

CUSTOMER MANUAL

**NORMAL OPERATION, MAINTENANCE, SAFETY,
AND EMERGENCY RESPONSE**

FOR

LIQUID STORAGE SYSTEM

FOR SUPPLY OF LIQUID OR GASEOUS PRODUCT

PRODUCT: LIQUID CARBON DIOXIDE (LCO₂)

CUSTOMER: Viridia

LOCATION: 1319 Hwy 182

Raceland,
LA
70394

Date: 4/21/2016

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This guideline applies to permanently fixed storage tanks at Customer Locations.

Air Products has designed and built its Liquid Storage and Supply Systems to operate safely and efficiently while totally unattended.

IN THE EVENT OF AN UPSET OR FAILURE, DO NOT ATTEMPT TO GO NEAR OR MANIPULATE THE EQUIPMENT. CALL AIR PRODUCTS IMMEDIATELY, AT ANY OF THE TELEPHONE NUMBERS SHOWN BELOW:

(800) 224-2724 Product Dispatch and Customer Stations
Maintenance Service

(800) 523-9374 Nationwide Emergency Service

The following two key points should be known by the customer personnel who will respond to any emergency:

1. Air Products' piping and safety relief systems are designed "fail-safe" so that any and all valves can be closed at any time without creating a hazard to the storage system. The flow of product may be interrupted, which could create a hazard in the customer's operation, but the tank and piping will remain fail-safe with all safety systems on line. Relief devices may actuate, but these have been installed so that all product relieved is vented safely with no danger to personnel.
2. **DO NOT SPRAY WATER ON ANY TANK PIPING OR TANK SHELL OPENINGS** as this may result in freeze-plugging of the safety relief devices and subsequent vessel over-pressure (however, it is acceptable to spray water on the tank shell itself).

I. OPERATION

1. System Description

a. Overview

The storage and supply system consists of the following:

- 50 Ton Vacuum Jacketed Cryogenic Liquid Storage Tank with tank mounted 30 kW electric pressure build circuit with electric actuated valve
- Two (2) Electric Direct To Process Vaporizers (28 kW/Each) sized for 520 lb/hr, piped in parallel with integral low temp shutoff solenoid valve on each
- One (1) Pressure Control Manifold with back pressure regulator, pressure reducing regulator, check valve, bleed valves, and isolation and bypass valves

2. Operating Procedure

a. Normal Operation

Each system is sized and designed to handle the customer's expected demand cycle. Significant changes in product usage volume, pressure settings, flow rate, or system control and instrumentation should be reported to Air Products.

The product is stored as a liquid in the vacuum jacketed tank. The minimum tank pressure is determined by the setting of the pressure building circuit, which allows liquid to be vaporized into a gas in the pressure building coil, and then returned to repressurize the tank (280 - 300 psig). The maximum tank pressure in normal operation is determined by the setting of the tank back pressure regulator, set at 330psig, just below the set-point of the tank safety relief valves (350psig and 368psig). The normal design conditions, however, are for liquid to flow to the vaporizers, where it is converted to a gas by absorbing heat from the electric vaporizer. This system is designed to convert liquid CO₂ to 70 F gaseous CO₂ and will cutoff the flow of CO₂ gas if the temperature of the gas at the outlet of the vaporizers falls below 35 F. The final pressure control manifold contains a back pressure regulator to maintain tank pressure above 200 psig, a pressure reducing regulator to reduce pressure to 75 psig supply, check valve to prevent backflow, pressure gauges, and isolation and bypass valve for maintenance requirements. The upset pressure of the system is 385psig, and customer should protect their downstream piping with a safety relief valve if the MAWP of those components and/or piping is below 385psig. Customer's safety relief valve should be set at the MAWP of the lowest rated component in the distribution line. The bypass valve on the pressure control manifold will be locked closed and should never be manipulated by customer. This bypass serves for maintenance purposes only by a trained APCI technician. Risk of depressurizing the tank or overdrawing the vaporizers can occur if this valve is left opened.

The customer is responsible for daily monitoring of the system, mainly for tank level and pressure readings.

The other requirement of the daily walk-by is a visual check for leaks, or any other change in the system. Most leaks are audible, however, the presence of a vapor cloud or ice build-up will also indicate a leak on the portions of the system. In all cases, Air Products is responsible for all interface with the system for adjustment or maintenance, so it is important to call Air Products.

During normal operation, the main interface which the customer has with the system is to monitor the tank inventory via the liquid level gauge, which can be one of three types: dial and needle, digital LED, or digital LCD as part of a telemetry system, which telephones readings directly to our delivery terminal.

The gauge is marked for "full" and "re-order" levels. The tank pressure can also be monitored on a standard pressure gauge located on the tank, near the level gauge.

By contract, it is the customer's responsibility to monitor the tank levels and order product from the delivery terminal at the established re-order level. In actuality, as the customer's usage pattern becomes established, we are able to forecast deliveries, however, it is still required that the customer report tank levels because of possible changes in use, such as heavy draw periods or shutdowns. It should be noted that a telemetry system is included, which automatically telephones tank levels to the terminal, but this system should only be considered a back-up or "insurance" system. It does **not** relieve the customer of the need to re-order product.

Air Products' distribution terminals operate 24 hrs./day, 7 days/week, so deliveries will be made at all hours of the day or night. When a tanker truck arrives to make a delivery, the driver will perform the delivery with no attendance required by the customer. During the delivery process, the "full trycock" level monitor valve is open so that escaping gas and a small vapor cloud are present. This is normal. At the end of the delivery, someone at the customer's plant should be designated to sign the delivery ticket.

The storage and supply equipment is designed to operate automatically and totally unattended, with a few minor exceptions:

For those systems with special electrical control panels, a power failure may require the "RESET" and the "SYSTEM START" buttons to be pressed. No harm or unsafe conditions can be caused by doing this because alarm conditions, if they exist, cannot be reset. We ask the customer to attempt this simple restart before calling for service.

The system is designed to vent, safely and automatically, any excess pressure build-up in the tank. This will sound like a hissing whisper and will exit through either an "autovent" regulator (for tanks which are expected to vent constantly), or the spring-loaded safety relief valves. **CHECK THE TANK PRESSURE.** Normal venting

should occur only within 95 to 110% of the MAWP (Maximum Allowable Working Pressure) of the tank or at the "autovent" setting somewhere below that. If the tank is venting violently from the safety valve tree, refer to the Emergency Response Section of this Manual, Section III, Item 2.

As a general rule in diagnosing how the system is operating, look for areas of frost or ice which indicates that flow is occurring in those locations.

In all cases, if you have a question or concern, please call Air Products.

b. Start-up Procedures

The system is designed to supply product on a demand basis at all times. There are no start-up procedures necessary once the original mechanical check of the equipment is made, the initial pressure regulation settings are completed, and the manual supply valves are opened. When the demand for product stops, i.e., by the closure of valves by the customer, the system will simply sit idle and be ready to supply product again when needed.

c. Shut-down Procedures

There are no shut-down procedures in normal operation. When the demand for product stops, the system will sit idle, ready to supply product again when needed. The tank is self-regulating and self-relieving of pressure build-up, by means of an "auto-vent" regulator. During periods of non-use, this regulator will be heard flowing and will show some small ice formation.

All product flow for the tank can be isolated by closing the manual valves at the tank withdrawal connections. Contact Air Products if, for any reason, product would need to be removed from the tank.

In all cases, if you have a question or concern, call Air Products.

II. MAINTENANCE

Most systems are owned by Air Products and leased to the customer. As such, maintenance is the responsibility of Air Products. There are no customer requirements for maintenance except for snow removal in snow areas, and general housekeeping to keep the area free from debris, weeds and vegetation.

1. Ongoing Maintenance

Air Products responds on a 24 hour basis to all needs for maintenance, as well as to any specific customer request or concern. Our delivery drivers, who do not make mechanical repairs, are instructed to report all repair requests to the maintenance department after each delivery of product. Our goal is to maintain a totally reliable and functional system with little or no effort on the part of the customer.

2. Preventive Maintenance and Inspections

We perform regular maintenance inspections on all systems. In addition to inspecting for leaks, integrity and general condition of the system, we also have adopted the following key maintenance standards within Air Products. In all cases, Federal, State, or Local regulations take precedence if they are more stringent. Whenever individual customer requirements supersede these, an agreement can be reached. These intervals have been set based on historical performance, system complexity, and product safety.

- a. The pressure vessels are ASME Section 8 in dry service so no periodic retest is required or deemed necessary.
- b. Any problems with the outer vessel insulation will be apparent by pressure rise in the tank or condensation on the outer shell.
- c. Level gauges are zeroed at each maintenance inspection, but are not spanned. These gauges are not the primary device for filling and have no safety function. Based on this and our operating experience, we do not span or calibrate the gauges. They are replaced-on-failure.
- d. Some ice build up is normal and to be expected. Contact Air Products if any of the following conditions exist:
 - 1) Tank piping begins to encase any operating device such as relief valves or valve handles.
 - 2) Any ice forms on the outside of the tank and the foundation at any point.
 - 3) Ice forms on overhead lines, creating a possible hazard of ice falling off or adding excess weight to the pipe. Generally, if the ice thickness exceeds the pipe diameter, there is reason for concern. For lines supported at grade, there is

no practical limit of ice thickness. Ice can be removed by either allowing it to defrost naturally (by stopping the flow of product), with a water hose, or with steam.

DO NOT ATTEMPT TO REMOVE ICE BY HAMMERING OR CHIPPING AS THIS WILL RUPTURE PIPING AND DAMAGE EQUIPMENT. WHEN USING WATER, BE CERTAIN NOT TO APPLY IT IN A DIRECTION WHICH COULD FREEZE THE OUTLET OF ANY SAFETY RELIEF VALVE(S).

- e. The system will shut down on loss of steam. The loss of steam is determined by a pressure switch which closes a solenoid on the gas line.
- e. Settings are checked and adjusted if necessary during the preventative maintenance inspections.
- f. All other components are replaced or repaired as required.

III. NORMAL HAZARDS

Every product has inherent hazards associated with it, such as cold burns for liquids and asphyxiation for Carbon Dioxide. These hazards are well known and are easily and consistently managed by system design and proper training. There are a number of sources of information about these hazards, the most common being the Safety Data Sheet and the Air Products' SAFETYGRAM, which are attached for reference. **Only personnel who are properly trained and are wearing the proper personnel protection equipment should directly handle or interface with these products.**

The National Fire Protection Association (NFPA) has established a standard system for the identification of the fire hazards of materials (NFPA Pamphlet 704). This is known as the "Colored Diamond" system because it utilizes four colored diamond shaped boxes to signify the level of hazard. The order of severity is given by the numerical ranking of zero for no hazard to four for a severe hazard. The top box indicates flammability, the left is health hazard, the right reactivity, and the bottom is used to show special reactivity with water, oxidizing properties, or simple asphyxiant. The chart below gives the proper ratings to be used for each product.

<u>Product</u>	<u>Top (Red) Flammability</u>	<u>Left (Blue) Health</u>	<u>Right (Yellow) Reactivity</u>	<u>Bottom (White) Specific</u>
LCO2	0	1	0	SA

SA = simple asphyxiant.

The installation and maintenance of these placards, if required by local authorities, is the responsibility of the customer.

IV. EMERGENCY RESPONSE

There are, of course, any number of emergency scenarios that could be considered. Our systems are designed with such large safety factors and in anticipation of all likely problems, that even the worst scenarios should create no extreme hazard. The following scenarios are listed in order of likelihood of occurrence, followed by the appropriate emergency response measures.

This information represents first-level responder information, as defined by the Federal HAZWOPER Regulations.

Keep all spectators (and other personnel not directly involved with handling the emergency) the following distances from the perimeter of any incident and upwind if at all possible. Spills, releases, and other emergencies: 150 feet

Please be reminded that the information given below is intended for personnel who are designated and trained to respond to emergency situations. In all instances, CALL AIR PRODUCTS FIRST!

1. EMERGENCY: Small piping leaks.

SYMPTOMS: Vapor cloud or hissing noise.

PROPER RESPONSE: Contact Air Products, Customer Stations Service. Do not attempt to stop the leak by tightening, or with wet rags, as larger leaks or personal injury from freezing may result.

DO NOT SPRAY WATER ON THE TANK AS THE WATER WILL DAMAGE THE TANK INSULATION.

The tank pressure will also rise because of the added heat leak to the tank. The tank safety valves are sized to handle added venting due to loss of vacuum. There is no physical danger in this situation, and no emergency response required, except to contact Air Products.

4. EMERGENCY: Major rupture or failure of tank piping.

SYMPTOM: Major rupture or piping failure will be apparent by a loud rush of high pressure cold gas and water vapor cloud. The piping associated with the rupture will also become frosted. At the same time, the tank pressure may fall.

PROPER RESPONSE: The first effort must be directed at keeping personnel out of the danger area (which in most cases very nearly approximates the vapor cloud). After that, the next goal is to shut off the flow at its source if a valve is available. Remote shutoffs are not installed on liquid systems. If the flow cannot be stopped, then simply allow the product to vaporize and dissipate. A water hose is an excellent agent for accomplishing this. Keep all fluids away from yard drains, sewers and buildings. There are no toxic or lasting effects of such spills. If possible, keep any liquid from contacting steel support structures as the cold can cause brittle fractures under stress.

5. EMERGENCY: Fire.

SYMPTOM: Heat striations, sound, or charred piping.

PROPER RESPONSE: The danger of fire is to our system from the surroundings, as neither this product nor any of the system's components are flammable. Our tank safety valves are sized to handle simultaneous loss of vacuum and a skin temperature of 1200°F on the entire tank shell. The tank piping is either stainless steel welded or silver soldered copper (which has a melting point of 1250-1370° F) so the piping will remain intact up to this temperature. Water can be applied to the shell as a precaution, but **KEEP WATER AWAY FROM THE SAFETY VALVES AND ALL OTHER SHELL OPENINGS.**

6. EMERGENCY: Driver injury during fill.

PROPER RESPONSE: If the driver should become disabled while the delivery transfer is in process, the tank will overfill and vent out the safety valves and rupture discs, which are sized to accommodate the maximum pumping capacity. Attend first to the driver's safety. After that, attempt to shut off the pump. The liquid delivery trailers can be shut off at a switch in the rear cabinet near the pump labeled "Emergency Shutoff". Call Air Products, Product Dispatch. In addition, there is an emergency 800 telephone number on the trailer.

7. EMERGENCY: Lightning.

PROPER RESPONSE: We have never experienced any damage due to lightning strikes. Our systems are not grounded directly, depending on the piping or anchor bolts for grounding.

8. EMERGENCY: Major rupture or overturn of tank due to external collision, wind, earthquake, or flood.

PROPER RESPONSE: We design the equipment, foundation(s), and anchoring systems to meet the seismic and wind conditions defined in the appropriate local codes, such as UBC, BOCA or SBC. Other extraordinary events such as airplane or vehicle impacts, or "floating" calculations in flood areas and such must be individually assessed. We always require that our storage systems be protected from external collisions by pipe bollards or guard rails. Siting requirements as spelled out by UBC and NFPA are also used to minimize exposure to other hazards. In the event of a major spill, the following actions should be taken:

- a. Keep all spectators and other personnel at least 150 feet away from the perimeter of the spill and upwind if possible.

9. EMERGENCY: Rollover of Delivery Liquid Tanker Truck

PROPER RESPONSE: First and foremost, contact Air Products, Product Dispatch, or call the 800 emergency number on the trailer. We have an emergency response network of people trained and ready for this situation. Generally, if the trailer is intact, there are several safe hours available during which we can travel to the site. If the trailer has cracked or burst and is leaking product, there is no hazard other than direct personnel contact for Liquid Carbon Dioxide. In this situation, simply keep all personnel 500 to 1,000 feet away, and allow the liquid to vaporize and disperse. **DO NOT SPRAY WATER ON THE EQUIPMENT.** Water can be used to speed the dispersal of the vapor cloud or pools of liquid. If the trailer is intact, the following guidelines apply:

ONLY AIR PRODUCTS' PERSONNEL SHOULD PERFORM THE FOLLOWING:

- a. The greatest danger is always from over pressure and rupture of the tank, therefore, keeping the tank vented to atmosphere is critical. Every tanker has vapor and liquid penetrations which, of course, will reverse when the tanker is upside down. On the liquid delivery tankers, there are no internal valves or check valves, so if the product can be directed to a safe area, the fail-safe thing is to open all valves. The ideal procedure is to only open a vapor valve.
- b. Once the pressure can be controlled, the next objective is to right the trailer with the contents intact, using a crane or cranes. The potential of liquid sloshing during up righting must be considered. The trailer does have crossways baffles so the greatest sloshing danger is side to side.

V. SAFETY DATA SHEET AND SAFETY GRAM

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1. PRODUCT AND COMPANY IDENTIFICATION

Product name : Carbon dioxide (Refrigerated)

Chemical formula : CO₂

Synonyms : Carbon dioxide (refrigerated)

Product Use Description : General Industrial

Manufacturer/Importer/Distributor : Air Products and Chemicals, Inc
7201 Hamilton Blvd.
Allentown, PA 18195-1501
GST No. 123600835 RT0001
QST No. 102753981 TQ0001

Telephone : 1-610-481-4911 Corporate
1-800-345-3148 Chemicals Cust Serv
1-800-752-1597 Gases/Electronics Cust Serv

Emergency telephone number (24h) : 800-523-9374 USA
+1 610 481 7711 International

2. HAZARDS IDENTIFICATION

GHS classification

Gases under pressure - Refrigerated liquefied gas
Simple Asphyxiant

GHS label elements

Hazard pictograms/symbols



Signal Word: Warning

Hazard Statements:

H281:Contains refrigerated gas; may cause cryogenic burns or injury.

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May displace oxygen and cause rapid suffocation.
May increase respiration and heartrate.

Precautionary Statements:

Prevention : P282:Wear cold insulating gloves/face shield/eye protection.

Response : P315 :Get immediate medical advice/attention.
P336 :Thaw frosted parts with lukewarm water. Do not rub affected area.

Storage : P403:Store in a well-ventilated place.

Hazards not otherwise classified

Extremely cold liquid and gas under pressure.
Direct contact with liquid can cause frostbite.
Can cause rapid suffocation.
Avoid breathing gas.
Self contained breathing apparatus (SCBA) may be required.

3. COMPOSITION/INFORMATION ON INGREDIENTS

Components	CAS Number	Concentration (Volume)
Carbon Dioxide	124-38-9	100 %

Concentration is nominal. For the exact product composition, please refer to Air Products technical specifications.

4. FIRST AID MEASURES

General advice : Remove victim to uncontaminated area wearing self contained breathing apparatus. Keep victim warm and rested. Call a doctor. Apply artificial respiration if breathing stopped.

Eye contact : In the case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
Keep eye wide open while rinsing.

Skin contact : In case of frostbite, obtain medical treatment immediately. As soon as practical, place the affected area in a warm water bath- which has a temperature not to exceed 40 °C (105 °F). Do not rub frozen parts as tissue damage may result. Cover wound with sterile dressing.

Ingestion : Ingestion is not considered a potential route of exposure.

Inhalation : Move to fresh air. If breathing has stopped or is labored, give assisted respirations. Supplemental oxygen may be indicated. If the heart has stopped,

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trained personnel should begin cardiopulmonary resuscitation immediately. In case of shortness of breath, give oxygen.

Most important symptoms/effects - acute and delayed : Exposure to oxygen deficient atmosphere may cause the following symptoms: Dizziness. Salivation. Nausea. Vomiting. Loss of mobility/consciousness. Shivering fit. Sweating. Blurred vision. Headache. Increased pulse rate. Shortness of breath. Rapid respiration.

5. FIRE-FIGHTING MEASURES

Suitable extinguishing media : All known extinguishing media can be used.

Specific hazards : Spill will rapidly vaporize forming an oxygen deficient vapor cloud. Vapor cloud may obscure visibility. Do not direct water spray at container vent. Move away from container and cool with water from a protected position. Keep containers and surroundings cool with water spray.

Special protective equipment for fire-fighters : Wear self contained breathing apparatus for fire fighting if necessary.

6. ACCIDENTAL RELEASE MEASURES

Personal Precautions, Protective Equipment, and Emergency Procedures : Monitor carbon dioxide level. Evacuate personnel to safe areas. Ventilate the area. Monitor oxygen level. Wear self-contained breathing apparatus when entering area unless atmosphere is proved to be safe.

Environmental precautions : Prevent further leakage or spillage. Prevent from entering sewers, basements and workpits, or any place where its accumulation can be dangerous. Do not discharge into any place where its accumulation could be dangerous.

Methods for cleaning up : Ventilate the area.

Additional advice : If possible, stop flow of product. Increase ventilation to the release area and monitor oxygen level. Vapor cloud may obscure visibility. Do not spray water directly at leak. If leak is from cylinder or cylinder valve, call the Air Products emergency telephone number. If the leak is in the user's system, close the cylinder valve and safely vent the pressure before attempting repairs.

7. HANDLING AND STORAGE

Handling

Know and understand the properties and hazards of the product before use. Only experienced and properly instructed persons should handle compressed gases/cryogenic liquids. Before using the product, determine its identity by reading the label. Do not remove or deface labels provided by the supplier for the identification of the cylinder contents. Before connecting the container, check the complete gas system for suitability, particularly for pressure rating and materials. Before connecting the container for use, ensure that back feed from the system into the container is prevented. Close container valve after each use and when empty, even if still connected to equipment. Never attempt to repair or modify container valves or safety relief devices. Damaged valves should

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be reported immediately to the supplier. If user experiences any difficulty operating cylinder valve discontinue use and contact supplier. Do not remove or interchange connections. Ensure the complete gas system has been checked for leaks before use. Prevent entrapment of cryogenic liquid in closed systems not protected with relief device. A small quantity of liquid produces large volumes of vaporized gas at atmospheric pressure. Containers used in shipment, storage, and transfer of cryogenic liquid are specially designed, well-insulated containers equipped with a pressure relief device and valves to control pressure. Under normal conditions, these containers will periodically vent product to limit pressure buildup. Ensure that the container is in a well-ventilated area to avoid creating an oxygen-deficient atmosphere. Use adequate pressure relief in systems and piping to prevent pressure buildup; liquid in a closed container can generate extremely high pressures when vaporized by warming. Employ suitable pressure regulating devices on all containers when the gas is being emitted to systems with lower pressure rating than that of the container. Only transfer lines designed for cryogenic liquids shall be used. Do not subject containers to abnormal mechanical shock. When moving cylinders, even for short distances, use a cart (trolley, hand truck, etc.) designed to transport cylinders. When doubt exists as to the correct handling procedure for a particular gas, contact the supplier.

Storage

Open/close valve slowly. Close when not in use. Wear Safety Eye Protection. Check Safety Data Sheet before use. Use a back flow preventative device in the piping. Do not change or force fit connections. Close valve after each use and when empty. Always keep container in upright position. Read and follow the Safety Data Sheet (SDS) before use. Do not allow storage temperature to exceed 50°C (122°F). Containers should be stored in a purpose build compound which should be well ventilated, preferably in the open air. Full containers should be stored so that oldest stock is used first. Do not store in a confined space. Full and empty cylinders should be segregated. Store containers in location free from fire risk and away from sources of heat and ignition. Return empty containers in a timely manner. Stored containers should be periodically checked for general condition and leakage. Protect containers stored in the open against rusting and extremes of weather. Containers should not be stored in conditions likely to encourage corrosion. Cryogenic containers are equipped with pressure relief devices to control internal pressure. Under normal conditions these containers will periodically vent product. All vents should be piped to the exterior of the building. Observe all regulations and local requirements regarding storage of containers.

8. EXPOSURE CONTROLS / PERSONAL PROTECTION

Engineering measures

Provide natural or mechanical ventilation to prevent accumulation above exposure limits.
Natural or mechanical to prevent oxygen deficient atmospheres below 19.5% oxygen.
Keep self contained breathing apparatus readily available for emergency use.

Personal protective equipment

Respiratory protection : Self contained breathing apparatus (SCBA) or positive pressure airline with mask are to be used in oxygen-deficient atmosphere.
Air purifying respirators will not provide protection. Users of breathing apparatus must be trained.

Hand protection : Wear working gloves when handling gas containers.
If the operation involves possible exposure to a cryogenic liquid, wear loose fitting thermal insulated or cryo-gloves.
Chemical-resistant, impervious gloves complying with an approved standard should be worn at all times when handling chemical products if a risk assessment indicates this is necessary.

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- Eye protection : Safety glasses recommended when handling cylinders. Protect eyes, face and skin from liquid splashes. Wear goggles and a face shield when transfilling or breaking transfer connections.
- Skin and body protection : Never allow any unprotected part of the body to touch uninsulated pipes or vessels which contain cryogenic fluids. The extremely cold metal will cause the flesh to stick fast and tear when one attempts to withdraw from it. Safety shoes are recommended when handling cylinders.
- Special instructions for protection and hygiene : Ensure adequate ventilation, especially in confined areas.

Exposure limit(s)

Carbon Dioxide	Time Weighted Average (TWA): ACGIH	5,000 ppm	-
Carbon Dioxide	Short Term Exposure Limit (STEL): ACGIH	30,000 ppm	-
Carbon Dioxide	Recommended exposure limit (REL): NIOSH	5,000 ppm	9,000 mg/m3
Carbon Dioxide	Short Term Exposure Limit (STEL): NIOSH	30,000 ppm	54,000 mg/m3
Carbon Dioxide	Permissible exposure limit: OSHA Z1	5,000 ppm	9,000 mg/m3
Carbon Dioxide	Time Weighted Average (TWA): TN OEL	10,000 ppm	18,000 mg/m3
Carbon Dioxide	Short Term Exposure Limit (STEL): TN OEL	30,000 ppm	54,000 mg/m3

Remarks : Simple asphyxiant.

9. PHYSICAL AND CHEMICAL PROPERTIES

- Appearance : Liquefied gas. Colorless.
- Odor : No odor warning properties.
- Odor threshold : No data available.
- pH : Not applicable.
- Melting point/range : -70 °F (-56.6 °C)
- Boiling point/range : -1,381 °F (-78,5 °C)
- Flash point : Not applicable.
- Evaporation rate : Not applicable.
- Flammability (solid, gas) : Refer to product classification in Section 2
- Upper/lower explosion/flammability limit : No data available.
- Vapor pressure : 831.04 psia (57.30 bara) at 68 °F (20 °C)

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Water solubility	: 2.000 g/l
Relative vapor density	: 1.52 (air = 1)
Relative density	: 1.03 (water = 1)
Partition coefficient (n-octanol/water)	: Not applicable.
Auto-ignition temperature	: No data available.
Decomposition temperature	: No data available.
Viscosity	: Not applicable.
Molecular Weight	: 44 g/mol

10. STABILITY AND REACTIVITY

Chemical Stability	: Stable under normal conditions.
Conditions to avoid	: No data available.
Materials to avoid	: Carbon steel.
Hazardous decomposition products	: No data available.
Possibility of hazardous Reactions/Reactivity	: No data available.

11. TOXICOLOGICAL INFORMATION

11.1 Information on toxicological effects

Likely routes of exposure

Effects on Eye	: Contact with liquid may cause cold burns/frostbite.
Effects on Skin	: Contact with liquid may cause cold burns/frostbite. May cause severe frostbite.
Inhalation Effects	: Concentrations of 10% CO ₂ or more can produce unconsciousness or death. Unlike simple asphyxiants, carbon dioxide has the ability to cause death even when normal oxygen levels (20-21%) are maintained. Carbon Dioxide is physiologically active, affecting circulation and breathing. At concentrations between 2 and 10%, carbon dioxide can cause nausea, dizziness, headache, mental confusion, increased blood pressure and respiratory rate. In high concentrations may cause asphyxiation. Symptoms may include loss of mobility/consciousness. Victim may not be aware of asphyxiation. Asphyxiation

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may bring about unconsciousness without warning and so rapidly that victim may be unable to protect themselves.

Ingestion Effects : Ingestion is not considered a potential route of exposure.

Symptoms : Exposure to oxygen deficient atmosphere may cause the following symptoms: Dizziness. Salivation. Nausea. Vomiting. Loss of mobility/consciousness. Shivering fit. Sweating. Blurred vision. Headache. Increased pulse rate. Shortness of breath. Rapid respiration.

Acute toxicity

Acute Oral Toxicity : No data is available on the product itself.

Inhalation : Unlike simple asphyxiants, carbon dioxide has the ability to cause death even when normal oxygen levels (20-21%) are maintained. 5% CO₂ has been found to act synergistically to increase the toxicity of certain other gases (CO, NO₂). CO₂ has been shown to enhance the production of carboxy- or met-hemoglobin by these gases possibly due to carbon dioxide's stimulatory effects on the respiratory and circulatory systems.

Acute Dermal Toxicity : No data is available on the product itself.

Skin corrosion/irritation : No data available.

Serious eye damage/eye irritation : No data available.

Sensitization. : No data available.

Chronic toxicity or effects from long term exposures

Carcinogenicity : No data available.

Reproductive toxicity : No data is available on the product itself.

Germ cell mutagenicity : No data is available on the product itself.

Specific target organ systemic toxicity (single exposure) : No data available.

Specific target organ systemic toxicity (repeated exposure) : No data available.

Aspiration hazard : No data available.

Delayed and Immediate Effects and Chronic Effects from Short and Long Term Exposure

Not applicable.

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12. ECOLOGICAL INFORMATION

Ecotoxicity effects

Aquatic toxicity : Not applicable.

Toxicity to fish - Components
Carbon Dioxide

LC50 (1 h) : 240 mg/l

Species : Rainbow trout (Oncorhynchus mykiss).

Carbon Dioxide

LC50 (96 h) : 35 mg/l

Species : Rainbow trout (Oncorhynchus mykiss).

Toxicity to other organisms : Not applicable.

Persistence and degradability

Biodegradability : No data is available on the product itself.

Mobility : No data available.

Bioaccumulation : No data is available on the product itself.

Further information

When discharged in large quantities may contribute to the greenhouse effect.

13. DISPOSAL CONSIDERATIONS

Waste from residues / unused products : Return unused product in original cylinder to supplier. Contact supplier if guidance is required.

Contaminated packaging : Return cylinder to supplier.

14. TRANSPORT INFORMATION

DOT

UN/ID No. : UN2187

Proper shipping name : Carbon dioxide, refrigerated liquid

Class or Division : 2.2

Label(s) : 2.2

Marine Pollutant : No

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IATA

UN/ID No. : UN2187
Proper shipping name : Carbon dioxide, refrigerated liquid
Class or Division : 2.2
Label(s) : 2.2
Marine Pollutant : No

IMDG

UN/ID No. : UN2187
Proper shipping name : CARBON DIOXIDE, REFRIGERATED LIQUID
Class or Division : 2.2
Label(s) : 2.2
Marine Pollutant : No

TDG

UN/ID No. : UN2187
Proper shipping name : CARBON DIOXIDE, REFRIGERATED LIQUID
Class or Division : 2.2
Label(s) : 2.2
Marine Pollutant : No

Further Information

Avoid transport on vehicles where the load space is not separated from the driver's compartment. Ensure vehicle driver is aware of the potential hazards of the load and knows what to do in the event of an accident or an emergency. The transportation information is not intended to convey all specific regulatory data relating to this material. For complete transportation information, contact an Air Products customer service representative.

15. REGULATORY INFORMATION

Toxic Substance Control Act (TSCA) 12(b) Component(s):

None.

Country	Regulatory list	Notification
USA	TSCA	Included on Inventory.
EU	EINECS	Included on Inventory.
Canada	DSL	Included on Inventory.
Australia	AICS	Included on Inventory.
Japan	ENCS	Included on Inventory.
South Korea	ECL	Included on Inventory.
China	SEPA	Included on Inventory.
Philippines	PICCS	Included on Inventory.

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EPA SARA Title III Section 312 (40 CFR 370) Hazard Classification
Acute Health Hazard

US. California Safe Drinking Water & Toxic Enforcement Act (Proposition 65)

This product does not contain any chemicals known to State of California to cause cancer, birth defects or any other harm.

16. OTHER INFORMATION

Prepared by : Air Products and Chemicals, Inc. Global EH&S Product Safety Department

Telephone : 1-610-481-4911 Corporate
1-800-345-3148 Chemicals Cust Serv
1-800-752-1597 Gases/Electronics Cust Serv

Preparation Date : 04/04/2016

For additional information, please visit our Product Stewardship web site at
<http://www.airproducts.com/productstewardship/>

Carbon dioxide

Carbon dioxide is nonflammable, colorless, and odorless in the gaseous and liquid states. Carbon dioxide is a minor but important constituent of the atmosphere, averaging about 0.036% or 360 ppm by volume. It is also a normal end-product of human and animal metabolism.

Dry carbon dioxide is a relatively inert gas. In the event moisture is present in high concentrations, carbonic acid may be formed and materials resistant to this acid should be used. High flow rates or rapid depressurization of a system can cause temperatures approaching the sublimation point (-109.3°F [-78.5°C]) to be attained within the system. Carbon dioxide will convert directly from a liquid to a solid if the liquid is depressurized below 76 psia (61 psig). The use of materials which become brittle at low temperatures should be avoided in applications where temperatures less than -20°F (-29°C) are expected. Vessels and piping used in carbon dioxide service should be designed to the American Society of Mechanical Engineers (ASME) or Department of Transportation (DOT) codes for the pressures and temperatures involved.

Physical properties are listed in Table 1. Carbon dioxide in the gaseous state is colorless and odorless and not easily detectable. Gaseous carbon dioxide is 1.5 times denser than air and therefore is found in greater concentrations at low levels. Ventilation systems should be designed to exhaust from the lowest levels and allow make-up air to enter at a higher level.

Manufacture

Carbon dioxide is produced as a crude by-product of a number of manufacturing processes. Carbon dioxide is a by-product of steam reforming of methane, propane or naphtha. The fermentation of sugar to alcohol and the production of lime and sodium phosphate also generate carbon dioxide. Additionally, carbon dioxide exists in natural wells. Once the product has been isolated, impurities are filtered out, moisture is removed in driers, and the purified carbon dioxide is compressed for liquefaction.

Uses

Liquid carbon dioxide is used widely in the food industry for freezing meats, poultry, vegetables, and fruits. Solid carbon dioxide (dry ice) is used to cool meats prior to grinding and also to refrigerate meat and poultry during transit. Soft drinks, wines, and beers are produced using gaseous carbon dioxide for carbonation. Carbon dioxide is used in water treatment to neutralize alkaline water. Liquid carbon dioxide is also used to increase recovery from oil and gas wells. Other industrial uses include the production of chemicals, plastics, rubber, metals, and electronic components.

Health Effects

The physiological effects of carbon dioxide are unique because it is an end-product of metabolism, a vital component of the acid-base mechanism that controls blood pH, and an active messenger substance in the linking of respiration, circulation, and vascular response.

The blood and cellular fluids are actually a solutions of sodium bicarbonate and other substances. Severe exposure to carbon dioxide forms carbonic acid in the blood that exceeds buffering capacity of the sodium bicarbonate. The decrease in pH has a rapid toxic effect because the neural control systems are excessively driven. These effects are independent of the amount of oxygen in the atmosphere.

Low concentration of carbon dioxide can be tolerated for a considerable period of time without noticeable effect, or may merely cause an unnatural feeling of shortness of breath. Sustained exposure of 5% carbon dioxide produces stressful rapid breathing. When the carbon dioxide level exceeds 7%, the rapid breathing becomes labored and restlessness, faintness, severe headache, and dulling of consciousness occur. At 15%, unconsciousness accompanied by rigidity and tremors occurs in less than 1 minute and in the 20% to 30% range it produces unconsciousness and convulsions in less than 30 seconds. The effects occur quickly since the carbon dioxide diffuses in the tissue fluids at a rate approximately 20 times more rapidly than oxygen. High concentrations of carbon dioxide can asphyxiate quickly without warning and not possibility of self-rescue regardless of the oxygen concentration.

Table 1: Carbon Dioxide Physical and Chemical Properties

Molecular Formula	CO ₂
Molecular Weight	44.01
Boiling Point @ 1 atm (sublimes)	-109.3°F (-78.5°C)
Freezing Point @ 76 psia	-69.9°F (-56.6°C)
Critical Temperature	87.9°F (31.0°C)
Critical Pressure	1,070 psia (72.9 atm)
Density, Liquid @ -35°F (-37°C), 11 atm	68.74 lb/cu. ft.
Density, Gas @ 68°F (20°C), 1 atm	0.115 lb/cu. ft.
Density, Solid @ -110°F (-79°C), 1 atm	97.4 lb/cu. ft.
Specific Gravity, Gas (air=1) @ 68°F (20°C), 1 atm	1.53
Specific Gravity, Liquid @ -35°F (-37°C), 11 atm	1.10
Specific Volume @ 68°F (20°C), 1 atm	8.7 cu. ft./lb
Latent Heat of Sublimation	10,900 Btu/lb mole
Solubility in Water @ 68°F (20°C), 1 atm	87.8% by volume

Occupation Exposure Limit Containers

U.S. OSHA specifies that employee exposure to carbon dioxide in any 8-hour shift of a 40-hour work week shall not exceed the 8-hour time-weighted average (TWA-PEL) of 5,000 ppm (0.5%; 9,000 mg/m³). According the American Conference of Governmental Industrial Hygienists (ACGIH), the short-term exposure limit (STEL/Ceiling) for 15 minutes of less is 30,000 ppm (3%; 54,000 mg/m³). Since oxygen exposure limits and definitions vary by region/country, consult relevant legislation for the appropriate limits.

Bulk carbon dioxide is typically stored as a liquid in storage tanks with capacities of 6, 14, 26, and 50 tons. Tanks are insulated by polyurethane foam with a vapor barrier, which provides weather protection. The tanks are fabricated from carbon steel according to ASME Standards. Carbon dioxide is maintained below 305 psig by a refrigeration unit and above 245 psig with a pressure buildup coil so that carbon dioxide can be stored for an indefinite period without venting. Smaller liquid quantities are stored and shipped in cryogenic liquid cylinders with a capacity of 384 pounds (3352 standard cubic feet). Cryogenic liquid cylinders are vacuum-jacketed and can hold product for long periods without venting. Cryogenic liquid cylinders can either supply liquid or gas and liquid.

Carbon dioxide is shipped and stored as a liquefied compressed gas in hollow steel and aluminum cylinders. The cylinders have a concave base which allows the cylinders to stand upright and are tapered to a small opening on the top. The tapered or open end is threaded to receive a cylinder valve or other suitable outlet connection. Safety relief devices are part of the cylinder valve or the outlet connections. A threaded neck ring is secured to the tapered end of the cylinder to allow a protective cylinder cap to be installed. Cylinders are manufactured according to Department of Transportation (DOT) specifications. Cylinders in carbon dioxide service are hydrostatically tested upon manufacture, and every five years thereafter at 5/3 times the service pressure.

Gas cylinder valves

Carbon dioxide cylinder valve connection standards have been adopted by CGA. Carbon dioxide cylinders use a CGA 320 outlet connection. For additional information on cylinder valves, consult Air Products' "Safetygram-23: Cylinder Valves."

Safety devices

Bulk liquid storage tanks are protected against excessive pressures, which may result from heat leak, by reseatable relief devices. Cryogenic liquid cylinders are equipped with reseatable relief devices and are additionally protected with burst discs. Gas cylinders are protected from rupture due to fire by a frangible disc sometimes backed by a fusible metal with a melting temperature of about 212°F (100°C).

Shipment of carbon dioxide

In the United States, the transportation of carbon dioxide in interstate commerce by rail, highway, air and water is governed by federal authority under regulations promulgated by DOT.

- For bulk shipments by road DOT 10¾" x 10¾" nonflammable gas placards are required on the trailer.
- For gas cylinders a DOT 4" x 4" nonflammable gas label or tag is required
- Cryogenic liquid carbon dioxide cylinders are shipped under DOT Exemption Number 7638. A copy of this exemption must be carried aboard each vessel, aircraft or motor vehicle used to transport the cylinders. Each cryogenic cylinder must be plainly marked on both sides near the middle, in letters at least two inches high on a contrasting background, "DOT-E 7638." The DOT 4" x 4" green nonflammable gas label or tag is also required for common carrier shipments.

Safety considerations

Carbon dioxide is stored and transported as a liquefied compressed gas. The following hazards are associated with liquefied compressed carbon dioxide.

1. High pressure involved in storage and service equipment.
2. Carbon dioxide is 1.5 times heavier than air and will not readily disperse in the atmosphere. Asphyxiation may be a hazard in confined areas.
3. Carbon dioxide in high concentrations is toxic to humans as described in the health effects section.
4. Vaporizing carbon dioxide can produce very cold temperatures. Liquid carbon dioxide that contacts the skin can cause freeze burn or frostbite. Carbon dioxide, solid below 61 psig, is very cold and sublimates so quickly that prolonged contact with the skin causes freeze burn or frostbite.

Buildings

1. Provide adequate ventilation.
2. The atmosphere in areas in which carbon dioxide gas may be vented and collect should be tested with a portable or continuous monitoring carbon dioxide gas analyzer to ensure ventilation is adequate.

Handling and storage

Personnel should be trained in the proper storage, handling and use of carbon dioxide cylinders. For additional information, see CGA P-1, "Safe Handling of Compressed Gases in Containers," CGA G-6, "Carbon Dioxide," and CGA G-6.3, "Carbon Dioxide Cylinder Filling and Handling Procedures." Cylinders should always be stored in assigned locations.

Personnel equipment

Personnel must be thoroughly familiar with properties and safety considerations before being allowed to handle carbon dioxide and its associated equipment. Safety glasses, safety shoes, and leather work gloves are recommended when handling cylinders.

Where exposure to liquefied compressed gas may occur, employees should also wear a full face-shield and clean, loose-fitting, thermal-insulated gloves to protect the eyes, face and hands.

Emergency response

If carbon dioxide is present, its level must be monitored by a carbon dioxide specific detector, rather than relying on oxygen monitoring. Carbon dioxide presents a unique hazard, since a dangerous concentration of carbon dioxide may exist even when there is apparently adequate oxygen to support life.

Rescue personnel must wear a self-contained breathing apparatus (SCBA) or supplied air respirator in oxygen-deficient atmospheres or where the carbon dioxide concentration exceeds 3%.

First aid

People suffering from carbon dioxide exposure should be moved to fresh air. If the victim is not breathing, artificial respiration should be administered immediately. If the victim is breathing, give supplemental oxygen.

For skin contact with liquid or solids carbon dioxide, place the affected area in a warm water bath that has a temperature not in excess of 105°F (40°C). Do not rub the area. Never use dry heat. For any cold contact burn, seek medical attention immediately.

Fighting fires

Carbon dioxide is nonflammable and is an extinguishing agent for Class B & C fires.

Emergency Response System

T 800-523-9374 (Continental U.S. and Puerto Rico)

T +1-610-481-7711 (other locations)

For regional ER telephone numbers, please refer to the local SDS 24 hours a day, 7 days a week for assistance involving Air Products and Chemicals, Inc. products

Technical Information Center

T 800-752-1597 (U.S.)

T +1-610-481-8565 (other locations)

Monday–Friday, 8:00 a.m.–5:00 p.m. EST

F 610-481-8690

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