

Cryogenic Materials

Cryogenics is the study and use of materials at ultra low temperatures (less than -150°C), and includes chemicals which are normally gases at room temperature. In many FSU labs, cryogenic use involves small amounts of material (a few liters of liquid nitrogen or a few pounds of dry ice). Some laboratories use liquid oxygen, hydrogen or helium whether in small quantities or in bulk.

Cryogenic Hazards

All cryogenic liquids are liquefied gases. In addition to the hazard of extreme cold, the hazards associated with the chemical pose a risk: reactivity, corrosivity, toxicity, asphyxiation, and vigorous flammability.

Tissue destruction

Frostbite resulting in damaged skin or eye tissue may result from contact with cryogenic materials. Even brief contact with small amounts of cryogenic material may permanently damage eyes or skin. Tissues that are frozen may be painless until thawed. Cryogenically cooled materials are hazardous to touch; they may freeze and tear skin if in contact.

Skin and Eye Hazards

Never make direct contact with cryogenic liquids, un-insulated cryogenic pipes, or un-insulated cryogenic equipment because contact can cause freeze burns and tissue damage. In addition, a jet of cryogen vapors can freeze the skin or eyes faster than liquid or metal contact.

The eyes contain fluids and are especially sensitive to cryogen exposure. These fluids will freeze upon contact with a cryogen causing permanent eye damage.

Personal Protection for eyes and skin is required. The precautions listed below shall be followed to protect the eyes and skin from the hazards associated with cryogens.

- Insulate all containment system pipes.
- Use care when filling portable dewars.
- Always wear protective gloves over jewelry because if exposed to cryogenic fluids, the ring can freeze to the finger.
- Protect your eyes by wearing safety goggles or a face shield whenever working with cryogen fluids.
- Wear a cryogen apron when working with cryogen liquids.
- Always wear a face shield when working around pressurized cryogenic systems, connecting or disconnecting cryogenic equipment lines, or when venting containment systems.
- Wear insulated gloves whenever working around un-insulated pipes or handling dewars.
- Try to cover all exposed skin by wearing long sleeve shirts, cuff-less pants, safety boots, and gloves. Gloves should be loose-fitting so that they can be quickly removed if cryogenic fluids are spilled on them.

Asphyxiation

Asphyxiation may occur when cryogenic materials are stored, transported or handled without adequate ventilation. Cryogens will rapidly boil and convert from a liquid to a gas at room temperature. As the gas warms to the temperature of the surrounding air, it expands. In confined or poorly ventilated areas, the

expanding gas will displace oxygen and can cause rapid asphyxiation or death. Therefore, you should use caution when using liquid nitrogen and helium indoors. These gases are colorless, odorless, and tasteless. OSHA specifies that workers cannot be inside a work space that contains less than 19.5% oxygen without supplied air respiratory protection. Below this level, workers start to experience early warning signs of oxygen deficiency. Specifically between 15- 19% oxygen workers may feel:

- An increase in pulse rate and breathing.
- A sense of euphoria and clumsiness. At oxygen levels between 12- 14% the worker's:
- Breathing becomes much deeper and faster.
- Judgment becomes impaired.
- Physical coordination is deteriorated.
- Lips turn blue. Usually at levels below 12% the worker will become unconscious and eventually die.

Preventing Asphyxiation Hazards

When using cryogenics indoors make sure the room is well ventilated and you have the cryogen stored in proper containment systems. If cryogenics are used in enclosed or poorly ventilated work areas (or confined spaces) special procedures may be needed. Do not enter confined spaces. Contact EH&S for evaluation of ventilation or for development of special handling protocols. Areas suspected of being oxygen deficient due to the release of large quantities of cryogenic vapors shall be evacuated immediately. Never vent a cryogenic dewar or system toward yourself or others. The vapor will quickly displace the oxygen, causing an oxygen deficient atmosphere.

Cold Embrittlement

Cold embrittlement (and failure) of materials may occur when inappropriate materials are subjected to extreme cold. At cryogenic temperatures, materials such as rubber, plastic and carbon steel can become so brittle that very little stress can break the material. To avoid problems with cold embrittlement, materials like stainless steel, copper, brass and most alloys of aluminum should be used in the cryogen containment systems.

Volume Increase from Warming

Cryogenic gases will significantly expand upon warming. Liquid nitrogen expands to the gas form at a rate of 1:700. Rapid expansion may create extreme pressure buildup in a capped vessel, which may result in vessel rupture or failure. Sudden release into the environment will displace oxygen and may create a life-threatening situation. The cold cryogenic gas condensing moisture in the air causes the visible fog that appears when cryogen is released to atmosphere. The fog is a visible indicator of cryogenic release. Users shall stay clear of this area.

Flammability

Nitrogen is not flammable, however when liquid nitrogen is released, air around the cryogen may condense when allowed to stand in an open container, which may create an oxygen rich atmosphere that is combustible. The resulting liquid mixture should be handled as though it is as hazardous as pure liquid oxygen. If liquid oxygen or oxygen contaminated liquid nitrogen were spilled on combustible materials (cloth, wood, cardboard), the oxygen (now a gas) can remain close to the solid surface for several hours, and can explode if an ignition source is provided.

Controlling Air Condensation

Insulating system components not only reduces air condensation but also protects workers by preventing contact with cold surfaces.

Also, the frost that accumulates on cryogenic system components is important in controlling air condensation. It insulates the containment system from surrounding air, reducing the possibility that the air will condense.

Cryogen Storage

- Cryogenics are stored or transported in dewars, which are insulated containers specifically made for storage of extremely cold materials. Dewars are designed to protect workers from contacting cryogenic fluids or vapors and maintain the cryogen in its liquid state.
- All pressurized dewars are equipped with pressure relief valves to prevent high pressures from building inside the dewars. When the pressure gets too high within the dewar, the pressure relief valve will open and expel cryogen vapor into the surrounding atmosphere. When the pressure drops to a safe level again, the relief valve will close.
- Frangible disks rupture when the pressure inside of the dewar gets too high, again expelling cryogen gas into the surrounding environment. When a disk ruptures, the entire contents of the dewar will be expelled. This is a very hazardous situation, as large amounts of expanding gas can displace oxygen in the room. Any sudden discharge of vapor from the dewar should indicate to lab workers that they must leave the room immediately, and contact others in the area to advise them of the hazard.
- Dewar Vacuum Jackets - The vacuum jacket acts as an insulating layer for the cryogenic fluid and sometimes includes a system of coiled pipes between the inner and outer walls. The vapors from the cryogenic fluid circulate through the piping system and cool the inner and outer wall of the containment. The vacuum jacket protects workers from the extreme cold of the cryogenic liquid and insulates the fluid from the ambient, surrounding temperature.
- Transfer Lines - Transfer lines are used to transport a cryogenic fluid from one vessel (dewar) to another. Transfer lines designed specifically for cryogen transfer shall be used. Some types of transfer lines include, small un-insulated copper or stainless steel lines, large diameter rigid lines, vacuum jacketed lines, or other lines made from appropriate materials.

Safe Handling of Cryogenics

- Always handle in well ventilated area!
- Do not store or use in a confined space
- Check oxygen monitor when entering cryogen storage area (oxygen monitors are required if more than a few liters of cryogenic materials is used or stored.)
- Immediately depart area where low oxygen alarm is sounding or oxygen reading indicates less than 19.5% oxygen
- Wear face shield AND safety goggles, cryogen protective gloves (loose-fitting insulated gloves) and lab coat or apron when handling liquid nitrogen; wear loose, long sleeves and pants without cuffs, and close-toed shoes. Pant cuffs should overlap the shoes or boots to prevent materials from contacting feet. Gloves should be loose-fitting so that they can be removed immediately if cryogenics splash inside the gloves. Use cryogen rated PPE when filling, venting or transferring cryogenics.

- Do not allow cryogen to touch any part of your body or become trapped in clothing near the skin. Even brief skin contact may result in severely damaged tissue.
- Do not touch any item that has been immersed in cryogen until it has warmed to room temperature
- Remove watches and other jewelry on the hands and wrists before working with cryogenics, as ultra cooled materials may freeze and tear skin on contact.
- Use containers that are made specifically for ultra low temperatures, such as Dewar flasks.
- Fill containers slowly to minimize thermal shock to the container, and do not overfill; allow for expansion of gases.
- When filling dewars or transferring cryogenic liquid, use a phase separator or special filling funnel. The top of the funnel should be partly covered to reduce splashing. If the liquid cannot be poured, use a cryogenic liquid withdrawal device for the transfer.
- Cover dewars when the liquid is not being transferred, but do not tightly plug, as warming cryogenics will expand and increase the pressure inside the container, which could result in explosion or vessel rupture.
- Keep the dewar upright. Do not bump or drop.
- When using a hand truck or fork truck for dewar transport, the dewar must be strapped onto a dewar transport pallet. Never refill dewars or transfer cryogen when emergency assistance is not available.
- Know the first aid procedures for frostbite before handling cryogenics
- If gloves become contaminated with cryogenic liquid, be aware of potential flammability of gloves.
- Avoid inhaling air that has been cooled to near cryogenic temperatures.
- If there is a potential for vapors from cryogenics to have accumulated in pits or low-lying areas, the environment may be oxygen deficient. An oxygen-supplying respirator (not just a mask) must be worn in these areas. Contact EH&S for information about the respirator program.
- **Personnel should never occupy an elevator being used for the transportation of cryogenics;** a release of cryogenic material will displace oxygen and can create an asphyxiating environment – 1L of liquid N₂, if completely sublimated where there is no air exchange, will displace 700L of air. In an elevator that is 4' x 4' x 8', 700L of air displaced by gaseous N₂ would lower the oxygen content of the elevator air from 21% to 17%, a potentially fatal level. This type of transport should be accomplished by securing the material in the elevator and using a coordinated team positioned outside the elevator doors on each floor to send and receive the material while ensuring that other individuals do not unknowingly get on the elevator (on other floors) while it is being used for this purpose. Contact EH&S for guidance.
- Learn properties of materials to be cooled by cryogen, as these may become brittle.
- Position dewars so that pressure relief valves and rupture disks vent paths are directed away from personnel, critical equipment or work areas.
- The fill and vent ports of the dewar should be kept closed at all times to minimize the formation of ice which may plug the pressure relief devices. Pressure relief devices should be periodically inspected for ice.

- Immediately evacuate area where sudden release or cryogenic liquid or vapor has occurred.
- Ensure that Dewars are properly labeled with name of cryogen. Do not cross-contaminate in service dewars with other cryogenic liquids.
- FSU laboratory workers MUST contact EH&S before initiating the use of toxic cryogenic materials.

Flammable Cryogenic Materials

Do not permit liquid oxygen, liquid hydrogen or oxygen-enriched air to come in contact with organic materials or flammable or combustible substances of any kind. Some organic materials that can react violently with flammable cryogens when ignited by a spark or even a mechanical shock are oil, grease, asphalt, kerosene, cloth, tar, and dirt that may contain oil or grease. There is potential for fire hazards due to oxygen enrichment of the surrounding atmosphere and the possibility of a combustion reaction if the oxygen or other flammable materials is permitted to contact a non-compatible material.

Important note: before you may work with liquid oxygen or hydrogen, you must be trained to deal with those hazards specifically!

- Store and use flammable cryogens with adequate ventilation. Do not store in a confined space.
- Where outside storage is used, provide for protection against the extremes of weather.
- Flammable cryogens must be separated from flammables and combustibles by 20 feet or a half-hour fire wall. Post "No Smoking" and "No Open Flames" signs.
- Customer storage sites having a capacity of more than 20,000 scf must be installed in accordance with the National Fire Protection Association (NFPA) Standard 50 (contact EH&S for guidance).
- Use only compatible lubricants.
- Do not permit liquid oxygen, hydrogen or oxygen enriched air to come in contact with any organic or combustible material.

Release or Spill of Cryogens

- If there are associated injuries, call emergency personnel at 911.
- Immediately evacuate the area of the spill or leak. Evacuate students and staff from labs adjacent to location of spill.
- Report the spill or leak to your supervisor immediately.
- Never re-enter the area until it has been determined "Safe" by a Safety Coordinator or your supervisor.

Personnel Injuries from Cryogens

It is extremely important to use caution when approaching someone injured or unconscious near a cryogenic system. If the system is leaking, there could be an oxygen deficient atmosphere around the injured person, which would make it dangerous for others to get close. Entering the oxygen deficient atmosphere could cause the rescuer to become unconscious as well.

If you see an injured or unconscious person near a cryogenic system:

- Call emergency personnel immediately.

- Determine if the cryogenic system is leaking.
- Determine if an oxygen deficient atmosphere might be present.
- If there is a potential for an oxygen deficient atmosphere, evacuate the area until it is ventilated.
- If safe to do so, shut-off the cryogenic system to stop the leak.
- If safe to do so, remove the injured person to a well-ventilated area.
- Give the injured person appropriate First Aid or CPR until emergency personnel arrive.

First Aid Procedures for Contact

Any time cryogen's come in contact with your skin, you should obtain medical assistance as soon as possible.

Immediately after exposure, the frozen skin appears waxy and yellow and usually is not painful to the worker. As the skin thaws, it painfully swells and blisters. When this occurs, immediate emergency treatment is required. While waiting for medical assistance, follow these first aid procedures:

- Remove the victim from the cryogen hazard.
- Remove any clothing that may interfere with the circulation of blood to the frozen tissues. The clothing must be removed in a slow, careful manner to prevent salvageable skin from being pulled off.
- Do not rub the affect areas of skin. Rubbing may further damage the tissue.
- Immerse the affected area in a warm water bath (approx. 105°F). Do not apply dry heat, such as electric heaters, because it may superimpose a thermal burn, further damaging injured tissue.
- If the worker has experienced a massive exposure such that overall body temperature is reduced, the worker should be wrapped in blankets until paramedics arrive. In cases of extreme exposure, the worker should be totally immersed in warm water. Treatment for shock may be necessary.
- The re-warming, or thawing, of affected area(s) should be done gradually. It may take up to 60 minutes to thaw the affected area(s) and bring back the natural colors of the skin.
- If the frozen tissue thaws before medical help arrives, cover the area with dry sterile dressings and large bulky protective clothing. Do not apply ointments.
- Do not allow the exposed worker to drink alcohol or smoke. Alcohol and nicotine decrease blood flow to the frozen tissues. You may give the effected worker warm drinks and food.
- Try to make the worker feel as comfortable as possible.

Even minor burns must be reported to your supervisor. Obtain medical attention if appropriate. For emergency treatment, call 911.

Additional Information and Resources

- [Video-Filling and Maintenance of Liquid Nitrogen Tanks](#)
- [Compressed Gas Association](#)
- [Cryogenic Safety](#)

- [Liquid Nitrogen](#)
- [Liquid Hydrogen](#)
- [Helium](#)
- [Argon](#)
- [Cryogenic Containers](#)
- [Sandia National Laboratories – Safe Handling of Cryogenic Fluids](#)
- [Hydrogen](#)
- The following handbooks are available through EH&S
 - Handbook of Compressed Gases – Fourth Edition
 - Safe Handling of Compressed Gases in Containers
 - Standards for Visual Inspection of Steel Compressed Gas Cylinders
 - Standards for Visual Inspection of High Pressure Aluminum Compressed Gas Cylinders
 - Guidelines for Visual Inspection 7 Requalification of Fiber Reinforced High Pressure Cylinders
 - Pressure Relief Device Standards – Part 1 – Cylinders for Compressed Gases
 - Pressure Relief Device Standards – Part 2 – Cargo and Portable Tanks for Compressed Gases
 - Standard for Requalification of DOT-3HT, CTC-3HT, and TC-3HTM Seamless Steel Cylinders