Selection Tips for Environmentally Safe Refrigerants

Course No: C02-026

Credit: 2 PDH

A. Bhatia

Continuing Education and Development, Inc.
22 Stonewall Court
Woodcliff Lake, NJ 07677

P: (877) 322-5800
info@cedengineering.com

SELECTION TIPS FOR ENVIRONMENTALLY SAFE REFRIGERANTS

A refrigerant is a fluid used in a refrigeration system to extract heat at low temperature and low pressure during evaporation and reject heat at high temperature and high pressure during condensation. Fluids suitable for refrigeration purposes can be classified into primary and secondary refrigerants.

Primary Refrigerants: Primary refrigerants are those fluids, which are used directly as working fluids, for example in vapour compression and vapour absorption refrigeration systems. Primary refrigerants provide refrigeration by undergoing a phase change process in the evaporator.

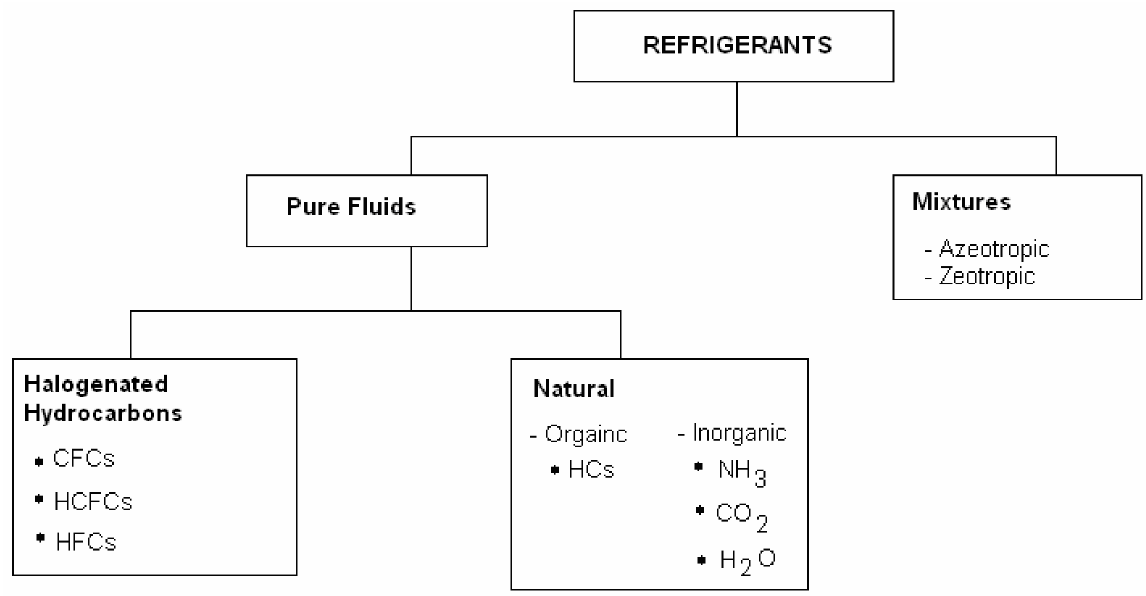
Secondary Refrigerants: As the name implies, secondary refrigerants are those liquids, which are used for transporting thermal energy from one location to other. Unlike primary refrigerants, the secondary refrigerants do not undergo phase change as they transport energy from one location to other.

The commonly used secondary refrigerants are the solutions of water and ethylene glycol, propylene glycol or calcium chloride. These solutions are known under the general name of brines. An important property of a secondary refrigerant is its freezing point. Of course, if the operating temperatures are above 0°C, then pure water can also be used as secondary refrigerant for example in large air conditioning systems. Antifreezes or brines are used when refrigeration is required at sub-zero temperatures. The temperature at which freezing of “brine” takes place depends on its concentration and the concentration at which a lowest temperature can be reached without solidification is called as eutectic point.

In this course attention is focused on primary refrigerants used mainly in vapour compression refrigeration systems.

COMMON REFRIGERANTS

Refrigerants in vapor compression refrigeration systems can be classified as pure fluids and mixtures. Pure fluids are further categorized as halogenated hydrocabons or natural compounds.



Early refrigerants used in vapor compression refrigeration applications were Halogenated Hydrocarbons predominately made up of chlorofluorocarbons (CFCs), Hydrochloro-fluorocarbons (HCFCs) and Hydrofluorocarbon (HFCs).

1) **Chlorofluorocarbons (CFCs)** -The acronym CFC stands for chlorofluorocarbons and refers to family of refrigerants containing chlorine, fluorine, and carbon. Since they contain NO hydrogen, CFCs are chemically very stable, even when released into the atmosphere, these are found to be long-lived in the atmosphere. In the lower atmosphere, the CFC molecules absorb infrared radiation and contribute to atmospheric warming. Once in the upper atmosphere, the CFC molecule breaks down to release chlorine that destroys ozone and, consequently damages the atmospheric ozone layer. Ozone found high up in the atmosphere, called "stratospheric ozone"; 15-40 km above earth surface, helps filter out damaging ultraviolet radiation from the sun. The ozone layer acts like a giant sunshade that shields the earth from the sun's harmful ultraviolet radiation.

   This phenomenon of Ozone Layer Depletion was first observed in 1974 and was largely attributed to chlorine and bromine containing CFC compounds. Owing to harmful effects of ozone layer depletion on a global level, it has been agreed by the global community (under Montreal Protocol - a landmark international agreement designed to protect the stratospheric ozone layer) to phase out the ozone depleting substances (ODS). The manufacture of CFC refrigerants was discontinued after December 31, 1995.

Prior to the environmental issues of ozone layer depletion, the most widely used CFC refrigerants were: R11, R12, R113, R114, R115…. Of these, R11 was primarily used with centrifugal compressors in air conditioning applications and R12 was used primarily in small capacity refrigeration and cold storage applications.

2) **Hydrochloro-fluorocarbons (HCFCs)** - Researchers found that by modifying the chemical compound of CFCs by substituting a hydrogen atom for one or more of the chlorine or fluorine atoms resulted in a significant reduction in the life of the molecule and, thus, reduced the negative environmental impact it may have.

   This category of refrigerants contains both chlorine and hydrogen. Even though they contain chlorine which is damaging to the ozone layer, they also contain hydrogen which makes them chemically less stable when they enter the atmosphere. These refrigerants decompose when released in the lower atmosphere so very little ever reaches the ozone layer. HCFCs, therefore, have a lower ozone-depletion potential. The most widely used HCFC refrigerants are: R22 and R 123. R-22 finds its use in most residential and small commercial air conditioning systems whereas R 123 has wide applications in low pressure centrifugal chillers. HCFC production for use in new equipment in developed countries is mandated to cease in year 2020 with total halt to manufacturing and importing mandated by year 2030.

3) **Hydrofluorocarbon (HFC)** - HFC refrigerants contain NO chlorine. Although these refrigerants have an ozone-depletion potential of zero, they probably still contribute to the global warming problem. Two HFC's that are replacing CFC12 and HCFC22 are HFC134a (Tetrafluoroethane CF_3CH_2F) and HFC410A (HFC32 & HFC125).

   Hydro fluorocarbons (HFCs), are not regulated by international treaty and are considered, at least for the interim, to be the most environmentally benign compounds in HVAC refrigeration systems.

Note that it is the chlorine that makes a substance ozone-depleting; CFCs and HCFCs (partly) are a threat to the ozone layer but HFCs are not.

Generally all halogenated refrigerants used in refrigeration, cold storage and air conditioning applications are non-toxic and non-flammable.

Refrigerant Number Designation

Since a large number of refrigerants exist and have a very complex chemical name, a numbering system has been adopted to designate various refrigerants. From the number, one can get some useful information about the type of refrigerant, its chemical composition, molecular weight etc.

The first step, and one that will provide a valuable way to check the results, is to understand the prefixes CFC, HCFC and HFC.

Prefix	Meaning	Atoms in the Molecule
CFC	chlorofluorocarbon	Cl, F, C
HCFC	hydrochlorofluorocarbon	H, Cl, F, C
HFC	hydrofluorocarbon	H, F, C
HC	hydrocarbon	H, C

Compounds used as refrigerants may be described using either the appropriate prefix above or with the prefixes "R-" or "Refrigerant." Thus, CFC-12 may also be written as R-12 or Refrigerant 12.

Decoding the Number

Now that we understand that the prefix describes what kinds of atoms are in a particular molecule, the next step is to calculate the number of each type of atom.

- The key to the code is to add **90** to the number; the result gives three digits which stand for the number of carbon, hydrogen and fluorine atoms respectively.
- Remaining bonds not accounted for are occupied by chlorine atoms. All of these refrigerants are saturated; that is, they contain only single bonds. The number of bonds available in a carbon-based molecule is 2C + 2 (i.e. for 1 carbon atom, there are 4 bonds; for 2 carbon atoms there are 6 bonds and for 3 carbon atoms there are 8 bonds).
- Chlorine atoms occupy bonds remaining after the F and H atoms.

- A suffix of a lower-case letters a, b, or c indicates increasingly unsymmetrical isomers.

Let's see few examples.

Example #1:

What is the chemical formula of HCFC141b?

141 + 90	=	2	3	1
		#C	#H	#F

Now to decipher number of chlorine atoms:

- C atoms = 2
- Number of bonds = 6 [2C + 2]
- H atoms = 3
- F atoms = 1

Since all of the carbon bonds are not occupied by fluorine or hydrogen atoms, the remainder is attached to chlorine, thus:

- Cl atoms = 6 – (3 + 1) = 2

So HCFC-141b has 2C, 3H, 1F, and 2Cl or the chemical formula for HCFC -141b is therefore **$C_2H_3FCl_2$**

Notice that the HCFC designation (h ydro c hloro f luoro c arbon) is a good double-check on the decoding; this molecule does, indeed, contain H, Cl, F, and C.

The "b" at the end describes how these atoms are arranged; different "isomers" contain the same atoms, but they are arranged differently. The letter designation for isomers is discussed below in another example.

Example # 2:

What is the chemical formula of HFC134a?

134 + 90	=	2	2	4
		#C	#H	#F

Now to decipher number of chlorine atoms:

- C atoms = 2
- Number of bonds = 6 [2C + 2]
- H atoms = 2
- F atoms = 4

There are 6 bonds. But in this case, there are no bonds left over after F and H, so there are no chlorine atoms. Thus chemical formula for HFC 134a is: $C_2H_2F_4$

In this case, too, the prefix is accurate: this is an HFC (h ydro f luoro c arbon), so it contains only H, F, and C, but no chlorine.

Letter “a” stands for isomer, e.g. molecules having same chemical composition but different atomic arrangement. The "a" suffix indicates that the isomer is unbalanced by one atom, giving 1, 1, 1, 2-Tetrafluoroethane. R-134 without the "a" suffix would have a molecular structure of 1, 1, 2, 2-Tetrafluoroethane—a compound not especially effective as a refrigerant.

Assigning a chemical name to the refrigerant number

We can reverse this method of designating a refrigerant by number. The following rules apply:

- Let the refrigerant number is X
- From the chemical formula derive a number in order of Carbon, Hydrogen, Fluorine atoms.
- Find X by deducting 90 in above

Example # 3:

What is the refrigerant number for $CHClF_2$?

- Number of C atoms = 1
- Number of H atoms = 1
- Number of F atoms = 2
- Arrange this in order of C H F = 112

Deduct 90 from above to arrive at refrigerant number;

Refrigerant number = 112 – 90 = 22 or the refrigerant can be designated as **HCFC22.**

<u>Example # 4</u>:

What is the refrigerant number for $CHCl_2CF_3$?

- Number of C atoms = 2
- Number of H atoms = 1
- Number of F atoms = 3
- Arrange this in order of C H F = 213

Deduct 90 from above to arrive at refrigerant number;

Refrigerant number = 213 – 90 = 123 or

The refrigerant can be designated as **CFC123**

<u>Note</u>

Any molecule with only 1C (e.g., CFC-12) will have a 2-digit number, while those with 2C or 3C will have a 3-digit number.

Inorganic or Natural Refrigerants

Inorganic refrigerants do not deplete the ozone layer and find use in industrial applications. These are designated by number 7 followed by the molecular weight of the refrigerant (rounded-off). For example:

- <u>Ammonia</u>: Molecular weight is 17, thus the designation is R717
- <u>Carbon dioxide</u>: Molecular weight is 44, thus the designation is R744

- Water: Molecular weight is 18, thus the designation is R718

Ammonia is one of the oldest known refrigerants that has very good thermodynamic, thermo-physical and environmental properties. However, it is toxic and is not compatible with some of the common materials of construction such as copper, which somewhat restricts its application. Other natural refrigerant carbon dioxide (R-744) have some specific problems owing to their eco-friendliness, they are being studied widely and are likely to play a prominent role in future. Water is refrigerant in the absorption based refrigeration systems.

Mixtures

A number of refrigerants are made up of blends or chemically prepared mixtures of refrigerants. These are called “Azeotropic” mixtures (designated by 500 series) and “Zeotropic” refrigerants (e.g. non-azeotropic mixtures designated by 400 series).

Azeotropic mixtures:

An azeotropic is a mixture of multiple components of volatilities (refrigerants) that do not change volumetric composition or saturation temperature when they evaporate or condense at constant pressure. In simpler terms azeotropic blends act as single substance, are very stable i.e. difficult to separate and have a negligible glide. These can be charged in vapour or liquid state. These refrigerants are designated by 500 series. For example:

- R500: Mixture of R12 (73.8 %) and R152a (26.2%)
- R502: Mixture of R22 (48.8 %) and R115 (51.2%)
- R503: Mixture of R23 (40.1 %) and R13 (59.9%)
- R507A: Mixture of R125 (50%) and R143a (50%)

A near azeotropic is a mixture of refrigerants whose characteristics are near those of an azeotropic. Because the change in volumetric composition or saturation temperature is rather small for a near azeotropic, such as, 1 to 2°F, it is thus named.

Zeotropic mixtures:

Zeotropic or non-azeotropic, including near azeotropic, shows a change in composition due to the difference between liquid and vapor phases, leaks, and the difference between charge and circulation. These can be separated easier than azeotropic mixtures, have some glide and can only be liquid charged.

A shift in composition causes the change in evaporating and condensing temperature/pressure. The difference in dew point and bubble point during evaporation and condensation is called glide, expressed in °F. Near azeotropic has a smaller glide than zeotropic. The midpoint between the dew point and bubble point is often taken as the evaporating and condensing temperature for refrigerant blends. The designated numbers are 400 series:

- R404A: Mixture of R125 (44%), R143a (52%) and R134a (4%)
- R407A: Mixture of R32 (20%), R125 (40%) and R134a (40%)
- R407B: Mixture of R32 (10%), R125 (70%) and R134a (20%)
- R410A: Mixture of R32 (50%) and R125 (50%)

Hydrocarbons:

- Propane (C_3H_8): R290
- n-butane (C_4H_{10}): R600
- Iso-butane (C_4H_{10}): R600a
- Unsaturated Hydrocarbons: R1150 (C_2H_4), R1270 (C_3H_6)

A complete discussion of the number designation and safety classification of the refrigerants is presented in ASHRAE Standard 34-1992.

REFRIGERANT SELECTION CRITERIA

Key considerations for any new refrigerant are chemical stability, toxicity, flammability, thermal characteristics, efficiency, ease of detection when searching for leaks, environmental effects, compatibility with system materials, compatibility with lubricants, and cost. In general, the selection of refrigerant for a particular application is based on the following requirements:

- Thermodynamic and thermo-physical properties
- Environmental and safety properties

Thermodynamic & Thermo-Physical Properties:

The requirements are:

1. **Suction pressure:** At a given evaporator temperature, the saturation pressure should be above atmospheric for prevention of air or moisture ingress into the system and ease of leak detection. Higher suction pressure is better as it leads to smaller compressor displacement.
2. **Discharge pressure:** At a given condenser temperature, the discharge pressure should be as small as possible to allow light-weight construction of compressor, condenser etc.
3. **Pressure ratio:** Should be as small as possible for high volumetric efficiency and low power consumption.
4. **Latent heat of vaporization:** Should be as large as possible so that the required mass flow rate per unit cooling capacity will be small.

The above requirements are somewhat contradictory, as the operating pressures, temperatures and latent heat of vaporization are related by Clausius-Clapeyron Equation:

$$\ln(P_{sat}) = -\frac{h_{fg}}{RT} + \frac{s_{fg}}{R}$$

In the above equation, Psat is the saturation pressure (in atm.) at a temperature T(in Kelvin), hfg and sfg are enthalpy and entropy of vaporization and R is the gas constant. Since the change in entropy of vaporization is relatively small, from the above equation it can be shown that:

$$\frac{P_c}{P_e} = \exp\left[\frac{h_{fg}}{R}\left(\frac{1}{T_e} - \frac{1}{T_c}\right)\right]$$

In the above equation, Pc and Pe are the condenser and evaporator pressures, Tc and Te are condenser and evaporator temperatures. From the above equation, it can be seen that for given condenser and evaporator temperatures as the latent heat of vaporization increases, the pressure ratio also increases. Hence a trade-off is required between the latent heat of vaporization and pressure ratio.

In addition to the above properties; the following properties are also important:

5. **Isentropic index of compression:** Should be as small as possible so that the temperature rise during compression will be small.
6. **Liquid specific heat:** Should be small so that degree of sub-cooling will be large leading to smaller amount of flash gas at evaporator inlet.
7. **Vapour specific heat:** Should be large so that the degree of superheating will be small.
8. **Thermal conductivity:** Thermal conductivity in both liquid as well as vapour phase should be high for higher heat transfer coefficients.
9. **Viscosity:** Viscosity should be small in both liquid and vapour phases for smaller frictional pressure drops.

The thermodynamic properties are interrelated and mainly depend on normal boiling point, critical temperature, molecular weight and structure.

The normal boiling point indicates the useful temperature levels as it is directly related to the operating pressures. A high critical temperature yields higher COP due to smaller compressor superheat and smaller flash gas losses. On the other hand since the vapour pressure will be low when critical temperature is high, the volumetric capacity will be lower for refrigerants with high critical temperatures. This once again shows a need for trade-off between high COP and high volumetric capacity. It is observed that for most of the refrigerants the ratio of normal boiling point to critical temperature is in the range of 0.6 to 0.7. Thus the normal boiling point is a good indicator of the critical temperature of the refrigerant.

The important properties such as latent heat of vaporization and specific heat depend on the molecular weight and structure of the molecule. Trouton's rule shows that the latent heat of vaporization will be high for refrigerants having lower molecular weight. The specific heat of refrigerant is related to the structure of the molecule. If specific heat of refrigerant vapour is low then the shape of the vapour dome will be such that the compression process starting with a saturated point terminates in the superheated zone (i.e. compression process will be dry). However, a small value of vapour specific heat indicates higher degree of superheat. Since vapour and liquid specific heats are also related, a large value of vapour specific heat results in a higher value of liquid specific heat, leading to higher flash gas losses. Studies show that in general the optimum value of molar vapour specific heat lies in the range of 40 to 100 kJ/kmol.K.

The freezing point of the refrigerant should be lower than the lowest operating temperature of the cycle to prevent blockage of refrigerant pipelines.

Other Desired properties:

- Evaporating pressure should be higher than atmospheric. Then non condensable gas will not leak into the system.
- Lower condensing pressure for lighter construction of compressor, condenser, piping, etc.
- A high thermal conductivity and therefore a high heat transfer coefficient in the evaporator and condenser.
- Dielectric constant should be compatible with air when the refrigerant is in direct contact with motor windings in hermetic compressors.
- It should have a critical temperature (temperature above which a gas cannot be liquefied by pressure alone) which is high enough to enable the refrigerant to condense either by cooling water or, preferably, air from the surroundings.
- It should have a freezing point lower than the lowest operational evaporating temperature.
- An inert refrigerant that does not react chemically with material will avoid corrosion, erosion, or damage to system components. Halocarbons are compatible with all containment materials except magnesium alloys. Ammonia, in the presence of moisture, is corrosive to copper and brass.

Environmental & Safety Properties:

Next to thermodynamic and thermo-physical properties, the environmental and safety properties are very important. In fact, at present the environment friendliness of the refrigerant is a major factor in deciding the usefulness of a particular refrigerant. The important environmental and safety properties are:

1. **Ozone Depletion Potential (ODP) -** Ozone depletion potential (ODP) is index to compare the relative ozone depletion of various refrigerants. It is defined as the ratio of the rate of ozone depletion of 1 pound of any halocarbon to that of 1 pound of refrigerant R-11. For R-11, ODP = 1.

   According to the Montreal protocol, the ODP of refrigerants should be ZERO, i.e., they should be non-ozone depleting substances. Since ODP depends mainly on the presence of chlorine or bromine in the molecules, refrigerants having either chlorine (i.e., CFCs and HCFCs) or bromine cannot be used under the new regulations. Refrigerants having non-zero ODP have either already been phased-out (e.g. R11, R12) or will be phased-out in near-future (e.g. R22).

   Note that the CFC refrigerants have a high ODP; the HCFC refrigerants have a low ODP and the HFC refrigerants have a zero ODP.

2. **Global Warming Potential (GWP) -** Similar to the ODP, Global warming potential (GWP) is an index used to compare the global warming effect of a halocarbon refrigerant with the effect of refrigerant R-11.

   Refrigerants should have as low a GWP value as possible to minimize the problem of global warming. Refrigerants with zero ODP but a high value of GWP (e.g. R134a) are likely to be regulated in future.

3. **Total Equivalent Warming Index (TEWI):** The Total Equivalent Warming Impact (TEWI) is a holistic measurement tool for assessing the overall environmental impact of equipment from energy use and refrigerant emissions. It allows the comparison of technologies and provides guidance for targeting improvements in environmental impact. The factor TEWI considers both direct (due to release into atmosphere) and indirect (through energy consumption) contributions of refrigerants to global warming. Naturally, refrigerants with as a low a value of TEWI are preferable from global warming point of view.

4. **Toxicity:** Ideally, refrigerants used in a refrigeration system should be non-toxic. However, all fluids other than air can be called as toxic as they will cause suffocation

when their concentration is large enough. Thus toxicity is a relative term, which becomes meaningful only when the degree of concentration and time of exposure required to produce harmful effects are specified. Some fluids are toxic even in small concentrations. Some fluids are mildly toxic, i.e., they are dangerous only when the concentration is large and duration of exposure is long. Some refrigerants such as CFCs and HCFCs are non-toxic when mixed with air in normal condition. However, when they come in contact with an open flame or an electrical heating element, they decompose forming highly toxic elements (e.g. phosgene-$COCl_2$). In general the degree of hazard depends on:

- Amount of refrigerant used v/s total space
- Type of occupancy
- Presence of open flames
- Odor of refrigerant, and
- Maintenance condition

Thus from toxicity point-of-view, the usefulness of a particular refrigerant depends on the specific application. ANSI/ASHRAE Standard 34-1992 classifies the *toxicity* of refrigerants as Class A and Class B. Class A refrigerants are of low toxicity. No toxicity was identified when their time-weighted average concentration was less than or equal to 400 ppm, to which workers can be exposed for an 8-hr workday and 40-hr work week without adverse effect. Class B refrigerants are of higher toxicity and produce evidence of toxicity.

5. **Flammability -** The refrigerants should preferably be non-flammable and non-explosive. ANSI/ASHRAE Standard 34-1982 classifies the *flammability* of refrigerants as Class 1, no flame propagation; Class 2, lower flammability; and Class 3, higher flammability

   The safety classification of refrigerants is based on the combination of toxicity and flammability. The newer ASHRAE 34a-1992 standard includes two alphanumeric characters A1, A2, A3, B1, B2, and B3. The capital letter (either A-Non-Toxic or B-Toxic) indicates the toxicity and the numeral (1-non-flammable, 2-slightly-flammable, and 3-highly-flammable) denotes the flammability.

- Refrigerants belonging to Group A1 (e.g. R11, R12, R22, R134a, R744, R718) are least hazardous i.e. have lower toxicity and nonflammable,
- Refrigerants belonging to Group B3 (e.g. R1140) are most hazardous (higher toxicity and high flammability.
- R123 in the B1 group, higher toxicity and nonflammable; and R717 (ammonia) in the B2 group, higher toxicity and lower flammability.

For HVAC refrigeration systems, only A1 refrigerants should be considered.

<u>Other important properties are:</u>

6. **Chemical stability:** The refrigerants should be chemically stable as long as they are inside the refrigeration system.
7. **Compatibility:** The refrigerants should be compatible with common materials of construction (both metals and non-metals)
8. **Miscibility with lubricating oils:** Refrigerant should be miscible with mineral lubricant oil because a mixture of refrigerant and oil helps to lubricate pistons and discharge valves, bearings, and other moving parts of a compressor. Oil should also be returned from the condenser and evaporator for continuous lubrication. Refrigerants that are completely miscible with oils are easier to handle (e.g. R12). R-22 is partially miscible. R-134a is hardly miscible with mineral oil; therefore, special precautions should be taken while designing the system to ensure oil return to the compressor. One option is to add synthetic lubricant of polyolester to the refrigerant.
9. **Dielectric strength:** This is an important property for systems using hermetic compressors. For these systems the refrigerants should have as high a dielectric strength as possible
10. **Ease of leak detection:** In the event of leakage of refrigerant from the system, it should be easy to detect the leaks.

REGULATIONS

Environmental concerns about depletion of the Earth's protective stratospheric ozone layer and the effect of CFC on this depletion have resulted in a halt in CFC production since December 31, 1995 and supplies of CFC refrigerant for equipment servicing can ONLY come from recovery, recycling, and reclamation.

On September 16, 1987, the European Economic Community and 24 nations, including the United States, signed a document called the **Montreal Protocol**. It is an agreement to restrict the production and consumption of CFCs in the 1990s.

The Clean Air Act amendments, signed into law in the United States on November 15, 1990, concern two important issues: the phaseout of CFCs and the prohibition of deliberate venting of CFCs and HCFCs.

In February 1992, President Bush called for an accelerated ban of CFCs in the United States. In late November 1992, representatives of 93 nations meeting in Copenhagen agreed to phase out CFCs beginning January 1, 1996.

While HFCs and PFCs are not ozone-depleting substances, they have been identified as potent greenhouse gases with long atmospheric lifetimes and are part of the six gases included in the **Kyoto Protocol**. The Kyoto Protocol calls for the aggregate emissions of the six gases to be reduced to an average of 5% below 1990 levels in developed countries in the 2008-2012 timeframe. The HCFC production for use in new equipment in developed countries will cease in 2020 with total halt to manufacturing and importing mandated by 2030.

Implementation of HCFC Refrigerant Phase-out in the United States

Year to be implemented	Clean air act regulations
2010	No production and no importing of HCFC R-22 except for use in equipment manufactured prior to January 1, 2010. (Consequently, there will be no production or importing of new refrigeration equipment using R-22. Existing equipment must depend on stockpiles or recycling for refrigerant supplies)
2015	No production and no importing of any HCFC refrigerants except for use in equipment manufactured before January 1, 2020
2020	No production or importing of HCFC R-22. (Since this is the cutoff date for new equipment using HCFC refrigerants other than R-22, this should end the installation of new chillers using R-123).

Year to be implemented	Clean air act regulations
2030	No production or importing of any HCFC refrigerant. (While it is anticipated that the vast majority of packaged equipment using R-22 will have been replaced by this date, there will still be a significant number of water chillers using R-123 still in operation. These chillers must depend on stockpiles or recycling for refrigerant supplies).

Hydro fluorocarbons (HFCs), are not regulated by international treaty and are considered, at least for the interim, to be the most environmentally benign compounds and are now widely used in HVAC refrigeration systems.

Recovery, Recycling and Reclamation of Refrigerants

EPA standards for recovery, recycling, and reclamation of refrigerants include the following key guidelines:

As of December 31, 1995, CFCs can no longer be legally manufactured or imported into the United States. Supplies of CFC refrigerant for equipment servicing can ONLY come from recovery, recycling, and reclamation.

- Recycling is defined as the cleaning of refrigerant for reuse by oil separation and single or multiple passes through moisture absorption devices.
- Reclamation is defined as processing refrigerant to a level equal to new product specifications as determined by chemical analysis (testing to ARI-700 standards).
- Recovery is defined as transferring refrigerant in any condition from a system to a storage container without testing or purifying the refrigerant in any way (according to ARI -740 standards). Recovery of refrigerants is necessary to provide adequate refrigeration supplies for service applications after the production bans, as well as to prevent venting to the atmosphere and the resulting ozone depletion. Since, November 14, 1994, technicians servicing refrigeration hardware must be certified in refrigerant recovery and the sale of CFC and HCFC refrigerants has been restricted to technicians certified in refrigerant recovery.

EPA requires recovering the refrigerant before you dispose any air conditioning and refrigeration equipment or any other appliance containing CFC, HCFC, and HFC refrigerants. Venting of substitutes for CFC and HCFC refrigerants, including HFC-134a, is now illegal and mandatory recovery is required for all refrigerants (including HFCs).

Violation of the Clean Air Act, including the knowing release of refrigerant during the maintenance, service, repair, or disposal of appliances, can result in fines up to $32,500 per day per violation. An award of up to $10,000 may be paid to any person supplying information that leads to a penalty against a technician who is intentionally venting refrigerant.

For information concerning regulations related to stratospheric ozone protection, please visit web site: **http://www.epa.gov/** or call the EPA Stratospheric Ozone Hotline: 800-296-1996 (10am-4pm eastern).

CURRENT REFRIGERANT OPTIONS

Several refrigerants are used in the refrigeration and air conditioning sector that have differing impacts on the environment. The common theme is that they all need to be contained to ensure efficient operation and minimal impact on the environment, “responsible use” in other words. Based on the HCFC refrigerant phase-out schedule, there will be no production or importing of new refrigeration equipment using R22 after January 1, 2010. The choices of refrigerants include:

HFCs (hydrofluorocarbons)

HFCs are the leading candidates of chlorine-free, non-toxic, low to non- flammable refrigerants which may be applied in any of the new installations, and indeed are the only ones which can realistically be considered for a large majority of air conditioning applications are R134A, R 407C and R410A, and their main characteristics are summarized below:

Summary of the major characteristics of R134a, R407C and R410A

Properties	**R134A**	**R407C**	**R410A**
Glide (K)	0	6	0.2
100 year GWP	1300	1530	1730

Properties	R134A	R407C	R410A
Pressure @ 50°C bar Abs	13.2	19.6	30.9
Critical Temperature (°C)	101	87	72
Compressor Displacement (%R22)	54% larger	About same	30% lower
Pressure Drop (%R22)	~30% higher	About same	~ 30% lower
Evap Heat Transfer (%R22)	~10% lower	~10% lower	~ 35% higher
System Cost	Higher	About same	Potentially lower

R134A

R -134A has the best theoretical performance and compressors optimized for it give very good COPs. But because of its lower pressure, about 50% larger displacement is required and this can make any compressor more costly when a larger body or shell size is needed. Also it needs larger tubing and components resulting in higher system cost. R134A has been very successfully used in screw chillers where short pipe lengths minimize costs associated with larger tubing. R134a also finds a niche where extra high condensing temperatures are needed and in many transport applications.

R407C and R410A

Both R407C and R410A are non-azeotropic HFC refrigerant blends. Non-azeotropic blends (400 series) means that they experience a temperature glide during evaporation and condensation. In contrast, a pure refrigerant or an azeotropic (500 series) refrigerant blend has a single boiling point temperature at a given pressure. However, as discussed below R-410A is a near azeotropic refrigerant.

- R407C has properties close to those of R22, and is for this reason is seeing extensive use world over. Its glide and heat transfer properties generally penalize the system performance, although counter flow heat exchange can deliver some benefit with plate heat exchangers.

- R410A looks discouraging at first because of its poor theoretical performance, low critical temperature, high pressure, and non-availability (until recently) of compressors. These factors would seem to indicate a low score on most criteria. However, the refrigerant side heat transfer is about 35% better than with R22 whereas for the other two it is poorer. The pressure drop effect in equivalent heat exchangers will be approximately 30% less.

R 417A

R 417A is another HFC designed primarily for retrofitting into existing R22 systems although some OEMs have been considering it for new product. When retrofitted in a system previously optimized for R22 the heat exchangers become effectively 5-10% oversized. This will tend to cause an adjustment of evaporating temperature upwards and condensing temperature downwards. It is not surprising that R 417A has been reported to deliver better system COPs than R22. A major concern is oil return when using mineral oil. Adequate oil return under all commonly encountered conditions is unproven, and users are strongly recommended to verify that proper oil levels are maintained under all conditions if R417A is to be considered.

HCs (hydrocarbons)

HCs (hydrocarbons) have a low global warming potential, are energy efficient, but are highly inflammable. R290 (propane) is an example. Being inflammable, the charge size is regulated by refrigeration safety standards, which establish maximum allowable charge sizes as a function of the occupancy category and air conditioned space volume. In practice, for many applications, these charge size constraints preclude the use of flammable refrigerants for direct air conditioning systems.

Inorganic Refrigerants

Ammonia is a non-halocarbon refrigerant and is currently widely used. The benefits of ammonia as a refrigerant are:

- Is not a contributor to ozone depletion, greenhouse effect, or global warming;
- Is naturally released into the atmosphere from many sources
- Is energy efficient
- Has a pungent odor that gives it a self-alarming property.

Ammonia is widely used in the food processing and pharmaceutical industries. However, local-permitting authorities may restrict the use of ammonia due to its toxicity and flammability. R717 (ammonia) has best theoretical COP. In practice, compressor COP tends to be only a few percent better than R22. System design for the best system COP may result in high cost, particularly when taking into account necessary items to ensure safety. Ammonia's B2 category makes it suitable only for indirect (chiller) systems. Within the chiller market it finds its place mainly in the Screw Chiller sector. Scroll and Reciprocating Chillers are generally smaller size and less able to bear the safety costs and scrolls are not available for R717.

Carbon dioxide is a greenhouse gas, but is not very energy efficient and as requires very high pressure equipment. However CO_2 is emerging as a good refrigerant for specific applications like heat pumps for water heaters. In this case the use of CO_2 is based on an objective assessment of its performance from all the refrigerants available. In contrast, in conventional air-conditioning and refrigeration systems HFCs remains the optimal solution, which is why it is important to maintain refrigerant choice.

Table in Annexure – 1 provides the suggested replacements for CFCs and HCFCs.

Concluding…..

The perfect refrigerant does not exist but to come up with the optimum solution for any given application users must make an assessment, which balances the characteristics of different refrigerants. An essential part of this decision is the consideration of competing technology on the markets. Any choice must be guided by regulation and procedures, which ensure refrigerants are used responsibly.

Annexure – 1

RESUME OF THE REFRIGERANT OPTIONS

HVAC refrigeration equipment is currently undergoing transition in the use of refrigerants. In the earlier 1990s, R11 was widely used for centrifugal chillers, R12 for small and medium-size vapor compression systems, R22 for all vapor compression systems, and CFC/HCFC blend R502 for low-temperature vapor compression systems. Because of the phaseout of CFCs and BFCs before 1996 and HCFCs in the early years of the next century, alternative refrigerants have been developed to replace them:

1. R123 (an HCFC of ODP = 0.02) to replace R11 is a short-term replacement that causes a slight reduction in capacity and efficiency. R245ca (ODP = 0) may be the long-term alternative to R11.
2. R134A (an HFC with ODP = 0) to replace R12 in broad applications. R134A is not miscible with mineral oil; therefore, a synthetic lubricant of polyolester is used.
3. R404A (R-125/R-134a/143a) and R407C (R32/R-125/R134a) are both HFCs near azeotropic of ODP = 0. They are long-term alternatives to R22. For R-407C, the composition of R-32 in the mixture is usually less than 30% so that the blend will not be flammable. R-407C has a drop of only 1 to 2% in capacity compared with R22.
4. R507 (R-125/R-143a), an HFC's azeotropic with ODP = 0, is a long-term alternative to R-502.
5. Synthetic polyolester lubricant oil will be used for R-507. There is no major performance difference between R507 and R502. R402A (R22 /R125 /R290), an HCFC's near azeotropic, is a short-term immediate replacement, and drop-in of R-502 requires minimum change of existing equipment except for reset of a higher condensing pressure.

Acceptable Substitutes for CFCs

Substitute (Name Used in the Federal Register)	Trade Name	Refrigerant Being Replaced	Retrofit/ New Uses (R / N)
Evaporative/Desiccant		all CFCs	N

Cooling			
R-407C	Suva 407C, Klea 407C	502	R, N
R-422C	ICOR XLT1	502	R, N
KDD6	KDD6	12	R, N

Acceptable Substitutes for HCFCs

Substitute (Name Used in the Federal Register)	Trade Name	Refrigerant Being Replaced	Retrofit/ New Uses (R / N)
HFC-134a		22	N
THR-03		22	N NOTE: this determination applies ONLY to window-unit residential air conditioning, and not to central air conditioning systems.
ISCEON 59, NU-22, R-417A	ISCEON 59, NU-22	22	R, N
R-410A, R-410B	AZ-20, Suva 9100, Puron	22	N
R-407C	Suva 9000, Klea	22	R, N

	66		
R-507, R-507A	AZ-50	22	R, N
NU-22	NU-22	22	R, N
Ammonia Absorption		22	N
Evaporative/Desiccant Cooling		all HCFCs	N
R-404A	HP62	22	R, N
R-125/134a/600a (28.1/70.0/1.9)		22	R, N
RS-44	RS-44	22	R, N
R-421A	Choice R421A	22	R, N
R-422D	ISCEON MO29	22	R, N
R-424A	RS-44	22	R, N
R-125/290/134a/600a (55.0/1.0/42.5/1.5)	ICOR AT-22	22	R, N
R-422C	ICOR XLT1	22	R, N
R-422B	ICOR XAC1	22	R, N

KDD5, R-438A	ISCEON MO99	22	R, N
R-434A	RS-45	22	R, N
R-125/290/134a/600a (55.0/1.0/42.5/1.5)	ICOR AT-22	22	R, N
R-422B	XAC1, NU-22B	22	R, N
R-422C	XLT1	22, 402A, 402B, 408A	R, N
R-407A	KLEA 60, KLEA 407A	22, 22 blends including R-401A, -401B, -402A, and -402B	R, N
R-427A	Forane 427A	22	R