McMaster University, Hamilton,Canada MEPP Program

MARKET RESEARCH INTO REPLACEMENT GASES FOR HFCs AND HFOs AND INTO SF_6 FOR SWITCHGEAR APPLICATIONS

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Vipul

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ABBREVIATIONS

A C: AIR CONDITIONER

CO_2: CARBON DIOXIDE

EPA: ENVIRONMENT PROTECTION ACT

FCT: FIELDING CHEMICAL TECHNOLOGY

GWP: GLOBAL WARMING POTENTIAL

HC: HYDROCARBONS

HCl: HYDROCHLORIC ACID

HCFC: HYDROCHLOROFLUOROCARBONS

HF: HYDROFLUORIC ACID

HFO: HYDROFLUOROCARBON

NH_3: AMMONIA

ODP: OZONE DEPLETION PROPERTY

OEM: ORIGINAL EQUIPMENT MANUFACTURER

P O: PURCHASE ORDER

RMC: REFRIGERANT MANAGEMENT CANADA

SF_6: Sulphur HEXAFLUORIDE

V P: VICE PRESIDENT

1. MONTHLY MILESTONES:

Month 1 – Create a detailed outline of official project – Interview key Fielding staff and tour facilities to understand the nature of FCT's business, the company methodology for evaluating business lines, FCT equipment capabilities and utilization, and FCT capabilities and competitive positioning.

- Develop a list of questions for interviews and for literature search and get approval of relevant Fielding staff.

- Start literature research on gases including SF_6.

Month 2 – Phase 1 Draft–Prepare Phase 1 draft and review results with Fielding staff to determine gaps and other required research.

- Start research on industry, manufacturers or users of the alternate gases and SF_6, the regulatory environment in the various large geographic markets, and the key trends

- Commence contacting manufacturers to set up meetings and start interviews.

Month 3 - Phase 2 Draft–Complete industry interviews and search on buying patterns.

- Prepare Phase 2 draft and review results with Fielding staff to determine gaps and other required research.

Month 4 – Final Draft – Review with Fielding staff, research to fill gaps, and complete Final Report.

2. AIM:

Fielding Chemical Technology is facing an increasing competition which is putting pressure on margins on some of its core commodity products so it would like to diversify into higher margined products with a more diversified customer base in markets where it can play a dominant role. Therefore, FCT is proactively looking for significant new market opportunities that will allow it to continue to grow its business and that are consistent with its corporate mission as a provider of innovative and environmentally protective solutions to recover and sell valuable chemicals, thereby diverting pollutants from waste streams and building a sustainable value chain for chemical use. Until this market research is done, it is too early for Fielding to commit finite capital, equipment and people resources towards building these two new business segments. This research may lead to identification of potential new IP as well.

The aim of this study is to help FCT develop recycling programmes for alternate gases in refrigeration and SF_6 used in switchgear application.

3. ABSTRACT:

Hydrochlorofluorocarbons (HCFCs) are being phased out globally under the Montreal protocol, due to their high global warming potential (GWP) and Ozone Depletion Potential, this initiated the search for more eco-friendly refrigerants with properties like low flammability and toxicity, compatibility with compressor lubricating oils and metal, good heat transferring and refrigeration performance and with attribute that help reduce green house gas emissions. An extensive literature research has been done to find details of the refrigerant industry focusing on the recycling sector and market research for alternatives along with the research into details of FCT's operations to understand the nature of FCT's business, their evaluation methodology, equipment capabilities and utilization, and competitive positioning. Interviews were conducted with key employees of FCT working in the gas sector so as to give the project technical expertise and valuable information to support the findings. The purchase pattern of raw materials and inclination of the FCT towards the GHG emission reduction have been evaluated. Staff members supported and guided the project development and also highlighted the key points to focus and to ensure a better understanding. Another important aspect of the study was to examine the possibility of setting up of a recycling plant for Sulphur hexafluoride (SF_6); a gas which has switchgear applications and is identified as a most potent non-CO_2 Green House Gas (GHG) with high GWP. Canada, at present does not have a recycling facility for SF_6, hence it is planned to evaluate prospects of setting up this facility here. This report comprises intensive study into market research of alternative refrigeration gases like HFO, HC, CO_2, NH_3 and recycling of SF_6, an important gas of electricity industry. Chemical Conversion Technology to convert refrigerant gases into its basic components i.e. CO_2, H_2O, HF, HCl has also been discussed. The study suggests that FCT can focus on introducing natural refrigerants like CO_2 NH_3, Propane and Isobutane in refrigeration sector which have zero ODP and GWP. Further investigation into using CO_2 in mobile air conditioning is recommended. Recycling of HFO-1234 yf blend for car air conditioning system should be explored. Another blend HFO-1233 zd is still in development stages. A fully automated SF_6 recycling plant using cryogenic techniques can be set up which would be a first of its kind in Canada. However, the recent introduction of CO_2 as a replacement of SF_6 in switch-gears should also be kept in mind.

4. INTRODUCTION:

Fielding Chemicals Technology (FCT) is a clean tech company specializing in the recycling of waste solvents, glycols and refrigerants. Through innovative custom processing, Fielding has been serving the paint and coatings, manufacturing, pharmaceutical, aviation, printing and HVAC industries by giving new life to waste solvent, glycols and refrigerants. FCT has a unique capability as the only company in Canada that can fractionate solvents and one of two companies in Canada that can recycle refrigerants. It annually repurposes over 25 million litres of waste solvent and over 250,000 kg of refrigerant which is the largest refrigerant repurposing program in Canada. FCT also has a state-of-the-art infrastructure with 7 fractional distillation units for separation, a large fleet of collection cylinders, and expertise in batch distillation that allows customized separation solutions for customers. FCT has a track record for safe materials handling, extraction, purification, storage and distribution of a variety of chemicals. It has a reputation for innovation and analytical capability with an on-site world class solvent and refrigerant lab, able to do a variety of solvent, metals and gas analysis.

This company now plans to step into recycling of SF_6, which is not available in Canada and introduce some of the replacement gases in the field of refrigeration and car air conditioning system.

5. BUYING PATTERN OF REFRIGERANTS IN CANADA: INTERVIEWS FOR UNDERSTANDING THE INCLINATION TOWARDS NEW INDUSTRY TRENDS IN CARBON EMISSION REDUCTION:

VP: FCT

Detailed discussion was done with the VP, FCT regarding alternate refrigerant gases which have low GWP and ODS. Key findings are:

- **Regarding understanding of the International commitment of Carbon emission reduction:** The policies currently in place clearly state the guidelines to be followed by the industries, customers and users in order to achieve the final goal of reduced carbon emission. Reductions in Australia are - 25% by 2020 compared to 2000 levels, U.K. - 80% by 2050 compared to 1990 levels and U.S. - 30% by 2030 as compared to 2005 levels. On the other hand, Canada, U.S. and Mexico are aiming towards carbon emission reduction by 2035 by a certain level but nothing has been approved by the legislature **(UNFCCC, 2009)**.

- **Regarding gases used in commercial refrigeration systems in supermarkets:** There are many gases which are being currently used such as R 502, R 22, R 408 A, these are commercial refrigeration gases. There are various HFC gases such as R 507, R 404A as well being used in similar applications. Supermarket owners in most European countries prefer freezers using these gases, in majority of the stores, thus promoting the idea of reduction of GHG emissions. However, there are other gases which have still lower GWP and hence some companies are looking to replace R507, R 404A with the R 407A or natural refrigerants like CO_2 or HFC, propane blends as their global warming potential (GWP) are a lot less than R 404 and R 507. Walmart has been phasing out R 404 and moving to R 407A and Sobeys intends to move to CO2 from R 404 **(Black, 2012).**

- **Regarding reclamations, destruction or conversion of refrigerants**: Sometimes, refrigerants that are brought back for reclamation are unable to reach to the AHRI-700 purity standards. Approaches include destruction - having a considerable track record and a more recent approach is conversion of fluorocarbons to basic compounds like CO_2, NH_3,HF and HCl.

FCT : SALES

An FCT official was interviewed for gathering knowledge about the pattern of buying consumables and non-consumables required to run the plant. Vender evaluation is done by the supervisor-Gases (Sales). For preparing purchase orders FCT uses an internal software system Called “Dynamics”. Large volumes of supplies are ordered in order to get a considerable price break and higher savings margin. Once the supplier is fixed, the supervisor-gases (Sales) generate a P.O. This whole process takes approximately 3-6 months. Final purchases of machines and other consumables are done through the purchase department after the approval of the Plant Manager.

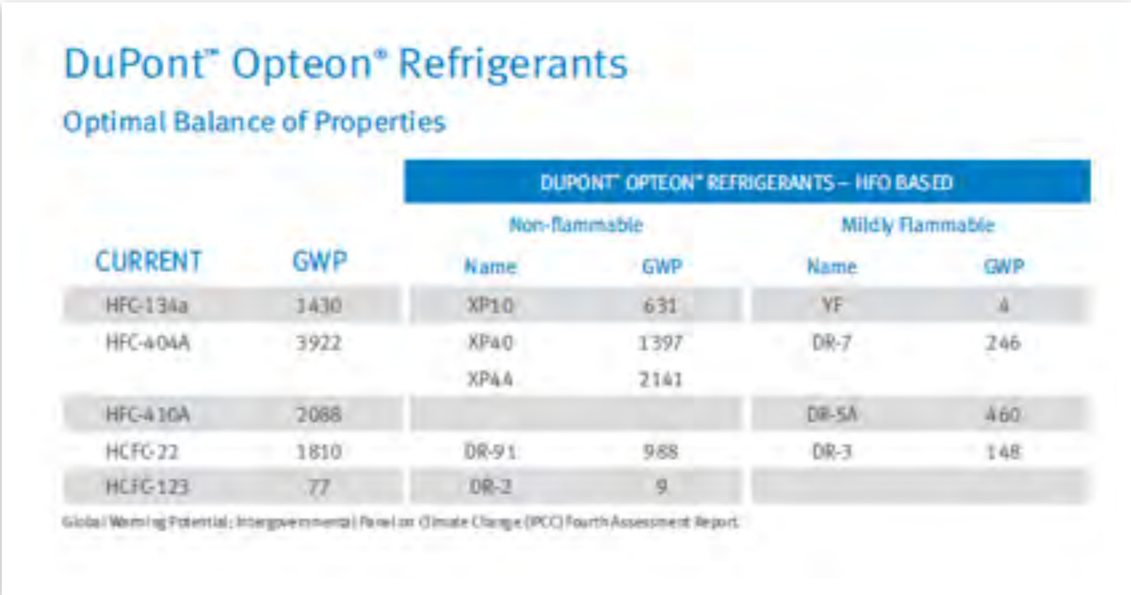
If a suppliers status stays inactive for a period of two years it is automatically removed from the system. If there are any complaints with the products and FCT is unable to fix the problem, the product is returned and a complaint is registered. If the problem is with faulty cylinders or their contents, it’s the Supervisor’s prerogative to remove the supplier from the list of suppliers. Infringement on any of the products is strictly not allowed, patent lawyers are consulted to make sure whether a particular company is authorized to blend any particular refrigerant or not.

DUPONT REFRIGERANTS: SALES

I was told by an official from the Market Development, DuPont, Canada that R-123 is the only refrigerant manufactured in Canada by DuPont.
He explained the company’s direction towards the phasing out of R22 and other gases with higher GWP & ODP and desire to find alternatives to replace those gases. Their R&D department is also looking into HFO-HFC blends and DuPont is selling the newest HFO in the market under the trade name of Opteon yf. Customers for HFO-1234yf include the

FIG 1: DUPONT OPTEON REFRIGERANTS

Source:Opteon.http://www2.dupont.com/Refrigerants/en_US/assets/downloads k26492_Opteon_refrigerants.pdf (FIG. 1)



DuPont™ Opteon® Refrigerants

Optimal Balance of Properties

CURRENT	GWP	DUPONT™ OPTEON® REFRIGERANTS – HFO BASED			
		Non-flammable		Mildly Flammable	
		Name	GWP	Name	GWP
HFC-134a	1430	XP10	631	YF	4
HFC-404A	3922	XP40	1397	DR-7	246
		XP44	2141		
HFC-410A	2088			DR-5A	460
HCFC-22	1810	DR-91	988	DR-3	148
HCFC-123	77	DR-2	9		

Global Warming Potential: Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report

automotive industry Ford, GM etc He also noted that according to A2L standards, HFO-1234yf is mildly flammable albeit being a robust replacement for HFCs; DuPont has also developed a range of Low GWP Replacements such as Opteon XP 40, XP 10, and XP44 According to him manufacturers, importers and reclaim companies have made a commitment to the RMC program and remit a levy to RMC on all sales of HCFC refrigerants **(RMC participants, 2014)**. He explained that DuPont's customer network is spread throughout Canada via a wholesaler refrigerant network and they have clients like Eastern Refrigeration, RSL located in western Canada.

ARKEMA CANADA: SALES

Arkema Canada purchases refrigerant gases from its sister company in the USA. These are sold to OEMs (General Motors for instance) or to wholesalers who then resell them to refrigerant/AC contractors. The purchases are made only from their sister company, Arkema Inc. No vendor evaluation is done.

Product arrives in cylinders and supplies depend upon the availability of the material. Warehouse personnel examine the product to ensure its correctness, correct quantity, intactness (not damaged) and it is labeled properly before entering their warehouse.

Arkema is dealing with refrigerant gases like Forane 22, 408a, 409a, 123, 404a, 134a, 507a, 407c, 410a, 427a, 365mfc/227ea blends, 407a. An Arkema interviewee stated HFO-1234yf and HFO-1233zd are for refrigeration to replace HFCs but research is still ongoing. HFO-1233zd is not commercially available.

They do not purchase or handle machinery and do not market SF_6.

ENERVAC CORPORATION (SF_6): SALES

An interview with an official of Enervac Corporation was held to gather information about the company and their operations in the field of SF_6. SF_6 is used as a dielectric (electrical insulation) in high voltage equipment (switched and breakers). Enervac builds equipment for transferring of gas during commissioning and maintenance of these electrical systems. Enervac has markets around the globe in countries including Australia, Japan, Republic of Korea, New Zealand and in over 30 states in United States of America; furthermore they are actively pursuing the expansion in United Kingdom, New Mexico and in other remaining provinces of the United States. Their clientele include Siemens, ABB, AREVA, Alstom, Duke Energy, TVA, CG International, Hydro One, BC Hydro, Armed Forces, Mining, Steel Plants, Pulp & Paper Mills of Canada. Currently they are operating joint ventures in U.A.E and Brazil and continue to pursue global expansion.

6. REFRIGERANTS:

There are a small number of replacement gases available which are most efficient with low GWP and Ozone depleting capacity. HFCs can be used in all refrigeration, air conditioning and heat pump (RACHP) applications. However due to their high global warming potential (GWP), HFCs have environmental implications in the event of refrigerant emissions into the atmosphere **(AREA, 2011).** Ammonia, CO_2 and HCs are well known refrigerants which have pros and cons, however, these refrigerants are natural and will stay competitive **(Jurgensen, 2013)**. HFO is a new refrigerant and will be widely used by all carmakers following EU Directive 2006/40/EC on mobile air conditioning **(AREA, 2011).**

There are several refrigeration systems available in the world which are based on CO_2, hydrocarbons and unsaturated HFC refrigerants as well as those that deploy ammonia (**Table 1**). All these refrigerants still have many challenges that should be considered in the design of refrigeration system such as their flammability, toxicity, lower efficiencies in some cases, and cost. Balancing the safety, energy efficiency, cost, and environmental impact of refrigerants using a consistent and comprehensive methodology across all refrigerants and system types, is essential in assessing alternatives. Good design is also important for reducing refrigerant emissions and preventing refrigerant loss during installation, operation, maintenance, decommissioning and end-of-life disposal. There are also several ways to reduce the refrigerant charge in a supermarket, such as proper piping design, type of condenser used, use of electronic expansion valves, and an efficiently designed distributed system. All these are measures to reduce refrigerant charges and therefore decrease the overall CO_2 footprint of the system **(United Nations Environment Programme, 2014)**.

TABLE 1: APPLICATION OF VARIOUS REFRIGERANTS

Application	Refrigerant
Industrial Refrigeration All kind of Industrial Ref.	Ammonia
Cascade systems	Carbon Dioxide + Ammonia
Secondary fluids	Carbon Dioxide
Commercial Refrigeration Cabinets	Hydrocarbons
Bottle coolers	Hydrocarbons
Supermarkets	Carbon Dioxide
Domestic Refrigeration freezers	Hydrocarbons
Air Conditioning	Hydrocarbons
Heat Pumps Hot Water	Carbon dioxide transcritical
Automotive	Carbon Dioxide or HFO1234yf
Large Chillers	Ammonia
Small Monobloc AC	Hydrocarbons

Source: AREA, 2011

A few of the refrigerant systems that use natural refrigerants are as follows:

1. CarrefourSA Express Kurtköy, Turkey: Transition from High-GWP refrigerant R 404 A to CO_2.
2. Sobeys, IGA Cookshire, Quebec, Canada: Transcritical CO_2 refrigerant system.
3. Supermercado Verdemar – Nova Lima Store,Brazil: CO_2 cascade system with HFC (R-134a) refrigerant as the high side fluid. The new installation uses a cascade system composed of a

twin primary system using 75 kg of R-134a (GWP=1430), and a secondary system using 100 kg of CO_2

4. Waitrose, Bromley South, Kent, U.K. Honeywell SolsticeTm ze, R-1234ze, HFO-1234ze.This case study has the world's first HFO chillers.
5. H-E-B at Mueller, Austin, Texas, U S: Propane Self-Contained Cases **(United Nations Environment Programme, 2014).**
6. Flanagan Food service, a leading distribution service, company located in Kitchener, Ontario, Canada: NH_3 / CO_2 fluid refrigeration package system supplied by MAYEKAWA. **(Maratou and Masson, 2013).**

❖ MERITS AND LIMITATIONS OF VARIOUS REFRIGERANTS

There are two broad classes of refrigerants:

A. NATURAL Refrigerants (AREA, 2011)

NH_3 (R717)

TABLE 2: MERITS AND LIMITATIONS OF NH3 (R717)

MERITS	LIMITATIONS
10-20% less costs to build the refrigeration plant, due to narrower-diameter piping usage as compared to CFC refrigeration systems.	Copper, Brass and Bronze cannot be used with ammonia refrigeration systems. Metal choices are mild steels, stainless steels and nickel
3-10% more energy efficient than CFCs hence lower operating costs	Poisonous in high concentrations.
Ozone Depleting Potential (ODP) - zero	Lighter than air hence spreads very fast in atmosphere if leakage occurs.
Global Warming Potential - zero	Ammonia systems have slightly higher maintenance costs - due to two factors: first

Distinctive smell detectable at small concentrations.	maintenance costs - due to two factors. First is in returning compressor oil that naturally migrates through the system. Oil return is a manual operation with an ammonia system requiring the collecting of the oil in a special pressure vessel, and draining that oil on a regular basis for disposal. A second major maintenance issue is that in low temperature plants, the "low side" or "cold side" of the system operates at pressures below atmospheric, which means that minor leaks that develop around valve stems pull air and moisture into the system. The air requires a special purging operation (or special equipment that does the purging automatically). The moisture infiltration in ammonia systems is more problematic, and requires special attention and equipment to remove **(Greenquist R, 2012).**
Less expensive than CFCs or HCFCs. It dissipitates faster in atmosphere and breaks down fast.	
Useful as a fertilizer in the form of nitrogen or urea manure.	

Applications for Ammonia:

Ammonia based refrigeration systems include thermal storage systems, HVAC chillers, process cooling and air conditioning, district cooling systems, supermarkets, convenience stores, air conditioning for the International Space Station and Biosphere II, and increasing output efficiencies for power generation facilities.

CO_2 (R744):

History of the use of CO_2 as a refrigerant is century old however R744 is now regaining popularity due to its low environmental impact.

TABLE 3: MERITS AND LIMITATIONS OF CO_2 (R744)

MERITS	LIMITATIONS
Safety classification of A1 - non flammable	Low cost but high pressure adds cost up due to certain system's needs
Lower toxicity than other greenhouse gases	Greater drop in capacity at higher ambient conditions
Ozone Depleting Potential- Zero	Dedicated training and tooling required to use them by engineers
Global Warming Potential – one	CO_2 vapour is heavier than air, so a leak in unventilated rooms would cause oxygen to be dispersed from the floor level upwards. This, together with the fact that smell, increases the resulting risk of casualties by suffocation.
Greater vapour pressure compared to other refrigerants which increases the heat absorbing capacity per unit volume flow rate of the refrigerant.	

Application of CO_2:

- CO_2 as primary refrigerant in cascade with ammonia or other refrigerant.
- CO_2 as secondary refrigerant

Carbon dioxide has been used in refrigeration and cooling in solid and liquid form because it sublimates to gas at very low temperature of -78.5^{o}C **(Hoge, 2013).** It is widely used in brewing of soft drinks, beers, other alcoholic drinks. Recently, it is being used in softening water to avoid corrosion problems in long water distribution lines and also in producing potable drinking water. The use of carbon dioxide as fire extinguisher is well known. It also finds application in petroleum industry to bubble out crude oil, sand blasting and hardening of metal castings **(Momin, 2013).**

The use of CO_2 into mobile air conditioning is still in nascent stages although many European companies are trying to implement its use in the air conditioning of cars **(Longden and Chasserot, 2007)**.Small cars like Fiat Panda and Ford Ka have the fitted CO_2 air conditioning system named B-COOL, that are however in research stages**(B-Cool, 2014).** A project from European Commission Research and Innovation transport is coming up with B-COOL using low-cost and high-efficiency CO_2 mobile air conditioning system for lower segment cars. The project aims at developing a new high-efficiency, low-cost air-conditioning system using CO_2 as a refrigerant for small cars (A and B segments). Methods to assess performance, annual fuel consumption and environmental impact will be identified, constituting a preliminary step for new EU standards **(B-Cool, 2014).**

HYDROCARBONS [PROPANE (R 290) AND ISO-BUTANE (R600a)]:

Along with other natural refrigerants, hydrocarbons such as R290 were used in refrigeration from the mid 1800s through to the 1930s. Due to its low environmental impact, R290 has been regaining popularity since the 1990s, and is now a common alternative to fluorocarbons in a wide range of applications **(Linde, n.d.)**

Application of HCs:

Refrigerants R290 and R600a are possible alternatives to other refrigerants with high GWP in small hermetic systems, like factory-made commercial refrigerators and freezers. They have also been used in refrigeration plants in the past, and are still used in some industrial plants. R290, in particular, is a possible refrigerant for such an application with good energy efficiency, but special care has to be taken regarding flammability.

Based on the safety aspects of hydrocarbons which make them very different to handle from an installation, maintenance and commissioning point of view, one could conclude that:

- R600a applications could be alternatives to HFC R134a
- R290 application could be alternatives to HCFC R22 **(AREA, 2011)**

TABLE 4: MERITS AND LIMITATIONS OF HYDROCARBONS [PROPANE (R 290) AND ISO-BUTANE (R600a)]

MERITS	LIMITATIONS
Low global warming potential(GWP)	Expensive to use as compared to NH_3
They have zero ozone depletion potential.	High flammability hence special care is required in use.
Petrol gases obtained from natural sources.	
Good energy efficiency hence used in household refrigeration.	
Easy availability throughout the world makes them good replacement for CFC, HCFC **(Danfoss application guideline, 2009).**	
Atmospheric lifetime is less than one year **(Hychill hydrocarbon refrigerants, n.d.)**	

B. SYNTHETIC Refrigerants

HFOs :

Carmakers around the world are seeking a globally compliant replacement for R134a refrigerant, the use of which is prohibited under the MAC Directive **(European Commission, 2014)**. A near drop-in replacement solution has been developed: HFO-1234yf (Hydro-Fluoro-Olefin, 2,2,2,3 Tetrafluoroprop-1-ene) enables carmakers to meet EU low GWP requirements.

These new fluids have potential in small commercial and residential applications where a medium pressure refrigerant can be efficiently employed and where low GWP is needed or desired. HFOs could allow use of current technologies minimizing conversion cost for the industry. HFOs and new blends of HFO–HFC (with reduced GWP 300-600, not flammable) may be available for applications that currently use R134a, R404A, and R410A (AREA, 2011).

EPA has approved three main low-GWP candidates for use as air conditioner refrigerants in new light-duty vehicles **(Sciance, 2013)**, they are:

1. R-152a GWP=124
2. R-744 GWP=1
3. R-1234yf GWP=4

Construction of production capacity for HFO-1234yf was delayed which was earlier planned in 2011 and is still a constraint. Honeywell and DuPont are currently the only HFO-1234yf suppliers. Honeywell will construct a high capacity plant to manufacture this refrigerant at the company's existing Geismar, Louisiana, refrigerants manufacturing plant which is expected to be fully operational by 2016 **(Honeywell, 2013)**. All cars in Europe will start using this refrigerant after 2017. Honeywell and DuPont claim intellectual property rights over the use of HFO-1234yf in vehicle air conditioners, although this is under dispute by Daimler because tests by Obrist Engineering in 2008 assessed the performance of different refrigerants, R134a, R744 (CO_2), and HFO-1234yf, under realistic conditions simulating a vehicle front end collision, where the mixture of refrigerant and oil would leak. While CO_2 would be safe at different temperature ranges, using the new HFO-1234yf will significantly increase the risk of fire **(Green Cooling Association, 2008).** In September 2012, Daimler claimed that recent testing had discovered unexpected risks in HFO-1234yf **(Apra global Connection, 2013)**. Daimler conducted a voluntary recall of the relatively small number of vehicles it had already sold in North America and Europe with HFO-1234yf, converting them to R-134a. Daimler stated that it would continue to use R-134a.The German Automobile Manufacturers Association (VDA) restarted development activity for R-744 systems. However, GM did intensive research on the use of this gas in air conditioning and now over 100,000 GM HFO-1234yf vehicles are already on the roads globally. An even larger combined number of vehicles are on the roads in Europe with HFO-1234yf from other OEMs such as Hyundai, Subaru, Ford, BMW. However, HFO-1234yf refrigerant prices have been higher than expected. It is ten times more costly than the R-134a due to less production by both the companies.

Production capacity for this gas is still not sufficient to cope with the present number of vehicles, however stricter environmental law of US and Europe for cutting down GHG emissions will help in promoting this blend in car air conditioning industry **(Sciance, 2013).**

❖ DESIRABLE REFRIGERANT CHARACTERISTICS TO FIND THE BEST REFRIGERANT

The choice of the best refrigerant for a given application is complex and it involves the evaluation of a number of competing characteristics **(RAC-7 alternatives, 2011)**

An “ideal” refrigerant would **(Table 5):**

- ❖ Have excellent global environmental characteristics i.e. zero ODP and zero or very low GWP.
- ❖ Be non-toxic and non-flammable.

- ❖ Have excellent thermodynamic properties for the given application. This means that the refrigeration cycle efficiency would be as high as possible.
- ❖ Be a “practical” fluid to incorporate in the plant design. This includes factors such as materials compatibility (it is helpful if the refrigerant is compatible with a wide range of metals and other materials such as seals and gaskets), lubricating oil compatibility and operating pressure level (evaporating pressure must not be too low and condensing pressure must not be too high).
- ❖ Be low cost, widely available and familiar to designers, installers and maintenance contractors.
- ❖ There is no single refrigerant or family of refrigerants currently available that possess all these characteristics.

All refrigerants have been characterized as “good” in terms of efficiency. All these refrigerant types have the potential to have “very good” efficiency if the system design is carefully optimized. However, poor design could lead to poor efficiency.

TABLE 5: A COMPARISON OF HFC, NATURALS AND HFO

	HFC	**NATURALS**			**HFO**
REFRIGE- -RANT		**HCs**	**NH**	**CO**	**1234yf**
GWP (100 YEARS)	×× R134a -1300 R410A -1725	√ 3-5	√√ 0	√√ 1	√ 4
TOXICITY	√√	√√	××	√	√√
FLAMMA BILITY	√√	××	×	√√	×
EFFICIENCY	√	√	√	√	√
MATERIALS	√	√	×	√	√
PRESSURE	√	√	√	××	√
COST	√	√√	√√	√√	?
AVAILABILITY	√√	√	√	√	××
FAMILIARITY	√√	√	√	×	×

Source: (RAC alternatives, 2011)

√GOOD √√VERY GOOD ×POOR ××VERY POOR

❖ RECENT ADVANCES IN THE FIELD OF RECYCLING OF REFRIGERANTS

➢ Midwest Refrigerants (Powell, 2013):

- The most recent advancements in dealing with refrigerants in U.S. have come from Midwest Refrigerants **(Powell, 2013),** which will be listed by the U.S. EPA as an approved facility for chemical-conversion once their first U.S. facility opens (probable date was in early 2013, no updates are available thereafter).

- Since chemical conversion is considered part of the chemical manufacturing process, not destruction by combustion, the conversion process is environmentally favourable, Moreover, used ODSs are not subjected to the rules of the hazardous waste because they are chemically transformed to the basic compounds like CO_2, H_2O, HF and HCl which are prevented from being harmful, by not being released into the atmosphere in this process.

- The Midwest refrigerant conversion plant will be able to convert 2 million pounds (2.5MT) annually and is being engineered to handle up to 12-15 million pounds (5,500 to 7,500 MT) annually **(Powell,2013).**

- Their technology includes chemical reaction with hydrogen and carbon dioxide that manipulates the ODS/GHG gas molecules and converts it into their original source chemicals, 99.99+% anhydrous HF, HCL and CO_2 for new uses, e.g. hybrid car batteries, electronics, oil sand industry.

- The Technology and Economic Assessment Panel (TEAP) allows a maximum of 0.2ng/m3 (0.2 nano grams per cubic meter) of toxic dioxins and furans output, whereas Mid-west achieves much lower levels of this toxic output of approximately 0.0095ng/m3.

- This system is asserted to be as a closed loop, no atmospheric venting, no waste stream, and energy efficient. This process is also effective on CFCs, HCFCs, HFCs, PFCs and HFOs, halons, methyl bromide, and most Persistent Organic Pollutants.

- In November 2011, Midwest Chemical Conversion Process **(Midwest refrigerants, 2013)**, received approval as an accepted destruction technology for ozone depleting and GHG substances, during the Montreal Protocol Member's meeting in Indonesia which made it one of the first technology approved by UNEP-TEAP that does not use combustion/incineration to achieve ODS/GHG destruction **(Midwest refrigerants, 2013).**

- The refrigerant manufacturing process leads to fluorocarbon waste which is normally eliminated inside the facility by thermal oxidizers. Midwest Refrigerants takes these waste streams and converts them back into their source chemicals for re-use.

➢ Use of HF and HCl Produced in the Midwest refrigerants Chemical Conversion Technique

HF:

- Serves as a catalyst in alkylation processes in oil refineries to extract Gasoline **(Aigueperse et al, 2005).**
- Is used as a solvent in the electrochemical fluorination of organic compounds to produce Sulphonic acid.
- Is used in the production of linear alkyl benzene.
- Several millions kilograms of Fluorine gas is prepared by electrolysis of a solution of HF and potassium bifluoride. It's used in the production of the atom bomb and other nuclear energy projects made it necessary to produce large quantities **(Jaccaudet al 2005)**.
- Is often used in the palynology.
- Is extensively used in the cleaning of stainless steel ,a process called pickling**(Galvez et al 2007)** etching glass, removing oxides from metals, exotic extraction of metals, and purification of quartz **(Hance et al 1997)** Manufacturers market large quantities of HF as drummed or packaged products.

- Car washing is one of the most chemically intensive activities and car wash facilities continue to use HF in their daily wash routine.
- Is used to prepare refrigerants.
- Is also used for digestion of geological samples containing radioactive elements. Following digestion of samples with HF, HF was eluted along with Pt group elements **(Genuino et al, 2012).**

HCl (Hudson,2012):

- Is used to 'pickle' steel. This is a process whereby rust and scale is removed from steel sheet or coil with the use of a dilute solution of Hydrochloric Acid. The metal can then be processed.
- Is used to manufacture organic compounds such as Vinyl Chloride and Dichloroethane which are used to produce PVC (Poly Vinyl Chloride)
- To regulate the pH level in a wide range of manufacturing and treatment processes including the production of drinking water, pharmaceuticals, beverages and foods
- Is used in the processing of additives for the food industry including fructose, citric acid and hydrolyzed vegetable protein.
- Is used to produce inorganic compounds for water treatment including drinking water and waste water.
- Is used to neutralize the water in swimming pools making it safe for bathers
- Is used to regenerate ion exchangers
- Is used to process leathers in the tanning industry
- Is used to purify common salt.
- Is used in North Sea oil production where it is used to facilitate oil well acidizing **(Hudson,2012).**

➢ **Refrigerant Management Canada (RMC participants,2014)**

- Refrigerants that are not usable anymore are administered by Refrigerant Management Canada (RMC), which is setup by The Heating, Refrigeration and Air conditioning institute of Canada (HRAI) and holds a non-profit organization status in Canada. They deal with disposal of surplus refrigerants with ozone depleting properties from stationary refrigeration and air-conditioning industry like HCFCs.

- In 2012, RMC stated that they verified and registered 170,000 ODS-derived registered emission reductions (RERs) on the Canadian Standards Associations (CSA) reductions registry, which marked the first verification of a successful ODS destruction project in Canada.

- RMC also verified significant GHG reductions along with the help of their partners, ensuring the proper recovery and destruction of potent GHGs with some of the highest GWP values.

- Post first verification, RMC delivered 60,000 RERs to natural gas and electricity retailer. The revenue generated from selling these offsets was critically important to the financial viability of the program that ensures proper management and destruction of ODS in Canada **(Powell, 2013).**

DuPont is the only company in Canada that manufactures a HCFC refrigerant viz; R – 123. It is used in building chillers and feed stock purposes. When question raised about the HCFC phase out, the interviewee stated that R-123 is treated as directed in its MSDS sheet **(DuPont Workplace Guidelines, 2013)** and fairly unique with its ODS of 0.02 and GWP of 120.It also has benefits like OEM acceptance and endorsement, however it will be phased out in 2030. This has the lower overall operational costs in new equipments and is an R-11 replacement in chiller systems worldwide.

➢ Putting global warming Fluorochemicals to beneficial uses (Global Scenario)

Fluorine-based compounds are a continuing threat to the environment and while they can be recycled but they are often warehoused and incinerated at high costs or just vented illegally **(Reisch, 2013).**

- A former, Environmental Protection Agency (EPA) scientist reported that ODS with global warming potential of higher than 6 billion tons of CO_2 are stored in refrigeration and air-conditioning equipment and commercial and residential infrastructure in the world, that's equivalent to carbon emissions from every car, house and factory in the U.S **(Reisch, 2013).**

- A San Francisco-based firm, EOS Climate is helping users get acquainted with and adopt the advanced refrigeration technologies with lower ODP and GWP in chilling equipment's **(EOS Climate, 2014).**

- EOS is collaborating with DuPont **(P R Newswire, 2014)** to help the users capture and eliminate CFCs which are destroyed at a waste incineration facility. Carbon credits can be earned in exchange and is included under California's new carbon trading program, California's Cap and Trade programme **(C&EN, 2014 and Powell, 2013).**

- HFCs and HCFCs are delivered to companies like Indianapolis-based Icor International, which purifies, distills, and resells old refrigerants **(Icor International, n.d**).

- Veolia Environmental Services receive many 30,000 lb shipments each year of discarded refrigerants, which cost $45,000 to destroy in a rotary kiln at 870 degree Celsius **(Veolia, n.d.**).

- The UNEP-TEAP, United Nations Environment Programme - Technology and Economic Assessment Panel **(United Nations Environment Programme, n.d.)** has approved the refrigerant conversion technologies from two firms - Midwest as discussed above **(Midwest refrigerants, 2013)** and Australia-based Pacifitech **(High Beam Research, 2011).**

- By using Midwest chemical conversion technology, the cost of destroying the discarded refrigerants would be reduced to $7,500 as compared to $45,000, as mentioned above using the Veolia facilities. This technology will also yield useful chemicals worth $30 thousand approximately **(Powell, 2013).**
- Midwest's technology can be used to destroy HFC-23(high GWP). This product is made in large quantities during the manufacturing of HCFC-22 and DuPont's Teflonflouropolymer **(Midwest refrigerants, 2013).**
- HFC-23 is a valuable source of HF and fluorine. These can be extracted off HFC-23 using the Midwest refrigerant conversion technique **(Midwest refrigerants, 2013).**
- Pacifitech's technology, converts a mix of fluorochemicals to vinylidene diflouride at temperatures between 725 and 900 degree celsius. VDF is the precursor of polyvinylidene fluoride, an elastomer used to make durable wire insulation and other coatings **(High Beam Research, 2011).**
- Another emerging technology with potential to have a large commercial asset is being developed by Suryaprakash and his team in University of Southern California, Loss Angeles. It is still at a nascent stage of development and includes a process to use HFC-23 as a catalyst and raw material for pharmaceuticals and agrochemicals **(Reisch, 2013).**
- This team has been able to use triflouromethane to react with sulphur to yield triflouromethane sulfonic acid that sells for about $300/lb as a catalyst **(Reisch, 2013).**

7. Sulphur HEXAFLUORIDE (SF_6):

❖ Size and trend of the industry - Domestically and Internationally

SF_6 is chemically inert, non-flammable, and nontoxic. Although SF_6 gas is not detrimental to the ozone layer, it is a highly potent greenhouse gas. It is 23,900 times more effective at trapping infrared radiation than carbon dioxide and is stable in the atmosphere for some 3,200 years. SF_6 is currently listed by the International Panel on Climate Change (IPCC) as the most potent greenhouse gas **(IPCC, 2007).** SF_6 does not contain chlorine atoms as do CFCs, hence has no ozone layer depletion potential. Measurements show that current concentration of $SF_6$is 3.2 parts per trillion by volume (PPMV). Concentrations of CO_2 are estimated to be 355 PPMV, which makes the relative contribution of SF6 to global warming close to about 0.01%, and it is estimated to be less than 0.1% in 100 years **(Van der Zel, 2003).**

Although the percentage of SF_6 found in the atmosphere is relatively small, the rate of growth is alarming because there is no legislative rule to curtail the SF_6 from heavy electrical industry emissions from where the SF_6 leaks out to the atmosphere. SF_6 gas is heavier than air such that in enclosed areas e.g. in power plants, it can displace breathable air. The toxic byproducts released when SF_6 gas interrupts the arc plasma in a circuit breaker are also of concern. Decomposition products in the form of metallic fluoride powder are toxic to humans who breathe or touch them, and adequate personal protective equipment (PPE) and training are essential for personnel safety **(US Bureau of reclamation, 2004).**

❖ Electricity Industry

SF_6 has been widely used for insulating purposes in high voltage equipment and as a cover gas and for oxidation prevention in the magnesium industry to protect combustion of molten magnesium. It is also used for semi conductors manufacturing and for gas dispersion studies in the industrial and laboratory setups but in much lesser amounts. The main issue with sulphur hexafluoride is the huge heat trapping capacity **(Environment Canada, 2013).**

An advantage of SF_6 is that it allows the transmission of higher power levels in a smaller footprint compared with other insulating mediums. Such advantages are particularly important for electricity transmission in city substations or offshore wind applications. SF_6 filled devices have continually decreased in size and increased in capacity over time. Pressurized SF_6 gas is used for the safe and reliable operation of gas insulated switchgear (GIS) as it has a much higher dielectric strength than air or dry nitrogen, making it possible to significantly reduce the physical footprint of the equipment and enable installation in constrained spaces. GIS also has the advantage of being more resistant to hostile operating environment , which makes this a more reliable and sustainable operating device **(Alexander et al, 2013).** Worldwide, the electric utility industry is the dominant user of SF_6–using 70%-80% of all SF_6 produced. There is growing environmental interest in the use of SF_6 due to the fact that it is a powerful and long-lived greenhouse gas. Even though the present share of SF_6 from the electricity industry in man-made greenhouse gas emissions is low (it was estimated in 1999 as 0.1%), there is concern over the long-term impact of SF_6 on global warming **(Van der Zel, 2003).**

❖ SF_6 Advantages

The electric power industry uses SF_6 as a dielectric and insulating material due to its physical and electrical properties that include **(AccuDri, 1995 and EPA Conference Proceedings, 1995):**

- Twice the dielectric strength that of air
- Nontoxic, nonflammable and noncorrosive
- Chemically stable with high breakdown strength and SF_6 molecules provide excellent arc extinction during electrical operations minimizing contact wear and maintenance.
- Excellent thermal conductivity; High heat transfer permits lower operating temperatures.
- Ease of availability in commercial locations
- For distribution voltage switchgear, SF_6 provides these important advantages:
- Size reduction
- Weight reduction

- Reliable operation
- Ease of installation
- Ease and reduction of maintenance

Common applications

Almost 80% of the annual composition of SF_6 is used for gas insulated substation (GIS) equipment and medium voltage switchgear including circuit breakers and load break switches. Of the 80% medium voltage switch gear accounts for approximately 10%. In both electrical applications, the equipment is designed to contain the gas in sealed pressure systems, which are assembled, filled and tested in a controlled environment. The other 20% of the annual consumption of SF_6 is used in applications that require release of gas into the atmosphere **(G and W, n.d.).**

❖ SF_6 Leakage

With increase in the age of equipment, the leaks of SF_6also increase which continue through the various stages of equipment's life cycle. Nevertheless, it can also accidentally get released during installation and servicing. It is still being permitted in medium and high voltage applications switchgear (till 52kV and above), which are also not leak proof and the gas still emits out into the atmosphere. SF_6 is on the Kyoto list of substances (**GHG protocol, 2013**), In fact, SF6 is now banned in most of applications **(European Environmental Bureau, 2012)**, but it is still permitted in medium-voltage (up to 52 kV) and high-voltage (above 52 kV) switchgear which emit SF6 in atmosphere due to leakage in ailing equipment or accidental leakages **(Electrical review,2011).** It is stated that the use and emission of the gas must be minimized and the trend expounds an approximate annual declination rate of 2.8% **(Pennsylvania state of independence, 2013)**.

Utilities are required to recharge their equipment so as to avoid the leakage from electrical equipment and to make up for the SF_6 gas that has escaped/leaked.

Potential SF_6 emissions occur during/from:

(1) Gas handling and transferring operations

(2) Equipment operation

(3) Equipment mechanical failure

SF_6 equipment has low pressure alarms that trigger when there's a 7-10% pressure loss which marks the top-up requirement. Under normal operating conditions, gas can be lost with a loss of up to 0.5% of the nameplate capacity for newer and 5% for older equipment, annually **(Enervac Corporation,n.d.)**. The newer GIS equipment is considered to be leak proof for a 5 to 10 year period. Variability depends upon the quality and age of seal materials and environmental factors. Cold conditions do create problems in the equipment operation that might lead to emissions because of seals being stiff and not sealing tightly. A mechanical failure can cause an immediate release of SF_6 or may also take up to 1 year to get the alarm get triggered.

Usually purification processes of SF_6 gas do not produce SF_6emissions.

On March 22, 2007, the Canadian Electricity Association (CEA) and the Greenhouse Gas Division (GHGD) on SF_6 emissions from electric utilities in Canada (Environmental Canada, 2008) signed a Memorandum of Understanding (MOU). It agreed upon the establishment of a joint committee to prepare a Sulphur Hexafluoride (SF_6) emission data collection and reporting protocol.

The idea behind the protocol is to provide a guidance document for estimating SF_6emissions from electric utilities that is consistent with the Intergovernmental Panel on Climate Change (IPCC) Guidelines. The methodology described will be used by all CEA member electric utilities in Canada to estimate their annual SF_6 emissions from in-service electrical equipment and report the results to the GHGD **(Environmental Canada, 2008)**.

❖ Methodology for Quantification of SF_6 Releases in Canada

The Canadian electricity sector will use following formula to estimate the release of SF_6emissions **(Environment Canada, 2008):**

Total Emissions = Σ Equipment Manufacturing Emissions + Σ Equipment Installation Emissions + Σ Equipment Use Emissions + Σ Equipment Decommissioning and Failure Emissions+ Σ Emissions from SF_6 Recycling and Destruction

❖ Equipment Manufacturing Emissions

Since Canadian electric utilities do not manufacture their transmission and distribution equipment, they are not responsible for the SF_6 released during the manufacturing stage. In fact, according to some utilities, electrical equipment purchased by the Canadian electricity sector is manufactured in the United States, Europe or Asia, and hence, emissions associated with manufacturing would have occurred mainly outside of Canada. As such, emissions from equipment manufacturing (i.e. the first term of Equation 1) are assumed to be not applicable to the electricity sector.

❖ Equipment Installation Emissions

SF_6 equipment is delivered to utilities pre-charged with some SF_6 and it is charged to full capacity at installation. In the Canadian electricity industry, the potential for SF_6 emissions during equipment installation is considered to be extremely rare occurrence. A vacuum hold check is typically performed prior to the installation of new equipment to ensure the equipment is gas tight **(Environment Canada, 2008)**.

❖ Equipment Use Emissions

The primary source of SF_6 releases is associated with the cumulative minute releases that occur during normal equipment operation. Gas releases could potentially occur during gas handling and transfer operations although such releases would be significantly smaller in magnitude than emissions that occur during normal operations.

Due to the SF_6 leakage that occurs during the above circumstances, utilities are required to "top up" their equipment to keep their equipment properly charged and operational. By topping up equipment with SF_6 gas, utilities are able to replace the amount of gas that has escaped.

❖ Equipment Decommissioning and Failure Emissions

During the decommissioning of retired equipment SF_6 gas must be recovered from the retired equipment prior to disposal. As SF_6 gas releases may occur from the way in which the gas is transferred out of the equipment during gas recovery, decommissioning of retired equipment becomes a potential source of SF_6 releases.

When catastrophic failures of equipment occur, a significant amount of SF_6 is leaked out of the equipment. Hence, equipment damages are a potential source of emissions.
Retired equipment and damaged equipment that cannot be repaired are sent off site for disposal.

❖ Emissions from SF_6 Recycling

When $SF_6$is recovered from equipment, it is filtered through a gas cart or other filtering equipment to remove moisture and impurities before it is reused. Hence, emissions from SF_6 recycling are eliminated from the calculation of total emissions.
Given the reasoning above, the Canadian electricity sector uses the modified following formula **(Environmental Canada, 2008).**

Total Utility SF_6 Emissions = Σ Equipment Use Emissions + Σ Equipment Decommissioning and Failure Emissions)

❖ Regulations or policies regarding the handling of SF_6 in Canada

$SF_6$was added to Schedule 1 of Canada Environment protection act (CEPA) 1999(Canadian Environmental Protection Act,1999) in November 2005 in order to enable the Government to use a variety of preventive or control actions on the use or emissions of SF_6 as related to various industrial and commercial sources. Under subsection 90(1) of CEPA 1999, a substance that meets the criteria set out in section 64 of CEPA 1999 can be added to Schedule 1 of CEPA 1999 by the Governor in Council on the recommendation of the ministers **(Environment Canada, 2013)**. SF_6 storage and release is subject of a proposed Environmental Emergency (E2) regulation, which obligates facilities that store SF_6 in large amounts to report the quantities, kept at the storage sites and the amounts of releases caused by accidents. The reporting on releases of SF_6 to the atmosphere is also regulated under section 46 of CEPA 1999 and is required from large industrial and commercial facilities that meet a certain threshold for their combined emissions in CO_2 equivalent of the six Kyoto Protocol Greenhouse Gases **(Environment Canada, 2013).**

❖ What happens to used gas in Canada?

When SF_6 gas is recovered from equipment, it is filtered through a gas cart or other filtering equipment to remove moisture and impurities before it is reused. When SF_6 gas has been contaminated with air and impurities, and has a purity of less than a certain level (the acceptable level can vary between 95-99%, depending on utility practices), it cannot be reused and is sent for offsite purification in the U.S. There are no facilities in Canada that perform SF_6 gas purification **(Environment Canada, 2008).**

At present, there are few companies in Canada, that are working on cleaning the used gas and again refilling the clean gas into the instruments. Enervac Corporation in Ontario is involved in cleaning used SF_6 gas **(Industry Canada, n.d.).**

❖ SF_6 Recycling (Environment Canada, 2008)

Enervac Corporation cleans the SF_6 gas in Canada. There is no company ,which does the recycling in Canada.

ENERVAC is divided into two divisions:

1. Environmental Technology Group

2. Utility Group

The Environmental Technology Group manages the Trampoil Separators, Coolant Recycling Systems, Sump Cleaners, Reverse Osmosis Systems, Ultra filtration Systems, Filters as well as consulting on water, coolant and waste water issues.

The Utility Group manages Dehydrators, Degasifiers, Dryers, Mobile Oil Filters, Fuller's Earth Systems, Sulphur Hexafluoride (SF_6) Processing Systems, Oil Filters and Air Filters, Centralized Lubrication Systems and consultations for the needs of oil, air and SF_6. Enervac has SF_6Gas Servicing Cart which is designed for the processing of SF_6 used in high voltage metal clad switch gear, bus ducts, accelerators, circuit breakers and transformers that are charged during normal operation with SF_6 Gas as a dielectric.

This cart performs following functions:

1. Removal of SF_6gas from the serviced equipment, liquefaction and storage of gas into system storage tank.

2. System evacuation for dry-out prior to re-charging.

3. Re-evaporating SF_6Gas and re-filling evacuated equipment.

4. Purification of SF_6 Gas by absorption and removal of decomposition products and moisture.

Enervac has SF_6 servicing carts, trailer-mounted for large volumes or compact and portable for small volumes. These servicing carts will remove the gas from the circuit breaker, purify it to remove water, particulate and degradation products, store it in liquid form while repairs are made, and fill the breaker with clean gas **(Enervac Corporation, n.d.).**

❖ Environmental Protection Act Position on SF_6

EPA has a voluntary program to reduce the emission of SF_6 into the atmosphere driving users and suppliers towards sustainability by gathering data on usage, upgrading old equipment, recovering and recycling the gas and improving the sealing methods of gas pressure vessels **(Environmental protection act,2010).**

❖ What is required technically to recover and process this gas? global Scenario:

AREVA T&D France is involved in cleaning and recycling of SF_6. They are major world producer of high voltage switchgear, and have been collaborating with AVANTEC, a company specialized in performance chemicals to develop a new approach to treat SF_6

containing a high amount of decomposition products due to electrical normal interruption (Bessede et al, n.d.).Onsite detection of byproducts of SF_6 is being done by gas chromatography. AVANTEC has developed the recycling of SF_6, using a liquid phase filtration technology. Laboratory analytical methods, also developed by AVANTEC, appeared to be very precise and reliable to guaranty the final composition of the purified gas. This concept, now running successfully in France since 2011 is slated to adoption in other countries of Europe. A further expansion in the America via AREVA T&D and AVANTEC subsidiaries and its partners is under consideration **(Bessede et al, n.d.).**

Recycling of SF_6 by this company is done efficiently by following method **(Bessede et al ,n.d.).**

AVANTEC has developed a SF_6 gas treatment technology, which aims at avoiding its destruction by a proper recycling of the polluted SF_6 gas. A pilot installation was set, based on selective adsorption of chemicals in the liquid phase, able to decrease the amount of decomposition products contained in the polluted SF_6 gas. AREVA T&D has developed an analytical method for onsite analysis of polluted SF_6 gas based on Gas Chromatography technique .As a pre-treatment, when the content of non-condensable gases in SF6 is too high (more than 10,000 ppm weight), a process of distillation has to be used by separation between the gas phases of air and of SF_6 at very low temperature. Then the purification is run on the equipment that has been studied and designed by AVANTEC. It allows the regeneration of SF_6 in the liquid phase. A large column is filled with successive layers of various adsorbents like soda ash, activated alumina, active charcoal, molecular sieves, in order to come to an optimal adsorption. Tissue rings separate these adsorbents and are displayed according to a certain order and precise quantities. In addition to the filtration capacity of the absorbents, a 5 microns particles filter is added at the end of the column. The polluted SF_6 in liquid form is pushed with a pneumatic pump, then rises inside the column, passes through adsorbents layers, is filtered through the safety 5 microns filter and is recovered. At the end of the equipment, a valve allows a direct sampling in order to determine the level of purity of the recovered product. Finally, this device, an improvement of a micro pilot unit already available in the factory, has been optimized by a special choice of i) the quality of the adsorbents, including the dedicated choice of the suppliers, ii) the order of placing the absorbents in the column, iii) the quantity of each component, iv) the dimensions of the several layers, v) the speed of the liquid SF_6 through the various layers, and vi) the pressure and its control. From time to time, when the performance of the process decreases, the adsorbents are taken away, are placed in tight containers, and are sent, for destruction to specialized company certified for this type of destruction. According to this company, when the SF_6 gas contains too much decomposition products, due to arc switching, the reclaiming of the gas, on site, with the help of the movable devices is not possible. In this case the gas has to be treated in another way and many reclaiming techniques have been developed worldwide that could avoid destruction of the gas.

In Japan, gas-reclaiming equipment has been developed to separate SF_6 gas from mixed gas. This system concentrates SF_6 gas, which is sent into a gas liquefaction system. Then a filter refines the SF_6 (Takahiro et al 2001). Another type of equipment has also been developed based on different filtering stages, a liquefaction system and also analytical system ,Gas Phase Chromatography in particular **(Tamata and Al,n.d.)**. In Germany too, a reuse concept has been developed, based on permanent quality control and a device for purifying and storing of the used SF_6 gas **(Lauzon et al, 2002)**. Other systems using separative membranes for the purification of the SF_6 have also been developed. These systems are found in France and Germany **(Pittroff et al, 2002).**

- **Removal of air or nitrogen from SF_6 as an aid to SF_6 Recycling and Re-use in USA:**

The main contaminants of this gas are nitrogen and air. One of the methods utilized to purify SF_6 gas is the use of a cryogenic process to separate and remove the air/nitrogen from the SF_6 gas. Users of SF_6 faced the problem of handling SF_6 that has been mixed with air or nitrogen or CF_4. In the case of nitrogen or CF_4, the mixture was likely intentionally performed to prevent liquefaction of the SF_6in colder climates. In the case of air, the mixture was likely unintentional and due to handling errors or gas handling equipment leaks. The handling of these mixtures needs to be performed in isolation from the handling of the pure SF_6 **(Van der Zel, 2003).**

Utilities are often not equipped to deal with two different categories of gas (Pure SF_6 and mixtures) and the inclination may be to vent of the mixture rather than deal with the complications and risks. Traditionally, SF_6 purification is carried out using cryogenic means. Some purification is possible in the field using gas carts if the SF_6 is always drawn from the liquid phase. However, the vast majority of the air will remain in the vapour phase and as the air content increases as the cart is used, higher pressures will be required to liquefy the SF_6. If the air content is high enough, the compressor will be unable to liquefy the SF_6 and the contents will require disposal. Retrofitting a purification unit to the gas cart will remove this air contamination in situ and allow not only withdrawal of clean gas from the vapour phase, but could eliminate having to remove contaminated gas for further processing **(Van der Zel, 2003).**

Two methods of cleaning of this gas have been testified in USA . They are:

Membrane separation - involves separation modules containing bundles of hollow fibres. Flowing contaminated gas through the hollow fibres allow the air to pass through the walls of the fibre but not the SF_6. Depending on the hollow fibre, the process works by either passing the gas through the fibres or flowing around the outside of the fibres and letting the air to permeate inside. The mechanism is one of size exclusion, the SF_6molecule being much larger than the oxygen or nitrogen (air) molecules, will be retained **(Van der Zel, 2003).**

Pressure Swing Adsorption (PSA) - is the separation of air from SF_6using adsorption processes with the use of modules packed with a specific adsorbent. The process is similar to the desiccant towers used traditionally for drying and removal of decomposition products from SF_6. The main difference is that the impurities in the desiccant towers (moisture, decomposition products) are permanently retained and the SF_6 just passes through. In a purification process utilizing PSA, the contaminants (oxygen, nitrogen) are retained more strongly, but not permanently, than the SF_6. This is due to differing molecular interactions between the adsorbent and the gases. The process begins by flowing of a fixed volume of a contaminated mixture (air and SF_6) through a module packed with the appropriate adsorbent.

The SF_6passes quickly through separating from the air and before the air has the time to come through the adsorbent, the flow is reversed and the air is collected in another vessel.

Based on the literature survey and evaluation, ten different adsorbents, which were examined and named on the basis of numbers 1-10. These were tested for the suitability of SF_6/air (nitrogen) separation. Table 6 has been obtained from the literature **(Van der Zel,2003).**

TABLE 6: SEPARATION FACTORS AT ROOM TEMPERATURE

Adsorbent	**SF_6**	**SF**	**SF**
1	1.86	4.14	9.05
2	1.47	3.68	8.13
3	0.114	0.314	-
4	21.74	21.74	7.06
5	2.38	2.38	2.24
6	>>25	>>25	-
7	>>25	>>25	-
8	>>25	>>25	-
9	4.55	4.55	-
10	2.68	5.73	10.17

The separation factors are the ratio of the retention times of each impurity (N_2, O_2, and CF_4) to that of SF_6 when a mixture of these gases is introduced into a packed column of the particular absorbent that has an inert gas flowing through it. These experiments apply gas chromatography and are useful in determining suitable absorbents to be further tested in the PSA apparatus. The higher the separation factor, the greater the difference in retention time and the better the two can be separated using a given adsorbent with PSA. Only one adsorbent (number 4) turned out to be suitable for the separation of $SF_6$from air or nitrogen in a gas mix containing higher amounts of SF_6. This has the separation factors at room temperature of 21.74, 21.74, 7.06 for SF_6/N_2, SF_6/O_2, SF_6/CF_4 respectively as shown in

Table **6 (Van der Zel,2003).**

Other types of adsorbents allow the air to pass through quickly and the $SF_6$to be retained. Ideally, the component in highest concentration is not retained, and the impurities are. Therefore, depending on the degree of air contamination (less than 20% compared to greater than 80%), the choice of absorbent is critical. The timing of the solenoid valves is critical to the process. Retrofitting this to a gas cart will be made easier by utilizing vacuum pumps and compressors on the cart **(Van der Zel, 2003).**

Only a few new technologies/concepts regarding SF_6 separation from air or nitrogen have emerged in the past five years. Just six patents were found and a few publications. Basically, all the research dealt with applying membrane separation, or adsorption processes, or in some cases a combination of both. Even though SF_6purification or separation was the main objective of these initiatives, some methods were applicable for very low (less than 1%) or low (10-20%) SF_6concentrations (for removing SF_6 from vented emissions) while only a few were applicable for concentration of SF_6in the feed stream higher than 60%. With the exception of one application, which is at the prototype stage, all adsorption processes were energy intensive (the purified SF_6gas was at low pressure). That is, the gas was treated at a lower pressure than the source and required recompressing. This requires more energy than if the purification were possible at the feed pressure. The same was true for membrane separation. These separation processes wasted the pressure of the SF_6 feed gas mixture during the separation process. The exceptions were a membrane process involving a molecular sieve separation principle and an adsorption process involving an adsorbent that had smaller pore openings than the kinetic diameter of SF_6 gas. Therefore, the product SF_6 gas stayed at approximately the same pressure as the feed gas, hence conserving the initial feed energy. The adsorption process was very similar to one that will best be suited for electrical utility applications. However, based on the prototype size, the process proposed will be smaller and lighter and more efficient.

❖ Recent Developments in recycling of SF_6:ABB Research Company,Australia

There is a recent development in recycling of SF_6. ABB Research Company has set up an automated recycling plant of Sydney, Australia. According to them, the purity of recycled SF_6gas using the newly developed technology is about 99.99 percent and is in accordance with technical grade IEC 60376 (the standard for new gas), which enables SF_6 to be reused again and again. Using recycled SF_6 gas will help reduce carbon emissions and could result in a cost savings potential of up to 30 percent **(Alexander et al, 2012).** Initially a manual cryogenic process for purifying SF_6 had been identified that had several limitations. These were primarily poorly reproducible product, quality and safety concerns regarding exposure of operators to liquid nitrogen. As a result, a new research and development project was initiated to develop a safer, better controlled and largely automated process. The outcome of this project was the first fully automated cryogenic SF_6 purification plant in the world. The entire project represents an innovation in itself; some of the individual innovations are:

–A novel gas separation chamber to freeze SF_6 under cryogenic conditions

–A rigorous automated process control system that balances inventory and prevents leakage

This resulted in a new process **(Alexander et al, 2012)** that involves a cryogenic step to remove non-condensable gases, chiefly nitrogen, from the used gas, and a filtration process to remove contaminants including water, various acids, toxic by products and oil. The greatest technical advantage of the new process in comparison with existing technology is that it can efficiently recycle SF_6 irrespective of the type or level of contamination. Existing technologies suffer from an inability to treat all contaminants and all contamination levels in one process. Furthermore, the level of automation present in the new process allows significantly greater throughput and energy efficiency.

While SF_6 is relied upon for its insulating and arc-quenching capabilities, over time the gas can deteriorate, particularly if the equipment has experienced regular switching. Inferior gas quality can diminish the above mentioned capabilities, which compromises the performance and safety of the equipment. Checking the quality of the gas in equipment, as part of a preventative maintenance program, can extend the product life **(Alexander et al,2012).**

ABB Research has announced the launch of its next generation LTA carbon dioxide (CO2) live tank high-voltage circuit breaker platform, starting from 72.5 kilovolt (kV), at the Cigre technical exhibition held in Paris in August 2012. Sulphur hexafluoride (SF_6) gas has higher global warming potential (GWP) than CO_2. By substituting it with CO_2 as the insulating and arc extinguishing medium, each new 72.5 kV LTA breaker has the potential to reduce CO_2 emissions by 10 tons through the product life cycle which is 18 percent less than its predecessor**(ABB,2012).**

8. CUSTOMER FEEDBACK:

Senior official at VIARAIL, CANADA has described company profile. They are priority customer of FCT. It is a government funded company, using refrigerants for air-conditioning. Their policy is to not use the contaminated/impure refrigerants at all. They are currently using R-22 as a refrigerant which is being recycled by FCT. He mentioned that R-421a was introduced to them by FCT which is a HFC and are prepared for its phase out in near future. Compatibility tests for this gas were acceptable and they intend to switch to this once R - 22 becomes obsolete. They are willing to shift to other refrigerants with FCT if government approves their use.

9. CONCLUSION:

This study reveals intention of Canadian refrigerant industry to switchover to more eco-friendly gases with zero GWP and ozone depletion properties to reduce GHGs. FCT can focus on introducing natural refrigerants like CO_2, NH_3, Propane and Isobutane in refrigeration sector which have zero ODS and GWP. Use of HFO-1234 yf blend and its recycling for car air conditioning system can be explored. Further investigation into using CO_2 in mobile air conditioning is recommended which is in nascent stages in Europe. The fully automated SF_6 recycling plant using cryogenic techniques can be set up which will be a first of its kind in Canada, However the recent introduction of CO_2 as a replacement of SF_6 in switchgear industry should also be kept in mind.

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ANNEX

A. Interview questions for sales departments:

1. How orders for various consumables and non-consumables are placed?
2. Who does the vendor evaluation?
3. How the vendor evaluation report is made?
4. Who approves the final purchases of machines and other consumables?
5. Who are the suppliers?
6. How are purchase orders placed?
7. How many days are taken for supply, once the orders are placed?
8. If any supplies are not acceptable what is the clause to remove the suppliers from the list?
9. What are the criteria for rejecting orders?
10. What are the criteria for releasing payments?
11. How soon the suppliers are paid?

B. Alternate refrigerants (Pearson, 2003)

Acoustic Refrigeration

Acoustic refrigeration depends on the fact that the energy travelling through gas in sound consists of pressure fluctuations in the gas, which themselves produce variations in temperature. If the sound is produced within a pressurized tube it is possible to cool an object within the tube and to refrigerate a fluid passing through the object.

Magnetic Refrigeration

Magnetic refrigeration is used to produce very low temperatures in the region of absolute zero. It works by extracting energy from already cold substances by de-magnetizing them.

Thermo-Electric Refrigeration

Thermo-electric refrigeration is thoroughly practicable on a small scale. It depends on the Peltier effect, which is that when a current is passed round a circuit containing two dissimilar materials, there is rejection of heat at one junction and absorption of heat at the other. When the dissimilar materials are metallic, as in a thermocouple, the conductivity of the metals is so high that the apparent cooling and heating effects are negligible. However, if materials of low conductivity, such as semi-conductors, are used, then the heating and cooling effects can clearly be demonstrated at the junctions. At present, thermo-electric refrigeration is not appropriate for building services but the situation could change if better semi-conductors were found.

Air Cycle Refrigeration

Air is a natural refrigerant. It has low efficiency. The market dominated by air cycle refrigeration is that of cabin air conditioning for aircraft. Compressed air at appropriate pressure is available from the jet engines and the running gear is very light. Air cycle has not dominated any other market though it has been demonstrated for rail carriage air conditioning and, on a large scale, for low temperature freezing.

Water Vapour Compression

Water is also a natural refrigerant. Water has a very high latent heat of evaporation and a high critical temperature. It is therefore potentially a very efficient refrigerant. However, water suffers from the enormous disadvantage of having an extremely high specific volume. Valiant efforts have been made to overcome this disadvantage by using high speed, multi-stage, axial compressors.

Evaporative Cooling

Evaporating water is also used as a refrigerant in evaporative cooling systems. Such systems are effective in arid regions where the relative humidity is low. No work has been done on the relative cooling effectiveness of various trees.

Absorption Refrigeration

Absorption refrigeration produces its refrigerating effect by evaporating a refrigerant, which is then absorbed into solution in a suitable liquid. The concentrated solution is pumped to high pressure and the refrigerant driven out of solution by heat, to be condensed at the higher pressure in a condenser. The condensed liquid is fed through an expansion valve to the evaporator, where the cycle recommences. The absorption refrigerator does not require a compressor but it tends to be bulky and inefficient. The fluid pairs in general use are ammonia/water and water/lithium bromide. Ammonia is the refrigerant in the water/ammonia system, which can operate at low temperature. Water is the refrigerant in the water/lithium bromide system, which consequently cannot operate below 0^{o} C. The water/lithium bromide system is more efficiency than the ammonia/water system and is widely used for air conditioning in Japan, where the heat source is usually natural gas. Absorption refrigeration has a place in some modern buildings. The main drawback is the low efficiency and the large amount of heat which has to be rejected compared to a vapour compression system.

Stirling Cycle Refrigeration

The Stirling Cycle machine is, in principle, a very efficient refrigerator. However Stirling Cycle machines are rather complex, containing compression pistons, displacer pistons and regenerative heat exchangers, together with a mechanism of some sort to regulate the relative motion of the power pistons and the displacer pistons. The main field of operation of the Stirling Cycle refrigerator has so far been in the efficient production of low temperature on a relatively small scale. It is possible to purchase standard Stirling Cycle machines which will produce liquid nitrogen and liquid oxygen from atmospheric air.

Hydrogen is the best gas to use in a Stirling Cycle refrigerator because of its low molecular weight but nitrogen is often used in standard commercial machines because it is much cheaper and safer.

The Vortex Tube Refrigerator

The vortex tube is an extremely simple device which works in a very complex manner. The device consists of a tube with a tangential entry for compressed air. The vortex tube is very inefficient but it is so robust and simple that it is often the best means of providing a small amount of spot cooling in a harsh, high temperature, environment.