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R-32 as an Alternative to Ammonia in Industrial Refrigeration

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ABSTRACT

Ammonia is recognised to be the most commonly used refrigerant in industrial systems however it is limited in some applications by its toxicity. R-32 has similar flammability characteristics and a similar pressure-temperature relationship, and through its use as a blend component it has become widely used and readily available. This paper compares and contrasts ammonia and R-32 with specific reference to industrial applications. The analysis includes comparison of refrigerating effect, heat transfer performance and equipment size and looks at a variety of applications from low temperature freezers to high temperature heat pumps. Commercial factors such as price and availability are also considered. Opportunities for the adoption of new processes and materials, currently not feasible with ammonia are explored and the possible future trends in the industrial market are identified and evaluated.

A hazard analysis for an industrial installation is described, showing the similarities to the type of analysis required for ammonia systems and identifying where the R-32 hazard analysis is different.

The paper concludes with an assessment of the benefits that would be gained by the use of R-32 instead of ammonia, the constraints that would be required to make this happen and the likely probability of widespread adoption of R-32 in the industrial market.

1. INTRODUCTION

Ammonia (R-717) has been used in vapor-compression (Perkins cycle) refrigeration systems since 1872, and indeed its excellent cooling capability was recognized as early as 1755 in the first ever report of experiments in mechanical refrigeration (Pearson, 2012). R-32 (difluoromethane) is a single molecule refrigerant and is one of the group of substances investigated by Thomas Midgley Jr and his co-workers in the 1920s although it was not commercialized at that time (Midgley *et al*, 1930). In some respects the two chemicals are similar and they each make an excellent refrigerant for low temperature applications, but there are also significant differences. The question addressed by this paper is therefore “Can R-32 be considered to be a suitable replacement for ammonia in industrial refrigeration systems?”

Some basic properties of the two fluids are given in Table 1. These are parameters which have specific significance to refrigeration and their relevance is explained later in the paper.

Table 1: Basic properties of the compounds

Parameter	Units	R-717	R-32
Formula	-	NH ₃	CH ₂ F ₂
Molecular Weight	g mol ⁻¹	17.031	52.02
Triple point	°C	-77.75	-136.81
Critical temperature	°C	132.3	78.4
Critical pressure	MPa	11.3	5.38
Normal boiling point	°C	-33.4	-51.65
Latent heat at 0°C	kJ kg ⁻¹	1260.66	315.3
Density at 0°C, saturated gas	kg m ⁻³	3.46	21.985
Volumic capacity at 0°C	kJ m ⁻³	4362.45	6931.87
Ratio of spec. ht.(1.013 bar, 25 °C)	-	1.316	1.253

Industrial refrigeration systems operate in the evaporating temperature range -30°C to $+10^{\circ}\text{C}$, with some specialist freezer plants running at lower temperatures. The design condensing temperature is usually between 30°C and 50°C depending on the type of condensers with some high ambient installations requiring higher condensing temperatures. It can be seen that both compounds are suitable for these ranges, although in specialist freezers and other low temperature applications the R-717 low pressure side will be below atmospheric pressure. The condensing pressure for the R-32 is typically about 60% higher than for R-717, resulting in a need for higher design pressures on the high side of the plant; usually 30 bar (G) for evaporative cooled equipment and 35 bar (G) for air cooled, compared with 20 bar (G) and 25 bar (G) respectively for R-717. However, as with R-744, the higher operating pressure brings the benefit for R-32 of dense suction gas and high volumic capacity (i.e. smaller compressors for a given heat duty). The refrigerating capacity achieved with a given swept volume is about 60% higher with R-32 than with R-717. Also like carbon dioxide, the pressure ratio required for a particular temperature lift is rather lower for R-32 than R-717, for example a lift from -25°C to $+35^{\circ}\text{C}$ produces a pressure ratio of 8.92 in R-717 but only 6.54 with R-32. This suggests that compressors will tend to be more efficient for R-32, although of course many other factors are relevant too. The ratio of specific heats (or index of compression) is relatively high for both compounds, and much higher than for most other fluorinated compounds, so the scope for single stage compression without excessive discharge temperature is limited. In this respect R-32 again is slightly better than R-717. The pressure – temperature curves for carbon dioxide (R-744) and R-123 are also given, for comparison, in Figure 1, illustrating that R-32 and ammonia are relatively close compared to the range of fluids used as refrigerants.

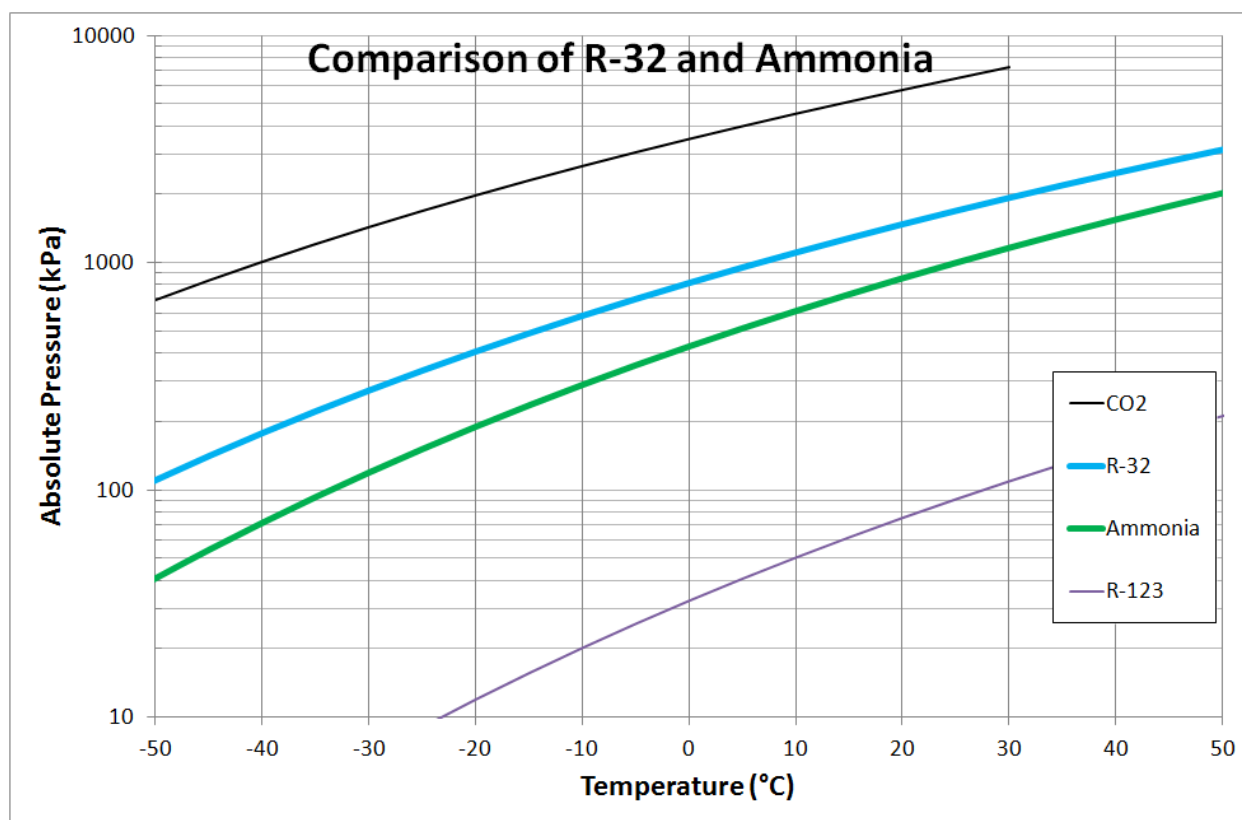


Figure 1: Pressure – temperature curves

It has been observed that smaller, lighter molecules tend to have a more symmetrical “dome” when the saturated liquid and vapour lines are plotted on a pressure-enthalpy graph. The extent to which the dome is skewed has two consequences in the design of refrigeration systems. Firstly the amount of superheat produced by compression is greater if the dome is less skewed. In extreme cases, when the dome is very skewed, for example with R-245fa, it is even possible to produce wet compression, i.e. to cross the saturated vapour line during the compression process, if the suction gas is not sufficiently superheated. Secondly, the extent to which subcooling of the condenser outlet is

beneficial, for example by economizing a screw compressor, depends on the extent to which the dome is skewed. Table 2 shows some of the common refrigerants including the molecular weight and a “skew factor”, ψ , which is defined as the enthalpy difference between the critical point and the centre of the latent heat at atmospheric pressure, expressed as a fraction of the latent heat, as shown in equation (1)

$$\psi = \frac{H_c - H_m}{L_a^*} \quad (1)$$

* L_a is the latent heat at atmospheric pressure except in the case of carbon dioxide where it is taken as the heat of vaporisation at the triple point

Table 2: Molecular weight and skew factor for various refrigerants

Refrigerant	Mol wt.	Crit P (kPa)	H_c (kJ kg ⁻¹)	H_f (kJ kg ⁻¹)	H_g (kJ kg ⁻¹)	H_m (kJ kg ⁻¹)	ψ
CO ₂	44	7377.3	332.25	80.21	430.45	255.33	0.2196
R-717	17	11333	1262.38	190.75	1561.01	875.88	0.2821
R-32	52	5782	414.15	114.18	496.32	305.25	0.2850
methane	16	4599.2	415.59	-0.56	510.56	255.00	0.3142
ethane	30	4871.8	438.26	-0.59	489.20	244.30	0.3960
R-22	86.5	4990	366.90	153.70	387.62	270.66	0.4114
R-134a	102	4059.28	389.64	165.44	382.60	274.02	0.5324
R-125	120	3617.7	318.06	143.04	307.29	225.17	0.5655
propane	44	4247.09	558.75	99.35	525.49	312.42	0.5780
R-245fa	125	3640	463.06	219.01	415.89	317.45	0.7396
butane	58	3796	694.91	197.92	583.24	390.58	0.7898

The skew factor indicates the extent to which the critical point is offset from the middle of the phase change path; if $\psi = 0$ then the critical point is directly above the midpoint and if $\psi = 0.5$ the critical point is directly above the saturated vapour line. Where $\psi > 0.5$ adiabatic expansion from the critical point would result in superheated gas at atmospheric pressure because H_c is greater than H_g . R-717 and R-32 have very similar, and very low skew factors. This indicates that they are unlikely to produce wet compression, they will have relatively high compressor discharge superheat and they will not benefit much from additional subcooling (compared with more skewed refrigerants such as R-134a).

2. FLAMMABILITY

Both of the compounds are flammable, and both are classed as 2L (lower flammability) in ISO817 and related standards. The limits which define this class are that the heat of combustion (HoC) is less than 19,000 kJ kg⁻¹, the lower flammable limit is greater than 3.5% v/v and the burning velocity (as measured by an approved test) is less than 10 cm s⁻¹. These classifications are found in ISO817:2014. Researchers have noted that “the combustion behavior of R-32 is quite different from that of propane” (Kataoka *et al*, 1996)

Flammability ratings are specified by the Globally Harmonized System for Classification and Labelling of Chemicals (GHS) which is administered by the United Nations Economic Commission for Europe (UNECE). It is not at first obvious why R-32 has such a more severe flammability rating than R-717 however it would be a mistake to write this off as a classification error. It should be noted that while both gases have a lower flammable limit greater than 13% v/v in air the range between LFL and UFL is 10.5% for R-717 and 16.6% for R-32. The GHS classification of highly flammable applies if the LFL is less than 13% v/v (both gases are higher than this) or the flammable range is greater than 12% irrespective of the LFL. It is therefore its relatively wide flammable range that gives R-32 the “highly flammable” tag. The difference in the NFPA704 codes is perhaps related to the exceptionally high latent heat of R-717 which means that it does not “rapidly or completely vaporize at normal atmospheric pressure and temperature”.

There is also a considerable difference in the substances produced by combustion of the compounds. R-717 produces nitrogen and water when it is fully combusted at atmospheric pressure whereas R-32 produces hydrogen fluoride (HF) and carbonyl fluoride (COF₂) (Smith and Tufts, 1996). The IDLH value of HF is 30ppm (one-tenth of

the value for R-717) and the short term exposure limit for COF₂ is 5ppm (one-seventh of the value for R-717). A key difference therefore in comparing and contrasting combustion events for the two fluids is that the products of combustion for R-717 are more benign than the fuel, whereas the reverse is true for R-32. However neither the refrigerant classification standard ISO817 nor the safety standard ISO5149 (and their related standards) address the issues presented by possible products of combustion so safety in the event of ignition must be ensured by taking measures that are not detailed in those documents.

Table 3: Flammability characteristics of the compounds

Parameter	Units	R-717	R-32
Heat of Combustion	kJ kg ⁻¹	18,600	9,400
Lower Flammable Limit	% v/v	16.7%	14.4%
Burning Velocity	cm s ⁻¹	7.2	6.7
Upper Flammable Limit	% v/v	27.2%	31.0%
Flammable range	% v/v	10.5%	16.6%
NFPA704 Flammability code ¹	-	1	4
GHS Hazard number ²	-	H221	H220
Directive 67/548/EEC Risk Number	-	R10	R11
Risk Phrase	-	Flammable	Highly Flammable
Autoignition temperature	°C	651	648
Products of combustion		N ₂ , H ₂ O	HF, COF ₂

Notes:

1. NFPA704 code 1 means “Materials that require considerable preheating, under all ambient temperature conditions, before ignition and combustion can occur” and code 4 means “Will rapidly or completely vaporize at normal atmospheric pressure and temperature, or is readily dispersed in air and will burn readily”.
2. GHS Hazard number H221 means “Flammable” and H220 means “Highly Flammable”. The key difference between R-717 and R-32 is in the width of the flammable range.

In order to use a flammable fluid in an industrial system in Europe it is necessary to conform to national regulations which are harmonized with the ATEX directive. In the United Kingdom this is the Dangerous Substances and Explosive Atmospheres Regulations (DSEAR) of 2002. Compliance with DSEAR for R-717 systems is described in detail by Young (2015). The main consideration is that all installations require a risk assessment to be conducted. If the risk assessment establishes that a flammable atmosphere cannot occur, or that it will be of limited size and hence the consequence of ignition of that atmosphere is negligible then no further precautions are necessary. However to ensure that the flammable zone is of negligible extent under all conceivable operating conditions (including non-running) it is likely to be necessary to provide a certain level of background ventilation to the equipment in all places where a leak in normal operation can be envisaged. Young conducted extensive modeling of various R-717 leakage scenarios to establish the extent of the zone which might arise in the event of a leak in operation. This modeling used software developed by the Health and Safety Laboratories (HSL) in the United Kingdom, on behalf of the Health and Safety Executive (HSE). A brief check using the HSL software for R-32 leakage scenarios indicated that hazard range for R-32 is slightly lower than for R-717, as is the volume of the hazardous zone. For example, considering a leak of gas at 13 bar (G) through a hole of 0.25mm² cross section the hazard range for R-717 is 0.121m whereas for R-32 it is 0.082m. Since on the other hand the operating pressure for a given temperature condition is somewhat higher with R-32 than with R-717 and the lower flammable limit is slightly less (see table 3) it was concluded that there is no significant difference between the two in terms of the measures which must be adopted to ensure compliance with DSEAR. However it must be clearly understood by all proponents of R-32 as a refrigerant that compliance with DSEAR in the United Kingdom (and equivalent laws in other jurisdictions) is mandatory, not advisory or optional.

3. TOXICITY

There are two toxicity classes in ISO817:2014. They are denoted “class A (lower chronic toxicity)” and “Class B (higher chronic toxicity)” although they are more generally called “non-toxic” and “toxic” respectively. As Paracelsus observed “sola dosis facit venenum” (the dose makes the poison). The threshold between class A and class B is an occupational exposure limit (based on OSHA, ACGIH, TERA or MAK) of 0.04% v/v (400ppm).

The 8 hour time weighted occupational exposure limit recommended for R-717 is 25ppm. For R-32 it is 1,000ppm, as is the case for most class A refrigerants. These values indicate a clear difference between the two refrigerants but as with many “single number” descriptions there is more to it.

The acute toxicity exposure level (ATEL) of R-32 is listed in ISO817:2014 as 220,000ppm (22% v/v) which is the highest value of all the refrigerants listed in Table 5 of the standard. In contrast R-134a has an ATEL of 5,000ppm (0.5% v/v) because it can produce cardiac sensitization. It is normal to use 140,000ppm (14% v/v) as the RCL for refrigerants with high ATEL values as this represents the limit of oxygen deprivation (ODL). This is not done for R-32 because the refrigerant concentration limit (RCL) is determined by the lower flammable limit; the RCL is 29,000ppm, which is 20% of 14.4%. If toxicity calculations are to be performed for R-32 then the ODL of 140,000ppm should be used, not the ATEL.

The acute toxicity exposure level for R-717 is given in ISO817:2014 as 320ppm. The source of this figure is not stated but it is largely irrelevant since the B classification means that R-717 can only be used in industrial systems or in outdoor installations, for example with air-cooled chillers. It is not feasible to use ammonia in a direct system for access category a or b as defined in EN378 and ISO5149 so the ATEL is not used for charge calculations. However for access category c, described as “authorized access” in EN378 which are “Rooms, parts of buildings, buildings where only authorized persons have access” it is feasible to design and construct large direct R-717 systems.

The refrigerant concentration limit for R-32 is equivalent to 300 g m⁻³ whereas for R-717 it is 0.22 g m⁻³.

4. PRICE

The price of R-717 for use in industrial refrigeration systems has been very stable for many years. The price per kg for purchasing wholesale in 59kg cylinders is approximately £1.50 per kg. R-32 is becoming more readily available and is priced at about £6.30 per kg, about the same as R-410A. In comparing prices the effect of liquid density should be borne in mind; a system requiring a certain volume of ammonia liquid would require a higher mass of R-32 to produce the same effect. At -30°C the density of R-32 liquid is 1151 kg m⁻³ whereas for R-717 it is 678 kg m⁻³. Hence in rough terms on a like-for-like basis a system that requires 5,000kg of R-717 to charge correctly will require about 8,500kg of R-32 costing seven times more than the R-717 charge.

5. INDUSTRIAL APPLICATIONS

5.1 Low temperature freezers

R-717 has been used in industrial freezer plants of all types for many years. It generally gives good efficiencies compared with the CFC blend R-502 and the HCFC R-22 which were widely used thirty years ago. Although it is at sub-atmospheric pressure for boiling temperatures below -33°C there is not usually a problem in operating down to about -50°C. The limiting factors on low suction pressure are the size of compressor required, the penalizing effect of suction line pressure drop and the high discharge temperatures which result from operating over a wide pressure ratio. R-32 seems to offer advantages in all these areas, although it has not been used for industrial freezers to date. It is at positive pressure down to -50°C and therefore the suction gas is significantly more dense than R-717, meaning that small pressure drops are less critical. The pressure ratio is lower so discharge temperature is not such an issue. If the refrigeration system only serves one or two freezers with no additional plant then the cost of refrigerant will not be a significant part of the total project cost.

5.2 Cold Storage

The same comments apply to cold stores as to freezers with the added consideration that the system charge is likely to be larger for a distributed cold store than a single freezer system and so the cost disparity for the refrigerant will be more significant. The R-717 charge for a pumped circulation cold store might be 10,000kg which would cost about £15,000 whereas the equivalent system on R-32 would cost over £100,000. There is therefore a greater imperative to develop low charge R-32 systems than R717, even though it is toxicity class A.

5.3 Chillers

Both R-717 and R-32 have a rather low molecular weight so neither is well suited to centrifugal compressors. The higher volumic capacity of R-32 (see Table 1) means that smaller compressors could be used, but the relatively low

critical temperature of R-32 means that it is likely to be significantly less efficient in air-cooled systems, particularly in high ambient temperatures.

5.4 High temperature heat pumps

The efficiency of R-717 systems when used for water heating to 90°C is unrivalled. To reach this temperature with R-32 the system would have to operate transcritically however the form of the isotherms as plotted on a pressure enthalpy chart are less suitable for this sort of operation with R-32 than they are with the more familiar R-744 systems. A comparison of heating coefficient of performance for R-717 and R-32 across the range at which they can be compared is given in Table 4, showing the percentage benefit in efficiency for using R-717, with R-32 as the baseline.

Table 4: Heating CoP (for evaporation temperature of 0°C)

Condensing Temperature	R-717	R-32	Benefit %
45°C	4.76	4.42	7.7%
50°C	4.31	3.94	9.4%
55°C	3.94	3.55	11.0%
60°C	3.63	3.20	13.4%
65°C	3.37	2.90	16.2%
70°C	3.14	2.62	19.8%
75°C	2.95	2.33	26.6%

5.5 Supermarkets

For the same reasons given in 5.5 R-717 is not considered suitable for direct use in supermarket systems, whether in integral cases or a central pack serving display cases. It can be used as the primary refrigerant in secondary systems provided all of the R-717 is kept out of the publicly accessible areas of the store. R-32 could be considered for direct use in cases, but the charge would be restricted to 20% x LFL x room volume with an upper limit of 12kg or up to 60kg if additional measures were used. For large sized systems, although the charge calculation process seems complicated there is in practice no difference between access category a and b or between applications for human comfort and other applications. This charge calculation method was the subject of much criticism in the last version of ISO5149 and it is now under review for possible further revision to try to resolve the adverse comments. However it is by no means certain that the revision will increase the chances of R-32 being adopted for industrial and heavy commercial systems.

5.6 Other applications

Consider the application of these refrigerants to a chilled beam system in a large publicly accessible space. R-717 is not applied in publicly accessible areas such as supermarkets and theatres or in areas such as offices because the restrictions on toxicity class B are so severe that it is impossible to design even a low charge system with a sufficiently low charge. For example the charge of R-717 allowed for a chilled beam system in shopping mall of 3,000m³ would be 660 g. In contrast a charge of 900kg of R-32 would be permitted if toxicity were the only factor. However the refrigerant concentration limit (RCL) for R-32 is lower than the ATEL due to the flammability. If the charge of R-32 permitted for the chilled beam system was calculated based simply on ensuring that the average concentration in the space could not exceed 20% of LFL then it would be restricted to 183kg. In addition there are further constraints based upon the likelihood of the refrigerant pooling or stagnating so the actual limit for the case described would be 12kg (1.5 x m₂ according to the ISO5149 part 1 Annex A method), possibly extending to 60kg if additional safety measures are applied. If the same size of room were treated with chilled beams and used as an office (access category b) there would be no further relaxation in the charge limits if the system was primarily intended for human comfort. However if the same system was primarily for other applications, for example IT cooling in the office environment, then the charge limits would be 25kg, still extending to 60kg with additional measures.

The main advantage of bringing R-32 into use in these applications would be the opportunity to use commercial refrigeration construction techniques in industrial applications, for example use of copper pipe with brazed connections. However for very large systems there are not the pipe sizes and fittings available in copper, brazing

large pipes is more difficult and it is also difficult to get valves and other components for industrial systems with brazing tails. It would be a mistake to introduce many additional flanged joints or a large number of transition pieces. If the suction line on the system needs to be installed in welded steel or stainless steel then it is difficult to justify running smaller bore pipes in copper, unless they can be prefabricated. In this case it is conceivable, particularly for a central plant with a large number of small air-coolers, that the main pipe headers would be installed in steel or stainless steel with branch pipes, valves, fittings, components and air coolers made of copper or copper alloys.

6. HAZARD ANALYSIS

Whenever a substance is present in a workplace and is classed as “dangerous” it is necessary to understand the risks and take appropriate control measures. The Health and Safety Executive in the UK state that dangerous substances are “any substances used or present at work that could, if not properly controlled, cause harm to people as a result of a fire or explosion or corrosion of metal.” In the case of flammable substances reference is made to the CLP regulations (European Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures). Both ammonia and difluoromethane are covered by CLP and so both R-717 and R-32 require conformity with DSEAR.

Step one of this conformity is for the employer to understand the fire and explosion risks, so it is necessary in all cases to complete a hazard analysis. The initial analysis will identify the equipment, its location, the refrigerant and the circumstances under which there might be a release of flammable material. Typical release scenarios include from a relief valve vent, from a compressor shaft seal, from a liquid pump, from a flanged connection, from a threaded connection, from an oil drain or from a fracture or failure that could reasonably have been foreseen. An example of a reasonably foreseeable fracture is where a length of pipe is located close to a vehicular route and is not adequately protected against mechanical damage which could be caused by a vehicle hitting the pipe.

Taking the quantity of refrigerant that can conceivably leak from the system under each of these failure scenarios into consideration and examining each of the areas of the plant which contain the “dangerous substance” a table of potential leakages can be drawn up. This does not need to include every possible leak in every part of the site, but it should be based on the foreseeable “worst case” within the leakage scenarios covered by ISO 60079-10-1. If the leakage scenario is trivial, for example if the charge within that part of the system is so small that it would not be possible to reach 20% of the lower flammable limit if that quantity were transferred to the space in question, then no further action is required. If more refrigerant could leak then an assessment of the likely effect of ignition is required. Where the background ventilation is sufficient to ensure that the consequences of ignition would be of negligible extent (NE) then no further action is required. However if this is not the case then the system designer will need to implement additional measures (which might be as simple as increasing the ventilation rate to ensure that the hazardous zone reduces in size until it can be classed as NE).

Some additional considerations should be built into the R-32 hazard analysis. R-32 is heavier than air and has no odor so it might be appropriate in industrial systems to put refrigerant detectors into occupied spaces, particularly in low lying parts such as cellars, pits and culverts, where leaked refrigerant might accumulate. Flow down to lower floors should be considered even if they are not directly served by the system. Greater care to ensure adequate ventilation of these areas may be required to ensure that a flammable hazardous zone cannot be created. Consideration should also be given to arc discharges and naked flames in these areas as they could result in the build up of toxic decomposition products.

6. CONCLUSIONS

R-32 provides a higher refrigeration capacity than R-717 with the suction side of a refrigerating system at positive pressure down to -50°C. It offers the prospect of miscible lubricants used with semi-hermetic motor-compressors and could lead to simpler, cheaper industrial installations. However the refrigerant itself is not as cheap as R-717 and it could still become a target of climate change phasedown limits as the GWP is 675, classed as “moderate GWP” in the UNEP RTOC report (2014). The risk of a burnout in a centralized semi-hermetic system might lead to the development of low charge modules with a cascade approach for low temperature plant, perhaps coupled with R-

744 as a volatile secondary. The prospect of significant displacement of R-32 by R-717 in the industrial market seems however remote in the short term future because

- It is still too expensive
- Hazard assessment requirements are less well understood
- There is a fear of future HFC phase down
- Industrial equipment is not widely available
- End users are not unwilling to use R-717 in industrial systems
- R-717 has a good track record of safety, efficiency, ease of maintenance and reliability

A significant shift towards greater use of R-32 in the industrial market would therefore only be likely to happen if there was a strong imperative to move away from R-717. This would most likely be on grounds of toxicity but since ammonia is so widely used in other industries and is so familiar and well-understood a sudden move against it seems improbable.

NOMENCLATURE

H	enthalpy	(kJ kg ⁻¹)
L	latent heat	(kJ kg ⁻¹)
P	pressure	(kPa)
ψ	skew factor	(-)

Subscript

c	critical point
f	liquid
g	vapour
m	mid-point

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