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Environment, Safety, and Health

Volume II

Part 18: Pressure/Noise/Hazardous Atmospheres

Document 18.5
Cryogens

Recommended for approval by the ES&H Working Group

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New document or new requirements

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18.5

Cryogens*

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Cryogens

1.0 Introduction

Work with cryogens (liquids with boiling points below –73°C (–99°F]) and cryogen systems require established controls to be in place because of the hazards involved. This document describes the hazards and provides work controls, including training requirements, for all LLNL operations involving the use of cryogens. It also includes the requirements that were in “Safe Handling of Cryogens” (H&SM S22.01), as this document was rescinded.

Other related Laboratory requirements are detailed in Document 18.1, “Pressure”, Document 18.7, “Working in Confined Spaces”, and Document 18.2, “Pressure Vessel and System Design,” in the *Environment, Safety, and Health (ES&H) Manual*. Industry guidelines can be found in the Compressed Gas Association Pamphlet P-12, “Safe Handling of Cryogenic Liquids.”

2.0 Hazards of Cryogens

All persons working with cryogens must be familiar with the properties of cryogens and must observe safe handling practices. Following are some of the hazards associated with cryogens:

- Burns to the skin can result from direct contact with a cryogen, uninsulated piping, or equipment containing a cryogen.
- Permanent damage can occur if liquid cryogen gets into the eye.
- The properties of some materials change drastically at very cold temperatures: ductile materials can become brittle, material shrinkage can exceed anticipated values, and leaks can develop that are undetectable even under pressure.
- Liquid cryogens warmed above critical temperatures will generate high pressures. This can cause a confining vessel to rupture or even explode. For example, small containers such as stoppered test tubes have overpressured and produced flying fragments. Fully containing a cryogenic fluid as a liquid at room temperature is usually not feasible—e.g., the pressure required to maintain liquid nitrogen at room temperature is 296 MPa (43,000 psi).

- Cryogens can create oxygen deficiency because they have large liquid-to-gas expansion ratios (generally >700). A small liquid spill produces a large volume of gas that can displace the air in a confined space, thus creating a serious oxygen deficiency that can suffocate occupants of the area.
- Helium and hydrogen can solidify atmospheric air. If air is not excluded from systems containing these cryogens, vents or exhaust ports to the atmosphere—relied upon for pressure relief—may become plugged by solidified air and lead to system overpressure and vessel failure. Also, if air condenses between the exterior metal surface of the system and the insulating layer, when it warms and vaporizes it can rip off the insulation with explosive force.
- Some cryogens are chemically very reactive (e.g., O_2); others are flammable (e.g., H_2 and CH_4).
- Cryogenic fluids with a boiling point below that of liquid oxygen may condense oxygen from the air if exposed to the atmosphere. Because oxygen does not evaporate as rapidly as liquid nitrogen, it will accumulate and may cause violent reactions with incompatible materials in the system.

Table 1 provides the physical properties of some cryogens used at LLNL.

Table 1. Physical properties of some cryogens.

Properties	**Cryogen**							
	Ar	**He**	**H_2**	**Ne**	**N_2**	**O_2**	**CH_4**	**CO_2**
Boiling point (1 atm)								
°C	–186	–269	–253	–246	–196	–183	–161	–78
°F	–303	–452	–423	–411	–321	–297	–256	–108
Critical temperature								
°C	–122	–268		–229	–147	–118	–82	31
°F	–188	–450		–379	–232	–181	–116	88
Critical pressure								
MPa	4.89	0.23	1.30	2.65	3.39	5.08	4.64	7. 37
(psig)	(710)	(34)	(188)	(385)	(492)	(736)	(673)	(1070)
Liquid density, g/l	1402	125	71	1206	808	1410	425	1560
Gas density (27°C), g/l	1.63	0.16	0.082	0.82	2.25	1.4	0.72	2.0
Liquid-to-gas expansion ratio	860	780	865	1470	710	875	650	790
Flammable	No	No	Yes	No	No	No[a]	Yes	No

[a] Although oxygen does not burn, it will support combustion. Oxygen-enriched atmospheres may lead to violent reactions, such as rapid combustion or explosions, with incompatible materials.

3.0 Prework Planning

The responsible user and the area ES&H Team should evaluate all intended use of cryogens. Factors such as those listed below shall be considered during this evaluation.

- The quantity and intended use of a cryogen.
- The location of dewars and piping.
- Operating and nearby staff who may be affected by cryogen work.
- Potential hazards from oxygen deficiency, skin contact, pressure, and flammability.

System designers and project leaders must understand the hazards of cryogenic materials and analyze the consequences of spills and system leaks. The analysis may require modification to the original work plan for reasons such as the following:

- System relocation or implementation of additional access controls due to the presence of nearby confined space.
- Special monitoring provisions (e.g., for oxygen deficiency) may be necessary for continuous operation of a system during off hours.
- Training of workers assigned to operate the system to assure they know the emergency shut-off procedures.

4.0 Engineered Controls

Because of their inherent dangers, cryogenic-fluid systems shall be designed, installed, and used in a manner that takes into consideration each of the hazards detailed in Section 2. Only personnel fully aware of the properties of cryogen should handle cryogenic fluids and equipment.

4.1 Design of Cryogenic Systems

Cold temperatures can cause the properties of some materials to change drastically. Thus, the suitability of materials must be carefully investigated before using them for cryogenic work.

LLNL cryogenic systems shall be designed, manufactured or supplied and installed in accordance with the design criteria specified in Section 5.5 (Cryogen Systems) of the LLNL Mechanical Engineering Department's *Design Safety Standards*.

Heat flux into cryogen is unavoidable. Therefore, pressure relief shall be provided to permit routing of off-gasing vapors. Such relief is best provided by spring-loaded relief devices or an open passage to the atmosphere. Frangible disks are recommended as additional relief devices when the capacity of the operational relief device is not adequate to take care of unusual or accidental conditions. This is especially true when insulation of the system is dependent upon maintaining a vacuum in any part of the system, including permanently sealed dewars. In any case, a relief device shall be capable of handling the maximum volume of gas that could be produced under the most adverse condition.

Each and every portion of the cryogenic system shall have uninterrupted pressure relief. Any part of the system that can be valved off from the remainder shall have a separate pressure relief device. Parts that usually require a separate pressure relief device include

- Pressurized supply dewars.
- Tubing and hoses used to transfer cryogen, unless an air gap is provided.
- Bath space surrounding experimental volume.
- Experimental volume, even if cryogen is in contact only with the exterior.
- Vacuum spaces in contact with cryogen.

Pressure relief devices shall be used in the last two cases because cracks may develop at cryogenic temperatures, thus allowing cryogen or air to leak into sealed spaces. If these cracks close on warming, the vaporizing fluid could expand and shatter the vessel.

Adequate ventilation shall be provided where toxic or flammable cryogens are used. Systems shall be designed so that the discharge from pressure relief devices and purge lines does not create a hazardous concentration. Section 4.2 provides detailed information on preventing oxygen-deficient atmospheres.

Each part of a cryogen system must be engineered for pressure in accordance with the requirements specified in Document 18.1 and Document 18.2. Pressure relief devices shall not be set higher than the maximum allowable working pressure, with the safety factor at the temperature of minimum strength.

Sufficient access shall be allowed so that work (e.g., routine filling, periodic inspection, and maintenance) can be performed safely on cryogen systems and equipment. Access to cryogen fill locations shall be free of obstacles.

4.2 Preventing Oxygen Deficiency

A small liquid spill produces a large volume of gas and displaces the air in a confined space, thus creating a serious oxygen deficiency that can suffocate occupants of the area. Calculations shall therefore be made to determine whether a given situation of cryogen storage or use will pose an oxygen-deficiency hazard in a worst-case credible accident. Where cryogen use requires remote piping, special care shall be taken to examine the piping to determine whether or not tunnels, pits, or trenches can develop an oxygen deficiency from a broken line, and appropriate safety procedures shall be implemented.

If the area of cryogen storage or use is designated a confined space, the provisions of Document 18.7, "Working in Confined Spaces," in the *ES&H Manual* shall be met. This may include installation of oxygen-deficiency sensors, positioned at the lowest point in the area and wired to audible alarms and the Emergency Management (Fire) Department. Proper use of ventilation can minimize potential oxygen deficiency. If the system has routine bleed-off relief devices, they should be vented to the outdoors.

If dry ice (solidified CO_2) or a dewar containing cryogen fluids must be transported via an elevator, it shall not be accompanied by personnel. These materials shall be transported alone, and measures shall be taken to assure that passengers do not board the vehicle on intervening floors. In a typical elevator car with poor air mixing, as little as 1lb of dry ice can create a CO_2 concentration of 3% (30,000 ppm) and double the breathing rate. A concentration of 0.5% (5000 ppm) will stimulate more rapid breathing.

4.3 Preventing System Overpressure

Certain cryogens (e.g., helium and hydrogen) are cold enough to solidify atmospheric air. Thus, air shall be prevented from entering into cryostats.

Vents or exhaust ports to the atmosphere may become plugged by solidified air. This could lead to overpressure and vessel failure, if the ports are relied upon for pressure relief. In case of maximum possible heat flux into the system, adequate pressure-relief devices shall be provided to vent all gas produced.

Cryogen fluids that are not handled in a vacuum-jacketed vessel and piping will cause air to condense on the exterior of the system. This can result in frostbite from touching the cold surface, dripping liquid air, and exploding insulation when air condenses between the metal surface and the insulating layer. When air warms, it vaporizes and can rip off insulation with explosive force.

4.4 Oxygen Enrichment

Cryogenic fluids with a boiling point below that of liquid oxygen may condense oxygen from the air if exposed to the atmosphere. Because oxygen does not evaporate as rapidly as liquid nitrogen, when cryogenic fluids are replenished to make up for evaporation, oxygen will accumulate and may cause violent reactions with incompatible materials in the system.

4.5 Inspection of Cryogenic Storage Systems

To ensure safe operations, high reliability, and satisfaction of code requirements, Plant Engineering will inspect annually all bulk stationary liquefied nitrogen, argon, and oxygen storage systems at LLNL. Inspections will cover the liquid storage cylinder and supporting vacuum system as well as all piping, valves, gages, relief devices, regulators, dewars, and evaporators associated with the cryogen system.

Plant Engineering will report findings resulting from these inspections to the program or facility owner of the system, who then must ensure that the necessary repairs are made or that the system is taken out of service.

System owners and operators shall conduct frequent work area observations to ensure that no hazardous condition is overlooked and that a safe environment is maintained.

5.0 Administrative Controls

5.1 Safety Documents

If cryogenic fluids are to be used in pressurized vessels or piping systems not certified or built to the requirements of the American Society of Mechanical Engineers (ASME) or the Department of Transportation, a safety note and an Operational Safety Plan (OSP) are required. Requirements for safety notes are given in Document 18.2.

An Emergency Plan is recommended to guide personnel actions in the event the equipment malfunctions or a mishap occurs while working with cryogens. The plan shall include shutdown, alarms/notification, and evacuation procedures for likely incidents.

5.2 Labeling

Many cryogens are chemically reactive; some are flammable. Thus, storage dewars, process vessels, piping, and other associated hardware containing such materials shall be labeled with the common name of the contents. In addition, the material safety data sheet (MSDS) shall be located in the immediate area where each cryogen is used or stored. MSDSs can be found at the Intranet address given below. It is also desirable to post emergency instructions and phone numbers.

http://ctmsds.llnl.gov:1650/livehtml/MSDS/MSDS1.html

5.3 Training

Training. Only personnel who are fully aware of the properties of cryogenic fluids shall handle cryogens and associated equipment. A formal training program, including hands-on training with experienced workers and operators, should be considered for large cryogen systems.

Course HS5030-W, "Pressure Safety Orientation", is recommended for all cryogen users. This web-based training course can be found at the following Intranet address:

http://www-training.llnl.gov/wbt/

6.0 Personal Protective Equipment

The hazard evaluation performed for each cryogen operation shall determine the appropriate type of personal protective equipment (PPE) necessary. Following are minimum PPE requirements for cryogen operations where personnel contact is possible:

- Eye, hand, and body protection shall be worn to prevent contact with liquid cryogens.
- At minimum, safety glasses with side shields are required any time cryogenic liquids, exposed to the atmosphere, are present. Goggles provide the best protection for the eyes.
- Full face shields shall be used in the following situations:
    - When a cryogen is poured.
    - For open transfers.
    - If fluid in an open container is likely to bubble.

Table 2 provides guidelines for selecting additional PPE. Consult the ES&H Team for assistance with selecting the proper equipment.

Table 2. Guidelines for selection of personal protective equipment.

Hands	Loose, nonasbestos insulating gloves that can be tossed off readily. Special gloves made for cryogenic work. Leather gloves without gauntlets that can be tossed off readily. Tongs or other tools to lift objects out of the liquid or liquid baths.
Feet	Closed-toe shoes that cover the top of the foot. Boots (extend trousers over the boot).
Body	Long-sleeved clothing made of nonabsorbent material. Cuffless trousers worn outside boots or over high-top shoes. Leather or other nonasbestos apron when handling large quantities of cryogens. Full protective suits where exposure to drenching is possible.
Respiratory organs	Supplied air where drenching is possible and where oxygen deficiency or asphyxiation may occur. (These types of exposures should be prevented through the implementation of engineered controls.)
Ears	Ear plugs or ear muffs where excessive noise levels may occur near filling and venting operations.

7.0 Emergency Procedures

7.1 Frostbite

The most likely cause of frostbite to the hands and body is contact with cold metal surfaces. Frostbite is almost instantaneous when the skin is moist. Call 911 (or 447-6880, from a cellular phone) for immediate treatment or report promptly to the Health Services Department for medical attention.

If an emergency occurs and definitive medical care is not readily available (e.g., offsite), the following emergency measures are recommended:

- Call 911 for assistance.
- Warm the affected area rapidly by immersion in water not to exceed 105 °F, body heat, or exposure to warm air. Showers with warm water should be provided where there is a sufficient probability of such an accident occurring. In the event of massive exposure, remove clothing while showering. Do not expose the body to open flame. Maintain the affected area of the victim at normal body temperature until professional help arrives.
- Calm the victim and avoid aggravating the injury. People with frostbitten feet should not walk on them. Do not rub or massage the affected parts of the body.

- To prevent infection, use a mild soap to clean the affected area. Dressing need not be applied if the skin is intact. However, protect the affected area from further pressure or trauma.
- If the eyes are affected, flush them with warm water for at least 15 minutes.
- Seek medical attention in all instances.

7.2 Cryogen Spill and Oxygen Deficiency

Personnel shall immediately evacuate an area if

- An alarm signals an oxygen deficiency or other emergency condition.
- They believe a cryogen spill has caused significant oxygen depletion.
- They feel light-headed or nauseous following a cryogen spill.
- A spill of any highly toxic or flammable cryogen occurs.

Personnel re-entering the area shall wear self-contained breathing apparatus (SCBA) or air-line equipment with a self-contained escape unit until the oxygen content of the atmosphere is at least 19.5% and no toxic or flammable mixture is present.

8.0 Responsibilities

General responsibilities for all workers are described in Document 2.1, "Laboratory & ES&H Policies, General Worker Responsibilities, and Integrated Safety Management," in the *ES&H Manual*. Specific responsibilities are listed under each title below.

8.1 Supervisors

Payroll supervisors are responsible for assuring that workers are familiar with the properties and hazards common to all cryogens in use.

Supervisors shall ensure that personnel handling cryogens and those working nearby who may be affected by a spill or emergency are trained in safe operating techniques; emergency procedures; and the use of protective equipment, including respiratory protective devices.

8.2 Workers

- Know the properties of cryogens.

- Observe safe handling practices.
- Take appropriate training and work with an experienced person if you are not familiar with cryogen use to gain the knowledge and experience necessary.

8.3 Cryogenic System Owners

- Maintain systems and make repairs when necessary.
- Notify the area ES&H Team and the Plant Engineering Maintenance and Operations Department when cryogen systems are installed or removed from service.

8.4 Plant Engineering Department

Plant Engineering will perform annual inspections of cryogenic bulk storage dewars as described in the Plant Engineering Maintenance Operations Procedure, "Inspection of Cryogenic Storage Systems" (MOP-15029).

8.5 Hazards Control Department

Hazards Control ES&H Teams can perform hazard evaluations to determine the proper PPE.

9.0 Work Standards

8 CCR § 450– 560, "Unfired Pressure Vessel Safety Orders (propane tanks, Air Receivers)."

29 CFR 1910.101, "Compressed gases general requirements."

29 CFR 1910.103, "Hydrogen."

29 CFR 1910.110, "Design and Construction of LPG Tanks."

29 CFR 1910.132, Subpart I, "Personal Protective Equipment."

29 CFR 1910, Subpart J, "General Environmental Controls."

29 CFR 1910, Subpart M, "Compressed Gas and Air Equipment."

29 CFR 1910, Subpart Q,, "Welding, Cutting, and Brazing."

49 CFR 100 -199, Research and Special Programs Administration."

ACGIH TLVs and BEIs: Threshold Limit Values for Chemical Substances and Physical Agents, 2002 (excluding Biological Exposure Indices, TLVs for Physical Agents, and Biologically Derived Airborne Contaminants).

ASME Boiler and Pressure Vessel Codes, Section VIII, Div. 1 and 2, "Rules for Construction of Pressure Vessels."

ANSI/ B 31.1, "Power Piping, ASME Code for Pressure Piping."

Compress Gas Association Pamphlet P-1, *Safe Handling of Compressed Gases in Containers*, 1991.

Compressed Gas Association Pamphlet P-12, *Safe Handling of Cryogenic Liquids*.

Compressed Gas Association Pamphlet S-1.2, *Pressure Relief Device Standards*, Part 2, "Cargo and Portable Tanks for Compressed Gases" 1995.

Compressed Gas Association Pamphlet S-1.3, *Pressure Relief Device Standards*, Part 3, "Compressed Gas Storage Containers," 1995.

DOE M 440.1-1, *DOE Explosives Safety Manual.*

NFPA 45, "Laboratories Using Chemicals.

NFPA 51B, "Standard for Fire Prevention in Use of Cutting and Welding Processes" (1999 edition).

UCRL AR 128970, "LLNL Pressure Safety Standard."

Public Law 91-596, OSHA Act of 1970, § 5 (a) (1).

10.0 Resources for More Information

10.1 Contacts

Refer questions regarding cryogens to the following:

- Area ES&H Team
- Plant Engineering Maintenance and Operations Department
- Mechanical Engineering Department

10.2 Lessons Learned

Refer to the following Internet address for a list of applicable lessons learned:

http://www-r.llnl.gov/es_and_h/lessons/lessons.shtml

10.3 Other Sources

DOE Order 440.1A, "Worker Protection Management for DOE Federal and Contractor Employees", Attachment 2, "Contractor Requirements Document", Sections 1–11, 13–16, 18 (delete item 19.a), (delete item 19.d.3) and 22.

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Compressed Gas Association, Pamphlet G-5.2, *Standard for Liquefied Hydrogen Systems at Consumer Sites*, CGA: New York (latest revision).

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Lawrence Livermore National Laboratory, *Design Safety Standards*, Section 5.5, "Cryogenic Systems," Mechanical Engineering Department, LLNL, Livermore, CA, M-012 (latest revision).

Neary, R. M., "Air-Condensing Cryogenic Fluids," *National Safety Council Transactions 1963*, Vol. 5, "Chemical and Fertilizer Industries," National Safety Council, Chicago, IL (1963).

Reider, R., "Handling and Use of Cryogenics," J. *Chem. Ed.,* 47(7), (July 1970).

Scott, R. B., *Cryogenic Engineering*, Library of Congress No. 599765, D. Van Nostrand Co., Inc., Princeton, NJ (1959).

Union Carbide Industrial Gases, Inc., *Safety Precautions for Oxygen, Nitrogen, Argon, Helium, Carbon Dioxide, Hydrogen, Fuel Gases*, Linde Division, Union Carbide Industrial Gases, Inc., Danbury, CT, Pamphlet L-3499H (latest revision).

Zabetakis, M. G. and D. S. Burgess, *Research on the Hazards Associated with the Production and Handling of Liquid Hydrogen*, U. S. Department of the Interior, Bureau of Mines, Washington D.C., Bureau of Mines Report of Investigation 5707 (1961).

Zabetakis, M. G., *Safety with Cryogenic Fluids*, Plenum Press, New York (1967).

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