ASHRAE Position Document on Refrigerants and their Responsible Use

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HISTORY OF REVISION/REAFFIRMATION/WITHDRAWAL DATES

The following summarizes this document's revision, reaffirmation, or withdrawal dates:

1/25/2012—BOD approves Position Document titled *Refrigerants and their Responsible Use*

7/2/2014—Technology Council approves reaffirmation of Position Document titled *Refrigerants and their Responsible Use*

Note: ASHRAE's Technology Council and the cognizant committee recommend revision, reaffirmation, or withdrawal every 30 months.

ABSTRACT

Refrigeration and air conditioning provide many benefits to society, but these benefits carry environmental and societal consequences. Many of these consequences stem directly from the refrigerant chosen for each application. ASHRAE has a direct interest in this issue because the operation of refrigerating and air-conditioning equipment depends on refrigerants. Environmental concerns have caused ozone-depleting potential, global warming potential, energy efficiency, and life-cycle climate performance to become important factors. This often results in conflicts between choices: if a lower global warming potential (GWP) refrigerants less efficient than the fluid which it replaces, any direct global warming benefit maybe offset by increased energy consumption. ASHRAE's position is that the selection of refrigerants and their operating systems be based on a holistic analysis of multiple criteria. ASHRAE promotes responsible use of refrigerants and supports the efforts to advance technologies that minimize impact on the environment while enhancing performance, cost effectiveness, and safety.

Note: ASHRAE position documents are approved by the Board of Directors and express the views of the Society on a specific issue. The purpose of these documents is to provide objective, authoritative background information to persons interested in issues within ASHRAE's expertise, particularly in areas where such information will be helpful in drafting sound public policy. A related purpose is also to serve as an educational tool clarifying ASHRAE's position for its members and professionals, in general, advancing the arts and sciences of HVAC&R.

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EXECUTIVE SUMMARY

"Refrigerants are the working fluids in refrigeration, air-conditioning, and heat-pumping systems. They absorb heat from one area, such as an air-conditioned space, and reject it into another, such as outdoors, usually through evaporation and condensation, respectively."

–ASHRAE Handbook—Fundamentals[1]

Refrigeration and air conditioning provide many benefits to society, but these benefits carry environmental and societal consequences, many of which stem directly from the refrigerant chosen for each application. This document represents ASHRAE's position on the selection and management of refrigerants.

Throughout the history of air conditioning and refrigeration, numerous substances have been used as refrigerants. However, choosing a refrigerant has become more complex in recent years. Earlier generations of refrigerants—chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs)—contributed to the depletion of stratospheric ozone and are being phased out under international treaty. CFCs and HCFCs largely have been replaced with hydrofluorocarbons (HFCs). Some of these HFCs have high global warming potentials (GWP) and are becoming subject to use restrictions in some European countries as the world deals with global climate change. Recently, lower GWP HFCs (referred to as hydrofluoroolefins or HFOs) have been introduced. They have zero ozone depleting potential (ODP) and very low GWP, but some of them are mildly flammable.

Natural refrigerants include ammonia, carbon dioxide, hydrocarbons, water, and air. Some of the natural refrigerants have been used in the market place for many decades although at varying degrees of application. Although environmentally superior favorable, natural refrigerants are not free of other concerns, such as corrosion, toxicity, high pressures, flammability, or in some cases lower operating efficiencies.

In addition, the energy that refrigeration systems consume is often produced from fossil fuels which results in emissions of CO_2, a contributor to global climate change. This indirect effect, associated with electrical generation, frequently presents larger environmental carbon footprint impact than the direct effect of refrigerant emissions.

ASHRAE's position is that the selection of refrigerants and their operating systems be based on a holistic analysis of multiple criteria. The criteria must include energy efficiency, system performance, potential impact on community safety, risk to personal safety, and minimization of direct and indirect environmental impacts. Additionally, the economic and social impacts of any fluid should also be considered. Technical and operational efforts to prevent refrigerant emissions must continue to be developed and implemented.

ASHRAE encourages and supports the ongoing effort to develop new refrigerants and improve the application of existing refrigerants to meet these criteria.

ASHRAE is committed to being a leader in the research to develop and advance HVAC&R technologies that enhance performance and safety and minimize negative environmental impact as well as the development of guidelines and standards to reduce direct and indirect emissions while improving energy efficiency.

1. ISSUES

Choosing a refrigerant for a given application has become more complex in recent years. Flammability and toxicity requirements are covered by the ASHRAE safety standards (Standard 15[2], Standard 34[3]) and their international equivalents (ISO 5149[4], ISO 817[5]), and environmental concerns have caused ozone depleting potential (ODP), global warming potential (GWP), energy efficiency, and life cycle climate performance (LCCP) to become important factors for consideration. Some countries have developed regulatory constraints, international protocols, or voluntary agreements in response. Although, conflicts may occur as a result of choices made. For example, if a lower GWP refrigerant is less efficient than the fluid it replaces then any direct global warming benefit maybe partially or totally offset by increased energy consumption. Since the implementation of the 1987 Montreal Protocol, fluids containing chlorine (e.g., CFC-11, CFC-12, HCFC-22, R-502, HCFC-123) have been restricted due to their ODP, resulting in the transition to alternatives such as hydrofluorocarbons (HFCs) and "natural refrigerants". Figure1 shows how the use of refrigerants is evolving.

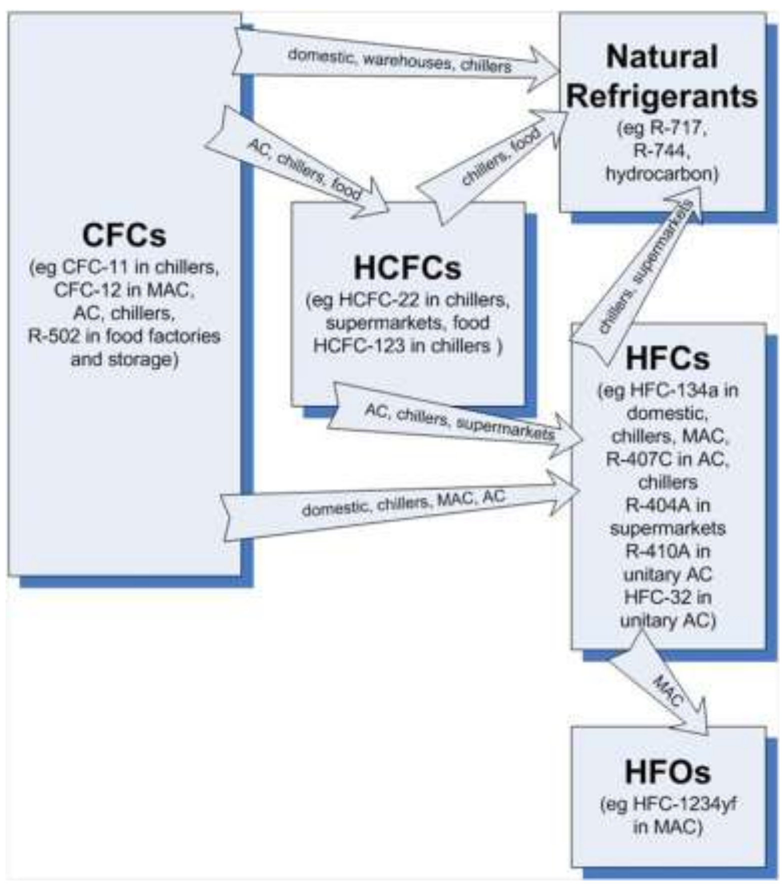

Figure 1 **Map of Refrigerant Change.** This map shows some of the routes that are being taken in the phase-out of CFCs and HCFCs. The process is moving at different speeds around the world: In some countries CFCs are already prohibited, in others their use is in decline as these countries move to complete prohibition. At present, the refrigerants that are likely to be used in the future are the natural refrigerants, the HFCs, the unsaturated HFCs (also known as HFOs), and possibly blends of these refrigerants.

The shift from CFCs was relatively rapid in the developed countries and has been more measured in the developing world. Metrics such as LCCP have been developed to enable comparisons between fluids [6]. (The LCCP methodology includes the environmental impact from the energy used by the refrigeration/air-conditioning system during its lifetime and the life cycle environmental impact of the system's refrigerant.) As such, LCCP can be used as an environmental assessment approach to compare alternative systems. In addition, systems are being designed to reduce the refrigerant charge, and procedures and equipment are being developed to monitor and minimize refrigerant leaks. The emphasis on corporate social responsibility (CSR) from end-users and manufacturers has led to an increased focus on energy efficiency and in some cases, an expressed preference for natural refrigerants. As a result, safety standards have been reassessed and are being updated to reflect the increasing interest in flammable or mildly flammable working fluids.

While each class of refrigerants has favorable performance and/or environmental aspects, none provide an ideal solution. Issues with natural refrigerants include flammability, toxicity, high pressures, or, in some cases, lower operating efficiencies, depending on the fluid. Concern about the high GWP of some HFCs has recently led to calls for a reduction in their use. This is spurring research to extend lower-GWP HFCs into new applications. The reduction has been proposed as a phase-down, however no country has formally adopted a proposal nor is it currently included in either the Kyoto or the Montreal Protocols. At the present time, some hydrofluoroolefins (HFOs) are available in limited quantities, but they are not yet fully tested in all applications. In addition, some HFOs and lower-GWP HFCs have mild flammability. Research is also investigating blends across these refrigerant classes to identify combinations that may optimize performance and minimize negative aspects.

End-of-life disposal of refrigeration and air-conditioning systems is another important issue. At that time, refrigerant should be recovered and recycled or disposed of safely to prevent loss of the charge to the atmosphere.

2. BACKGROUND

Refrigeration and air conditioning provide a broad range of benefits to society, including the preservation of food, comfort conditioning of living spaces and workplaces, and temperature control of industrial processes. The vast majority of refrigeration and air-conditioning equipment operates via the application of the vapor-compression cycle, and such cycles require a working fluid or refrigerant to operate. Refrigerants are thus at the heart of most modern refrigeration and air-conditioning equipment, and the careful selection of refrigerant has a significant impact on the safety, reliability, and energy consumption of the equipment.

A refrigerant must satisfy a number of requirements related to safety, chemical stability, environmental properties, thermodynamic characteristics, and compatibility among materials. There is no single setoff optimum characteristics (especially for thermodynamic properties), and often there are tradeoffs among desirable characteristics. Thus, a variety of refrigerants having a range of properties is needed to meet the requirements of various applications.

A broad range of fluids has been used as refrigerants over the years, and current usage is dominated by a range of fluorinated chemicals, known as HFCs, in addition to hydrocarbons and several inorganic compounds, including ammonia and carbon dioxide (CO_2). An earlier generation of refrigerants, the chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) contained chlorine, and environmental impacts related to ozone depletion resulted in the scheduled phase out of the CFC and HCFC refrigerants under the Montreal Protocol. And now, global climate change concerns have focused attention on the HFC refrigerants; in some countries, the HFCs are facing restrictions in certain applications.

The net climate impact of a refrigerant is dependent on direct and indirect effects. The direct effect is from the global warming impact of a refrigerant emitted to the atmosphere (either from a leak, accident, or from improper handling or disposal). The indirect effect is associated with the energy consumed during the operation of the heating, ventilating, air-conditioning, and refrigerating (HVAC&R) equipment. This indirect effect, which occurs as a result of the CO_2 produced from fossil fuel power plants, is usually much greater than the direct effect due to the GWP of the refrigerant itself. The refrigerant is contained within a sealed system and should not be emitted to the atmosphere at all under normal operation and with proper end-of-life disposal. In actual practice, systems are subject to leakage and breaks and require proper maintenance to minimize losses. Both direct and indirect effects are considered in metrics such as the total equivalent warming impact (TEWI)[7] and LCCP[6]. The total climate impact of a refrigeration system may increase in switching to a lower-GWP refrigerant if the energy efficiency is lower.

A more thorough discussion of the history of refrigerants, the classes of refrigerants and their attributes and tradeoffs, and means of mitigating risks associated with different classes of refrigerants is presented in the Appendix of this document.

2.1 ASHRAE Activities

ASHRAE has a direct interest in this issue because the operation of much of the heating, refrigerating, and air-conditioning equipment depends on refrigerants. ASHRAE contributed to the successful effort to phase out the ozone-depleting CFC and HCFC refrigerants, and it has a significant role to play in encouraging the proper and safe use of refrigerants going forward. ASHRAE is active in the following areas: policy, research, standards, codes and guidelines, and technology transfer and education.

ASHRAE plays a major role in the development of voluntary standards and guidelines governing the application and use of all types of refrigerants. Other organizations adopt the technical requirements developed by ASHRAE into various codes and regulations. The most important ASHRAE standards dealing with refrigerants are ANSI/ASHRAE Standard 34, *Designation and Safety Classification of Refrigerants* [3], ANSI/ASHRAE Standard 15, *Safety Standard for Refrigeration Systems* [2], and ANSI/ASHRAE Standard 147, *Reducing the Release of Halogenated Refrigerants from Refrigerating and Air-Conditioning Equipment* [8].

ASHRAE plays an important role in providing technical information on the proper application of refrigerants and in educating the technical community. These activities are carried out through handbooks, journals, technical meetings, special publications, and educational training. Local ASHRAE chapters also host refrigerant-related programs and speakers. Technical activities in this area are addressed within ASHRAE by the Refrigeration Committee, by committees responsible for the maintenance and revision of the Standards mentioned above, and by numerous technical committees.

ASHRAE is unique among technical engineering societies in sponsoring an extensive member-supported research program. The 2010–2015 research plan for the Society includes items to facilitate the application of low-GWP refrigerants, to investigate methods to reduce refrigerant charge in systems, and to improve system efficiency.

A major focus of ASHRAE's activities is on improving the energy efficiency of buildings. Reducing the heating and cooling load of buildings implies smaller HVAC&R systems with smaller charges of refrigerant and smaller indirect climate impacts resulting from energy generation.

3. RECOMMENDATIONS

ASHRAE acknowledges that HVAC&R systems have environmental consequences and ASHRAE is committed to making these systems more sustainable. Because of their environmental impacts, ASHRAE holds to the principle that refrigerants should be used prudently to provide best value to society.

3.1 ASHRAE's Strong Position

ASHRAE holds a strong position that:

- selection of refrigerants and their operating systems be based on a holistic analysis including energy efficiency and performance attributes; environmental impacts; community and personal safety; and economic considerations (e.g., a refrigerant should not be selected based on any one single factor such as GWP, operating pressure, flammability, etc., a variety of refrigerants are required to meet the range of HVAC&R applications);
- the HVAC&R industry should comply with all applicable regulations;
- refrigerant emissions should be reduced through research, education, improved design and maintenance procedures, and enforcement;
- at the end equipment life, all refrigerants should be recovered for reuse, reclamation or destruction

3.2 ASHRAE's Research Recommendations

ASHRAE recommends that further research be conducted on:

- balancing the safety, energy efficiency, cost, and environmental impact for refrigerants using a consistent and comprehensive methodology across all refrigerants and system types using benchmarks like LCCP, life cycle assessment (LCA) or TEWI;
- advancing the design and development of refrigeration and air conditioning equipment that facilitate reduced refrigerant emissions
- developing methodologies and practices to minimize or prevent refrigerant loss during installation, operation, maintenance, and decommissioning of refrigeration systems;
- developing tools, equipment, and approaches to identify, and thus minimize, refrigerant emissions during system operation
- developing new refrigerants that minimize environmental impacts and safety concerns

3.3 ASHRAE's Commitment

ASHRAE is committed to:

- supporting research to develop and advance HVAC&R technologies that minimize impact on the environment while enhancing performance, cost effectiveness, and safety;
- supporting development of guidelines and standards to improve energy efficiency and to reduce refrigerant emissions;
- supporting responsible refrigerant use through education, information dissemination, and proper technician training;
- being a leader of those dedicated to advancing responsible refrigerant use by working with societies, universities, and government agencies
- promoting responsible use of refrigerants

APPENDIX—BACKGROUND

Refrigeration and air conditioning provides a broad range of benefits to society, including the preservation of food, comfort conditioning of living spaces and workplaces, and temperature control of industrial processes.

The vast majority of refrigeration and air-conditioning equipment operates by application of the vapor-compression cycle wherein a working fluid, i.e., a refrigerant, is alternately compressed and condensed (releasing heat) and then expanded and evaporated (absorbing heat) thereby transferring heat from a low-temperature volume (e.g., a refrigerator) to a higher-temperature volume (such as ambient air). The same process can be used as a heat pump to extract low-temperature heat from an ambient source and "upgrade" it to provide heating. These processes require the input of work (usually in the form of electricity) to drive the compressor and auxiliary fans and pumps. Vapor-compression equipment is responsible for a significant portion of total global energy consumption.

Refrigerants are thus at the heart of most modern refrigeration and air-conditioning equipment, and the careful choice of the refrigerant has a significant impact on the safety, reliability, and energy consumption of the equipment.

History of Refrigerants

Mechanical refrigeration based on the vapor compression cycle was first demonstrated in the 1830s and for the next century a broad range of substances were used; these included toxic compounds, such as sulfur dioxide, as well as refrigerants still in widespread use, such as ammonia. Calm and Hourahan[9,10] characterized this "first generation" of refrigerants as "whatever worked." The widespread adoption of home refrigerators in the 1930s spurred the development of nonflammable and low-toxicity refrigerants, and the CFC (chlorofluorocarbon) and later HCFC refrigerants dominated this "second generation" of fluids.

Ozone Issue and the Montreal Protocol

CFCs and HCFCs contain chlorine, and chlorine in the stratosphere (the region of the atmosphere between about 10 and 50 km above the surface) was established as one of the primary causes of the depletion of stratospheric ozone which led to the formation of the Antarctic ozone hole each spring, along with smaller losses at high latitudes in both hemispheres. Ozone absorbs harmful ultraviolet radiation from the sun, protecting the earth's surface. The mere presence of chlorine in a molecule is not sufficient to threaten stratospheric ozone—the molecule must first be released to the atmosphere and then remain intact in the atmosphere sufficiently long for it to be transported to the stratosphere. A metric termed the ozone depletion potential (ODP) quantifies the destructive effect on ozone of a chemical released to the atmosphere relative to that of CFC-11, which is assigned an ODP value of 1.

On all counts, the properties and usage of the CFC and HCFC refrigerants combined to make them significant contributors to ozone depletion. They contain chlorine. They were relatively inexpensive chemicals and thus there was little incentive to fix leaks or recover them from equipment, leading to emissions to the atmosphere. They have significant atmospheric lifetimes—on the order of decades to centuries.

In response to this environmental concern, the Montreal Protocol on Substances That Deplete the Ozone Layer was adopted in September 1987 under the auspices of the United Nations and entered into force January 1, 1989.It has now been ratified by every member country of the United Nations. The original Protocol called only for a 50% phasedown of the CFCs, but subsequent changes to the Protocol mandate a complete phase out of both the CFC and HCFC refrigerants.

One of the initial responses to the Montreal Protocol was to transition certain applications of CFCs to HCFCs, which have ODP values that are significantly lower than CFCs, although not zero. The transition to HCFCs was recognized as an interim measure and allowed for a rapid phase out of the more detrimental CFCs. Concurrently, a range of HFCs (which have ODPs of zero) and blends of HFCs were developed to meet the requirements of most refrigeration applications. In addition, increased attention was given to reducing emissions from refrigeration equipment and recovering refrigerant during servicing and at disposal; in some cases these are mandated by regulations.

Although the primary purpose of the Montreal Protocol was to protect ozone, it also resulted in a large reduction in greenhouse gas emissions. This is because the CFCs were, as a class, much more potent greenhouse gases than the HFCs that replaced them. The IPCC reports: "In 2010, the decrease in annual ODS emissions under the Montreal Protocol is estimated to be about10 gigatonnes of avoided CO_2-equivalent emissions per year, which is about five times larger than the annual emissions reduction target for the first commitment period (2008–2012) of the Kyoto Protocol." [11].

Global Climate Change: The Kyoto Protocol and F-Gas Legislation

The HFCs are greenhouse gases due to their absorption of infrared (heat) radiation. CO_2 also absorbs IR radiation, but an HFC molecule is more effective than a molecule of CO_2 in contributing to climate change in part because HFCs absorb at wavelengths where the atmosphere is otherwise largely transparent. A metric termed the "global warming potential" or GWP quantifies this effect; GWP values are relative to CO_2, which is assigned a GWP value of 1. This is a time-dependent process, and an "integration time horizon" must be defined for every GWP value; a 100-year time horizon is most commonly used (GWP_{100}).

In response to the impacts that global climate change would have on human societies and the global ecosystem, the United Nations Framework Convention on Climate Change (UNFCCC) was develop data summit held in Rio de Janeiro in June 1992.The UNFCCC did not set limits on greenhouse gases but did provide for updates (or "protocols") that would mandate limits. The first of these was the Kyoto Protocol, which was adopted December 1997 and entered into force in February 2005. The Kyoto Protocol has been ratified by 191 nations; the United States signed the Protocol but has not ratified it. The Protocol set limits for developed countries only for four greenhouse gases (CO_2, methane, nitrous oxide, and SF_6) and two groups of gases (perfluorocarbons and hydrofluorocarbons); emissions of these gases were converted to their CO_2 equivalent (using GWP values), and the emission limits for a given country were in terms of the total CO_2 equivalent. The CFCs and HCFCs were not included because a phaseout of these chemicals was already mandated by the Montreal Protocol. Thus, under the Kyoto Protocol, there are no specific mandates for reductions or phase out of the HFCs or any other refrigerants.

The climate impact of refrigeration equipment is much larger than the direct global warming impact of a refrigerant emitted to the atmosphere (either from a leak, accident, or from improper handling or disposal). Refrigeration equipment consumes energy during its operation, and when this energy is produced by fossil fuels, CO_2 is produced. In some applications, this “indirect” effect of producing energy is much greater than the direct effect due to the GWP of the refrigerant itself. The refrigerant is contained within a sealed system and should not be emitted to the atmosphere at all under normal operation and with proper end-of-life disposal. In actual practice, systems are subject to leakage and accidents and require proper maintenance to minimize losses.

The concept of total equivalent warming impact (TEWI)[7] was developed to include both direct and indirect impacts of refrigeration systems. This has been modified to the LCCP through addition of the (direct and indirect) impacts from refrigerant and component manufacturing. Both TEWI and LCCP are much more complicated metrics than the direct GWP of the refrigerant itself. They must include (and make assumptions about) the energy efficiency of equipment, local CO_2 equivalent of energy generation, system charge, emission rates during operation, average lifetime of equipment, and the recovery (or not) of refrigerant from equipment prior to disposal. TEWI and LCCP values are thus specific to a particular application and may differ from region to region.

HFCs, in all applications, presently contribute only about 2% of the total anthropogenic warming[12]. However, HFC emissions are increasing due to the last of the CFC-and HCFC-based equipment being replaced with HFCs and the increased use of air conditioning worldwide. Assuming “business as usual” with regards to refrigeration and a significant replacement of fossil fuels with renewable energy, the HFCs could account for a significant fraction of total GHG emissions (on a CO_2 equivalent basis) by the middle of the century[13]. This concern has resulted in the European Union enacting regulations covering HFCs, perfluorocarbons, and SF_6 in all their applications. This so-called F-Gas Legislation provides for inspection, recovery, reporting, and training requirements when these gases are used in all but small refrigeration systems. The associated Mobile Air-Conditioning Directive bans the use of HFC-134a in new vehicle models beginning in 2011 and in all new vehicles beginning in 2017.This Directive also requires that the replacement refrigerant must have a GWP_{100} less than 150.

In 2010, the United States co-sponsored (with Canada and Mexico) a proposed amendment to the Montreal Protocol that would phase down by 2033 the use of HFCs to 15% of the combined 2005–2008 consumption of HFCs plus 85% of HCFCs based on GWP weightings[14]. This proposal explicitly recognizes that there are not alternatives for all HFC applications and therefore calls for a phasedown as opposed to a phaseout. The baseline includes HCFCs due to the continuing transition from HCFCs to HFCs. Although the Montreal Protocol addressed ozone depletion, it resulted in a universally accepted program for restrictions on refrigerants, and thus provides a mechanism for including HFCs. A total of 91 countries signaled their readiness to regulate HFCs through the Montreal Protocol by signing a declaration that recognized that the projected increase in the use of HFCs poses a major challenge for the world’s climate system.

These developments have led to renewed and increased interest in natural refrigerants and the development of new low-GWP options, as discussed in following sections.

Requirements of a Refrigerant

A refrigerant must satisfy a number of (sometimes conflicting) requirements as discussed by McLinden and Didion[15].The most essential requirement is chemical stability; a refrigeration system is expected to operate many years, and all other properties would be meaningless if the refrigerant decomposed or reacted to form something else. The next most important criteria relates to health and safety; the ideal refrigerant would have low toxicity and be nonflammable. ASHRAE Standard 34[3] classifies refrigerants according to their toxicity (with “A” being a “lower degree of toxicity” as indicated by a “permissible exposure limit” of 400 ppm or greater, while “B” refrigerants have a “higher degree of toxicity”) and flammability (ranging from “1” for nonflammable fluids to “3” for highly flammable fluids, such as the hydrocarbons). Flammability class“2” has a further subclass (“2L”) for refrigerants of very low flammability, as defined by a burning velocity of less than 10 cm/s. Thus, an ideal refrigerant would be class “A1,” and such refrigerants can be used with minimal health and safety restrictions. Other classes are restricted, such as maximum limits on the system charge or restriction to use in dedicated machine rooms. Such restrictions are enunciated in mechanical codes, many of which are based on ASHRAE Standards 34[3] and 15[2] and corresponding international standards, such as ISO/FDIS 817[5] and ISO/FDIS 5149[4].

Another important set of criteria relate to the performance (i.e., energy efficiency and capacity) of a system. The thermodynamic characteristics (most importantly normal boiling point, critical temperature, and heat capacity) must be matched to the application for the system to operate efficiently. Here there is no single set of optimum values, and a variety of refrigerants having a range of properties is needed to meet the requirements of various applications. Favorable transport properties (low viscosity and high thermal conductivity) have an impact on the size of the heat exchangers and thus cost of the overall system. Energy efficiency, along with the ozone depletion potential and global warming potential are key environmental criteria. Environmental impacts related to ozone depletion drove the phase out of the CFC and HCFC refrigerants. Global climate change concerns have focused attention on the HFC refrigerants. The atmospheric lifetime of a refrigerant affects both ODP and GWP; low values are associated with short atmospheric lifetimes. Here there is often a direct conflict between the need for chemical stability (within the sealed refrigeration system) and the need for chemical breakdown if a refrigerant is released to the atmosphere.

A final set of practical criteria relate to materials and impact the long-term reliability of a system. The refrigerant must be compatible with common materials of construction, including metals and seals. A suitable compressor lubricant must be available.

Classes of Refrigerants

Hydrocarbons and Inorganic Compounds

These include ammonia, CO_2, simple hydrocarbons, and water; they are often referred to as “natural refrigerants.” (Although these molecules are found in nature, generating sufficient quantities for refrigeration requires industrial separation processes or, in the case of ammonia, industrial synthesis.) They have zero ODP and low GWP values. There has been increased interest and application of these refrigerants in recent years, although all of these fluids present one or more drawbacks (such as toxicity, flammability, corrosivity, high pressures, and/or lower efficiency) that require consideration when designing systems.

Ammonia has been used as a refrigerant for more than 150 years. It has excellent thermodynamic characteristics and provides a very high refrigeration effect per mass, but the volumetric cooling capacity is similar to many halocarbon refrigerants. It also has a very high discharge temperature from the compressor, and this has to be taken into account when designing systems. It is applicable to a wide range of cold-side temperatures. Ammonia has a toxicity classification of B according to ASHRAE Standard 34 [3] and has an ASHRAE flammability rating of 2L. It is not compatible with copper and copper alloys.

Ammonia is very common in large beverage processing, food storage, and industrial refrigeration systems where its thermodynamic characteristics and low cost outweigh the regulatory burdens. Interest in small ammonia systems has increased in recent years, and compressors and other components compatible with ammonia are commercially available. For additional information see the [ASHRAE Position Document on Ammonia as a Refrigerant] [16].

Absorption chillers with ammonia/water mixture are suitable and cost effective for some specific applications, especially using a waste heat, in Combined Chilling, Heat and Power (CCHP) systems and district cooling.

Ammonia used in refrigeration is produced as anhydrous ammonia for fertilizer. Ammonia has a production process has a carbon equivalent of 2 kg CO_2 eq per kg[17].

CO_2 is nonflammable and has low toxicity; its ODP is zero, and it has a GWP_{100} of one; it has an ASHRAE classification of A1. The pressure/temperature characteristics of CO_2, however, have two major implications for refrigeration system design. First, it operates at very high pressures, approximately ten times the pressure of halocarbon or ammonia systems. Second, the low critical temperature of 31.0 ˚C implies a trans-critical cycle in many applications requiring direct heat exchange with the outdoor environment. While transcritical operation may lead to low operating efficiency at higher ambient temperatures in cooling mode, a trans-critical cycle, with its gliding temperature across the condenser gas cooler, can increase the efficiency of applications such as water-heating heat pumps that have gliding temperatures of the sink fluid. The high operating pressure simply a dense refrigerant that requires smaller piping and compressor sizes and reduced penalties from pressure drops can yield operation and design benefit particularly when evaporator temperatures drop to the -30 to -50°C..

CO_2 has been used as a refrigerant since the mid-19th century, but was largely displaced by ammonia and the CFC and HCFC refrigerants by the mid-20th century. There has been a resurgence of interest since the early 1990s as an alternative to the halocarbon refrigerants. It is being used in heat pump water heater applications (primarily in Japan). CO_2 is experiencing high growth in supermarket refrigeration systems either in a transcritical cycle or in the low-temperature stage of a cascade system that allows this refrigerant to operate in a sub-critical mode (i.e. a normal vapor-compression cycle). CO_2 is also being used as the heat-transfer fluid in secondary heat-transfer loops (also termed “pumped CO_2”).

The carbon dioxide used as a refrigerant is generally of industrial or scientific grade, and is typically recovered from the waste streams of industrial processes. The embedded energy required to reclaim, clean, liquefy and transport carbon dioxide is estimated to have a carbon equivalent of 1 kg CO_2 eq per kg [17].

Hydrocarbons are constituents of natural gas and petroleum. The most common hydrocarbon refrigerants are propane, butane, and isobutane. They generally have good thermodynamic properties. Hydrocarbons with a wide range of boiling points are available to meet refrigeration requirements over a wide range of temperatures. These refrigerants have zero ODP, low GWP, and are generally of low toxicity. However, they are highly flammable, and this is the major impediment to their wider use.

Hydrocarbons have long been used for process refrigeration in the petrochemical industry; here flammability of the refrigerant is not an issue because the products being produced are of similar hazard. Household refrigerators using isobutane as the refrigerant were introduced in Europe in1992 and now account for more than one-third of global production. The growth of hydrocarbons as refrigerants is rapid in China and India, countries with high GWP tax on refrigerants (Australia) are also adding hydrocarbons to mainstream use. The growth of hydrocarbons is limited by the current state of safety training for service personal and the additional costs involved in flammability safety mitigation.

Hydrocarbons used as a refrigerant are generally of industrial or scientific grade. They are recovered from the natural gas industry and the embedded energy required to clean, liquefy and transport are less than a carbon equivalent of 1 kg CO_2 eq per kg [17].

Water could be considered the ultimate in safe and environmentally benign refrigerants, but it has a very low vapor density, requiring large compressor and piping sizes. Pressure drops across components extracts a larger efficiency penalty compared to higher-pressure equipment. The equipment operates under a vacuum posing the problem of drawing air into a system. Development of prototype vapor-compression equipment using water is underway for large chilled-water systems (such as those used in large building air-conditioning).Water is used in absorption-type refrigeration equipment (with lithium bromide as the absorbent), but this type of refrigeration cycle has low energy efficiency and is typically used only when a waste heat source is available at very low cost. The lower temperature limit for water is 0˚C.

Halocarbon Refrigerants

The halocarbon refrigerants include one or more of the halogens (i.e., the elements fluorine, chlorine, or much less frequently, bromine or iodine) in a molecule with a carbon backbone. These chemicals were first commercialized in the 1930s and include CFCs (i.e., containing carbon, fluorine, and chlorine), HCFCs (also containing hydrogen), and HFCs (which do not contain chlorine).

The most commonly used CFCs used CFC refrigerants were CFC-12 and CFC-11. CFC-12wasusedinamultitudeof applications ranging from automotive air conditioning and various refrigeration applications to large centrifugal water chillers. It possessed very good performance characteristics and was widely available and affordable. The refrigerant application of CFC-11 was in low-pressure centrifugal chillers. As discussed previously, the production of these refrigerants was phased out by year end 1995 in developed countries and by year end 2009 in developing countries due to their impact on stratospheric ozone.

The most common HCFC is HCFC-22. It was extensively employed in a wide array of stationary air-conditioning systems that ranged from small window units, ducted and duct-less split systems, to large screw water chillers and even some very large centrifugal chillers. It also found use in a number of refrigeration applications from walk-in coolers/freezers to large industrial refrigeration systems. It performs well over a wide range of application temperatures. Its only performance drawback is a high compressor discharge temperature when applied in low temperature refrigeration systems. As mentioned previously, it does have an ODP (0.055) and is being phased out. No new equipment containing HCFC-22 is being produced in the US, Europe and Japan. HCFC-123 replaced CFC-11 in low pressure centrifugal chiller applications. Chillers using this refrigerant have very good efficiency. Both the ODP and GWP of this refrigerant are quite low (0.02 and 77 respectively), but it is scheduled to be phased-out under the Montreal Protocol in the developed countries for new equipment in 2020. It is classified by ASHRAE as having higher toxicity (“B1”), but this has not been an issue in low emission equipment such as chillers which are typically located in machine rooms.

The most common HFCs in use are HFC-134a and the blended refrigerants R-410A, R-404A, and R-507. HFC-134a is currently being used for automotive air conditioning, in small refrigeration systems such as home refrigerators and vending machines, and in larger water chillers where screw and centrifugal compressors are employed. R-410A (a blend of HFC-32 and HFC-125) is used in many residential and small commercial air-conditioning systems as the replacement for HCFC-22. It operates at approximately 50% higher pressure, which dictates redesign of equipment, but this higher pressure does allow for more compact equipment to meet specified efficiency targets. In some equipment where redesign was not practical, a blend of HFC-32, HFC-125, and HFC-134a (designated R-407C) is used. This refrigerant operates at pressures that are similar to HCFC-22. The only drawback of this refrigerant is the higher temperature glide that can cause fractionation concerns and its somewhat lower efficiency relative to either HCFC-22 or R-410A. R-404A (R-125/143a/134a) and R-507 (R-125/143a) are used in commercial refrigeration systems such as supermarkets and replace R-502 (a CFC/ HCFC blend). Their low discharge temperature allows reliable operation of low temperature systems, however their efficiency is somewhat less than HCFC-22 in medium temperature refrigeration application and their GWP_{100} are fairly high (above 3900). Lower GWP HFC blends (e.g.R-407A) have been used mainly to retrofit and replace older HCFC-22 systems but have also been used in place of R-404A.

In an attempt to retain the desirable properties of the widely used HFC refrigerants, but with low GWP values, a new class of HFCs has recently been introduced. These incorporate a carbon-carbon double bond into the molecular structure; thus they belong to the chemical class of “olefins” and these new refrigerants are termed HFOs, for “hydrofluoroolefin.” The double bond provides a mechanism for rapid degradation in the atmosphere, leading to low GWP values. As of early 2011, two such HFOs (HFO-1234yf with a GWP_{100} of 4 and HFO-1234ze (E) with a GWP_{100} of 6) have been publicly disclosed; additional HFOs are under development. These two fluids have low toxicity and very low flammability (ASHRAE classification A2L). HFO 1234yf is offered as a low-GWP option for automotive air-conditioning applications, and has been approved for this use in the US. The HFOs are being actively investigated for many other applications, but much research remains to determine their application suitability.

Fluorocarbons and fluoroolefins are specially made for the application in air conditioning and refrigeration systems. The embedded energy required to manufacture these materials are typically about a carbon equivalent of 9 kg CO_2 eq per kg[17].

Lower-GWP Options

There is no generally accepted definition for what constitutes a “low-GWP” refrigerant. A regulatory inferred definition comes from the MAC directive of the European Union, which stipulates that only refrigerants with a direct global warming potential of 150 or lower (relative to CO_2 on a 100-year time horizon) may be used in automotive air-conditioning systems. This is an arbitrary value that was chosen to allow the use of HFC-152a but this is not based on a rigorous analysis nor does it denote an environmentally benign refrigerant. It should be noted that this limit was set only for auto air-conditioning applications, which are generally more leak prone than many other applications.

The UNEP Technical Options Committee for Refrigeration, Air-conditioning, and Heat Pumps [18] proposed seven groups based on the refrigerants GWP* and defines low-GWP as less than 300. These GWP groups, although proposed in 2010, have not been adopted by others. The difficulty arises from the fact that based on the current refrigerants in use each application has a different baseline and what constitutes '"low-GWP" is often referenced to the refrigerant that has traditionally been used in that application. It should be noted that the proposed amendment to the Montreal Protocol by the U.S., Canada, and Mexico does not set GWP limits but instead would introduce a GWP-weighted phase-down of all HFCs. This would allow flexibility for multiple GWP options as long as a country remains below its reduction target.

The refrigerants currently being evaluated to replace the higher-GWP HFCs all have drawbacks. HFC-32 has a GWP_{100} value of 675, and, like HFO-1234yf and HFO-1234ze (E), has an ASHRAE classification of A2L, which means that it is mildly flammable. Of the refrigerants with a GWP_{100} value less than 150, HFC-152a and the hydrocarbons are flammable. Ammonia is toxic. CO_2 operates at very high pressures and, often, in a trans-critical cycle (with generally lower efficiency).

In addition to the HFOs used as single-component refrigerants, blends of HFOs with conventional HFCs are being investigated. Such blends are tailored to match, as closely as possible, the characteristics of current refrigerants and thus meet the requirements of various applications. These blends have GWP_{100} values higher than the HFOs but lower than the HFCs they are intended to replace.

As pointed out earlier in this report, GWP should not be used as the sole criterion of environmental acceptability. If a lower GWP refrigerant is less efficient than the fluid which it replaces, any direct global warming benefit maybe offset by increased energy consumption. It is also clear that in order to meet the range of HVAC&R applications, a variety of refrigerants are required.

Mitigation of Risk

Risks of all types can be lessened by reduction of total system charge. Smaller charges can reduce the safety risks of a flammable refrigerant (a gas will not ignite in air below a finite concentration known as the "lower flammability limit" or LFL), and may allow the use of such refrigerants in many more applications. Reduction of charge would reduce the environmental consequences of refrigerant release due to leaks, accident, or improper disposal.

Ideally, refrigerants should not be emitted from equipment during normal operation. In practice, refrigerant losses are a function of system size, design, installation, and maintenance of the equipment. In general, small factory-sealed systems such as refrigerators can operate to the end-of-life without loss of refrigerant charge. Automotive air-conditioning systems may require recharging due to losses through hoses. Larger field-erected systems, such as those used in supermarkets, are more vulnerable to refrigerant losses due to the magnitude of components and piping required to meet their refrigeration loads. Proper design, fabrication, installation, maintenance and disposal procedures can greatly reduce the emissions and environmental impact of refrigerants.

*- The 2010 Assessment Report of the Technical Options Committee for Refrigeration, Air-conditioning, and Heat Pumps, published by UNEP, has proposed a classification scheme that distinguishes between very low (or ultra-low) with GWP ≤30,very low with GWP ≤100,low with GWP ≤300, moderate with GWP ≤1000, high with GWP ≤3,000,very high with GWP ≤10,000,and ultra-high with GWP ≤10,000.

To address these issues, ASHRAE has published Standard 147,*Reducing the Release of Halogenated Refrigerants from Refrigerating and Air-Conditioning Equipment*[8]. An example of a best practices guide is also available from the EPA[19].

One strategy for reducing both system charge and emissions that has been successfully applied in supermarkets is to locate the refrigeration equipment outside or in a machine room with heat exchange loops circulating a secondary coolant (e.g., CO_2 or a glycol/water solution) to the refrigerated display cases. This approach can also be applied to other systems, and requires good design practice to offset any energy penalty from the additional heat exchange loop [20].

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