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Safety Aspects of CO_2 as a Refrigerant

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ABSTRACT
Safety is a major concern in any refrigeration application and it is the main reason why synthetic refrigerants dominated the refrigeration industry for several decades. In the specific application of refrigeration system, safety is more carefully considered because of the large number of people that might be affected in the case of leakage. This study analyses some safety aspects related to the usage of CO2 in large systems.

Keywords **–** *Safety Aspects, Risk analysis,* CO_2

I.INTRODUCTION

Carbon dioxide (CO_2) is a colorless, odorless, non-flammable gas that is a product of cellular respiration and burning of fossil fuels. It has a molecular weight of 44.01g/mol (NIOSH 1976). Although it is typically present as a gas, carbon dioxide also can be a solid form as dry ice and liquefied, depending on temperature and pressure (Nelson 2000).

CO2 is relatively inexpensive and unique among the natural refrigerants in its good safety characteristics. In relation to the environment, as a natural substance CO2 has no Ozone Depletion Potential (ODP), a Global Warming Potential (GWP) of 1 and no unforeseen threat to the environment. All these factors combined make it almost an ideal fluid (from safety and environment points of view) for applications where relatively large refrigerant quantities are needed.

CO_2 is present in the atmosphere at 0.035% (Aerias 2005; CCOHS 2005). In terms of worker safety, Occupational Safety and Health Administration (OSHA) has set a permissible exposure limit (PEL) for CO_2 of 5,000 parts per million (ppm) over an 8-hour work day, which is equivalent to 0.5% by volume of air. Similarly, the American Conference of Governmental Industrial Hygienists (ACGIH) TLV (threshold limit value) is 5,000 ppm for an 8-hour workday, with a ceiling exposure limit of 30,000 ppm for a 10-minute period based on acute inhalation data (MDPH 2005; NIOSH 1976). A value of 40,000 ppm is considered immediately dangerous to life and health based on the fact that a 30-minute exposure to 50,000 ppm produces intoxication, and concentrations greater than that (7-10%) produce unconsciousness (NIOSH 1996; Tox. Review 2005).

II.EFFECTS OF CO_2

Carbon dioxide replaces air, and causes lack of oxygen. At presence of sufficient oxygen, CO2 has a narcotic effect at stronger concentration. With smaller amounts, CO2 has a stimulating effect on the respiratory center. Due to the acidic characteristics of CO2, a certain local irritating can appear, particularly on the mucous membrane of nose, throat and eyes as well as induce coughing.

The symptoms associated with the inhalation of air containing carbon dioxide are, with increasing carbon dioxide concentrations. The data, valued for adults with good health, are as follows (source: AGA Gas Handbook)

2%	50% increase in breathing rate
3%	10 Minutes short term exposure limit; 100% increase in breathing rate
5%	300% increase in breathing rate, headache and sweating may begin after about an hour (Com.: this will tolerated by most persons, but it is physical burdening)
8%	Short time exposure limit
8-10%	Headache after 10 or 15 minutes. Dizziness, buzzing in the ears, blood pressure increase, high pulse rate, excitation, and nausea.
10-18%	After a few minutes, cramps similar to epileptic fits, loss of consciousness, and shock (i.e.; a sharp drop in blood pressure) The victims recover very quickly in fresh air.
18-20%	Symptoms similar those of a stroke

Carbon dioxide can be lethal at concentration at about 12%, the lowest ever reported lethal concentration of CO_2 is 9% for 5 minutes.

At CO_2 levels greater than 0.5%, adverse health effects are present in humans, animals, and plants. Plants utilize CO_2 as a primary ingredient in photosynthesis and depend on the gas for survival. However, under concentrated conditions, plant roots can actually be suffocated, which inhibits the uptake of nutrients, and subsequently kills the plants (Farrar et al. 1999; NIOSH 1976). This phenomenon was noted in Mammoth, California, recognized for infrequent, yet recent volcanic activity. Researchers investigating this phenomenon discovered concentrations as high as 95% CO_2 by volume from magmatic emissions (Farrar et al. 1999). These elevated concentrations were measured in pits in the snow and soil, buildings with poor ventilation, and in belowground valve boxes in the vicinity of Mammoth Mountain. Accumulation in pits and wells occurs due to the fact that CO_2 is denser than air and may slowly accumulate (IVHHN 2005). Specifically, soil gas levels of CO_2 in a snow well in Mammoth were measured at 70% after the death of a skier in the vicinity of the well (Farrar et al. 1999; IVHHN 2005).

CO_2 is considered to be a potential inhalation toxicant and a simple asphyxiate (Aerias 2005; NIOSH 1976; Priestly 2003). It enters the body from the atmosphere through the lungs, is distributed to the blood, and may cause an acid-base imbalance, or acidosis, with subsequent CNS depression (Nelson 2000; Priestly 2003). Acidosis is caused by an overabundance of CO_2 in the blood. Under normal physiological circumstances, there is a higher concentration of CO_2 in the blood than in the lungs, forming a concentration gradient, where blood CO_2 diffuses into the lungs and then is exhaled. An increase in inhaled CO_2 and subsequent reaction with water in the blood forms carbonic acid (H_2CO_3), which then dissociates into hydrogen ions [H^+] and bicarbonate[HCO_3^-]. The excess CO_2 shifts the equilibrium toward the creation of more hydrogen ions, thus creating an acidic environment (see equation below). During respiratory acidosis, the pH of the blood becomes less than 7.35 (Priestly 2003).

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

Electrolyte imbalance occurs due to decreased blood plasma chloride, potassium, and calcium and increased blood plasma sodium. Furthermore, the oxygen depleted environment does not allow for cells in the body to obtain the oxygen they need to survive. Fortunately, the body compensates for the excess in H^+ ions by binding of the protons to hemoglobin. In addition, the lungs attempt to compensate by removing the excess CO_2, which is the reason rapid breathing is apparent during acute CO_2 exposure. After prolonged exposure, the kidney begins to balance blood pH by retaining bicarbonate and excreting hydrogen ions to correct acidosis (Priestly 2003).

III.SAFETY ASPECTS OF CO_2

A common issue for CO_2 systems in supermarkets is the high pressure at standstill. If the plant would be stopped for maintenance, component failure, power cut or any other reason, then the refrigerant inside the plant will start to gain heat from the ambient and the pressure inside the plant will consequently increase. Components of the indirect system and the low temperature level of the cascade and trans-critical systems will not stand the high pressure as they are usually designed for a maximum pressure of 40 bars.

The most common and easiest protective technique is to release some of the CO_2 charge from the plant when the pressure reaches a certain preset value, consequently, the pressure and temperature of CO_2 in the plant will be reduced. If the plant remains at standstill, then the process will be repeated and subsequently the plant must be charged again to compensate for the lost CO_2 charge. The fact that CO2 is inexpensive favours this solution over other more expensive ones such as auxiliary cooling unit or thermal storage vessel. The position of the relief valve must be carefully selected so liquid CO_2 would not pass through it, otherwise solid CO_2 (dry ice) will be formed which might block the valve. Dry ice will be formed when the pressure is reduced below the triple point pressure, 5.2 bars, as clarified in Figure 1.

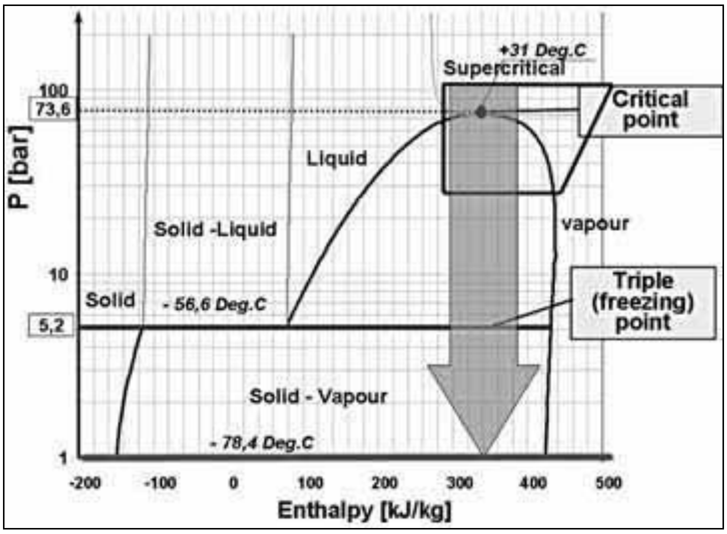

Figure 1: CO2 Log P-h diagram

IV.VEHICLE TEST

A medium sized car, three doors, without A/C system has been chosen as test vehicle. A hose leads from the CO2 bottle though the engine compartment into the inlet of recirculated air of the HVAC. The inlet of fresh air is permanently closed. The mass of spilled CO2 is measured as difference in weight with a highly sensible scale. Additionally the CO_2 volume flow is measured with a flow meter. The CO_2 concentration will be measured with an infrared (IR) sensor. The IR CO2 sensor is a transducer for the measurement of the CO2 partial pressure in the atmosphere, by the absorption of infra-red radiation. The accuracy is ± 5 % of the measured value.
The following parameters were regarded :
a) concentration profile inside the passenger compartment,
b) reduction of inner volume due to passengers sitting in the car
c) influence of release time
d) blower off
An instantaneous release of a certain amount of CO2 inside the passenger compartment would result in a theoretical maximum peak concentration inside the cabin as listed in Table 2.

Refrigerant	Passenger compartment Volume [m^3]	AC System Charge [g]	Refrigerant conc. ppm vol/vol if total AC charge leaks [%]
CO2	1.5	240	8.9
	2.5	225	5
	2.5	400	8.9
	4	600	8.3
Notes: *Theoretical, for illustration only, actual refrigerant charges and passenger compartment volume may be different. Assumes a total leakage of refrigerant charge.*			

Table 2 Refrigerant leakage: theoretical concentrations within passenger compartments

500g gaseous CO_2were released with 1500 liter/hr into the passenger compartment (see Figure 2.) The maximum measured concentration of 6.3 % vol. was at the vent center just before stopping the release. The difference in CO_2 concentration on different positions inside the car was in the range of the statistical error (0.3%). After the spill stopped, the concentration decreased rapidly. Concentrations lower than 1 % are reached after approximately 50 Minutes.

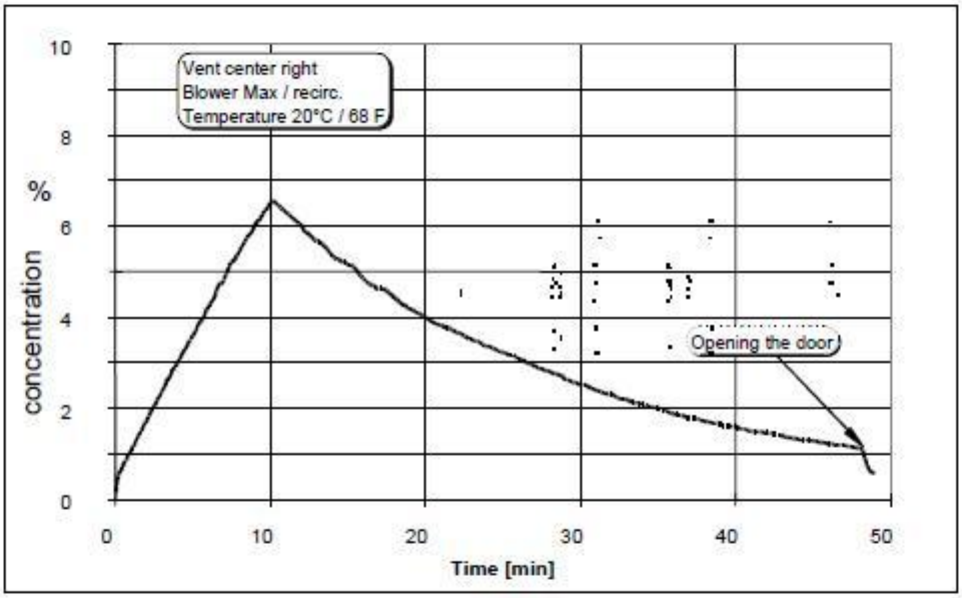

Figure 2: Experimental results of a continuous release of 500 g CO_2 with 1500 l/h into the passenger compartment of a midsize vehicle.

The release rate has the most significant influence on the measured CO_2 peak concentration. By decreasing the rate from 1500 liter/hr down to 500 l/h the peak concentration of CO_2 drops from 6.3 % vol. to 3.9 % vol. (see Figure 3). One test was conducted with 5 Dummies inside the passenger compartment, each with a volume of approximately 70 liters. The measured peak concentration after releasing 500 g CO_2 with 1500 liter/hr was 6.7 % vol. That's approximately 0.4 % higher than without Dummies.

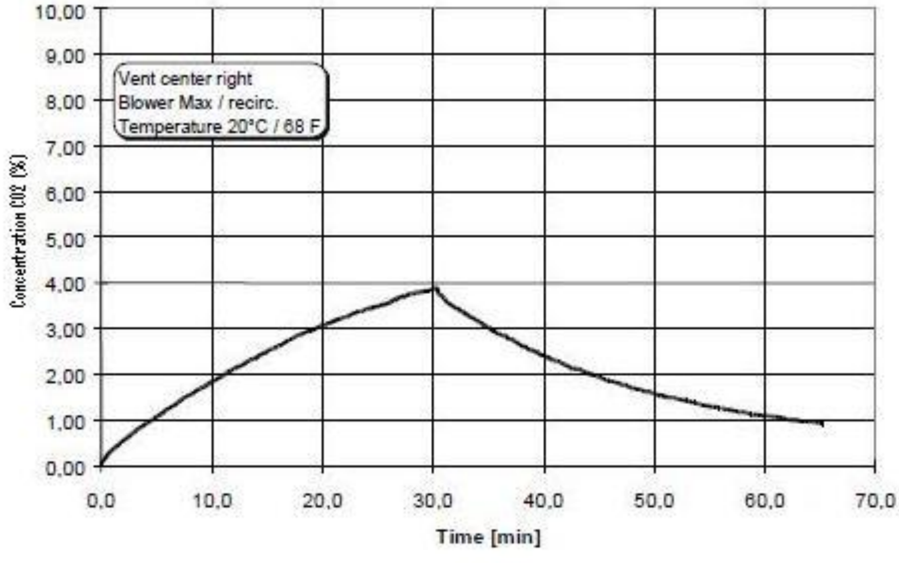

Figure 3: Experimental results of a continuous release of 500 g CO2 with 500 l/h into the passenger compartment of midsize vehicle.

The peak concentration at the seat level decreases within 10 minutes from 4% vol. to values lower than 2 % vol. In all cases the opening of the door lead to a very rapid decrease of the CO_2 concentration inside the car. However, with closed doors CO_2 disappears with a rate of 1.5 % vol. per 10minutes.

V.SUMMARY

It must be emphasized that CO_2 is a refrigerant with low toxicity. The concentrations of CO_2 that can lead to any effects are very high and these could only result in the event of a leak of refrigerant into the passenger compartment under conditions of low fresh air ventilation rates.

The physiological effects on Carbon Dioxide effects are apparent at exposure limits above 2%. Above 5% the change is marked and the human control means system effects became apparent. While not like threatening, at such concentrations this reaction may cause further stress in the subject, who may well be aware of breathing changes, but be enable to detect any cause. The lowest ever reported lethal concentration of carbon dioxide is 9%.

VI.CONCLUSION

$CO_2$is a naturally occurring atmospheric gas that is considered safe at levels below 0.5% according to OSHA standards (CCOHS 2005). However, occupational hazards related to CO_2 exposure may occur under certain conditions.

From the analysis, it is clear that using CO_2 does not enclose exceptional health risks for the customers and the workers in the specific area. Yet, CO_2 detectors are recommended to be installed in the specific area, especially in places where leakage is possible and high local concentrations is expected in case of a leak. Evidently, safety requirements such as proper ventilation and alarm system are a must in the specific area.

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