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Petroleum and natural gas industries — Characteristics of LNG, influencing the design, and material selection

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National foreword

This British Standard is the UK implementation of EN ISO 16903:2015. It supersedes BS EN 1160:1997 which is withdrawn.

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European foreword

This document (EN ISO 16903:2015) has been prepared by Technical Committee ISO/TC 67 "Materials, equipment and offshore structures for petroleum, petrochemical and natural gas industries" in collaboration with Technical Committee CEN/TC 282 “Installation and equipment for LNG” the secretariat of which is held by AFNOR.

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The text of ISO 16903:2015 has been approved by CEN as EN ISO 16903:2015 without any modification.

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Foreword

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The committee responsible for this document is ISO/TC 67, *Materials, equipment and offshore structures for petroleum, petrochemical and natural gas industries*.

Petroleum and natural gas industries — Characteristics of LNG, influencing the design, and material selection

1 Scope

This International Standard gives guidance on the characteristics of liquefied natural gas (LNG) and the cryogenic materials used in the LNG industry. It also gives guidance on health and safety matters. It is intended to act as a reference document for the implementation of other standards in the liquefied natural gas field. It is intended as a reference for use by persons who design or operate LNG facilities.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies

EN 1473, *Installation and equipment for liquefied natural gas — Design of onshore installations*

NFPA 59A, *Standard for the production, storage, and handling of liquefied natural gas (LNG)*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
boil-off gas
gas generated during the storage or handling of volatile liquefied gases

3.2
condensate
hydrocarbon liquid that forms by condensation from natural gas, consisting primarily of pentanes (C_5H_{12}) and heavier components

Note 1 to entry: There will be some propane and butane dissolved within the mixture.

3.3
liquefied natural gas
LNG
colourless and odourless cryogenic fluid in the liquid state at normal pressure composed predominantly of methane which can contain minor quantities of ethane, propane, butane, nitrogen, or other components normally found in natural gas

3.4
liquefied petroleum gas
LPG
gaseous hydrocarbons at normal temperatures and pressures, but that readily turns into liquids under moderate pressure at normal temperatures, e.g. propane and butane

3.5
natural gas liquids
NGL
liquid hydrocarbons, such as ethane, propane, butane, pentane, and natural gasoline, extracted from field natural gas

4 Abbreviated terms

For the purposes of this International Standard, the following abbreviations apply.

BLEVE	boiling liquid expanding vapour explosion
LPG	liquid petroleum gas
QRA	quantitative risk analysis
RPT	rapid phase transition
SEP	surface emissive power

5 General characteristics of LNG

5.1 General

It is recommended that all personnel concerned with the handling of LNG should be familiar with both the characteristics of the liquid and the gas produced.

The potential hazard in handling LNG stems mainly from three important properties.

a) It is extremely cold. At atmospheric pressure, depending upon composition, LNG boils at about –160 °C. At this temperature, the vapour is denser than ambient air.

b) Very small quantities of liquid are converted into large volumes of gas. One volume of LNG produces approximately 600 volumes of gas.

c) Natural gas, similar to other gaseous hydrocarbons, is flammable. At ambient conditions, the flammable mixture range with air is from approximately 5 % to 15 % gas by volume. If vapour accumulates in a confined space, ignition can result in detonation and shock wave overpressure.

This International Standard focuses on LNG, its properties, and resultant hazards. When evaluating the hazards at an LNG site, designers need to consider all systems present. Often, the LNG itself does not present the greatest hazard; other systems such as LPG-based refrigeration at the liquefaction plant or high pressure gas send out at a regasification plant can dominate the overall site risk profile.

5.2 Properties of LNG

5.2.1 Composition

LNG is a mixture of hydrocarbons composed predominantly of methane and which can contain minor quantities of ethane, propane, butane, nitrogen, or other components, normally found in natural gas. The physical and thermodynamic properties of methane and other components of natural gas can be found in reference books (see Annex A) and thermodynamic calculation codes. Although the major constituent of LNG is methane, it should not be assumed that LNG is pure methane for the purpose of estimating its behaviour. When analysing the composition of LNG, special care should be taken to obtain representative samples not causing false analysis results due to distillation effects. The most common method is to analyse a small stream of continuously evaporated product using a specific LNG sampling device that is designed to provide a representative gas sample of liquid without fractionation. Another method is to take a sample from the outlet of the main product vaporizers. This sample can then be analysed by normal gas chromatographic methods, such as those described in ISO 6568 or ISO 6974.

5.2.2 Density

The density of LNG depends on the composition and usually ranges from 420 kg/m^3 to 470 kg/m^3, but in some cases can be as high as 520 kg/m^3. Density is also a function of the liquid temperature with a gradient of about 1,4 kg/m^3/K. Density can be measured directly but is generally calculated from composition determined by gas chromatographic analysis. The method as defined in ISO 6578 is recommended.

NOTE This method is generally known as revised Klosek-McKinley method.

5.2.3 Temperature

LNG has a boiling temperature depending on composition and usually ranging from –166 °C to –157 °C at atmospheric pressure. The variation of the boiling temperature with the vapour pressure is about 1,25 × 10^{-4} °C/Pa. The temperature of LNG is commonly measured by using copper/copper nickel thermocouples or using platinum resistance thermometers such as those defined in ISO 8310.

5.2.4 Viscosity

The viscosity of LNG depends on the composition and is usually from 1,0 × 10^{-4} to 2,0 × 10^{-4} Pat –160 °C, which is nearly 1/10 to 1/5 of the water. Viscosity is also a function of the liquid temperature.

5.2.5 Examples of LNG

Three typical examples of LNG are shown in Table 1 below which demonstrates the property variations with different compositions[1)].

Table 1 — Examples of LNG

Properties at boiling temperature at normal pressure	LNG Example 1	LNG Example 2	LNG Example 3
Molar content (%)			
N_2	0,13	1,79	0,36
CH_4	99,8	93,9	87,20
C_2H_6	0,07	3,26	8,61
C_3H_8	—	0,69	2,74
i C_4H_{10}	—	0,12	0,42
n C_4H_{10}	—	0,15	0,65
C_5H_{12}	—	0,09	0,02
Molecular weight (kg/kmol)	16,07	17,07	18,52
Boiling temperature (°C)	–161,9	–166,5	–161,3
Density (kg/m^3)	422	448,8	468,7
Volume of gas measured at 0 °C and 101 325 Pa/volume of liquid (m^3/m^3)	588	590	568
Volume of gas measured at 0 °C and 101 325 Pa/mass of liquid (m^3/10^3 kg)	1 392	1 314	1 211
Mass heat of vaporization (kJ/kg)	525,6	679,5	675,5
Gross heating value (MJ/m^3)	37,75	38,76	42,59

5.3 Physical properties

5.3.1 Physical properties of boil-off gas

LNG is stored in bulk as a boiling liquid in large, thermally insulated tanks. Any heat leak into the tank causes some of the liquid to evaporate as a gas. This gas is known as boil-off gas. The composition of the boil-off gas depends on the composition of the liquid. As an example, the boil-off gas could contain 20 %

1) Values are given from simulations.

nitrogen, 80 % methane, and traces of ethane; the nitrogen content of the boil-off gas could be about 20 times that in the LNG.

As LNG evaporates, the nitrogen and methane are preferentially lost leaving the liquid with a larger fraction of the higher hydrocarbons. Boil-off gases below about −113 °C for pure methane and −85 °C for methane with 20 % nitrogen are heavier than ambient air. At normal conditions, the density of these boil-off gases is approximately 0,6 of air.

5.3.2 Flash

As any fluid, if pressurized LNG is lowered in pressure below its boiling pressure, for example by passing through a valve, then some of the liquid evaporates and the liquid temperature drops to its new boiling point at that pressure. This is known as flash. Since LNG is a multi-component mixture, the composition of the flash gas and the remaining liquid differ for similar reasons from those discussed in 5.3.1.

As a guide, a 10^3 Pa flash of 1 m^3 liquid at its boiling point corresponding to a pressure ranging from 1×10^5 Pa to 2×10^5 Pa produces approximately 0,4 kg of gas. More accurate calculation of both the quantity and composition of the liquid and gas products of flashing multi-component fluids such as LNG are complex. Validated thermodynamic or plant simulation packages for use on computers incorporating an appropriate database should be used for such flash calculations.

5.3.3 Spillage of LNG

When LNG is poured on the ground (as an accidental spillage), there is an initial period of intense boiling, after which the rate of evaporation decays rapidly to a constant value that is determined by the thermal characteristics of the ground and heat gained from surrounding air. This rate can be significantly reduced by the use of thermally insulated surfaces where spillages are likely to occur as shown in Table 2. These figures are given for examples, but should be checked when used for QRA or detail engineering.

Table 2 — Rate of evaporation

Material	**Rate per unit area after 60 s** kg / (m^2h)
Aggregate	480
Wet sand	240
Dry sand	195
Water	600
Standard concrete	130
Light colloidal concrete	65

Small quantities of liquid can be converted into large volumes of gas when spillage occurs. One volume of liquid produces approximately 600 volumes of gas at ambient conditions (see Table 1). When spillage occurs on water, the convection in the water is so intense that the rate of evaporation related to the area remains constant. The size of the LNG spillage extends until the evaporating amount of gas equals the amount of liquid gas produced by the leak.

5.3.4 Expansion and dispersion of gas clouds

Initially, the gas produced by evaporation is at nearly the same temperature as the LNG and is denser than ambient air. Such gas is, at first, subjected to gravity spreading by flowing in a layer along the ground until it warms sufficiently by absorbing heat from the soil and mixing with the ambient air.

The dilution with warm air increases temperature and decreases the molecular weight of the mixture. As a result, the cloud is in general denser than ambient air until diluted well below the flammable limit. Only in case of high water content of the atmosphere (high humidity and temperature) can the condensation of water during the mixing with the cold LNG vapours heat-up the mixture as such that it becomes lighter than air and results in a buoyant cloud. Spillage, expansion, and dispersion of vapour clouds are complex subjects and are usually predicted by computer models. Such predictions should only be undertaken by a body competent in the subject. Following a spillage, 'fog' clouds are formed by condensation of water vapour in the ambient air. When the fog can be seen (by day and without natural fog) and if the relative humidity of the ambient air is sufficiently high, the visible fog is a useful indicator of the travel of the vaporized gas and the cloud gives a first indication of the extent of flammability of the mixture of gas and air as the visibility of the cloud is a function of the humidity and ambient temperature, not a function of the natural gas release.

In the case of a leak in pressure vessels or in piping, LNG sprays as a jet stream into the atmosphere under simultaneous throttling (expansion) and vaporization. This process coincides with intense mixing with air. A large part of the LNG is contained in the gas cloud initially as an aerosol. This eventually vaporizes by further mixing with air.

5.3.5 Ignition

A natural gas/air cloud can be ignited when the natural gas concentration is in the range from 5 % to 15 % by volume.

5.3.6 Pool fires

The surface emissive power (SEP) of a flame from an ignited pool of LNG with greater diameter than 10 m can be very high and shall be calculated from the measured values of the incident radiative flux and a defined flame area. The SEP depends on pool size, smoke emission, and methods of measurement. With increased footing, the SEP decreases. The Bibliography contains a list of references which can be used to ascertain the SEP for a given circumstance.

5.3.7 Development and consequences of pressure waves

In a free cloud, natural gas burns at low velocities resulting in low overpressures of less than 5×10^3 Pa within the cloud. Higher pressures can occur in areas of high congestion or confinement such as densely installed equipment or buildings.

5.3.8 Containment

Natural gas cannot be liquefied by applying pressure at ambient temperature. In fact, it shall be reduced in temperature below about −80 °C before it liquefies at any pressure. This means that any quantity of LNG that is contained, for example between two valves or in a vessel with no vent, and is then allowed to warm up increases in pressure until failure of the containment system occurs. Plant and equipment shall therefore be designed with adequately sized vents and/or relief valves.

Designers need to pay attention to eliminating the potential to shut in even small volumes of cryogenic liquid, including attention to details such as cavity venting of ball valves.

5.3.9 Rollover

The term rollover refers to a process whereby large quantities of gas can be emitted from an LNG tank over a short period. This could cause over pressurization of the tank unless prevented or designed for. It is possible in LNG storage tanks for two stably stratified layers or cells to be established, usually as a result of incomplete mixing of fresh LNG with a heel of different density. Within cells, the liquid density is uniform but the bottom cell is composed of liquid that is denser than the liquid in the cell above. Subsequently, due to the heat leak into the tank, heat and mass transfer between cells and evaporation at the liquid surface, the cells equalize in density and spontaneously mix. This spontaneous mixing is called rollover and if, as is often the case, the liquid at the bottom cell has become superheated with respect to the pressure in the tank vapour space, the rollover is accompanied by an increase in vapour evolution. Sometimes, the increase is rapid and large. In a few instances, the pressure rise in the tank has been sufficient to cause pressure relief valves to lift.

An early hypothesis was that when the density of the top layer exceeded that of the lower layer, an inversion would occur, hence the name rollover. More recent research suggests that this is not the case and that, as described above, it is rapid mixing that occurs. Potential rollover incidents are usually preceded by a period during which the boil-off gas production rate is significantly lower than normal. Boil-off rates should therefore be closely monitored to ensure that the liquid is not storing heat. If this is suspected, attempts should be made to circulate liquid from the bottom layer into the top layer to promote mixing. Rollover can be prevented by good stock management. LNG from different sources and having different compositions should preferably be stored in separate tanks. If this is not practical, good mixing should be ensured during tank filling. High nitrogen content in peak shaving LNG installations can also cause a rollover to occur soon after the cessation of tank filling, due to the preferential evaporation of the nitrogen. Experience shows that this type of rollover can best be prevented by keeping the nitrogen content of LNG below 1 % and by closely monitoring the boil-off rate.

Therefore, the LNG density in the tank should be monitored if there is any suspicion of stratification due to different LNG sources, as an example. In case of stratification is detected, mitigation measure shall apply.

5.3.10 RPT

When two liquids at two different temperatures come into contact, shock wave forces can occur, given certain circumstances. This phenomenon, called rapid phase transition (RPT), can occur when LNG and water come into contact. Although no combustion occurs, it produces a pressure wave like an explosion. RPTs resulting from an LNG spill on water have been both rare and with relatively limited consequences. A theory that agrees with the experimental results can be summarized as follows. When two liquids with very different temperatures come into direct contact, if the temperature (expressed in Kelvin) of the warmer of the two is greater than 1,1 times the boiling point of the cooler one, the rise in temperature of the latter is so rapid that the temperature of the surface layer can exceed the spontaneous nucleation temperature (when bubbles appear in the liquid). In some circumstances, this superheated liquid vaporizes within a short time via a complex chain reaction mechanism and thus produces vapour at a shock wave rate.

For example, liquids can be brought into intimate contact by mechanical impact, and this has been known to initiate RPTs in experiments with LNG or liquid nitrogen on water. Recent research programs gained a better understanding of RPTs, to quantify the severity of the phenomena and to ascertain whether prevention measures are warranted.

5.3.11 BLEVE

Any liquid at or near its boiling point and above a certain pressure vaporises extremely rapidly if suddenly released due to failure of the pressure system. This violent expansion process has been known to propel whole sections of failed vessels several hundred metres. This is known as a boiling liquid expanding vapour explosion (BLEVE). A BLEVE is highly unlikely to occur on an LNG installation because either the LNG is stored in a vessel which fails at a low pressure (see Bibliography) and where the rate of vapour evolution is small, or it is stored and transferred in insulated pressure vessels and pipes which are inherently protected from fire damage.

6 Health and safety

6.1 General

The following recommendations are given in order to provide guidance to persons involved in operating LNG plants and are not intended to supersede national legal requirements.

6.2 Exposure to cold

6.2.1 Warning notice

The low temperatures associated with LNG can result in a variety of effects on exposed parts of the body. If a person is not suitably protected against low ambient temperatures, the person's reactions and capabilities can be adversely affected.

6.2.2 Handling, cold contact burns

Contact with LNG can produce a blistering effect on the skin similar to a burn. The gas issuing from LNG is also extremely cold and can produce burns. Delicate tissues, such as those of the eyes, can be damaged by exposure to this cold gas even though it would be too brief to affect the skin of the face and hands. Unprotected parts of the body should not be allowed to touch un-insulated pipes or vessels containing LNG. The extremely cold metal can adhere and the flesh can be torn when attempts are made to withdraw from it.

6.2.3 Frostbite

Severe or prolonged exposure to cold vapours and gases can cause frostbite. Local pain usually gives warning of freezing but sometimes no pain is experienced.

6.2.4 Effect of cold on the lungs

Prolonged breathing of extremely cold atmospheres can damage the lungs. Short exposure can produce breathing discomfort.

6.2.5 Hypothermia

The danger from hypothermia can be present at temperatures up to 10 °C. Persons apparently suffering from the effects of hypothermia should be removed from the cold area and rapidly warmed up in a warm bath with the temperature between 40 °C and 42 °C. Dry heat shall not be used for warming.

6.2.6 Recommended protective clothing

When handling LNG, the eyes should be protected with an appropriate face shield or safety goggles if exposure to LNG is reasonably foreseeable. Leather gloves should always be worn when handling anything that is, or could have been, in contact with the cold liquid or gas. Gloves should be a loose fit so that they can be readily removed should liquid splash in or on them. Even when using gloves, equipment should only be held for a short time.

Tight fitting overalls or similar type of clothing should be worn, preferably without pockets or turn-ups, and trousers should be worn outside boots or shoes. Clothing which has been contaminated with cold liquid or vapour should be ventilated before the wearer goes into a confined space or near an ignition source. Operating personnel should be aware that protective clothing only gives a measure of protection against occasional splashes of LNG and contact with LNG should be avoided.

6.3 Exposure to gas

6.3.1 Toxicity

LNG and natural gas are not toxic.

6.3.2 Asphyxia

Natural gas is a simple asphyxiant. The normal oxygen content of the air is 20,9 % by volume, atmospheres containing less than 18 % oxygen by volume are potentially asphyxian. In the case of high concentrations of gas, there can be nausea or dizziness due to anoxia. However, removal from exposure normally causes the symptoms to disappear rapidly. The oxygen and hydrocarbon content of atmospheres where natural gas could be present should be measured prior to entry.

Even if the oxygen content is shown to be adequate to prevent asphyxia, a flammability test should be made before entry. Only instruments made for this purpose should be used for such tests.

6.4 Fire precautions and protection

It is recommended that fire extinguishers of the dry powder type (preferably potassium carbonate) are conveniently available when handling LNG. Personnel involved in handling LNG should be trained in the use of dry powder extinguishers on liquid fires. High expansion foam or foamed glass blocks can be useful in covering LNG pool fires, and hence greatly reducing the radiation from them. A water supply should be available for cooling purposes and for foam generation if equipment is available. Water should not be used to extinguish fires. The design of fire precautions and protection shall comply with EN 1473 or NFPA 59A, other internationally recognised standards or national standards/regulations.

Fire extinguishers should be dry chemical powder type.

6.5 Colour

LNG vapour is colourless. However, when released into atmosphere, white cloud will form as result of ambient air humidity condensation.

6.6 Odour

LNG vapour is odourless.

7 Materials of construction

7.1 Materials used in the LNG industry

7.1.1 General

Most common materials of construction fail in brittle fracture when they are exposed to very low temperature. In particular, the fracture toughness of carbon steel is very low at LNG temperatures (–160 °C). Materials used in contact with LNG should be proved resistant to brittle fracture.

7.1.2 Materials in direct contact

The main materials which are not embrittled by direct contact with LNG and their general use are listed in Table 3. This list is not exhaustive.

Table 3 — Main materials used in direct contact and general use

Material	General use
Austenitic stainless steel	Tanks, unloading arms, nuts and bolts, pipes and fittings, pumps, heat exchangers
9 % Ni steel	Tanks
Nickel alloys, ferronickel alloys	Tanks, nuts, and bolts
Fe- 36 % Ni steel (Invar)	Pipes, tanks
Aluminium alloys	Tanks, heat exchangers
Copper and copper alloys	Seals, wearing surfaces
[a] Stellite: Co 55 %, Cr 33 %, W 10 %, C 2 %.	

Table 3 *(continued)*

Material	General use
Elastomer	Seals, gaskets
Concrete (pre-stressed)	Tanks
Graphite	Seals, stuffing boxes
Fluoroethylene propylene (FEP)	Electrical insulation
Polytetrafluoroethylene (PTFE)	Seals, stuffing boxes, bearing surfaces
Polytrifluoromonochloroethylene (Kel F)	Bearing surfaces
Stellite[a]	Bearing surfaces
[a] Stellite: Co 55 %, Cr 33 %, W 10 %, C 2 %.	

7.1.3 Materials not in direct contact under normal operation

The main materials used in construction at low temperature but not designed for direct contact under normal operation are given in Table 4. This list is not exhaustive.

Table 4 — Main materials not in direct contact under normal operations with LNG

Material	General use
Low alloyed stainless steel	Ball bearings
Concrete (pre-stressed, reinforced)	Tanks
Colloid concrete	Retention dykes
Wood (balsa, plywood, cork)	Thermal insulation
Elastomer	Mastic, glue
Glass wool	Thermal insulation
Exfoliated mica	Thermal insulation
Polyvinylchloride	Thermal insulation
Polystyrene	Thermal insulation
Polyurethane	Thermal insulation
Polyisocyanurate	Thermal insulation
Sand	Thermal insulation
Calcium silicate	Retention dykes
Silica (glass)	Thermal insulation
Cellular glass	Thermal insulation, retention dykes
Perlite	Thermal insulation

7.1.4 Other information

Aluminium is often used for heat exchangers. Such aluminium can be used in contact with LNG provided that LNG does not content any contaminant that could create corrosion, such as mercury as an example.

Liquefaction plant tube and plate exchangers are protected by a steel chamber called a cold box.

Aluminium is also used for inner tank suspended roofs.

Equipment and material specifically designed for liquid oxygen or liquid nitrogen are normally also suitable for LNG.

Equipment designed for normal operation on LNG at higher pressure and temperature should also be designed to take account of the drop in temperature of the fluid in the event of depressurization.

7.2 Thermal stresses

Most cryogenic equipment used in LNG facilities undergoes fast cooling from ambient temperature down to LNG temperature.

Temperature gradients occur during these cooling down operations producing thermal stresses which are transient, cyclical, and maximal along the walls directly in contact with LNG. These stresses increase with the thickness of the materials, and when this thickness exceeds approximately 10 mm, they can become significant. For especially critical points, transition or shock stresses can be calculated using an approved method and tested for brittle fracture.

The extreme temperature ranges encountered in LNG facilities result in significant thermal expansion or contraction. Piping and structural designs need to accommodate resultant movement to avoid excessive stresses. Also, if piping is only partially filled with LNG, the resulting temperature gradient from the top to the bottom of the pipe can cause bending stresses and permanent deformations, potentially resulting in loss of containment, mainly in flanged connections.

Flexibility studies shall be carried out for equipment and piping systems to ensure minimum flexibility, and thus preventing excessive stress due to temperature changes throughout all operating modes (cool down, warm-up, transient conditions, etc.). This flexibility analysis will combine all normal, accidental, and exceptional load cases (weight, wind, snow, earthquake, etc.).

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