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Council

Cryogenics Safety Manual

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Cryogenics Safety Manual
A guide to good practice

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Safety Committee
British Cryogenics Council

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Notice

This manual has been produced for the guidance of all who are concerned with the operation, maintenance, and supervision of plant for producing, storing, and handling industrial gases at relatively low temperatures. While every attempt has been made to deal with all foreseeable hazards, the final responsibility for safety must remain with those designing, maintaining, and operating the equipment. The British Cryogenics Council accepts no liability for any errors in, or omissions from, the manual.

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1 General safety requirements

Cryogenics is widely and simply described today as ‘the Science and Technology of Low Temperatures’ [1]. A cryogen is the fluid or, under appropriate conditions, solid phase of one of the single component gases, or multi-component mixtures such as air and natural liquid hydrocarbons, which have a normal boiling point (or sublimation temperature) below ambient temperature. In terms of fluid dynamic properties, the storage and handling behaviours of all cryogens are determined significantly:

- by heat flow into the cold liquid from the ambient environment via conduction, convection and radiation and
- by the rapid changes in their physical properties, viscosity, density, thermal conductivity, specific heat, etc. with decreasing temperatures.

For the purposes of this manual, a cryogen (or cryogenic fluid) is defined as one which is normally manufactured, stored, handled and processed at temperatures below 250 K or -23 °C (i.e. colder than the refrigeration and air-conditioning working temperature range) down to the lowest attainable temperatures approaching absolute zero at -273.15 °C. The properties of various cryogens are given in Table 2 in Section 1.2.4.

1.1 Health

1.1.1 Cryogenic burns and frostbite

Exposure of the skin to low temperature can produce effects on the skin similar to a burn. These will vary in severity with temperature and the time of exposure.

Naked or insufficiently protected parts of the body coming into contact with very cold uninsulated pipes or vessels may stick fast by virtue of the freezing of available moisture, and the flesh may be torn on removal. The use of wet gloves must be avoided under all circumstances. The low viscosity of cryogenic liquids means that they will penetrate woven or other porous clothing materials much faster than other liquids, for example, water.

Prolonged exposure to cold can result in frostbite. There may well be insufficient warning through local pain while the freezing action is taking place. All cold burns should be checked by a first aider to confirm the extent of damage and by a medical expert if there is any concern over the injuries.

Prolonged inhalation of cold vapour or gas can damage the lungs. Under no circumstances should cryogens be ingested. Cryogenic liquids and vapour can also damage the eyes.

1.1.1.1 Precautions

Protective clothing for handling low-temperature liquefied gases serves mainly to protect against cold burns.

A risk assessment should be performed in order to determine the hazards of use. Non-absorbent gloves (e.g. PVC or leather) should always be worn when handling anything that is or may have been in contact with cold liquids or vapours. Gloves should be a loose fit so that they may be readily removed should liquid splash on to them or into them. Gloves should be in conformance with the European Standard EN 511 [2]. However, it should be noted that this specification is for temperatures down to -50 °C. For situations where colder cryogens are being used, this standard should be met, but confirmation should be obtained from the glove manufacturers that their product is suitable for the

temperatures which may be encountered. When selecting the appropriate gloves, consideration must be given to the level of dexterity required during the work, as the lower the temperature capability of the glove, the lower the level of dexterity in the glove. This may result in a re-assessment of equipment controls to enable the activity to be carried out safely.

If severe spraying or splashing is likely to occur, eyes should be protected with a face shield and suitable goggles. Trousers should be worn outside boots and have no pockets or turn-ups. No open footwear, such as sandals, or lace-up shoes/boots should be used. The use of aprons may be necessary depending on the application.

1.1.1.2 First aid (cryogenic burns)

Flush the affected areas of skin with copious quantities of tepid water, but do not apply any form of direct heat, e.g. hot water, room heaters, etc. Move the casualty to a warm place (about 22°C; 295 K). If medical attention is not immediately available, arrange for the casualty to be transported to hospital without delay. Treatment for shock may be necessary.

While waiting for transport:

- (a) Loosen any restrictive clothing.
- (b) Continue to flush the affected areas of skin with copious quantities of tepid water.
- (c) Protect frozen parts with bulky, dry, sterile dressings. Do not apply too tightly so as to cause restriction of blood circulation.
- (d) Keep the patient warm and at rest.
- (e) The patient should not be administered pain killers.
- (f) The patient can be given oxygen if available.
- (g) Ensure ambulance crew or hospital is advised of details of accident and first aid treatment already administered.
- (h) Smoking and alcoholic beverages reduce the blood supply to the affected part and should be avoided.

1.1.2 Oxygen deficiency (anoxia)

None of the gaseous forms of the common cryogenics (Table 2 in Section 1.2.4.) have any odour, and therefore they cannot be detected by smell. Apart from oxygen, all the gases are asphyxiants. Accounts of the symptoms arising from the sudden and gradual onset of oxygen deficiency in the atmosphere are given below.

1.1.2.1 Sudden asphyxia

In sudden and acute asphyxia, such as that from inhalation of a gas containing practically no oxygen, unconsciousness is immediate. The victim falls as if struck down by a blow on the head and may die in a few minutes, unless immediate curative action is taken.

1.1.2.2 Gradual asphyxia

Sudden asphyxia is the most common form encountered in practice but degrees of asphyxia will occur when the atmosphere contains less than 20.9 % (volume) of oxygen.

The four stages of asphyxia are described below [3]. It should be appreciated that the concentrations given are rough guides only and may vary with individuals and ambient conditions.

- (a) *1st stage* – oxygen reduced to 14 %. The first perceptible signs of anoxaemia (oxygen deficiency) develop. The volume of breathing increases and the pulse rate is accelerated. The

ability to maintain attention and think clearly is diminished, a fact that may not be noticed by the individual. Muscular co-ordination is somewhat disturbed.

- (b) *2nd stage* – oxygen reduced to range 14–10 %. Consciousness continues but judgement becomes impaired. Severe injuries may cause no pain. Muscular efforts lead to rapid fatigue. Emotions, are heightened particularly ill-temper.
- (c) *3rd stage* – oxygen reduced to range 10–6 %. Nausea and vomiting may appear. Victim loses ability to perform any vigorous muscular movements or even to move at all. Up to or during this stage, the victim may be wholly unaware that anything is wrong. Then the legs give way, leaving the victim unable to stand, walk or even crawl. This is often the first and only warning, and it comes too late. The victim may realise that death is imminent, but does not greatly care. No pain will be experienced. Even if resuscitation is possible, permanent damage to the brain may result.
- (d) *4th stage* – oxygen reduced below 6 %. Respiration consists of gasps, separated by periods of increasing duration. Convulsive movements may occur. Breathing then stops but the heart may continue to beat a few minutes longer.

1.1.2.3 Exhaustion of oxygen due to breathing in enclosed space

It is worth noting that the effects (described in 1.1.2.2 above) resulting from oxygen deficiency due to addition of inert or asphyxiant gas are very different to those which result from consuming oxygen in an enclosed space by respiration. In the latter case, oxygen absorbed is replaced by exhaled carbon dioxide. This causes discomfort and panting, thus giving early warning of oxygen depletion.

1.1.2.4 Safe systems of work - entry into confined spaces

Oxygen-deficient atmospheres can arise from venting and purging operations. Note that inert gases which are heavier than air, e.g. argon and cold nitrogen present a special risk because of their tendency to accumulate in low places such as pits, gullies, etc.

In the United Kingdom the Confined Spaces Regulations 1997 [4] state that 'no person at work shall enter or carry out any work in or (other than as a result of an emergency) leave a confined space otherwise than in accordance with a safe system of work which, in relation to any relevant specified risks, renders that work safe and without risks to health'. The Regulations also require that adequate arrangements must be made for the rescue of persons in the event of an emergency.

The Management of Health and Safety at Work Regulations 1999 [5] require that a competent person (typically a shift manager) will be responsible for identifying the hazards present, assessing the risks and determining what precautions to take. The assessment will include:

- (a) The job to be carried out.
- (b) The working environment.
- (c) Working materials and tools (e.g. harnesses, breathing apparatus).
- (d) Oxygen deficiency monitoring via personal monitors.
- (e) Gas monitoring for specific flammable / toxic gas which may be encountered (e.g. methane)
- (e) The competence and training of those carrying out the work.
- (f) An emergency rescue plan that is documented and rehearsed.

Entry to a confined space will normally be conditional on the issue of a "Permit to Work" certificate which will require that a formal check is undertaken by a competent person to ensure that all elements of a safe system of work are in place before persons are allowed to enter or work in the confined space. The permit to work certificate (signed by the competent person) should state, among other requirements, that any equipment used is properly isolated from live systems, does not contain potentially hazardous substances and is adequately ventilated. The gas in the confined space should be monitored to assess the reduction in oxygen level and the ingress of flammable or toxic gas during the work period. This should be conducted continuously by using personal gas monitors which detect

oxygen levels and the gas likely to be encountered. The rescue plan should be prepared and rehearsed before the issue of the permit certificate.

The permit certificate should be retained by the competent person for inspection on request by any supervisor. The supervisor must make sure that any person working on a job covered by a permit to work certificate understands:

- (a) The conditions stated on the certificate.
- (b) The fact that the certificate is valid only while these conditions apply.
- (c) The fact that the certificate is withdrawn automatically if there is any change in these conditions or in the job itself or when time expires.

1.1.2.5 Rescue and first aid

Rescue personnel should ensure that they are adequately trained and equipped with breathing apparatus, air supply lines, etc., before attempting to remove anybody overcome in an oxygen-deficient atmosphere. Victims should be removed immediately to a normal atmosphere. If they are not breathing, it is vitally important to start artificial respiration at the first opportunity, preferably by the use of an automatic resuscitator employing oxygen gas, or alternatively by the mouth or other unaided method.

1.1.2.6 Hazard warning signs

There is no approved hazard warning sign for asphyxiant gases but the symbol in Fig. 1 is generally accepted throughout the EU and other European countries [6].



Fig.1 Asphyxiation hazard warning sign

1.1.3 Toxicity

With the exception of carbon monoxide, the gases dealt with in this manual may be regarded as non-toxic. Abnormally prolonged exposure to some of them, however, may result in adverse effects. High concentrations, especially of hydrocarbons, may cause some nausea, drowsiness, or dizziness. Removal from exposure usually causes the symptoms to disappear rapidly.

1.1.4 Hot burns

Hot burns can arise from leaking flammable liquids and gases which have ignited, such as liquid or gaseous hydrogen, natural gas, ethane, LPG or ethylene. Burns may be caused either by direct flame impingement or thermal radiation. Whereas flames from hydrocarbon gases are mostly luminous, hydrogen flames emit only very little visible radiation and are therefore difficult to see in a well-lit situation.

Maintenance of any cryogenic plant handling flammable gases should include prompt attention to product leakage.

1.1.4.1 First aid (burns arising from exposure to high temperatures)

The affected areas should be treated with cold water for at least 20 minutes, and a sterile gauze dressing applied. In serious cases medical help should be summoned immediately.

1.1.5 General cold exposure (hypothermia)

Hypothermia occurs due to the body being unable to maintain its normal temperature due to prolonged exposure to low temperatures. The dangers of hypothermia may be present at temperatures below 10 °C (283 K).

Individuals not suitably protected against low ambient temperatures may be adversely affected so far as their reactions and capabilities are concerned.

1.1.5.1 Precautions

Personnel should be protected by suitable Personal Protective Equipment (PPE) against low ambient temperatures which may occur, for example, in confined spaces and large cold storage units i.e. freezers.

1.1.5.2 First aid (hypothermia)

Persons apparently suffering from the effects of hypothermia should be removed from the cold area to a warm environment, ~22 °C (295 K).

1.2 Safety

1.2.1 Safety devices

Safety devices are installed on plant and equipment to provide protection in the event of emergencies or abnormal operating conditions which may otherwise result in equipment failure, fire or damage. Provided the plant and equipment are operated properly, such devices will seldom be called upon to operate.

1.2.1.1 Pressure relief devices

- (a) Pressure relief devices may be either spring-loaded safety valves, pilot operated safety valves or rupture discs.
- (b) The volumes of gas released from unit volumes of liquid as given in Table 2 show that a vessel initially containing a cryogenic liquid at 1 bar which warms to ambient temperature may result in a pressure increase of between 400 and 1400 bar. Therefore, vessels and piping containing cryogenic liquids must be protected by suitable relief devices adhering to the relevant codes of practice [7].

- (c) Vents from pressure relief devices should discharge fluids and gases to a safe area away from personnel and equipment or structures, in compliance with prescribed safety distances [8].
- (d) All pressure relief valves should be operationally inspected and checked on a regular basis for leakage and frosting. Relief valves which are leaking or 'feathering' below their set pressure will result in excessive ice formation on the valve body, which may prevent the proper operation of the valve and which also may indicate an operational problem on the pressure system itself. In extreme situations plugging of the discharge line may occur, rendering the pressure relief system inoperable.
- (e) Rupture discs should be visually inspected on a regular basis.

1.2.1.2 Alarm and shutdown systems

Devices such as pressure, flow, temperature, atmosphere monitoring or level switches will be designed to activate audible or visual alarms and/or shut down the equipment in an emergency. The audible differentiation between the various types of alarms should be considered.

1.2.1.3 Proof testing of safety devices

- (a) Pressure relief devices should be visually inspected at 12-monthly intervals and tested every 3 to 6 years. The frequency of inspection and testing will depend on the nature of the pressure system, the relevant scheme of testing required and the applicable codes of practice.
- (b) The proof testing frequency for alarm and shutdown systems should be based on a quantitative risk assessment of the system [9].

1.2.2 Fire hazards

For a fire or explosion to occur, three elements are required: the igniter; the fuel; and the oxidant. These are commonly represented in the fire triangle (Fig.2). The following are examples of factors leading to fire and explosion hazards:

(a) *The igniter*

Any source of heat must be regarded as an igniter in the presence of air and fuel gas. Examples are:

- (i) Naked flame.
- (ii) Lit cigarette.
- (iii) Sparks.
- (iv) Molten metal from cutting and/or welding.
- (v) Friction.
- (vi) Static electricity.
- (vii) Electrical equipment (outside its certified area).

(b) *The fuel*

- (i) Combustible gases.
- (ii) Combustible liquids.
- (iii) Oils.
- (iv) Rags.
- (v) Timber.
- (vi) Paper.
- (vii) Organic-based insulants and solvents.

(c) *The oxidant*

- (i) Air.
- (ii) Oxygen.
- (iii) Nitrous oxide
- (iv) Certain acids, and their salts, e.g. nitric acid, ammonium nitrate.

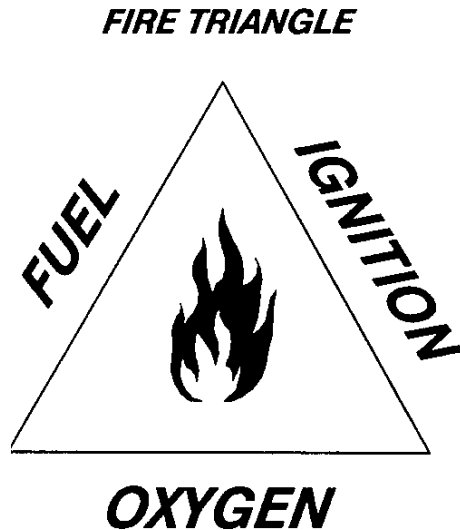


Fig.2 The Fire Triangle - the three components necessary for fires to occur

1.2.2.1 Flammability Limits of Gases

It is important to understand that for flammable gases there are, under given physical conditions, both 'lower' (LFL) and 'upper' (UFL) limits of flammability [10]. Within, but not outside, these limits self-propagation of a flame can occur once ignition has occurred. These limits depend on:

- (a) Dimensions of the vessel or containment involved
- (b) Direction of flame propagation
- (c) The system pressure
- (d) The temperature of the gas mixture
- (e) The quantity of inert gases in the mixture

In practice, flammable gas hazards normally arise at atmospheric pressures and temperatures where small temperature/pressure variations have little effect on the flammability limits. The flammability limits for different cryogenic related air-gas mixtures per cent by volume are presented in Table 1.

Table 1. The lower and upper flammability limits of various cryogenic gases.

Gas	LFL %	UFL %
Ammonia	15.0	28.0
Butane	1.8	8.4
Carbon Monoxide	12.5	74.0
Deuterium	4.9	75.0
Ethane	3.0	12.4
Ethylene	2.7	36.0
Hydrogen	4.0	74.0
Isobutane	1.8	8.4
Methane	5.0	15.0
Propane	2.1	9.5

1.2.2.2 *Emergencies*

Where a fire occurs in an installation containing a flammable cryogenic fluid the emergency fire services should be contacted without delay. The subsequent means of containing the fire is to cut off the supply of fuel to the fire. If this is not possible, it may be preferable to let the fire burn itself out. If the fire is extinguished without stopping the escape of fuel, large volumes of a flammable gas/air mixture may be formed and subsequently ignited by either a local or remote source.

Information on fire precautions for specific cryogenic fluids is given in the appropriate parts of this manual. All installations with a specific fire risk should have a formally prepared and agreed fire-fighting plan with personnel trained in its implementation. Fire practices should be held at regular intervals. Regular meetings should be held with the local fire brigade to ensure awareness of any special fire risks and the recommended means of countering them.

1.2.3 **Oxygen enrichment**

In situations where oxygen enrichment of the atmosphere can occur, a potential fire hazard exists. The atmosphere normally contains 21 % (volume) of oxygen. Enrichment to only 25 % may give rise to a significant increase in the rate of combustion of burning materials exposed to such an atmosphere. Many materials, including some common metals which are not flammable in air, may burn in oxygen enriched atmospheres when ignited. Hazards arising from oxygen enrichment are further explained in Chapter 2.

1.2.4 **Properties of fluids, solids and gases at low temperatures**

1.2.4.1 *Cryogenic fluids*

The physical properties for liquid cryogenics are presented in Table 2.

1.2.4.2 *Mechanical properties of solid materials*

The physical properties of many solid engineering materials can change significantly as temperatures fall. In particular, the toughness of materials may be considerably reduced at low temperatures and allowance must be made for this in the design of cryogenic plant (see Fig.3).

The change in mechanical properties with reducing temperature is often very abrupt. Many materials undergo a ductile to brittle transformation at a characteristic transition temperature. Carbon and certain steel alloys are examples of metals exhibiting such behaviour. Below the transition temperature, toughness is considerably reduced, and relatively low levels of stress or shock loading may result in brittle failure. Similar behaviour may be observed in other materials, including many elastomers, polymers and composites. Even if a material does not undergo a ductile to brittle transition, repeated thermal cycling may result in stress cracking and ultimately fatigue failure.

There are records of incidents where carbon steel pipelines, designed solely for warm gas service, were inadvertently exposed to cryogenic liquid either as a result of leaking valves or poor system design. In each case, the sudden cooling of the carbon steel below its transition temperature, in combination with the elevated operating pressure and residual stresses in the piping, resulted in a catastrophic failure of the pipeline [12].

When servicing or modifying cryogenic plants, it is essential that only components correctly specified for the conditions of service are used. In the absence of any new recommendations, or revisions of existing codes of practice that might be relevant, adherence to the original material and design specifications must be maintained. Consideration must be given to the lowest possible temperature that equipment might experience under fault conditions, and an appropriate margin of safety included in any design [13]. It must be emphasised that cryogenic plant may not be as durable as systems operating at ambient temperatures [14].

Table 2 Physical properties of various cryogenes

	Helium	Hydrogen	Neon	Nitrogen	Air	Argon	Oxygen	Methane	Krypton	Xenon	Ethylene	Ethane	Propane	Butane
Chemical symbol	He	n-H ₂	Ne	N ₂		Ar	O ₂	CH ₄	Kr	Xe	C ₂ H ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀
Molecular weight	4	2	20	28	28.9	40	32	16	84	131	28	30	44	58
Normal boiling point °C (K)	-269 (4.2)	-253 (20.2)	-246 (27.2)	-196 (77.2)	-199.3 (78.9)	-186 (87.2)	-183 (90.2)	-161 (112.2)	-152 (121.2)	-109 (164.2)	-104 (169.2)	-89 (184.2)	-42.1 (231.1)	-0.6 (272.6)
Freezing temperature °C (K)	-	-259 (14.2)	-249 (24.2)	-210 (63.2)	-	-189 (84.2)	-219 (54.2)	-183 (90.2)	-169 (104.2)	-140 (133.2)	-169 (104.2)	-183 (90.2)	-187.75 (85.45)	-135.2 (138)
Critical temperature °C (K)	-268 (5.2)	-240 (33.2)	-229 (44.2)	-147 (126)	-140.7 (132.5)	-122 (151)	-119 (154)	-82 (191)	-63 (210)	+17 (290)	+10 (283)	+32 (305)	+97 (370)	+152.8 (426)
Critical pressure, bars	2.3	12.8	26.5	34.0	37.9	49.0	50.4	46.0	55.0	58.2	50.4	48.7	42.1	36.0
Volume of gas at 1 bar, 15°C released from liquid boiling at 1 bar	739	826	1417	678	713	824	843	613	689	533	482	430	312	241
Density of saturated liquid at 1 bar (kg m ⁻³)	125	71	1206	807	875	1395	1142	423	2415	2942	568	544	581	601
Gas density relative to dry air. (at 1 bar, 15°C)	0.14	0.07	0.70	0.98	1.00	1.40	1.12	0.56	2.93	4.61.	0.97	1.05	1.52	2.00
Latent heat of vaporisation at 1 bar (cooling potential of phase change) (h _{fg} kJ kg ⁻¹)	20.7	446	85.7	199.0	202	161.4	213.1	510.6	108.0	96.5	482.9	488.5	426	386
Fire/explosion hazard	no	flammable	no	no	Yes	no	yes	flammable	no	no	flammable	flammable	flammable	flammable
Air liquefaction hazard	yes	yes	yes	yes	yes	no	no	no	no	no	no	no	no	no

Notes: Pressures are in bars absolute.

With the exception of liquid oxygen, which is light blue, all the liquid cryogenes referenced above are colourless. All the cryogenes referenced above are considered to be non-toxic except for ethylene and ethane both of which have a slight anaesthetic effect.

The thermo-physical properties have been reproduced from the software package GASPAK by kind permission of Cryodata Inc. [11].

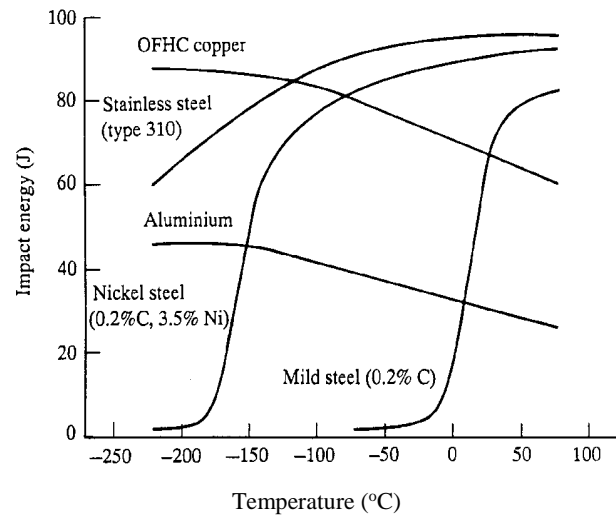


Fig.3 Toughness (impact energy) as a function of temperature for various materials

(Note: These data for Charpy V-notch impact tests have been compiled from a number of different sources and should be used for comparative purposes only)

When designing new process plants, or planning modifications to existing units, it is important to identify the potential hazards that could arise during operation. Established techniques, such as Hazard and Operability studies (HAZOP) [15] and/or Hazards Analysis (HAZAN) [16] should be used for this purpose. The results of these studies will then enable engineers to introduce necessary safety systems, such as pressure relief devices, alarms, trips etc., to mitigate the effects of the hazards and prevent serious incidents that might cause injury to personnel or damage to equipment.

1.2.4.3 Contraction of solid materials

Most materials contract when cooled. In cooling from ambient temperature to liquid nitrogen temperature, -196 °C (77 K), the metals and alloys commonly employed in the construction of a cryogenic plant might typically contract by up to 0.3 % (3 mm per metre). Unless such contraction has been allowed for in the design, leakage due to movement of joints may result.

Stresses due to thermal contraction can be significant and in extreme cases complete failure can occur. Fatigue failure due to thermal cycling is also possible. Coefficients of expansion (contraction) for some of the materials used in cryogenic plant are given in Table 3.

Table 3 Coefficients of expansion for various materials

Temperature (°C)	Aluminium	Brass	Invar (63.8 %Fe, 36.0 %Ni, 0.2 %C)	Stainless Steel (Austenitic)	Pyrex Glass	PTFE
-250	0	1	0	0	-1.0	37
-200	18	26	1	13	-0.5	186
-150	75	88	10	62	9	395
-100	162	168	21	120	21	691
-50	262	256	30	190	34	1216
0	370	347	47	265	49	1487
+15	430	396	53	306	56	1596

Note: The numbers in the table must be multiplied by 10^{-5} to give the coefficient (α), $\Delta l = l_0 \alpha \Delta T$, [K^{-1}] [17]

1.2.4.4 *Ice formation of liquids*

Water may be present in a cryogenic plant as a result of condensation or liquid ingress from an external source. If an accumulation of water freezes in the pipework or vessels of the plant, the expansion that occurs during the phase change to ice may be sufficient to rupture that part of the system. Such damage may remain undetected until cryogen is introduced to the system when leakage and subsequent damage can occur. Such damage can be avoided by ensuring that the plant is thoroughly dried out with warm air before cool-down.

Damage may also be caused to external insulation following the ingress of either damp air or water. In addition to increasing the rate of heat leak, such deterioration may affect the structural integrity of the insulation and result in corrosion of underlying metal that might escape detection.

1.2.4.5 *Gaseous expansion in containers*

Equipment and pipework containing a cryogenic liquid could be subject to severe overpressure due to thermal expansion of the liquid or vaporisation of the liquid in a closed system. This will result from heat leak or, in the case of liquid expansion, loss of secondary cooling. Specification guidance for spacing and sizing of relief valves should be followed with care.

1.2.5 Cryogen leakage and consequent hazards

The leakage of any cryogenic substance must be considered potentially hazardous. In addition to the hazards associated with the very low temperatures, the leakage of cryogenics such as hydrogen and oxygen present major fire and explosion hazards. The implications of a leak, both in terms of injury to personnel, cryogen loss, subsequent damage and repair costs, must also be considered. Two main causes of leakage may be identified: leakage resulting from contraction and leakage following damage due to freezing. The likelihood of leakage will be minimised in a plant that is correctly designed, assembled and maintained.

1.2.6 Gas detection

1.2.6.1 *Oxygen*

Instruments used for oxygen detection employ either the paramagnetic, zirconia or electrochemical principle. The instruments may be either fixed installations, for continuous gas analysis, or portable, for carrying out spot checks of atmospheres in or around various items of plant equipment.

The lightest and most portable instruments, including those of the personal pocket-sized variety, are generally of the electrochemical cell type and are battery-operated. With these types of instrument care must be taken to ensure that both the cell and battery are in good order before attempting to measure atmospheric oxygen concentration. The life of the cell as quoted by the supplier should not be exceeded and the battery should be replaced when it is approaching exhaustion. Some instruments incorporate battery test circuits.

The paramagnetic types of analyser are also available as portable instruments. Although they are usually heavier than the electrochemical cell type, they require less maintenance and can be operated from either standard mains power supply or batteries.

The zirconia types of analyser are available only as fixed instruments for continuous process monitoring.

Whichever type of instrument is used, it is important to ensure that it is well maintained and calibrated at frequent intervals. When checking atmospheres with portable analysers, it is advisable to ensure the instrument is calibrated, and the instrument has been 'bump tested' (i.e. exposed to a target gas sample) before use; with most portable analysers calibration can be effectively carried out using atmospheric air, without the need for special calibration gas mixtures.

1.2.6.2 Flammable gas detectors

Most flammable gas detectors rely on combustion of the gas in question on the surface of a heated catalytic element. This raises the temperature of the element, and the difference between the normal running temperature of the element and that in the presence of the burning fuel gas sample is displayed on a meter, which is usually calibrated in percentage of the lower explosive limit for a given kind of gas.

Types of instrument vary. Some operate continuously in a fixed installation to give warning of excessive gas concentration at any of several measuring points; others are battery-driven and portable and switched on only when a test is required. It is important to ensure that the gas detector is well maintained and within its calibration period, and the instrument has been 'bump tested' before use

Alarms, either audible or visual or both, may be provided.

1.2.6.3 Toxic gas detectors

These, by definition, cover a broader range of compounds than those described in the two preceding sections. The most common toxic gas encountered in cryogenic gas separation plants, e.g. hydrogen separation plants, is carbon monoxide. Monitoring and detection of toxic gases in the atmosphere can be achieved on a continuous basis by permanently installed process analysers linked to gas alarm systems, or on an intermittent basis by using portable detectors. The latter type should be used with caution, depending upon the risk and degree of exposure of the operator to toxic gases.

Portable detectors can be either battery-operated instruments or in the form of reagent tubes. The reagent tube is the cheapest method of detection and is generally reliable as a means of obtaining a quick, approximate indication of toxic gas concentration, but only at that point in time. Battery powered portable gas detectors may also be used, but it is important to ensure that they are equipped with the appropriate sensor for the gas expected to be encountered. It is important to ensure that the gas detector is well maintained and within its calibration period, and the instrument has been 'bump tested' before use.

1.2.6.4 Multi-gas portable detectors

These gas detectors are capable of measuring high and low oxygen levels, flammable gas and toxic gas, all within one unit.

Care must be taken to ensure that the gas detector is equipped with the appropriate flammable and toxic sensors for the gases likely to be encountered. The gas detector must be maintained and within its calibration period, and the instrument 'bump tested' before use.

1.2.7 Distribution of cryogenics

Cryogenic liquids are stored and distributed using purpose-designed equipment for each product. Transport of large quantities of cryogen may be by road tanker, ISO containers, ship or pipeline. Smaller quantities are conveniently handled in portable cryogenic storage dewars, transportable liquid cylinders and other insulated vessels. Cryogenic vessels should not be transported in passenger vehicles due to the potential hazards posed by liquid leakage and asphyxiation. The design and construction of the equipment used to transport cryogenics takes into account the physical and chemical properties of the specific products. In all cases, distribution must be accomplished in complete safety and with minimum loss of cryogen.

1.2.7.1 Pipelines

Insulated pipelines may be used to convey cryogenics over distances from a few metres to several hundred metres. The maximum distance will depend on the product and the quality of insulation. For short distances, solid insulant is most commonly employed; however over longer distances or for

using with liquid helium vacuum insulated pipelines are more commonly used. The general safety considerations relating to cold surfaces and insulation breakdown are obviously applicable, but the operation and maintenance of a pipeline is a specialised undertaking and in every case the designated operating procedures must be strictly followed. An inspection, testing and recording schedule should be implemented in accordance with the correct regulations.

1.2.7.2 Road tankers

These are relatively sophisticated vehicles. Drivers and operators must receive formal training in correct operating procedures, including those for preventing product contamination or loading of the wrong product. This is particularly important where flammable or oxidising products are concerned. All road tankers must be clearly identified with the product name and carry appropriate safety and emergency instructions. A typical cryogenic liquid road tanker is shown in Fig.4.



Fig.4 Typical cryogenic road tanker (courtesy BOC)

1.2.7.3 ISO containers

ISO (International Standards Organization) shipping containers are manufactured to strict size specifications in terms of exterior height, exterior width, and exterior length to ensure that all containers can be accommodated by all equipment handlers, chassis, rail cars, and slot spaces on vessels. Fig 5 shows an example of a vacuum insulated ISO container for the transport of cryogenics.



Fig.5 Typical ISO container (courtesy of Wessington Cryogenics)

1.2.7.4 Dewars and insulated vessels

Insulated containers, or dewars, for the storage and distribution of smaller quantities of cryogen are simple open top vessels, typically of aluminium or stainless steel construction, which are designed to hold up to about 50 litres of cryogen (primarily nitrogen or argon) for short periods of time. See Figure 6. Small capacity glass dewars are also available for laboratory use.

The containers are portable and relatively inexpensive but suffer relatively high rates of boil-off. These containers are durable but must be handled with care to avoid damage. The only significant hazard associated with this type of container is the ease with which they may be knocked over, particularly when only part full, owing to their light weight.

Many designs of vacuum insulated dewar vessels include additional materials in the vacuum space to enhance the quality of insulation. Dewars designed for helium may use a liquid nitrogen-cooled outer vessel. The use of such dewars for liquid hydrogen service, or any other flammable cryogen, would not normally be recommended because of the attendant fire risks.

The majority of dewars are not designed to operate at pressures significantly above or below ambient. Blockage of the neck of a dewar or a loss of vacuum (and hence insulation) can lead to an increase in internal pressure, resulting in catastrophic failure. Partial loss of vacuum may also result in the ingress of atmospheric air, which may condense in the vacuum space. When the dewar subsequently warms up, the trapped liquid air will evaporate and may not be able to escape fast enough to prevent an increase in pressure sufficient to burst the vacuum shell.

In the case of helium dewars, care must be taken to prevent air diffusing down the neck where it can freeze to form a plug. In dewars containing the higher boiling point cryogenics (see Figure 7), such as nitrogen, argon or LNG, ice plugs forming from atmospheric water vapour are the major danger. All dewars should have some form of pressure relief system, but this should not be relied upon. In the event of a dewar becoming blocked the manufacturer's instructions should be followed. Fortunately the rate of pressure increase within a blocked dewar is usually quite slow, provided the insulation is maintained.

1.2.7.5 Transportable liquid cylinders

Liquid cylinders are a special type of dewar designed to hold up to about 1000 litres of cryogenic liquid and to deliver a gaseous product at moderate pressures. Such cylinders are commonly used for all cryogenics. Transport and storage of a product in liquid form has many advantages over the use of high pressure gas cylinders.

Liquid cylinders have inbuilt evaporator and pressure raising circuits. The cylinders are designed to cope with fault conditions, with excess pressure being vented via safety valves. It is important that the safety devices are inspected regularly and that the cylinder is only operated within its rated capacity. In common with all dewars, liquid cylinders should always be handled with care and not subjected to any undue shock or loading.

1.2.7.6 Sea Transport

Following a period of rapid international expansion of the LNG business back in the 1970s, the Society of Gas Tanker and Terminal Operators (SIGTTO; <http://www.sigtto.org/>) was formed. Based in London, and formed originally with thirteen members, SIGTTO has grown to a membership of over 170, representing nearly all the world's LNG business (and more than half the global LPG business). Member companies are concerned to share experiences, address common problems, derive agreed criteria for best practice and essential common standards for the industry, to aid its expansion and underpin public confidence.

The Society publishes studies and produces information papers and works of reference on safety, technical and other topics for the guidance of industry members. It maintains working relationships with other industry bodies, governmental and intergovernmental agencies, including the International Maritime Organisation (IMO), to better promote the safety and integrity of gas transportation and storage schemes. Details of the publications available are shown on the SIGTTO website.



Fig.6 Selection of open-top cryogenic containers



Fig.7 Selection of transportable cryogenic containers for liquid nitrogen.

1.2.8 Operational hazards associated with specific cryogenics related equipment

1.2.8.1 Cryo-cooler maintenance and operation.

Cryo-coolers are used to cool some applications (such as cryogen-free cryostats, magnets, dilution refrigerators, cryo-detectors etc.) to cryogenic temperatures. A recent review is given by Radebaugh [18].

Always refer to the cryo-cooler operating and/or maintenance manuals for safety guidance concerning a specific system.

1.2.8.1.1 High pressure gas hazards

- (a) Gas lines should only be disconnected when the compressor is not running.
- (b) The cold head can be disconnected only at ambient temperature. Disconnecting it while it is cold can create excessively high internal pressure because of helium fluid expansion during warming. Uncontrolled pressure releases due to material failure can cause injury.
- (c) Compressed helium gas can be supplied only from a cylinder with a proper regulator. Overpressure can cause system equipment ruptures which can lead to personal injury.
- (d) Loosening of the cold head coupling (when disconnecting a gas line coupling by using two wrenches) should be avoided. A gas-charged component should always be vented before the disassembly of its couplings. Gas pressure can propel the loose coupling with enough force to cause injury.

- (e) When releasing the vacuum with dry air or nitrogen, the cold head can be filled only to atmospheric pressure.
- (f) Eye protection should always be worn during the handling of pressurised gas lines and other pressurised components.
- (g) Heat should never be applied to a pressurised gas line or other pressurised components.

1.2.8.1.2 Injury from burns

- (a) During operation, some compressor components under the system cover become hot.
- (b) Allow the compressor to cool for ~ 30 minutes after switching off before removing the cover.

1.2.8.1.3 High voltage hazards

- (a) Disconnect the power to the system before troubleshooting the electrical components.
- (b) Permit only qualified personnel to open electrical enclosures to perform electrical checks, maintenance or repairing procedures of electrical equipment. Failure to observe this warning can result in injury or death.
- (c) All supply connection needs to be installed by qualified personnel and must meet applicable codes.

1.2.8.2 Superconducting magnets and magnetic fields [19]

A superconducting magnet is an electromagnet made from coils of superconducting wire. This kind of magnets requires a cryogenic environment during operation in order to maintain the superconducting state. Superconducting magnets are used in Magnetic Resonance Imaging (MRI) machines in hospitals, and in scientific equipment such as Nuclear Magnetic Resonance (NMR) spectrometers, mass spectrometers, magnetic field sample environment and particle accelerators. The strong magnetic field hazard warning sign is presented in Fig.8.



Fig.8 Strong magnetic field hazard warning sign.

1.2.8.2.1 Collision Hazards A danger frequently encountered in a strong static magnetic field comes from unfixed magnetic objects. The field may be strong enough to attract such objects and to cause them to fly along the field lines towards the magnet - the 'missile effect' - which may lead to crushing injuries. Therefore metallic objects, particularly magnetic objects with sharp edges, keys, scissors, tools, gas cylinders, trolleys etc. may become dangerous projectiles and their use should be controlled in any areas where the magnetic field exceeds 0.2 T. Consideration should be given to

establishing systematic search protocols before such magnetic fields are started up to ensure that relevant areas are free from loose magnetic objects.

1.2.8.2.2 Permanent Magnets Permanent magnets, particularly rare earth magnets, can pose extra hazards if they are in close proximity to high field cryogenic magnets. Extra precautions need to be taken when handling them in such an environment.

1.2.8.2.3 Movement of conducting materials in static magnetic fields The movement of conducting materials in strong static magnetic fields can result in the generation of eddy currents in the conductor which should be considered if assessing hazards.

1.2.8.2.4 Effect on medical implants Persons having artificial metallic implants may feel painful sensations. Owners of heart pacemakers, for instance, should be aware of the possibility of interference from magnetic fields. The warning sign for owners of heart pacemakers is presented in Fig.9.

According to the International Commission on Non-Ionizing Radiation Protection (ICNIRP): “practical policies need to be implemented to prevent inadvertent harmful exposure of people with implanted electronic medical devices and implants containing ferromagnetic materials, and injuries due to flying ferromagnetic objects, and these considerations can lead to much lower restriction levels, such as 0.5 mT” [20].



Fig.9 Warning sign for owners of heart pacemakers.

1.2.8.2.5 Biological Hazards Although present knowledge of the possible biological effects of strong static magnetic fields is still somewhat uncertain, some evidence has been obtained which indicates that simple biological systems may be affected by exposure to strong static magnetic fields. There is no specific information regarding possible long term health effects from exposure and none have been observed so far.

Investigations have been carried out to ascertain the effect of magnetic fields on humans, and very few have shown any effect; in one or two cases associated with high magnetic fields it has been claimed that slight headaches, disorientation and slight feelings of nausea have ensued especially when there is movement in a static magnetic field. The only effect on which there appears to be some agreement is that of a taste sensation, possibly due to loose metal fillings in teeth, when exposed to high magnetic fields.

The World Health Organization (WHO) states that: "For static magnetic fields in excess of 2-4 T, physical movement in static field gradient will induce sensations of vertigo and nausea that, although

transient, may adversely affect people. Together with possible effects on eye-hand co-ordination, the optimal performance of workers executing delicate procedures could be reduced, with a concomitant impact on safety. Other acute effects are less clearly established; cardiovascular responses, such as changes in blood pressure and heart rate, have occasionally been observed in volunteer and animal studies, but lie within the normal range below 8 T." [21]

It is therefore recommended, wherever possible, that reasonable and simple measures to limit such exposure should be adopted, particularly exposure of the head or whole body. Where exposure to high magnetic fields in working situations cannot be avoided then the ICNIRP limits (spatial peak exposure limits) given in Table 4 should be considered.

Table 4 International Commission on Non-Ionizing Radiation Protection (ICNIRP) limits [20]

Category	Exposure characteristics	Magnetic flux density (B)	Commentary
Occupational	Exposure of head and trunk	2 T	For specific work applications, exposure up to 8T can be justified, if the environment is controlled and appropriate work practices are implemented to control movement induced effects.
	Exposure of limbs	8 T	
Public	Exposure of any part of the body	0.4 T	Because of potential indirect adverse effects, ICNIRP recognises that practical policies need to be implemented to prevent inadvertent harmful exposure of persons with implanted medical devices and implants containing magnetic material, and dangers from flying objects, which can lead to much lower restriction levels such as 0.5mT.

1.2.9 Safety control procedures

1.2.9.1 Work permit systems

There will be occasions when it will be necessary, either on a planned or emergency basis, to carry out work either on or in the vicinity of a gas processing plant which may call for inspection, modification, maintenance, or repair, and which usually requires a departure from normal production routine. Under these conditions plant maintenance personnel or contractors may be exposed to danger purely as a result of ignorance of the potential hazards which may exist. Such hazards, which have already been described, include pressurised systems, low temperature fluids, and flammable, asphyxiating or oxygen-rich atmospheres.

If accidents are to be prevented, it is vital that the closest possible understanding exists between those responsible for production and those carrying out the repair and maintenance work. Experience has shown that the maximum degree of safety can be achieved by using a 'permit to work' system as a formal and disciplined procedure. This requires that a competent person is assigned to identify the hazards, assess the risks and determine what precautions must be taken. [9]

The work permit certificate will require that a formal check is undertaken to ensure that all the elements of a safe system of work are in place before persons are allowed to start the work. The work permit certificate will normally be prepared by a competent person following which it will be signed by that person, and the individual in charge of the maintenance operation, to the effect that the particular section of plant or piece of equipment is safe for work to begin.

The plant manager should be responsible for ensuring that procedures for operating the work permit system are established and that they are understood and adhered to by all personnel and contractors engaged in the maintenance operation.

1.2.9.2 Checklists

A checklist should be used to ensure that the plant and equipment has been made safe for work to be carried out and that the appropriate safety precautions have been considered. This list may either be built into the work permit itself or used separately as a reminder to those persons responsible for issuing work permits.

Although checklists will not cater for every conceivable hazard, it is possible to itemise the fundamental actions that must be taken to make equipment safe but which can easily be forgotten under pressure of work. The principal items that should be included in a checklist are the following:

1.2.9.2.1 Actions to make plant and equipment safe

- (a) A review of the process flow sheet and of the actual area and equipment where the work is to be carried out.
- (b) Effective isolation of equipment from other parts of the plant or process which may still be 'live' and which could create a hazard by inadvertent operation of a valve, switch, or control system. The checklist shall carefully identify the isolation measures to be taken such as:
 - (i) Isolation valves.
 - (ii) Double block and bleed valves.
 - (iii) Blind flanges or spectacle plates.
 - (iv) Locks, valve tags and/or signs.
- (c) The effective isolation of the power supply from prime movers, e.g. electric motors, steam turbines.
- (d) Effective depressurisation of equipment and provision of adequate arrangements to ensure that it remains depressurised during the entire maintenance operation.
- (e) Normalisation of temperature, to ensure that personnel are not exposed to excessively high or low temperatures.
- (f) Removal of flammable, toxic, or otherwise harmful fluids and materials from process lines, equipment and working environments.
- (g) Analysis of surrounding atmosphere to check on any change of the oxygen content, or existence of explosive or toxic mixtures. This requirement is of prime importance when it is necessary for persons to enter process vessels or equipment, or if hot work is to be carried out.
- (h) Specification of requirements for the carrying out of periodic analyses of the atmosphere. It will be necessary that production staff are aware of the acceptable limits for safe working. A clear statement as to whether work requiring naked flames or other sources of ignition is permitted.
- (k) Provision of emergency arrangements, e.g. fire extinguishers, means of escape, standby personnel.
- (l) A clear statement of any special precautions that may be necessary.
- (m) A reminder that the specified and special safety precautions required do not release the personnel carrying out the work from the responsibility of taking general precautions (signs, area roped off, manholes covered, etc.).

1.2.9.2.2 Protective cryogenic clothing and equipment Some or all of the following, as appropriate:

- (a) Safety glasses and/or face shield.
- (b) Apron.
- (c) Suitable Cryogenic gloves/gauntlets (manufacturers certification required for work with cryogenics below -50°C (223 K))
- (d) Oxygen analyser.
- (e) Flammable gas detector
- (f) Toxic gas detector
- (h) Multi gas detector, equipped with appropriate flammable and toxic sensors
- (g) Suitable footwear

- (h) Ear protection
- (i) Self-contained breathing apparatus or fresh air masks

1.2.9.3 *Special precautions*

Although a general purpose permit system will be adequate for most situations which are liable to be encountered, it may be advisable to introduce additional permit systems to cover specialised areas, examples of which are:

- (a) High voltage electrical equipment.
- (b) Entry into vessels or confined spaces (see 1.1.2.4).
- (c) Work requiring hot work, i.e. the use of flames or other potential sources of ignition.
- (d) Working at height.

1.2.10 **Rapid changes in operating parameters**

When plant handling or processing cryogenic liquids is started up or shut down, rapid changes occur within the system. Rapid changes of flow, pressure, temperature or composition are often the precursor to the realisation of the hazards described in this section. It is important that all personnel involved in the design, operation and maintenance of cryogenic liquid systems recognise this fact.

1.3 **Legislation**

1.3.1 **Major hazards**

The storage of large quantities of cryogenic flammable gases, toxic gases and liquid oxygen is covered by specific safety requirements in European and UK legislation.

An EU Council Directive (96/82/EC) on the 'Control of Major-Accident Hazards Involving Dangerous Substances' was passed in 1996 which set the standard for major hazard legislation in EU countries. In the UK, the EC Directive was initially implemented by the Control of Major Accident Hazards (COMAH) Regulations 1999 which has now been superseded by COMAH 2015 [22]. In addition, the Control of Industrial Major Accident Hazards Regulations 1984 (CIMAH), had specific requirements. This legislation has now been revoked, with the current legislative requirements from this incorporated in the COMAH 2015 Regulations.

In certain circumstances, installations handling cryogenic liquids will be subject to the Dangerous Substances (Notification and Marking of Sites) Regulations 1990 (NAMOS) as amended, 2013. [23]

1.3.2 **Planning/Siting controls**

Planning restrictions will almost certainly apply to locations where storage of the quantities covered by the COMAH regulations is proposed. The storage of smaller quantities of cryogenic flammable gases, toxic gases and liquid oxygen may also be subjected to planning control under the current Planning and Building Control legislation, and it is advisable to consult with these authorities at an early stage.

1.3.3 **Dangerous Substances (Notification and Marking of Sites) Regulations 1990 (as amended 2013) [23]**

Sites containing 25 tonnes or more of dangerous substances must:

- (a) Erect suitable signs at access points to warn those entering the site of the existence of those dangerous substances.

- (b) Notify the appropriate fire and enforcing authorities, giving information specified in the regulations.
- (c) Erect suitable signs at individual locations on site warning of the presence and nature of the hazard of those dangerous substances, as directed by an inspector.

The 25 tonne threshold is an aggregate total.

The following cryogenic liquids are defined as dangerous substances for the purposes of these regulations:

- (a) Liquid oxygen
- (b) Liquid natural gas
- (c) Liquid ethylene
- (d) Liquid ethane
- (e) Liquid carbon monoxide
- (f) Liquid hydrogen

1.3.4 Pressure Systems Safety Regulations 2000 [24] and Carriage of Dangerous Goods and Use of Transportable Pressure Equipment Regulations 2004 [25]

The overall intention of these Regulations is to prevent the risk of serious injury as a result of the failure of a pressure system or part of it. The main requirements of the Regulations are:

- (a) The appointment of competent persons to prepare schemes of periodic examination and testing of the plant and equipment to ensure its fitness for continued use.
- (b) To ensure the proper design and installation of pressure systems with respect to protective devices, safe operation, access and maintenance.
- (c) To establish and maintain records of examination, testing, repairs and modifications to the plant and equipment.
- (d) To ensure the correct marking and identification of pressure vessels.

1.3.5 Control of Substances Hazardous to Health Regulations 2002 [26]

The Regulations place the following duties on employers:

- (a) Not to carry on any work which exposes employees to substances hazardous to health unless an adequate assessment of the risks to health arising from the work have been made and the measures for controlling or preventing exposure identified.
- (b) To make full use of control measures and protective equipment and maintain them in good condition and efficient working order.
- (c) To monitor exposure of employees to substances hazardous to health and implement health surveillance as appropriate.
- (d) To provide employees with information and training in respect of the risks to health and the precautions to be taken.

1.3.6 General Health and Safety Legislation

In the U.K., long standing detailed safety legislation specific to particular industries and work activities is gradually being replaced by general health and safety regulations covering matters such as the prevention of accidents, safety management systems, the assessment of risks, the reporting of incidents and construction safety. Activities involving cryogenic fluids will be subject to this general legislation.

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2 Oxygen, nitrogen and argon

Chapter 2 deals with special precautions which must be observed in the operation and maintenance of air separation plants and product handling and storage equipment. For the purpose of this guide an air separation plant includes all machinery and equipment for the production of oxygen, nitrogen, argon or rare gases by the purification and distillation of liquid air. Handling and storage equipment refers to all pumps, compressors, vessels, and ancillary equipment in service with the gases and liquids produced by the air separation plant. This chapter supplements the general safety requirements of Chapter 1.

2.1 Properties of oxygen, nitrogen and argon at low temperatures

The physical properties for oxygen, nitrogen and argon are presented in Table 5 (taken from Table 2 in Section 1.2.4).

Table 5 Physical properties of oxygen, nitrogen and argon

	Oxygen	Nitrogen	Argon
Chemical symbol	O ₂	N ₂	Ar
Molecular weight	32	28	40
Normal boiling point °C (K)	-183 (90.2)	-196 (77.2)	-186 (87.2)
Freezing temperature °C (K)	-219 (54.2)	-210 (63.2)	-189 (84.2)
Critical temperature °C (K)	-119 (154)	-147 (126)	-122 (151)
Critical pressure, bars	50.4	34.0	49.0
Volume of gas at 1 bar, 15°C released from liquid boiling at 1 bar	843	678	824
Density of saturated liquid at 1 bar (kg m ⁻³)	1142	807	1395
Gas density relative to dry air. (Reference conditions 1 bar, 15°C)	1.12	0.98	1.40
Latent heat of vaporisation at 1 bar (cooling potential of phase change) (h _{fg} kJ kg ⁻¹)	213.1	199.0	161.4
Fire/explosion hazard	yes	no	no
Air liquefaction hazard	no	yes	no

2.2 Specific hazards

2.2.1 Oxygen

2.2.1.1 Fire and explosion hazard

Oxygen is not itself a flammable gas, but vigorously supports combustion. Combustible materials ignite more easily and burn more rapidly and intensely in an atmosphere that contains a higher concentration of oxygen than that of air, i.e. 20.9 % by volume. These effects intensify with increase of oxygen concentration, pressure and temperature. Many commonly used materials not normally combustible in air may burn in pure oxygen or oxygen-enriched atmospheres. Special precautions are therefore essential when using equipment in service with either gaseous or liquid oxygen if fires or explosions are to be avoided. [1, 2]

2.2.1.2 Selection of materials for oxygen service

Only materials which have been properly tested and approved may be used in service with oxygen. Information regarding the selection of such materials should be obtained either from the industrial gas suppliers or published data.

The behaviour of several common substances in contact with gaseous or liquid oxygen is summarised below. The list is not exhaustive, but serves as an indication of the types of materials which may be safely used in oxygen service and those which are not acceptable for use [3].

- (a) *Materials that are highly dangerous*
Flammable liquids and gases; porous flammable materials that will absorb oxygen; bitumen based substances; hydrocarbon-based oils and greases.
- (b) *Materials that are unsafe (will ignite easily)*
Wood; asphalt; paint; clothing materials; cotton waste; finely divided metals and carbon; cork; organic solvents.
- (c) *Materials that will normally be safe (will not ignite easily)*
Stainless steels; mild steel; cast iron and cast steel; aluminium; aluminium bronzes; zinc; PTFE.
Note. Although these materials are normally safe for approved applications, they can ignite under some conditions, particularly in the finely divided state. Particle impingement coincident with high gas velocities is a common cause of ignition. Combustion of such materials in these circumstances can be extremely violent [4].
- (d) *Materials safe under practically all conditions (will not normally ignite in solid form)*
Copper; brass; bronze; gold; silver; nickel; monel and other non-ferrous nickel alloys; oil-free silicate-based insulants.

2.2.1.3 Hazards to personnel

Oxygen is odourless, colourless, and tasteless; therefore atmospheres enriched in oxygen cannot be readily detected by the normal human senses. In general, oxygen should never be released into confined spaces where there is inadequate ventilation [5]. Liquid oxygen and gaseous oxygen are heavier than air and can accumulate in low-lying areas, such as pits and trenches, where the gas may be slow to disperse. Liquid oxygen can also migrate and seep through porous materials, fissures in the soil, cracks in concrete and roadways, drains, and ducts.

Personnel should not enter areas where oxygen enrichment of the atmosphere is suspected without first testing the atmosphere with a suitable gas detector to ensure that the oxygen content lies between 20 and 22 per cent by volume. The principal danger is that body hair, clothing and porous substances may become saturated with oxygen, whereupon they will burn violently if ignited.

Clothing which has been contaminated with an enriched oxygen atmosphere should be well ventilated in the open air for about 15 minutes before the wearer approaches a source of ignition.

2.2.1.4 *Misuse of oxygen*

It is extremely dangerous to use oxygen gas as a substitute for compressed air, nitrogen or other gases. Oxygen should never be used for any of the following or similar applications:

- (a) Starting internal combustion engines.
- (b) Pressurising oil reservoirs.
- (c) Operating pneumatic tools.
- (d) Paint-spraying.
- (e) Inflation of vehicle tyres.
- (f) Blowing out pipelines, etc. (other than oxygen service lines, which may be purged with oxygen).
- (g) Freshening the air or clearing the fumes in a confined space.

The Health and Safety Executive leaflet “Oxygen use in the workplace” INDG459 contains further information on this hazard [6].

2.2.2 **Argon and nitrogen**

2.2.2.1 *Asphyxiation hazards*

Both argon and nitrogen are colourless, odourless, and tasteless, and cannot be detected by the normal human senses. They are non-flammable, but act as asphyxiants by displacing the oxygen from the atmosphere [7]. Argon and cold gaseous nitrogen are heavier than air and may accumulate at low points in pits and trenches. Before entering areas or equipment suspected of being deficient in oxygen, test the atmosphere with an oxygen detector. Personnel should not be exposed to atmospheres containing less than 20 per cent by volume of oxygen.

2.2.2.2 *Fire and explosion hazards*

Oil-lubricated compressors operating continually on nitrogen or argon service for a prolonged period should not be switched to air service without thorough cleaning; otherwise there is a danger that unoxidized pyrophoric deposits which may have formed in the machine will explode violently on contact with compressed air.

At equal pressures, the boiling point of liquid nitrogen is lower than that of liquid air. Air will condense on the external surfaces of vessels or pipework containing liquid nitrogen at an equilibrium pressure less than 1.5 bar absolute if the vessels are either uninsulated or insulated with a porous cellular type material which has not been properly vapour-sealed. The liquid air produced can result in oxygen enrichment of the atmosphere local to the equipment, and if the insulant is combustible, there is a serious risk of fire. Special care must therefore be taken before any maintenance or repair work is started, particularly where the use of open flames or other potential sources of ignition is intended.

2.2.3 **Liquid Air**

Liquid air is not normally supplied commercially. However, if it is intended to use liquid air for any particular reason it must be recognised that it can suffer oxygen enrichment during both condensation and evaporation. For this reason liquid air must be treated in the same way as liquid oxygen and, as such, it must not be used in place of liquid nitrogen as a cold store or for other applications. [8]

2.3 **Safety in the operation of air separation plants**

The operating instructions provided by the plant manufacturer for an air separation plant will usually contain the general safety requirements, together with the particular safety precautions relating to specific operating procedures. It is vital that the plant management and operating personnel both understand and familiarise themselves with all safety requirements and adhere to them in practice.

The basic operation of an air separation plant includes the liquefaction of air inside an insulated enclosure, a cold box. By rectification and distillation it is separated into its main constituents: nitrogen, oxygen and argon. The liquid components are either stored in thermally insulated cryogenic vessels or evaporated and compressed into pipelines for onward distribution. A schematic diagram of a typical air separation process is shown in Fig.10.

The purpose of this section of the manual is to emphasise those areas of operational safety which are of fundamental importance and generally applicable to all air separation plants and handling and storage equipment. [9]

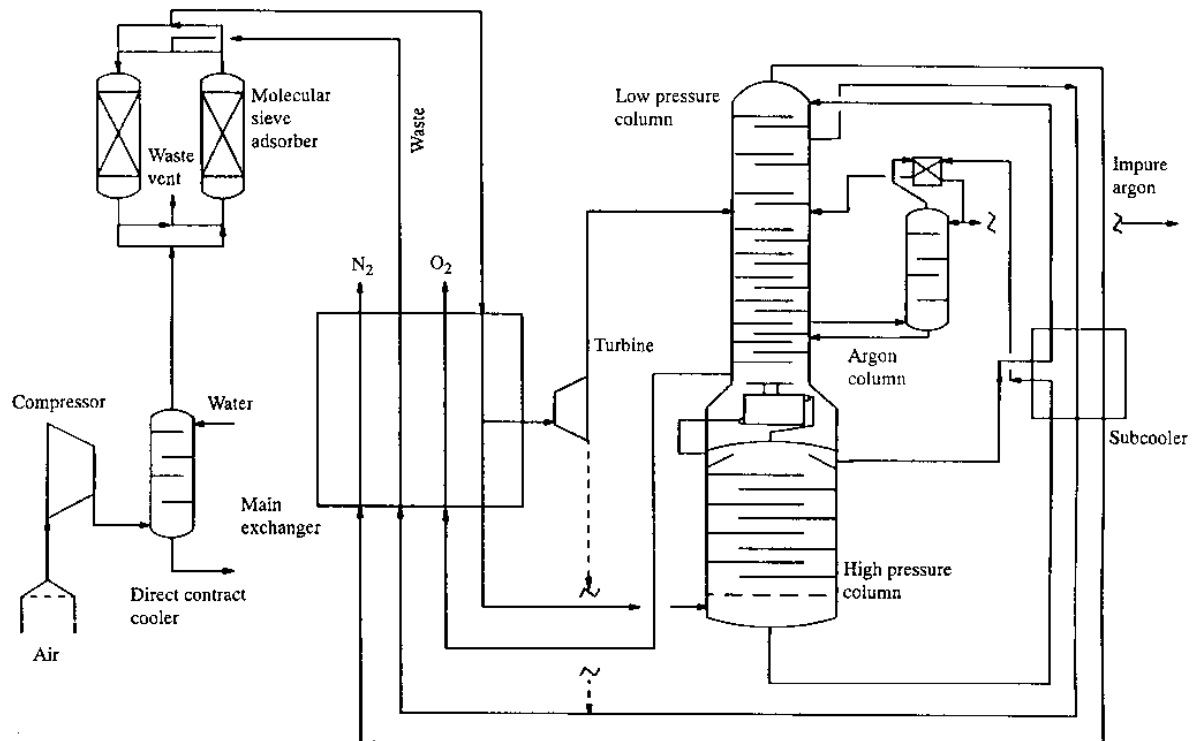


Fig.10 Schematic diagram of a typical air separation process

2.3.1 General

2.3.1.1 Housekeeping

For reasons of general safety and because of the hazards associated with oxygen, it is important to ensure that high standards of housekeeping and cleanliness are maintained throughout the entire factory.

Storage of equipment, spare parts, and potentially hazardous materials such as oil and grease should be located as far away as practically possible from the plant operating area, particularly the sections of plant handling the gaseous and liquid products. Safety and separation distances are prescribed in guidelines such as BCGA CP36 and EIGA Doc.75/07 [10, 11].

2.3.1.2 Prohibition of smoking, open flames or other ignition sources.

Smoking and the use of open flames are forbidden in the vicinity of the plant while it is in operation or contains liquid or gaseous oxygen. It is the responsibility of the management to define:

- (a) The areas where smoking is prohibited.

- (b) The areas and conditions under which open flames or other potential ignition sources, e.g. cutting or welding operations, may be used.

Where maintenance or repair work using heat or open flames is to be carried out in the plant operating area, the use of a 'permit to work' system is essential.

2.3.2 Contaminants in the process stream

Oxygen, because it can react with many substances, must be manufactured and stored in equipment which is kept free of contamination. Where contaminants cannot be completely eliminated, sound design and safe operating practices enable them to be controlled within acceptable limits.

Contaminants may be introduced into air separation plants by way of the air-feed stream, by plant equipment malfunction, or inadvertently during maintenance or construction.

The information given in this section is intended to provide general guidance on measures for controlling and monitoring contaminant levels. However, it must be stressed that in all cases professional advice must be sought from the plant manufacturer or supplier regarding the precise instructions, methods and procedures for ensuring correct, safe and reliable operation.

2.3.2.1 Control of airborne contaminants

A knowledge of the nature and concentration of the contaminants in the process air is of fundamental importance in the safe operation of the plant.

Non-flammable contaminants, such as carbon dioxide and water, are always present, but do not normally create safety problems unless, through plant maloperation or process instability, carbon dioxide passes through to the low-pressure column and plugs the reboiler passages. Under these circumstances local dry boiling and concentration of potentially hazardous contaminants, such as acetylene, can occur.

Particulate matter is normally removed from the air-feed stream by filters located on the suction side of the main air compressors and on the discharge side of vessels containing particulate adsorbent material such as molecular sieves.

The presence of corrosive gases, such as sulphur dioxide or oxides of nitrogen, in the atmosphere can, over a period of time, cause severe corrosion of the warm end sections of the plant unless proper controls are introduced. Periodic monitoring of the condensate from the aftercooler of the air-feed compressor for pH level will serve as a useful indication of the degree of acid contamination in the atmosphere. In severe cases it may be necessary to provide cleaning or scrubbing equipment to reduce the acid-gas concentration in the air either before it enters the feed compressor or before it enters the process system.

The contaminants of greatest concern are those which are flammable, such as hydrocarbons, and which can pass through to the oxygen-rich sections of the process system. Acetylene is of particular concern, because of its relatively low solubility and high reactivity in liquid oxygen. Although air separation plants normally incorporate equipment for removal of hydrocarbon contaminants from the gas and liquid streams, the design of which is based on measured or estimated pollution levels, it is advisable to be aware of local sources of contamination which may on occasions reach levels significantly in excess of those used as the design basis and jeopardise the safety of the plant.

Common sources of environmental contamination are:

- (a) Chemical and oil refining processes.
- (b) Exhausts from internal combustion engines.
- (c) Acetylene generating equipment.
- (d) Other local industries or processes.

Air separation plants are frequently located in industrial areas where a degree of atmospheric contamination will always be present. The initial selection of the plant location is therefore of great importance in minimising the levels of undesirable materials in the air-feed stream. In industrial areas,

where hydrocarbon pollution can be high, periodic evaluation or testing of air quality may be necessary which could dictate changes to process equipment, monitoring equipment, frequency of analysis or operating procedures. In some cases, particularly where there is an increased risk of hydrocarbon release and contamination, the use of continuous monitoring equipment linked to alarm and shut-down systems may be necessary.

It is of the utmost importance that correct operating procedures are maintained to ensure that the levels of contaminants in the various sections of the plant are controlled within acceptable limits. Particular attention should be paid to the following items:

2.3.2.1.1 The use of molecular sieve adsorbers. Modern plants are normally fitted with molecular sieve adsorption units to remove water and carbon dioxide from the air feed to the plant. A secondary function of a molecular sieve adsorption unit is to remove certain hydrocarbon impurities present in the air.

It is essential that the operating cycle times, regeneration temperatures and flows, and the temperature of the air entering the units, are maintained within the limits specified by the manufacturers. If the plant is stopped for any reason, the outlet of the sieve unit should be shut off to prevent desorbed contaminants passing forward into the plant.

2.3.2.1.2 Use of liquid phase hydrocarbon absorbers. It is important that the specified operating period of an adsorber vessel is not exceeded, and that the required reactivation gas flow rate and outlet temperature are achieved.

2.3.2.1.3 Reboiler-condenser operation. The reboiler-condenser in the low-pressure column of an air separation plant is a heat exchanger which condenses air or nitrogen vapours against constantly boiling liquid oxygen. Reboiler-condensers are usually of the thermosyphon or downflow type. [12]

Plugging of oxygen passages with foreign material, including carbon dioxide or ice, can, under some conditions, cause hazardous concentrations of hydrocarbons to build up while the plant is operating at normal liquid levels.

Acetylene, because of its low solubility in liquid oxygen (approx. 9 ppm), can present a problem, particularly with older plants, where acetylene may not be effectively removed in the front end system. When its concentration exceeds the solubility limit, solid acetylene can collect on the surface of the liquid or on the walls of the reboiler passages, where it creates high local concentrations capable of detonating. The presence of acetylene in liquid oxygen, when detected, requires immediate investigation and corrective action as recommended by the plant supplier.

In plants with thermo-syphon reboilers, a decrease in the reboiler liquid level below a certain point has the potential to concentrate hydrocarbon contaminants to a hazardous level. It is therefore important to operate the reboiler at the full submergence level to maintain the boiling surfaces fully wetted. Alarms and trips should be provided to guard against extended periods of operation at low levels. Changes in plant operating requirements may cause the reboiler liquid level to vary temporarily. During these changes, variation in level can be tolerated for short periods of time without affecting safe operation of the unit. It is also important to maintain the recommended minimum purge flow from the liquid oxygen bath to control the hydrocarbon and carbon dioxide concentrations at acceptable levels. Particular attention must be given to the reboiler liquid level when the air separation plant is on cold shutdown. The plant liquid should be disposed of whenever the liquid level falls appreciably or when the total carbon dioxide or hydrocarbon content exceeds the limit recommended by the supplier.

For plants supplied with downflow reboilers, the flow of liquid oxygen from the base of the reboiler must be maintained at the recommended minimum value to prevent accumulation of hydrocarbons. A low-flow alarm should be provided or inferred. In the same way as for thermosyphon reboilers, the purge flow from the liquid oxygen bath should be maintained at the minimum recommended level.

Liquid of acceptable quality may be transferred to the low-pressure column from storage, if available, to maintain a satisfactory liquid level and dilute the hydrocarbon concentration.

When starting a plant containing liquid after a cold shutdown, take special care not to boil away existing plant liquid or to permit desorbed hydrocarbons from the hydrocarbon adsorber to enter the

low-pressure column. The plant operating manual should be consulted for the correct start-up procedures.

2.3.2.1.4 Monitoring of contaminants. Most hydrocarbon gases entering the plant, including acetylene, are removed by the front end purification system (molecular sieve unit) and, depending on the plant design, by cryogenic liquid phase adsorbers. Hydrocarbons, such as methane and ethane, which are not readily removed by the front end system, and which can enter the low-pressure column, are readily soluble in liquid oxygen. A gas chromatograph or total hydrocarbon analyser can be used for continuous monitoring of the parts-per-million level of hydrocarbons within the reboiler and other oxygen rich sections of the plant. The analyser selected for this duty should be set to alarm and shut down the plant at pre-determined levels (as recommended by the plant supplier) should a potentially hazardous situation develop. In the event of an alarm the operator should investigate the reason for the deviation and take corrective action. The analyser should normally be used on a continuous basis to monitor a representative sample of liquid oxygen from the column sump, because hydrocarbons tend to concentrate at this part of the plant. For environments where atmosphere pollution levels are known to be high, the quality of the air-feed stream should be checked periodically, or even continuously, to give early warning of increasing hydrocarbon contamination. On plants fitted with liquid phase hydrocarbon adsorbers, the liquid on the downstream side can also be subject to periodic sampling and analysis.

For plants designed with front end molecular sieve units, which effectively remove acetylene from the process air feed stream, it is not necessary to conduct regular tests specifically for acetylene.

Plant upsets can result in higher than normal concentrations of carbon dioxide in the reboiler sections of the plant. The solubility of carbon dioxide in liquid oxygen is relatively low (5 to 9 ppm depending on liquid temperature) and there is a risk of forming solid carbon dioxide which, in extreme circumstances can block reboiler passages and cause dry boiling. The liquid oxygen purge from the reboiler should normally be sufficient to maintain the carbon dioxide level below the solubility limit but verification of the actual concentration should be obtained by either periodic or continuous monitoring of the reboiler liquid using a suitable analyser.

There will normally be a certain level of contaminants dissolved in the column sump liquid, but, provided the concentration is within the specified limit, the plant will operate safely under these conditions. Any significant increase above the normal background level will warrant an immediate investigation to trace the cause of the problem and take appropriate corrective action. If the corrective action (increasing liquid oxygen purge rate, draining liquids, hydrocarbon adsorber changes, etc.) does not reduce the contaminant level, and the concentration of total hydrocarbons or carbon dioxide reaches the maximum recommended by the plant manufacturer, the plant should be shut down and the liquid in the columns drained off to the disposal system.

2.3.2.1.5 Draining of plant liquid after shutdown. When the plant is shut down for an extended period, i.e. over 24 hours, all liquid in vessels and process lines, except the main condenser, should be drained. The main condenser level should not normally decrease by much over a few days, but if it falls to half the normal operating level, the draining and disposal of all liquid will be necessary.

2.3.2.2 Contaminants introduced by equipment

Lubricants from the plant's machinery (compressors or expanders) are possible contaminants of the process stream. On high-pressure plants equipped with oil-lubricated reciprocating air compressors or expanders, lubricant carry-over from the cylinders is removed in the compressor entrainment separators, the air driers, adsorbers or purpose-designed oil removal systems. However, periodic solvent washing of the plant may still be necessary to remove trace quantities of lubricant carried over into the cryogenic sections of the plant.

For reciprocating machinery with dry-lubricated cylinders and oil lubricated crank cases, it is important to maintain crank case, cylinders, oil slingers, piston-rod wipers, and similar devices in good condition to prevent the migration of oil from the crank case into the process stream via the rods and cylinders.

Low-pressure plants are equipped with centrifugal compressors and expanders which are designed to prevent lubricants entering the process gas by a more positive separation of oil-lubricated bearings from the process stream using combinations of distance pieces, seal gas systems, labyrinths, vents and purges. Purge, vent and seal gas systems must be operational on such equipment when the lubricating system is operating, to prevent contamination of the process gas stream. Consideration should be given to the use of alarm and trip systems to shut down the equipment in the event of purge or seal gas system failure.

2.3.2.3 *Contaminants introduced during maintenance and construction*

Maintenance work that requires opening the process system may accidentally permit entry of contaminants or unsuitable materials. Particular care must be taken during maintenance so that only proper materials and parts are used and that all new systems, parts and components have been appropriately cleaned. A system of inspection and checks should be used to avoid errors.

Parts, assemblies, accessories, and materials must be stored carefully to prevent contamination by dirt, mud, grease, oil, weld spatter, or as a result of the normal work environment or by bad weather. Material already prepared for oxygen service must be sealed and protected to avoid contamination during storage, and should be tagged and marked: "Clean for oxygen service".

Personnel engaged in maintenance of plant machinery should wear clean overalls, preferably with zip fasteners and no external pockets.

2.3.3 **Cold box purge and leak detection**

The insulation spaces of air separation plant cold boxes are normally purged on a continuous basis with dry gaseous nitrogen. The prime purpose of the purge gas is to keep the insulating material dry by preventing ingress of water vapour from the atmosphere, but it also serves to prevent condensation of air on the external surfaces of equipment operating at liquid nitrogen temperatures. The presence of excessive quantities of ice in the cold box not only diminishes the thermal properties of the insulation but can also result in increased stress on internal piping and fittings.

The purge gas flow should be maintained at the specified rate, except when it is necessary to enter the cold box for repairs or when the plant has been shut down, drained and defrosted.

From time to time it is possible that leaks, either of gas or cold liquid, can develop within the cold box. Minor leaks may go undetected but those of an appreciable nature will become apparent in one or all of the following ways:

- (a) Formation of white frost spots on the external surface of the cold box.
- (b) An increase in pressure of the gas in the cold box insulation space.
- (c) If the leak is oxygen, an increase in the oxygen content of the purge gas in the insulation space.
- (d) In the event of a severe liquid leak, the cracking of mild steel panels and presence of vapour fog and liquid outside the cold box local to the area of leakage.

Regular monitoring of the cold-box surfaces and the pressure and oxygen concentration of the gas in the cold-box insulation space is recommended. This will increase the chance of detecting the development of a leak as early as possible. Naked lights, cigarettes, or similar heated sources must not be used to detect any suspected leaks on oxygen producing or handling plants. Gas analysis equipment will generally be the first means of confirming that an oxygen leak is present. Leaks on external pipe joints which are not obvious to the hand, eye or ear may be located by applying a suitable liquid detergent to the suspected area.

2.3.3.1 *Notification of leaks*

When there is evidence of enriched air due to oxygen or liquid air leakage in an air separation unit or from external oxygen lines, the supervisor in charge of the plant must be notified immediately so that he may decide the appropriate action to be taken.

2.3.3.2 Operation of plant with liquid leakage

If a gas-producing air separation unit has not sufficient refrigeration capacity to maintain correct reboiler operating level, and this is known or suspected to be due to internal liquid leakage, the plant must be shut down to rectify the fault. To maintain the plant in operation under such conditions by feeding in liquid from an external source is extremely dangerous.

2.3.3.3 Areas affected by leaks

Areas affected by leaks must be regarded as danger areas and the necessary precautions must be taken. Leaks of cold vapours or gases that are heavier than air, such as oxygen or argon, may accumulate in pits or trenches. If entry to these areas is contemplated, the atmosphere should be checked beforehand for oxygen content.

Large liquid leaks may cause freezing and movement of the foundations (frost heave) which can result in vertical displacement of the cold box. Such an event can give rise to process performance problems and/or damage to piping and equipment.

2.3.4 Disposal of cryogenic liquids

The presence in the plant of liquid oxygen which has been heavily contaminated with hydrocarbons represents a potential hazard to equipment and personnel. Therefore quick action is required to dispose of such liquids to reduce the hazard. Collecting the liquid in a vessel outside the air plant does not eliminate the hazard, because the vaporising liquid in the collecting vessel will also concentrate the contaminants.

Oxygen, air or nitrogen in liquid form must never be drained into trenches, pits, road drains, confined spaces or near personnel. The disposal system must vaporise the liquid without allowing any contaminants to accumulate. The heat supplied to the disposal vaporiser may be from water, steam, or ambient air. The vaporised liquid should be vented in a manner that will not expose personnel, work areas or equipment to increasing oxygen concentrations, which can contribute to the potential for fire; or to decreasing oxygen concentrations, which may give rise to an asphyxiation hazard.

Vents should be directed away from structures liable to mechanical failure on exposure to low temperatures [13].

2.3.5 Vapour fog clouds

Vapour fog clouds can form during certain phases of plant operation, such as draining hydrocarbon adsorbers of liquid before reactivation or transferring product from storage to liquid transport vehicles. The vapour fog is composed of atmospheric water vapour condensed by the cooling effect of the liquid being vaporised. The fog should also be assumed to contain a possible hazardous concentration of the vaporised liquid. Depending upon the quantity of product being vaporised, and climatic conditions, the fog can travel considerable distances, causing visibility problems for plant operators. Vehicle accidents may also occur if vapour clouds are blown across nearby public highways. Tests and calculations show that the extremities of the visible cloud are non-hazardous. If liquid oxygen is released into the atmosphere, the possibility of fire exists. The dispersion of oxygen vapour clouds can be calculated by referring to the BCGA Technical Report [14]. If the product is inert, then asphyxiation can be a potential hazard.

Elevated vents from process equipment and control of the venting rate can reduce exposure to vapour fog clouds. Fans can inject air into the vents to dilute and heat the vapour and to enhance dispersal into the atmosphere. In this way the hazard to operating personnel or the public is minimised [13].

Ambient air vaporisers, when used for plant liquid disposal or as product vaporisers, can generate vapour clouds from the contact of air moisture with the cold metal portion of the vaporiser. The fog is not as dense as that caused by liquid venting direct to the atmosphere, but under certain atmospheric conditions the fog may collect in operating or public areas adjacent to the plant, and reduce visibility.

2.3.6 Thermal expansion

A hazard exists in a process system whenever cryogenic liquid can be trapped between closed valves. As the liquid vaporises through normal heat leak, the pressure generated may cause the trapped section of piping or equipment to fail. Pressure relief valves, are provided in these sections of the system to relieve the pressure generated by trapped liquid. Consideration should be given to whether a manual blow down valve is also required.

2.3.7 Modifications to plant

Proposed modifications to an air separation plant should be thoroughly reviewed to determine whether they affect the safety of the system or introduce new hazards. Modifications undertaken without the advice and experience of competent cryogenic engineers and operators can unknowingly introduce hazards, through improper choice or use of materials for the conditions of service, or through introduction of contaminants. Proposed changes in operating procedures should also be reviewed in the same way. A HAZOP/HAZAN study should be considered (see Chapter 1 and [15]).

2.3.8 Special equipment hazards

The mechanical equipment for handling the oxygen and nitrogen products of an air separation plant and the transmission system for the gaseous oxygen product require special consideration because of oxygen's ability to support combustion. Such equipment contains recognised ignition energy sources, and it is therefore essential that clean components are used to eliminate the presence of easily ignitable fuels. Oxygen compressors, oxygen pumps, nitrogen compressors, and oxygen piping systems are examples of equipment containing recognised ignition sources.

2.3.8.1 Centrifugal oxygen compressors

Within a centrifugal oxygen compressor energy is being introduced to increase the pressure of the product, and components with very small clearances are moving at high relative speeds [16]. Balance and stability of rotating parts are essential. Instabilities may be caused by surging, passing through critical speeds, and/or sudden unexpected shutdowns. Even momentary rubbing or impact between rotating and stationary elements may create temperatures sufficiently high to ignite the metal in the oxygen atmosphere and cause damage to the compressor.

Bearing wear occurring during normal operation or as a result of lubricating system failure is a condition which can lead to instability of the rotating elements of the oxygen compressor.

Failure of the seal gas supply to the labyrinth seals of the compressor increases the possibility of lubricating oil migrating into the process stream. Oil is a recognised low ignition temperature fuel which is capable of reacting with oxygen.

The most critical periods of instability and also the periods of greatest potential hazard exist during start-up and shutdown of the compressor.

- (a) Vibration sensors to detect axial and radial movement which alarm and shut down the compressor.
- (b) Interstage high-temperature gas alarm and shutdown instrumentation.
- (c) Seal gas pressure with alarm and shutdown points.
- (d) Lubrication system pressure and temperature control system with alarm and shutdown points and an auxiliary oil pump to supply compressor bearing lubrication when the main lubricating oil pump is not operating.
- (e) A purge system for start-up and shutdown, using clean, dry, oil-free nitrogen or air instead of oxygen.
- (f) Location of the compressor behind a non-combustible barrier for personnel protection. Low-pressure oxygen blowers may require shielding only at critical areas of the machine.
- (g) Location of the compressor where the potential fire exposure to other plant activities is minimised.

- (h) Location of the control panel and critical instrumentation for the compressor outside the non-combustible barrier.
- (i) Filters/screens in the compressor gas inlet lines to prevent particles from entering.
- (j) Mandatory checklists must be completed before start-up.
- (k) Compressor should preferably be started up on nitrogen before oxygen is introduced.
- (l) All operating characteristics must be normal after start-up before oxygen is put through the compressor.
- (m) All personnel must be outside the barrier before switching to oxygen and while compressing oxygen.
- (n) Compressor maintenance must be rigidly controlled.
- (o) Logged data to be periodically reviewed to detect trends.

2.3.8.2 *Reciprocating oxygen compressors*

The design requirements and operating procedures applicable to high-pressure centrifugal compressors apply also to high-pressure reciprocating compressors, except for the vibration, seal gas and surge control requirements [17]. Complete enclosure of the compressor by personnel barriers may not be necessary with some applications.

Attention must be given to prevent oil migration along the piston rods. Slings, distance pieces, and crankcase eductors are some of the devices used to control lubricant migration. In addition, a permanently mounted ultraviolet inspection light may be used to detect, by fluorescence, the presence of lubricating oil on the piston rods. A fluorescent additive can be added to the lubricating oil to improve ease of detection. If lubricating oil migrates as far as the cylinder end of the piston rods, a potentially hazardous situation exists, and the compressor must be shut down to investigate and correct the fault.

Compressor valve cover temperatures may also be monitored to detect changes in valve performance.

2.3.8.3 *Liquid oxygen pumps*

Both centrifugal and reciprocating type pumps are used for handling and transferring liquid oxygen [18]. Although the materials of construction of liquid oxygen pumps are carefully chosen, particularly those of the stationary and moving parts in contact with the fluid, a potential fire hazard can exist in the event of an abnormal operating condition. Insufficient cooling of the pump, cavitation or mechanical failure of shafts, pistons or bearings may create sufficient energy in the form of frictional heat to ignite or melt moving and stationary components in contact with oxygen.

Pump installations, particularly those having high speed or high head pumps, should incorporate features designed to protect the equipment and minimise the potential hazard. The following important safety measures should be considered for inclusion, as appropriate, in a liquid oxygen pump installation:

- (a) Personnel protection barriers for high speed or high head pumps which are not located within a cold box or below ground level.
- (b) Suction line filters, the mesh sizes of which are governed by the clearances between the moving and stationary parts.
- (c) Safety devices to shut down the pump in the event of cavitation or loss of prime.
- (d) The location of the control station at a reasonable distance away from the pump (3-5 m).
- (e) Provision of automatic devices to shut off the liquid flow to the pump in the event of pump failure.
- (f) Use of ignition resistant materials, e.g. tin bronze, for the pump casing and impeller.

2.3.8.4 Nitrogen compressors

Nitrogen compressors present a unique problem. Fires have occurred in reciprocating oil-lubricated compressors pumping high purity nitrogen when the oxygen content has suddenly increased due to plant upset conditions.

Ignition can occur in centrifugal compressors pumping nitrogen through interference of rotating parts, and in reciprocating compressors through ring or valve failure, but only in the presence of sufficient oxygen. Fuel for the reaction can be lubricating oil or accumulated organic material which has normally been exposed only to an inert atmosphere.

Continuous analysis of oxygen in the nitrogen stream, coupled with alarms and shutdown switches, provide the necessary operating information and protection to reduce the risk of an ignition due to increasing oxygen content.

2.3.8.5 Pipelines

High velocity flow of oxygen gas in a pipeline is recognised as a potential hazard [4]. Any dirt, metal scale, or other particle travelling with the high velocity flow represents a potential energy source (impact) capable of starting a reaction.

Several historical observations that have been made from studies of fires in oxygen service are listed:

- (a) No ignition has been known to occur in oxygen-clean carbon steel or stainless steel systems sized for limited gas velocities unless initiated by the presence of a foreign substance.
- (b) Ignition has occurred several times in carbon steel and stainless steel systems operating at, or near, sonic velocity. Friction from high-velocity particles is considered to be the most probable cause of ignition.
- (c) Copper, brass and nickel alloys have a low heat of combustion relative to steels and iron, and are resistant to ignition in oxygen service. Once ignited, these materials burn at a much slower rate than carbon or stainless steels.
- (d) Aluminium is resistant to ignition, although under certain conditions it can ignite in the presence of oxygen and rust from carbon steel, resulting in rapid combustion. The use of aluminium for gaseous oxygen pipelines is therefore avoided.

The velocity of oxygen in steel pipelines is limited to 200 ft/s (60 m/s) at pressures up to about 14 bar. Normally, velocities are considerably lower, to limit pressure drop and power consumption. At valves, orifices, and line sections where the velocity can exceed 200 ft/s (60 m/s), copper, brass, or nickel alloys should be used. Monel tees should be used at points of abrupt change in flow direction.

In general, oxygen gas pipelines should be kept free of contaminants and all valves in the system should be operated slowly to avoid sudden changes in flow and pressure.

2.3.8.6 Liquid storage containers

Product liquids are stored and transported in purpose designed and constructed containers of capacities ranging from a few litres to several hundred thousand litres. Containers are of two types: vacuum insulated, operating at pressures in the region of 16 bar, and flat-bottomed tanks that are also double-skinned, use conventional thermal insulating media and operate at lower pressures in the region of 0.5 bar.

Normally, cryogenic liquid storage tanks are installed and located in accordance with established codes of practice [19-22], which include measures for minimising the effects of liquid spillage. Nevertheless, sudden and uncontrolled releases of large quantities of cryogenic liquid to the atmosphere are undesirable events that pose significant potential hazards, and every endeavour should be made to ensure that they are prevented.

Apart from basic design and manufacturing faults on the storage tanks, which are extremely rare, the principal causes of uncontrolled liquid spills are the following:

2.3.8.6.1 Overfilling. This may occur during transfer of liquid to a tank, either from a production plant or from a road tanker. Overfilling can cause discharge of liquid from vent lines normally discharging vapour, and can also cause a rapid build-up of the tank pressure, resulting in the discharge of liquid to atmosphere by way of the vapour space pressure relief devices. In an extreme situation tank rupture could occur, owing to excessive hydrostatic pressure.

In general, overfilling can be avoided by training of personnel in correct operating procedures, proper positioning, marking and maintenance of liquid level indicators and, where necessary, the provision of high level alarm and trip systems.

2.3.8.6.2 Overpressure. The development of excessive pressure in the tank vapour space can only occur if for some reason the pressure safety valves either fail to operate at their set pressures or their capacity is inadequate to handle the upset condition. Although pressure safety devices should be maintained and tested at regular intervals to ensure as far as possible that they are in working order, it is desirable to reduce to a minimum the number of demands upon them to operate.

The situations that usually give rise to an increase in pressure in cryogenic storage tanks are as follows:

- (a) Heat leak. There will normally be a steady flow of heat into the tank that will determine the liquid boil-off rate. However, the rate of heat input may rise, owing to deterioration of the thermal insulation, or, in the case of vacuum insulated tanks, failure of the vacuum. The latter situation can occur suddenly, resulting in a rapid increase in the rate of heat leak, with subsequent increase in the liquid boil-off rate and rise in pressure.
- (b) Overfilling as discussed above.
- (c) Flash vapour due to the injection of relatively warm liquid into the tank vapour space. The liquid may be from a production plant, a road tanker or recycled from a liquid pump. Excessive liquid injection rates will clearly result in increased flash vapour and a tendency to raise the tank pressure. Most vacuum-insulated tanks are equipped with a liquid fill connection at the bottom of the tank as well as at the top. The bottom fill connection can be used when filling from a road tanker to control the rate of rise in pressure in the tank vapour space.
- (d) Failure of the pressure build-up valve in the open position. Most cryogenic liquid tanks are fitted with an automatically controlled pressure build-up system to maintain the pressure in the vapour space during periods of high liquid withdrawal rates. Failure of the automatic valve in the open position will clearly result in a continuing build-up of pressure in the tank until corrective action is taken or the pressure safety valve operates.

2.3.8.6.3 Underpressure. Low-pressure tanks are vulnerable to damage by the development of partial vacuum conditions in the vapour space, owing to the nature of the tank construction and the pressure at which they normally operate. Partial vacuum conditions can arise because of excessive liquid withdrawal rates or, under certain conditions, sudden increases in atmospheric pressure. In general the creation of partial vacuum conditions can be avoided by adherence to correct operating procedures, ensuring that the pressure build-up system is operating correctly and that the vacuum relief valve is in working order. It must be recognised that frequent demands on the vacuum relief valve may give rise to ingress of excessive quantities of moist air, resulting in accumulation of ice and subsequent blockage of the relief valve piping.

2.3.8.6.4 Failure of ancillary equipment. Failure of valves, piping and fittings on liquid off-take lines from the base of liquid storage tanks can clearly result in large uncontrolled spillages of liquid. Liquid lines on larger capacity tanks may be provided with internal or external emergency shut-off valves to minimise the extent of liquid spillage in the event of such failures. However, demands on emergency devices should be minimised by ensuring that liquid lines, valves and fittings external to the tank are properly inspected and maintained and, as far as is practicable, protected from mechanical damage.

2.3.8.6.5 *Failure of purge gas flows to insulation space.* The insulation spaces of cryogenic liquid storage tanks of the non-vacuum insulated type are normally purged with dry gaseous nitrogen in the same way as the cold box of an air separation plant (see section 2.3.3).

Failure to maintain adequate flow of purge gas may result in ingress of air, causing accumulation of ice and, in the case of low pressure liquid nitrogen storage tanks, condensation of air on the external surfaces of the inner vessel. In extreme cases these conditions may adversely affect the integrity of the tank and internal piping.

2.3.8.6.6 *Tow-away.* Incidents have occurred when road tankers containing cryogenic liquids have been driven away from the tank fill point with the flexible transfer hose still connected. Such incidents have led not only to damage to piping and equipment but also to large spillages of liquid.

Although tow-away incidents can largely be prevented by proper training of drivers and other personnel responsible for liquid transfer operations, the experience of several companies has shown that this is not always sufficient and that the potential consequences of a tow-away warrant the introduction of further safeguards. Such safeguards include the use of breakaway couplings, flag warnings and various interlock systems, the latter of which give audible warnings or prevent release of the vehicle brakes until the transfer hose is disconnected [23].

2.3.8.7 *Road tankers*

Road tankers used for the transport of cryogenic liquid should be maintained and operated in accordance with the manufacturers' instructions and any relevant statutory requirements.

Liquid transfer hoses should be capped when not in use to prevent ingress of water and dirt. Hose couplings used for the transfer of a particular cryogenic liquid should be non-interchangeable with those used for other liquids. The practice of changing the service of a road tanker from one cryogenic liquid to another on a frequent basis should be avoided. Such situations, unless carefully controlled, can lead to problems with product contamination, particularly where it is necessary to use adaptors for connecting hose couplings normally used for one liquid to fill points designed for another. Strict controls are required when tankers in inert gas service are converted to liquid oxygen service.

It is essential to ensure that drivers and other personnel engaged in road tanker and liquid transfer operations receive formal education and training in the potential hazards and the correct operating procedures [24].

2.4 Safety in the maintenance of air separation plants

The establishing of proper maintenance programmes and practices is of vital importance to ensure the continuing safe operation of an air separation plant. However, the unique features of air separation plants and the nature of the gaseous and liquid products require that certain special safety precautions are taken, both in the workshop and when carrying out maintenance operations on plant equipment *in situ*.

The purpose of this section of the guide is to identify those key areas of safety which are recognised by the industry as being of particular importance for the successful implementation of a maintenance programme.

2.4.1 Equipment

The main items of equipment that will require regular attention to maintain them in good order are:

- (a) Machinery, e.g. compressors, pumps.
- (b) Heat exchangers and vaporisers
- (c) Vessels, piping and valves.
- (d) Insulation.
- (e) Instruments.

- (f) Safety devices.
- (g) Yard areas.
- (h) Auxiliary services (water, steam, power, instrument air).

In view of the high degree of reliability which is required of continuous process plants it is essential that a well-planned preventive maintenance programme is prepared and implemented. Regular attention to key areas is vital to minimise the occurrence of accidents or major breakdowns, which can be costly in terms of injury, repairs and business interruption.

2.4.2 Cleanliness

It has already been stated that oxygen vigorously supports combustion and, under the right conditions, can react violently with certain materials, particularly oils and greases. For this reason cleanliness is of critical importance for all equipment in service with oxygen or oxygen-enriched fluids.

It is therefore necessary to start with a clean plant and to maintain the same standard of cleanliness by periodic cleaning and decontaminating procedures. Initially, all materials of construction, sub-assemblies and individual components comprising the air separation plant and product storage equipment will be subjected to cleaning processes. Once clean, all equipment and components should be protected during construction and thereafter protected or re-cleaned in accordance with established repair or maintenance procedures [25-28].

2.4.2.1 Maintenance facilities

2.4.2.1.1 Special maintenance area. An area for final cleaning and assembly of air separation plant components and other equipment in service with oxygen must be clearly defined, segregated from other maintenance areas, and kept in a clean, oil-free condition. The use and storage of combustible materials in this area should be kept to a practicable minimum. Dismantling and initial cleaning of equipment and components must be carried out before they are taken to the clean area for repair.

For maintenance of special items of equipment, such as liquid oxygen pumps, which require the highest standards of cleanliness, a special clean room should be provided to minimise the likelihood of contamination during repair and re-assembly.

2.4.2.1.2 Work benches. Work benches in the special maintenance areas must be covered with stainless steel or other non-combustible, non-absorbent material, and kept clean and free of oil and grease. Relatively soft materials such as wood or aluminium, are not recommended.

2.4.2.1.3 Tools. Tools for maintaining and assembling air separation plant components must be kept thoroughly clean and used only for this purpose. Tools that are used for general maintenance work, such as crankcase overhaul, must not be used for maintenance or assembly of air separation plant components or equipment which have been cleaned for oxygen service.

2.4.2.1.4 Protective clothing. Protective clothing, such as overalls, footwear, gloves, etc., used when carrying out maintenance operations on air separation plant components and equipment, must be clean and free from oil and grease. This is of prime importance when carrying out work on special items of equipment such as oxygen turbocompressors. Overalls without external buttons or pockets are best, to minimise the chances of foreign objects such as pens, buttons, etc., entering clean equipment.

2.4.2.1.5 Personal cleanliness. Personnel must cleanse hands thoroughly and change into approved protective clothing before transferring from general maintenance work involving dirt, oil, or grease, to air separation plant maintenance. Barrier protection creams usually contain combustible components, and must not be applied to the hands before handling components that have already been cleaned for air separation plant service.

2.4.2.2 Standards of cleanliness

Guidance on the frequency and methods of cleaning and on the degree of cleanliness required should be obtained from the plant manufacturer, and the instructions should be carefully followed. In general, all equipment should be free of hydrocarbon oils and greases, loose material, scale, metallic chips, solvent residue and other foreign material before use in oxygen service.

2.4.2.3 Inspection techniques

Various techniques are used for inspecting equipment and components to determine whether an acceptable standard of cleanliness has been achieved. Such methods include:

- (a) Bright white light to inspect surfaces for particles, fibres and liquid films.
- (b) Ultraviolet light ('black light') to detect fluorescent oil or grease deposits.
- (c) Wipe tests with clean white filter paper for detecting residues not detectable by ultraviolet light.
- (d) Solvent extraction test to check inaccessible surfaces by washing and subsequent quantitative analysis for contaminants.

The criteria for the required degree of cleanliness of equipment for oxygen service, as determined by the above inspection methods, should be obtained from the plant manufacturer.

2.4.2.4 Cleaning methods

2.4.2.4.1 Method selection criteria. Selection of the most practical and efficient methods for cleaning equipment and components for oxygen service will depend on the size, nature and construction of the equipment to be cleaned.

In general, cleaning of equipment may be accomplished by any method which satisfies the acceptance criteria as recommended by the plant manufacturer. Any solvent or chemical agent used in the cleaning process should be a commercially approved type of satisfactory grade and quality, compatible with the materials of construction of the equipment being cleaned and used in accordance with the manufacturer's instructions. However, the use of combustible fluids, such as paraffin, acetone, or petrol, is not recommended for cleaning equipment for oxygen service.

2.4.2.4.2 Cleaning processes. The principal methods used for cleaning process equipment include:

- (a) Steam or hot water cleaning.
- (b) Mechanical cleaning.
- (c) Caustic cleaning using strong alkaline solutions.
- (d) Acid cleaning.
- (e) Solvent washing.
- (f) Vapour degreasing.

2.4.2.4.3 Rinsing, drying and packaging. On completion of any cleaning process it is essential that all traces of chemical agents or solvents are completely removed from the equipment by draining and either rinsing with clean, oil-free water or purging with clean, dry, oil-free air or nitrogen as appropriate. The latter media may also be used to thoroughly dry equipment that has been rinsed with water.

It should be noted that chlorinated solvents can form flammable atmospheres in the presence of oxygen, and it is therefore of great importance to ensure that all traces of solvent are removed from the equipment or system after cleaning.

Once equipment has been inspected to ensure that the required standard of cleanliness has been achieved, it should be packaged or sealed in nitrogen to protect the surfaces from contamination until such time as it is put back into service.

2.4.2.4.4 Precautions. Practically all the cleaning methods described above call for the use of chemicals, solvents, or processes which are potentially hazardous. It is therefore essential that cleaning operations are carried out by properly trained and experienced personnel using suitable purpose-designed equipment. Personnel should be aware of the nature of the hazards, e.g. whether toxic or corrosive, and use appropriate protective equipment.

Cleaning agents should be used only if their performance and application are known, or after discussion with the cleaning agent manufacturers. The manufacturers' instructions for use, including the means for disposal of used solvents, should be strictly followed.

2.4.3 Precautions when handling perlite

Where maintenance or repair is required on a pipe, vessel or associated equipment which has contained a cryogenic liquid, insulating material must be removed before work can begin. For large-scale vessels and pipes in air separation unit cold boxes and low pressure cryogenic liquid storage tanks, an insulating medium called 'perlite' is used. Perlite is an inert material made from expanded volcanic rock, which is pumped as very fine granules into the interspace of cold boxes or storage tanks. The density of the perlite is an important consideration in relation to thermal insulating properties and pipe stress. As perlite is inert, it is difficult to envisage any risks when handling it, but experience has shown that there are potential hazards associated with the material. Perlite can be discharged from the interspace of a cold box in the event of box failure and produce a cloud of particles which can reduce visibility, particularly on adjacent roads. Because it flows so easily, perlite can cause death by choking if ingested; this could occur if a person fell into a container filled with perlite.

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3. Natural gas

Chapter 3 deals with special precautions that must be observed in the supervision, operation and maintenance of liquefaction, product handling and storage of natural gas. The general term 'plant' is used in the following sections to define liquefaction, storage, boil-off control, and vaporisation to generate gas for export from storage. Table 6 gives some of the important properties of methane. This chapter supplements the general safety requirements of Chapter 1.

Table 6 Thermo-physical properties of methane.

Gas Property	Methane
Chemical symbol	CH ₄
Molecular weight	16
Normal boiling point °C (K)	-161 (112.2)
Freezing temperature °C (K)	-183 (90.2)
Critical temperature °C (K)	-82 (191.2)
Critical pressure, bars	46
Volume of gas at 1 bar, 15°C released from liquid boiling at 1 bar	613
Density of saturated liquid at 1 bar (kg/m ³)	423
Gas density relative to dry air (Reference conditions 1 bar, 15°C)	0.56
Latent heat of vaporisation at 1 bar (cooling potential of phase change) kJ/kg	510.6
Air liquefaction hazard	No
Flammable limits in air (vol. %)	5-15
Spontaneous ignition temperature in air °C (K)	540 (813)
Minimum ignition energy (mJ)	0.28
Flame temperature °C (K)	1880 (2153)
Limiting oxygen index (vol. %)	11.5

Note: Pressures in bars absolute

3.1 Specific hazards

3.1.1 Fire and explosion hazard

3.1.1.1 General

Natural gas in concentrations between 5% and 15% with air or oxygen forms a flammable mixture; care must therefore be taken to prevent uncontrolled releases to atmosphere. The composition of natural gas is predominantly methane with approximately 5% by volume of higher hydrocarbons. However, the composition will vary depending on the source of the gas.

Because of the low temperatures at which the liquids are stored, any release is initially heavier than air and will fall to ground level and spread until the gas temperature rises to a point at which the gases are lighter than air or neutrally buoyant. A liquid release will quickly boil off to gas, giving a large volume increase.

3.1.1.2 Ignition and burning characteristics

3.1.1.2.1 Spontaneous ignition temperature (SIT). Natural gas has a spontaneous ignition temperature of about 540 °C (813 K). This value depends on the purity of the gas and to some extent on the measurement conditions.

3.1.1.2.2 Laminar burning velocity and significance of confinement. The laminar burning velocity of natural gas is low compared with other hydrocarbons (less than 0.5 ms⁻¹). The burning velocity is an indication of the tendency of a flame to 'run up' to deflagration.

It has been shown that, given the appropriate degree of confinement and congestion, this fuel can 'run up' to a deflagration. Detonation, although not impossible, is unlikely.

3.1.1.2.3 Minimum ignition energy. Spark ignition energies may be used as a measure of sensitivity to ignition by localised sources. Various sources quote slightly different values. However, natural gas is quoted as 0.28 mJ.

3.1.1.2.4 Flammable range. In air at atmospheric pressure natural gas has a flammable range of 4.9 to 15 per cent by volume.

3.1.1.2.5 Limiting oxygen index. The limiting oxygen index is the minimum concentration of oxygen to support flame propagation when a stoichiometric fuel-air mixture is diluted with nitrogen, that is, it is the least amount of oxygen required to support combustion. For methane the value is 11.5 per cent by volume.

3.1.1.2.6 Quenching distance. This is the minimum gap between two parallel surfaces which will just permit a flame to pass without cooling it to extinction. The smaller the quenching distance, the greater resistance the flame has to cooling, and the more difficult it will be to extinguish. The maximum experimental safe gap for natural gas is 1.14 mm.

3.1.1.2.7 Flame characteristics. Non-aerated hydrocarbon flames have a yellow tinge. The flame temperature of natural gas is 1880 °C.

3.1.1.2.8 Thermal expansion. Equipment and pipework containing a cryogenic liquid can be subject to severe overpressure, owing to thermal expansion of the liquid, in the event of liquid being trapped in a closed system. This will result from heat in-leak or loss of secondary cooling.

Overpressure can also be generated by vaporisation of a cryogenic liquid in a closed system. Pressure relief valves are provided in these sections of the system.

3.1.2 Oxidants and their avoidance

The oxidising agents which may exist in plant are air and cold box atmosphere containing air diluted with nitrogen. It should be remembered that air will initially be present in cold boxes, process vessels, and pipework.

3.1.2.1 Purging

The limiting oxygen index is relevant only to the problem of flammability. Considerations such as solubility, liquefaction, or freezing at the process temperature may require limiting the oxygen to much lower concentrations than those dictated by flammability alone.

Before the introduction of a hydrocarbon into processing equipment, air should be eliminated by nitrogen purge to give an exit oxygen concentration of no more than 2% oxygen, i.e. approximately 20% of the minimum oxygen index. To allow for sampling errors, a figure lower than this may be used in practice.

3.1.2.2 *Air ingress*

Operation below atmospheric pressure should be avoided unless the plant is designed for vacuum conditions, as this could lead to the ingress of air and the formation of flammable mixtures. Suitable safeguards in operating instructions or hardware should be provided to prevent operation below atmospheric pressure where applicable.

3.1.2.3 *Condensation of air and other gases*

Natural gas at its boiling point will not cause atmospheric oxygen to condense, but at its melting point it is close to the boiling point of oxygen.

On the other hand, when liquefied, it can solidify carbon dioxide. Hence it is important to remove carbon dioxide from plant by purging, and from the gas to be liquefied by pre-treatment, otherwise blockages may occur in the process.

3.1.3 **Electrostatic effects**

Electrostatic charges can build up as a result of friction in pipes which can cause ignition where gas is venting to atmosphere.

3.1.3.1 *Safeguard against electrostatic build-up*

Routine inspection to ensure the integrity of electrical earthing and bonding systems on plant equipment is essential. When maintenance work has been carried out, the electrical bonding should be checked before re-commissioning.

3.1.3.2 *Road tanker operations*

Before transfer is begun, tankers carrying the subject cryogenics must be equipped with an earth cable, which must be connected to the earth terminal of the receiving equipment and remain connected until transfer is completed.

3.1.4 **Firefighting**

Natural gas fires need to be fought from a safe distance and from the upwind side of the fire.

Even relatively small hydrocarbon fires are difficult to extinguish, the only reliable approach being to shut off the supply. In fact, until the source can be shut off, it may well be inadvisable to attempt to extinguish the flame, as this could result in the formation of potentially explosive mixtures. The following points are important:

- (a) Liquid hydrocarbon when exposed to the atmosphere will produce a cloud of ice/fog from the air. The flammable mixture will probably be inside the vapour cloud and it is advisable that personnel keep well outside the area of visible moisture.
- (b) Use large quantities of water, preferably in the form of a spray, to cool adjacent equipment and any burning material below the ignition point. Do not apply directly to a pool of burning liquid hydrocarbon, as water will evaporate additional gas.
- (c) Depending upon the circumstances, it is not usually advisable to extinguish a hydrocarbon flame in confined areas if the hydrocarbon supply cannot be shut off. The continued escape of unburned hydrocarbon can create an explosive mixture which may be ignited by other burning material or hot surfaces. It is better to allow hydrocarbons to burn in localised areas and keep adjacent objects cool with water rather than risk the possibility of an explosion.
- (d) If electrical equipment is in danger from the fire, disconnect the supply or use carbon dioxide or dry chemical extinguishers above, and not directly on to, the fire.

3.1.5 Secondary hazards

These take the following forms:

- (a) Pressure rupture (thermal expansion), due to trapping of cold liquid or vapour.
- (b) Brittle fracture, due to metals being used below their transition temperatures.
- (c) Ice formation - if water is present in plant and equipment before cooling down, fractures may occur, owing to the expansion of ice formed. Plant dryness is therefore vital.
- (d) Contraction leakage - sudden cooling can lead to contraction and leakage from bolted flanges and pipework. The system should be specially designed to overcome this problem, provided cooling down is carried out at a specified uniform rate.

3.1.6 Health hazards

The hazards to health of natural gas stem from its low temperatures in the liquid phase and the exclusion of oxygen arising from vaporisation in enclosed spaces.

Serious tissue destruction similar to that caused by burns can occur when the liquid comes into direct contact with body surfaces, owing to the low temperature of the liquid. Similar effects can arise from body contact with uninsulated equipment containing cold fluids. The cold gases can cause damage to the lungs if inhaled.

Natural gas is non-toxic, but oxygen exclusion will result in asphyxiation, and it should be noted that this can often occur so rapidly that the victims may be unable to escape even if they realise that something is wrong.

3.2 Safety in operation

3.2.1 General

It is essential to maintain safe working conditions by minimising the possibility of release to atmosphere of natural gas in liquid or gaseous form [1]. Also, it is important to prevent oil, grease, aromatic hydrocarbons, carbon dioxide, or water from entering the cold parts of the plant where blockage due to freezing may occur and lead to subsequent equipment malfunction. Similar attention should be paid to the cleanliness of equipment before re-commissioning. Compressor suction lines are particularly vulnerable areas, where special care is required to ensure mill scale and other debris are removed and cannot be carried forward to the compressor. Serious damage and plant malfunction could occur either in the main working parts or in the protective and lubrication systems, which are designed to operate with fine clearances.

3.2.2 Ventilation of plant buildings

The plants usually include three distinct types of building where specific safety considerations apply, i.e. control rooms, compressor houses, and analyser houses.

It is claimed, not without justification, that the safest plant building is one with 'no roof and no sides'. Buildings in which flammable fluids are handled should be as open as possible to permit safe operation with good natural ventilation in order to dilute any potential leakage to a safe concentration. Care should be taken to ensure that natural ventilation, as allowed for in the design, is not reduced by temporary or other modifications. Where forced ventilation systems are installed, the equipment, associated alarms and protective devices should be regularly tested and maintained.

3.2.2.1 Control rooms

Generally, these are designed not to contain any flammable gases, but because of their location relative to the plant, the ventilation systems may be required to ensure safe conditions in the event of

any atmospheric release of flammable gas. In the case where the control room is pressurised or swept to prevent entry of flammable gas, safe operating conditions should be maintained by ensuring that the ventilation equipment alarms are regularly tested and that immediate action is taken in the event of system failure. Control rooms should be designed and located to minimise exposure to the effects of gas release, fire or explosion within the process equipment or storage areas.

3.2.2.2 Compressor houses

To achieve maximum safety, compressor house design will give a substantially open building, with side walls having a large free space on all sides and with substantial free area in the roof, e.g. a ridge ventilator.

Natural ventilation of buildings should not be restricted by temporary or permanent plant modifications when flammable gases/liquids are present. Where noise levels are a problem and acoustic enclosure of the compressors is necessary, adequate ventilation and noise control can be achieved simultaneously by the use of acoustic louvres.

3.2.2.3 Analyser houses

Closed analyser houses normally contain specialised and non-flameproof equipment. In the event of ventilation failure or build-up of flammable concentrations of gas, the equipment has to be automatically isolated to maintain safe conditions. Ventilation equipment, alarm and trip systems should be regularly tested and maintained to ensure continued correct and reliable operation.

3.2.3 Road tanker operations

The loading and off-loading of tankers requires special care to ensure that safety in operation is maintained. While each installation will have individual details in design and operation methods, the main areas requiring close attention are given below.

- (a) *Filling.* It is essential to avoid overfilling. The tanker should be weighed before filling, or filled with a metered quantity of product, or both. The maximum filling level may be dictated either by the maximum tanker barrel capacity or by the total road weight of the tanker. The Safe Working Capacity should be displayed on the compartment or tanker & should not be exceeded. Compartment or tanker should be proved to be empty prior to refill.
- (b) *Product compatibility.* Each tanker should be checked for previous cargo to establish if it is safe to load, whether inerting is required, and that the product to be loaded is fully compatible with the tanker.
- (c) *Overpressure.* The operating pressure of the tankers during the filling, venting and purging operations should be known, and the systems set up to ensure that overpressure is avoided by adequate relief valves as well as by the operating procedures.
- (d) *Tanker connection and disconnection.* Before connection for loading, the tanker documentation procedures should have been cleared. Before loading, all safety interlocks, earthing, venting, etc., should be checked as operational; procedures to prevent the tanker being driven away with hoses still connected should be completed; and the tanker and loading system should be checked for leaks. To prevent spillage in the event of hose breaks, the ends of the hose should be protected from forward or reverse flow by means of emergency isolation valves and non-return valves respectively. To minimise the pressure in the hose and avoid running the tanker engine, site offloading pumps rather than a tanker mounted pump should be used. The reverse interlock procedure should be carried out before the tanker is allowed to leave.
- (e) *Personnel Protective Equipment (PPE).* As with handling of all cryogenic substances, appropriate PPE must be utilised. Consideration needs to be given to the type of gloves, eye and face protection, coveralls/aprons and footwear which should not be the lace up variety.

3.2.4 Road tankers and small storage installations

A typical small facility to supply liquid fuel gas (LFG) should include the following features:

- (a) Concrete bund wall to contain the total contents 110% of the storage tank (see section 3.4.1).
- (b) Fixed, dry-powder, fire-extinguisher installation at the tanker loading bay.
- (c) Catchment pit to contain a potential spillage and thus minimise evaporation area.
- (d) Portable dry-powder extinguishers for fighting small LFG fires.
- (e) Water hydrant points for the supply of water to cool adjacent equipment exposed to heat from a fire.
- (f) Vehicle barrier (Armco or similar) to safeguard installation from impact by vehicles.

3.2.5 Vehicle entry into plant areas

3.2.5.1 Administrative precautions

This section covers some basic precautions regarding entry of non-routine and maintenance vehicles into safe plant areas. Entry into high risk areas is covered in section 3.2.5.2. In general, vehicles may be classified in three groups:

- (a) Vehicles passing through for short periods, where adequate control can be achieved by administrative procedures and access restricted to safe areas only (e.g. escorted).
- (b) Part-time vehicles, e.g. cranes, where in addition to administrative procedures, a degree of protection to the vehicle is required (e.g. escorted).
- (c) Vehicles requiring regular entry e.g. a forklift truck, where thorough protection of the vehicle is required.

All vehicles should be checked before entry. Vehicles and their destinations on the plant site should be logged on entry and cancelled on exit in order that in the event of an emergency the operator is aware of the number and whereabouts of vehicles on the plant.

Drivers should be made aware of the route to and from the location in the plant to which they require access. If the vehicle requires access to or is taking a route through a high-risk area, the control room operator should be notified before the vehicle proceeds from the plant gate in the event that a vehicle escort is required.

Before entry, the reason for entry should be established, the driver de-matched, and a check made that the vehicle is carrying an appropriate fire extinguisher. Once on the plant the vehicle should not be allowed to block the plant roads or be left unattended with the engine running.

3.2.5.2 Vehicle entry to high risk areas

A high risk area in this context is a Zone I or Zone 2 area as defined in the 'Institute of Petroleum Electrical Safety Code' and by BS EN 60079-14 [2, 3]. Additional administrative procedures may be required to cover the need for issue of fire permits in certain circumstances, positioning of gas detectors, and suitable supervision and inspection of the vehicle such that at any time it may be shut down safely.

With regard to protection of the vehicle itself, where frequent entry is required reference to BS 5908 [4] will give details of protection considered necessary. Briefly, the requirements cover air intake protection to avoid overrunning, spark arresters and a positive shut-off, exhaust protection to avoid sparks and excessive temperatures, and electrical-equipment modifications to achieve the required safety level.

3.3 Safety in maintenance

3.3.1 Responsibility for maintenance

The manager of the facility is responsible for the safe condition of the plant, and should ensure that regular maintenance and testing of the plant equipment and safety systems are carried out by competent personnel. Any plant modifications should be checked for their safety implications and authorised by a competent authority before installation and commissioning. Vessels containing steam, air and other fluids are subject to periodic statutory inspections in accordance with the current version of the Pressure Systems Safety Regulations [5].

Other pressure vessels and systems containing hydrocarbons require inspections at set frequencies which should be established before initial plant commissioning in line with the current industry practice.

3.3.2 Routine safety maintenance - frequencies

Safe operation of the plant relies, in particular, on the correct operation of reliable safety instrumentation, which demands regular inspection and testing. As a minimum, all instruments, relief valves, and major equipment controls, e.g. for compressors and their drives, should be checked and tested in the first year of plant operation. More frequent testing, usually monthly, will be required on certain defined safety systems to ensure that an acceptable standard of operation is achieved.

3.3.3 Conditions for safe entry and working under permit

When carrying out work on plant containing natural gas, either in a cryogenic state or ambient temperature, a permit to work system should be applied. See Section 1.2.9.5 of this manual.

3.4 Storage systems

3.4.1 General

The physical properties of liquefied flammable gas fluids dictate the need to use materials of construction which are resistant to brittle fracture at low temperatures [6-9]. Typical materials, for service at -100 °C and below, range from magnesium aluminium alloy, 9% nickel steel and stainless steels. Specific choice depends upon the application. Small volumes of LNG may be contained under pressure within a vacuum-insulated vessel, the vacuum being of the order of 0.01 mbar or less [10]. Any leakage into the interspace would adversely affect the insulating properties. Hence potential leak sources are minimised where possible by the use of welded connections.

In contrast, a large refrigerated volume at near atmospheric pressure is contained within a double-walled, flat-bottomed metal tank [11]. The annular space between the two tanks is filled with special insulating material, such as expanded perlite.

The inner tank, in contact with the cryogen, is made of a suitable material, as described above, while the outer tank can be constructed of similar material, concrete or carbon steel plate, depending on the integrity requirements of the system. The outer tank contains the gas pressure and insulating materials.

Secondary containment is provided by a bund surrounding the storage tank. As a low earth bund offers little or no protection against a gas cloud spreading from a liquefied gas spill in the bund, some form of high level concrete bund, designed for cold shock from the release of the tank contents close to the storage tanks, is installed in modern storage designs. The bund can be a separate wall or an integral part of the tank design to form a double containment system. In addition, the whole system may be buried (excepting the roof) by provision of an earthen berm.

3.4.2 Liquefied Natural Gas (LNG) storage

Fig.11 shows an LNG storage tank (it may be noted that in this design the tank is surrounded by a high bund wall).

A large LNG facility to supply gas should incorporate the following features:

- (a) Two approaches to bund design for containment of the total tank inventory:
 - (i) A two spillage level arrangement, i.e. 10% and 110% of the total tank contents.
 - (ii) A high pre-stressed bund wall.
- (b) High expansion foam monitors located at the 10% periphery to minimise the evaporation rate.
- (c) Fixed water deluge facilities to cool the roof and wall of the tank exposed to heat from a possible fire in adjacent plant.
- (d) Low temperature sensors situated within the bund for potential LNG spillage detection and activation of the foam system.
- (e) Two approaches to liquid removal:
 - (i) A single outlet line at the base of the tank protected by a fail-safe shut-off isolation valve, with remote activation in addition to the normal isolation valve.
 - (ii) In-tank pumps with 'over the top' outlet line, avoiding the need to breach the tank wall.



Fig.11 LNG storage tank and bund wall. (Courtesy of BG Storage)

3.4.3 Large tank operations

3.4.3.1 Rollover

Rollover occurs when adjacent layers of LNG in a storage tank reach the same density and mix suddenly. The material in the lower layer is then under less head of pressure and consequently produces vapour rapidly. The total amount of extra vapour is proportional to the mass and supersaturation temperature of the lower layer.

In a 'normal' tank of LNG it is well established that there exists a very thin top layer whose temperature is slightly colder than the bulk of the LNG. Heat leak through the base and walls causes the adjacent LNG to be slightly warmer than the bulk, and this warmed LNG therefore rises to the surface, where it 'flashes' (creating boil-off). The LNG remaining after loss of boil-off is colder and therefore sinks through the bulk and mixes with it. This mechanism is aided by the density rise associated with the preferential evaporation of low molecular weight methane during boil-off. The tank is therefore in a state of dynamic equilibrium, the bulk of LNG being well mixed by these convection currents, while the surface layer is being constantly replenished.

If the tank pressure changes, the top layer responds virtually immediately, its temperature rising or falling accordingly. For example, if the boil-off compressor loading is increased, the pressure drops and the top layer temperature falls to a value which is in equilibrium with the lower tank pressure. The LNG rising to the surface now flashes off more than before (because the pressure is lower), and the colder LNG sinking into the bulk gradually results in a cooling of the bulk over a long period. Likewise, when the tank pressure is increased, there is less boil-off and the bulk LNG warms over a long period.

Over a long period of operation of an LNG tank the average boil-off is determined by the average heat leak into the tank. The top layer effect means that there can be variations in boil-off, the bulk of the LNG acting as a heat store or reserve of boil-off. The longer the period that boil-off is held below average by maintaining a high pressure, using a reduced compressor loading, the longer the period of high boil-off will tend to be when the pressure is reduced.

A prerequisite to rollover is the stratification of LNG in a storage tank [12, 13]. This may be caused by either of the following:

- (a) The loading of fresh LNG into a tank containing a liquid residue (a 'heel'). This is more likely to cause stratification if a denser liquid is added underneath a less dense fluid, or a denser fluid is added on top of a lighter one.

Normally, liquid coming from the liquefaction plants is colder than the liquid in the tank, and hence is invariably denser (whatever the weathering, i.e. density vs time, characteristics). Denser liquids should always be top-filled to ensure good mixing.

- (b) Auto-stratification. When LNG in a tank contains a higher proportion of nitrogen, greater than approximately 0.8 %, auto-stratification is theoretically possible [12]. As the LNG reaching the surface flashes, the boil-off vapour contains a high proportion of nitrogen. The LNG remaining, although colder, can be less dense because of the fall in molecular weight caused by loss of nitrogen. Hence there is no tendency for the top layer to sink into the bulk of the LNG. Under some circumstances therefore, the top layer, instead of being in dynamic equilibrium and being continually replenished, builds up as a stratified layer.

In this situation, the bulk of the LNG cannot reach the surface, owing to the layer above, and it gradually warms through heat leak into the tank. The top layer continues to boil-off, as it is warmed by heat transfer from the layer below, but at a much reduced rate.

Hence the pressure can be maintained with very low compressor loadings. This stratified condition cannot continue indefinitely. The top layer eventually loses so much methane that its molecular weight starts to rise again and its density increases (or at least decreases more slowly). The bulk of the LNG falls in density because its temperature is rising, and eventually the densities of top and bottom layers equalise. This is a metastable situation, and any disturbance, e.g. a change in compressor loading, will promote sudden mixing of the two layers. The bulk LNG, which was superheated, can now boil-off. This is a classic 'rollover', and results in a surge of boil-off over a period. The duration and rate of boil-off during a rollover are notoriously difficult to predict.

Prevention and removal of stratification are the appropriate actions for avoiding rollover. Instrumentation for detecting stratification should be provided in each tank. If stratification is suspected then mixing procedures should be implemented without delay. [13]

3.5 Firefighting

3.5.1 Fire situations

Identifications and risk of accidental fires on process plant will have been systematically studied at the project design stage. Some of the simpler aspects and principles are discussed below. Often other flammable liquids are present on a site as well as cryogenics, and it is therefore important to appreciate that different fire situations may arise.

3.5.2 Fire initiation

It is the vapour phase of a liquid which takes part in the flame production. The readiness of liquids to form a vapour at ambient condition is therefore of prime importance. For example, an LNG liquid spill on the ground instantly creates a vapour at a high rate which then decays to a much slower rate, depending on heat leakage from soil/atmosphere. Following ignition, a short-lived flash fire would occur, followed by steady burning from the pool. However, vapour evolution can be undesirably increased by breaking up a surface liquid pool, e.g. by fireman's jet hose, or if the liquid is discharged as a spray from a pressurised leak source.

In contrast, a flammable liquid such as diesel oil produces vapour much more slowly.

3.5.3 Fire extent

The pool diameter size gives guidance towards possible flame height. With most ignited spills, flame height will be limited to 1-2 times pool diameter. As the pool diameter increases, there is a tendency for the flame to break up into a number of smaller pool flames, as distinct from one main flame.

3.5.4 Fire duration

The duration of the fire is dictated by the regression rate and the depth of liquid.

3.5.4.1 Flammable leaks/ delayed ignition

Serious consequences can result from small leaks, e.g. the escape from a failure of a 15mm line, if allowed to accumulate in confined environments. Should the accumulation be subsequently ignited, an overpressure or explosion could be created. Potential confined spaces include built-up process areas and spaces within buildings.

The importance of shutting off the fuel supply to the fire cannot be overemphasised. Equipment which experience shows is particularly liable to leak should be fitted with remotely operated emergency isolation valves.

3.5.5 Practical situations

3.5.5.1 Minor leaks

Leaks can occur during operation from pipe flanges, pump seals, and valve glands. In the design, consideration must be given to the possibility of a leak, ignition, and the consequences of flame impingement on associated plant.

3.5.5.2 Major leaks

Large quantities of hydrocarbon liquids need special consideration. For example, with a potential LNG tank fire it may not be possible to extinguish it, and hence the emphasis should be to protect surrounding plant. With storage tank farms, fixed water deluge systems may be provided on each tank, which will reduce the chance of a fire in one tank spreading to others.

Caution is needed with high pre-stressed concrete bunds, as an adverse external tank hydraulic overpressure could result if the deluge water was allowed to accumulate in the tank/bund interspace.

High-pressure storage introduces different requirements. The characteristics of a fire would be a torch-like flame. If the flame is vertical, the effects of thermal radiation will have to be considered. With a horizontal flame, spread to adjacent process equipment is a possibility.

Flames impinging on equipment may soften the metal and lead to a failure, with a subsequent boiling liquid expanding vapour explosion (Bleve). In both situations priority must be given to isolating the fuel supply. Remotely operated isolation valves may be located on the inlet and outlet tank liquid lines to minimise spill duration.

A practice observed with some pressurised liquid storage systems is to provide a catchment pit situated away from the storage area to collect major spills. In this way it may be possible to transform a potentially serious fire situation into a controlled situation.

3.5.6 Firefighting agents and equipment

The two principal agents are water and foam.

Water is used for cooling adjacent plant in the vicinity of a fire and also for foam production. It is not a suitable firefighting agent for flammable liquids, but when used as fogging spray, it can be effective as a heat shield to assist access to the equipment near a fire.

Foam is the most effective means of suppressing and extinguishing flammable liquids when burning. For installations of 10,000 tonnes and above, a fixed foam distribution system should be installed.

3.5.6.1 Foams

Water in the foam provides a heat-resistant blanket of lower density than that of a flammable liquid, and is able to extinguish fire by:

- (a) Cooling.
- (b) Suppressing vaporisation.
- (c) Preventing the ingress of oxygen.

Foams are normally categorised in terms of their expansion ratio.

3.5.6.1.1 Low expansion foams. These are normally of the protein type and used for fighting fires where the process liquids are non-miscible in water, e.g. fuel oils, particularly those with a flash point below 100°C. Special 'alcohol-resistant' foam is required when dealing with water-miscible liquids, for which normal grades of foam would need extremely high application ratios.

3.5.6.1.2 Medium expansion foams. These are normally of the detergent type and have been found to be the best type of foam for fighting LNG fires as they provide very rapid blanket coverage over a large area. The foam compound has a good shelf life and requires less storage space than low expansion foams. Compared with low expansion foams, however, they have poor 'throw' i.e. cannot be projected any great distance from the generator. In addition, they are easily carried away by wind and are broken down by fire and by some chemicals.

3.5.6.1.3 High expansion foams. High expansion foams are particularly useful for extinguishing fires in large contained volumes, where the whole volume can be filled with the foam, i.e. by flooding buildings and other enclosures.

3.5.6.1.4 Aqueous film forming foam (AFFF). This foam is available in two forms - standard and alcohol-resistant. The experience with these foams is at present limited, but evidence currently available indicates that although they are more expensive than 'conventional' protein foams, the required application rates are lower; they are also less toxic and they do not deteriorate in storage.

3.5.6.2 Hand-held and mobile firefighting equipment

Advice and agreement of the local fire authority should be obtained in arriving at requirements to ensure compatibility with its equipment. Where equipment such as extinguishers, nozzles, etc., is kept out of doors, it is important that adequate weather protection is provided. The locations of all such fire points should be numbered and each location number shown on a layout drawing.

All equipment should be regularly inspected and maintained and a record kept of all such work. It should be noted that this is a legal responsibility of the occupier.

3.5.6.2.1 Dry powder extinguishers. For general use a suitable size of hand-held extinguisher is preferred. All extinguishers should be permanently and distinctly marked to identify the type of powder. At specific locations on a site where hand-held extinguishers are not considered to be adequate, larger trolley-mounted units should be provided. All continuously manned sites should be equipped with a minimum of two trolley-mounted units. For installations which require a fire certificate, such as an LNG site, all dry powder extinguishers should be filled with a potassium powder (monnex or equivalent).

3.5.6.2.2 Monitors. For sites with low manning levels, portable water monitors should be provided where a firefighting main is installed. These monitors will enable cooling water to be applied on plant and equipment with minimal effort. A minimum of two such units should be available on each site.

3.5.6.2.3 Foam units. On sites where quantities of flammable liquids in excess of 2000 litres are stored, a minimum of one trolley-mounted foam unit of at least 100 litres foam-concentrate capacity should be provided.

3.5.6.2.4 Fire suits. A minimum of 2 fire protection suits should be provided on all permanently manned sites.

3.5.6.2.5 Firefighting equipment cabinets. Fire cabinets should be provided to store valve handles, hoses and nozzles, etc. Where it is necessary to provide a standpipe hydrant leg, this equipment should be housed in a suitable weather-protected cabinet.

3.6 Detection systems

3.6.1 Leak detection

Detection is normally used in order to give early warning of leaks, and is particularly important when manning is minimal. The effectiveness of a system can be determined only after careful consideration of the suitability of the sensing detectors for the envisaged situation.

For pressurised fluid leaks, the movement of liquid/gas causes a change of energy. It may be possible to identify and detect this particular change of energy within the pipework or where the gas/liquid is leaking from the pipework. With LNG the 'cold' can be used as the basis of a detection system. In this instance, thermocouples or optic fibres are employed as sensing elements in the field.

The final physical change that occurs, in terms of time, is vaporisation of the liquid to a gas and the formation of a flammable mixture with air. When a specific ratio of gas to air is present at the detector head (gas detection), the detection system becomes active.

3.6.1.1 Flammable-gas detection

Gas-detection systems have been developed for use in storage areas and plant areas where an undetected release of flammable gas or vapour could occur. A gas-detection system is basically used to give early warning of leakage, and is particularly useful in storage areas where operator cover is minimal, owing to the large area covered by the installations and the automatic action of the installed equipment.

3.6.1.1.1 General. In areas where more than one gas is to be detected the instruments should be calibrated for the least sensitive gas in that area.

Where the detectors depend on an effective catalyst, care should be taken to use the correct detector type to avoid poisoning of the catalyst. For example, in areas where silicone grease or oil is used, 'normal' detectors will require filter elements to be fitted.

As a general requirement, the operator should check that gases present, other than flammable gas being detected, are compatible with, and not likely to inhibit, the detector catalyst.

In practice, devices require fitting with draught cones and weather protection when mounted in the open.

As with most safety systems, the integrity of the gas-detection systems can only be maintained by regular testing of the equipment by trained personnel.

3.6.1.1.2 Gas-detection systems. There are basically three ways to use gas detection systems:

- (a) The area is ringed on the periphery with gas detectors calibrated to read out percentages of the LFL (lower flammable limit) for the particular gas being measured. The detectors are spaced to cover the plant area, assuming that leaks have an angle of spread of 30 degrees.
Usually these detectors are connected to a control room annunciator panel, together with wind speed and direction indicator, such that an alarm is given and the operator can take the appropriate action, which can be to actuate emergency valves, call the fire brigade or activate steam curtains or other protective systems. Alternatively, the detectors can be used to start the protective systems automatically, such as steam curtains, to disperse the gas cloud.
Open-path infra-red sensors which can detect flammable gases at any point along their beams are being developed.
- (b) Point source detectors may be used around equipment, such as pumps, separator pits, etc., which may have shown a high potential for developing gas releases, to give the operators, in a remote control room, early warning of danger. Another application is in analyser buildings, where the detector would be used to shut off automatically any power supplies feeding non-classified electrical equipment in the event of flammable gas being detected.
- (c) Where maintenance work, especially hot work, is being carried out in a live plant area under a fire permit, portable gas detectors which give local audible and visible alarms may be used around the area of work to ensure that conditions remain safe for the duration of the maintenance activity, and that the work is stopped if the conditions change.

3.6.2 Fire detection

A similar approach can be made for the detection of fire. Important parameters are smoke particles, combustion products, and energy (convection and radiant heat).

Infra-red/ultraviolet detection in theory affords the fastest response, since the signal arrives at the detector instantaneously. Other types of detector can take the form of simple plastic tubes filled with air under pressure which burst at high temperature, release internal pressure and trigger an alarm system. In practice, a combination of detectors may be used after careful evaluation of the flame characteristics of the material in question.

Transmission of the alarm signal must be engineered for reliability and protected from foreseeable hazards, such as power failure, fire, explosion or vehicle impact.

3.7 Standards, codes of practice and detailed guidance

The siting, design and construction of plant and storage facilities for liquefied natural gas are covered by various standards and codes of practice [14-16]. Reference can be made to these documents for guidance on design considerations.

The general precautions for handling flammable cryogenic fluids given in this Manual also apply to their handling during bulk transport by sea in special vessels, or gas carriers, and to the offloading of such vessels. Guidance on the safe handling of LNG is published in the British Compressed Gases Association (BCGA) Codes of Practice CP46 [17]. Revised BCGA CP41 Code of Practice has been extended to include LNG [18]. The safe design, construction and management of gas carriers are covered by various Conventions of the International Maritime Organisation [19, 20]. Guidance on the safe handling of liquefied gases on gas carriers and at marine terminals is also published by the Society of Gas Tanker and Terminal Operators (SIGTTO) [21, 22].

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4. Hydrogen

This part supplements the general safety requirements in Chapter 1 to cover the special precautions to be observed in the operation and maintenance of plant and equipment used in the handling of liquid and gaseous hydrogen at low temperatures [1-5]. The greatest hazards are those of fire or explosion. Other hazards, resulting from high pressures, low temperatures, and atmospheres other than normal, will be referred to as secondary hazards [1–14].

4.1 Properties

Below we present the physical properties of hydrogen (H₂) and, for comparison, the physical properties of methane which is the main constituent of Liquid Natural Gas (LNG) broadly used in modern technology [14].

Table 7 Thermo-physical properties of hydrogen (H₂) and, for comparison, the physical properties of methane

Property	Hydrogen	Methane
Normal boiling point (K)	20.3	111.7
Density of saturated liquid at 1 bar (kg/m ³)	70.8	422.5
Gas density relative to dry air (at 1 bar, 15°C)	0.07	0.56
Static thermal conductivity at 15°C (mW/mK)	188	35.5
Latent heat of vaporisation at 1 bar (cooling potential of phase change) kJ/kg	445	510.6
Volume ratio of evaporated vapour/liquid at 15°C	828	622
Flammable limits in air at 1 bar, 15°C (vol. %)	4-75	5.3-17
Ignition energy (mJ)	0.017	0.274
Heat of combustion (MJ/kg)	142	55

Note: Pressures in bars absolute

4.2 Specific hazards

4.2.1 The fire and explosion hazard

4.2.1.1 General

Hydrogen is a high energy fuel which, when mixed with air or other oxidisers, releases large amounts of energy in the form of heat or explosive force when ignited [6-11].

The gas is very light and travels rapidly upwards at ambient temperature. Release under eaves outside a building can therefore present a problem, as the gas may find its way into the building. Within buildings, high-level ventilation should always be provided.

Special care is necessary in any part of a process necessitating possible operation below atmospheric pressure, as this can quickly lead to the formation of an explosive mixture due to ingress of air.

4.2.1.2 Ignition and burning characteristics

4.2.1.2.1 *Spontaneous ignition temperature (SIT).* Hydrogen has a spontaneous ignition temperature of about 450 °C (723 K), but this value depends on measurement conditions.

4.2.1.2.2 *Laminar burning velocity and significance of confinement.* The laminar burning velocity is relevant to the violence of explosions and to the tendency of a flame to 'run up' into a detonation. The burning velocity of hydrogen is markedly greater than that of other common fuels, indicating that the hazard of explosions and detonations must be carefully considered. A practical consideration that affects the probability of 'run up' is the degree of confinement of the flammable mixture; the greater the degree of confinement, the greater the probability of explosion. It has been shown that even with partial confinement, burning to detonation of hydrogen/air mixture can be expected.

4.2.1.2.3 *Minimum ignition energy.* Spark ignition energies may be used as a measure of sensitivity to ignition by local sources. Hydrogen differs from many other flammable gases in that it requires significantly less energy for ignition, e.g. in air, the minimum ignition energy for methane is 0.28 mJ, as opposed to 0.02 mJ for hydrogen. This is borne out by the fact that venting or leaking hydrogen can ignite spontaneously. The presence of dust in a vent stack can cause ignition of hydrogen by discharge of static electricity.

4.2.1.2.4 *Flammable range.* Appreciation of the wide range of concentrations in air or oxygen in which hydrogen is flammable is very important. The flammable range at 1 bar of hydrogen in air is 4-75 per cent by volume; in oxygen it is 4-94 per cent. Compared to other flammable gases, this is very wide. Note that methane has a range of 5-17 per cent in air; for propane, the range is 2.1-9.5 per cent. At pressures and temperatures above ambient or with inert gases other than nitrogen, e.g. argon, the range can be widened.

4.2.1.2.5 *Limiting oxygen index.* The limiting oxygen index is the minimum concentration of oxygen to support flame propagation when a stoichiometric fuel-air mixture is diluted with nitrogen. In other words, it is the least amount of oxygen required to support combustion. In general, gaseous hydrocarbons require 10-12 per cent oxygen by volume in the original atmosphere to support combustion, but hydrogen requires only 5 per cent oxygen.

This value, of course, sets a limit on the quantity of oxygen that can be tolerated when purging or inerting equipment. (Note: air contains 21 per cent oxygen by volume.)

4.2.1.2.6 *Quenching distance.* This is the minimum gap between two parallel surfaces which will just permit a flame to pass without cooling it to extinction. The smaller the quenching distance, the greater resistance the flame has to cooling, and the more difficult it will be to extinguish. The quenching distance for hydrogen is about one-third that for hydrocarbons such as propane. Thus, flameproof equipment for hydrogen has to be designed to a much higher standard than for other flammable gases.

4.2.1.2.7 *Flame characteristics.* Hydrogen burns at higher temperatures, but generally gives off much less radiant heat than propane or other hydrocarbons. The flames are colourless or nearly colourless. Both these characteristics make it more difficult to detect a hydrogen fire. Detection of burning hydrogen is easier at night or in subdued lighting. Ultraviolet sensors, linked to alarm systems, can be used to detect and give warning of the presence of hydrogen flames.

4.2.1.3 Oxidants and their avoidance

The oxidising agents which may exist in a hydrogen plant are air, cold-box atmospheres containing air diluted with nitrogen, or oxygen-enriched air. It should be remembered that air will initially be present in cold boxes, process vessels, and pipework. When air condenses on cold equipment, the liquid produced is substantially enriched in oxygen and is therefore a more powerful oxidant than air.

4.2.1.3.1 Purging. The limiting oxygen index is relevant only to the problem of flammability. Considerations such as solubility, liquefaction, or freezing at the process temperature involved, may require limiting the oxygen to much lower concentrations than those dictated by flammability alone.

Before the introduction of hydrogen into processing equipment, air should be eliminated by nitrogen purge to give an exit oxygen concentration of less than 20 per cent of the minimum oxygen index.

4.2.1.3.2 Air ingress. Hydrogen plants should never be operated below atmospheric pressure, as this could lead to the ingress of air and the formation of flammable mixtures. Suitable safeguards should be provided to prevent operation below atmospheric pressure.

4.2.1.3.3 Oxidant removal. Hydrogen feed gas that may contain oxygen should have the oxygen removed by catalytic conversion at ambient temperatures. In addition, low-temperature adsorbers should be provided to remove trace quantities of oxygen or other oxidisers where concentrations warrant it. At liquid hydrogen temperatures, oxygen is soluble in liquid hydrogen to the extent of only a fraction of a part per million, so small concentrations of oxygen can cause accumulations of solid oxygen with a potential explosion hazard.

Other potential oxidants such as nitrogen oxides should be removed by adsorption, catalyst, or other means.

4.2.1.3.4 Monitoring. Analysis by low-temperature adsorption and chromatography or other means should be provided to give maximum assurance of freedom from potential hazards due to contaminants.

4.2.1.4 Condensation of air and other gases

The low temperature of liquid hydrogen can solidify any gas except helium. The solidified gases could plug restricted areas, such as valves or small openings, and cause equipment failure. If air or oxygen is allowed to condense and solidify in liquid hydrogen, a potential explosion hazard can result. Because air (oxygen) will condense into it, liquid hydrogen should generally be handled in closed systems provided with safety relief devices which exclude air. An exception may be made where, with proper precautions, as outlined below, quantities of a few litres of liquid hydrogen are handled in laboratory or test operations in open Dewar vessels properly stoppered and vented.

The venting systems on liquid hydrogen containers should be examined periodically to make sure that they do not become plugged with moisture frozen from the air.

4.2.1.5 Electrostatic effects

Electrostatic charges can build up as result of friction in pipes or by the break-up of liquid hydrogen to droplet size. This can cause ignition where gas is venting to atmosphere.

4.2.1.5.1 Safeguard against electrostatic build-up. Routine inspection to ensure the integrity of electrical earthing and bonding systems on plant equipment is essential. When maintenance work has been carried out, the electrical bonding should be checked before re-commissioning.

4.2.1.5.2 Road tanker operation. Before transfer begins, tankers carrying liquid hydrogen must be equipped with an earth cable for connection to the earth terminal of the receiving equipment, and remain connected until transfer is completed.

4.2.1.5.3 Electrostatic ignition risks. When gaseous hydrogen and air are mixed within the limits of flammability, the threshold ignition energy can be as low as 0.02 mJ.

The maximum electrostatic energy which can be acquired by a man standing on an earthed plate in insulating footwear is about 15 mJ; thus it is desirable to dissipate this body charge. This can conveniently be done by wearing anti-static, non-sparking footwear having a leakage path of not more than 5 M Ω to earth.

4.2.1.6 *Electrical equipment*

All electrical equipment, such as switches, motors, instruments and portable testing devices, used and installed within the boundary of the hydrogen installation shall be suitable for the requirements of the area classification. The classification of areas will be in accordance with the definitions in BS EN 60079 [15].

4.2.1.7 *Firefighting*

Hydrogen fires burn with an almost invisible flame. Hence the particular need to fight from a safe distance and from the upwind side.

The most effective way of dealing with a hydrogen fire is to shut off the hydrogen supply. Depending upon the circumstances, it is not usually advisable to extinguish a hydrogen flame in confined areas if the hydrogen supply cannot be shut off. The continued escape of unburned hydrogen can create an explosive mixture which may be ignited by other burning material or hot surfaces. It is better to allow hydrogen to burn in localised areas and keep adjacent objects cool with water rather than risk the possibility of an explosion. Proceed as follows:

- (a) Use large quantities of water, preferably in the form of a spray, to cool adjacent equipment and to cool any burning material below its ignition point. Do not apply directly to a pool of burning liquid hydrogen, as water will evaporate additional gas.
- (b) Liquid hydrogen when exposed to the atmosphere will produce a cloud of ice/fog from the air. The flammable mixture will probably extend beyond this vapour cloud, and personnel should therefore keep well outside the area of visible cloud.
- (c) If electrical equipment is affected by the fire, disconnect the supply or use carbon dioxide or dry chemical extinguishers above and not directly on to the fire.

4.2.2 **Secondary hazards**

These take the following forms:

- (a) Mechanical hazards arising from embrittlement of materials caused by exposure to a hydrogen environment and the very low temperature at which hydrogen is processed.
- (b) Over-pressurisation hazard caused by additional liquid hydrogen boil off due to ortho-para conversion.
- (c) Health hazards applicable to hydrogen.
- (d) Health hazards due to other gases associated with hydrogen processing.

4.2.2.1 *Mechanical hazards*

These hazards may take the following forms:

- (a) Pressure rupture - due to trapping cold liquid or vapour.
- (b) Brittle fracture - due to metals being used below their transition temperatures. Brittle fracture can be also caused by hydrogen embrittlement of a material exposed to the hydrogen environment.
- (c) Freezing leakage. If water is present before cooling down, plant and equipment fractures may occur, owing to the expansion of ice formed. Plant dryness is therefore vital.
- (d) Contraction leakage. Sudden cooling down can lead to contraction and leakage from bolted flanges, which may have to be specially designed to overcome this problem.
- (e) Hydrogen embrittlement – metals such as steel become brittle, and subsequently may fracture, as a result of hydrogen diffusion.

These hazards have been dealt with in more detail in Chapter 1 (except point e) but it should be remembered that, owing to the very low temperatures involved in liquid hydrogen plants, the effects

of the various hazards are liable to be more pronounced than they would be in the case of other gases, except helium.

4.2.2.2 *Over-pressurisation hazard caused by ortho-para conversion.*

Hydrogen is essentially a mixture of ortho- and para- hydrogen, with an equilibrium concentration of 75% ortho- to 25% para- at ambient temperature [14, 16]. However, when liquefied at 20 K, there is a slow but continuous transformation of the ortho- hydrogen to the lower energy para- hydrogen.

The heat of transformation is around 120% of the latent heat of evaporation. The boil-off generated to the complete transformation over a few days might evaporate around 70% of the liquid hydrogen tank. The standard way out of this problem is to catalyse the ortho-para conversion to a final state of 95–99% para during the cooling and liquefaction from ambient temperature.

In addition, the co-existence of ortho- rich and para- rich liquid with different densities may lead to stratification and subsequent rollover with sudden and uncontrolled boil off. Thus the tanks used for storage and shipping must be able to vent freely to avoid mechanical failure.

4.2.2.3 *Health hazards - hydrogen*

The hazards to health of gaseous hydrogen and liquid hydrogen stem from their low temperatures and the exclusion of oxygen arising from vaporisation in enclosed spaces.

Serious tissue destruction similar to that caused by burns can occur when liquid hydrogen comes into direct contact with body surfaces, owing to the low temperature of the liquid. Similar effects can arise from body contact with uninsulated equipment containing cold fluids.

Hydrogen is non-toxic, but oxygen exclusion will result in asphyxiation, and it should be noted that this can often occur so rapidly that the victim may be unable to escape even if he/she realises that something is wrong.

4.3 Hydrogen plants

The term 'hydrogen plant' is used to define any plant designed primarily for the low-temperature separation and/or liquefaction of hydrogen.

Such plants have both hot and cold sections. The low-temperature construction in which the cryogenic process equipment is contained is known as the 'cold box'. It requires the same general construction considerations as other cryogenic process plants, except that a flammable product is being dealt with, and temperatures considerably lower than the liquefaction points of oxygen and nitrogen are encountered.

4.4 Liquid hydrogen storage, transport and handling equipment

Liquid hydrogen storage, transport and handling equipment includes all component parts, assemblies, sub-assemblies, piping, and instruments in contact with the gaseous or liquid hydrogen, including:

- (a) Storage and transport tank inner vessels, piping, safety valves, fittings, and instruments.
- (b) High pressure piping, safety valves and instruments.
- (c) Evaporator inner vessels, evaporator coils, connecting piping, valves, safety valves, fittings, and instruments.
- (d) Piping and valves for liquid storage manifold system.

It is essential that personnel concerned with maintenance and operation of liquid hydrogen storage, transport, and handling equipment should be familiar with Chapter 1 of this guide.

Liquid hydrogen storage and handling equipment should be designed and installed in accordance with established codes and safe practices [4, 6, 8] which incorporate all necessary features for their safe operation. A bulk storage tank for liquid hydrogen is illustrated in Fig.12.

Operators should be properly trained in the operation of equipment and in dealing with emergencies, e.g. spillage, fire. The line system and the fluid being handled should be clearly identified at all times.

Clear access for vehicles should be provided. Hard standing for plant and for filling vehicles should comprise impermeable non-combustible material. In covered areas adequate ventilation must be maintained. Where possible, installations should be located outside. Areas for liquid hydrogen storage must be adequately guarded and posted to prevent access by unauthorised personnel and must be defined as a 'no smoking, no naked lights' areas.



Fig.12 Liquid hydrogen storage tank (Courtesy Air Products)

Liquid hydrogen in bulk quantity presents extremely hazardous properties as a medium for energy storage in the public domain [14]. Safety standards for shipping bulk liquid hydrogen are currently in preparation.

4.4.1 Protective clothing

During transfer operations personnel should wear gloves and goggles, or preferably full face-shields appropriate for the temperatures which will be encountered, to prevent liquid hydrogen contact with the skin and eyes. Cold burns may result from contact of liquid hydrogen with the skin after only a few seconds. If liquid hydrogen contacts the skin, irrigate the affected area with cold water and obtain prompt medical attention. The wearing of flame resistant overalls can provide additional protection in the event of fire.

4.4.2 Use of correct transfer equipment

Only containers specifically designed to hold liquid hydrogen or approved for liquid-hydrogen service by the manufacturer should be used. Such containers are made from materials which can withstand the rapid changes and extreme differences in temperature encountered in working with the liquid.

They should, however, be filled as slowly as possible, to minimise the thermal shocks which occur when any material is cooled.

Quantities of liquid hydrogen considerably greater than 5 litres should always be handled in enclosed vessels equipped with suitable relief valves or vents. All containers for liquid hydrogen service should be vented or protected by a safety device which permits the escape of vapour but excludes entry of air. The vent should be checked at regular intervals to ensure that it does not become plugged with ice. Inadequate vent capacity can result in excessive gas pressure, which may damage or burst the container. It is recommended that, to prevent air ingress, containers are not completely emptied before being returned for refilling.

Use transfer equipment which has been designed for liquid hydrogen service. Unlike most other liquefied gases, liquid hydrogen should not be poured from one container to another or transferred in an atmosphere of air. If this is done, oxygen from the air will condense into the liquid hydrogen, adulterating it and presenting a possible explosion hazard. Pressurised withdrawal through an insulated tube is recommended. The liquid should be pressurised with very pure, dry, regulated hydrogen or helium only - not with air or nitrogen.

4.5 Liquid/Cold gas hydrogen - Land vehicle fuelling system interface

The International Standard ISO 13984 [17] specifies the characteristics of liquid hydrogen refuelling and dispensing systems on land vehicles of all types in order to reduce the risk of fire and explosion during the refuelling procedure and thus to provide a reasonable level of protection from loss of life and property. This International Standard is applicable to the design and installation of liquid hydrogen (LH₂) fuelling and dispensing systems. It describes the system intended for the dispensing of liquid hydrogen to a vehicle, including that portion of the system that handles cold gaseous hydrogen coming from the vehicle tank, that is, the system located between the land vehicle and the storage tank.

Recently Society of Automotive Engineers (SAE) has established hydrogen fuelling standards known as J2601 [18]. These standards establish a fast hydrogen fuelling protocol enabling a driving range equivalent to internal combustion gasoline engine vehicles. SAE J2601 includes protocols for two pressure classes (35 and 70 MPa), three fuel delivery temperatures (-40°C, -30°C, -20°C) and compressed hydrogen storage system sizes from 49.7 to 248.6 L. Future versions of J2601 may incorporate warmer fuel delivery temperatures (-10°C and ambient) and smaller compressed hydrogen storage system for motorcycles.

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5. Helium and other rare gases

Chapter 5 deals with special precautions which must be observed in the handling of helium, neon, krypton and xenon. This section supplements the general safety requirements of Chapter 1.

5.1 Helium, neon, krypton and xenon

Liquid helium and the liquid phases of rare gases such as neon, krypton and xenon are usually encountered in much smaller quantities than other cryogenics. However, the nature and uses of these products demand special care and procedures in their handling [1, 2]. This is particularly the case in small scale and research systems, where the application is such that only a very limited amount of prior experience may be available. For example, reference to Table 2 (Section 1.2.4.1) will show that helium has the lowest boiling point of any substance, $-268.9\text{ }^{\circ}\text{C}$ (4.2 K) at 1 bar absolute, while the only other substance with a lower boiling point than neon, $-246\text{ }^{\circ}\text{C}$ (27.2 K) at 1 bar absolute, is hydrogen.

The extremes of density associated with these substances should also be noted. Helium is the second lightest of the elements with a liquid density of 125 kg/m^3 at its normal boiling point. By contrast, neon, krypton and xenon are the heaviest of the cryogenics, with liquid densities of 1206 kg/m^3 , 2415 kg/m^3 and 2942 kg/m^3 respectively.

Taking the extreme case, liquid xenon is therefore almost three times the density of liquid nitrogen and more than twenty-four times as dense as liquid helium.

5.1.1 Applications

Products such as neon, krypton and xenon, although produced and stored as cryogenics, will ultimately be used in their gaseous form at ambient temperatures, the main application being in lasers, discharge tubes and other light emitters. However, all cryogenics could be employed as refrigerants if required. In practice only nitrogen and helium are commonly used, other cryogenics being used as refrigerants only in special circumstances, usually where intermediate temperatures are required. For example, the normal boiling point of neon lies conveniently between that of helium and nitrogen, and neon offers a safe alternative to hydrogen. Helium is expensive but offers the lowest temperature of any of the cryogenics. Large-scale use of helium, greater than a few litres, is limited to the cooling of superconducting magnets and superconducting microwave cavities used in particle accelerators.

5.1.2 Potential hazards

The potential hazards in handling liquid helium, neon, krypton and xenon are similar:

- (a) The liquids are extremely cold.
- (b) The very low temperatures of helium and neon can condense, and possibly solidify, other gases. This may be a particular hazard in the case of poorly insulated transfer lines.
- (c) The volume increase from liquid to vapour is considerable and may lead to high pressures in closed systems.
- (d) Low temperature embrittlement of materials may occur, particularly at helium and neon temperatures.
- (e) These substances will not support life, so all these gases are asphyxiants.
- (f) The high densities of neon, krypton and xenon are such that dewars designed for helium or nitrogen service are not usually suitable and may be unsafe.

Although the very low temperatures associated with helium and neon can present particular design and material problems, the procedures for safe handling of these rare gas cryogenics are generally as outlined in Chapter 1. More specific information is given in the following sections.

5.1.3 Health and general safety

The precautions outlined in Chapter 1 of this manual concerning first aid, protective clothing, materials compatibility and fire and oxygen hazards apply to the handling of all cryogenics, and should be followed. However, the nature of likely applications of these particular cryogenics, perhaps including prototype or research systems, and the very low temperatures associated with helium and neon, demand that special care be taken.

5.1.4 Specific hazards

5.1.4.1 Condensation and solidification (helium and neon)

The temperature of liquid helium is sufficiently low to condense and freeze any other gas; neon is sufficiently cold to condense and freeze all gases with the exception of hydrogen and helium. Consequently, there is a danger of pipes or vents becoming plugged, and an air liquefaction hazard. Liquid helium and liquid neon must therefore be stored and handled under positive pressure or in closed systems to prevent the infiltration and solidification of air or other gases. As explained in Chapter 1, a plugged dewar or storage vessel may develop sufficient internal pressure to cause catastrophic failure.

5.1.4.2 Oxygen enrichment (helium and neon)

Since air will condense on helium- or neon-cooled surfaces, there is a potential oxygen-enrichment hazard. At its dew point liquid air contains about 50 per cent oxygen by volume, and the oxygen content of any accumulation of liquid air will rise still further as the lower-boiling-point nitrogen component evaporates. Surfaces on which condensation might occur must be cleaned to oxygen service standards and must be kept free of oil, grease or other combustible material. Ideally, all cold surfaces should be vacuum-insulated, but if a solid insulant is used at any point, this should be oxygen-compatible and non-combustible.

5.1.4.3 Materials compatibility (helium and neon)

Many of the materials qualified for nitrogen service may not be suitable for use with liquid helium or liquid neon, because of their significantly lower temperatures. Care must therefore be taken to ensure that even equipment designed for cryogenic use is in fact suitable for the extremely low temperatures associated with these cryogenics.

5.1.4.4 Risk of asphyxiation

Helium, neon, krypton and xenon are odourless, and therefore cannot be detected by smell. All these gases are asphyxiants (please see Section 2.1).

5.1.5 Handling equipment

5.1.5.1 Supply system design

Because of their limited quantities, cryogenics such as helium, neon, krypton and xenon are conveniently transported and stored in small dewars or liquid cylinders with capacities up to about 500 litres. Depending on the application, the product may be drawn directly from the main storage vessel or decanted into a smaller dewar for subsequent use. It should be appreciated, however, that each transfer process will incur a loss of product; hence the number of transfers should be minimised

by appropriate design wherever possible. A typical storage dewar and supply system is shown in Fig.13. If the product is to be used as a refrigerant, a recovery system will be added if the quantities are significant.

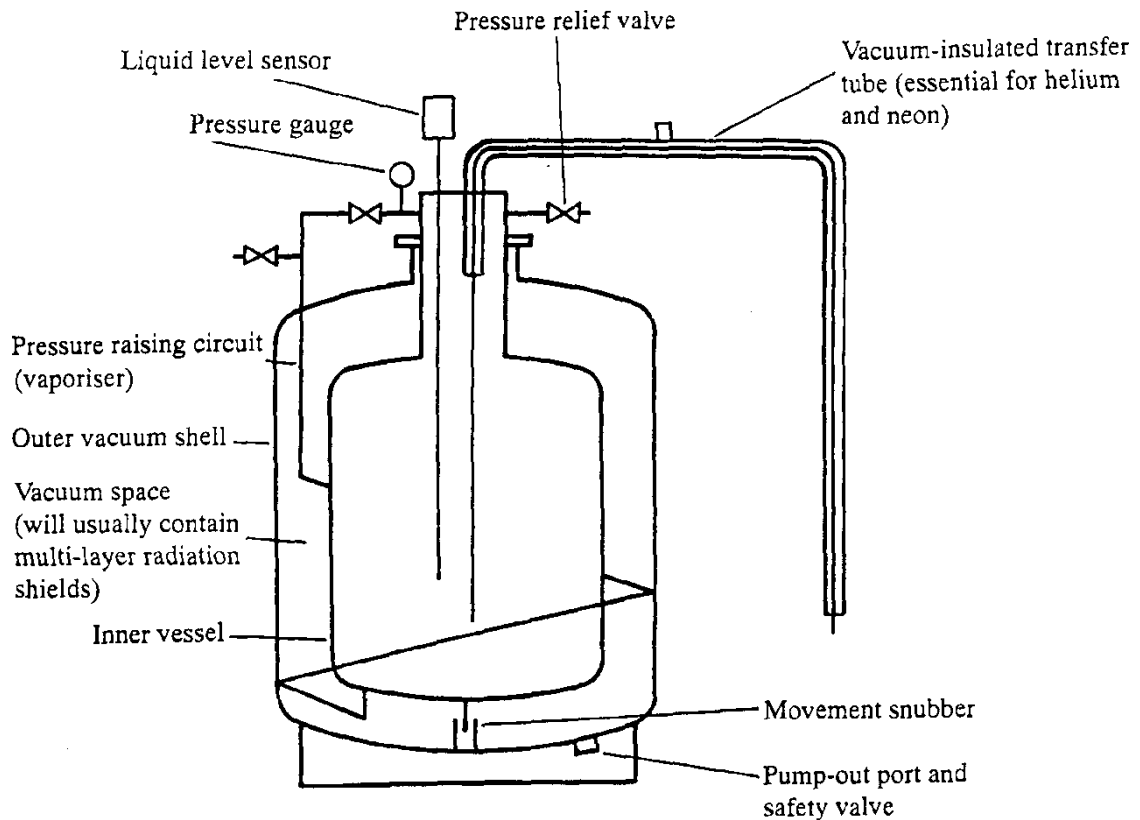


Fig.13 Typical liquid storage dewar vessel and transfer tube

5.1.5.2 Precautions when handling dewars

In addition to observing the general safety considerations relating to dewars and insulated vessels outlined in Chapter I it must be appreciated that the dewars used to contain helium and the other rare gases may demand special care in handling. Dewar vessels are designed and constructed to minimise heat in-leak, and, while not exactly delicate, do need to be treated with care. Most of the internal support is built into the neck, and the dimensions of all parts linking the inner and outer vessels will be a minimum in order to reduce conduction losses. It is therefore important not to subject dewars to mechanical shock or, in the case of certain designs, use them in other than the vertical position, especially when full. A 50 litre dewar full of krypton would weigh in excess of 150 kg. Dewars designed for helium service should not be used for any other purpose. Since the density of liquid helium is low, the vessel may not be adequately stressed to contain other cryogenics.

Dewars and many other storage vessels are designed to work over a very limited range of pressures. Care must be taken to ensure that overpressurisation is avoided. Effective safety vents must be fitted and operational to minimise this risk. In all cases the manufacturer's operating instructions must be followed [3].

5.1.5.3 Transfer processes

It is good practice to transfer all liquid cryogenics through insulated lines. Non-insulated transfer lines will result in loss of liquid and may give rise to problems associated with condensation of air and

other gases. The use of vacuum-insulated lines is essential for helium transfer and desirable for other cryogenics. If liquid loss is to be minimised, transfer lines should be pre-cooled with liquid nitrogen.

Before liquid transfer, all lines and receiving vessels should be purged with dry gas. Particular care must be taken to purge joints before assembly, and ensure that no foreign gases remain in closed-ended areas of a system.

Pressure for transfer may be provided by pressure build-up due to natural heat leak, a pressure raising circuit using a vaporiser, or by supply of pure gas from a regulated cylinder. In most cases low pressure transfer is to be preferred. The exit of a transfer line should be below the final liquid level. The cryogen should be directed towards the bottom of the receiving vessel to avoid excessive boiling and splashing. Where possible, the insertion of the transfer line should be delayed until cold vapour issues from the outlet, in order to avoid a build-up of back pressure in the line during cool-down.

If oscillations occur during transfer, the process should be stopped. This phenomenon of thermo-acoustic oscillation results from a particular combination of temperature gradient, heat transfer, system configuration and fluid properties. The oscillations are most often observed in helium transfer lines, where they can lead to a serious loss of liquid and, in extreme cases, even mechanical damage. The problem can usually be overcome by repositioning the transfer tube within the warm receiving vessel. Persistent oscillations may be eliminated by changing the volume of the receiving vessel. The phenomenon may be usefully employed in a liquid level sensing device.

5.2 Liquid helium

Liquid helium has many unique properties, and in particular has the lowest boiling point of all the cryogenics [2]. Helium gas is less dense than air and is present in the atmosphere in the ratio of about five parts per million. Practically all commercial helium, however, is obtained from natural gas, where it is typically found in concentrations of between 0.5 and 2.5 per cent by volume, although particular gas reserves may contain as much as 7 per cent helium.

Helium exists as several isotopes, the most common being He^4 . The next most abundant isotope is He^3 , although this is rarely found outside the research laboratory (ordinary helium gas contains only about 0.3 parts per million He^3). Whenever helium is referred to without any isotope designation it can be assumed to be He^4 . Mixtures of He^3 and He^4 are used in dilution refrigerators to reach temperatures below $-272\text{ }^\circ\text{C}$ (1.2 K).

In liquid form helium exhibits two very different characteristics, depending on temperature (Fig.14). Between the critical temperature of $-268\text{ }^\circ\text{C}$ (5.2 K) and the lambda (λ) line it is known as liquid helium I and, apart from its very low temperature, exhibits characteristics typical of many liquids. However, at the lambda line the liquid undergoes a transition (the lambda transition) and at lower temperatures becomes helium II. This colder liquid exhibits the phenomenon of superfluidity, having virtually zero viscosity, and in addition has an extremely high effective thermal conductivity (over 1000 times as great as that of copper) near the lambda line. Among the various applications for liquid helium are the cooling of superconducting magnets, quantum computers, microwave cavities, space simulation and the production of ultra-high vacuum.

Although high concentrations of gaseous helium are used in certain breathing gas mixtures by divers, in its pure form it will not support life and must therefore be treated as an asphyxiant. Density differences between air and released helium gas from cryogenic systems require special oxygen deficiency hazard control measures. It is not uncommon to assume that helium spills will quickly collect at the ceiling of a building or enclosure and will efficiently exit at the nearest vertical penetration or vent. However, as it has been shown that helium gas, more readily than expected, diffused through an air column in the direction opposing buoyancy [4]. This effect should be taken into account during helium gas asphyxiation risk assessment.

In general, the properties of liquid helium are sufficiently unusual to demand special equipment and handling techniques.

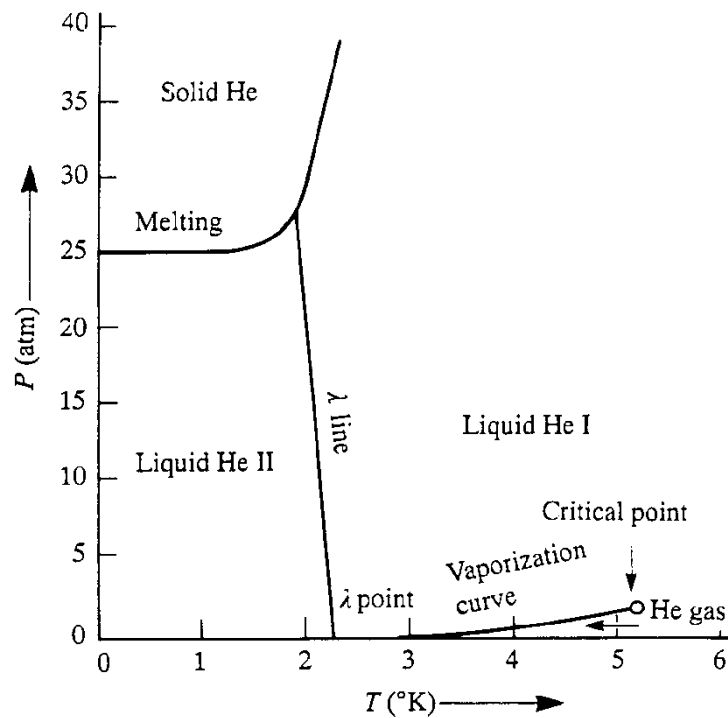


Fig.14 Phase diagram for helium

5.2.1 Vaporisation of liquid helium

Owing to its relatively low latent heat of vaporisation (less than 1/50th that of liquid nitrogen) liquid helium will evaporate rapidly when heated (for example, due to the quench of a superconducting magnet) or when liquid is first transferred into warm or partially cooled equipment. Similarly, only a very limited deterioration in the insulating vacuum of a storage vessel will result in a large increase in the rate of boiling of the liquid. Pressure relief devices for liquid helium systems must therefore be of adequate capacity to release the large quantities of vapour that may result under such circumstances.

5.2.2 Special precautions with helium dewars

The very low density of liquid helium is such that helium dewars may be of particularly light internal construction, thus minimising conduction paths and thermal mass [5]. It should be emphasised that this mechanical specification does mean that helium dewars should never be used for other cryogenes, as discussed in Section 5.1.5.2.

Hazard analysis, safety concepts, the design and operation of safety relief devices of helium dewars have been reviewed in details [6]. Currently, the safety of liquid helium cryostats is also the main subject of a joint Karlsruhe Institute of Technology (KIT) – CERN Horizon 2020 project proposal [7].

5.3 Grouping of neon, krypton and xenon

It is appropriate that neon, krypton and xenon should be grouped together, since these products are used in similar applications, at least in their gaseous forms. The gases are produced commercially as a by-product of air liquefaction, although the yield is small because they are only present in the atmosphere in very low concentrations. The cooling capacity of liquid neon is forty times that of liquid helium per unit volume, and more than three times that of liquid hydrogen. Further, neon has a higher latent heat capacity than helium, and, unlike hydrogen, is non-flammable. Despite these

desirable properties, its use as a refrigerant is still limited. Other than in very special circumstances it is unlikely that krypton or xenon would be used as refrigerants.

The normal boiling point of neon, $-246\text{ }^{\circ}\text{C}$ (27.2 K), is considerably lower than that of krypton, $-152\text{ }^{\circ}\text{C}$ (121.2 K) or xenon, $-109\text{ }^{\circ}\text{C}$ (164.2 K), and as such imposes more stringent requirements on system design and operation. In general, the procedures for handling liquid neon are similar to those for helium while for krypton and xenon, procedures used for nitrogen are appropriate. Neon, krypton and xenon are not in themselves harmful, but all will act as asphyxiants by displacing oxygen.

5.3.1 General properties

Neon	Abundance in dry air: 15.5ppm. Three stable isotopes. Inert (under most conditions). Non-toxic. Asphyxiant.
Krypton	Abundance in dry air: 0.14ppm. Six stable isotopes. Inert (under most conditions). Currently used to define SI standard of length. Non-toxic. Asphyxiant.
Xenon	Abundance in dry air 0.9ppm. Nine stable isotopes. Often considered inert but rare compounds are possible which may be toxic and even explosive. However, these are unlikely to be encountered in cryogenic plant. Non-toxic in pure form. Asphyxiant.

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