THE LINDE GROUP

Safety Advice.
1 – Handling of cryogenic liquefied gases.

1. Introduction

This safety advice provides recommendations based on practical experience gained during the safe handling of cryogenic liquefied gases. It does not replace any mandatory regulations.
A gas or liquid is in a cryogenic state when its temperature is below its boiling point. The table below shows some of the gases which are frequently handled in the cryogenic state.

2. Properties

When a gas is cooled sufficiently it will liquefy and change into a liquid, with the addition of heat this liquid will change back to a gas. So the term "cryogenic liquefied gas" may indicate a physical state of a liquid or gas depending mainly on its temperature.

The chemical properties of gases in the cryogenic liquefied state are principally the same as in the "warm" state. In their cryogenic state there is also an additional physical property, extreme cold or "cryogenic". Therefore it is important that the extreme cold temperature when handling these cryogenic liquefied gases is considered.

- **Contact:** Direct contact with a cryogenic liquefied gas can cause severe frostbite and / or cryogenic burns. Splashing cryogenic liquid can cause severe damage especially to the eyes.

- **Contact with equipment:** Pipes etc. containing cryogenic liquefied gas will be extremely cold. Naked or insufficiently protected parts of the body coming into contact with uninsulated pipes or vessels in service with a cryogenic liquefied gas may stick fast by virtue of the freezing any available moisture and the flesh may be torn away on removal. The wearing of wet clothing should therefore be avoided.

- **Embrittlement:** Materials, e.g. most plastics, ferritic steels are embrittled due to the effects of low temperatures.

3. Precautions

These are applicable to all cryogenic liquefied gases. They must be applied together with those gas specific safety measures which are given in the Safety Data Sheets and other relevant Safety Advices, e.g. Oxygen Deficiency, Oxygen Enrichment etc.

3.1. Personal protective equipment

Personal protective equipment protects against contact with cryogenic gases, liquids or exposed parts of equipment.
The clothing should be clean, dry and made from natural fibres. It should be well-fitting, yet easy to remove if impregnated with a It should cover arms and legs completely. Protruding pockets, turned-up trousers or sleeves, or coveralls tucked into boots should be avoided. As these may trap a cryogenic liquid increasing the local exposure time and therefore the cooling.

Gloves providing good insulation made from dry low-embrittling materials (e.g. leather, Kevlar®) should be worn when handling cold equipment or when splashing of liquid is possible. Gloves should be well-fitting and easy to remove if a cryogenic liquid penetrates them. Gauntlets or cuffs should be of a type to prevent the

Physical properties of some cryogenic gases

Gas	Oxygen	Nitrogen	Argon	Hydrogen	Helium	LNG	Carbondioxide
Chemical symbol	O_2	N_2	Ar	H_2	He	CH_4	CO_2
Boiling point at 1013 mbar [°C]	–183	–196	–186	–253	–269	–161	–78,5 *)
Density of the liquid at 1013 mbar [°C]	1,142	0,808	1,40	0,071	0,125	0,42	1,178 **)
Density of the gas at 15°C, 1013 mbar [kg/m3]	1,34	1,17	1,67	0,084	0,167	0,72	1,85
Relative density (Related to air) at 15°C, 1013 mbar	1,09	0,95	1,36	0,0685	0,136	0,55	1,5
Gas quantity vaporized from 1 litre liquid [l]	853	691	839	845	749	587	632

* temperature of sublimation ** at 5,18 bar

easy ingress of cryogenic liquid.
If splashing cryogenic liquid might reach the eyes a face shield should be worn, e.g. when cryogenic liquid is decanted, when hoses are connected or disconnected or when parts are immersed in the liquid. Goggles can be used but do not offer the same good protection.

When handling cryogenic liquids safety shoes should be worn. When handling flammable cryogenic gases (e.g. liquid hydrogen, LNG) shoes with conductive (so-called antistatic) soles should be worn.

Breathing equipment may be required when vaporizing cryogenic gases are displacing atmospheric oxygen, see Oxygen Deficiency.

3.2. Advices when handling liquefied cryogenic gases

Cryogenic liquefied gases are in a boiling state at atmospheric pressure. When filled into open containers at ambient temperature boiling is at first violent, as the liquid vaporizers as the container is cooled. During this phase large amounts of vaporized cryogenic gas, which may contain some liquid, are produced.and may splash out of the container. The same applies when immersing warm objects into cryogenic liquefied gases.
When the vessels or objects have reached the temperature of the cryogenic liquefied gas, vaporization becomes less violent but the cryogenic liquefied gas remains in the boiling state. The ambient temperature surrounding the vessel makes the cryogenic liquid boil off into a gas, leaving it if it is open (e.g. dewar). If the vessel is closed then the pressure inside will rise. The better the vessel is insulated the slower the rise in pressure will be.

One litre of cryogenic liquefied gas generates considerable quantities of gas (see table page 1). Working areas where cryogenic liquefied gases in open vessels are handled, require adequate ventilation which can remove at least the amount of gas generated. Adequate ventilation should prevent substantial changes in the oxygen concentration of the air: An oxygen enrichment from (normally) 21% by to in excess of 23% considerably increases the risk of fire. Therefore, cryogenic liquefied oxygen should not be kept in open vessels.

The cryogenic liquefied gas as in table 1 do not cause intoxication. However, these gases (except oxygen) might displace atmospheric oxygen which may result in suffocation if oxygen concentration drops below 15%. It should be kept in mind that low concentrations of carbon dioxide (CO_2) in air can lead to severe respiratory disorder. CO_2 concentrations in excess of 20% can lead to death within seconds. Apart from the increased risk of fire oxygen enrichment of the air to more than 23 % is not dangerous. Further information on this subject is given in Safety Advice 3 – Oxygen Deficiency and / or Oxygen Enrichment.

Exposure to an atmosphere cooled by cryogenic gases may lead to undercooling of the body, inhaling of a cryogenic gas may result in freezing of the respiratory tract including the lungs.

"Gas" clouds may form when cold cryogenic gases are mixed with warm air, because the moisture in the air will condense when it is cooled down. In the event of major leaks of cryogenic liquefied gases formation of these clouds may result in obscured visibility.
Attention should be given to the fact that even outside the cloud a significant change in atmosphere composition must be expected.

Low temperature warning

At boiling temperature, all gases given in the table are heavier than air. Areas where significant leakage of cryogenic liquid gases is expected, must not have sewer entries without liquid seal, open deep-level windows or other open entries into deep level rooms or pits. The heavy gases might accumulate in these deep-level areas, where special risks of suffocation or fire may arise. Handling of inert gases (e.g. nitrogen, argon, helium, CO_2) does not involve any risk of fire. These gases might even be used for fire fighting. Fire or explosion hazards may arise in the event of leaking flammable cryogenic liquefied gases (e.g. liquid hydrogen, LNG), because these gases evaporate forming an explosive mixture with air. Therefore, an efficient natural or artificial ventilation is absolutely necessary.

Oxygen is not flammable but supports combustion. Materials that are not flammable in air can be flammable in an oxygen enriched atmosphere. Once ignited they burn very vigorously. See Safety Advice Oxygen enrichment.

When handling cryogenic gases having a temperature below the boiling point of oxygen (see table, line 1) condensing of atmospheric oxygen and local enrichment is possible. See Safety Advice "Oxygen enrichment".

Materials coming into contact with cryogenic liquefied gases must be suitable for use at low temperatures, i.e. they should not embrittle. Suitable materials are copper, austenitic steels, some aluminium alloys and special plastics.

If a cryogenic liquefied gases is trapped between two valves an adequately sized pressure relief devices should be installed. As the trapped liquid warms up it will vaporise and the pressure will increase, and unless it is relieved the pipework will fail. Vessels, pipework, equipment etc. must be thoroughly dried before receiving cryogenic liquefied gases. If not the cold nature of the cryogenic liquefied gas may cause freezing of any moisture or humidity which in turn may cause failure of safety valves or pressure gauges.

It should be noted that any material will shrink when exposed to lower temperatures. The extent of shrinkage depends on the material and the extent of temperature drop. Different shrinkage of different materials may result in leaks or even lead to failure e.g. of flange connections or similar.

4. Environmental protection

All gases indicated in the table (except hydrogen and LNG) are contained in the air in different concentrations. Small quantities of cryogenic liquefied gases evaporating into the atmosphere will not cause pollution. Inadvertently spilled cryogenic liquefied gases do not contaminate the ground because they evaporate quickly and do not – or only slightly – soak into the ground. The temporary local ground freezing does not permanently damage it.

5. First-aid treatment

If a person has been in contact with a cryogenic liquefied gas.

- Move the victim to a warm place (about 22°C) but do not apply direct heat.
- If qualified medical attention is not immediately available arrange for the victim to be transported to hospital without delay.

In the meantime:

- Loosen any clothing that may restrict blood circulation to the affected area.
- Flush the affected areas of the skin with large quantities of lukewarm water.

Note:
Do not use hot water or any other form of direct heat!

- Protect the affected areas of the skin with bulky dry sterile dressings. Do not apply too tightly so as to restrict blood circulation. Keep the affected part at rest.
- Treat patient generally for shock.
- Do not give patients alcohol to drink or tobacco to smoke. Both of these cause restriction in the blood flow.
- Do not pull off "stuck" clothing.

6. Treatment by medical practitioner or hospital

- Immediately place the part of the body

First Aid

exposed to the cold temperature in a water bath with a temperature of, ideally, not less than 40°C but certainly not more than 42°C.

Note:
Never use hot water or dry heat! Temperatures in excess of 45°C will suppose a burn on the frozen tissue:

- If there has been extensive body exposure to cryogenic temperatures such that the general body temperature is depressed the patient must be re-warmed without delay. The patient should be placed in a bath of warm water at a temperature between 40–42°C. It is important that the temperature of the bath is maintained at a level of not less than 40°C to maximise the rate of re-warming.
- In the absence of facilities for this treatment the patient should be taken to a warm atmosphere, preferably at a temperature of 22°C, kept at rest and lightly covered with one or two blankets.
- Shock may occur during the re-warming process.
- Frozen tissues are often painless and appear waxy with a pallid, yellowish colour. They become painful, swollen and very prone to infection when thawed. Thawing may take from 15–60 minutes and should be continued until the pale colour of the skin turns to pink or red. The thawing operation dependent on the degree of exposure, can be painful and it may be necessary to administer drugs to control the pain.
- If the frozen part of the body is thawed by the time medical attention has been obtained do not re-warm. Under these circumstances cover the area with dry sterile dressings with a large bulky protective covering.
- Administering of a tetanus booster is recommended.
- Consideration should be given in the case of an accident for the transportation of the patient to a hospital with special facilities and experienced personnel in the treatment of burns.

7. Conclusion

Safe handling of cryogenic liquefied gases is only possible if the specific properties of these gases are known. Inadequately used cryogenic gases can for instance cause frostbite.

Cryogenic liquefied gases have neither good nor bad properties. What matters is the knowledge of there physical and chemical properties, and using them in a safe way.

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