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New Refrigerants Impact Standards and Codes

The HVAC industry has gone through tremendous growth and a great number of changes since its inception in the early 1900s. Not only have the hardware and technology evolved, but also the refrigerants used in them. Most, if not all, of the changes have been driven by a need to improve the safety of the end users either directly when technicians or other people come into contact with the equipment, or indirectly by affecting the environment.

Manufacturers, design engineers and legislators have addressed various issues and continue to do so today. Refrigerants transitioned first from toxic, flammable and unstable substances to safer ones in the form of CFCs and HCFCs. However, they were found to harm the environment by thinning the ozone layer and were gradually banned by the United Nations Environment Programme (UNEP) Montreal Protocol. They were replaced by HFCs, but HFCs were also found to have problems because they were greenhouse gases which contributed to global warming. Refrigerants are now being regulated by an amended version of the Montreal Protocol called the Kigali Amendment.

This newsletter will discuss the Montreal Protocol and its amended version, along with their implementation at the US federal and state level, EPA's strategy for implementation and new emerging refrigerants.

Refrigerants in the HVAC Industry

The first attempts at using the vapor compression cycle in refrigeration and air conditioning relied on available substances at the time. These substances, while able to perform in the system as required to produce cooling, had a number of negative aspects including high toxicity, high flammability (or both) and a chemical instability that resulted in the creation of dangerous by-products when they were released and/or burned. Several fatal accidents and severe injuries were reported during the early days of HVAC system development. It is important to note that today's engineering know-how needed to mitigate safety concerns has vastly improved.

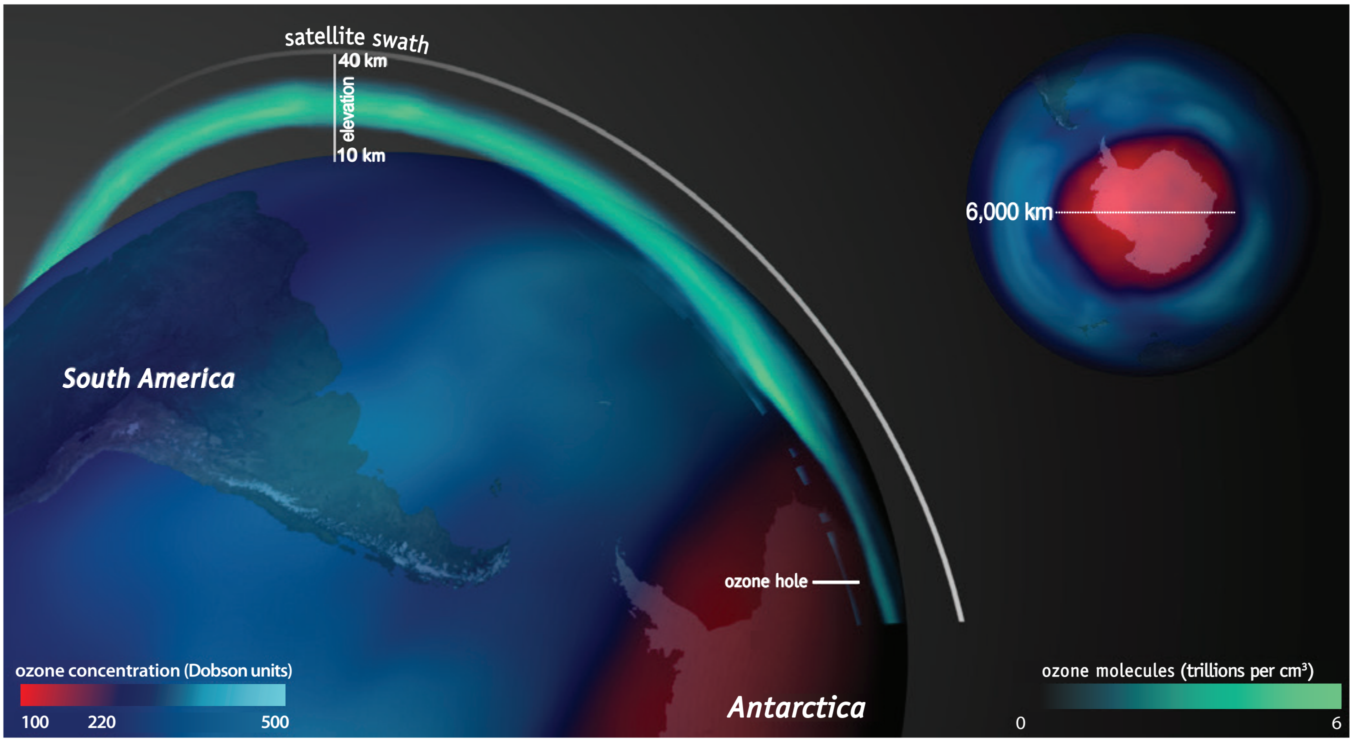
CFC and HCFC Refrigerants: History and Environmental Issues

Thomas Midgley, under the direction of Charles Kettering at the General Motors Research Labs, is credited with the invention of the refrigerants known as Chloro-Fluoro-Carbons (CFCs) in 1928. CFCs and their close relatives, the Hydro-Chloro-Fluoro-Carbons (HCFCs) were the safest non-flammable and non-toxic alternatives to the refrigerants that were then commonly used. CFCs and HCFCs, such as CFC-11, CFC-12 and HCFC-22 for example, almost completely replaced the common flammable and toxic refrigerants used until then, such as Sulfur Dioxide (SO_2), Methyl Chloride (CH_3Cl) and Ammonia (NH_3). These new refrigerants began to be manufactured by the DuPont Company under license from General Motors under the trade name Freon.® In 1932, the Carrier Engineering Corporation released its first unit using Freon as its refrigerant.

CFCs and HCFCs were safe from a flammability and toxicity standpoint; however, in 1974, Frank Rowland and Mario Molina suggested that due to the high stability and lifetime of CFCs and HCFCs they were able to travel to the upper layers of the atmosphere, in particular the stratosphere, where they would decompose due to exposure to UV light and release chlorine atoms. They also proposed a chemical reaction whereby the free atoms of chlorine would eventually break up ozone molecules (O_3) thus reducing the amount of ozone in the stratosphere. This reduction of ozone was responsible for what was termed the ozone hole that was forming over the earth's South Pole (see Figure 1).

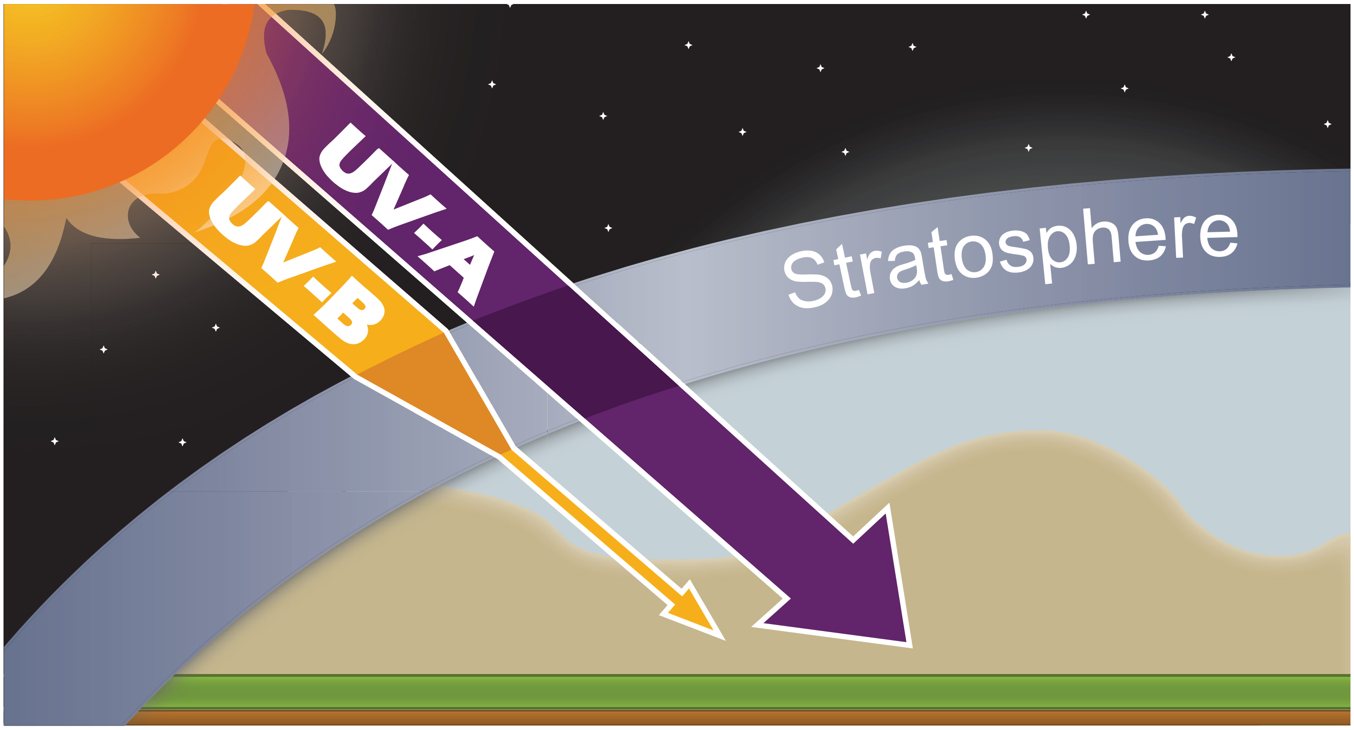
Stratospheric Ozone plays an important role in human quality of life, since it filters a great portion of the UV-B rays entering the atmosphere (see Figure 2) and prevents them from reaching the surface. Excessive UV-B light is linked with adverse health effects ranging from moderate like sunburn to more severe such as eye cataracts, skin aging and cancer, immune system suppression and macular degeneration among others.

Figure 1: A depiction of the ozone hole



(from https://www.climate.gov/sites/default/files/OzoneProject-Layers_lrg.png, an NOAA site)

Figure 2: Effect of the stratosphere's ozone layer filtering UV-B light



The Montreal Protocol

After Rowland and Molina's discovery, the United Nations Environmental Programme (UNEP) organized a series of meetings of scientists and representatives from around the world that culminated in the signing of the "Montreal Protocol on Substances that Deplete the Ozone Layer" in 1987. This treaty is considered as the most successful international agreement ever sponsored by the United Nations. It has been signed and ratified by every participating country and is enforced worldwide. The agreement is responsible for the gradual elimination of all CFCs and HCFCs everywhere in the world. In the US, the only HCFC still in production is R-123 but it will be phased out completely by the end of 2019. No new piece of equipment will be built in the US using either CFCs or HCFCs starting in 2020. This is the case also for every other developed country and many developing countries (referred to as article 5 countries in the treaty). The usage of CFC/HCFC even in developing countries has been drastically reduced and will be completely eliminated within a relatively short time. In practical terms, it means that except for a very few cases, only the CFCs and HCFCs already made or imported can be used for servicing older units, but no new refrigerants of these types can be manufactured.

Hydro-Fluoro-Carbon (HFC) Refrigerants

Due to the ban on production of CFCs and HCFCs, the industry began using HFCs. HFCs, such as R-134a and R-410A for example, are also fluorocarbons, but they do not contain any chlorine atoms in their molecular make up and thus do not destroy the ozone layer. HFCs are considered 3rd generation refrigerants and were intended as the solution tor eplace all applications of CFCs and HCFCs in new equipment.

Natural Refrigerants

Another group of refrigerants, while not new, is enjoying renewed interest in the industry: natural refrigerants. The group is made up of refrigerants that are not synthetized as fluorochemicals are, but rather extracted or refined from naturally occurring sources. The most common ones are ammonia (NH_3), propane (C_3H_5) and carbon dioxide (CO_2). The main advantage to using them is that they pose a minimal risk to the environment if they leak from a system: they cause no ozone depletion and have very low global warming potential. As a disadvantage, their use may require special mitigation for high flammability, toxicity or high operating pressures.

Ammonia (R-717): Typically used in large industrial or commercial refrigeration settings, but can also be found in some chiller applications and even some small appliances. It is incompatiblewith copper and its initial cost is high. It is flammable and toxic. It has good capacity and efficiency and a strong smell detected at very low ppm levels. The use of ammonia has been growing in selected applications.

Propane (R-290): A hydrocarbon (HC) that can be used in a wide variety of refrigeration and air conditioning applications, much like R-22. One of its biggest downsides is its high flammability, rated A3 by ASHRAE. This limits its maximum charge to 150 grams in the US. It is low cost.

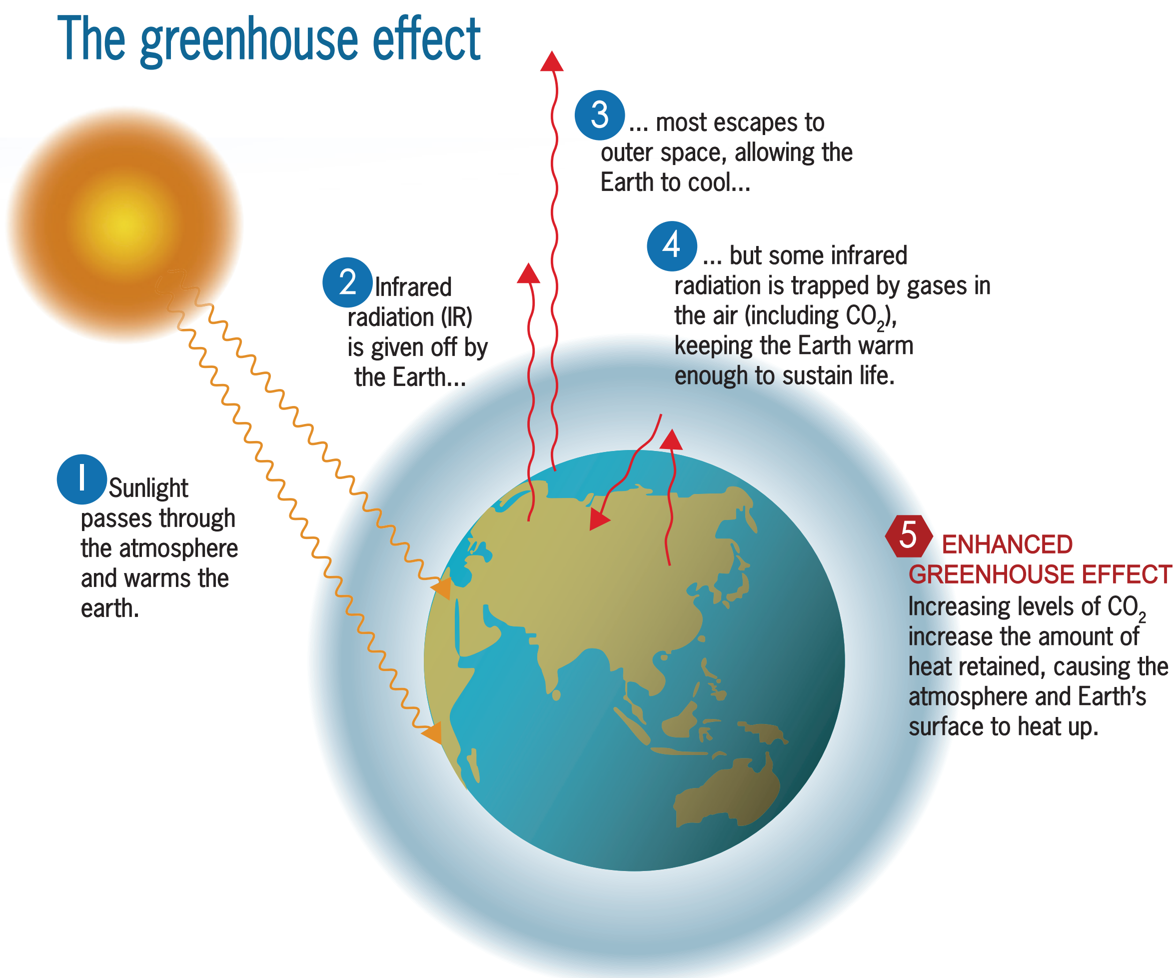
Carbon Dioxide (R-744): This refrigerant is used in very low temperature cascade systems or as a secondary loop fluidwhere it is seeing an increase in use, as in supermarket refrigeration. It suffers rapid performance degradation with increased condensing temperatures but recent technology advances, such as those seen in Carrier's CO_2OLtec® refrigeration products, help overcome this issue.

Global Warming and the Greenhouse Effect

The Intergovernmental Panel on Climate Change (IPCC), an intergovernmental body of the United Nations, published a report in 1995 indicating that man-made greenhouse gases (GHG) were responsible for global warming. Refrigerants, in particular HFCs, were deemed as GHGs and contributors to the greenhouse effect warming up the earth (see Figure 3).

The earth's surface is warmed by sunlight that comes through the atmosphere. At the same time, the earth radiates back to space some heat in the form of infrared radiation (IR). A fine balance between the heat coming in and the heat radiated back maintains a constant average earth temperature. When excessive amounts of greenhouse gases are present, they will trap a larger portion of the heat which will no longer be radiated back out to space. This enhanced greenhouse effect causes the earth to warm up and raises its average temperature. It is estimated that even seemingly small temperature increases (less than 2°F) could have a devastating effect on climate. Scientists attribute some of the climate changes we seem to be experiencing to an increase in the earth temperature.

Figure 3: How the greenhouse effect works



(from the CO2CRC website at http://www.co2crc.com.au/gallery/general-ccs/)

Total Equivalent Warming Impact (TEWI)

It is difficult to evaluate the real effect of a HVAC system to the environment unless a metric like TEWI is used. Other metrics such as Life Cycle Climate Performance (LCCP) can be used as well, but TEWI is the most common one used in the US. TEWI measures the impact of direct emissions (refrigerant leaking from a system) and indirect emissions (caused by generation of electricity at power plants to run a system through its lifetime). The lower the TEWI, the lower impact on the environment.

Reducing the GWP of a refrigerant works on reducing the direct emissions portion, while improving a system's efficiency works on reducing the indirect emissions portion. It is estimated, as a rule of thumb, that for tight systems such as chillers, direct emissions account for about 2% of the total, while indirect emissions account for up to 98%. It is easy to see that while both portions need to be reduced, the key is to improve system efficiency to gain the most benefit from a system change or redesign. Using a lower GWP refrigerant that will result in a less efficient system is not sensible and is counter to the goal of improving the environment. Sensible regulations will deal with both direct and indirect portions of TEWI.

The Kyoto Protocol

Trying to capitalize on the success of the Montreal Protocol, the UNEP sponsored a series of meetings of interested parties that concluded with the drafting of the Kyoto Protocol in December, 1997. The Kyoto Protocol's goal was to reduce the emission of any GHGs, including HFCs, to reduce their effect on global warming. The Kyoto Protocol was signed and ratified by a number of countries (US did not ratify it), but it was nowhere near the success that the Montreal Protocol had been, and while it went into effect, it did not really play a role worldwide since it was not truly enforced. The Kyoto Protocol's complexity made it difficult to verify compliance, to follow, and to enforce.

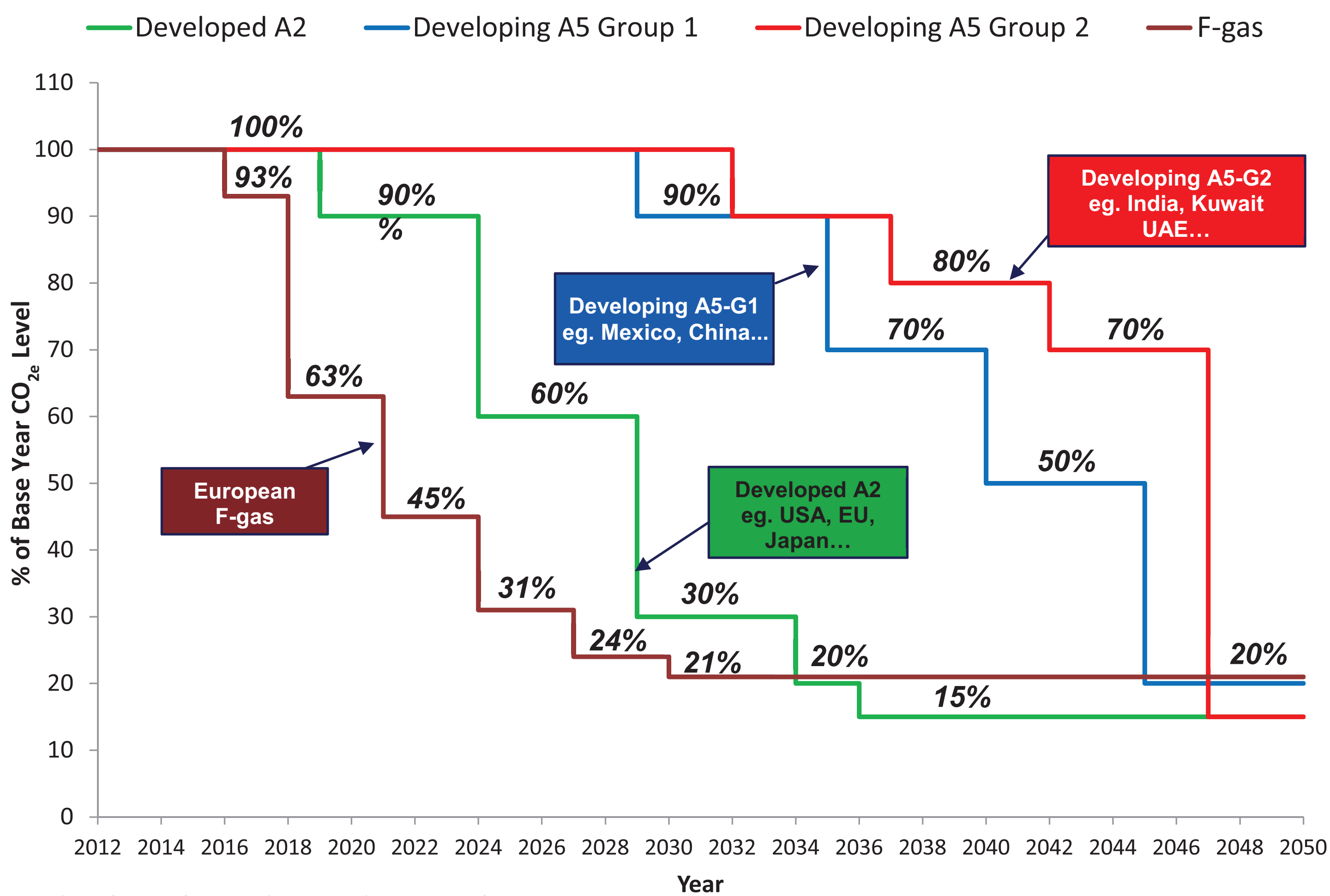
The Kigali Amendment to the Montreal Protocol

In spite of the failure of the Kyoto Protocol, the world community was still interested in curbing GHG emissions. After a great many discussions, the world parties decided to amend the original Montreal Protocol to also include GHG reductions. The agreement, signed in Kigali, the capital of Rwanda, in October of 2016 set very specific reduction levels for HFCs measured in carbon dioxide equivalents (CO_{2eq}). It only regulated HFCs and did not eliminate any specific refrigerants, unlike the original Montreal Protocol that resulted in the elimination of CFCs and HCFCs. In fact, the new amendment did not alter the previously set phase-out of chlorinated refrigerants, which continues to be on track.

The reductions are gradual over approximately 30 years and differ for countries depending on their development level. (Developed countries would see the faster reductions, followed by developing countries, group 1 and group 2). European specific rules that apply to fluorinated gases, known as the F-Gas rules are also shown for reference as well. (See Figure 4.)

Note that no specific refrigerant is singled out for elimination, and in fact HFCs are only regulated but not altogether eliminated. Reductions are based on total carbon dioxide equivalents (CO_{2eq}), which is calculated based on weight of refrigerant times its GWP (CO_{2eq} = wt of refrigerant x GWP). The treaty needed to be ratified by a minimum of 20 countries to go into effect, and that threshold has already been met. The Kigali amendment took effect on January 1st, 2019. For the particular case of the US, it needs to be ratified by the Senate with a 2/3 majority; however, it has not been presented for a vote yet. There is no indication as to if or when this may happen.

Figure 4: Kigali amendment phase down schedule for HFCs by country group.



Based on the Kigali Amendment and F-gas Regulation

The US EPA SNAP and the Courts

International treaties like the Kigali amendment, even if approved by the US representatives, are not US law. Treaties need to first be ratified by the Senate and then codified into laws before they can be enforced. The original portion of the Montreal Protocol was incorporated into the Clean Air Act (CAA) and enforced by the EPA. However, the Kigali Amendment has not been ratified or made into a law, therefore, regardless of whether the treaty has gone into force or not, it is not binding in the US.

The EPA has a program in place called the Significant New Alternatives Policy (SNAP) created under the CAA and used to regulate the use of refrigerants from a safety perspective (not performance). SNAP allows the use of specific refrigerants only in specific types of equipment. Only matched pairs are legal to use. For example, the use of R-410A in residential A/C is a SNAP approved match; however, R-410A in residential refrigeration is not and it would be illegal to use it that way. For a refrigerant to be used in a specific application, a petition has to be made to the EPA, including required supporting information, and the EPA rules whether the match is approved.

In 2014, the EPA began unilaterally delisting refrigerant/equipment applications. The agency was trying to take a proactive role in the regulation of HFCs to reduce their use in the US. A summary of the changes to the program is contained in SNAP Rules 20 and 21. One particular case of the many changes was the delisting of R-134a and R-410A in chiller applications after 2024, but it did not affect the use of R-410A in residential A/C at all.

Two large refrigerant manufacturers, Mexichem and Arkema, sued the EPA in federal court, claiming that it had exceeded its authority granted by the CAA. The claim was that the CAA could only be used to regulate ozone depleting substances but its mandate did not extend to regulation due to global warming concerns. The EPA lost the original ruling and a subsequent appeal. The end result is that Rule 20 has been vacated and Rule 21 is on hold in the Washington DC circuit courts pending a final ruling.

The California Air Resources Board (CARB) supported the EPA during its court battles and pledged to follow the Kigali Amendment reductions and to adopt SNAP Rules 20 and 21 regardless of the federal court rulings. The California legislature has passed bill SB1013 called the California Cooling Act. It adopts all of the provisions of the SNAP rules and sets additional limits for stationary refrigeration and A/C equipment based on charge size and refrigerant global warming potential (GWP) values. Other states such as New York, Maryland and Connecticut have made similar supporting statements, but have not issued any specific rules yet.

A New Generation of Refrigerants: HFOs

In order to cover the gap that a reduction in the availability of HFCs would create, the HVAC industry has developed a new generation of refrigerants called Hydro-Fluoro-Olefins (HFO), such as R-1233zd(E) and R-1234ze(E) for example. They are very similar to HFC refrigerants in their molecular make-up and share the fact that they also have no Chlorine atoms that could cause ozone depletion. However, they have a big difference with HFCs: HFOs have a double bond that makes the molecule more unstable and drastically reduces its atmospheric lifetime. It may seem counterintuitive to use refrigerants that are more unstable; however, that is not an issue when they are in containment in storage tanks or in the system itself. The instability occurs only when the refrigerant is exposed to sunlight if it leaks. Having a lifetime that is measured in days instead of years means that the potential effects of these refrigerants as greenhouse gases is drastically reduced by orders of magnitude. Some of the GWP values of these new refrigerants are referred to as “ultra-low” and their GWP in many cases is in the single digits. However, other HFO refrigerant GWP values may be much higher.

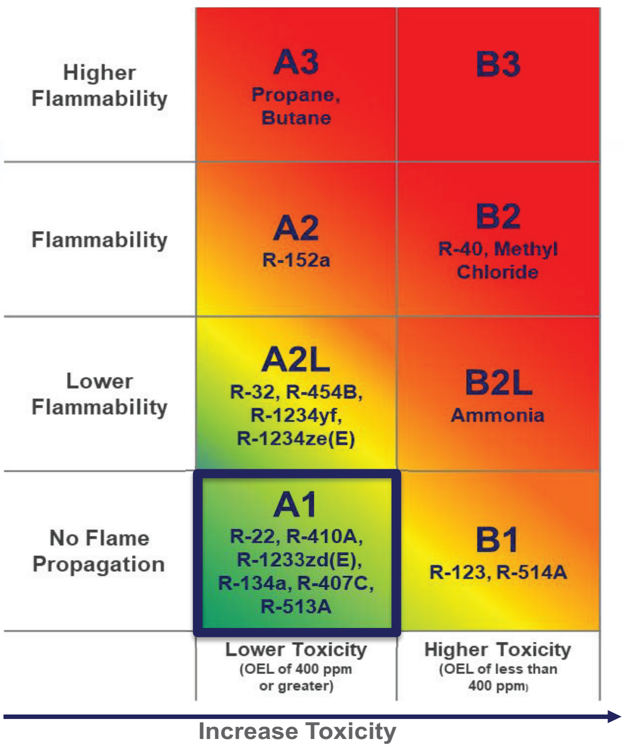
Many new low GWP refrigerants now coming into the market are either pure HFOs or blends of HFOs and HFCs. By mixing selective refrigerants in a blend, it is possible to achieve certain properties that a single refrigerant could not achieve on its own. It is also important to note that by having HFCs as components of these long term refrigerant solutions shows HFCs are NOT being eliminated and are part of the global future solution to global warming.

Refrigerant Safety Classifications

In order to discuss some of the more notable low GWP refrigerants in the market, we will review safety classifications as set by ASHRAE’s Standard 34. (See Figure 5.)

The standard evaluates each refrigerant’s flammability and toxicity and gives it a class referenced as a letter and number combination. For toxicity it has two classes A: lower toxicity and B: higher toxicity. The toxicity class is based on the refrigerant’s Occupational Exposure Limit (OEL) and it assigns refrigerants with an OEL of 400 ppm or greater an A and for less than 400 ppm a B. For flammability, the standard uses data based on the burning velocity (BV), heat of combustion (HOC) and lower flammability limits (LFL) of each refrigerant. A class of 1 would be the lowest flammability and a 3 would be the highest. In recent years, the second class was broken into 2L and 2. A rating of 2L indicates that while the refrigerant is still considered flammable, its flammability is much lower than that of a class 2 or 3.

Figure 5: ASHRAE Standard 34 safety classes



New Replacement Refrigerants in the Market

Table 1 illustrates some of the new low GWP refrigerants emerging in the HVAC market. The list is not all inclusive but just a sample of the most significant players with special emphasis on Carrier systems. Table 1 below shows the composition of those low GWP refrigerants that are blends.

In addition to the refrigerants above, we will also cover the single component HFOs R-1234yf, R-1234ze(E) and R-1233zd(E).

Table 1: Composition in weight percentages of some low GWP refrigerants

	R-454B	R-513A	R-514A	R-1233zd(E)	R-1234yf	R-1234ze(E)
Pure Fluid?	No	No	No	Yes	Yes	Yes
R-134a		44%				
R-32	68.9%					
R-1234yf	31.1%	56%			100%	
R-1130			25.3%			
R-1336mzz			74.7%			
GWP	466	631	3.71	1.34	4	0.97
ASHRAE 34 Rating	A2L	A1	B2	A1	A2L	A2L

Low Pressure Low GWP R-11 Refrigerant Replacements

R-1233zd(E): A low pressure single component HFO replacement for R-11 in new system designs. It cannot be used to retrofit R-11 or R-123 machines. It has an ultra-low GWP of 1.34. It is neither flammable nor toxic so it carries an A1 ASHRAE safety rating. Being a single component it has no glide. Another advantage is that it has high efficiency. Carrier, as well as other chiller manufacturers, have announced new chiller designs with R-1233zd(E). R-1233zd(E) is US EPA SNAP approved for use in low pressure chillers.

R-514A: A low pressure zeotropic blend (having a range of boiling points for a given pressure as opposed to an azeotropic blend that has a unique boiling point) intended to be used as a replacement for R-123. R-514A can be used to retrofit older R-123 units or in new systems. The refrigerant is non-flammable but is toxic, although it has lower toxicity than R-123. It is rated as B1 by ASHRAE. Carrier does not use it, or have plans to use it, in any of its units. R-514A is SNAP approved for use in low pressure chillers.

Medium Pressure Low GWP R-134a Refrigerant Replacements

R-513A: A medium pressure zeotropic blend of a HFO and a HFC. It has a low GWP of 631, just under 50% that of R-134a at 1430. It is mostly intended as a retrofit refrigerant that can be used with relatively minor modifications in R-134a units. R-134a units retrofitted to R-513A can experience a drop in capacity and efficiency, but the losses can be lessened by optimizing the unit and its controls to the new refrigerant. Its safety classification by ASHRAE is A1 (nonflammable and nontoxic) and it is SNAP approved for use in chillers. Carrier has approved its use in several of its R-134a units. Please note that although Carrier has approved the use of R-513A in some of its units, it is not recommending retrofits.

R-1234ze(E): A medium pressure, single component HFO intended as an OEM replacement for R-134a in several of its applications, in particular, chillers. It has an ultra-low GWP of 0.97. With an ASHRAE safety classification A2L, it is non-toxic but slightly flammable. Due to building codes, its use is not allowed in the US; however, Carrier's European division has commercial units based on this refrigerant. The refrigerant is also a component in certain low GWP blends as well. It has a lower volumetric capacity than R-134a, so a higher mass flow rate is required; therefore, it cannot be used as a direct retrofit for R-134a unless modifications to the unit are made.

R-1234yf: A single component, medium pressure HFO replacement for R-134a in certain applications. The most significant use of R-1234yf is in the mobile A/C market, and several new car models already use it. R-1234yf is NOT SNAP approved for use in any chiller application; however, it is used as a component in low GWP blends such as R-513A.

High Pressure Low GWP R-410A Refrigerant Replacements

Replacing R-410A is one of the toughest challenges for the industry so far. There does not seem to be any suitable A1 available replacements for R-410A that matches its properties and performance. Most of the new candidates seem to be either flammable, exhibit lower performance or have compatibility issues. There are no Carrier approved replacements for R-410A in chillers; however, R-454B (Puron Advance™) has been announced by Carrier as a replacement refrigerant for residential and unitary air conditioning applications.

R-454B: A near azeotropic, low GWP blend of an HFC and an HFO medium pressure replacement for R-410A. This refrigerant is not approved for use in any Carrier chillers and it is not SNAP approved for that application. R-454B has been approved by Carrier as a replacement for R-410A in new units but is not approved for R-410A retrofits. (See full announcement posted on the Carrier website). It is marketed as Puron Advance.™ It has an ASHRAE safety classification of A2L, so it is nontoxic but slightly flammable. New units using R-454B are not expected to be commercially available until the 2023 to 2024 timeframe.

Standards and Building Codes

Standards are established to harmonize requirements and guidelines when working with HVAC equipment. Refrigerant, Equipment and Applications standards provide best methods to use and handle refrigerants, design and install new equipment or modify existing installations. By following the standards, engineers are given the tools needed to install, operate, maintain and modify HVAC systems in the safest and most economical way. Standards also align information across installations, trades and sometimes even geographies. ASHRAE and UL are responsible for most of the standards used in the US. CEN (European Committee for Standardization) is responsible for EN (European Norms) standards in Europe. ISO works in conjunction with the international standard writing bodies and tries to develop a harmonized standard. There are also many other standard writing organizations around the world, such as GB for China.

Due to the changes in regulations and treaties like the Kigali Amendment, many of these standards are now being updated to reflect new technologies and products:

ASHRAE Standard 34: A safety standard which has been modified to include a new flammability subclass: 2L (see Figure 5). This class is being used for refrigerants that are still considered flammable and part of class 2, but are at the lowest risk levels. Standard 34 has also been updated to assign safety classifications to a large number of new refrigerants considered low GWP that are coming to the market. While this standard is in continuous maintenance assigning new safety classifications to new refrigerants, its main body is considered complete.

ASHRAE Standard 15: Application standard that has recently been completed and modified to deal with the new flammability subclass, among other changes. While it is considered complete, it will continue to undergo reviews to improve it.

UL 60335-2-40: An electrical safety compliance standard still being modified to incorporate changes due to the new refrigerants in the market, the new safety flammability subclass and charge limits for flammable refrigerants. Work on this standard is not complete.

Update to the Building Codes Revision Process: Standards are the technical basis upon which codes are built. Once all the standards are completed, they are taken up by the groups that write the building codes. They are responsible for revising and modifying the International Building Code (IBC), International Fire Code (IFC) and International Mechanical Code (IMC) that in essence put the standards into a practical, organized, consistent, verifiable and enforceable set of rules. These rules are used by engineers, architects, installers and others to design and install the safest and most cost efficient systems, and by inspectors that verify compliance. It is important to note that while some localities (states, counties, cities, etc.) may just use the IBC, IFC and IMC codes as is, others may modify them in order to make them stricter or to adapt to a particular geographical condition or insurance requirement. Building codes are on a 3-year cycle, which means that for codes to allow for the use of A2L refrigerants in places where they are not allowed now (e.g. chillers in occupied buildings), all the standards need to be finalized by no later than 2021. The consensus seems to be that we are on track to complete all the necessary changes in time.

SUMMARY

The HVAC industry has undergone many changes, especially in the area of refrigerants. The discovery of the ozone hole led to the gradual banning of all CFCs and HCFCs per the original Montreal Protocol. The phase-out is on schedule, and for the US, 2019 is the last year any unit can be shipped with an HCFC (such as R-123).

New regulations, inspired by the modified Montreal Protocol and its Kigali Amendment, are focusing on global warming. There is still a lot of uncertainty as to what the final regulatory outcome will be, but it is expected that use of HFC refrigerants in new chiller equipment will slowly diminish over time as new HFO and HFO/HFC blends emerge. It is important to note that new regulations do not phase out any HFC refrigerants (such as R-134a or R-410A). HFCs can, and will, be used well into the future for many different applications. Further complicating the situation, states in the US are not in agreement with federal policies and may enact their own set of rules (California has already done so).

In the case of chillers, it appears that R-1233zd(E) is the best choice for low pressure systems, with Carrier and some other OEMs already announcing commercial units for sale. Alternatives for R-134a, such as R-513A, are available but come with the potential for lower performance which can hurt the overall TEWI rating. Due to this, retrofits are not recommended at this time. Replacing R-410A is the most challenging as many new candidates are flammable, exhibit lower performance or have compatibility issues. Their use may need changes in building codes due to flammability. Research in this area is still ongoing, with a number of refrigerants being actively evaluated, but R-454B looks promising.

R-134a and R-410A systems still provide some of the best overall options from a perspective of environmental protection and energy efficiency. They should be considered and evaluated when new units are needed.

Finally, work on standards and building codes is progressing rapidly with the goal of being completed by the end of 2023 when units with new refrigerants may be required by state and/or federal regulations.

The HVAC industry continues to evolve and Carrier is always ready for the future.

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United Technologies
turn to the experts