

Guidelines for the Use of Cryogenic Gases

Introduction

This section is to provide information and guidelines concerning the safe use of cryogenic fluids and to define the hazards associated with their use along with required safety precautions.

Definitions

A cryogenic liquid is defined as a liquid with a normal boiling point below -240 degree F (-150 degree C).

General

Cryogenic liquids will vent (boil off) from their storage containers as part of normal operation. As an example a 160-liter tank will vent the gas equivalent to 2 liters of liquid a day. Containers are typically of a vacuum jacketed design to minimize heat loss. Excessive venting and/or an isolated ice build-up on the vessel walls may indicate a fault in the vessel's integrity or a problem in the process line. A leaky container should be removed from service and taken to a safe, well-ventilated area immediately.

Precautions

There are a number of general precautions and safe practices that must be observed because of the extremely low temperatures and high rates of conversion into gas for all cryogenic liquids.

Extreme Cold Hazard

By definition, all cryogenic liquids are extremely cold. Cryogenic liquids and their vapors can rapidly freeze human tissue. Brief exposures that would not affect skin on the face or hands can damage delicate tissues such as the eyes. Prolonged exposure of the skin or contact with cold surfaces can cause frostbite. There is no initial pain but there is intense pain when frozen tissue thaws. Unprotected skin can stick to metal that is cooled by cryogenic liquids. The skin can then tear when pulled away. Even non-metallic materials are dangerous to touch at low temperature. Prolonged breathing of extremely cold air may damage the lungs.

Cryogenic liquids, can cause many common materials such as carbon steel, rubber and plastics to become brittle or even break under stress.

Asphyxiation Hazard

Use and store cryogenic fluids in well ventilated areas only. All cryogenic liquids produce large volumes of gas when they vaporize. For example, one volume of liquid nitrogen vaporizes to 694 volumes of nitrogen gas at 68o F @ 1 atm. Air is normally 21% oxygen by volume. When this is reduced to 15-16% oxygen, symptoms of asphyxia (below) will develop. At 12% oxygen, the individual will lose consciousness without warning and may be unaware of any danger. When there is not enough oxygen, asphyxiation and death can occur very quickly. When cryogenic liquids form a gas, that gas is very cold and usually heavier than air. This cold, heavy gas does not disperse very well and can accumulate near the floor. Even if the gas is non-toxic, it displaces the air. Oxygen deficiency is a serious hazard in enclosed or confined spaces.

Signs of asphyxiation are giddiness, mental confusion, loss of judgment, loss of coordination, weakness, nausea, fainting and up to and including death. Only a few breaths of oxygen-depleted air are required to cause a rapid drop in dissolved oxygen in the blood. Mental failure and coma follow within seconds. Symptoms or warnings are generally absent, but even if present, the loss of mental abilities, coordination and weakness may make it impossible for victims to help themselves or summon help from others.

Most cryogenic liquids are odorless, colorless and tasteless when vaporized into the gaseous state. Most liquids have no color except liquid oxygen, which is light blue. However, extremely cold liquids and their vapors have a built-in warning property that appears whenever they are exposed to the atmosphere. The cold “boil-off” gases condense the moisture in the surrounding air, creating a highly visible fog. Fog clouds do not define the vapor cloud. They define the area where vapors are still cold enough to condense the moisture in the air. The vapor cloud may extend well beyond the fog cloud. Although fog clouds may be indicative of a release, they must never be used to define the leak area, which should not be entered by anyone.

Because cryogenic vapors are undetectable to the human sensory system, never enter a suspected oxygen-deficient area without an external source of breathing air or a monitor for the atmosphere to ensure that oxygen levels are safe.

Oxygen Enriched Air

Vaporization of liquid oxygen in an enclosed area can cause oxygen enrichment, which could saturate combustibles in the area such as workers' clothing. This can cause a fire if an ignition source is present. Although oxygen is not flammable it will support and vigorously accelerate the combustion of other materials.

Liquids at or below the boiling point of liquefied air can actually condense the surrounding air causing a localized oxygen-enriched atmosphere. Extremely cold cryogenics such as Helium can even freeze or solidify the surrounding air.

Explosion Due to Rapid Expansion

Cryogenic liquids cannot be indefinitely maintained in the liquid state. If they are vaporized in sealed container they can produce enormous pressures that could rupture the container, for this reason pressurized cryogenic containers are normally protected with multiple devices for over-pressure prevention. A pressure relief device must protect all selected equipment that may allow for the liquid to become trapped.

Special Helium Precautions

The most critical safety issue in dealing with liquid helium is its temperature. It is so cold that it will **FREEZE ALL GASES** except Helium. This includes not only H₂O, but also N₂ and O₂; all of these can freeze inside a liquid helium dewar or delivery lines, forming an "ice" plug which can potentially close up the neck and create a bomb. For this reason, it is imperative that procedures be in place followed exactly to prevent air or other gases from entering the liquid delivery lines at any time. Should a blockage be suspected remove the dewar to a safe location and contact the vendor immediately. Attempting to transfer liquid helium in non-vacuum jacketed piping can cause air surrounding the outside of the transfer pipe to condense and liquefy. The nitrogen in this liquid will evaporate first, leaving an enriched oxygen liquid behind. The area where this liquid collects should be insulated and oxygen-compatible.

General Safety Practices

Storage and Use

All cryogenic liquids must be stored and used in a well-ventilated area.

1. Dewars: Non-pressurized, vacuum-walled containers which are equipped either with a loose-fitting cap or open top and are used for storage of small amounts of liquid.
2. Cryogenic Liquid Cylinders: These are sealed, vacuum-walled containers, which

do contain pressure up to 350 psig. Cryogenic liquids can also be extracted from these containers.

3. Cryogenic Storage Tanks: These tanks range in size from 500 to 420,000 gallons and are always pad mounted. Liquid and gas can be extracted from these containers.

Personal safety

The eyes are the most sensitive body part to the extreme cold of the liquid and vapors. The recommended Personal Protective Equipment (PPE) for handling cryogenics includes a full-face shield over safety glasses, loose-fitting thermal insulated or leather gloves, long sleeved shirts and trousers without cuffs. Gloves should be loose fitting to allow quick removal if liquid should be spilled inside. Gloves are not made to permit the hands to be immersed in a cryogenic liquid. They will only provide short-term protection from accidental contact with the liquid. No metal jewelry rings watches etc... should be worn on hands or wrist while transferring cryogenic liquids.

Safety Practices

1. Cryogenic liquids must be handled, stored and used only in containers or systems designed in accordance with applicable standards, procedures or proven safe practices.
2. All systems components piping, valves etc...must be of the appropriate materials to withstand the extreme temperatures.
3. Pressure relief valves must be in place in systems and piping to prevent pressure build up.
4. Any system section that could be valved off while containing cryogenic liquid must have a pressure relief valve. Pressure relief valve relief ports must be positioned to face toward a safe location.
5. Transfer operations involving open cryogenic containers, such as dewars must be done slowly, while wearing all required PPE. Care must be used not to contact non-insulated pipes and system components.
6. Open transfers will be allowed only in well-ventilated areas.
7. Do not use a funnel while transferring cryogenic liquids.
8. Use tongs or other similar devices to immerse and remove objects from cryogenic liquids.
9. Workplace Hazard Assessment reviews are required when using cryogenic materials.

TABLE I- Properties of Cryogenic Fluids.

Gas	Boiling Point Centigrade	Boiling Point Kelvin	Volume Expansion to Gas
Helium-3	-269.9	3.2	757 to 1
Helium-4	-268.9	4.2	757 to 1
Hydrogen	-252.7	20.4	851 to 1
Deuterium	-249.5	23.6	...
Tritium	-248.0	25.1	...
Neon	-245.9	27.2	1438 to 1
Nitrogen	-195.8	77.3	696 to 1
Carbon monoxide	-192.0	81.1	...
Fluorine	-187.0	86.0	888 to 1
Argon	-185.7	87.4	847 to 1
Oxygen	-183.0	90.1	860 to 1
Methane	-161.4	111.7	578 to 1
Krypton	-151.8	121.3	700 to 1
Tetrafluoromethane	-128	145	...
Ozone	-111.9	161.3	...
Xenon	-109.1	164.0	573 to 1
Ethylene	-103.8	169.3	...
Boron trifluoride	-100.3	172.7	...
Nitrous oxide	-89.5	183.6	666 to 1
Ethane	-88.3	184.8	...
Hydrogen chloride	-85.0	188.0	...
Acetylene	-84.0	189.1	...
Fluoroform	-84.0	189.1	...
1,1-Difluoroethylene	-83.0	190.0	...
Chlorotrifluoromethane	-81.4	191.6	...
Carbon dioxide	-78 5(b)	194.6	553 to 1

Emergency Procedures

Should a Dewar of cryogenic liquid be venting continuously call the supplying vendor immediately. Remember, oxygen-deficient atmospheres are an invisible danger. They have no warning properties.

Additional Information:

General information on Cryogenic fluids

<http://www.airproducts.com/nr/rdonlyres/c50df690-bd10-4348-a986-bf8a6e12ed2f/0/safetygram16.pdf>

<http://www.ccohs.ca/oshanswers/chemicals/cryogenic/cryogen1.html>

Oxygen deficient

<http://www.airproducts.com/nr/rdonlyres/35b1bc31-7c0e-455b-a723-8255ff28ddba/0/safetygram17.pdf>

Cryogenic Liquid Containers

<http://www.airproducts.com/nr/rdonlyres/38000ecf-e07b-4288-8ff9-73699c70c882/0/safetygram27.pdf>

Liquid Helium

<http://www.airproducts.com/nr/rdonlyres/f655730b-dfee-4eb0-a6c5-fac10d5ae480/0/safetygram22.pdf>

Liquid H₂

<http://www.airproducts.com/nr/rdonlyres/780e8a00-f1bf-435c-8219-6601da6632f0/0/safetygram09.pdf>