Safety Considerations for Carbon Dioxide Systems

Andy Pearson & Angus Gillies

Star Refrigeration Ltd., U.K.
Safety issues with CO$_2$

- Physiological effects
- Pressure and temperature
- Safe maintenance
- Materials selection
- Component installation
- Chemical reactions – ammonia
- Chemical reactions - water
Physiological Effects
Experts probe liquid nitrogen spill

Death gas rescuer praised by firefighters

Annette McCarr

One of the country's leading medical researchers has said that the use of liquid nitrogen in the transport of organs for transplantation has led to a significant decrease in tissue damage.

The researcher, who has recently published a study on the benefits of using liquid nitrogen in organ preservation, said that the technique is safe and effective. "The use of liquid nitrogen in organ preservation has been shown to significantly reduce tissue damage," she said.

The researcher added that the use of liquid nitrogen in organ preservation is not only effective but also cost-effective. "The cost of using liquid nitrogen in organ preservation is significantly lower than other preservation techniques," she said.

Experts have been quick to praise the rescuer's actions, describing them as "heroic" and "amazing." "The rescuer's actions were truly incredible," said one expert. "They saved many lives and deserve our highest praise."
Effect of reduced oxygen

- 21% - normal atmosphere
- 16% - breathing becomes laboured
- 14% - moving becomes an effort
- 12% - muddled thinking
- 10% - nausea, vomiting, collapse
- 8% - loss of consciousness
- 6% - respiratory failure
Air displacement

- Asphyxiants
- Nitrogen
- Argon
- CO2
- Oxygen
3 classes of refrigerant

• Those which smell strongly and have an acute toxic effect
  Ammonia, sulphur dioxide, methyl chloride

• Those which have no particular smell or taste, and no short-term toxic effect
  Fluorocarbons, hydrocarbons, nitrogen

• Those which are directly involved in the respiration process
  Carbon dioxide
Air displacement

- Asphyxiants
- Nitrogen
- Argon
- CO2
- Oxygen
Asphyxiation by nitrogen
Asphyxiation by CO$_2$
$\text{CO}_2$ and respiration

- $\text{O}_2$ releases energy by “burning” carbohydrates in cells
- $\text{CO}_2$ transferred from cells to lungs in carboxyhaemaglobin
- $\text{CO}_2$ used for pH control to ensure brain function
- Breathing rate is controlled by blood levels of $\text{CO}_2$
**CO₂ and respiration**

- Excess CO₂ causes increased breathing rate ("hyperventilation")
- Further CO₂ causes numbness and dizziness ("narcosis")
- At higher CO₂ levels the breathing reflex is disrupted ("hypoventilation")
- This is followed by "coma"
- …and "death"
CO$_2$ and respiration

- Return to fresh air (300ppm CO$_2$)
- Effects are dependent on rate of increase...
- ...and on physical condition
- Typically 3% (30,000ppm) causes hyperventilation,
- 5% causes narcosis
- 10% causes coma
Asphyxiation by CO$_2$
Conclusions

• CO$_2$ is different to all other gases....
• ...but it is not more or less safe!
• CO$_2$ effects are felt at lower levels than R134a or N$_2$...
• ...but the warning signs are as clear as NH$_3$ to those trained to spot them
Gas detectors for CO₂

Infra red technology has proved to be:

• accurate
• robust
• reliable
• …and doesn’t give false alarms!
Gas detectors for CO$_2$
COSH H Assessment CO₂

Health hazards:
• Increased respiration and headache
• Asphyxiation
• Freeze burns and frost bite
• Explosive release of pressure
COSH Assessment CO₂

Control measures:

• Ensure good ventilation
• Do not trap refrigerant
• Ensure all portable tools are suitable for high pressures
• Design staff training
• Commissioning and maintenance staff training
COSHH Assessment CO$_2$

Risk No and phrase:

- **RAs**  Asphyxiating in high concentrations.
- **RFb**  May cause frostbite
COSHH Assessment CO\textsubscript{2}

Safety No and phrase:

- **S9**: Keep container in well ventilated place.
- **S23**: Do not breathe the gas.
- **S36A**: Use suitable protective equipment
Pressure and Temperature
Physical properties

Pressure/Temperature curves for various refrigerants

- R-744
- R-410A
- R-717
- R-717
- R-134a

Critical Point
Triple Point
P-h chart for CO₂.
Pressure-enthalpy \((p, h)\)-diagram for \(\mathrm{CO}_2\)

can be used for an overview of the state of \(\mathrm{CO}_2\) at different pressures and enthalpies according to Flank and Kuprianoff.

At 273.15 K, \(h_{\text{liq}} = 418.7 \text{ kJ/kg}\)
\(s_{\text{liq}} = 4.187 \text{ kJ/(kg} \cdot \text{ K)}\)

For better overview in this diagram temperature is used as \(T = (T_0 - 0.15) \text{ K}\) except the critical temperature \(T_{\text{crit}}\) and the temperature of the triple point \(T_t\).
pressure issues with CO$_2$

- At $-50^\circ$C the pressure is 6 Bar(G)
- At $-20^\circ$C the pressure is 19 Bar(G)
- At $0^\circ$C the pressure is 34 Bar(G)
- At $20^\circ$C the pressure is 57 Bar(G)

It is the pressure/temperature relationship that is important!
pressure issues with CO$_2$

- HT cascade $P_s = 40$ Bar(G)
- LT cascade $P_s = 40$ Bar(G)
- Defrost system $P_s = 52$ Bar(G)
- Transcritical $P_s = 100$ Bar(G)
- Ambient standstill $P_s \approx 80$ Bar(G)
- Fade out vessel $\approx 90$ Bar(G)
Key temperatures for CO₂

+31.1°C – critical temperature
Key temperatures for CO$_2$

+25°C
0°C
-25°C
-50°C
-75°C
-100°C

+31.1°C – critical temperature

-56.6°C – triple point temperature
Key temperatures for $\text{CO}_2$

- $+25 \degree C$ -
- $0 \degree C$ -
- $-25 \degree C$ -
- $-50 \degree C$ -
- $-75 \degree C$ -
- $-100 \degree C$ -

$+31.1 \degree C$ – critical temperature

$-56.6 \degree C$ – triple point temperature

$-78.5 \degree C$ – atmospheric temperature
Safe Maintenance
Don’t trap vapour:

R744 Isotherm: Thermodynamic Properties

[Diagram of thermodynamic properties for R744 gas]
Solid formation in vents:
Solid CO$_2$ issues
Pumping out liquid CO$_2$
Venting liquid CO₂
Pressure issues with CO$_2$

Considerations with relief valves:

- Mount valve at the outside end of a high pressure line
- Size relief valve inlet for pressure drop <3% of actual relieving pressure (EN 13136:2001)
- Minimal valve outlet vent line to avoid blockage with solid CO$_2$
Venting a CO₂ system

Precautions:
• Vent to open air
• Do not vent liquid to atmosphere
• Always use a gauge to ensure line is vented before opening
Pumping out CO$_2$ liquid

**Precautions:**

• Never apply heat to a vent blocked with solid CO$_2$
• Always confirm a vent is not blocked with solid CO$_2$
• Beware of frost burn from solid CO$_2$
Charging a CO$_2$ system

Charging from a cylinder:

• Ensure appropriate quality refrigerant
• Ensure charging line can withstand circa 90 Bar
• Charge vapour until above 5 Bar(G)
Charging a CO$_2$ system

Charging from a tanker:

- Agree bulk delivery conditions with supplier well in advance
- Expect mechanical design review
- Agree charging method
- Expect tanker pressure circa 20 Bar
- Charge vapour until above 5 Bar(G)
Safe maintenance of CO$_2$

- Solid forms at $-56.6^\circ$C (4.2 Bar(G)), and can block vent valves
- Never apply heat to blockages...
- ...find another way to relieve pressure
- Beware of trapped liquid...
- ...and trapped gas
- Only vent to open air
Materials Selection and Component Installation
Materials selection for CO\textsubscript{2}

- Pipework and vessels can be carbon steel
- Can be LT50 (ASTM A333 Gr6) for most European design codes
- Or consider stainless steel.....

It is the pressure/temperature relationship that is important!
Valve choice

Details for ball valves:
• Petrochemical industry equipment
• “Floating ball” design
• Cavity relief is essential
• Avoid graphite reinforcement
• Glass fibre reinforcement is recommended
• Specify for dry CO₂
Valve choice

Details for globe valves:

- Refrigeration industry equipment
- Up to 52 Bar(G)
- Beware of stem seal leakage
- Reasonable cost
Valve choice

Details for solenoid valves:

• Refrigeration industry equipment
• 40 Bar designs common now
• 52 Bar designs coming soon
• High differential pressures can rupture diaphragms
Chemical Reaction with Ammonia
Refrigerant Shapes:
Ammonia

NH₃

Nitrogen
Hydrogen
Refrigerant Shapes:
Carbon Dioxide

CO₂

Carbon
Oxygen
Compound Shapes: Ammonium Carbamate

White crystalline
decomposes at 60°C
25% soluble at 15°C
When heated in open air....

$\text{CO}_2 + \text{NH}_3$
Conclusions

• \(\text{CO}_2/\text{ammonia} \) mixtures form \textit{Ammonium carbamate}
• This can easily block ports and valves, and withstand pressure
• Ventilating with hot air clears the solid to gases (\(\text{CO}_2\) and \(\text{NH}_3\))
• Ammonium carbamate also easily dissolves in water
• Increased corrosion rate of steel
Lessons learned....

• Deal with leaks quickly to prevent additional damage
• Design both sides for the same pressure to prevent overpressure or
• Include automatic isolation to protect the lower pressure ammonia system
• For simple systems hot air may be enough,
• ....but keep the system well ventilated
• For more complex systems wash with water then dry thoroughly.
CO$_2$/NH$_3$ issues
Chemical Reaction with Water
Water in CO$_2$ systems

$\text{CO}_2 + \text{H}_2\text{O}$
Water in $\text{CO}_2$ systems

$\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$ (Carbonic acid)
Water in CO$_2$ systems

H$_2$CO$_3$ + H$_2$O
Water in CO₂ systems

H₂CO₃ + H₂O = HCO₃⁻ + H₃O⁺ (Hydronium ion)
WATER IN CARBON DIOXIDE SYSTEMS

Picture courtesy of Danfoss
Water in CO$_2$ systems

- Iron + oxygen + water = rust
- Mineral oil + O$_2$ = organic acid + water
- Ester oil + H$_2$O = organic acid + alcohol
- Wear additive + H$_2$O = phosphoric acid + alkanol
Water in CO$_2$ systems

- Oxidation of mineral oils leads to formation of “short” organic acids (eg formic acid, acetic acid)
- Hydrolysis of polyol ester oils leads to formation of “long” organic acids (less harmful)
- …but both types are counted in the TAN (total acid number)
Water in CO$_2$ systems

- Carbonic acid + water = bicarbonate + hydronium ion
- Organic acid + water = carboxylate + hydronium ion
- Phosphoric acid + water = phosphate + hydronium ion

Any acid needs water to make it harmful!
Water in Carbon Dioxide Systems

Water Solubility in Refrigerants. Gas Phase

Temperature [°C]

mg of water/kg of refrigerant [ppm]
Water in CO₂

Water content in Carbon Dioxide

ppm by volume vs. temperature (°C)
Water in CO$_2$

• Ensure the moisture content is such that the water concentration remains below the amount that can dissolve in liquid CO$_2$.
• Corrosion is not a risk if there is no “free” water ie it is all dissolved in CO$_2$. 
Safety issues with CO$_2$

- Physiological effects
- Pressure and temperature
- Safe maintenance
- Materials selection
- Component installation
- Chemical reactions – ammonia
- Chemical reactions - water
* Any questions?