Safety of CO_2 in Large Refrigeration Systems

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Introduction

Safety is a major concern in any refrigeration application and it is the main reason why the synthetic refrigerants dominated in the refrigeration industry for several decades. When synthetic refrigerants were found to be harmful to the environment, several regulations were enforced on their usage. Natural refrigerants are seen as a potential permanent solution, among which CO_2 is the only non-flammable and non-toxic (to a certain degree that will be discussed in this study) that can operate in vapour compression cycle at evaporation temperature below 0°C so it can be directly used in public areas. When ammonia or propane are used in installations that serve public areas, indirect systems are usually applied where the public areas are served with secondary refrigerant, could be brine or CO_2, and the primary refrigerant, ammonia or propane, is kept in the machine room. In this case refrigerant leakage will be limited to the machine room area where the proper safety devices must be installed. Compared to direct expansion systems, indirect systems will have lower evaporation temperature due to the additional temperature difference in the heat exchanger in the indirect circuit. This will result in an additional temperature lift in the primary refrigeration circuit leading to an increase in the compressor power for the same refrigeration capacity. Moreover, the power needed to operate the secondary refrigerant circulation pump will add to the running cost of the indirect system.

CO_2 is relatively inexpensive and unique among the natural refrigerants in its good safety characteristics. In relation to the environment, as a natural substance CO_2 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. Supermarket refrigeration and other large sized refrigeration systems are applications where CO_2 is seen as a strong candidate to replace conventional options. It has been first used as secondary refrigerant in indirect systems. The knowledge learned from the early research work on CO_2 and the experiences gained from the early installations of CO_2 in commercial applications promoted its wider application in supermarkets with different system concepts. Cascade systems with CO_2 in the low stage and trans-critical systems where CO_2 is the only working fluid have been applied in recent years. Nowadays, for instance in Sweden, there are more than 100 installations of CO_2 in indirect systems, few cascade installations and at least 20 plants with trans-critical circuit.

In the specific application of supermarket refrigeration, safety is more carefully considered because of the large number of people that might be affected in case of leakage. Although considerable research has been devoted to the development and the performance analysis of CO_2 refrigeration systems in commercial applications, rather less attention has been paid to the detailed analysis of the safety aspects in this context. Some research work has been done through the RACE project for mobile air conditioning application (Amin, Dienhart et al. 1999). Investigations focused on the concentration levels in the passengers' compartment in case of leakage and on the level of the explosive energy in case of component failure.

This study analyses some safety aspects related to the usage of CO_2 in large systems, the case of supermarket application is chosen as a practical example. The concentration levels in the supermarket's shopping area and machine room that result from different accident scenarios are calculated for a selected practical example. The ventilation requirements in the supermarket under normal conditions and during a leakage accident are taken into consideration. The case study is chosen in Sweden due to the large number of CO_2 installations in Sweden, especially in supermarket application.

For the selected case, the analysis of the calculations' results showed that CO_2 does not pose exceptional health risks for the customers and the workers in the shopping area, whereas safety requirements expressed by efficient ventilation and proper alarm system must be installed in the machine room.

Safety characteristics 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 CO_2 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. Guidance for selection and positioning of the pressure relief valves can be found in EN 378: 2007 part 2.
On the other hand, the formation of the dry ice can be considered advantageous when leakage occurs in other parts of the system except the relief valves. The concentration rate increase in the space of the leak will be lower than the case of vapour leak owing to the fact that the formed dry ice will delay the mixing between CO_2 and air by the time that it will take the dry ice to sublime. Moreover, the formation of dry ice on the leakage point might block or limit the flow.

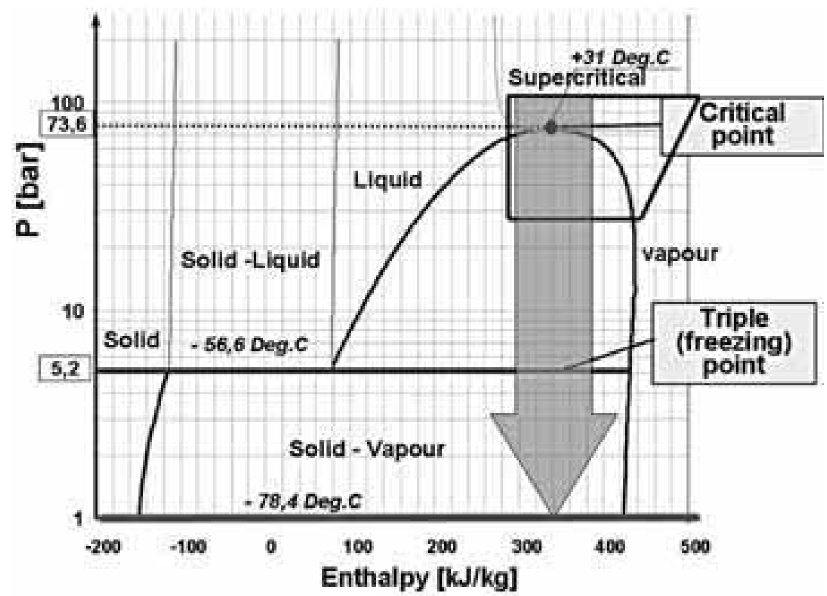

Figure 1: CO_2 Log P-h diagram

Supermarket refrigeration is a relatively large-scale application that requires long distribution lines and an accumulation tank for the solutions where the pump is used. This results in large system volume and consequently a considerable refrigerant charge. In case of a sudden leakage the concentration levels of the refrigerant might be high and the number of people in the shopping area who could be exposed to it is large. Therefore, safety concern is a major factor in the choice of the type of system and refrigerant to be used. CO_2 is a relatively safe refrigerant compared to natural and artificial working fluids. It is classified in group A1, according to ASHRAE Handbook-Fundamentals (ASHRAE 2005). This is the group that contains the refrigerants that are least hazardous and without an identified toxicity at concentrations below 400

PPM. Naturally, CO_2 exists in the atmosphere at concentrations around 350 PPM and for concentrations between 300 and 600 PPM people do not usually notice the difference. CO_2 has similar classification according to ISO 817: 2005, which is the international standard for refrigerant safety classification; it is classified in group A1 which are the refrigerants with low toxicity and non-flammable.

According to ASHRAE (ASHRAE 1989), a CO_2 concentration of 1000 PPM is the recommended limit to satisfy comfort for the occupants, where in a CO_2 controlled ventilation system fresh air should be supplied so that the CO_2 concentration level will not exceed this value. This is the case of an application when a small CO_2 generation rate is expected due to different human activities. However, in the case of high leakage rate that might occur in supermarket space or in the machine room, the consequences of serious health hazards, such as suffocation, must be taken into account.

The following table is a list of selected concentration levels of CO_2 and expected effects on the human health.

PPM	Effects on health	Reference
350	Normal value in the atmosphere	(Bearg 1993)
1,000	Recommended not to be exceeded for human comfort	(ASHRAE 1989)
5,000(1)	TLV-TWA(2)	(Rieberer 1998)
20,000	Can affect the respiration function and cause excitation followed by depression of the central nervous system. 50% increase in breathing rate	(Berghmans and Duprez 1999)
30,000(3)	100% increase in breathing rate after short time exposure	(Amin, Dienhart et al. 1999)
50,000 (40,000)(4)	IDLH(5) value	(Rieberer 1998)
100,000	Lowest lethal concentration	(Berghmans and Duprez 1999)
	Few minutes of exposure produces unconsciousness	(Hunter 1975)
200,000	Death accidents have been reported	(Berghmans and Duprez 1999)
300,000	Quickly results in an unconsciousness and convulsions	(Berghmans and Duprez 1999)

Table 1: Different concentrations of CO_2 and the expected health consequences

(1) The Occupational Safety and Health Administration (OSHA) revised Permissible Exposure Limit (PEL): Time-Weighted Average (TWA) concentration that must not be exceeded during any 8 hour per day 40 hour per week.
(2) Threshold Limit Value (TLV): TWA concentration to which one may be repeatedly exposed for 8 hours per day 40 hours per week without adverse effect.
(3) Short Term Exposure Limit (STEL): a 15-minute TWA exposure that should not be exceeded at any time during a workday.
(4) National Institute for Occupational Safety and Health (NIOSH) revised Immediately Dangerous to Life or Health (IDLH) value
(5) IDLH: maximum level for which one could escape within 30 minutes without any escape-impairing symptoms or any irreversible health effects.

CO_2 has a main drawback of not being self-alarming by lacking a distinctive odour or colour. This implies that facilities where CO_2 may leak must be equipped with sensors that trigger alarm when the concentration level exceeds 5000 PPM, above which CO_2 concentration may have effect on health. CO_2 is heavier than air and therefore will collect close to the floor when it leaks; thus, the sensors and the ventilators in the space where CO_2 might leak should be located close to the floor. Being inexpensive and relatively safe allows the usage of large charges of the refrigerant and provides flexibility in the design of the system. Hence, flooded evaporators which require large refrigerant charges can be used for the intermediate and low temperature levels. Nevertheless, the CO_2 charge is expected not to be very high compared to other refrigerants due to the fact that the compact size of the CO_2 components and delivery lines will contribute to minimizing the charge. Based on experiences from several installations, an estimation of how much charge of CO_2 will be needed in a supermarket can be found in Heinbok (Heinbokel 2001); about 5.25 and 1.7kg/kW for secondary and cascade systems respectively. Of course this should be considered a rough estimate because it will be different from one system solution and installation to another.

In case of component rupture, the fact that CO_2 has relatively high operating pressure compared to other refrigerants raises questions concerning the hazards of blast effects, shocks and flying fragments. As described and studied by Pettersen et al. (Pettersen, Armin et al. 2004), the extent of a potential damage can be characterized by first; the explosive energy which can be estimated as the energy released by expansion of the refrigerant contained in a component or system. Second; is the possible occurrence of a Boiling Liquid Expanding Vapour Explosion (BLEVE) which may create a more severe blast effect than by an ordinary refrigerant expansion. BLEVE may occur when a vessel containing pressurised saturated liquid is rapidly depressurised, e.g. due to a crack or initial rupture. The sudden depressurisation leads to explosive vaporisation and a transient overpressure peak that may burst the vessel. As Pettersen et al. (Pettersen, Armin et al. 2004) reported, the explosive energy per kg for CO_2 is high compared to R22. However, when the comparison is made for ductless residential air conditioning system with equal cooling or heating capacities and similar efficiencies then owing to the smaller volume and refrigerant charge of the CO_2 system the actual explosive energies are in the same range.

In the supermarket system the expected explosive energy may be higher than the cases with conventional systems. This is due to the presence of the accumulation tank in most of the CO_2 system solutions which increases the system's charge and volume. However, the explosive energy is more of a concern with systems where the occupants are close to the system's components; such as mobile air conditioning and residential air conditioning. In supermarket systems the high pressure components are in the machine room and the distribution lines are usually kept in a distance from the consumers.

Regarding the possible occurrence of BLEVE in CO_2 vessels, Pettersen (Pettersen 2004) reports that the maximum observed pressure spikes in the tests were only a few bars above the initial pressure. Therefore, it was concluded that there was no reason to expect BLEVE in CO_2 system accumulators or receivers.
In order to evaluate the risks attached to a leakage accident in a supermarket the possible concentration levels in the supermarket's shopping area and machine room that result from different accident scenarios has been calculated for a selected practical example. The theoretical analysis will show the limits for the highest concentration levels that could be reached in the supermarket.

The case study

The case of a supermarket in the small to medium size category (relative to the CO_2 installations in Sweden) was selected as the base for the calculations. The dimensions of the shopping area are around 40x30x5 m and the machine room's dimensions are 10x10x3 m. The capacity of the plant is around 30 kW at the low temperature level and 75 kW at the medium temperature level. CO_2 is used as secondary refrigerant at the low temperature level in an indirect system, the CO_2 charge in this installation is assumed to be 100 kg. These parameters are almost identical to a supermarket in Hedemora area, about 200 km North West of Stockholm. The concentration of CO_2 is calculated in different accident scenarios, which differ depending on two main parameters: The leakage position and the flow rate of the leaking CO_2.
The main two places in the supermarket where leakage could take place are the machine room and the shopping area. The risk analysis is performed for these two places. The refrigerant is assumed to leak with different flow rates which start with the hypothetical case that the refrigerant escapes instantaneously and completely from the plant resulting in the highest concentration possible. The lowest flow rate used in the calculations was based on two hours of leakage time. It is assumed in the calculations that good mixing occurs and that the refrigerant leaks with constant flow rate until all the charge escapes from the plant. The value of 365 PPM was used for the CO_2 concentration in the fresh air supply and as the initial value in the room.

Risk analysis in the shopping area

Based on the dimensions of the selected supermarket, if the CO_2 is assumed to escape completely within the shopping area in a very short time, then the maximum concentration of CO_2 will be around 9,270 PPM. This concentration level far exceeds the accepted levels for occupants in non-industrial facilities, the value of 1000 PPM in

Table 1. Until 1989 the Occupational Safety and Health Administration (OSHA) set the concentration value of 10,000 PPM to be the Permissible Exposure Limit (PEL). Most of the agencies, National Institute for Occupational Safety and Health (NIOSH), American Conference of Governmental Industrial Hygienists (ACGIH), and MAK-commission in Germany, that set the occupational safety standards used the TLV-TWA of 5000. The value of TLV-TWA is usually combined with the Short Term Exposure Limit (STEL) value of 30,000 PPM which is much higher than the highest concentration possible in the shopping area (9,270 PPM). Accordingly, leakage accident within the shopping area is not expected to result in any health hazard to the occupants. When the fresh air supply is taken into account, the CO_2 concentration in the space will drop after one hour of ventilation according to the equation below (Peterson 1986), which is represented by the curve in Figure 2. C_{1h} is the concentration after one hour (PPM), C_{max} is the maximum initial concentration (PPM) and is the air change rate (1/h).

$$\frac{C_{1h}}{C_{\max}} = \exp^{(-N)} \qquad (1)$$

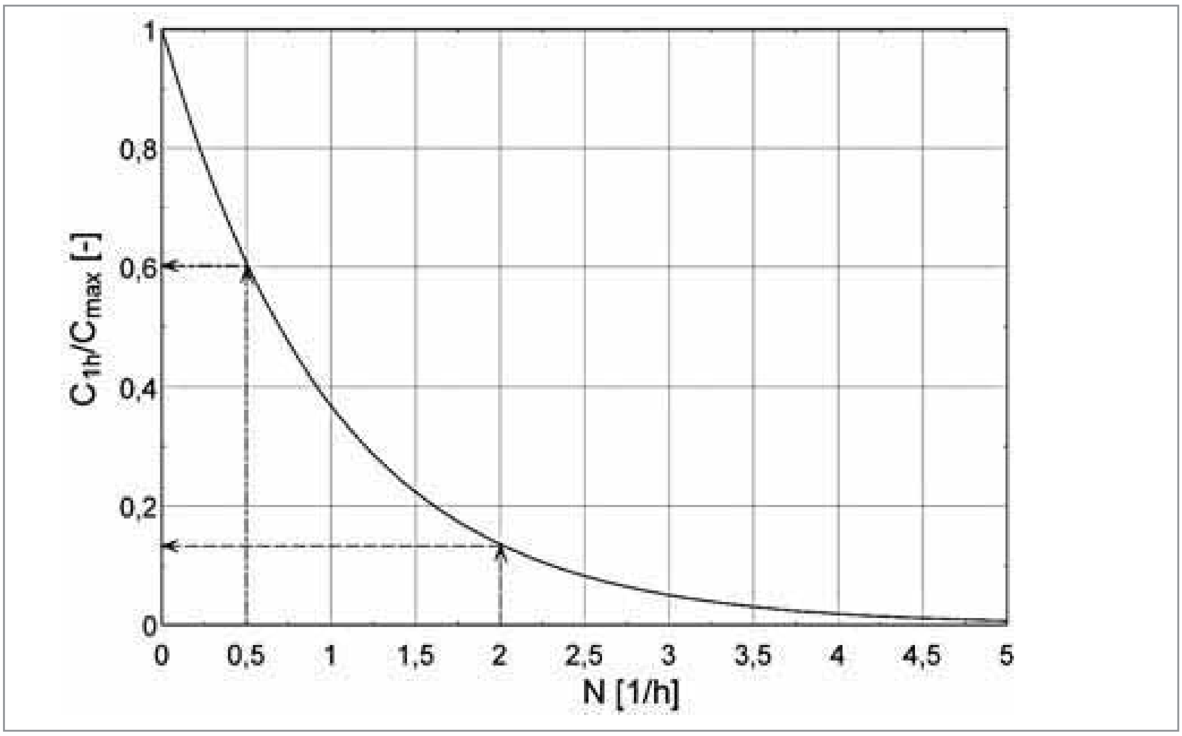

Figure 2: The influence of the ventilation rate on the concentration

For the shopping area, ASHRAE Standard 62 (1989) recommends about 0.5 air changes per hour (ACH), which results in approximately 40% reduction in the initial CO_2 concentration after one hour of ventilation, which can be seen in the figure above. If the CO_2 charge is assumed to escape with a constant flow rate then the concentration, in kg/m³, is calculated as a function of time according to the equation below (Peterson 1986) and the results, in PPM, are plotted in Figure 3 for the shopping area. It was assumed that the CO_2 charge escapes with constant flow rate during different durations of 15 minutes, 30 minutes, 1 hour, and 2 hours. CO_2 generation from the occupants was ignored in the calculations.

$$C_{(kg/m^3)} = \frac{\dot{m}_{CO2}}{N \times V} + C_{air} - \left\{ \frac{\dot{m}_{CO2}}{N \times V} + C_{air} - C_0 \right\}.\exp^{(-N.t)} \qquad (2)$$

Where $\dot{m}_{CO2}$ is the CO_2 mass flow rate (kg/h), V is the space volume (m³), C_{air} is the CO_2 concentration in fresh air (kg/m³), C_0 is the initial concentration (kg/m³) and is the time in hours.

In a CO_2 controlled ventilation, the ventilation rate in the shopping area must be increased when the concentration reaches a value close to 1000 PPM in order to bring the CO_2 concentration down to normal level. In these calculations the ventilation system was assumed to have constant value of 0.5 ACH regardless of the CO_2 concentration level.

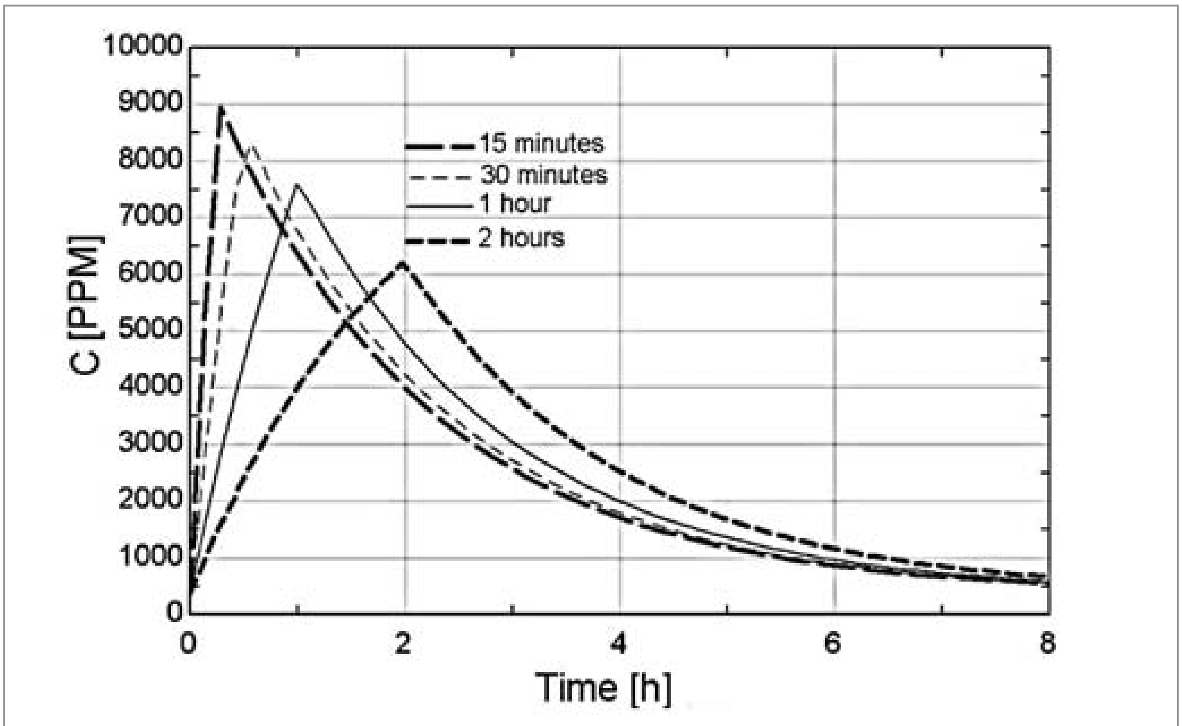

Figure 3: CO_2 concentration versus time in the shopping area for 15 minutes, 30 minutes, 1 hour, and 2 hours of leakage durations

The results in Figure 3 show that the CO_2 concentration sharply increases during the assumed leakage times. This is due to the fact that the CO_2 leakage rate is much higher than the rate of replacement of CO_2 contaminated air by fresh air supply via the ventilation. At the end of the leakage period (after 15, 30, 60, and 120 minutes) the CO_2 concentration reaches the peak because at that point the CO_2 charge escaped completely from the plant into the shopping area. Afterward, the CO_2 concentration decreases in an exponential manner due to the effect of the ventilation which replaces the CO_2 contaminated air by fresh air supply.

Looking at the accident scenario with the highest peak concentration, almost 9000 PPM at 15 minutes leakage duration, it is evident that the CO_2 concentration level in the shopping area does not enclose health risk to the customers and the workers in the supermarket. However, an alarm is necessary to warn of a leakage problem so proper procedures can be followed for occupants' safety and proper maintenance can be performed.

Risk analysis in the machine room

If the same scenario, that the charge escapes completely and instantaneously, is applied in the machine room then the concentration will be around 185,300 PPM. It is very high if compared to the value of 200,000 PPM, listed in Table 1 at which death accidents have been reported. Therefore, protective measures of a proper alarm system based on CO_2 detectors and efficient CO_2-controlled ventilation system must be implemented. According to the Swedish design codes (Svensk Kylnorm 2000), a minimum ventilation rate of 2 ACH is recommended in the machine room. This value results in 86% drop in the initial CO_2 concentration after one hour of fresh air supply, clarified in Figure 2. According to EN 378, if the machine room is occupied for significant periods, e.g. used as building maintenance workplace, then the ventilation rate must be at least 4 ACH. The ventilation system in the machine room must be a CO_2 controlled one; and, according to the Swedish safety codes when the concentration level in the machine room reaches the TLV, 5000 PPM, the fresh air supply flow rate (m^3/h) must be increased according to the formula:

$$\dot{V} = 50\sqrt[3]{M^2} \qquad (3)$$

Where *M* is the refrigerant charge (kg). The increase in the ventilation rate is accompanied with a low-alert alarm system, visual and acoustic, in the machine room and in a visible place from outside the room. When the concentration level reaches 50,000 PPM (the IDLH value) high-alert alarm system is triggered and the workers must leave the machine room immediately (SvenskKylnorm 2000).

This is also in good accordance with the European Standard EN 378, which states that refrigerant detection systems shall be fitted in machinery rooms if the system charge is greater than 25 kg. Refrigerant detection systems shall be fitted to raise alarms and initiate ventilation if the levels rise to 50% of the acute toxicity exposure limit (ATEL), which is about 20000 PPM (2 % by volume). The emergency ventilation system shall not to produce more than 15 ACH.
Figure 4 indicates that for the leakage duration of 2 hours there are no health consequences for the workers, since the IDLH value is not reached (the maximum value is approximately 26,150 PPM). The concentration curve levels off close to the value of 25,000 PPM due to the fact that the extraction rate of CO_2 is almost equal to the leakage rate. In the case of 1 hour leakage time, the highest value reached is approximately 50,500 PPM and the high-alert alarm will be triggered for only 4 minutes, when the IDLH value is exceeded.

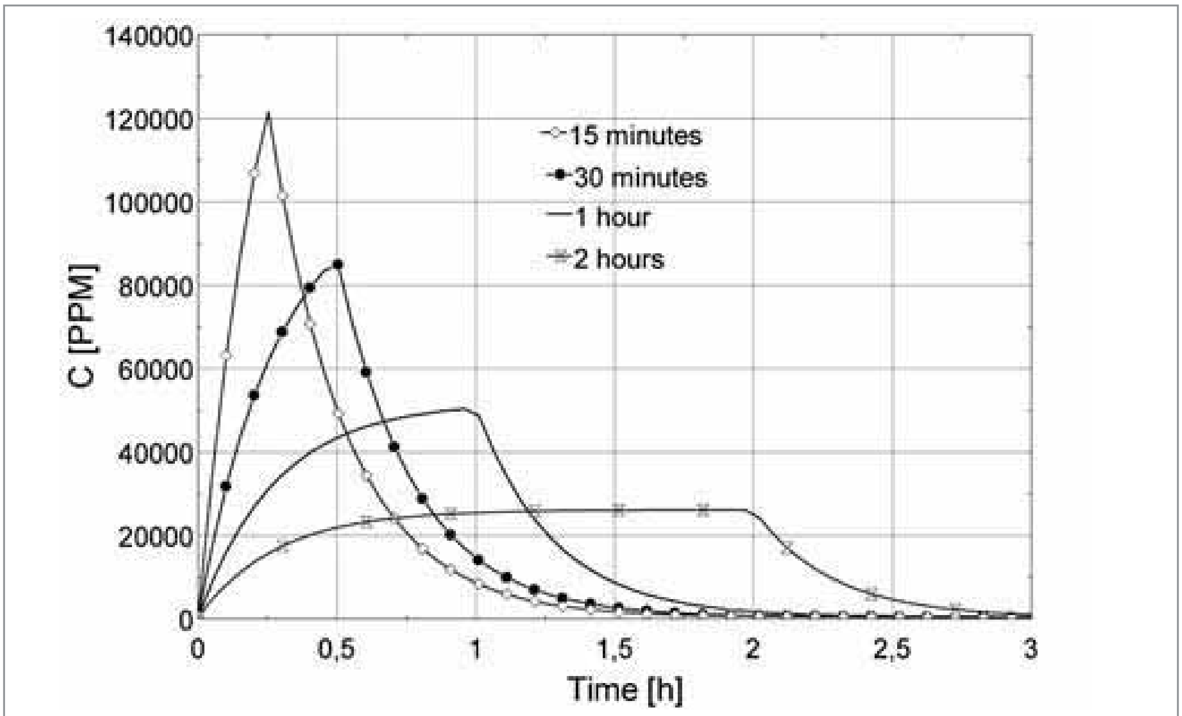

Figure 4: CO_2 concentration versus time in the machine room for 15 minutes, 30 minutes, 1 hour, and 2 hours of leakage durations

The concern is high in the case of short leakage time of the whole CO_2 charge, for 30 minutes of leakage time the value of 86,000 PPM is reached. According to the settings of the alarm system installed in the machine room, the low-alert alarm will be triggered after less than one minute from the moment that the leakage starts, and it will last for almost 12 minutes until the high-alert alarm is triggered. Which means that the workers have at least 12 minutes to leave the place before the critical CO_2 concentration levels are reached. In case of 15 minutes of leakage time, the low-alert alarm will be activated for at least 5 minutes before the high-alert alarm will start. This makes the time to escape from the machine room shorter, but it should be also noticed that the period where the IDLH value is exceeded is 25 minutes, which means that the exposure time for the high concentration levels of CO_2 is also short. The high concentrations reached in the machine room imply that specific safety procedures must be implemented. The fact that CO_2 is a colourless odourless gas means that proper detection system must be placed to determine the increase in gas concentration. Figure 5 clarifies the safety equipment that should be placed in the machine room, it is shown in the figure that acoustic and flashing light alarm devices must be provided in a visible place from inside and outside the room. The figure also shows that detectors and the exhaust fan are placed at low level close to the floor.

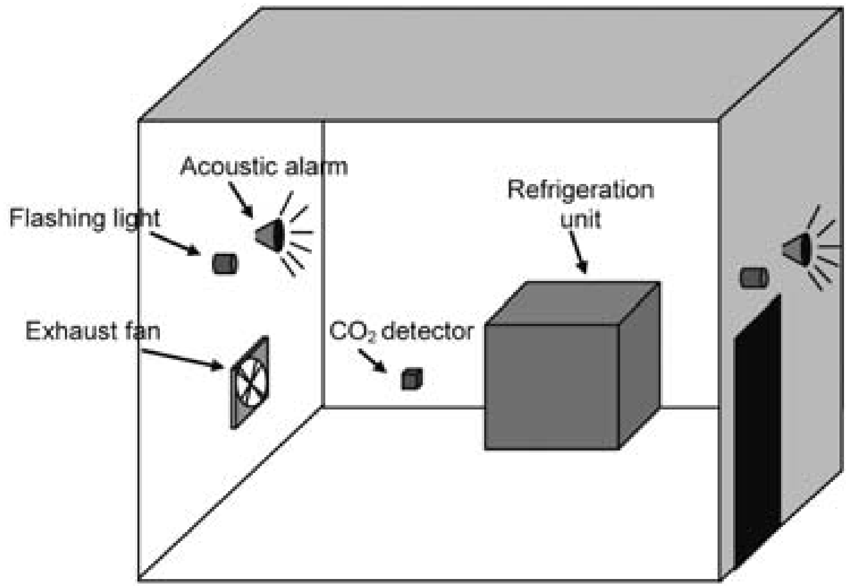

Figure 5: Simplified drawing of the machine room and the required safety equipment/devices

Discussion of the assumptions and results

The results presented in this chapter are based on simplified assumptions and aimed to give an indication of the situation in a practical case. It was assumed that the refrigerant leaks with constant flow rate, which is not the case in practice, where the flow rate is expected to be higher in the first stages of the leakage and then it will decay due to the reduction of the pressure in the system.

The refrigerant was assumed to escape completely from the system, it should be taken into account that when the pressure in the system drops to 5.2 bars then dry ice will be formed inside the system and will slowly sublimate. The same will occur to liquid CO_2 leaking from the system to the surroundings. Furthermore, the formation of dry ice at the leakage point may reduce the leakage flow rate and could block the leakage point. When the pressure inside the system drops to the ambient pressure, part of the refrigerant will be left in the volume of the system's components and distribution lines. The longest leakage time of two hours that is used in the calculations is considered to be very short. In practice complete leakage is rare to occur and if it happens then it would take place over several hours. Therefore, this will contribute to slower increase of concentration.

Due to the fact that CO_2 is 1.5 times heavier than air it will tend to pool; thus, CO_2 concentration distribution in air will not be homogenous as assumed in these calculations. The concentration values presented in this study does not necessarily present what a human would be subject to because the concentration at an average height of human body might be higher or lower than the calculated value using the good mixing assumption. The fact that the sensor must be installed on a level close to the floor means that it will measure higher concentration than at an average height of human body. This will give earlier warning and longer escape time than the resulting values from the homogenous concentration assumption. Based on the above discussion, it can be concluded that this model over predicts the average CO_2 concentration in the machine room and the shopping area. It also over predicts the rate of concentration increase and the escape time would be much longer than used in the calculations.

Moreover, the analysis in this chapter does not take into account specific cases of direct and close contact with leaking CO_2 stream which could happen for technicians in the machine room. This means that the person will be exposed to very high concentration for very short time which may result in loosing consciousness. Skin burns probably will not occur due to the fact that CO_2 does not evaporate at atmospheric pressure (Pettersen, Armin et al. 2004). Safety requirements in the machine room in large refrigeration systems will be similar to the discussed case in this study. However, concentration levels in the machine room and the public areas will depend on the given parameters of each individual case. Still, the analysis in this study can be used as guidelines for evaluation and can give an indication of possible risks.

Conclusions

From the analysis of the calculations' results, it is clear that using CO_2 in supermarkets refrigeration does not enclose exceptional health risks for the customers and the workers in the shopping area. Yet, CO_2 detectors are recommended to be installed in the shopping area, especially in places where leakage is possible and high local concentrations is expected in case of a leak. It must be pointed out that even if the CO_2 charge and the size of the supermarket's shopping area and machine room are identical to the modelled example, the case of every supermarket must be considered individually taking into consideration the geometrical variations and the locations of the distribution lines. Evidently, safety requirements such as proper ventilation and alarm system are a must in the machine room.

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