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**Dr R. A. Lamb**

# Refrigerant Choices For The Future – Small Industrial Refrigeration Applications


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## Why this topic?

- Provides a summary of the options and choices for small industrial refrigeration systems

### 1 Introduction

The first refrigerants were fluids such as ammonia, hydrocarbons and carbon dioxide. These had challenges including flammability, toxicity and high operating pressures and in the 1930s, Midgley et al [1] worked on the selection of synthetic refrigerants that would address these issues. This resulted in the commercialisation of chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) refrigerants that operated at acceptable pressures and were both non-flammable and non-toxic. Ammonia remained the refrigerant of choice for large industrial applications and CFCs and HCFCs were typically used for commercial and smaller industrial applications.

The link between chlorinated hydrocarbons and ozone depletion in the 1980s led to the phase out of CFCs and HCFCs under the Montreal Protocol. New zero ozone depletion potential (ODP) HFC refrigerants were introduced as replacement fluids both for new installations and retrofitting in existing systems. However, these fluids were found to have high global warming potentials (GWP) and availability is subject to phase down under the F-gas regulation in Europe (Figure 1) and, more recently, the Montreal Protocol across the rest of the world. This raises the question as to which refrigerant(s) will be used for smaller scale industrial applications in the future. The term 'small scale' is defined in this paper as system capacities up to 300kW for medium (MT) and high temperature (HT) applications operating with evaporating temperatures between -15˚C to +10˚C. For low temperature (LT) systems operating down to -40˚C, capacities up to 150kW.

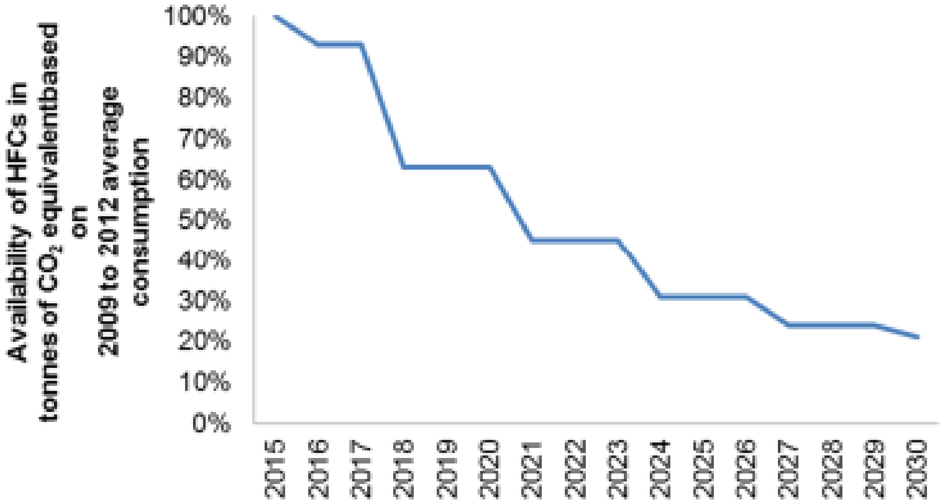


Figure 1: Phase down timetable for availability of global warming refrigerants

### 2 Refrigerant Selection

When considering new refrigerants, much of the work carried out by Midgley still applies today with added environmental restrictions of zero ODP and low GWP. The criteria set out by McLinden and Didion [2] and presented in Table 1 are an ideal starting point for refrigerant selection.

| | |
|---|---|
| Chemical | Stable and inert |
| Health and safety | Non-toxic and non-flammable |
| Environmental | Zero ozone depletion potential (ODP)<br>Zero or low global warming potential (GWP) |
| Thermodynamic and thermophysical | Appropriate critical/boiling point temperatures for the application<br>Low vapour heat capacity<br>Low viscosity<br>High thermal conductivity |
| Miscellaneous | Good oil solubility<br>Low freezing point<br>Reasonable containment materials<br>Easy leak detection<br>Low cost |

Table 1: Refrigerant Selection Criteria

Despite extensive research and development there is no single fluid that satisfies all these criteria and selection involves some level of compromise. Suitable refrigerant options are limited to a narrow group of fluorinated hydrocarbons, hydrofluoro-olefins, blends of these fluids and 'natural' fluids such as ammonia, hydrocarbons and carbon dioxide.

Certain selection criteria are fixed including zero ODP and inert when operating in a system. Other criteria such as critical and boiling temperatures can vary with application. Recent development of new chemical components has included fluids with reduced stability in order to ensure a shorter atmospheric life and lower global warming potential. Many of these refrigerants and their blends are also classified as mildly flammable. These characteristics are undesirable but represent the necessary compromise in order to meet the requirements of environmental legislation. The industry must learn to adapt to new requirements if it is to use alternative fluids but this change also brings opportunities for innovation.

***Health and Safety***
The introduction of flammability as a necessary compromise in refrigerant selection brings a new challenge to equipment manufacturers and installers. Refrigerant flammability classification is detailed in ISO817:2014 and shown in Table 2. The CFC, HFC and HCFC refrigerants used over the past 80 years have been safety Class 1 with no flame propagation at the specified test conditions. No special requirements have been necessary for equipment and installations.

| **Safety Classification** | **Lower Flammability Limit (LFL) % v/v** | **Heat of Combustion kJ $kg^{-1}$** | **Flame Propagation at 60ºC and 101.3kPa** |
|---|---|---|---|
| 1 | No flame propagation at 60°C and 101.3kPa | | |
| 2L lower flammability | >3.5 | <19,000 | Yes and burning velocity <10 cm $s^{-1}$ at 23ºC and 101.kPa |
| 2, flammable | >3.5 | <19,000 | Yes |
| 3, higher flammability | ≤3.5 | ≥19,000 | Yes |

Table 2: ISO817:2014 Safety Classification

It can be seen from Table 3 that moving to lower GWP alternatives below 1000 typically results in a newly developed 2L classification. These fluids exhibit characteristics similar to existing Class 2 in that they have a lower flammability limit >3.5% v/v and heat of combustion less than 19,000 kJ kg-1. The key difference in that the spread of flame is less than 10 cm $s^{-1}$at 23°C and 101.kPa.

The letters A and B that preceded the flammability classification relate to toxicity which is discussed later.

| Refrigerant | Chemical Formula /Composition | GWP (100 year) | Safety Class |
|---|---|---|---|
| R22 | $CHClF_2$ | 1810 | A1 |
| R32 | $CH_2F_2$ | 675 | A2L |
| R125 | $CHF_2CF_3$ | 3500 | A1 |
| R134a | $CH_2FCF_3$ | 1430 | A1 |
| R290 | $C_3H_8$ | 3 | A3 |
| R404A | R125/R143a/R134a (44/52/4) | 3922 | A1 |
| R407A | R32/R125/R134a (20/20/60) | 2107 | A1 |
| R407F | R32/R125/R134a (30/30/40) | 1825 | A1 |
| R717 | $NH_3$ | 0 | B2L |
| R744 | $CO_2$ | 1 | A1 |
| R1234yf | $CF_3CF=CH_2$ | 4 | A2L |
| R1234ze(E) | $CF_3CH=CHF$ | 7 | A2L |

Table 3: Refrigerant GWP and Safety Class

Although ISO817 recognises Class 2L refrigerants as ‘lower flammability’ no such definition exists in the European ATEX directive, which describes what equipment and work environment is allowed in an environment with an explosive atmosphere. Under ATEX there are flammable and non-flammable fluids and 2L refrigerants come under the former. This means that they must conform with national regulations which are harmonised with the directive. In the United Kingdom this is the Dangerous Substances and Explosive Atmospheres Regulations (DSEAR) 2002 which requires a risk assessment to be carried out for all installations using flammable fluids. If this assessment concludes that there is no risk of a flammable atmosphere occurring or the consequence of ignition is negligible then no further action is necessary. To achieve this under all operating conditions, including when the plant is off, requires ventilation to areas where there is potential for leakage. The result is that the measures required for the new 2L refrigerants are similar to those for ammonia installations to satisfy the requirements of DSEAR.

The need to carry out DSEAR risk assessments isn’t something that has been necessary in the past for most synthetic refrigerant installations, as they have been Class 1. This will require education and training of the industry to ensure compliance. It will also add cost to an installation both in terms of carrying out the assessment and incorporating the necessary ventilation and gas detection.

***Toxicity***
ISO817 has two classes of toxicity as seen in table 2. These are denoted as “Class A (lower chronic toxicity)” and “Class B (higher chronic toxicity). The threshold between these two classes is based on occupational exposure limit (OEL) and is set at 0.04% v/v (or 400ppm). Table 4 provides details of refrigerant and their OELs.

| Refrigerant | Safety Class | OEL v/v |
|---|---|---|
| R22 | A1 | 1000 |
| R32 | A2L | 1000 |
| R125 | A1 | 1000 |
| R134a | A1 | 1000 |
| R290 | A3 | 1000 |
| R717 | B2L | 25 |
| R744 | A1 | 5000 |
| R1234yf | A2L | 500 |
| R1234ze(E) | A2L | 800 |

Table 4: Refrigerant Safety Class and OELs

The majority of commercialised refrigerants are Class A including carbon dioxide and hydrocarbons. The notable exception is ammonia which has an OEL of 25ppm, limiting its use to industrial applications or in outdoor installations.

The focus of ISO817 is on the refrigerant but it is also worth considering the byproducts of combustion, particularly as many of the new fluids coming to market are Class A2L. The products of combustion of ammonia are nitrogen and water, which are themselves harmless compared to the fluid itself. The opposite is true for a fluorinated refrigerant such as R32 where the products of combustion are hydrogen fluoride (HF) and carbonyl fluoride ($COF_2$) (Smith and Tufts, 1996). Hydrogen fluoride is a highly dangerous gas, forming corrosive and penetrating hydrofluoric acid upon contact with moisture. The gas can also cause blindness if it comes into contact with eyes and has an immediate danger to life or health (IDLH) value of 30ppm. This is one tenth the level of ammonia. Carbonyl fluoride is similar to phosgene ($COCl_2$) in that it is colourless and highly toxic. It's short term exposure limit of 5ppm is one seventh that of ammonia. These products of combustions must be taken into account when designing refrigeration systems so that in the event of an ignition (or fire), the correct emergency procedures are followed.

## 3 Refrigerant Options

The F-gas regulation means that long term refrigerant solutions need to have low GWP. The available options can be categorised as either single component fluids or blends. Single component fluids include R32, a low GWP HFC, the HFOs R1234ze and R1234yf, ammonia, carbon dioxide and hydrocarbons.

### *R32*

Despite being considered by Midgley et al. during their research in the 1930s, R32 wasn't commercialised. Over the past 20 years it has played an important role as a component in refrigerant blends including the R407 (R32/R125/R134a) series and R410A (R32/R125).
R32 has more recently been used for air conditioning and heat pump applications in Japan, where it has replaced R410A. The need to reduce refrigerant GWPs under the F-gas regulation in Europe has resulted in a number of manufacturers launching R32 air conditioning equipment in 2016. More are expected to follow in 2017. So what about its use in industrial refrigeration?

Pearson [3] considers whether R32 could be a replacement for ammonia in industrial refrigeration systems. R32 has a number of positive attributes including positive pressure operation down to -50°C and 60% higher refrigeration capacity for the same swept volume. It is also compatible with materials used in existing HFC systems, albeit at higher operating pressures than many fluids.

Despite these positive attributes, Pearson concludes that flammability, refrigerant cost, lack of operating experience and uncertainty of the future of HFCs means that R32 is unlikely to displace ammonia for traditional industrial applications.

There is the potential that it could be used in smaller industrial applications where the refrigerant price is offset by the savings of using copper pipework and lower cost equipment.

***R1234yf and R1234ze(E)***
Both R1234yf and R1234ze(E) are isomers of tetrafluoropropene and were developed as refrigerants to replace R134a. R1234yf is used in the automotive industry for car air conditioning whereas ze(E) is used for foam blowing and in packaged chillers and heat pumps. Pearson [4] demonstrated that for a 250kW air cooled water chiller using magnetic bearing compressor technology, the efficiency of R1234ze was higher than R134a across a range of ambient temperatures and load conditions.

The price of R1234yf (between £100/kg to over £400/kg) is likely to limit its use in industrial refrigeration to a component in several new refrigerant blends. R1234ze(E) is more reasonably priced and is likely to be limited to small industrial applications requiring higher temperature packaged chiller and heat pumps.

***Refrigerant Blends***
The limited number of single component synthetic refrigerants has led to development of new multi-refrigerant blends. These consist of two or more components and are a balance of operating temperatures, pressures, efficiency, flammability and GWP. They are typically mixtures of HFC and HFO components and those with GWPs lower than 500 are A2L safety class. Major refrigerant manufacturers are developing their own branded solutions for different applications and are in the process of launching patented products. Table 5 shows a number of refrigerants currently on the market, their composition, refrigerant glide and target applications.

| **Refrigerant** | **Components** | **Composition %wt** | **Safety Class** | **GWP** | **'Glide' K** | **Application** |
|---|---|---|---|---|---|---|
| R448A | R32/R125/R134a/R1234ze/R1234yf | 26/26/21/7/20 | A1 | 1273 1386 | ≈5.5K | LT/MT |
| R449A | R32/R125/R1234yf/R134a | 24.3/24.7/25.3/25.7 | A1 | 1397 | ≈4K | MT/LT LT/MT |
| R-450A | R134a/R1234ze | 42/58 | A1 | 547 601 | ≈0.6K | MT/HT |
| R-452A | R32/R125/R1234yf | 11/59/30 | A1 | 2141 | ≈3K | LT/MT |
| R-454A | R32/R1234yf | 35/65 | A2L | 239 | ≈5K | LT/MT |
| R454B | R32/R1234yf | 69.9/31.1 | A2L | 466 | ≈1.5K | AC/HP |
| R-454C | R32/R1234yf | 21.5/78.5 | A2L | 148 | ≈6K | LT/MT |
| R-455A | R32/R1234yf/R744 | 75.7/21.5/3 | A2L | 145 | ≈12K | LT/MT/HT |
| R513A | R1234yf/R134a | 56/44 | A1 | 631 | 0 | MT/HT |

Table 5: Low GWP Refrigerant Blends

Many of the blends detailed in Table 5 are zeotropic, meaning they boil over a temperature range or 'glide'. This change in saturation temperature during evaporation and condensation varies with components and composition. Additional care is required when designing and commissioning systems using these refrigerants. For example, when commissioning direct expansion systems it is crucial that glide is accounted for when setting up superheat in the evaporator to avoid liquid carry over to the compressor suction. The potential for phase separation in areas of the system must also be avoided as this can lead to a variation in circulation composition, a change in capacity and reduced efficiency.

Through components and system design it is possible to overcome these challenges and develop solutions that deliver enhanced operating efficiency when using refrigerant blends. Work by Bensafi and Haselden [5] and Lamb [6] demonstrated the potential saving when using refrigerant blends with glide in air conditioning and water chiller applications. Their work focused on matching refrigerant glide to the temperature change of the fluid being cooled. Where this is achieved, the temperature lift across the compressor and associated power consumption are reduced for a given cooling capacity. Key to delivering these savings is additional heat transfer area, counter current flow in both the evaporator and condenser and good phase mixing through the evaporation and condensation process.

The proliferation of so many refrigerant blends onto the market is providing a headache for manufacturers in terms of testing and publishing performance information. In many cases, manufacturers are using software to predict refrigerant properties and performance in place of test data in order to keep up. History indicates that over time manufacturers and contractors will narrow down the number of blends use in the majority of applications but it is too early to say if this will happen this time and which fluids these will be.

**R744 - *Carbon Dioxide***

Carbon dioxide was one of the fluids used in early refrigeration but high operating pressures and transcritical operation in warmer ambient meant that it fell out of favour when lower pressure synthetic alternatives became available. Over the past 20 years, it has experience a revival in use due to environmental pressures. As the base fluid for GWP measurement, carbon dioxide is ideally placed to meet the challenges of refrigerant phase down.

Subcritical carbon dioxide systems in cascade with fluids such as ammonia for industrial applications have been described by Pearson and Cable [7] and Blackhurst [8] but the major growth in recent years has been in retail applications. There were more than 5,500 supermarkets operating on carbon dioxide at the end of 2015 and this figure is expected to double in 2016 due to the phase down of HFCs [9]. The rest of the world is expected to follow with growing numbers of $CO_2$ systems in Japan, the US and Canada.

There are examples of $CO_2$ being used in smaller industrial projects. This is certain to increase as end users look to find an alternative for R404A and R507A. Components including compressors, evaporators, gas coolers, valves, pipework, instrumentation and controls are widely available and prices are becoming more competitive as volumes increase. Reduction in pipe sizes with $CO_2$ coupled with the ability to use copper, means that installation costs are also competitive.

An increasing number of manufacturers are offering packaged equipment at capacities ranging from tens to hundreds of kilowatts. System designs include direct expansion single stage for medium/high temperature applications and two-stage for low temperature, often with a medium temperature load (Figure 2). Low pressure receiver systems provide an alternative to direct expansion, ensuring a small overfeed from each evaporator and the ability to maintain system charge at high ambient in the event of power loss. Both systems typically operate transcritically at design conditions but the UK's temperate climate has the benefit of enabling subcritical operation for the majority of the year. This helps boost efficiency. The availability of high grade waste heat is also of benefit for end users requiring hot water for cleaning processes and office heating.

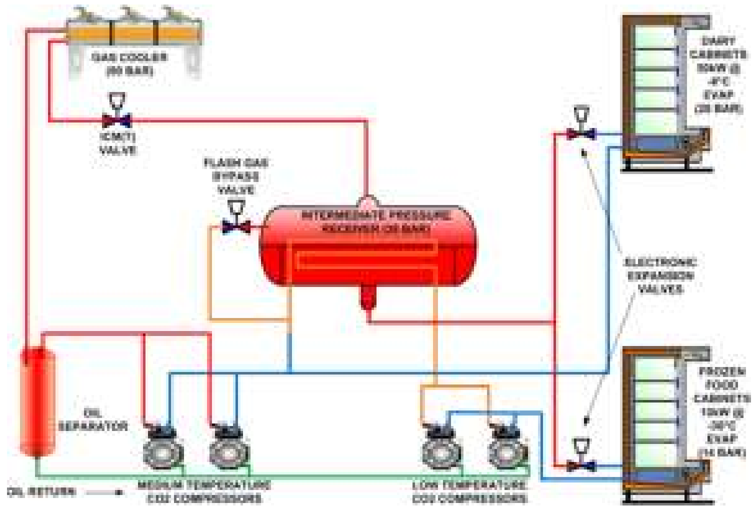


Figure 2: Transcritical Low Pressure Receiver $CO_2$ System

Other solutions include subcritical low temperature $CO_2$ and pumped volatile secondary $CO_2$ (Figure 3) systems, both of which condense against a primary refrigerant system operating with low GWP refrigerants.

Figure 3: Volatile $CO_2$ Secondary Pumping Station

A challenge to its use in small industrial refrigeration is longevity. At present, $CO_2$ packages are built for the retail market and have a life expectancy based around the refresh cycle for a supermarket which is typically 10 years. Industrial end users typically look to invest in equipment with 20+ years life from a new carbon dioxide solution. Experience with larger scale industrial systems indicates that this is achievable but will require a more robust approach to both the package design and installation.

**R717 – *Ammonia***
Despite the challenges of installation cost, flammability and toxicity, ammonia remains the refrigerant of choice for large industrial applications. Its excellent operating efficiency over a wide range of operating conditions from -40°C freezers to +90°C heat pumps is a major factor in its success along with the longevity of installations (typically >20 years).

The development of packaged ammonia chiller solutions has helped reduce the price per kW by reducing costs associated with connection of equipment on site. The complete package is factory assembled, commissioned and shipped to site pre-charged. Once in position, site works are reduced to connecting the secondary pipework and power supply.


Figure 4: Factory testing of a packaged ammonia chiller

The packaged approach has also reduced refrigerant charge and the potential for leakage. Air-cooled and water cooled chiller packages operating in conjunction with secondary fluids (e.g. glycol and brine) can reduce refrigerant charge to less than 0.1kg/kW. This has resulted in its use in smaller industrial projects and in new applications including HVAC, data centres and district heating.

Low charge ammonia is also available for direct applications. Jensen [10] demonstrated that by eliminating storage vessels and reducing circulation rates makes it possible to reduce charge by 75% to 80%. At the same time, it is possible to improve efficiency by 67% [11] through the system design and the use of variable speed technology. Nelson [12] describes how the use of aluminium coils can reduce refrigerant charge in low temperature evaporators by 95% when compared to stainless steel and pumped recirculation. Lamb [13] describes a packaged system using an air cooled condenser and low pressure receiver that provides pumpless overfeed to aluminium evaporators and reduces system charge to less than 0.5kg/kW.

Equipment and installation cost still remains a challenge to the use of ammonia in small industrial applications. The price per kg of new A2L refrigerants and requirements for similar levels of ventilation and gas detection will reduce the gap and is likely to see ammonia being used in smaller applications in the future.

***Hydrocarbons***
Hydrocarbons have historically been limited to petrochemical applications due to their Class 3 flammability rating. The development of low charge, multi-circuited hydrocarbon packaged chillers working with a secondary fluid has enabled refrigerants such as propane to be for HVAC applications. Small charge water cooled packages have also been used for retail applications. The requirements of the ATEX regulation when using hydrocarbons is likely to limit its use to secondary applications and outdoor packages but it will have place, albeit minor, in the small industrial market where customers are averse to using a synthetic fluid and don’t want ammonia due to its toxicity or cost.

**4 Conclusions**

The phase down of HFC refrigerant under the European F-gas regulations requires new solutions to small industrial refrigeration applications. There is no single fluid that will fulfil this requirement and whichever option is selected, it will require some form of compromise.

New synthetic refrigerants will permit the use of existing component technology and are likely to be used in condensing unit and smaller distributed systems. Their classification as A2L fluids under ISO817 will require consideration of flammability and the need for addition ventilation and gas detection. Temperature glide must also be considered for blends but innovation in heat exchanger design could provide attractive energy savings.

Carbon dioxide is likely to play an increasing part in smaller systems due to its low GWP, A1 classification and reducing installation costs. Food processors and process cooling customers may find the opportunity for high grade heat recovery attractive and seasonal efficiencies should be attractive in the UK's temperate climate.

There are likely to be more opportunities for package ammonia solution as innovation drives down the cost of equipment and installation. Reduction of refrigerant charge will also attract end users who have previously been concerned over flammability and toxicity.

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**About Rob Lamb**

Rob Lamb graduated from Leeds University in 1994 with a 1st Class Hons degree in Chemical Engineering. He continued his post graduate studies at Leeds under the supervision of past IOR Geoffrey Haselden, looking into the use of refrigerant blends for energy saving in water chilling applications and graduated with a PhD in 1997. On leaving university Rob joined Star Refrigeration as a Technical Sales Engineer working in Derby, Glasgow and Oxford where he became Regional Sales Director. In 2002 he returned to Derby becoming National Sales Director and in 2010 joined the Executive Board of Star where he currently holds the position of Group Sales & Marketing Director.

Rob chairs the IOR membership committee, represents Star at both the contractors section and council of the BRA council and is a member of eurammon, a European group supporting the wider use of natural fluids in refrigeration and air conditioning.

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