines. Although automatic emergency shutdown systems come into operation if the integrity of the cargo transfer lines is at risk, a small amount of liquefied gas may still be spilled before the supply is shut off. In these circumstances, the liquid may find its way overboard and form a pool on the sea surface between the ship and the berth. If the ship is lying alongside an open-piled jetty, then the spacing between the piles will offer no containment for the pool. If on the other hand, the jetty is a continuous wall, the pool may be confined between the jetty wall and the ship's side. If fenders are spaced at the water level along the ship's side, they will have a "booming effect" on the pool (see **Figure 25**). If ignition takes place, and assuming rapid shutdown of the transfer operation has taken place, the fire could be quite intense but should be short-lived.



***Figure 25 (Copyright Cedre). Illustration showing possible booming effect “of fixed fender system positioned alongside a ship's hull.***

Tank overfilling or piping failure (incl. failures of joints, seals etc.) may result in spillage on deck. Consequences may be minor if the leakage is detected quickly and corrective action taken immediately. Yet brittle cracking of adjacent steel structures and an accumulation of liquefied gas in void spaces with subsequent vaporization could still result.

In either case, spillage of toxic cargo will result in health hazards to personnel in the immediate areas.

### **1.3. Gaseous products in pipeline**

Accidents and associated impacts involving a pipeline leak or total rupture depend on many factors such as:

- Type of pipeline: aerial/subsea,
- Transport operating conditions: temperature, pressure,
- Nature of the gas,
- Origin of accident: gas pipeline wear, defects, metal fatigue, collision, etc.

It can be noticed that pipelines operating at low temperature may present a high risk, especially if they belong to industrial facilities, especially export/import units with liquefaction/regasification processes. In the case of subsea release near offshore units, blowout, leading to the formation of a plume of gas bubbles may lead to the loss of buoyancy of installations.

Possible consequences of a pipeline accident are the formation of cloud at risk at sea surface with potential vapor cloud explosion, flash fire and pool fire.

## 2. Hazards from spilled gases

In general terms, harm can be defined as injury or damage caused following exposure to the hazards of an accidental release of a product. The hazards faced by response pressure following exposure to an accidental release of a gaseous material could be due to:

- flammability;
- toxicity;
- reactivity;
- corrosively;
- cold burns;
- a combination of the different hazardous properties.

### 2.1. Detection of gas in the atmosphere

It is essential that first responders could assess rapidly potential risks and learn in real time without any knowledge of potential deadly hazards. Suitable instrumentation is thus systematically used by each responder to monitor concentration levels both for toxicity and explosive/inflammable. This is all the more important that they sometimes intervene without any knowledge of potential deadly hazards. In general, responders are equipped with a 4 gases sensor detecting the following risks:

- Anoxia/asphyxia with detection of oxygen ( $O_2$ ) concentration,
- Toxicity with detection of hydrogen sulphide ( $H_2S$ ), typically detected in oil and gas industry, and carbon monoxide (CO),
- Explosive atmosphere with Lower Explosive Limit based on the measurement of hydrocarbon gas as a percentage by volume of the total atmosphere being measured more risky gas potentially present.



***Figure 26 (Copyright SOBEGI). 4-gas sensor.***

Few different principles of detection are presented in **Table 6**:

Type of detection	Main features
<b>Flammable Gas Monitors (Explosimeters)</b>	Such sensor contains a poison resistant flammable pellistor as the sensing element. As pellistor rely on the presence of oxygen (minimum 11% by volume) they cannot operate efficiently for measuring hydrocarbon gas in inert atmospheres.
<b>Non-Catalytic Heated Filament Gas Indicators (Tanksopes)</b>	A non-catalytic hot filament is the sensitive element. The composition of the surrounding gas determines the rate of loss of heat from the filament, and hence its temperature and resistance.
<b>Interferometer (Refractive Index Meter)</b>	This type of sensor uses an optical device based on the difference between the refractive indices of the gas sample and air. The instrument is normally calibrated for a particular hydrocarbon gas mixture. As long as the use of the instrument is restricted to the calibration gas mixture, it provides accurate measurements of gas concentrations.
<b>Infra-red (IR) Instruments</b>	From a measurement based on infra-red radiation, the sensor indicates the concentration of hydrocarbons in the atmosphere.
<b>Chemical Indicator Tubes</b>	Each single-use tube allows measurement at very low concentrations of toxic gases onboard tankers, provided that no interfering gas is present.
<b>Electrochemical Sensors</b>	measure the concentration of a target gas by oxidizing or reducing it at an electrode and measuring the resulting current. Some interfering gases may modify accuracy.

***Table 6. Few examples of different principles of detection and main features.***

## 2.2. PPE for responders

Suitable equipment is required for responders to intervene in safe conditions. Depending on risk assessment and environment, the equipment required can be different, mostly depending on the route of penetration in human body, and must be properly selected to keep both mobility and sufficient protection. An example of PPE set equipment is shown in **Figure 27**.

- Respiratory equipment:
  - Facepieces,
  - Air pressure in facepieces,
  - Respirators,
  - Air-purifying respirators,
  - Atmosphere-supplying respirators,
  - Protection factors of respiratory equipment,
  - Common problems encountered when wearing respiratory equipment,
  - Maintenance and storage.
- Non-respiratory equipment:
  - Head and facial protection,
  - Hand protection,

- Foot protection,
- Body protection.

Any personnel who use protective equipment should be familiar with both its use and its limitations. A dedicated guideline, created by REMPEC and entitled Personal Protection Equipment and Monitoring Devices for Maritime Chemical Emergencies, can be consulted for further information.



***Figure 27 (Copyright Cedre). Example of PPE during phase of decontamination.***

### 2.3. Response equipment

Suitable response tactics and equipment must be deployed in case of gaseous release from marine incident. Some examples are presented below.

- Closure tightening of a valve or flange.
- Water curtain: one or several water curtains can be deployed to create a barrier and stop or mitigate diffusion of a toxic or explosive gas towards a sensitive area or target. This type of response can also be used preventively to mitigate radiation in case of fire.
- Fan: this type of equipment can be used to expulse gas from a confined area or dilute a gas located in a sensitive area.

*Practical guide for marine chemical spills* is a relevant guideline developed by REMPEC.

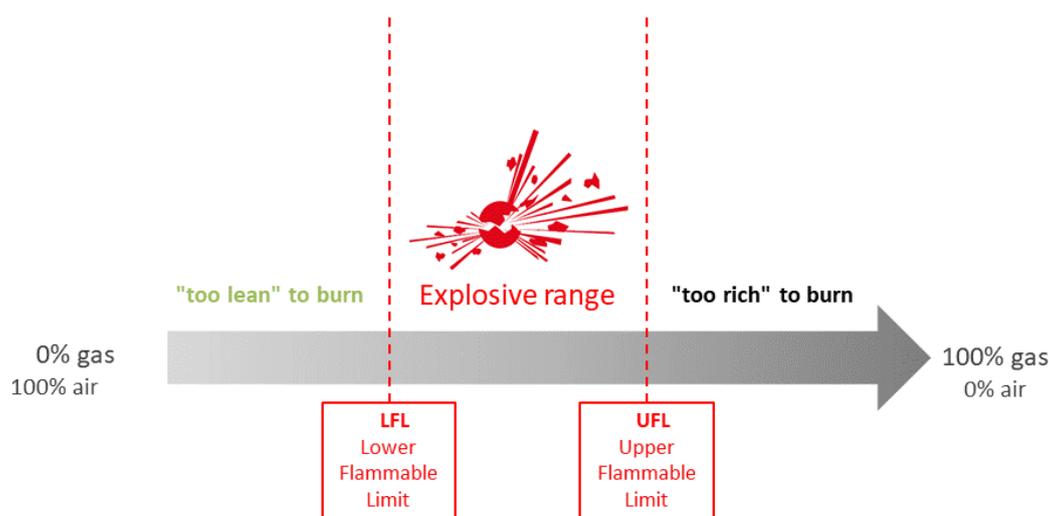
### 2.4. Fire hazards of spilled gases

A spill involving a gaseous product may pose fire hazards. The ease with which a gas will ignite, either spontaneously from exposure to high temperature or from exposure to a spark or open flame is termed the **flammability potential of the gas (Figure 28)**.

Some common measures quoted from the scientific and technical literature which can assist a responder in evaluating the flammability potential of a gas are:

- the **flash point** which is the lowest temperature of the material at which it will ignite and burn when exposed to an ignition source without self-sustaining combustion;
- the **fire point** which is the lowest temperature at which a substance, when once ignited will continue to burn without any additional source of heat (temperatures are available for a relatively few materials in the literature);
- the **flammable range or limit** which gives a measure of the ratio of flammable gas (or vapour) to air necessary for combustion; it is the difference between the upper and lower flammable (or explosive) limits; the lower flammable (or explosive) limit (LFL or LEL) is the minimum concentration of a gas in air that will ignite and propagate a flame and is usually expressed as a percentage by volume of gas in air whilst the upper flammable (or explosion) limit (UFL or UEL) is the maximum concentration of a gas in air that will ignite or propagate a flame. If the gas-to-air mixture is below the LFL, it is described as being "too lean" to burn and if it is above the UFL, it is "too rich" to burn; when the gas-to-air ratio is somewhere between the LFL and UFL, fires and explosions can occur and the mixture is said to be in the flammable range (see **Figure 2**).

*The words "flammable" and "explosion" are used interchangeably here; the reasoning behind this is that the concentration of a gas that will burn in air can also be expected to explode given the right conditions in particular when the products of gas combustion including the heat produced, are not removed from the reaction zone.*



**Figure 28. Flammable range set up from a liquefied gas spill.**

- the **autoignition temperature**: which is the ignition temperature required to cause self-sustained combustion in the absence of any source of ignition.(e.g. flame or spark).

Flammable properties of some gases which are commonly transported are shown in **Annex 2**.

#### **2.4.1. Types of fire**

Some of the types of fires associated with gaseous (or vapour) releases are:

- **flame jets** which can form when liberated gas (or vapour) encounters an ignition source whilst discharging or venting at high speeds entraining and mixing with air in the process;
- **fire balls** which can form following a Boiling Liquid Expanding Vapour Explosion (BLEVE);
- **vapour cloud fires** which can form when a cloud or plume of flammable gas (or vapour) contacts an ignition source at a point at which the gas (or vapour) concentration is within the flammable range; the fire may flash back to the spill source engulfing anything and everything in its path.

#### 2.4.2. Sources of ignition

Following an airborne release or likely release of a gaseous flammable product, it is essential to control all sources of ignition during the response since the occurrence of these sources whilst unexpected, their potential hazard is often underestimated. Sources of ignition could include:

- smoking including the use of cigarette lighters and matches;
- flash lights;
- safety tools which although may be "non-sparking" may have fragments of metal embedded in their heads;
- generators of static electricity such as helicopters used to transport response personnel to and from the stricken vessel;
- personal clothing such as shoes with metal cleats.

#### 2.4.3. Hazards from the products of combustion

A fire is but one of the products of the chemical reaction initiated between a flammable gas and oxygen (from the air). This chemical reaction is also known as "combustion". There are three major products of combustion, all of which are produced in varying degrees. These are:

- flame and heat which give rise to thermal radiation causing burns of different intensity, i.e. first-degree burns affect the outer layer of the skin, second-degree burns cause blistering and penetrate further into the skin, third-degree burns penetrate even further and damage nerve endings;
- smoke which consists of airborne particulate material, mostly of a carbonaceous nature, which results from the incomplete combustion of material and causes irritation to eyes and lungs and even death;
- fire gases which are the products of combustion and the resulting chemical rearrangements produced by the fire; invariably they will consist of carbon dioxide and, depending on the amount of available oxygen, carbon monoxide; irritating, corrosive and toxic products, such as hydrogen chloride and phosgene may be generated depending on the chemical composition of the material.

## 2.5. Toxic hazards from spilled gases

**Toxicity** can be defined as the property of a substance to cause damage to living tissue, impair the function of the central nervous system, cause severe illness or even death when inhaled, ingested, injected or absorbed by the skin. It is also important to distinguish between **acute effects** of a substance which are those that occur immediately after exposure and **chronic effects** which are those that occur and remain apparent for some time after the exposure.

### 2.5.1. Factors affecting the toxicity potential

Undoubtedly, the release of a gaseous product can pose toxicological threats and the immediate concern during an airborne gaseous discharge should be the protection of human life and health. The toxic hazard posed by the released material will depend on:

- the amount spilled;
- the toxicological properties of the substance;
- the route of exposure;
- the duration of exposure;
- the life-stage of the exposed individual(s).

Two common routes of exposure following an airborne release of a gas (or vapour) are **inhalation** and **absorption**.

Inhalation of a toxic gas (or vapour) may:

- dull the sense of smell;
- cause dizziness;
- cause headaches;
- irritate the eyes;
- cause unconsciousness;
- cause internal damage to vital organs
- cause cessation of breathing;
- cause death.

Absorption of a toxic gas (or vapour) may:

- irritate the skin;
- cause blood poisoning;
- cause internal damage;
- cause death.

### 2.5.2. Exposure limits for airborne release

One of the key tasks in preparing for and responding to an emergency involving a gaseous release is to select the airborne concentration that can be tolerated by all exposed personnel, including people in the vicinity, since it is this "target" concentration that will determine the extent of the hazardous zone.

The Protective Action Criteria for Chemicals, named PACs dataset, is a hierarchy-based system of the three common public exposure guideline systems: **AEGLs**, **ERPGs**, and **TEELs**. The order of priority proposed by this method is as follows:

1. 60-minute AEGL values
2. ERPG values
3. TEEL values

It can be noted that a particular hazardous substance may have values in any—or all—of these systems.

The PACs dataset has a single set of values (PAC-1, PAC-2, and PAC-3) for each chemical, but the source of those values can vary. The PACs dataset is created by the TEEL developers (Department of Energy, Subcommittee on Consequence Assessment and Protective Actions).

It must be recognized that:

- any toxicological value is continually being revised and updated and the latest revision of these values should be consulted;
- the values provide "guideposts" for identifying exposure limits in an emergency situation and should not be regarded as sharp dividing lines between what is safe and what is a dangerous concentration;
- the application of any value to an emergency situation requires specialist interpretation and any advice should be taken following a formal and total review of the toxicity of the substance.

## 2.6. Cold and chemical burns

Two possible additional health hazards from contact with gases are cold and chemical burns.

Cold burns are very much related to the way a gas cargo is carried rather than to the inherent properties of the cargo and are caused as a result of the direct contact with an extremely cold liquid. The mechanism that applies to brittle fracture of a steel structure on board a ship following a spillage of a cryogenic liquid would also apply to the production of cold burns. In this case, heat from the skin is taken to provide the latent heat the cold liquid needs to be able to evaporate.

On the other hand chemical burns are related to the corrosivity of the gases (or vapour) which causes visible destruction or irreversible alteration in human skin tissue at the site of contact. Chemical burns can be caused by ammonia, bromine, chlorine, ethylene oxide and propylene oxide.

## 2.7. Reactivity hazards of spilled gases

**Reactivity** is the ability of a material to change chemically, either by combination, replacement or decomposition. Reactivity hazards involve the release of energy in quantities and at rates too high to be absorbed by the reacting system. This results in possible adverse consequences such as the generation of toxic gases, heat, rupture of cargo tanks with an

overflow of material, fire and explosion. In the case of a spilled gas some of the basic types of reaction which could give rise to potentially hazardous situation are:

- **reactions with water** or air: for example ammonia will dissolve rapidly and exothermically to produce ammonium hydroxide whilst if any cryogenic gas spills onto the sea, large quantities of vapour will be generated by the heating effect of the water which if flammable may ignite in the presence of an ignition source;
- **polymerization reactions**: for example Vinyl Chloride Monomer (VCM) has a strong tendency to polymerize (self-react) under certain conditions and is therefore carried with a phenol inhibitor;
- **reactions with other materials**: for example methane and propylene are considered reactive with mild steel which is a common material of construction on most ships.

## 2.8. Environmental exposure limits for release in water

Environmental risk assessment is a process of predicting whether there may be a risk of adverse effects on the environment caused by a chemical substance. This involves determining a predicted no-effect concentration (PNEC) and comparing it with some estimate of exposure concentration (PEC).

Risk assessment of environmental effect of the aquatic compartment can be determined from acute or chronic toxicity from three trophic levels represented by algae (primary producers), invertebrates (primary consumers) and fish (higher level consumers and predators). Among these values is LD50, LD stands for Lethal Dose, and corresponds to the amount of a material, given all at once, which causes the death of 50% (one half) of a group of test animals. The LD50 is one way to measure the short-term poisoning potential (acute toxicity) of a material.

Another value of interest is the bioconcentration factor (BCF) which is the ratio of the concentration of the chemical in the organism to its concentration in the ambient environment. It reflects the ability of an organism to accumulate a chemical from the ambient environment.

A useful source of information is the Revised Hazard Evaluation Procedure from GESAMP, the Joint Group of Experts on the Scientific Aspects of Marine Environment Protection.

## 3. Behaviour airborne release

Because of the high vapour pressure of gases and rapid vaporization of spilled liquefied gases, response organization will frequently have to deal with how the liberated gas (or vapour) will spread and what the resulting airborne concentrations will be in the downwind location. The following will refer to airborne gas releases but equally applies to vapours.

It must be noted that different modelling tools have been developed to assess the fate of some chemicals in the atmospheric and/or aquatic environment.

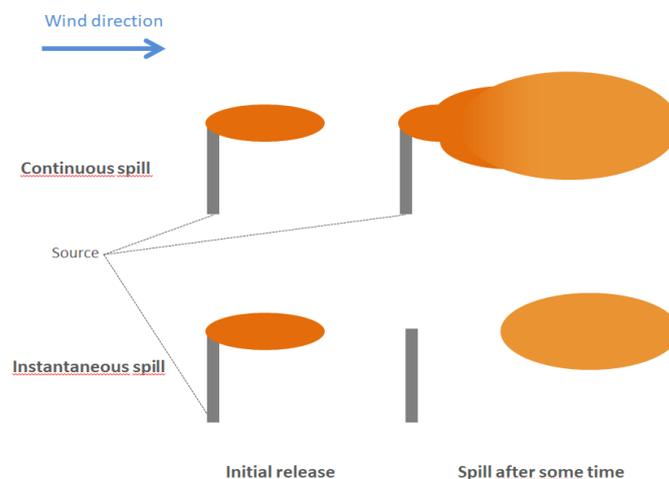
### 3.1. Types of gas dispersion

**Dispersion** is a term which incorporates advection (moving), diffusion (spreading) and mixture with air. An air borne release of gas will generally move in downwind direction and

spread in a crosswind (perpendicular to the wind) and vertical direction. Releases of gases into the atmosphere can be classified as:

- **instantaneous** which are those releases that take place over a short period of time and then stop; the result of such a type of release is a puff or a distinct cloud; as wind pushes the puff in the direction of the wind, air will begin to mix with the surface of the puff, thus diluting the surface concentration although the volume of the contaminated air space will become larger;
- **continuous** which are those releases which take place over a longer time and produce long stretched-out plumes; the results of such a type of release is that points downwind will eventually be exposed to a relatively constant airborne contaminant concentration for a period of time equal to the duration of the discharge as long as there is no shift in wind.

Illustrations of the two different types of gas dispersion are found in **Figure 29**.



**Figure 29 (Copyright Cedre). Illustration of plume (first row) and cloud formation (second row).**

Purely instantaneous or continuous spills do not readily occur in practice since many spills may be of too long duration to be characterized as truly instantaneous, yet too short in duration to establish a continuous plume. However this type of theoretical categorization enables simulated models to be developed which assist in assessing how a gas will be dispersed over time and therefore help a responder in determining the extent of the hazard zone affected by the gas.

## 3.2. Variables influencing atmospheric dispersion

Generally, a cloud or plume of a gas will drift in the direction of the prevailing wind, dispersing and becoming diluted as it mixes with the air, tending to broaden and becoming more diluted as it travels further.

There are a number of factors that influence the shape and size of a downwind zone affected by an airborne gaseous release. Although these variables will be discussed individually, several of them interact with each other so that the resultant hazard zone is a function of the combination of the different variables.

### 3.2.1. Effects of sources strength

In general larger release amounts or higher release rates will produce longer and larger downwind hazard zones. "Jet" momentum effects will also be experienced in the vicinity of a source if a gas is vented under high pressure. These effects become less significant as the gas moves away from the source.

### 3.2.2. Effects of fire

Thermal energy from a fire will cause a gas cloud or plume to rise. Furthermore a flammable gas, once released, will provide fuel for the fire and can itself be consumed in the process. This may result in a smaller overall hazard zone of the original released substance, especially if the fire is close to the source of release.

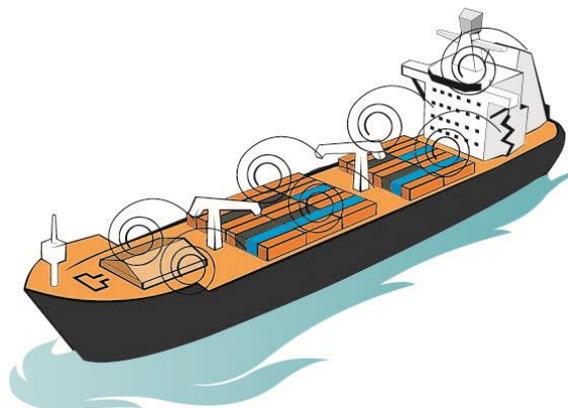
### 3.2.3. Effects of gas buoyancy

From a buoyancy perspective, gases can either be classified as lighter-than-air (e.g. LNG) or heavier-than-air (e.g. chlorine). Lighter-than-air gases, when released, will rise and mix with air. The rate at which a gas will rise as it moves downwind will, in part, be a function of the difference between the density of the gas and that of air as well as the prevailing wind speed. Strong winds tend to keep a lighter-than-air gas plume or a cloud closer to the ground for longer periods.

Heavier-than-air gases will have a tendency to initially collect at ground level. As the gas moves away from the point of discharge, it will become diluted as it mixes with air. As its density approaches that of air, it will begin to behave more like a neutrally buoyant gas. A gas that is lighter-than-air under normal ambient conditions, but is shipped as a cryogenic (low temperature) liquid, forms a heavy gas cloud on initial spillage because at the time of the release it is cold and therefore dense.

### 3.2.4. Effects of Terrain

Topographical features will influence the manner in which a gas will disperse. Topographical features are usually expressed as surface roughness. A rough surface causes more turbulence than a smooth surface promoting vertical mixing of gas. A rough surface tends to create obstacles thereby reducing the wind speed near the ground as is the case in an urban area near a port. Wind flowing around large obstacles will also create eddies and unstable wind-shifts which can influence the behaviour of gas release. This is of particular importance when air flows swiftly pass a ship's hull and its superstructure, swirling around the ship in the process (see **Figure 30**). The passing air causes a slight drop in pressure, drawing in currents of air (eddies) which can then drag the released gas onto the ship's deck.



**Figure 30 (Copyright Cedre). Formation of swirling currents (eddies) as air flows past a ship's superstructure.**

### 3.2.5. Effects of atmospheric stability

The time of day, cloud coverage, wind speeds, strength of sunlight determine the level of turbulence in the atmosphere and how a parcel of air will behave when it is displaced in the vertical direction. Unstable atmospheric conditions, characterized by strong sunlight and clear skies contribute to high levels of thermal turbulence in the atmosphere and promote rapid mixing. On the other hand, stable conditions characterized by light winds and night time cooling conditions contribute to low levels of thermal turbulence and would not promote mixing of the gas. When there is very little wind or when wind speed decreases, the wind direction may also become very inconsistent. The practical significance of this is that under low wind conditions, sudden shifts in wind direction may take place and the possibility exists that the gas cloud or plume may "hop" from one position or direction to another. At the other end of the scale, high wind speeds contribute to the generation of mechanical turbulence and hence rapid mixing. Thus, weather conditions will determine the direction of the plume or cloud and the amount of dilution in the plume as it moves downwind.

## 4. Response measures applicable to gaseous releases

Response measures are those actions which will minimize the risk to both life (including human health) and the environment in the early, critical stages of a spill or leak of gas. These actions could be directed to:

- the ship;
- the cargo;
- the released substance.

In responding to an emergency situation, any response action to be taken has to be evaluated on the basis of the circumstances of the particular incident and whether the action can be accomplished safely without detriment to those responding. The following paragraphs contain possible response options, giving an indication of what might be undertaken in the event of a gaseous release or likely gaseous release resulting from a maritime incident. These lists should not in any way be interpreted as a recipe to response operations for gaseous releases from accidents involving the transportation by sea in bulk or in package form of such products but should only act as guidance.

### 4.1. Response options – the vessel

The following is a list of response options focusing on the vessel.

THE VESSEL	
ACTION	MODE OF ACTION
Move (or tow) the ship	No. Towards the open sea No. Towards a safe anchorage No. Towards a safe haven No. To the prevailing wind direction, with accommodation upwind (if possible) No. Beach the ship
Extinguish fire	No. Use water spray No. Use high expansion foam No. Use dry chemicals No. Use high pressure CO2 gas

	No. Use sand
Reduce potential for fire	No. Eliminate ignition sources No. Eliminate heat sources No. Flood area of contact to cool hot metal (applicable mostly to collisions) No. Spray down deck/piping No. Spray down tanks
Scuttle the ship	
Instruct and warn approaching vessels as to safe approach and to remain upwind	
No direct action	No. Monitor the situation

#### 4.2. Response options – the cargo

The following is a list of response options focusing on the cargo.

THE CARGO	
ACTION	MODE OF ACTION
Move the cargo	No. Transfer cargo from damaged tanks No. Lighter the vessel (STS; STT) No. Remove containers/portable tanks
Stop the spill	No. Close valves No. Seal/plug the leaks/ruptures
Protect the cargo	No. Isolate damaged tanks No. Cool adjacent areas No. Add inert gas
Immobilize the cargo	No. Bury the containers/portable tanks, (capping) No. Anchor the containers/portable tanks
Release the cargo	No. Intentional jettison with mechanical air dilution No. Intentional jettison with water spray dispersion No. Controlled explosion of sunken containers No. Controlled flare-off
No direct action	No. Monitor the situation

#### 4.3. Response options – the released gas

The following is a list of response options focusing on the released gas.

THE RELEASED GAS	
ACTION	MODE OF ACTION
Chemical treatment	No. Use foam for vapour suppression No. Use water fog to knock down gas clouds using neutralizing agent to avoid pH overdosing, if necessary No. Make cloud visible
Restrict access to dangerous zone	
Evacuate non-response personnel from hazard zone	See Section 5
Shelter-in-place non-response personnel	See Section 5
Do nothing	No. Monitor the situation allowing the substance to evaporate and disperse naturally

## 5. Behaviour airborne release personnel (the civil protection)

There are essentially two ways to protect the civil population. One is evacuation and involves relocation of a threatened population to shelters in safer areas. The other involves giving people instructions to remain inside their homes or places of business until the danger passes (shelter-in-place).

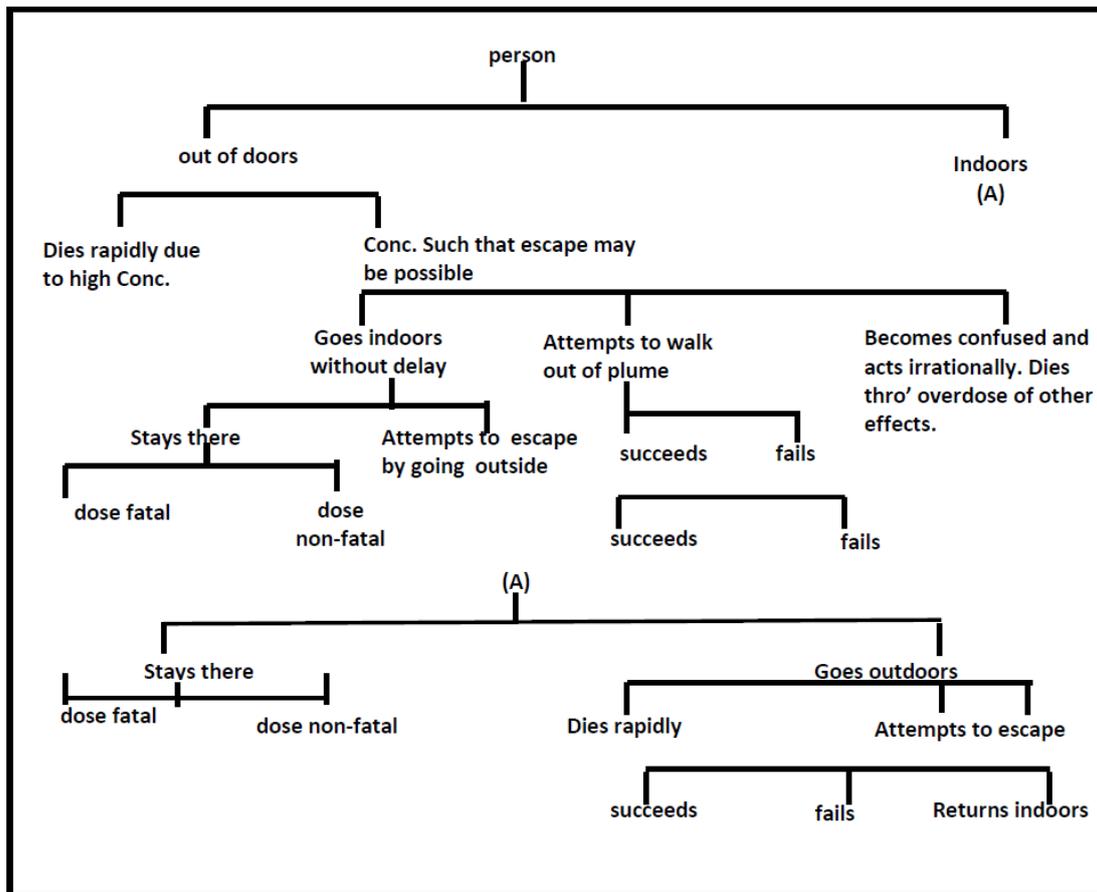
Both of these options have been used to protect the community from the effects of maritime-related accidents (see **Table 7**).

DATE	LOCATION	VESSEL	SUBSTANCE	DETAILS
20/4/95	Corpus Christi, Texas, USA	barge, DC-304	cumene/VCM	Bow of LPG carrier Maersk Shetland loaded with VCM struck barge near Ingleside naval station: small release of cumene: <b>locals evacuated</b> ; VCM cargo intact
9/01/93	nr Mandal, Norway	Stawfjord	explosives	Listing ship with 200 tonnes of dynamite in hold and deck containers of percussion caps overturned when tow broke: grounded; <b>100 evacuated</b> ; explosion
22/8/91	Coode Island, Australia	bulk liquids storage tank	methyl ethyl ketone	Explosion and fire in storage tanks spread to others. Port and railroad closed, <b>hundreds evacuated</b> . Workers and residents in nearby suburbs <b>were warned to stay indoors</b> , switch off air conditioners and seal windows to prevent entry of toxic fumes
3/05/91	Norfolk Coast, UK	Nordic Pride	ethyl acrylate	Two 24,000-litre ethyl acrylate tank containers beached; one leaked 1000 litres, <b>1000 residents evacuated</b>
27/7/89	Rotterdam, Holland	tank container	calcium hypochlorite	About <b>7000 people evacuated</b> from vessels and homes in port district following fire in container of calcium hypochlorite: chlorine given off

**Table 7. Example of cases of evacuation /in-place sheltering methods in maritime related accidents involving hazardous substances.**

### 5.1. Options facing a person caught in a toxic gas vapour

A person has a range of options at his disposal on whether he stays in or outdoors when faced with a toxic gas or vapour release (**Figure 31**).



**Figure 31. Options facing a person caught in toxic gas cloud or vapour.**

The options in **Figure 31**, when extrapolated to a whole population can be summarized as follows:

- the remain-indoors option and the use of the reservoir of clean indoor air to dilute contaminated air that infiltrates indoors;
- the evacuation of the area before the toxic release occurs (pre-incident evacuation);
- the rescue of people after the hazard reaches the area which involves supplying protective equipment to ensure their safety;
- the evacuation of the area after the outdoor concentration has decreased to a level lower than indoors (post-incident evacuation).

## 5.2. Aspects of an evacuation

Evacuation is a complex operation and is considered one of the most sweeping and aggressive response measures taken in an accidental chemical release. It is also important to distinguish between mass evacuation of an entire area and the selective evacuation of part of the area at risk.

### 5.2.1. Factors to consider for evacuation

There are a number of factors to consider when deciding on an evacuation;

- the optimum starting time;
- the number of evacuees (evacuation of the entire area or a selection of the area);
- the location and whereabouts of evacuees;
- the mobility of evacuees;
- the reaction of people who are informed that they are to be evacuated.

### 5.2.2. Resources required for evacuation

To accomplish a safe and effective evacuation operation, certain resources are imperative, such as

- evacuation assistance personnel;
- vehicles to move people out of the stricken area;
- equipment;
- agreements with nearby jurisdictions to receive evacuees.

### 5.2.3. Conducting an evacuation

An evacuation operation itself must be conducted in a well co-ordinated, thorough and safe manner and making prior arrangements (**at the preparedness level**) to ensure the availability of resources prior to the emergency will result in a more efficient evacuation operation.

## 5.3. Aspects of in-place sheltering

An alternative to evacuation is to seek shelter indoors. This could be a viable option to protect the public from the effects of toxic gas or vapour discharges into the atmosphere. The exposure of people inside a building to a toxic gas or vapour release which has taken place on the outside is a function of:

- the airtightness of the building;
- the rate of entry and exit of the contaminated air;
- the indoor mixing of the toxic load with the indoor clean air.

## 5.4. Summary – evacuation vs. shelter-in-place

It can be said that the decision to evacuate and/or shelter in-place is very incident specific and the use of judgement is necessary. **Evacuation remains a viable option of protecting the public when:**

- there appears to be time to relocate people;
- the discharge has already taken place but people are sufficiently far downwind to permit evacuation;
- long term releases take place, and the release is expected to occur over an extended period of time;

- a fire has also occurred which can get out of control;
- people not yet in the direct path of a cloud or plume are threatened by a future shift in wind direction;
- risks associated with in-place sheltering might not fully protect the people from the deleterious effects of the hazardous material release.

On the other hand, **in-place sheltering is also a viable option of protecting the public when:**

- the air borne contamination is moving so fast that there is no time to evacuate;
- a short-term release takes place and the toxic plume is expected to pass over quickly;
- climatic changes and duration of toxic plume movement are difficult to predict;
- it is anticipated that the most vulnerable populations such as the elderly and sick, may sustain injury during evacuation;
- risks associated with evacuation might not fully protect the evacuees from the deleterious effects of the hazardous material release.

Further detailed information on the aspects to consider in evacuation and in-place sheltering can be found in **Annex 3**.

## 6. Conclusion

Gases are distinguished from other hazardous cargoes in that their vapour pressure at ambient conditions exceeds that of the atmosphere. This characteristic imposes special requirements in their carriage at sea. Because of the volatility of gases together with their inherent toxic, flammable, corrosive and reactive properties, the possibility of spillages and accidental releases require special consideration. Preparing for maritime related accidents involving gaseous products whether they occur at a terminal facility or while a ship is on route requires an understanding of the chemistry of gases, the type of ships which carry such products, the type of accidental releases that might occur, the possible consequences from such releases and the countermeasures that may be feasible. Undoubtedly, once a spill of gas takes place it is very hard to combat.

**ANNEX I. CRITICAL TEMPERATURES AND PRESSURES  
OF SOME COMMON GASES**

<b>Substance</b>	<b>Critical Temperature (°C)</b>	<b>Critical Pressure (bars)</b>
Methane	-82.5	44.7
Ethane	32.1	48.7
Propane	96.8	42.6
n-Butane	153.0	38.1
I-Butane	133.7	38.2
Ethylene	9.9	50.5
Propylene	92.1	45.6
δ-Butylene	144.7	38.7
Butadiene	161.8	43.2
Isoprene	211.0	38.5
VCM	158.4	52.9
Ethylene oxide	195.7	74.4
Propylene oxide	209.1	47.7
Ammonia	132.4	113.0
Chlorine	144	77.1

VCM = Vinyl Chloride Monomer

## ANNEX II. FLAMMABLE PROPERTIES OF SOME GASES

Gas	Flash point (°C)	Flammable range (% by vol. in air)	Auto ignition temperature (°C)
Methane	-175	5.3 - 14	595
Ethane	-125	3.1 - 12.5	510
Propane	-105	2.1 - 9.5	468
n-Butane	- 60	1.8 - 8.5	365
i-Butane	- 76	1.8 - 8.5	500
Ethylene	-150	3 - 32	453
Propylene	-180	2 - 11.1	453
α-Butylene	- 80	1.6 - 9.3	440
β-Butylene	- 72	1.8 - 8.8	465
Butadiene	- 60	2 - 12.6	418
Isoprene	- 50	1 - 9.7	220
VCM	- 78	4 - 33	472
Ethylene oxide	- 18	3 - 100	429
Propylene oxide	- 37	2.8 - 37	465
Ammonia	- 57	16 - 25	615
Chlorine	Non-flammable		

## ANNEX III. EVACUATION VS IN-PLACE SHELTERING

### 1. Aspects of evacuation

Evacuation is a complex operation and is considered one of the most sweeping and aggressive response measures taken in an accidental chemical release. The physical difficulties of large scale evacuation should not be underestimated whilst in considering or carrying out an evacuation operation, care must be taken not to put people at risk by bringing them outdoors and being caught in the open when they might be more effectively protected by in-place sheltering. It is also important to distinguish between mass evacuation of an entire area and the selective evacuation of part of the area at risk.

#### 1.1 Factors to consider for evacuation

Issues to be considered are whether:

- people are evacuated before the release occurs and if there is enough time to permit relocation;
  - people are sufficiently downwind to permit time for evacuation;
  - people not yet in the direct path of a cloud or plume but threatened by a future shift in wind;
  - the release has already taken place, in this case the best time to leave is after the outdoor concentration has decreased below the indoor level;
- number of evacuees (evacuation of the entire area or a selection of the area);
- the location and whereabouts of evacuees such as:
    - private residences;
    - educational institutions;
    - medical institutions;
    - health care facilities;
    - child care facilities;
    - correctional facilities;
    - offices;
    - commercial establishments;
    - industrial establishments;
    - sporting and recreational facilities;
    - parks and similar open spaces;
    - roadways;
- the mobility of evacuees with special consideration to:
- persons lacking their own transport;
  - the elderly;
  - the children;
  - disabled persons;
  - the infirm;
  - prisoners;
  - persons not speaking the "local" language;
- the reaction of people who are informed that they are to be evacuated (Note: with the realization that a person is to be away from home for a considerable time, there is a tendency for a person to return to pick up valuables and supplies whilst relatives and friends concerned about the safety of people evacuating have a tendency to converge on the area compounding the whole operation the latter group of people should not be allowed in the stricken area. Persons with domestic pets may be unwilling to leave their homes unless arrangements include their pets).

## 1.2 Resources of required for evacuating

To accomplish a safe and effective evacuation operation, certain resources are imperative, such as:

- evacuation assistance personnel;
- vehicles, to include:
  - lift-equipped vehicles for disabled persons;
  - ambulances for the infirm;
  - transport means for moving people lacking their own transport;
- equipment, to include:
  - protective equipment for evacuation assistance personnel;
  - protective equipment for evacuees who may have to be taken through a heavily contaminated area;
- communication equipment, such as:
  - portable and mobile radios;
  - mobile public address systems;
  - bull-horns;
- evacuation tags or markers to indicate the occupants of a building have already been notified and the building has been evacuated;
  - maps (drawn to scale) with evacuation routes and alternatives
  - protective shelters for evacuees;
- agreements with nearby jurisdictions to receive evacuees.

Making prior arrangements (at the preparedness level) to ensure the availability of resources prior to the emergency will result in a more efficient evacuation operation.

## 1.3 Conducting an evacuation

An evacuation operation itself must be conducted in a well co-ordinated, thorough and safe manner. This involves a number of sequential steps.

- STEP 1:** Assigning tasks to evacuation assistance personnel such as their specific area of coverage.
- STEP 2:** Alerting the people that they must evacuate and give them with accurate instructions. This step could be accomplished by:
- door-to-door notification;
  - public address system e.g. mobile unit, broadcast system;
  - a combination of the two.
- STEP 3:** Moving the people and providing them with transport assistance. Consideration will need to be given to traffic control and the provision of alternate traffic routes. Traffic control involves auditing vehicle movement in and out of the evacuation area.
- STEP 4:** Sheltering the evacuees and providing them with a safe and comfortable building. When selecting the location of the building, it is imperative that the location is chosen beyond the current and anticipated area of contamination. If in the extreme case, the building has to be evacuated, alternate locations would need to be previously identified. A number of buildings should have been pre-identified which could function as shelter/rest centres in any

emergency. Some characteristics, facilities and services which should be available at shelter/rest centres are listed in **Appendix 1** to this Annex.

**STEP 5:** Securing the evacuated area to prevent unauthorized activities (e.g. looting, vandalism). Security personnel patrolling the area must be equipped with appropriate protective clothing.

**STEP 6:** Re-entering the evacuated area which can be considered as an evacuation operation in reverse. In this regard, once re-entry has taken place, it is important to advise people to report any lingering vapours or other hazards to emergency services as well as advise people to seek medical treatment for any unusual symptoms that they may experience (e.g. rashes, difficulty in breathing).

## 2. Aspects of in-place-sheltering

An alternative to evacuation is to seek shelter indoors. This could be a viable option to protect the public from the effects of toxic gas or vapour discharges into the atmosphere.

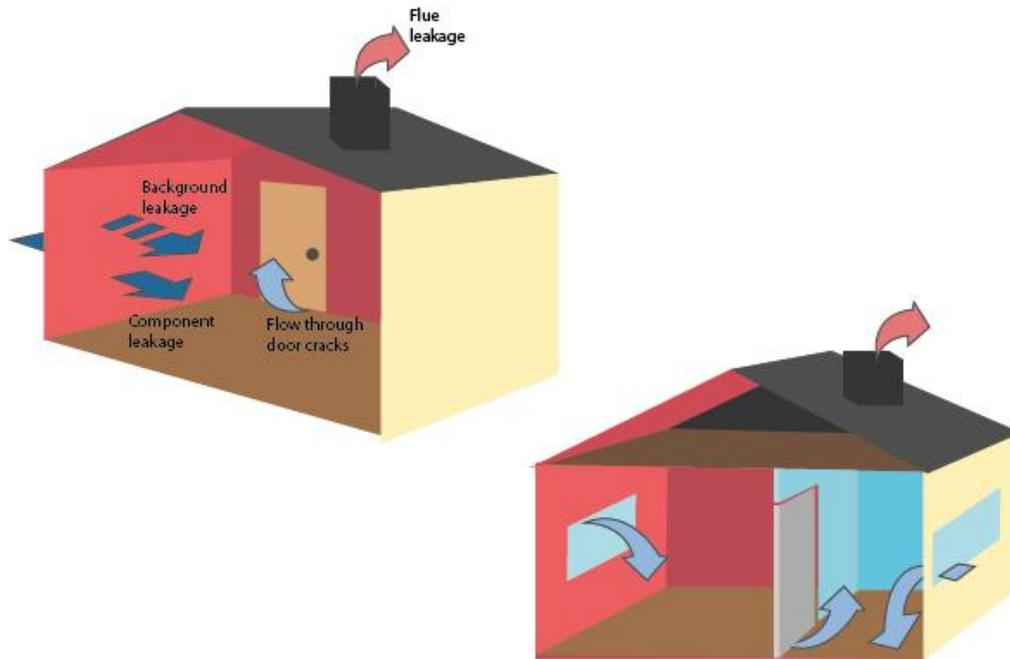
### 2.1 Factors to consider for in-place sheltering

If a building or other structure is airtight i.e. like a sealed box, anyone inside will not be exposed to any outside toxic gases or vapours. On the other hand, if severe leakages of contaminated air take place into a building, people will be exposed to the same level of contamination "indoors" as they would be if they were "outdoors". Therefore, the exposure of people inside a building to a toxic gas or vapour release which has taken place on the outside is a function of the "**airtightness**" of the building, the **rate of entry and exit of the contaminated air** and the **indoor mixing of the toxic load with the indoor clean air**.

#### 2.1.1 Air-tightness

Three ways air enters (and exits) structures are:

- natural ventilation which can be described as the entry of outdoor air into a building through open windows or doors without assistance; obviously, the more openings in a building, the greater the rate at which outdoor air can pass through; closing and opening the various windows and doors regulates the rate of entry/exit;
- forced-air ventilation which can be described as the entry of outdoor air into a building through the use of fans and other equipment, possibly heating, cooling, filtering the air and even circulating it several times and then exhausting it to the outside; regulation of the rate of entry and exit is done through the control of the system;
- infiltration which can be described as the air leakage into building through cracks and crevices around the openings around the windows and doors and through floors and walls; this type of infiltration is divided into two: background leakage which would include sources at the joints between the walls and the foundation, perforations such as electrical outlets and plumbing; and
- component leakage which would include localized sources such as for example cracks around window frames and openings for dryer vents (**Figure 32** illustrates the air infiltration and exfiltration leakage paths); this type of air entry is different from natural and mechanical ventilation in the sense that occupants are generally considered to exercise very little control over the rate of entry.



**Figure 32 (Copyright Cedre). Leakage pathways in a building.**

### 2.1.2 Total infiltration rate of buildings

The rate of entry of a toxic gas into a building is dependent on:

- different types of ventilation;
- wind and temperature conditions;
- air exchange rate of the building;
- terrain roughness;
- path of the toxic plume in relation to the buildings.

### 2.1.3 Indoor mixing

Certain factors that need to be borne in mind when considering indoor mixing of contaminated air in a building are:

- the dilution of contaminated air with indoor air which means that person sheltering indoors will be exposed to a diluted outdoor concentration;
- the direct displacement of indoor air due to the entry of an unmixed flow of cooler contaminated outdoor air which would be in direct conflict with the dilution effect;
- the potential for build-up of hot spots within a given space;
- the physical state of the airborne substance (gases and vapours travel greater distances and pass through smaller spaces than dusts and other aerosols).

## 2.2 Recommendations to follow when in-place sheltering

In order for in-place sheltering to be effective, minimization of the indoor toxic air load needs to take place. The following are a set of suggested instructions which can assist in making in-place sheltering an effective protective measure:

- doors to the outside should be closed, windows should be closed and locked (windows seal better when locked). Gaps under doorways and windows should be sealed with wet towels/clothes and those around doorways and windows with ducting (electrician's) tape or equivalent thick tape;
- ventilation systems should be set fully to the recirculation mode to avoid outside contaminated air being drawn into the building. A ventilation system should be turned off where this is not possible;
- heating systems and air conditioners should be turned off;

- the use of lifts should be minimized since they tend to "pump" outdoor air in and out of a building as they travel up and down a building;
- extractor and exhaust fans in kitchens, bathrooms, toilets should be switched off;
- obvious gaps to the outside around window-type air-conditioners, exhaust fans, kitchen hoods, dryer vents should be sealed using plastic sheeting, wax paper or aluminium foil wrap;
- internal doors (as many as is feasibly possible) should be closed;
- if the information available on the substance indicates that the material is soluble or even partial soluble in water, advise to hold a wet cloth over the nose and the mouth. Advise to move to the bathroom, to seal the door and any other openings, to turn on the shower, and to set the shower head to a strong spray "to knock-down" any contaminated air;
- if there is a chance of explosion outdoors, advise to close curtains and shades, to lie low and to move away from external windows to avoid being hit by flying glass and other shrapnel;
- open windows and ventilation systems as soon as the danger has passed to help in "flushing-out" any contaminated air lingering or trapped in the building;
- turn on the emergency broadcast system on the radio or television and follow the guidance given.

## **APPENDIX I. CHARACTERISTICS, FACILITIES AND SERVICES OF SHELTERS/ REST CENTRES**

The Appendix will cover some broad guidelines, which are considered necessary for establishing a shelter/rest centre. They are by no means comprehensive but concentrate on the most important features. The Annex is divided into two parts. Part A deals with the characteristics, facilities and services that should be provided by the shelter/rest centres whilst Part B lists in point form the stress induced to those accommodated within these places.

### **PART A – Characterises, facilities and services**

#### **Layout of building:**

- a single entrance and exit should be arranged even though more than one could be present in the building;
- entrance/reception area must be large enough to allow people to enter without having to wait outside especially at night or during inclement weather;
- a main living/sleeping area with sufficient space to avoid overcrowding;
- a room to store valuables and any other personal belongings evacuees may wish to protect;
- sufficient car park area and access to the premises which are large enough for buses or ambulances with easy access for the disabled;
- separate room for pet owners and their animals;
- rooms for medical examination and counselling.

#### **Facilities:**

- food preparation facilities;
- telephone or other communication facilities (e.g. two way radio);
- shower/washing/toilet facilities;
- basic furniture (e.g. chairs, tables, bedding);
- adequate lighting, temperature control, ventilation and uncontaminated water supply;
- provisions for the monitoring of hazards in and around the building.

#### **Management and organization:**

- a person to serve as a shelter/rest centre co-ordinator;
- provisions for registration and accountability of the whereabouts of the evacuees once received;
- arrangements to limit access where entry to parts of the premises is prohibited due to possible danger;
- provisions where regular, accurate and up-to-date information is displayed and given to the evacuees;
- provisions to have interpretation where necessary, this is particularly important in areas where evacuation has taken place of foreign nationals (e.g. hotels);

- provisions for medical prescriptions to be picked up and medical treatment continued for any chronic ailments suffered by evacuees;
- provisions to have assistant staff and workers to be relieved;
- provisions for certain basic items to be available (e.g. soap, towels, toothbrushes and toothpaste).

## **PART B – Possible Sources of Stress in Rest Centres**

### **Loss of dignity:**

- lack of privacy
- loss of false teeth, spectacles, etc.
- "being grateful"
- "having to ask"

### **Strange and unsatisfactory surroundings:**

- sanitation
- washing
- other people

### **Strange neighbourhood, loss of neighbours (social network):**

- news
- babysitting
- support

### **Disruption of services:**

- food
- information

### **Uncertainty:**

- how long here?
- what next?

### **Bureaucracy:**

- loss of control
- delay
- fading sympathy of others

### **Life changes:**

- work
- education
- culture

**Continuing psychological problems:**

- encounter with death
- bereavement
- need to adapt

**Family tension:**

- crowding
- no privacy
- no communication (fear of memories and distress)
- overuse of alcohol (tension release)
- worries over children (behaviour)

## LIST OF FIGURES

Figure 1. Main routes for Gas (magenta lines) ,LNG (dark blue lines) and LPG (light blue lines) tankers in the Mediterranean Sea and main ports (light blue dots) (Source <http://safemedqis.rempec.org/>).

Figure 2 (Copyright Cedre). Two-dimensional illustration of the different phases of matter.

Figure 3. Illustration of the behaviour of water when heated or cooled.

Figure 4 (Copyright Cedre). Phase diagram.

Figure 5 (Copyright Cedre). Phase diagram showing how a gas can be liquefied by removal of heat and/or pressurizing.

Figure 6. Key components of a LNG liquefaction plant (Source Petrowiki.org).

Figure 7 (Copyright Cedre). Standard European Behaviour Classification. G (Gas), E (Evaporator), F (Floater), D (Dissolver), S (Sinker) and behaviour combinations (e.g. FED for Floater and Evaporator and Dissolver).

Figure 8. Various types of gas cylinders (not to scale).

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## GLOSSARY AND ACRONYMS

**AEGLs (Acute Exposure Guideline Levels):** Toxicological reference values defined for a type of exposure, a route of exposure, a duration of exposure and a type of population.

**Auto ignition temperature:** temperature to which its vapour-in-air mixture must be heated to ignite spontaneously.

**Bar g:** unit of pressure under atmospheric pressure.

**Bar g:** unit of gauge pressure, i.e. pressure in bars above ambient or atmospheric pressure.

**BOG:** Boil Off Gas.

**Boiling point:** the temperature at which the vapour pressure of a liquid is equal to the pressure on its surface (the boiling point varies with pressure).

**Density:** the mass per unit volume of a substance at specified conditions of temperature and pressure.

**ERPGs (Emergency Response Planning Guidelines):** Toxicological reference values who are defined for a type of exposure, a route of exposure, a duration of exposure and a type of population.

**ESD:** Emergency ShutDown system.

**Flammable range:** the range of hydrocarbon gas concentrations in air between the Lower and Upper Flammable (Explosive) Limits. Mixtures within this range are capable of being ignited and of burning.

**Flash point:** the lowest temperature at which that liquid will evolve sufficient vapour to form a flammable mixture with air.

**LFL (Lower Flammable Limit):** the lower end of the concentration range over which a flammable mixture of gas or vapour in air can be ignited at a given temperature and pressure.

**LPG:** Liquefied Petroleum Gas or Liquid Petroleum Gas

**LEL (Lower Explosive Level):** the concentration of a hydrocarbon gas in air below which there is insufficient hydrocarbon to support and propagate combustion.

**MARPOL:** MARine POLLution, the International Convention for the Prevention of Pollution from Ships is the main international convention covering prevention of pollution of the marine environment by ships from operational or accidental causes.

**NGL:** Natural Gas Liquid.

**PEC (Predicted Environmental Concentration):** The prognosticated concentration of a chemical in the environment.

**PNEC (Predicted No Effect Concentration):** The concentration of a chemical which marks the limit at which below no adverse effects of exposure in an ecosystem are measured.

**PTS:** Terminal Port-To-Ship

**QCDC:** Quick Connect/Disconnect Coupler hydraulic system.

**STS:** Ship-To-Ship

**TEELs (Temporary Emergency Exposure Limit):** Toxicological reference values who are defined for a type of exposure, a route of exposure, a duration of exposure and a type of population.

**TTS:** Truck-To-Ship

**UEL (Upper Explosive Level) or UFL (Upper Flammability Limit):** the concentration of a hydrocarbon gas in air above which there is insufficient oxygen to support and propagate combustion.

**Vapour density:** the density of a vapour in relation to that of hydrogen (or of air depending on source). It has no dimension but commonly quoted in units of kilogrammes per cubic metre ( $\text{kg/m}^3$ ).

**Vapour pressure:** characterizes volatility of a product, generally quoted in Pascal.

**VCM:** Vinyl Chloride Monomer

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