History Of Refrigeration

- Refrigeration relates to the cooling of air or liquids, thus providing lower temperature to preserve food, cool beverages, make ice and for many other .
- Most evidence indicate that the Chinese were the first to store natural ice and snow to cool wine and other delicacies.
- Ancient people of India and Egypt cooled liquids in porous earthen jars.
- In 1834, Jacob Perkins, an American, developed a closed refrigeration system using liquid expansion and then compression to produce cooling. He used Ether as refrigerant, in a hand- operated compressor, a water-cooled condenser and an evaporator in liquid cooler.

Refrigerantion Principle

- Modern refrigeration and air-conditioning equipment is dominated by vapour compression refrigeration technology built upon the thermodynamic principles of the reverse Carnot cycle.
- Refrigerant Changes phases during cooling and used again and again.

What is a Refrigerant

- Refrigerants are used as working substances in a Refrigeration systems.
- Fluids suitable for refrigeration purposes can be classified into primary and secondary refrigerants.
- Primary refrigerants are those fluids, which are used directly as working fluids, for example in vapour compression and vapour absorption refrigeration systems.
- These fluids provide refrigeration by undergoing a phase change process in the evaporator.
- Secondary refrigerants are those liquids, which are used for transporting thermal energy from one location to other. Secondary refrigerants are also known under the name brines or antifreezes

What is ChloroFloroCarcons

- Today's refrigerants are predominantly from a group of compounds called halocarbons (halogenated hydrocarbons) or specifically fluorocarbons.
- Chlorofluorocarbons were first developed by General Motor's researchers in the 1920's and commercialized by Dupont as "Freons".

Halocarbon Refrigerants

- Halocarbon Refrigerant are all synthetically produced and were developed as the Freon family of refrigerants.

Examples :

- CFC's : R11, R12, R113, R114, R115

Freon Group Refrigerants Application and ODP Values

Refrigerant	Areas of Application	ODP
CFC 11(R11)	Air-conditioning Systems ranging from 200 to 2000 tons in capacity. It is used where low freezing point and non-corrosive properties are important.	1.0
CFC 12 (R 12)	It is used for most of the applications. Air-conditioning plants, refrigerators, freezers, ice-cream cabinets, water coolers, window air-conditioners, automobile air conditioners.	1.0
CFC 13 (R 13)	For low temp refrigeration up to – 90 °C in cascade system	1.0
CFC113 (R113)	Small to medium air-conditioning system and industrial cooling	1.07
CFC114 (R114)	In household refrigerators and in large industrial cooling	0.8 0.34
Blend of R22 and R115 (R502)	Frozen food ice-cream display cases and warehouses and food freezing plants. An excellent general low temp refrigerant	

What is Ozone Layer

- Ozone is an isotope of oxygen with three atoms instead of normal two. It is naturally occurring gas which is created by high energy radiation from the Sun.
- The greatest concentration of ozone are found from 12 km to 50 km above the earth forming a layer in the stratosphere which is called the ozone layer.
- This layer, which forms a semi-permeable blanket, protects the earth by reducing the intensity of harmful ultra-violet (UV) radiation from the sun.

Ozone Layer Depletion

- In the early70's,scientists Sherwood Roland and Mario Molina at the University of California at Irvine were the first to discover the loss of ozone in stratosphere while investigating the ozone layer from highflying aircraft and spacecraft.
- They postulated the theory that exceptionally stable chlorine containing fluorocarbons could, overtime, migrate to the upper reaches of the atmosphere and be broken by the intense radiation and release chlorine atoms responsible for catalytic ozone depletion.

OZONE LAYER DEPLETION

- NORMAL REACTION
- $O_2 = O + O$
- $O_2 + O = O_3$
- But CFC refrigerants leaked during the manufacturing and normal operation or at the time of servicing or repair, mix with surrounding air and rise to troposphere and then into stratosphere due to normal wind or storm. The Ultraviolet rays act on CFC releasing Cl atom, which retards the normal reaction:

- RETARDED REACTION
- $O_3 = O_2 + O$
- $CCL_2F_2 = CCLF_2 + CL$
- $O_3 + CL = CLO + O_2$
- $O + CLO = CL + O_2$

Harmful consequences of ozone depletion

- ***For Humans*** Increase in
- skin cancer
- snow blindness
- cataracts
- **Less immunity to**
- infectious diseases
- malaria
- herpes
- ***For plants***
- smaller size
- lower yield
- increased toxicity
- altered form
-
- ***For marine life***
- Reduced
- plankton
- juvenile fish
- larval crabs and shrimps

MONTREAL PROTOCOL

- SIGNED IN 1987 UNDER THE 'UNEP', AFTER MUCH DISCUSSIONS
- MORE THAN 170 COUNTRIES HAVE RATIFIED
- INDIA RATIFIED ON SEPT 17,1992
- ONE OF MOST SUCCESSFUL EXAMPLE OF INTERNATIONAL COOPERATION IN UN HISTORY

Montreal protocol- Control Schedule

Montréal Protocol- Control Schedule

ozone depleting substance	developed countries	developing countries
CFCs	phased out end of 1995	total phase out by 2010
halons	phased out end of 1993	total phase out by 2010
HCFCs	total phase out by 2020	total phase out by 2040

CFC Phase-out in India

- **What is to be phased out?**
- CFC-11, CFC-12 & CFC-113a.
- **How much and when?**

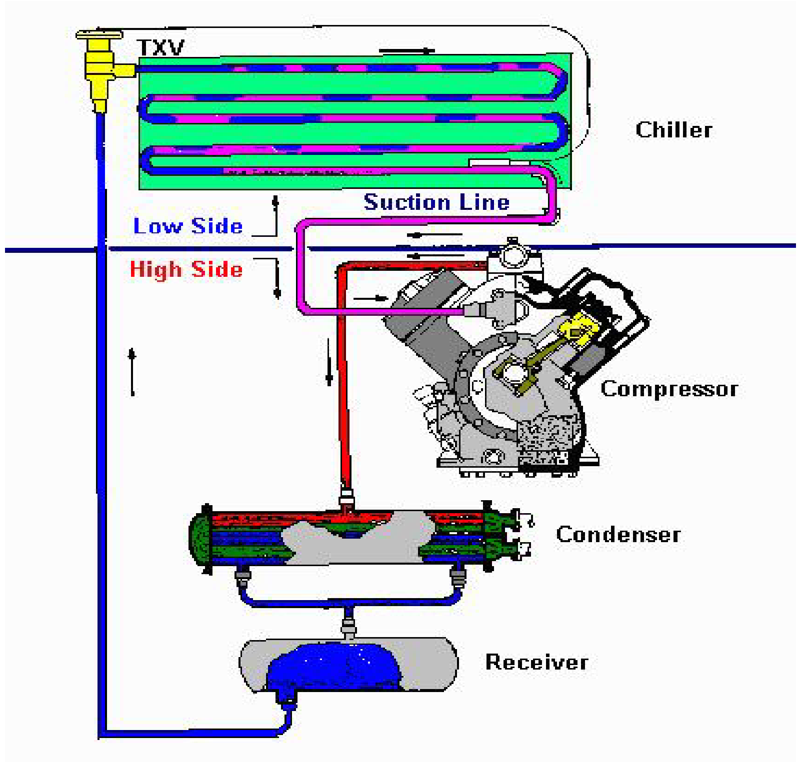
- **Year 1999** 22,588 MT
- 2005 11,294 MT
- 2010 0 MT
- **How to achieve the target?**
- Production is controlled through a production quota allocated to each producer every year. The Ozone Cell conducts audits twice a year to monitor the production.
- **How much has been Phaseout?** CFC has been completely phased out as on 1st August, 2008

Vapor compression refrigeration System

- In 1834 an American inventor named Jacob Perkins obtained the first patent for a vapor-compression refrigeration system, it used ether in a vapor compression cycle.
- Joule-Thomson (Kelvin) expansion
- Low pressure (1.5 atm) low temperature (-10 to +15 ℃) inside
- High pressure (7.5 atm) high temperature (+15 to +40 ℃) outside

Components

- Refrigerant
- Evaporator/Chiller
- Compressor
- Condenser
- Receiver
- Thermostatic expansion valve (TXV)



Circulation of Refrigerant

- Compressor
  cold vapor from the evaporator is compressed, raising it temperature and boiling point
  adiabatic compression
  T, b.p. ~ P
  work done on the gas
- Condenser
  hot vapor from the compressor condenses outside the cold box, releasing latent heat
  isothermal, isobaric condensation (horizontal line on PV diagram)
  high temperature
  T (hot)
  latent heat of vaporization *Q* (hot)
- Expansion valve (throttling valve)
  hot liquid from the condenser is depressurized, lowering its temperature and boiling point
  adiabatic, isochoric expansion (vertical line on PV diagram)
  T, b.p. ~ P
  no work done $W = 0$
- Evaporator
  cold liquid from the expansion valve boils inside the cold box, absorbing latent heat
  isothermal, isobaric boiling (horizontal line on PV diagram)
  low temperature
  T (cold)
  latent heat of vaporization *Q* (cold)

Importance of Refrigerant

- The thermodynamic efficiency of a refrigeration system depends mainly on its operating temperatures.
- However, important practical issues such as the system design, size, initial and operating costs, safety, reliability, and serviceability etc. depend very much on the type of refrigerant selected for a given application.
- Due to several environmental issues such as ozone layer depletion and global warming and their relation to the various refrigerants used, the selection of suitable refrigerant has become one of the most important issues in recent times.

Refrigerant selection criteria

- Selection of refrigerant for a particular application is based on the following requirements:
  - i. Thermodynamic and thermo-physical properties
  - ii. Environmental and safety properties
  - Iii. Economics

Thermodynamic and thermo-physical properties

- The requirements are:
- <u>a) Suction pressure: </u>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
- <u>b) Discharge pressure: </u>At a given condenser temperature, the discharge pressure should be as small as possible to allow light-weight construction of compressor, condenser etc.
- <u>c) Pressure ratio: </u>Should be as small as possible for high volumetric efficiency and low power consumption
- <u>d) Latent heat of vaporization: </u>Should be as large as possible so that the required mass flow rate per unit cooling capacity will be small

Thermodynamic and thermo-physical properties

- In addition to the above properties; the following properties are also important:
- e) Isentropic index of compression: Should be as small as possible so that the temperature rise during compression will be small
- f) Liquid specific heat: Should be small so that degree of subcooling will be large leading to smaller amount of flash gas at evaporator inlet
- g) Vapour specific heat: Should be large so that the degree of superheating will be small
- h) Thermal conductivity: Thermal conductivity in both liquid as well as vapour phase should be high for higher heat transfer coefficients
- i) 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.

Environmental and safety properties

- 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:
- a) Ozone Depletion Potential (ODP): According to the Montreal protocol, the ODP of refrigerants should be zero, i.e., they should be non-ozone depleting substances. Refrigerants having non-zero ODP have either already been phased-out (e.g. R 11, R 12) or will be phased-out in near-future(e.g. R22). 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

Environmental Effects of Refrigerants

Global warming :

Refrigerants directly contributing to global warming when released to the atmosphere

Indirect contribution based on the energy consumption of among others the compressors (CO_2 produced by power stations)

Environmental and safety properties

- <u>b) Global Warming Potential (GWP):</u> 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.
- <u>c) Total Equivalent Warming Index (TEWI):</u> 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.

Environmental and safety properties

- <u>d) Toxicity:</u> Ideally, refrigerants used in a refrigeration system should be non-toxic. 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. In general the degree of hazard depends on:
  - - Amount of refrigerant used vs total space
  - - Type of occupancy
  - - Presence of open flames
  - - Odor of refrigerant, and
  - - Maintenance condition

Environmental and safety properties

- <u>e) Flammability:</u> The refrigerants should preferably be non-flammable and non-explosive. For flammable refrigerants special precautions should be taken to avoid accidents.
- <u>f) Chemical stability:</u> The refrigerants should be chemically stable as long as they are inside the refrigeration system.
- g) <u>Compatibility</u> with common materials of construction (both metals and non-metals)
- <u>h) Miscibility with lubricating oils:</u> Oil separators have to be used if the refrigerant is not miscible with lubricating oil (e.g. ammonia). Refrigerants that are completely miscible with oils are easier to handle(R12).

Environmental and safety properties

- <u>Ease of leak detection: </u>In the event of leakage of refrigerant from the system, it should be easy to detect the leaks.

Economic properties:

- The refrigerant used should preferably be inexpensive and easily available.

ECO-FRIENDLY REFRIGERANTS

- CFC ALTERNATIVES.
  - HCFC
    R22,R124
  - HFC
    R134a,R152a
  - NATURAL REFRIGERANT
    NH_3, HC's

Halocarbon Refrigerants

- Halocarbon Refrigerant are all synthetically produced and were developed as the Freon family of refrigerants.

Examples :

- CFC's : R11, R12, R113, R114, R115
- HCFC's : R22, R123
- HFC's : R134a, R404a, R407C, R410a

HFCs

- Remain a popular choice
  - especially for R22 phase out
- Good efforts at improving leakage performance
  - e.g. Real Zero project
- Interest in R407A to replace R404A
  - 50% reduction in GWP

Inorganic Refrigerants

- Carbon Dioxide
- Water
- Ammonia
- Air
- Sulphur dioxide

Table 1: Environmental Effects of Some Refrigerants (UNEP, 2002)

Refrigerants		ODP	GWP (Time horizons of 100 yrs)
HCFC's	R-22	0.055	1,700
HFC's	R-134a	0	1,300
	R-404A (R125/143a/134a)	0	3,800
	R-410A (R32/125)	0	2,000
Natural Refrigerants	Carbon dioxide (R-744)	0	1
	Ammonia (R-717)	0	<1
	Propane (R-290)	0	20
	Isobutane (R-600a)	0	20
	Cyclopropane (RC-270)	0	n/a

HCFC

- Transitional compounds with low ODP
- Partially halogenated compounds of hydrocarbon
- Remaining hydrogen atom allows Hydrolysis and can be absorbed.
- R22, R123

HCFC

- Production frozen at 1996 level
- 35% cut by 2005,65% by 2010
- 90% by 2015,100 % by 2030
- 10 year grace period for developing countries.

R22

- ODP-0.05, GWP-1700
- R22 has 40% more refrigerating capacity
- Higher pressure and discharge temp and not suitable for low temp application
- Extensively used in commercial air-conditioning and frozen food storage and display cases

R123

- ODP-0.02,GWP-90
- As a replacement for R11 as similar thermodynamic properties.
- Very short atmospheric life but classified as carcinogen
- Retrofit alternative to R11

HFC

- Zero ODP as no chlorine atom contains only Hydrogen and Flurodine
- Very small GWP values
- No phase out date in Montreal Protocol
- R134a and R152 a – Very popular refrigerants
- HFC refrigerants are costly refrigerants

R134a

- ODP-0, GWP-1300
- Used as a substitute for R12 and to a limited range for R22
- Good performance in medium and high temp application
- Toxicity is very low
- Not miscible with mineral oil

R152a

- ODP-0,GWP-140
- R152a is another attractive HFC with similar properties to R12.
- GWP is one order less than HFC134a but it is slightly flammable.
- Also it has lower energy consumption. Hence the Environmental Protection Agency of Europe prefers HFC152a to HFC134a

Hydrocarbon

- Very promising non-halogenated organic compounds
- With no ODP and very small GWP values
- Their efficiency is slightly better than other leading alternative refrigerants
- They are fully compatible with lubricating oils conventionally used with CFC12.

Hydrocarbon Refrigerants

- Extraordinary reliability- The most convincing argument is the reliability of the hydrocarbon system because of fewer compressor failures.
- But most of the hydrocarbons are highly flammable and require additional safety precaution during its use as refrigerants.
- Virtually no refrigerant losses
- Hydrocarbons have been used since the beginning of the century and now being considered as long term solutions to environmental problems,

Hydrocarbons

- Dominant in domestic market like household refrigerators and freezers
- Growing use in very small commercial systems like car air-conditioning system
- Examples: R170, Ethane, C_2H_6

  R290 , Propane C_3H_3

  R600, Butane, C_4H_{10}

  R600a, Isobutane, C_4H_{10}

  Blends of the above Gases

R290

- ODP-0,GWP-3
- Compatible with copper.Miscible with mineral oil
- Highest latent heat and largest vapour density
- A third of original charge only is required when replacing halocarbons refrigerant in existing equipment
- Energy saving : up to 20% due to lower molecular mass and vapour pressure

R 600a

- ODP-0,GWP-3
- Higher boiling point hence lower evaporator pressure
- Discharge temp is lowest
- Very good compatibility with mineral oil

Flammability

- Approximate auto ignition temperatures
- R22 630 °C
- R12 750 °C
- R134a 740 °C
- R290 465 °C
- R600a 470 °C

Modifications of Electrical Equipment

- Replaced with solid state equivalents
- Sealed to ensure that any sparks do not come into contact with leaking gas
- Relocated to a position where the component would not come into contact with leaking gas

Modifications of Electrical Equipment

- Faulty components.
- Poor, corroded, loose, or dirty electrical connections.
- Missing or broken insulation which could cause arcing/sparks.
- Friction sparks, like a metal fan blade hitting a metal enclosure.

Blends & Mixtures

- Limited no of pure refrigerants with low ODP & GWP values
- To try a mixture of pure refrigerants to meet specific requirement

Azeotropic Refrigerants

- A stable mixture of two or several refrigerants whose vapour and liquid phases retain identical compositions over a wide range of temperatures.

- Examples : R-500 : 73.8% R12 and 26.2% R152

  R-502 : 8.8% R22 and 51.2% R115

  R-503 : 40.1% R23 and 59.9% R13

Zeotropic Refrigerants

- A zeotropic mixture is one whose composition in liquid phase differs to that in vapour phase. Zeotropic refrigerants therefore do not boil at constant temperatures unlike azeotropic refrigerants.
- Examples :R404a : R125/143a/134a (44%,52%,4%)

  R407c : R32/125/134a (23%, 25%, 52%)

  R410a : R32/125 (50%, 50%)

  R413a : R600a/218/134a (3%, 9%, 88%)

Inorganic Refrigerants

- Carbon Dioxide
- Water
- Ammonia
- Air
- Sulphur dioxide

Carbon Dioxide

- Zero ODP & GWP
- Non Flammable, Non toxic
- Inexpensive and widely available
- Its high operating pressure provides potential for system size and weight reducing potential.
- ***Drawbacks:***
- Operating pressure (high side) : 80 bars
- Low efficiency

Ammonia –A Natural Refrigerant

Ammonia is produced in a natural way by human beings and animals; 17 grams/day for humans.

Natural production	3000 million tons/year
Production in factories	120 million tons/year
Used in refrigeration	6 million tons/year

Ammonia as Refrigerant

- ODP = 0
- GWP = 0
- Excellent thermodynamic characteristics: small molecular mass, large latent heat, large vapour density and excellent heat transfer characteristics
- High critical temperature (132C) : highly efficient cycles at high condensing temperatures
- Its smell causes leaks to be detected and fixed before reaching dangerous concentration
- Relatively Low price

Some Drawbacks of Ammonia as Refrigerant

- Toxic
- Flammable (16 – 28% concentration)
- Not compatible with copper
- Temperature on discharge side of compressor is higher compared to other refrigerants

Water

- Zero ODP & GWP
- Water as refrigerant is used in absorption system .New developing technology has created space for it for use in compression cycles also.
- But higher than normal working pressure in the system can be a factor in restricted use of water as refrigerant

Application of New Eco-friendly Refrigerants

Application	HFCs used	Possible Eco-friendly refrigerant
Domestic refrigeration	R134a,R152a	HC600a and blends
Commercial refrigeration	R134a,R404A,R407C	HC blends,NH_3 ,CO_2 **
Cold storage ,food processing		
And industrial refrigeration	R134a,R404A,R507A	NH_3 ,HCs,CO_2 **
Unitary air conditioners	R410A,R407C	CO_2 , HC s
Centralized AC (chillers)	R134a,R410A,R407C	NH_3 ,HCs,CO_2, water **
Transport refrigeration	R134a,R404A	CO_2,
Mobile air conditioner	R134a	CO_2 ,HCs
Heat pumps	R134a,R152a,R404A R407C,R410A	NH_3 ,HCs,CO_2, water **

General Safety measures for refrigerating plants

- **Reduction of refrigerant contents:**
  - Components with reduced contents
  - Indirect systems with secondary refrigerant: distinction between generation and transport of cold

- **Scheduled maintenance and leak testing**

- **Governmental surveillance** – Refrigerant Audits for systems operating with HFC's. Recovery, Stock of used refrigerants, Recycling of refrigerants.

- For the Netherlands, the combined measures resulted in a leak rate reduction of 35% (1995) to 8% (2001) for R22-systems

Survey Of Refrigerants

Refrigerant	Group	Atmospheric life	ODP	GWP
R11	CFC	130	1	4000
R12	CFC	130	1	8500
R22	HCFC	15	.05	1500
R134a	HFC	16	0	1300
R404a	HFC	16	0	3260
R410a	HFC	16	0	1720
R507	HFC	130	1	3300
R717	NH3	-	0	0
R744	CO_2	-	0	1
R290	HC	< 1	0	8
R600a	HC	< 1	0	8

Comparison of Alternatives

F-GAS SUPPORT
Promoting Compliance with F-Gas and Ozone Regulations

Refrigerant	HFCs	HCs	Ammonia	CO_2	Low GWP FCs
GWP	✗✗	✓	✓✓	✓✓	✓
Toxicity	✓✓	✓✓	✗✗	✓	✓✓
Flammability	✓✓	✗✗	✗	✓✓	? ✗
Efficiency	✓	✓	✓	✓	✓
Materials	✓	✓	✗	✓	✓
Pressure	✓	✓	✓	✗✗	✓
Cost	✓	✓✓	✓✓	✓✓	?
Availability	✓✓	✓	✓	✓	✗✗
Familiarity	✓✓	✓	✓	✗	✗

Very poor ✗✗ Poor ✗ Good ✓ Very Good ✓✓

Conclusions

- In the aftermath of the Montreal protocole HFC's have predominantly replaced CFC's and HCFC's in RAC equipment.
- Due to their high GWP, HFC's are not a good replacement solution.
- The solution are the natural refrigerants :

  Ammonia, Hydrocarbons and Carbon dioxide
- System need to have low TEWI factor
- High efficiency with ammonia and lower power consumption with hydrocarbons

Environmental Effects of Refrigerants

Global warming :

Refrigerants directly contributing to global warming when released to the atmosphere

Indirect contribution based on the energy consumption of among others the compressors (CO_2 produced by power stations)