SAFE HANDLING OF LIQUID CARBON DIOXIDE CONTAINERS THAT HAVE LOST PRESSURE

AIGA 074/11

GLOBALLY HARMONISED DOCUMENT

Based on CGA G-6.7
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1 Introduction

This publication is one of a series compiled by the Compressed Gas Association, Inc. (CGA) to satisfy the demand for information on the production, handling, storage, transportation, and use of compressed and liquefied gases, cryogenic liquids, and related products.

As part of the programme of harmonization of industry standards, the Asia Industrial Gases Association (AIGA) has adopted the original CGA standard G-6.7 - 2009 as AIGA 074/11 This standard is intended as an international harmonized standard for the use and application by members of CGA, EIGA, JIMGA and AIGA. This edition has the same content as the CGA edition except for editorial changes in formatting, units, spelling and references to AIGA documents.

2 Scope and purpose

2.1 Scope

The scope of this publication is concerned primarily with the safe repressurization of stationary or transportable liquid carbon dioxide containers made of low alloy carbon steels and having a minimum design metal temperature above –110 °F (–78.9 °C).

2.2 Purpose

The purpose of this publication is to provide information to personnel to ensure that carbon dioxide containers that have lost pressure and may contain dry ice are safely repressurized before being returned to service.

Examples are given of repressurization procedures for containers manufactured under the American Society of Mechanical Engineers *ASME Boiler & Pressure Vessel Code*, Section VIII, Division 1, Pressure Vessels (ASME Code) [1].[1]

3 Definitions

For the purpose of this publication, the following definitions apply.

3.1 Autorefrigeration

The lowering of the temperature of carbon dioxide as the pressure reduces to maintain temperature and pressure equilibrium.

3.2 Brittle

The property of a material that causes it to break under load with little or no deformation.

3.3 Coincident temperature

The corresponding temperature for a substance at a given pressure at equilibrium.

3.4 Compressed gas

A substance existing only as a gas at a given temperature and pressure.

3.5 Condensation

The process by which a gas converts to a liquid.

3.6 Container

An insulated pressure vessel manufactured in accordance with the ASME Code for the storage of liquid carbon dioxide [1]. Container is interchangeable with vessel or tank.

3.7 Critical size

The size of a flaw in the container material that causes an uncontrolled increase of the length of a crack while under constant stress.

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[1] References are shown by bracketed numbers and are listed in order of appearance in the reference section.

3.8 Depressurization

A reduction of pressure in a container resulting in a container temperature below the minimum design metal temperature (MDMT) or the solidification of the carbon dioxide.

NOTE—Typical causes are the overdrawing of a pressure-building vaporizer, leaks, or a pressure relief device that did not reseat properly.

3.9 Dry ice

The common name for solid carbon dioxide.

NOTE—Its temperature is –109.3 °F (–78.5 °C) at atmospheric pressure.

3.10 Ductile

The property of a material that defines its ability to deform under load without breaking.

3.11 Elastic

The property of a material that defines its ability to deform under load without being permanently deformed.

3.12 Equilibrium

The physical state of a substance where the temperature and pressure will not change without an energy exchange.

3.13 Low-alloy carbon steel

A steel relatively low in carbon containing small amounts of other elements to enhance strength, ductility, and toughness.

3.14 Maximum allowable working pressure (MAWP)

The maximum gauge pressure permissible at the top of a vessel in its operating position for a designated temperature.

3.15 Melting

The process by which solid carbon dioxide converts to a liquid.

3.16 Minimum design metal temperature (MDMT)

The lowest temperature at which a container is designed to operate at a given pressure.

3.17 Nil ductility transition temperature (NDTT)

The temperature below which metals are brittle enough to fracture.

3.18 Plastic deformation

The deformation of a material that will remain permanent after removal of the load that caused it.

3.19 Pressure-building vaporizer

A heat exchanger that vaporizes liquid carbon dioxide from the container and returns it to the container as vapor to increase or maintain the pressure.

3.20 Qualified carbon dioxide technician

A person who by reason of education, training, and experience knows the properties of carbon dioxide; is familiar with the equipment used to store, transfer, and use carbon dioxide; and understands the precautions necessary to safely use carbon dioxide equipment.

3.21 Repressurization

The process of restoring a container to its design parameters when it has lost pressure and is below its MDMT.

3.22 Sublimation

The process of changing from the solid phase directly to the gas phase without passing through the liquid phase.

3.23 Toughness

The ability of a metal to absorb energy and undergo plastic deformation before fracturing.

3.24 Triple point

The temperature and pressure at which a material exists simultaneously as a solid, liquid, and gas.

NOTE—For carbon dioxide, the triple point is –69.9 °F, (–56.6 °C) and 60.4 psia (416 kPa).[2]

3.25 Ultimate tensile strength

The maximum stress level a material can sustain without fracturing.

3.26 Upset condition

Any condition outside the normal design parameters.

3.27 Vaporization

The process by which liquid carbon dioxide is converted to a gas.

4 Basis

The basis for this publication is actual testing performed under the auspices of CGA, who sponsored extensive testing on a horizontal 50-ton capacity carbon dioxide storage container in 1992 and 1993. The purpose of the testing was to obtain pressure, temperature, and flow rate data to allow CGA to evaluate prospective procedures that could be used to return a depressurized carbon dioxide container to normal service. Many different repressurization procedures were in use by the carbon dioxide industry, and the purpose of the testing was to evaluate their safety.

CGA provides these procedures and recommendations as its best available knowledge of carbon dioxide and its safe use. No single repressurization technique or procedure can be used for every container in service.

5 Warning

It is critical that persons attempting to return a carbon dioxide container from an upset condition (low pressure) be aware of the hazards involved, the metallurgical properties of the container, the quantity of liquid in the container before the upset, and the physical site conditions in order to choose the safest and best procedure for the circumstances.

A carbon dioxide container that has cooled below its minimum design metal temperature (MDMT) should be repressurized only by a qualified carbon dioxide technician. Knowledge of the container metallurgy and the properties of carbon dioxide are essential. The potential for catastrophic failure of a depressurized container being repressurized is much greater than normal if not properly handled.

6 Properties of carbon dioxide

Carbon dioxide is a compound of carbon and oxygen in proportions by weight of 27.3% carbon to 72.7% oxygen. A gas at normal atmospheric temperatures and pressures, carbon dioxide is colorless, odorless, and about 1.5 times as heavy as air. It is a slightly acid gas that can have a biting taste and faintly pungent odor. The physical constants of carbon dioxide are given in Table 1.

Carbon dioxide gas is relatively nonreactive and relatively nontoxic. It will not burn and it will not support combustion or life. When dissolved in water, carbonic acid (H_2CO_3) is formed. The pH of saturated carbonic acid varies from 3.7 at atmospheric pressure to 3.2 at 354 psig (2440 kPa).

Carbon dioxide can exist simultaneously as a solid, liquid, and gas at a temperature of –69.9 °F (–56.6 °C) and a pressure of 60.4 psig (416 kPa), which is its triple point. Figure 1 shows the triple point and full equilibrium curve for carbon dioxide.

At temperatures and pressures below the triple point, carbon dioxide can be either a solid (dry ice) or a gas, depending upon conditions. Solid carbon dioxide at a temperature of –109.3 °F (–78.5 °C) and at atmospheric pressure transforms directly to a gas (sublimes) without passing through the liquid phase. Lower temperatures result if solid carbon dioxide sublimes at pressures below atmospheric.

At temperatures and pressures above the triple point and below 87.9 °F (31.1 °C), carbon dioxide liquid and gas can exist in equilibrium in a closed container. Within this temperature range, the pressure in a closed container holding carbon dioxide liquid and gas in equilibrium bears a definite relationship to the temperature. Car-

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[2] kPa shall indicate gauge pressure unless otherwise noted as (kPa, abs) for absolute pressure or (kPa, differential) for differential pressure. All kPa values are rounded off per CGA P-11, Metric Practice Guide for the Compressed Gas Industry [2].

bon dioxide cannot exist as a liquid above its critical temperature of 87.9 °F (31.1 °C), regardless of the pressure.

Table 1—Physical constants of carbon dioxide

	U.S. Units	**SI Units**
Chemical formula	CO_2	CO_2
Molecular weight	44.01 lb/lb-mol	44.01 kg/kg-mol
Vapor pressure		
at 70 °F (21.1 °C)	838 psig	5778 kPa
at 32 °F (0 °C)	491 psig	3385 kPa
at 2 °F (–16.7°C)	302 psig	2082 kPa
at –20 °F (–28.9 °C)	200 psig	1379 kPa
at –69.9 °F (–56.6 °C)	60.4 psig	416 kPa
at –109.3 °F (–78.5 °C)	0 psig	0 kPa
Density of the gas		
at 70 °F (21.1 °C) and 1 atm	0.1144 lb/ft^3	1.833 kg/m^3
at 32 °F (0 °C) and 1 atm	0.1234 lb/ft^3	1.977 kg/m^3
Specific gravity of the gas		
at 70 °F (21.1 °C) and 1 atm (air = 1)	1.522	1.522
at 32 °F (0 °C) and 1 atm (air = 1)	1.524	1.524
Specific volume of the gas		
at 70 °F (21.1 °C) and 1 atm	8.741 ft^3/lb	0.5457 m^3/kg
at 32 °F (0 °C) and 1 atm	8.104 ft^3/lb	0.5059 m^3/kg
Density of liquid, saturated		
at 70 ° F (21.1 °C)	47.6 lb/ft^3	762 kg/m^3
at 32 °F (0 °C)	58.0 lb/ft^3	929 kg/m^3
at 2 °F (–16.7 °C)	63.3 lb/ft^3	1014 kg/m^3
at –20 °F (–28.9 °C)	66.8 lb/ft^3	1070 kg/m^3
at –69.9 °F (–56.6 °C)	73.5 lb/ft^3	1177 kg/m^3
Sublimation temperature (1 atm)	–109.3 °F	–78.5 °C
Critical temperature	87.9 °F	31.1 °C
Critical pressure	1070.6 psia	7381.8 kPa, abs
Critical density	29.2 lb/ft^3	468 kg/m^3
Triple point	–69.9 °F at 75.1 psia	–56.6 °C at 518 kPa, abs
Latent heat of vaporization		
at 32 °F (0 °C)	100.8 Btu/lb	234.5 kJ/kg
at 2 °F (–16.7 °C)	119.0 Btu/lb	276.8 kJ/kg
at –20 °F (–28.9 °C)	129.6 Btu/lb	301.4 kJ/kg
Latent heat of fusion at –69.9 °F (–56.6 °C)	85.6 Btu/lb	199 kJ/kg
Weight of liquid at 2 °F (–16.7 °C)	8.46 lb/gal	1014 kg/m^3
Latent heat of sublimation at –109.3 °F (–78.5 °C)	245.5 Btu/lb	571.0 kJ/kg

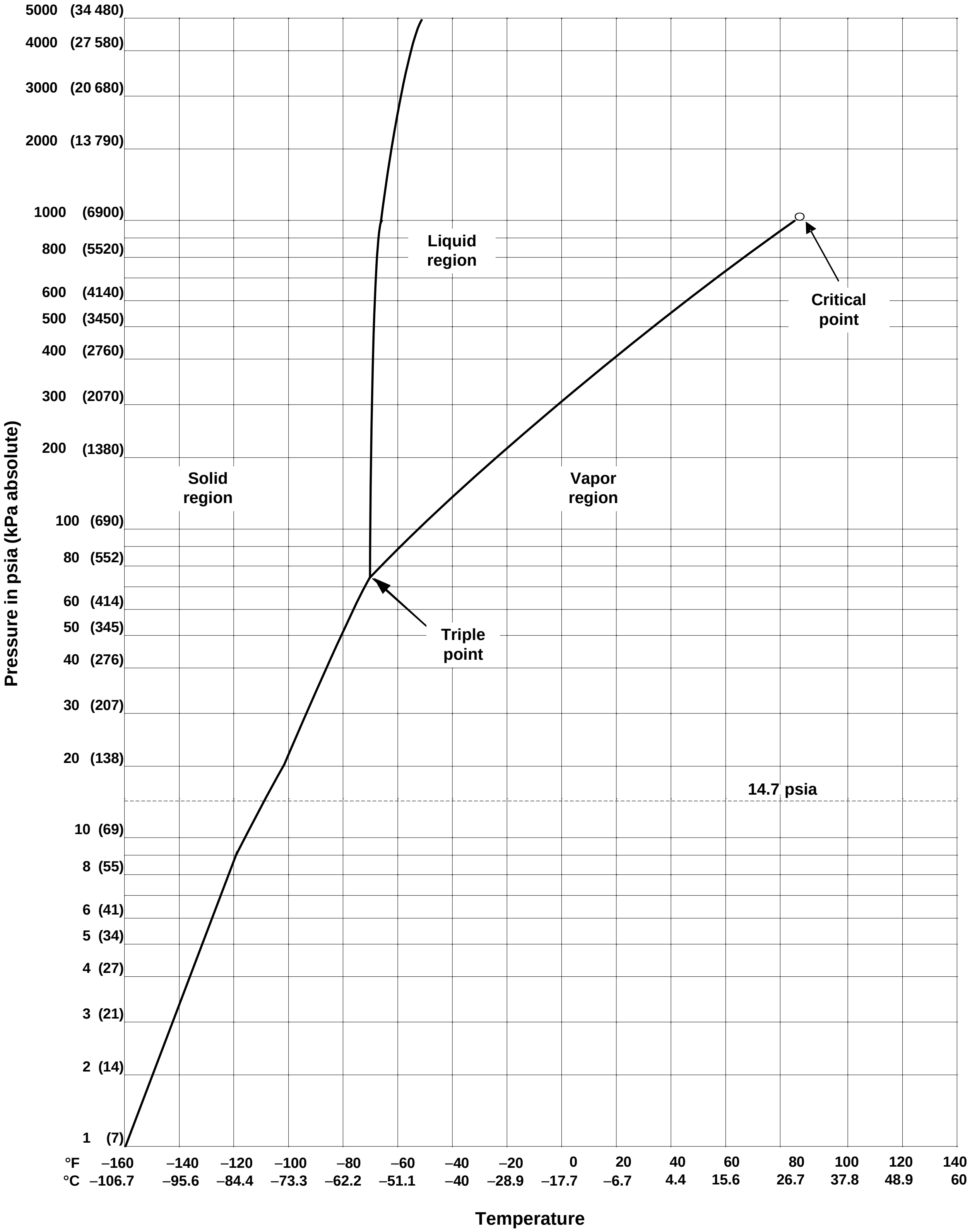


Figure 1—Phase diagram for carbon dioxide

7 Temperature and pressure

The temperature of liquid carbon dioxide and its container decreases as the pressure decreases due to autorefrigeration. The temperature and phases of the container contents during depressurization can be accurately determined by using the known pressure and the phase diagram shown in Figure 1. A conversion from liquid to dry ice begins to occur at 60.4 psig (416 kPa) with a coincident temperature of –69.9 °F (–56.6 °C). This is the triple point where gas, liquid, and solid carbon dioxide exist in equilibrium. As gas continues venting, energy is extracted from the liquid to generate the gas and solid required to maintain equilibrium. This converts more liquid to a solid. This process continues as long as venting occurs with temperature and pressure remaining constant, until only gas and dry ice remain. Continued venting below the triple point causes the pressure and temperature to continue to decline until at 0 psig (0 kPa) a temperature of –109.3 °F (–78.5 °C) is reached.

Container pressure losses can be caused by such things as a relief valve opening and failing to reclose, the rapid withdrawal of large volumes of carbon dioxide vapor, or the failure of a pressure-building vaporizer.

Carbon dioxide container owners and operators need to understand that the pressure/temperature equilibrium relationship does not apply when a container is being repressurized to return to normal service. It is possible for a container to be at 300 psig (2070 kPa) and to have liquid and dry ice at –69.9 °F (–56.6 °C) in the container because it is not at equilibrium. The liquid temperature will eventually warm up and the vapor pressure will decrease until they stabilize, but this can take days or weeks to occur.

Carbon dioxide storage containers are typically designed and constructed in accordance with the ASME Code, which is the recognized standard for pressure vessel construction in the United States and Canada [1]. The ASME Code provides a safety factor of 3.5, which means that at its maximum working pressure, the material is stressed to only 28.6% of its ultimate tensile strength. Carbon dioxide containers are typically fabricated using low-alloy carbon steels.

Low-alloy carbon steels at design operating conditions are both strong (have high tensile strength) and ductile. These materials remain strong as they become cold but become less ductile. A decrease in operating temperature can result in the container reaching its nil ductility transition temperature (NDTT). This means that a material that is normally considered ductile becomes brittle at temperatures below the NDTT. This condition is fully reversible when the metal temperature rises above the NDTT. As the temperature decreases, the container material also shrinks and can produce localized stresses. Ductile materials can accommodate localized stresses by slight deformation. The material will stretch in that area and not fail. Brittle materials are not able to stretch locally at low temperatures and can catastrophically fail. If a crack or material defect reaches a critical size in a pressurized brittle container, there is a greater likelihood of a total container failure similar to breaking a glass jar. Ductile materials can fail, but generally not catastrophically because the material tends to stretch, possibly crack and leak, but does not come apart.

Carbon dioxide is stored in insulated containers as a liquefied compressed gas. Normal container operating pressures range from 200 psig to 300 psig (1380 kPa to 2070 kPa), which corresponds to an equilibrium temperature of –20 °F (–28.9 °C) and 3 °F (–16.1 °C) respectively.

In North America, the majority of the containers in refrigerated carbon dioxide service are fabricated using low-alloy carbon steels such as SA-212, SA-515, SA-516, and SA-612. Containers manufactured before 1990 typically had an MDMT of –20 °F (–28.9 °C). When the container wall is at an operating temperature colder than the MDMT, it is out of its intended operating condition.

8 Physiology and toxicology of carbon dioxide

8.1 General

The physiology and toxicology of carbon dioxide are unique because carbon dioxide is a product of normal metabolism. It is a requirement of the body's normal internal chemical environment and an active messenger substance in the linking of respiration, circulation, and vascular response to the demands of metabolism both at rest and in exercise.

The respiratory control system maintains carbon dioxide pressure at a relatively high level of about 50 mm Hg pressure in the arterial blood and tissue fluids. This maintains the acidity of the tissue and cellular fluids at the proper level for the essential metabolic reactions and membrane functions. Changes in the normal carbon dioxide tissue pressure can be damaging. If tissue pressure becomes excessively low, which can occur from hyperventilation, failure of critical neuromuscular function or loss of consciousness can occur.

Inhaled carbon dioxide produces the same physiological effects as metabolically produced carbon dioxide. As the carbon dioxide tissue pressure rises from inhaling carbon dioxide, the body responds by using respiratory and adaptive processes to adjust to the change. These adaptive processes are limited and cannot cope with severe exposures that cause pH change to the body fluids.

Toxic effects of carbon dioxide, namely severe and disruptive acidosis, occur when high concentrations of carbon dioxide are inhaled.

The blood and cellular fluids are actually solutions of sodium bicarbonate containing numerous other substances. Severe exposure to carbon dioxide forms carbonic acid in the blood for which the sodium bicarbonate is not very effective as a buffer. The decrease in pH has a rapid toxic effect because the neural control systems are excessively driven. It is important to note that these effects are independent of the amount of oxygen in the atmosphere being breathed.

The effects produced by low and moderate concentrations of carbon dioxide are physiological and reversible, but the effects of high concentrations are toxic and damaging [3].

8.2 Physiological effects of carbon dioxide

The response to carbon dioxide inhalation depends on the degree and duration of exposure, and it varies greatly even in healthy normal individuals. The medical term for the physiological effects of excess carbon dioxide in the blood is hypercapnia. Carbon dioxide can be toxic even when normal oxygen levels are present. For example, low concentrations of inspired carbon dioxide can be tolerated for a considerable period without noticeable effect, or may merely cause an unnatural feeling of shortness of breath. Sustained exposure to 5% carbon dioxide produces stressful rapid breathing. When the level of inspired carbon dioxide exceeds 7%, the rapid breathing becomes labored (dyspnea) 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. These effects occur quickly because 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 with no possibility of self-rescue regardless of the oxygen concentration.

8.3 Physical effects of overexposure to carbon dioxide

Skin, mouth, or eye contact with solid carbon dioxide (dry ice) can cause severe frostbite, skin lesions, corneal burn, or more serious injury from deep freezing of the tissues due to the –109.3 °F (–78.5 °C) temperature. Liquid discharging from a container produces high-velocity carbon dioxide snow particles that are abrasive in addition to being cold and causes similar injuries.

8.4 Regulatory standards

Carbon dioxide naturally exists in the atmosphere at approximately 350 ppm by volume. The Occupational Safety and Health Administration (OSHA), as found in Title 29 of the U.S. *Code of Federal Regulations* (29 CFR) Part 1910.1000, lists an 8-hour Time-Weighted Average–Permissible Exposure Limit (TWA-PEL) of 5000 ppm (9000 mg/m^3) [4]. TWA-PEL is the exposure limit that shall not be exceeded by the 8-hour time-weighted average in any 8-hour workshift of a 40-hour workweek.

The American Conference of Governmental Industrial Hygienists (ACGIH) recommends a Threshold Limit Value–Time-Weighted Average (TLV®–TWA) of 5000 ppm [0.5%] (9000 mg/m^3). The TLV–TWA is the time-weighted average concentration for a normal 8-hour workday and a 40-hour workweek to which nearly all workers can be repeatedly exposed, day after day, without adverse effect [5].

Also, the ACGIH recommends a Threshold Limit Value–Short-Term Exposure Limit (TLV®–STEL) of 30 000 ppm [3%] (54 000 mg/m^3) [5]. The TLV–STEL is the 15-minute TWA exposure that should not be exceeded at any time during a workday even if the 8-hour TWA is within the TLV–TWA. Exposures above the TLV–TWA up to the STEL should not be longer than 15 minutes and should not occur more than 4 times per day. There should be at least 60 minutes between successive exposures in this range [5]. In Canada, similar limits are mandated by provincial legislation.

8.5 Safety precautions

Appropriate warning signs should be placed at entrances to confined areas where high concentrations of carbon dioxide gas can accumulate. A typical warning is shown below:

> ***CAUTION****—CARBON DIOXIDE GAS*
>
> *Ventilate the area before entering. A high carbon dioxide gas concentration can occur in this area and can cause asphyxiation.*

Carbon dioxide monitoring should be completed before entering any confined space or low area in which carbon dioxide gas may have accumulated. The carbon dioxide shall be removed by ventilation to a concentration below 3% (see 8.4) or a supplied-air respirator shall be worn before entering the confined area or low area (see CGA SB-15, *Managing Hazards in Confined Work Spaces During Maintenance, Construction, and Similar Activities*) [6] *and AIGA 008/04 Hazards of inert gases*

8.6 Rescue and first aid

Do not attempt to remove anyone exposed to high concentrations of carbon dioxide without using proper rescue equipment or you can also become a casualty. Rescuers account for over 60% of confined space fatalities. If the exposed person is unconscious, obtain assistance and use established emergency procedures.

If a person has inhaled large amounts of carbon dioxide and is exhibiting adverse effects, move the exposed individual to fresh air at once. If breathing has stopped, perform artificial respiration. Oxygen may be given but only by qualified personnel. Keep the affected person warm and at rest. Get medical attention as soon as possible. Fresh air and assisted breathing is appropriate for all cases of overexposure to gaseous carbon dioxide. With prompt response to a carbon dioxide emergency, recovery is usually complete and uneventful.

If dry ice or compressed carbon dioxide gas comes in contact with the skin or mouth, stop the exposure immediately. If frostbite has occurred, obtain medical attention. Do not rub the area. Immerse in warm water, 100 °F to 105 °F (37.8 °C to 40.6 °C).

9 Special hazards

9.1 General

Personnel handling liquid carbon dioxide should be thoroughly familiar with its associated hazards. There are several conditions in which extreme danger to personnel and equipment can exist. The following describes these conditions and offers procedures and guidelines to prevent dangerous conditions from developing.

9.2 Dry ice blocking or plugging

Dry ice plugs can be formed inside hoses and piping when liquid carbon dioxide is decreased below its triple point pressure of 60.4 psig (416 kPa). The dry ice can be compacted into a plug that can trap gas. The pressure behind or within a plug can increase as the dry ice sublimes until the plug is forcibly ejected or the hose or pipe ruptures. A dry ice plug can be ejected from an open end of any hose or pipe with enough force to cause serious injury to personnel, both from the impact of the dry ice plug and the sudden movement of the hose or pipe as the plug ejects.

Liquid carbon dioxide shall be purged from the hose or pipe before reducing the pressure below 60.4 psig (416 kPa). This is done by supplying carbon dioxide vapor to one end of the hose or piping system to maintain the pressure above the triple point while removing the remaining liquid from the other end.

9.3 Low temperature effects on materials

The low temperature effect of dry ice (–109.3 °F [–78.5 °C]) on the materials in the system is another hazard. At dry ice temperatures many materials used in hose and piping systems can become brittle and fail if highly stressed. Materials used in the construction of carbon dioxide transfer systems including hoses should be compatible with liquid carbon dioxide and the temperature and pressure conditions encountered.

9.4 Trapped liquid

Liquid carbon dioxide that is forced to occupy a fixed volume (i.e., between two closed valves) will increase in pressure as it warms and expands. A fixed volume of liquid carbon dioxide at 290 psig and 0 °F (2000 kPa and –17.8 °C) when warmed 10 °F (–12.2 °C) causes the pressure to increase to 2000 psig (13 790 kPa). As the temperature continues to increase, the pressure of the trapped liquid could exceed that which the piping and hoses can withstand. This can cause rupture of the hose or piping with possible injury and property damage.

All carbon dioxide piping shall be equipped with pressure relief devices located in all parts of the system in which liquid can be trapped (between valves, check valves, pumps, etc.). The pressure relief devices should be installed on a riser pipe extended from the cold liquid piping to create a vapor trap and prevent water ice from accumulating inside the pressure relief device and allow any condensation to drain (see Figure 2).

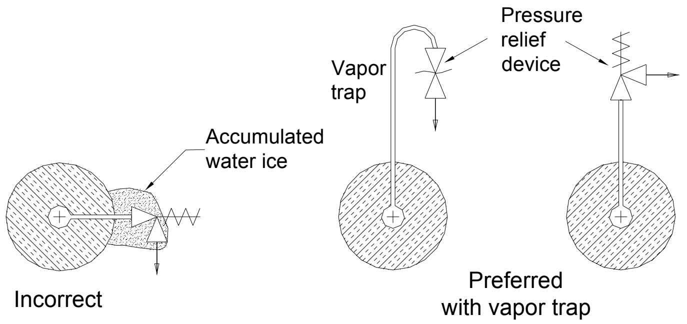


Figure 2—Examples of incorrect and preferred pressure relief device installations on liquid carbon dioxide piping

9.5 Personnel overexposure

When carbon dioxide is used in an enclosed area, it is necessary to ventilate the area adequately to maintain a safe working environment for personnel. Carbon dioxide in its 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 in confined areas or low elevations. Ventilation systems should be designed to exhaust from the lowest level and allow make-up air to enter at a higher point. Do not depend on measuring the oxygen content of the air alone because elevated levels of carbon dioxide can be toxic even with adequate oxygen for life support. For additional information, see Section 8.

10 Hazards of carbon dioxide container repressurization

10.1 Hazards

Depressurization of a container and the resulting autorefrigeration that occur will not likely result in the brittle fracture of an otherwise sound container. The highest stresses in the container are caused by the internal pressure exerted by the product. As the pressure and temperature decrease, the pressure-induced stresses also decrease.

Table 2 shows the relationship of the container wall stress and the internal pressure for both an ASME and EN carbon dioxide container. The ASME container is constructed from SA 516-70N having a tensile strength of 70 000 psi (483 MPa) with an MAWP of 350 psig (23.8 bar). The ASME Code requires a safety factor of 3.5; therefore the maximum allowable stress at MAWP is 70 000/3.5 = 20 000 psi. The EN example is constructed from a material having a guaranteed yield strength of 355 MPa (51 500 psi). EN 13458, *Cryogenic vessels—Part 2: Static vacuum insulated vessels: Design, fabrication, inspection and testing*, uses a safety factor of 2.5; therefore the maximum allowable stress at the MAWP of 22 bar (319 psig) is 225.6 MPa [7].

A pressure vessel risk assessment must be performed by a qualified carbon dioxide technician prior to choosing a container repressurization technique. This assessment shall include the following: the design code of the container, the ductility of the materials of construction, and wall stresses. Those users with vessels other than

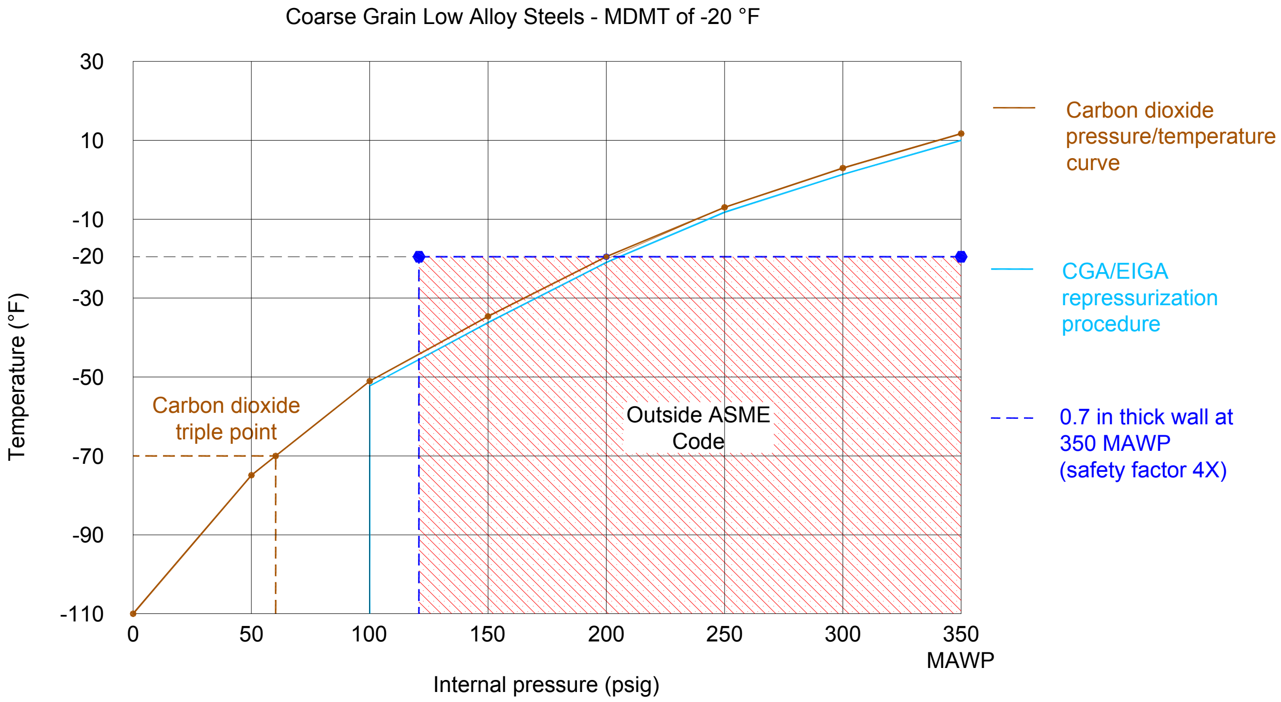
ASME-designed vessels shall perform a comparable assessment to ensure safe repressurization. See Appendix A for an example of an assessment for an EN-designed vessel.

Table 2—Carbon dioxide container pressure/wall stress relationships

Internal pressure			Equilibrium carbon dioxide temperature		Wall stress in container due to internal pressure		
					ASME 1)		EN 2)
psig	**kPa**	**Bar**	**°F**	**°C**	**psi**	**MPa**	**MPa**
350	2413	24.1	13	–11	20 000	138	——
319	2199	22	5	–15	18 250	125.8	225.6
300	2069	20.7	3	–16	17 143	118	212.2
250	1724	17.2	–8	–22	14 286	98.4	176.8
200	1379	13.8	–20	–29	11 429	78.8	141.4
150	1034	10.3	–35	–37	8571	59.1	106.1
100	690	6.9	–53	–47	5714	39.4	71.8
60	414	4.1	–69	–56	3429	23.6	56.1
0	0	0	–110	–78.9	0	0	0

1) At lower equilibrium temperatures/pressures and using the rules of the ASME Code and Figure UCS 66.1, it can be shown that the allowable reduction in MDMT is colder than the equilibrium temperature at reduced pressures [1]. See Figures 3 and 4 as examples for typical liquid carbon dioxide containers, which show the allowable temperature as a function of reduced pressure.

2) See Figure A-1 for additional information for EN-designed vessels.



NOTE—Coarse grain steels used for carbon dioxide containers included SA-212, SA-515, SA-516 (as rolled), and SA-612 (as rolled).

Figure 3—Allowable pressure-temperatures in an ASME liquid carbon dioxide container (pre-1976 safety factor 4X)

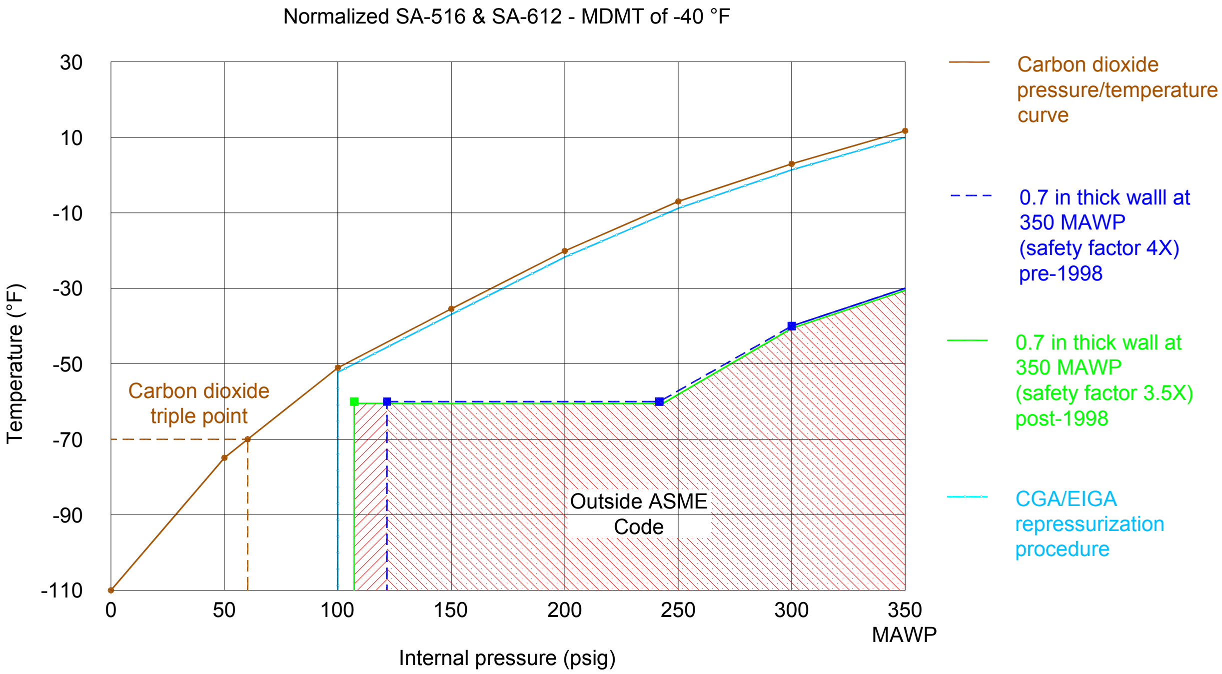


Figure 4—Allowable pressure-temperature in an ASME liquid carbon dioxide container (pre-1998 safety factor 4X, post-1998 safety factor 3.5X)

10.2 Warnings

Dangerous conditions can be caused by artificially increasing the pressure in a container that is depressurized and autorefrigerated below the container material's NDTT. A carbon dioxide container at a pressure below 60.4 psig (416 kPa) should be assumed to be at a temperature below –69.9 °F (–56.6 °C) and in a brittle condition and should not be moved or impacted.

Most carbon dioxide containers fabricated before 1976 in North America used coarse grain steels that have poor low temperature characteristics (see Figure 3). These containers remain in service and require special care when performing repressurization. Consideration should be given to installing backpressure control valves to prevent excessive vapor withdrawal, which is a common cause of depressurization. CGA recommends that the life of these vessels not be extended by overhauling (see CGA PS-5, *CGA Position Statement on the Suitability of Carbon Steel Containers for Stationary Carbon Dioxide Storage*) [8].

These containers were manufactured using SA-212 or SA-515 low-alloy steels with an MAWP of 350 psig to 363 psig (2410 kPa to 2500 kPa) in accordance with the ASME Code, which allowed MDMTs of –20 °F (–29 °C) without any impact testing. The ASME Code was revised in 1987 to reflect the fact that similar low-alloy steels did not have adequate ductility at temperatures colder than 10 °F (–12 °C). They were, and still are, within the ASME Code to operate at temperatures as cold as –20 °F (–29 °C), even though the container wall could be in a brittle condition.

Figure 3 illustrates where the pressure/temperature equilibrium curve for carbon dioxide passes through the zone outside the ASME Code at equilibrium temperatures between –20 °F and –44 °F (–29 °C and –42 °C) and corresponding equilibrium pressures of 200 psig and 120 psig (1380 kPa to 830 kPa).

Nevertheless, the repressurization procedure outlined in Methods 4 and 5 are acceptable for the following reasons:

- The pressure vessel safety factor of these containers is 4:1 versus the 3.5:1 safety factor adopted in 1987, which provides an additional level of safety;

- The stress level in the container wall from 120 psig to 200 psig (1380 kPa to 830 kPa) ranges from 33% to 55% of the design stress of the vessel. This means that even if operating in a brittle condition, the stress level is less than 8.3% to 13.7% of the ultimate strength of the material;
- The containers were typically fabricated with fractional inch thickness plate compared to the present day rolled to thickness plate. This effectively increased the container wall thickness thereby increasing the factor of safety beyond the minimum 4:1 required by ASME;
- The containers are protected from impact and external damage by insulation and an outer jacket, reducing the potential risk of a brittle failure caused by external stresses; and
- There have been no known failures or incidents on containers that have used these repressurization methods.

In addition, the following conditions shall be met:

- The repressurization procedure is performed by a qualified carbon dioxide technician;
- The procedure is continuously attended and monitored for unusual circumstances; and
- After completing the procedure, do not fill the container over 80% of rated capacity the first time (see 15.3.2 b).

Improper repressurization of a container that is in a brittle condition can result in catastrophic failure.

Escaping carbon dioxide can create an asphyxiation hazard in poorly ventilated spaces. Take adequate precautions before entering such an area (see Section 9).

11 Preliminary procedures for returning depressurized containers to service

Before returning depressurized containers to service, follow these preliminary procedures:

- discontinue all carbon dioxide withdrawal;
- close all service withdrawal valves and do not return the container to service until it is at or above the MDMT;
- shut off all pressure building vaporizer(s) and do not introduce pressure from another source;
- do not move or impact the container; and
- determine that the container has no residual liquid or dry ice.

11.1 Personnel requirements

A qualified carbon dioxide technician should determine the reason for loss of pressure and correct the problem before proceeding with repressurization procedures.

Repressurization should only be attempted by a qualified carbon dioxide technician or persons knowledgeable in the container design and physical properties of carbon dioxide. Safe, tested procedures should be developed for each case before proceeding with repressurization.

11.2 Provisions for alternate source

Returning a container to service can be a lengthy process, so arrangements may have to be made for an alternate source of carbon dioxide. Depending on the amount of dry ice in the container and the size of the container, a considerable amount of carbon dioxide can be required for the repressurization procedure. An evaluation should be made and an adequate source of carbon dioxide provided for this procedure.

11.3 Depressurized container evaluation

The container and its related piping, markings, Manufacturer's Data Report (U-1A), recent fill records, recent product use records, and events leading up to depressurization should be investigated before proceeding with repressurization. The ASME data plate can be found on the container in one of a number of locations such as on the legs, head, or manway. For an example of a depressurized container evaluation form see Figure 5.

Manufacturer__________ Year Built__________ Man. Serial No.__________

Natl Bd No.__________ Type Material__________ MAWP__________

Minimum Design Metal Temp__________ °F At__________ psi Impact Test__________

ASME Code__________ Capacity__________ Pressure In Container__________

Liquid Level__________ External Appearance__________

____

Piping External Appearance (e.g., frosted/water ice buildup or ambient temperature)__________

____

Signs of Product Discharge or Leakage__________

Last Known Contents Level__________ Date__________ Time__________

Last Known Pressure__________ Date__________ Time__________

Known Use Since Last Known Contents Level__________

Estimated Product Withdrawal Since Last Known Contents Level__________

Figure 5—Depressurized container evaluation form

11.4 Facts to consider in evaluating repressurization methods

Approximately 50% of the carbon dioxide in the container is lost during a complete depressurization.

To reliquefy and warm 1 lb (0.45 kg) of dry ice to approximately 150 psig (1030 kPa) saturated liquid, 9 lb to 10 lb of 250 psig (4.1 kg to 4.5 kg of 1720 kPa) saturated liquid is required.

Approximately 1 lb of 0 °F (0.45 kg of –17.8 °C) carbon dioxide vapor is required to return 1 lb (0.45 kg) of dry ice to about 150 psig (1030 kPa) saturated liquid. Some of the dry ice in the container melts and changes to liquid. The liquid level increases until the residual dry ice becomes completely submerged in the liquid. At this point, the container pressure increases, and continued addition of vapor can result in unsafe container pressures above the triple point as the heat transfer is reduced because the vapor is no longer in direct contact with the dry ice. Additional energy is required to melt the remaining solid and warm the liquid and the container wall.

The liquid level gauge (using differential pressure or floats) cannot be relied upon when a container has been depressurized below its design temperature and contains dense liquid, snow, or dry ice.

Several carbon dioxide cargo tanks can be required to supply sufficient carbon dioxide vapor to complete the repressurization procedure (see Table 3).

A heat exchanger, a pump, and a source of energy can be required to complete the procedure outlined in 13.5.

During repressurization, dry ice becomes submerged in liquid carbon dioxide at pressures greater than 60.4 psig (416 kPa); *therefore pressure can no longer be used as an indicator of container temperature.*

Pressure greater than that calculated using the ASME Code and Figure UCS 66.1 should not be applied to a vessel if the vessel's material is likely to be colder than the MDMT [1].

Table 3—Typical quantities of carbon dioxide and times needed for container repressurization
(Container fully depressurized to atmosphere)

Quantity of liquid CO_2 in container before depressurization	**CO_2 vapor required to pressurize to 100 psig (690 kPa)** (Section 13.4)		**Number of full 20-ton CO_2 cargo tanks required**	**Time to reliquefy residual dry ice and warm the liquid to –20 °F (–28.8 °C) (200 psig) (1380 kPa) using a 6 kW heater** (Section 13.4)	**Quantity of liquid CO_2 in container after repressurization**	**Time required to warm the liquid from –50 °F to –20 °F (–45.6 °C to –29 °C) (100 psig to 200 psig) (690 kPa to 1380 kPa) using a 6 kW heater** (Section 13.5) (No dry ice present)
(ton)	**(lb)**	**(kg)**		**(hr)**	**(ton)**	**(hr)**
6	1110	(503)	0.5	10	3.3	4.2
14	2590	(1175)	1.2	23.3	7.6	10.3
30	5550	(2517)	2.5	50	16.3	22
50	9250	(4196)	4.2	83.3	27.1	36.5

Flow rates as high as 120 lb/min (54 kg/min) were observed in tests using cargo tanks as the vapor source. To complete this step, approximately 185 lb of vapor is required per ton of liquid carbon dioxide (92.3 kg/tonne) that was in the container before depressurization. If *full* 20-ton cargo tanks are the vapor supply source, then 0.084 cargo tanks per ton of liquid depressurized is required.

Example: 50 tons of liquid depressurized to 0 psig would require:

- 185 lb/ton (83.9 kg/0.91 tonne) x 50 ton (45.4 tonnes) = 9250 lb of carbon dioxide vapor (4096 kg) (column 2); or
- 0.084 x 50 = 4.2 cargo tanks to pressurize to 100 psig (690 kPa) (column 3).

Example: A container that is totally depressurized should require about 10 kWh/ton liquid to melt all the dry ice and warm the liquid to 200 psig (1380 kPa), i.e., a container with 30 tons of liquid fully depressurized can be returned to 200 psig (1380 kPa) using a 6 kW heater in about 50 hrs:

- 10 kWh/ton x 30 ton / 6 kW = 50 hr (column 4).

Example: The energy required to warm liquid carbon dioxide is approximately 0.28 kWh/ton °F. A container with 10 tons of liquid at 131 psig (900 kPa) (–40 °F/ –40 °C) requires 112 kWh to warm up to 291 psig (2010 kPa) (0 °F/ –17.8 °C). (Temperature difference is 40 °F):

- 0.28 kWh/ton °F x (0 - [–40] °F) x 10 ton = 112 kWh.

12 Guidelines for evaluation of the condition of a depressurized container

A container that is below the pressure corresponding to its MDMT, typically 200 psig (1380 kPa), needs to be evaluated before proceeding. It is possible that the container is empty (no liquid) or it may hold cold liquid, a mixture of cold liquid and dry ice, or just dry ice. One of the most common causes of container pressures declining below 200 psig (1380 kPa) is an empty container. All of the liquid is consumed and only vapor pressure remains in the container. An empty container is not an upset condition but shall be treated as such until a proper evaluation is completed. The following guidelines should be used by a technician before proceeding with repressurization and a return to normal service.

12.1 Container pressure greater than 200 psig (1380 kPa)

The container is probably acceptable for normal service. However, if the container was depressurized earlier and the pressure continues to decrease over time with no product removal, cold liquid or dry ice are likely present. Do not maintain in normal service until all facts are known (see Section 11).

12.2 Container pressure less than 200 psig (1380 kPa) but greater than 60.4 psig (416 kPa)

The following procedure should be performed to determine whether the container is empty (no liquid present):

a) Check the consumption records to determine whether the container could possibly be empty;

b) Check liquid valve and piping for signs of frost, which can indicate the presence of liquid carbon dioxide; and

c) Confirm that the container is empty by opening either the liquid fill valve or a liquid use valve. If ONLY vapor exits, the container is empty and can be filled in accordance with CGA G-6.4, *Safe Transfer of Liquefied Carbon Dioxide in Insulated Cargo Tanks, Tank Cars, and Portable Containers* [9]. If liquid exits from either the liquid valve or, if the piping is obstructed by dry ice blockages, it must be assumed that low-temperature liquid and/or dry ice are present. See 13.1, 13.4, and 13.5 for further guidance.

12.2.1 Container minimum design metal temperature of –20 °F (–29 °C)

Containers holding liquid at pressures below 200 psig (1380 kPa) are in an upset condition and are colder than the minimum design condition. Repressurize using the procedures outlined in 13.4 and 13.5.

12.2.2 Container minimum design metal temperature of –40 °F (–40.0 °C)

Containers with pressures above 140 psig (970 kPa) can be returned to service. Containers with pressures below 140 psig (970 kPa) are in an upset condition and require the repressurization procedures as outlined in 13.4 and 13.5.

12.2.3 Container minimum design metal temperature of –50 °F (–46 °C)

Containers with pressures above 105 psig (724 kPa) can be returned to service. Containers with pressures below 105 psig (720 kPa) are in an upset condition and require the repressurization procedures in 13.4 and 13.5.

12.2.4 Containers with other minimum design metal temperature values

Containers with other MDMT values can be returned to service at pressures above the corresponding equilibrium carbon dioxide pressure (see Figure 1). Containers with temperatures below the MDMT are in an upset condition and require the repressurization procedures in 13.4 and 13.5.

12.3 Container pressure less than 60.4 psig (416 kPa)

The container could be empty of all liquid with vapor pressure only. The following procedure should be performed to determine whether the container is empty (no dry ice present):

a) Check the consumption records to determine whether the container could possibly be empty;

b) Check liquid valve and piping for signs of frost, which can indicate the presence of liquid carbon dioxide or dry ice;

c) Check the pressure and liquid level gauge for accuracy. Pulsations in the liquid level gauge can be an indication of the presence of dry ice;

d) Pressurize the container to 100 psig (690 kPa) with vapor (see 13.4). If the container pressure stays at 60 psig (414 kPa) for any length of time during this pressurization, dry ice is present inside the container; and

e) Open either the liquid fill valve or a liquid use valve and see if only vapor exits. If the liquid piping is obstructed by dry ice or discharges liquid, then the tank contains dry ice and must be repressurized using methods given in Section 13.

12.4 Special low-temperature containers

Containers made of materials that remain ductile at –109.3 °F (–78.5 °C) (for example TC/DOT-4L containers made of type 304 stainless steel) may be returned to service without some of the precautions necessary for containers made of materials that do experience a loss of ductility below –20 °F (–28.9 °C). The ASME data plate of such vessels should clearly identify them as having an MDMT colder than –109.3 °F (–78.5 °C).

Testing has demonstrated that solid carbon dioxide still exists although the pressure is above the point where solid carbon dioxide would exist if the contents were in an equilibrium condition. Even though some solid carbon dioxide exists in the container, it is likely that the pressure-building vaporizer can be activated and the container returned to service. *Do not fill to the normal liquid carbon dioxide level*. The first fill after a container has lost pressure should not exceed 80% of normal full. This allows room for any residual dry ice to melt and convert to liquid that will expand close to the normal 100% fill level. A container with residual dry ice will be overfull at designed conditions if filled to the normal fill settings. *The procedures suggested in this section only apply to containers with an MDMT colder than –109.3 °F (–78.5 °C)*.

13 Recommended repressurization methods

13.1 Recommendations

The following recommendations are provided based on the best information available at the time of publication. Each instance needs to be evaluated by a technician knowledgeable in the properties of carbon dioxide. The depressurization of a container is an upset condition. The assumption is made that only a pressure gauge, contents-level gauge, and liquid/vapor fill lines are available to the technician. It is also assumed that little or no instrumentation is available; limited electric power or alternate heat sources exist; cargo tanks are probably the only external sources of carbon dioxide vapor; and the container needs to be returned to normal service as rapidly as possible.

13.2 Unassisted natural repressurization (Method 1)

Remove the container from service, close all valves, and install a pressure control device to maintain the container's pressure at 100 psig (690 kPa). Ambient heat entering through the insulation will melt the dry ice and warm the resulting liquid to normal operating conditions.

This is a slow and gradual process. Pressure cannot be used to determine the liquid temperature during repressurization because dry ice and colder liquid tend to settle to the bottom of the container. This could maintain the temperature at the bottom of the container at the triple point irrespective of the pressure. This method should only be used if the pressure in the container is limited to 100 psig (690 kPa) (see Note 2 of Table 2).

The advantage of unassisted natural repressurization is that it is self-regulating.

The disadvantages of unassisted natural repressurization are:

- extremely slow; and
- may require up to 30 days depending upon the quantity of product, the ambient temperature, and the quality of the insulation.

13.3 Hot gas warming at no pressure (Method 2)

This procedure is the safest for containers fabricated with coarse grain steels because it does not go into the unsafe zone as illustrated in Figure 3.

Remove the container from service. If the container is above 60.4 psig (416 kPa), remove all the remaining liquid carbon dioxide through a liquid connection (see 9.2). Depressurize completely through a vapor connection.

Inject large quantities of warm, dry air or gas through an open manway or product-use connections and vent to the atmosphere.

Drain condensed moisture from the container and piping. Dry, clean, and purge after all the dry ice has sublimed. Pressurize the container with carbon dioxide vapor and fill as required for a first fill (see CGA G-6.4) [9].

The advantage of hot gas warming at no pressure is there are no container rupture hazards during the heating process.

The disadvantages of hot gas warming at no pressure are:

- discharges all remaining carbon dioxide;
- *can create large volumes of carbon dioxide gas creating a possible asphyxiation hazard;*

- requires approximately 238 000 Btu/ton (276 800 kJ/tonne) of liquid in the container before depressurization if complete conversion to dry ice has occurred;
- requires cleaning and purging of the container to remove moisture and contaminants; and
- *may require entry through the manway with confined space entry safety restrictions and procedures* [5].

13.4 Carbon dioxide gas pressurization up to 100 psig (690 kPa) (Method 3)

NOTE—This repressurizing method can be used on most ASME-designed tanks, but may not be applicable for EN or other design codes with lower factors of safety. The user must determine if this technique is acceptable (see the examples in 10.1 and Appendix A to determine the extent of the safe domain).

This procedure is step one of a two-step process outlined here and in 13.5. It is used to partially liquefy any dry ice inside a container when the pressure has decreased below 60.4 psig (416 kPa).

Pressurize the container to 100 psig (690 kPa) with carbon dioxide vapor from cargo tank(s) or other external vapor source (see Table 3). The vapor can be added as fast as the piping and hoses allow. If the container liquid piping is blocked by dry ice, the vapor equalization line should be used (see Figure 6). The vapor condenses as it melts some of the dry ice. The liquid level rises until all of the exposed dry ice is submerged. At this point, the container pressure increases rapidly because the incoming vapor cannot contact the dry ice directly. The liquid level gauge can show a reading, but is probably not accurate.

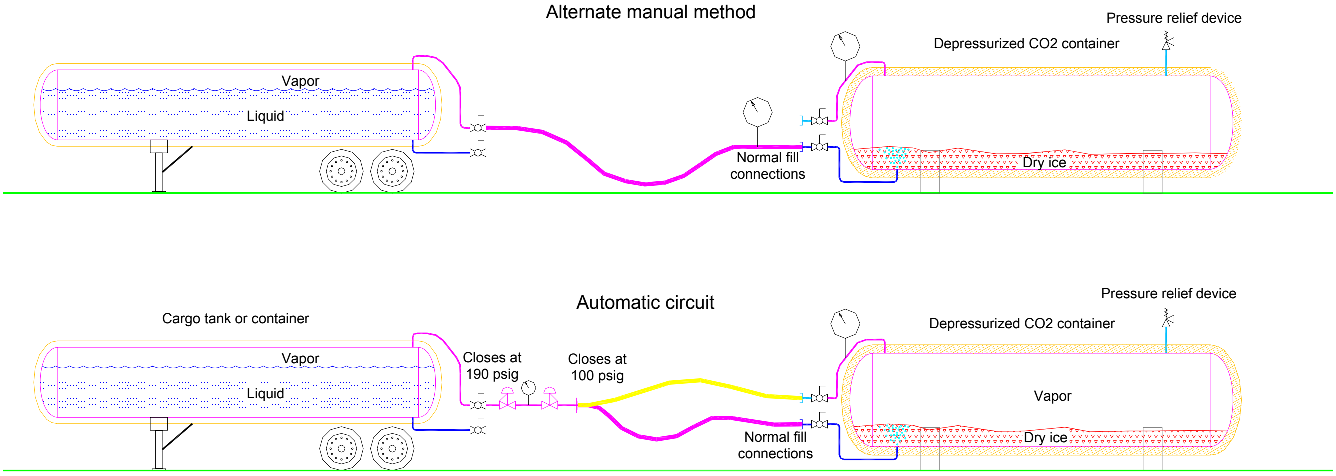


Figure 6—Carbon dioxide vapor pressurization up to 100 psig (690 kPa)
(Refer to 13.4 and 15.1.)

The vapor pressurization step described in the previous paragraph should not be used to increase the container pressure above 100 psig (690 kPa), and the vapor supply container shall be maintained above its MDMT. The first step of the repressurization is now complete and the second phase can begin (see 13.5).

The advantages of carbon dioxide gas pressurization up to 100 psig (690 kPa) are:

- Carbon steel pressure vessels subject to pressure levels less than 100 psig (690 kPa) are unlikely to fail in a catastrophic manner at dry ice temperatures. Table 2 indicates that a container with a 350 psig (2410 kPa) MAWP and a pressure of 100 psig (690 kPa) has a stress level in the steel wall of 5714 psi (39.4 MPa). Therefore, it is safe to pressurize such a container to 100 psig (690 kPa) with no risk of brittle fracture. At 100 psig (690 kPa), testing shows that there is enough liquid in the container to allow liquid to be pumped as recommended in 13.5; and
- no lost product.

The disadvantages of carbon dioxide gas pressurization up to 100 psig (690 kPa) are:

- requires large volumes of vapor to partially reliquefy the dry ice. To pressurize 185 lb/ton (92.3 kg/tonne) of vapor per ton of depressurized liquid, 100 psig (690 kPa) from atmospheric pressure is required. In most cases, electric vaporizers are not large enough to complete this step rapidly;
- only practical carbon dioxide vapor source readily available is from cargo tanks. Typical cargo tanks do not have a vaporizer or auxiliary heat source available, and therefore have a limited quantity of vapor available. Full cargo tanks are the best source but can deliver no more than 100 lb of vapor per ton of liquid (50 kg/tonne). The vapor removed from cargo tanks is supplied by the autorefrigeration of the liquid carbon dioxide. Vapor removal shall be limited to keep the pressure above the corresponding cargo tank MDMT; and
- insufficient warming of liquid. It does not provide the circulation of the liquid to ensure that all the dry ice is melted in a reasonable time, so recirculating liquid as described in 13.5 is necessary.

13.5 Recirculation of warmed liquid (Method 4)

This procedure is step two and shall be preceded by the one listed in Section 13.4 unless the container is at 100 psig (690 kPa) or above.

NOTE—Valves, nozzles, and piping can be blocked (or become blocked) with dry ice even after carbon dioxide in the container is partially liquefied (see 9.2).

WARNING: *Recirculation of liquid causes the temperature and pressure of containers fabricated with coarse grain steels to pass through the zone outside the ASME Code as illustrated in Figure 3 [1]. This procedure requires continuous supervision by a qualified carbon dioxide technician to monitor pump flow, heat input, and vessel protection from shock and/or impact for a slow, controlled pressure rise.*

Liquid carbon dioxide is pumped from either the liquid fill or a liquid use line through a vaporizer/vapor heater. The warmed liquid is returned to the container through the vapor fill connection (see Figure 7). Typical pump capacities range from 2 g/m to 10 g/m (7.6 L/m to 37.9 L/m) and typical heater capacities range from 3 kW to 18 kW. The preferred procedure is to pump liquid from one end of the container and to return the warmed liquid to the opposite end, if such a connection is available.

The container level gauge is typically not accurate until all the dry ice has melted.

The advantages to recirculation of warmed liquid are:

- minimizes the possibility that the vapor pressure in the container will exceed the equilibrium pressure of the circulated liquid. Any dry ice in the container will gradually melt. The liquid circulation causes a mixing action minimizing temperature gradients throughout the container;
- relatively fast – a container can be returned to normal service in one or more days;
- uses equipment readily available within the carbon dioxide industry. This procedure can be accomplished using only the two fill connections; and
- no lost product.

The disadvantages of recirculation of warm liquid are:

- requires bringing extra equipment to the site, which adds set up time;
- requires a compatible electric or energy supply with sufficient capacity to supply the pump and heater. Most carbon dioxide containers have an electric supply for the refrigeration unit that can be temporarily disconnected and used for the process; and
- requires time varying from hours to days depending on the circumstances.

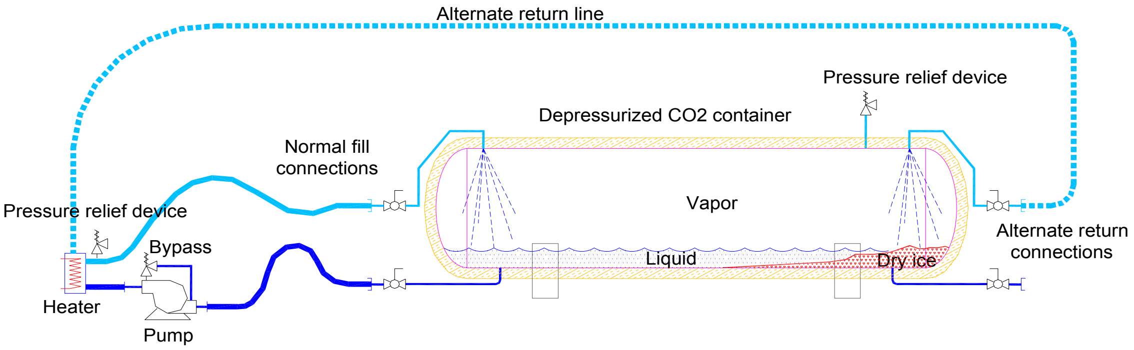


Figure 7—Recirculation of warmed liquid to 200 psig (1380 kPa)
(See 13.5 and 15.3.2)

14 Repressurization methods—not recommended

Some of the following procedures are known to have been used for repressurization in the past. Actual tests performed by CGA indicated that they are ineffective or unsafe and are therefore not recommended.

14.1 Transfer liquid carbon dioxide into the container to melt the dry ice and warm the liquid—not recommended

The reasons that this method is not recommended are:

- only works with partially filled containers (approximately 10% full before depressurization). More than a full 20-ton carbon dioxide trailer is required to restore a 50-ton container back to service if it contains 10% of liquid just before depressurization;
- no assurance that all the dry ice will melt after the liquid is added. The container can become overfilled after the dry ice melts; and
- may not be able to inject liquid through lines blocked by dry ice.

14.2 Pressure building vaporizer/internal heater method only—not recommended

The reasons that this method is not recommended are:

- Dry ice can still exist in areas away from the heater. The container pressure will not reliably indicate product and container temperature;
- can rapidly increase the vapor pressure in the container without melting the dry ice or warming the liquid in areas away from the heater;
- no liquid circulation to melt dry ice or warm liquid away from the vaporizer; and
- can cause the heating element to overheat or burn out inside an extremely cold and brittle container. Dry ice in the liquid supply piping (see 9.2) to an external vaporizer or the bridging of dry ice surrounding the internal heater could prevent the heater from being properly submerged in liquid causing overheating.

14.3 Transferring carbon dioxide vapor into the vapor connection of the depressurized container—not recommended

The reasons that this method is not recommended are:

- will warm up container contents only when incoming vapor can directly contact dry ice or snow. The pressure rises rapidly when dry ice is covered by liquid, and further melting of the dry ice or warming of the liquid is extremely slow;
- cannot restore container to service by this method alone; and
- does not promote any mixing of the liquid.

14.4 Remove liquid carbon dioxide from the container and transfer to cargo tanks—not recommended

The reasons that this method is not recommended are:

- requires contents to be in a liquid state before transfer;
- requires cargo tanks with a suitable MDMT; and
- requires a container with a suitable MDMT to receive the cold liquid from the cargo tank.

14.5 Manual removal of dry ice—not recommended

The reasons that this method is not recommended are:

- freezing and asphyxiation hazards to personnel; and
- requires confined space entry procedures.

15 Summary of suggested procedures

15.1 General

This is a summary of suggested procedures for qualified persons to repressurize carbon dioxide containers with MDMTs warmer than –109.3 °F (–78.5 °C). It does not address any particular container type or circumstance and each situation shall be evaluated by a qualified carbon dioxide technician. The objective is to warm the container material to the temperature at which it regains its ductility before the rising pressure causes critical stress levels around areas of stress concentration. Pressure surges and mechanical impacts or shocks shall be avoided when these containers are in a brittle condition. This publication recommends the use of one of three procedures. Single-step procedures are outlined in 13.2 and 13.3, and a two-step procedure is presented in 13.4 and 13.5, which are combined in 15.3.

15.2 Monitoring

Monitoring by a qualified technician is required during repressurization. Any sign of leakage, unusual noise, or other unexplained occurrence during these procedures is reason to discontinue repressurization and take other appropriate action.

15.3 Two-step repressurization procedure detailed description (Sections 13.4 and 13.5)

15.3.1 Step one (<100 psig [690 kPa])

a) Connect a hose from the vapor phase of a supply tank to the liquid phase of a depressurized container.

   A manifold similar to Figure 6 is suggested. The depressurized container pressure control regulator should be set at 100 psig (690 kPa), and the pressure relief regulator on the supply tank should be set no lower than 190 psig (621 kPa) or at the pressure coincident with the supply tank MDMT.

   Full-time monitoring of pressure gauges and manual control of pressure and flow is an acceptable alternative (Figure 6 alternative manual method);

b) Purge the hose and manifold; and

c) Slowly open the valves connecting the supply tank and the depressurized container. A single supply tank and vaporizer may be used as a vapor source instead of several cargo tanks.

   CAUTION: *Do not let the supply tank pressure fall below the pressure coincident with the MDMT of the supply tank. Without an external pressure building vaporizer, the supply tank pressure can fall to the point that the repressurization operation must be stopped until the supply tank pressure is restored. Large quantities of carbon dioxide may be required (see Table 3).*

   When the vapor pressure in the depressurized container approaches 100 psig (690 kPa), do not assume that the dry ice is completely melted. The container will have a significant amount of dry ice at –69.9 °F (–56.6 °C) remaining. The rising pressure seems to indicate the entire contents are above –69.9 °F (–56.6 °C), but experimentation has shown that the rate of condensation slows and the pressure begins to rise when the solid carbon dioxide becomes covered with liquid. As long as solid carbon dioxide remains in the container, the container is likely to be colder than its MDMT and should be treated accordingly.

15.3.2 Step two (>100 psig [690 kPa])

a) Discontinue the vapor transfer and connect the depressurized container liquid line to a pump and carbon dioxide heater/vaporizer circuit (see Figure 7). Ideally, the discharge from the pump-heater circuit should return to the opposite end of the container to promote mixing of the warm carbon dioxide with the container contents. Alternatively it could be routed to a vapor connection. The circulating operation should continue until the container pressure exceeds the pressure coincident with the MDMT or 200 psig (1380 kPa). The product heating and circulation can be discontinued at this time. When the pressure remains stable for 2 hours or is rising, the container contents should be at or near equilibrium. The container then may be returned to service; and

b) Do not fill the container over 80% of rated capacity the first time after completing this procedure. This allows sufficient volume for the expansion of the cold liquid if residual dry ice remains inside the container. The container pressure and level should be monitored until normal operation is observed.

16 References

Unless otherwise specified, the latest edition shall apply.

[1] *ASME Boiler & Pressure Vessel Code,* ASME International, Three Park Avenue, New York, NY 10016. www.asme.org

[2] CGA P-11, Metric Practice Guide for the Compressed Gas In*dustry*, Compressed Gas Association, Inc., 4221 Walney Rd., 5th Floor, Chantilly, VA 20151. www.cganet.com

[3] Quinn, E.L. and Charles L Jones, *Carbon Dioxide*, p. 97, American Chemical Society Monograph Series, Reinhold Publishing Corp., New York, NY 10036. www.umi.com

[4] *Code of Federal Regulations*, Title 29 (Labor) Part 1910, Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402. www.gpoaccess.gov

[5] *TLVs® and BEIs® Threshold Limit Values for Chemical Substances and Physical Agents & Biological Exposure Indices,* American Conference of Governmental Industrial Hygienists, 1330 Kemper Meadow Dr., Cincinnati, OH 45240. www.acgih.gov

[6] CGA SB-15, *Managing Hazards in Confined Work Spaces During Maintenance, Construction and Similar Activities*, Compressed Gas Association, Inc., 4221 Walney Rd., 5th Floor, Chantilly, VA 20151. www.cganet.com

[7] EN 13458 Parts 1-3, *Cryogenic vessels—Static vacuum insulated vessels*, American National Standards Institute, 25 West 43rd St., New York, NY 10036. www.ansi.org

[8] PS-5, *CGA Position Statement on the Suitability of Carbon Steel Containers for Stationary Carbon Dioxide Storage*, Compressed Gas Association, Inc., 4221 Walney Rd., 5th Floor, Chantilly, VA 20151. www.cganet.com

[9] CGA G-6.4, *Safe Transfer of Liquefied Carbon Dioxide in Insulated Cargo Tanks, Tank Cars, and Portable Containers*, Compressed Gas Association, Inc., 4221 Walney Rd., 5th Floor, Chantilly, VA 20151. www.cganet.com

[10] EN 1252-1, *Cryogenic vessels—Materials—Part 1: Toughness requirements for temperatures below –80 °C*, American National Standards Institute, 25 West 43rd St., New York, NY 10036. www.ansi.org

[11] ISO 21028-2, *Cryogenic vessels—Toughness requirements for materials at cryogenic temperature—Part 2: Temperatures between –80 °C and –20 °C*, Compressed Gas Association, Inc., 4221 Walney Rd., 5th Floor, Chantilly, VA 20151. www.cganet.com

[12] AD2000 Merkblatt W10 *Werkstoffe für tiefe Temperaturen Eisenwerkstoffe,* Carl Heymanns Verlag KG, Luxemburger Strasse 449, D-50939 Cologne

[13] EN 10028-3, *Flat products made of steels for pressure purposes—Part 3: Weldable fine grain steels, normalized*, American National Standards Institute, 25 West 43rd St., New York, NY 10036. www.ansi.org

17 Additional references

EN 14197 Parts 1-3, *Cryogenic vessels—Static non-vacuum insulated vessels*, American National Standards Institute, 25 West 43rd St., New York, NY 10036. www.ansi.org

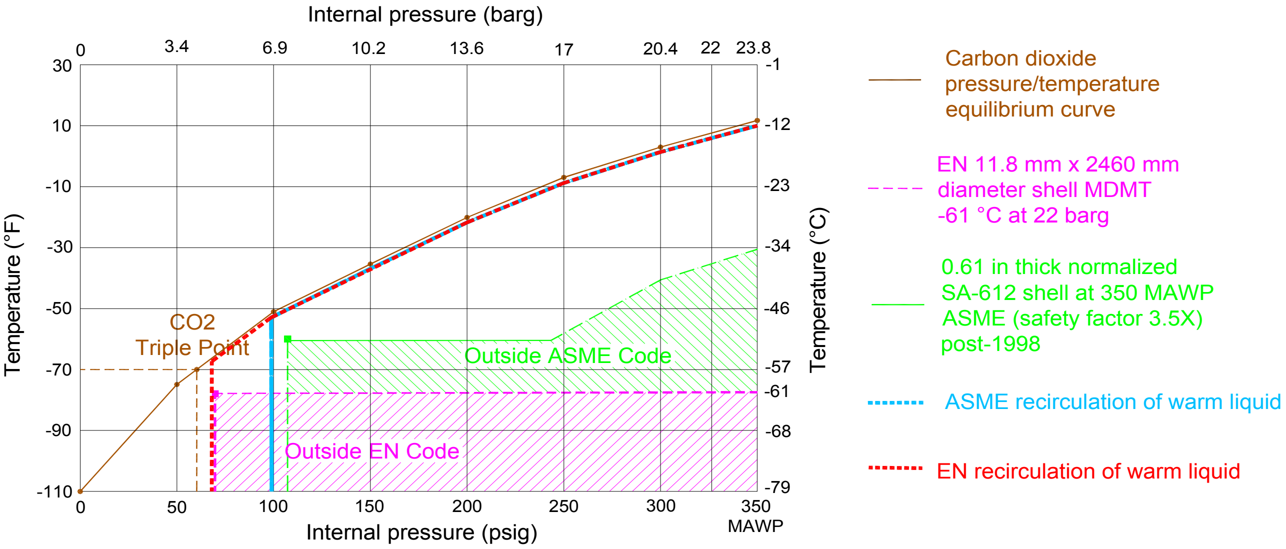
EIGA Doc 66/08, *Refrigerated CO2 storage at users' premises*, European Industrial Gases Association, Avenue des Arts 3-5, B 1210 Brussels, Belgium. www.eiga.eu

AIGA 008/11 *Hazards of inert gases and oxygen depletion*

Appendix A—EN pressure vessel material design information (Informative)

A1 EN standard pressure vessel

The EN example in Figure A-1 illustrates a 33 tonne carbon dioxide pressure, service pressure = 22 bar, outside diameter = 2460 mm, minimum wall thickness = 11.8 mm, manufactured with a steel having a minimum impact value of 27 J at –40 °C with an MDMT of –61 °C based upon Figure A-2.



NOTE—The vapor pressurization technique indicated in 13.4 to 7 barg (100 psig) falls outside the EN code allowable zone. Only vapor pressurization below 4.8 barg (70.5 psig) is acceptable.

Figure A-1—Comparison of EN and ASME allowable MDMT conditions for a carbon dioxide container being repressurized

Check the guaranteed impact properties of the steel at the lowest temperature in the material certificate or the material standard; in this example it is 27 J at –40 °C.

Check the wall thickness of the tank, the guaranteed yield stress (*Re*) of the steel used and whether the vessels has been heat treated after welding; for the example given in Figure A-1 with no post weld heat treatment, *Re* = 355 N/mm^2 and thickness equal 11.8 mm.

The vessel can be operated at temperatures lower than –61°C, but only at stress levels below 50 MPa per EN 1252-1, *Cryogenic vessels—Materials—Part 1: Toughness requirements for temperatures below –80 °C* [10]. The pressure that corresponds to a stress (S) of 50 MPa can be determined using the following formula:

$P = S \cdot 2\,e\,/D$

Where:

P = 4.8 MPa (4.8 barg) internal pressure

S = 50 MPa (stress level where lower operating temperature is allowed)

e = 11.8 mm wall thickness

D = 2460 mm diameter

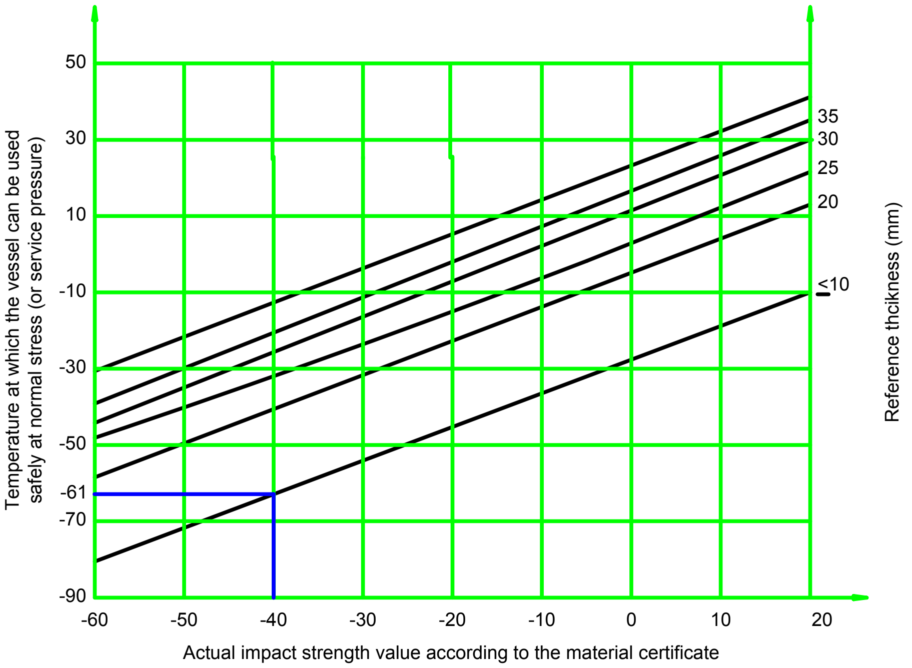
EN 1252 allows the operation of pressure vessels 40 °C colder than the MDMT as long as the wall stresses are less than 50 MPa. Therefore, the example vessel could operate as cold as –101 °C at pressures below

4.8 barg, which is well below the coldest dry ice temperature of –78 °C (i.e., –61 °C MDMT – 40 °C allowable temperature reduction = –101 °C minimum operating temperature at reduced pressure).

The boundaries of the shaded area on Figure A-1 labeled outside the EN code were determined using EN 1252-1. Any operating conditions colder than –61°C and greater than 4.8 barg would not be allowed by the EN code. This shaded area must be below the temperature/pressure curve for carbon dioxide (brown line) to allow safe operation of the tank during repressurization.

Method 3 found in 13.4 (pressurize to 6.9 barg [100psig]) can not be used on EN vessels where the pressure stress calculation at 50 MPa is less than 6.9 barg. Method 1 and 2 can be used (see 13.2 and 13.3).

A modified Method 3 can only be used for the EN example where the tank vapor pressurization step is maintained below 4.8 barg. This is very near the carbon dioxide triple point and therefore this method (liquid recirculation) is not recommended.



310 N/mm^2 < R_p ≤ 360 N/mm^2 : 27J

R_p = proof stress

NOTE—The minimum acceptable temperature according to the material certificate is –40° C, but because the wall thickness of the tank is approximately 10 mm, the tank can be used at normal stress (or service pressure) down to –61° C.

Figure A-2—Design reference and impact test temperatures as welded condition for and EN pressure vessel[3]

A2 AD2000 Merkblatt pressure vessel [12]

Check the type of the tank material and guaranteed impact properties of the steel at the lowest temperature in the material certificate or the material standard; for example fine grained steel P355ML1 its impact properties are 27 J at –40 °C. [12]

Check the MAWP and wall thickness of the tank and if the tank has been heat treated after welding; for example, no heat treatment and thickness equal 11.8 mm.

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Select the load case for the lowest expected operation temperature for the tank material on AD2000 Merkblatt W10, Table 1, Column 4, 5, or 6 which will be –78.5 °C if dry ice is in the tank: for example load case II has to be considered for the material P355NL1 because it allows a lowest operation temperature of –110 °C [12].

NOTE—Load case II may be selected for all low temperature fine grained steels of the grades P355NL1/2 or P355ML1/2 according to EN 10028, *Flat products made of steels for pressure purposes—Part 3: Weldable fine grain steels, normalized*, because their allowable operating temperature is below –90 °C [13].

Select the allowable pressure loads for the tank based on the wall thickness of the tank shell and their heat treatment according to AD2000 Merkblatt W10, Table 2 and/or Clause 3 [12]. As a general rule heat treatment is not required for wall thicknesses less than 20 mm if the test certificate shows sufficient impact properties for low temperature as required in the material standard.

The required test temperature is also indicated in Table 1, Column 9 of AD2000 Merkblatt W10 [12]. Example for the material P355NL1 is –40 °C.

For wall thicknesses equal or less than 10 mm the allowable pressure load is limited up to 75% of the calculation pressure (MAWP).

For wall thicknesses greater than 10 mm and equal or less than 20 mm the allowable pressure load is limited up to 50% of the calculation pressure (MAWP): for example, a tank with a thickness of 11.8 mm and a MAWP of 22 bar may be pressurized up to 11 bar.

NOTE—Load case I is allowed for temperatures below the triple point for some materials. Nevertheless the allowable pressure in the tank should be only increased during the repressurization procedure if the temperature of the tank wall is measured and well above the allowable value.