Environment global protection to the polluting action of refrigerants

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Abstract: In this paper are approached principal aspects of the environmental pollution, by working fluids of the refrigeration, air-conditioning and heat-pumping systems and a new utilization strategy of these refrigerants is described, in accordance with the international legislation. The refrigerants will be selected in order to be the best adapted for the desired application, based on few criteria which take into account the thermodynamic and thermophysical properties, the technological behavior, the cost and the use constraints. Also, the paper presents a study of the Romanian line up to the environment, refrigeration and air-conditioning EU legislation with the recommendation of using ammonia as a very eco-efficient alternative.

Key-Words: working fluids, pollution, environment protection, nonecological refrigerants, substitutes.

1 Introduction

The environment pollution represents a major risk for all that means life on our planet (men, flora, fauna), it consist not only in the local noxious effect of different pollutants but in the unbalances produced in a large scale on the whole planet.

The term "pollutant" appoints each solid, liquid or gaseous substance, microorganisms, sounds, vibrations, all kind or combination of radiations, that modifies the natural state of environment.

Environment protection represents the fundamental condition of the society's sustainable development, a priority purpose of national interest that is realized in institutional frame where the legal norms authoresses the development of activities with impact on environment and exert the control upon these.

The purpose of environment protection is to maintain the ecological balance, to maintain and improve the natural factors, to prevent and control pollution, the development of natural values, to assure better life and work condition for the present and future generations and it refers to all actions, means and measures undertaken for these purpose.

The atmosphere represents the surrounding air of earth, excluding the indoor air or the air in underground spaces. One of the minor components of atmosphere, the ozone has a special importance in maintaining the ecological balance. It is distributed in principal between the stratosphere (85…90%) and troposphere. Any perturbation of the atmospheric ozone concentration (it varies between 0 and 10 ppm, in function of the regions) has direct and immediately effect upon life.

The problems of forming and maintaining the earth ozone layer, represents a priority preoccupation of all states. In this context during the last 30 years, the European Union has adopted a great number of laws and regulations concerning environment protection, to correct the pollution effects, frequently by indirect directives, imposing allowable concentrations, asking for government collaboration, programs and projects for regulation of industrial activities and productions. The Alliance for Responsible Atmospheric Policy [21] maintains a brief summary of regulations for some countries.

2 Refrigerants action on the environment

Refrigerants are the working fluids in refrigeration, air-conditioning, and heat-pumping systems. They absorb heat from one area, such as an air-conditioned space, and reject it into another, such as outdoors, usually through evaporation and condensation, respectively. These phase changes occur both in absorption and mechanical vapor compression systems, but not in systems operating on a gas cycle using a fluid such as air. The design of the refrigeration equipment depends strongly on the properties of the selected refrigerant.

Refrigerant selection involves compromises between conflicting desirable thermophysical properties. A refrigerant must satisfy many requirements, some of which do not directly relate to its ability to transfer heat. Chemical stability under conditions of use is an essential characteristic. Safety codes may require a nonflammable refrigerant of low toxicity for some applications. Cost, availability, efficiency, and compatibility with compressor lubricants and equipment materials are other concerns.

The environmental consequences of refrigerant leaks must also be considered.

Minimizing all refrigerant releases from systems is important not only because of environmental impacts, but also because charge losses lead to insufficient system charge levels, which in turn results in suboptimal operation and lowered efficiency.

Working fluids escaped through leakages from refrigeration equipments, during the normal operating (filling, empting) or accidental (damages), gathers in significant quantities in high levels of the atmosphere (stratosphere). There, through catalytically decompounding they deplete the ozone layer that normally is filtering the ultraviolet sun radiations, dangerous for living creatures and plants on earth. Stratospheric ozone depletion has been linked to the presence of chlorine and bromine in the stratosphere. Supplementary, refrigerants contributed to the global warming of atmosphere, as gases with greenhouse effect. Some very stabile substances used as refrigerants have a long period of atmospherically live.

The average global temperature is determined by the balance of energy from the sun heating the earth and its atmosphere and of energy radiated from the earth and the atmosphere space. Greenhouse gases (GHGs), such as carbon dioxide (CO_2) and water vapor, as well as small particles trap heat at and near the surface, maintaining the average temperature of the Earth's surface about 34 K warmer than would be the case if these gases and particles were not present (the greenhouse effect).

Global warming is a concern because of an increase in the greenhouse effect from increasing concentrations of GHGs attributed to human activities.

Thus, the negative influences of refrigerants, especially of Freon's upon environment, can be synthesized by the two effects:

– depletion of the ozone layer;

– contribution to global warming at planetary level by the greenhouse effect.

The measure of a material's ability to deplete stratospheric ozone is its *ozone depletion potential* (ODP), a value relative to that of R-11 which is 1.0.

The *global warming potential* (GWP) of a GHG is an index decribing its relative ability to trap radiant energy compared to CO_2 (R-744), which has a very long atmospheric lifetime.

Therefore refrigerants will be select so that the ozone depletion potential will be zero and with a reduced atmospheric global warming potential.

The most utilized refrigerants are those who derivate from methane and ethane as presented in figure 1, where is evidenced even there toxicity and flammability according to the number of Cl and H atoms.

According to the polluting action upon environment, for atmospheric ozone view through the Montreal protocol (1987) and the further amendments, and for the green house effect according to the Kyoto protocol (1997), refrigerants can be classified as follows:

– with strong destructive action upon the ozone layer and with significant amplification of the greenhouse effect upon earth (Chlorofluorocarbons-CFCs);

– with reduced action upon the ozone layer and with moderate amplification of the greenhouse effect (Hydrochlorofluorocarbons-HCFCs);

– non harmless upon the ozone layer, with less influence on greenhouse effect (Hydrofluorocarbons-HFCs);

– non harmless upon the ozone layer, with less influence on greenhouse effect (ammonia-NH_3, carbon dioxide-CO_2, natural hydrocarbons)

Chlorofluorocarbons had been used as refrigerants since the 1930s because of their superior safety and performance characteristics. However, their production for use in developed countries has been eliminated because it has been shown that they deplete the ozone layer [18]. Production for use in developing countries will be eliminated by 2010, except as allowed under essential use exemptions or in feedstock applications.

Hydrochlorofluorocarbons also deplete the ozone layer, but to a much lesser extent than CFCs. Their production for use as refrigerants is scheduled for elimination by 2030 for developed countries, and by 2040 for developing countries.

Hydrofluorocarbons do not deplete the ozone layer and have many of the desirable properties of CFCs and HCFCs. They are being widely adopted as substitute refrigerants for CFCs and HCFCs. The HFC refrigerants have significant benefits regarding safety, stability and low toxicity, being proper for large applications.

The second influence of refrigerants upon the environment, preciously mentioned, guided to a new classification of refrigerants according to there contribution to the atmosphere warming. Comparison of this specific contribution to the greenhouse effect is realized even for R-11 (the most noxious even from point of view of ozone layer depletion) as well as for CO_2.

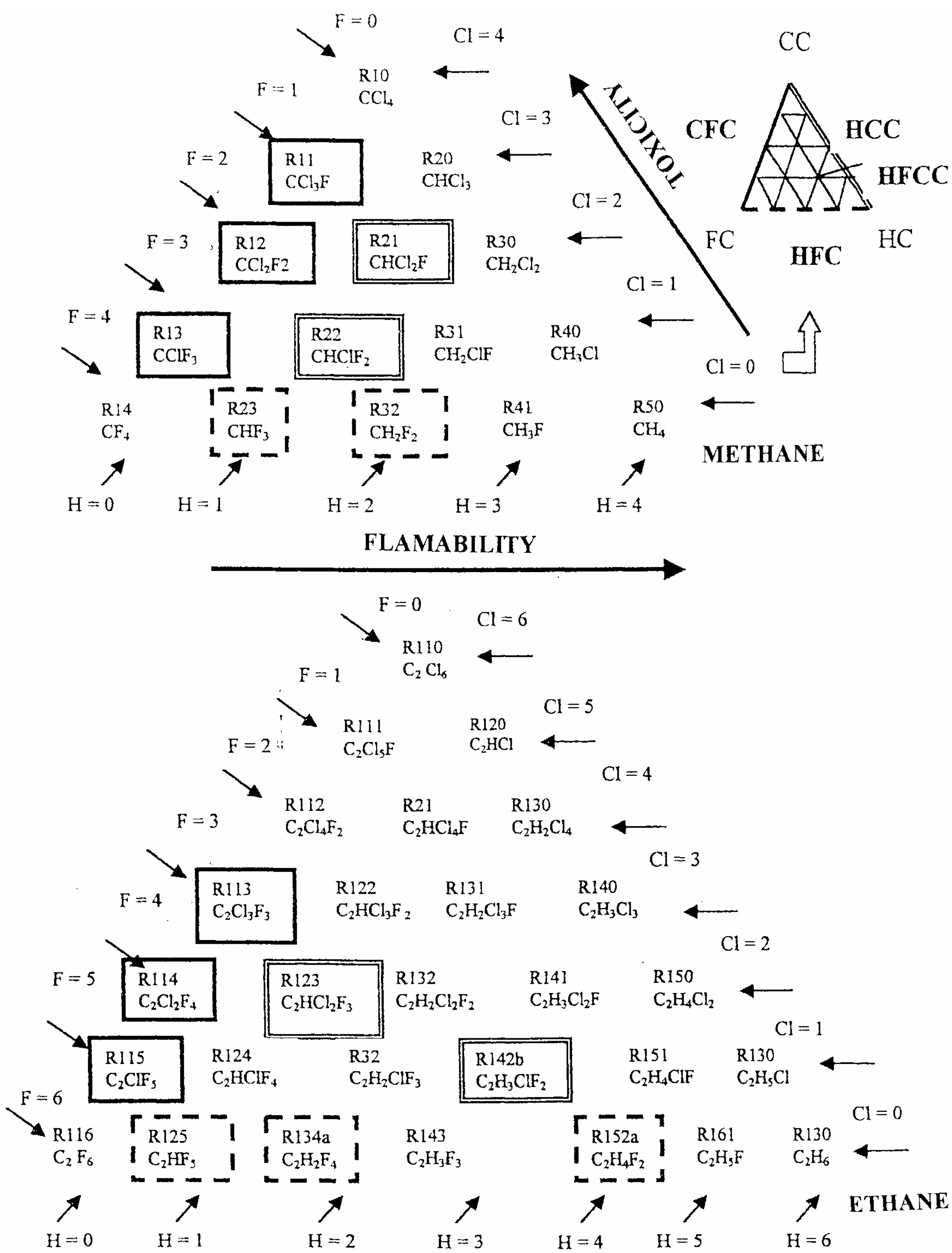

Fig. 1 Chlorofluoro compound derivate from methane and ethane

Freon's placed on the undesirable position 3 (14%) between the gases with green house effect, could be explained by there great absorption capacity of infrared radiation.

In table 1 are presented the principal Freon's (pure and blends), with the symbol for refrigerant, chemical name and formula, as well as there application domains.

In case of the refrigerating systems, supplementary with direct action to the green house effect, because of the refrigerants leakage in the atmosphere, it must be considered even the indirect action to global warming by the CO_2 quantity released in atmosphere during the transport of energy produced by the installation, obviously greater then the associated direct action. While the refrigerant quantity increases in the installation, the effect of direct action rises.

Table 1. Application domains of the freon's

Group	Refrigerant	Chemical Formula	Chemical Name	Vaporization temperature, [°C]		Applications
0	1	2	3	4	5	6
CFC	R11	CCl_3F	Trichlorofluoromethane	0	+60	Air-conditioning, Heat pumps
	R12	CCl_2F_2	Dichlorodifluoromethane	-40 +10	+10 +40	Household and industrial cooling, air conditioning, Heat pumps
	R12B$_1$	$CClBrF_2$	Bromochlorodifluoromethane	0	+50	Air-conditioning, Heat pumps
	R13	$CClF_3$	Chlorotrifluoromethane	-100	-60	Cascade refrigeration systems
	R13B$_1$	$CBrF_3$	Bromotrifluoromethane	-80	-40	Mono-, two stage- and in cascade refrigeration systems, for industrie
	R113	$C_2Cl_3F_3$	Trichlorotrifluoroethane	0 +15	+15 +50	Air-conditioning, Heat pumps
	R114	$C_2Cl_2F_4$	Dichlorotetrafluoroethane	-20 +10	+10 +80	Air-conditioning, Heat pumps
HCFC	R21	$CHCl_2F$	Dichlorofluoromethane	-20	+20	Air-conditioning, Heat pumps
	R22	$CHClF_2$	Chlorodifluoromethane	-50	+10	Industrial-, food-, naval-, commercial refrigeration, Air-conditioning
	R142b	$C_2H_3ClF_2$	Chlorodifluoroethane	-20 +10	+10 +60	Air-conditioning, Heat pumps
HFC	R23	CHF_3	Trifluoromethane	-100	-60	Cascade refrigeration systems for industrie and laboratory
	R32	CH_2F_2	Difluoromethane	-60	-10	Industrial and commercial refrigeration
	R125	C_2HF_5	Pentafluoroethane	-50	+10	Industrial and commercial refrigeration, Air-conditioning
	R134a	$C_2H_2F_4$	Tetrafluoroethane	-30	+20	Commercial-, household-, industrial refrigeration, Air-conditioning
	R152a	$C_2H_4F_2$	Difluoroethane	-30	+10	Industrial and commercial refrigeration, Air-conditioning
Blends	R500	(R12/R152a)	–	-40	+10	Household and industrial refrigeration, Heat pumps
	R502	(R22/R115)	–	-60	-20	Industrial and commercial refrigeration
	R507	(R125/R134a)	–	-50	-10	Industrial and commercial refrigeration
	R410A	(R32/R125)	–	-50	0	Industrial and commercial refrigeration
	R407C	(R32/R125/R134a)	–	-40	0	Industrial and commercial refrigeration

The total equivalent warming impact (TEWI) of an HVAC&R system is the sum of direct refrigerant emissions expressed in terms of CO_2 equivalents, and indirect emissions of CO_2 from the system's energy use over its service life. Another measure is *life-cycle climate performance* (LCCP), which includes TEWI and adds direct and indirect emissions effects associated with manufac-turing the refrigerant The analysis of TEWI index for refri-gerating systems, operating with divers refrigerants (CO_2, R22, NH_3, R134a, R404A) evidence that even the direct effect generated by CO_2 is negligible comparing with the other refrigerants [8]. The indirect effect generated by CO_2 is great because of the high condensation pressures that determine a great energy consumption and in consequence the maximum value of TEWI for CO_2.

Environmentally preferred refrigerants have:
– low or zero ODP;
– relatively short atmospheric lifetimes;
– low GWP;
– provide good system efficiency;
– appropriate safety proprties;

– yield a low TEWI or LCCP in system applications.

In Table 2 is presented the refrigerants effect upon the environment. Because HFCs do not contain chlorine or bromine, their ODP values are negligible and thus are shown as 0 in this table.

The European Union has a major contribution against the climate changes through the regulations regarding some fluorinated gases with green house effect and it is a real support in emission reducing resulted from these fluorinated gases all over Europe. These regulations establish a high protection level of the environment as well as an inside market for equipments containing fluorinated gases and for the members involved in this activities.

Table 2. Effect of refrigerants upon environment

Group	Fluid	ODP	GWP (basis R-11)	GWP (CO_2=1)	Atmospherically lifetime (years)
0	1	2	3	4	5
CFC	R-11	1	1	4000	50…60
	R-12	1	2.1…3.05	10600	102…130
	R-113	0.8…1.07	1.3	4200	90…110
	R-114	0.7…1	4.15	6900	130…220
	R-12B_1	3…13	-	1300	11…25
	R13-B_1	10…16	1.65	6900	65…110
HCFC	R-21	0.05	0.1	-	<10
	R-22	0.055	0.34	1900	11.8
	R-123	0.02	0.02	120	1.4…2
	R-142b	0.065	0.3…0.46	2000	19…22.4
HFC	R-23	0	6	14800	24.3
	R-32	0	0.14	580	6…7.3
	R-125	0	0.58…0.85	3200	32.6
	R-134a	0	0.28	1600	14…15.6
	R-143a	0	0.75…1.2	3900	55…64.2
	R-152a	0	0.03…0.04	140	1.5…8
Azeotropic blends	R500(R12/R152a)	0.63…0.75	2.2	6000	-
	R501(R12/R22)	0.53	1.7	4200	-
	R502(R22/R115)	0.3…0.34	4.01…5.1	5600	>100
	R507(R125/R143a)	0	0.68	3800	-
Cvasiazeotrope blends	R404A(0.44R125/0.52R143a/0.04R134a)	0	0.6…0.94	3750	-
	R410A(0.5R32/0.5R125)	0	0.5	1890	-
	FX40(0.1R32/0.45R125/0.45R143)	0	0.6	3350	-
Zeotropic blends	R407A(0.2R32/0.4R125/0.4 R134a)	0	0.14…0.45	1920	-
	R407B(0.1R32/R0.7R125/0.2R134a)	0	0.1…0.5	2560	-
	R407C(0.23R32/0.25R125/0.52R134a)	0	0.29…0.37	1610	-

3 Replacement of nonecological refrigerants

After the finding that CFCs, HCFCs and some other human-produced compounds deplete the ozone layer, most countries agreed to the Montreal protocol. This protocol is an international treaty, administered by the United Nations Environment Programme (UNEP) that controls consumption and production of ozone-depleting substances, including CFCs and HCFCs [18]. Hydrofluorocarbons (HFCs) do not deplete the ozone layer and have many of the desirable properties of CFCs and HCFCs. They are being widely adopted as substitute refrigerants for CFCs and HCFCs. However, HFCs are also associated with an environmental issue; they contribute to global warming if released into the atmosphere [19]. Countries, trade associations and companies are increasingly adopting regulations and voluntary programs to minimize these releases and, hence, minimize potential environmental effect while continuing to allow use of these refrigerants.

Consequently a new orientation appeared upon the utilization of working fluids. Thus, CFC refrigerants as R-11 and R-12 where substituted by simply compound refrigerants R-123 (HCFC) and R-134 (HFC) with a reduced even zero action upon the depletion of the ozone layer. This alternative is attractive because the substitutes have similar proprieties (temperature, pressure) with the replaced one, and the changes that took place directly on the existent installations will be realized with minimum of investments.

For other refrigerants it were not found simply compound fluids as for example for R-502 that could be replaced with a mixture of R-115 (CFC) and R-22 (HCFC) or in some cases only with R-22, that is a fluid for temporary replacement, conform with the international legislation.

By blending two or three pure Freon's we obtain new substances, better adaptable for desired cooling application. The first blends are named azeotropes while the others are named zeotropes. The use of blends could generate undesired aspects, especially by leakages of the working fluid, accidentally or during the installations filling.

Figure 2 presents the strategy concerning the refrigerants.

The substitutes for refrigerant R-22 could be R-134a, R-290, R-1270 and R-744, the HFC blends (R-407C, R-410A, R-417A, FX 90) and the ammonia (R-717).

None of these substances can efficiently substitute R-22, presenting a specific cooling power or a different saturation pressure, restricted application and specially demands in the installation design.

In new installations, for certain applications, R-143a is a good substitute, having a reduced delivering compressor pressure and temperature, but also an inferior specific cooling power being necessary a greater cylinder of the compressor.

The HFC zeotropic blends are considered substitutes for a short period. Between the natural fluids, the ammonia is the best substitute for R-22, having favorable thermodynamic proprieties, high heat transfer coefficient (3…4 times superior to R-22) and a performance coefficient similarly good for many applications, especially industrial one, with great cooling powers. It is cheap and ecological (ODP=0, GWP=0).

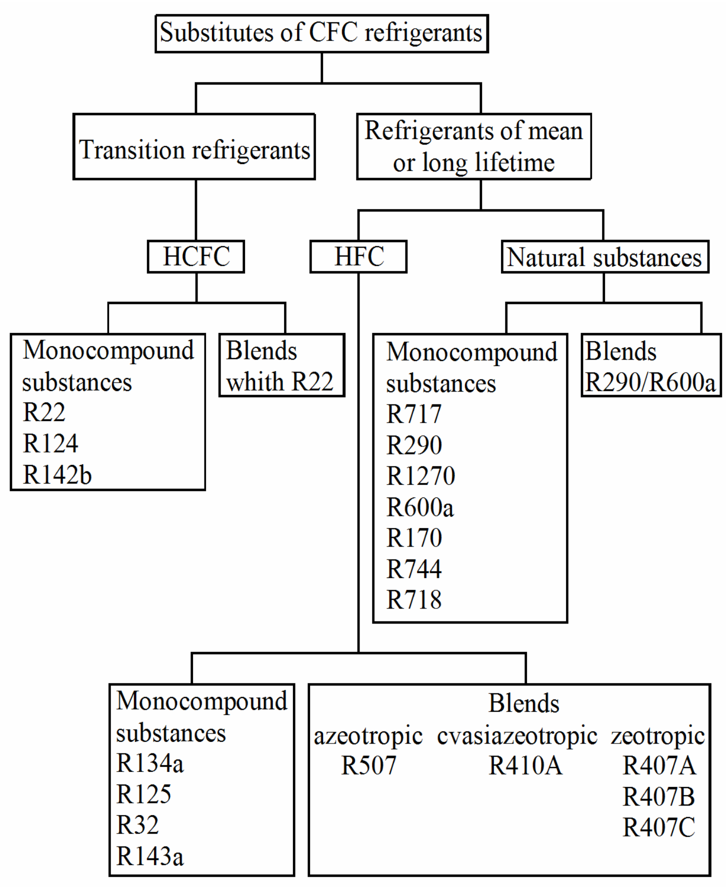

Fig. 2 Strategy concerning the refrigerants

Carbon dioxide (R-744) is a possible substitute for all refrigerants, being used even by low and high temperatures (cascade system, commercial cooling and air-conditioning). It is accessible, has a low cost and doesn't impact upon ozone, while his heating potential is negligible. His low critical temperature involves the use in supercritical cycles. The high saturation pressure and isotherm compression coefficient are considered as inconvenient.

Because thermodynamic and thermophysic proprieties influences the energetically performances of refrigerating systems and produces meantime the impact upon environment, they must be carefully analyzed and take in account by the installations conception and planning.

In figure 3 are indicated the normal vaporisation temperatures for the principal refrigerants and in table 3 are presented the principal thermodynamic proprieties of CO_2 and other natural refrigerants. These proprieties determine the advantages and also the disadvantages by using CO_2.

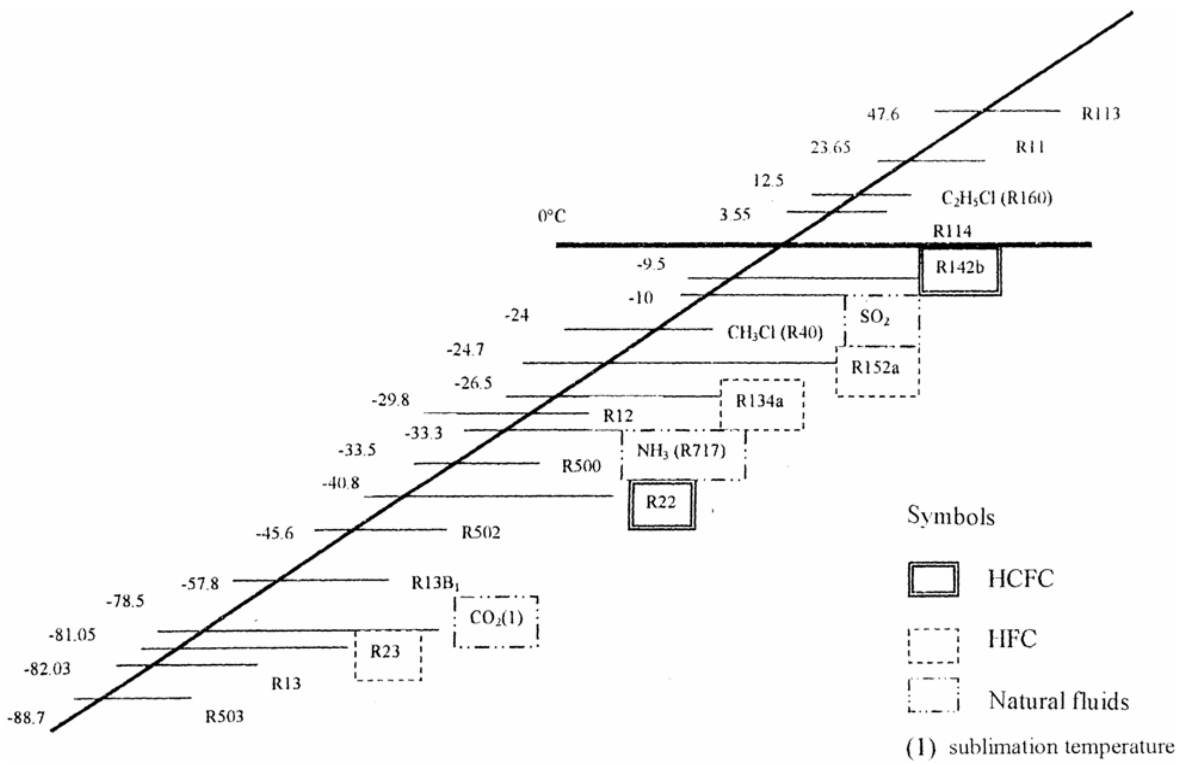

Fig. 3 Normal vaporization temperature of the refrigerants

Table 3. Thermodynamic proprieties of principal natural refrigerants

Propertye	Carbon dioxide R-744	Ammnonia R-717	Water R-718	Propane R-290	Isobutane R-600a
0	1	2	3	4	5
Molecular mass [g/mol]	44	17	18	44.1	58.1
Critical temperature [°C]	30.98	132.4	374	96.8	135
Critical pressure [bar]	73.75	113.5	221	44.1	36.5
Normal boiling point [°C]	-37	-33.5	100	-42.2	-11.7
Freezing point [°C]	-56.57	-77.9	0	-187.1	-159.6
Adiabatic compression index (c_p/c_v)	1.7015	1.400	-	1.140	1.110
Compression ratio (-15/35 °C)	3.147	5.72	-	4.21	-
Refrigeration volumetric capacity [kJ/m^3] (-15/35 °C)	4922	2156.4	-	450	130

4 Implementation of European legislation concerning refrigeration and air-conditioning in Romania

Romania is a country with great refrigerants consumption, it has not his own producers for CFC and it does not export CFC. The CFC consumption in Romania has decreased because of the number of activities in service and production fields. Along the last decade the Romanian industry was in a transition state from public enterprises to the private one, based on improvements of the economical situation. In this period in Romania appeared the variation of CFC consumption.

An important factor for stabilising the employers in this domain is the adoption of the Good Practice Code at international standard level and beginning with these the specialists will be easier adapted to introduce the norms and directives required by the European Union (EU). In the EU is developed the process regarding a correlation between the technical standards of the membership countries, that will renew the norms and standards at "Harmonized Standards" level. In the domain of refrigerating and air conditioning a major importance will have SR EN-378/1-4 and the new Norm CE 842-2006.

The realisation of Good Practice Code by the General Association of Refrigerants from Romania is part of a project that was implemented by United Nations Industrial Development Organisation (UNIDO), named "National CFC Elimination Program in Romania" (NCPP) and one of the recognised activities, required for CFC reducing in the services domain from Romania.

In Sweden the Environment Ministry assisted through the Stockholm Environment Institute (SEI) in preparing NCPP for the refrigerating and air conditioning sectors. Also, previously, UNIDO assisted Romania in implementing the Refrigerants Management Plan (RMP).

The most utilised refrigerant in industrial installations even national and worldwide is the ammonia. In the last five years Romania was in a continuous development of the domain of industrial refrigerating systems. In this country were built and modernized slaughter-houses, warehouses, chicken-, pork-, and beef farms, beer factories, skating rings and other industries. Part of these domains needs high cooling capacities while others need a reduced cooling capacity. Each refrigerating system was realised with equipments as: air cooler, condenser, pumps, heat exchanger, and liquid storage, high and low pressure separators, pipes, armatures and automatization systems.

In figures 4, 5 and 6 are evidenced the most utilised equipments on the Romanian market in the last five years, as: compressors, evaporators and condensers.

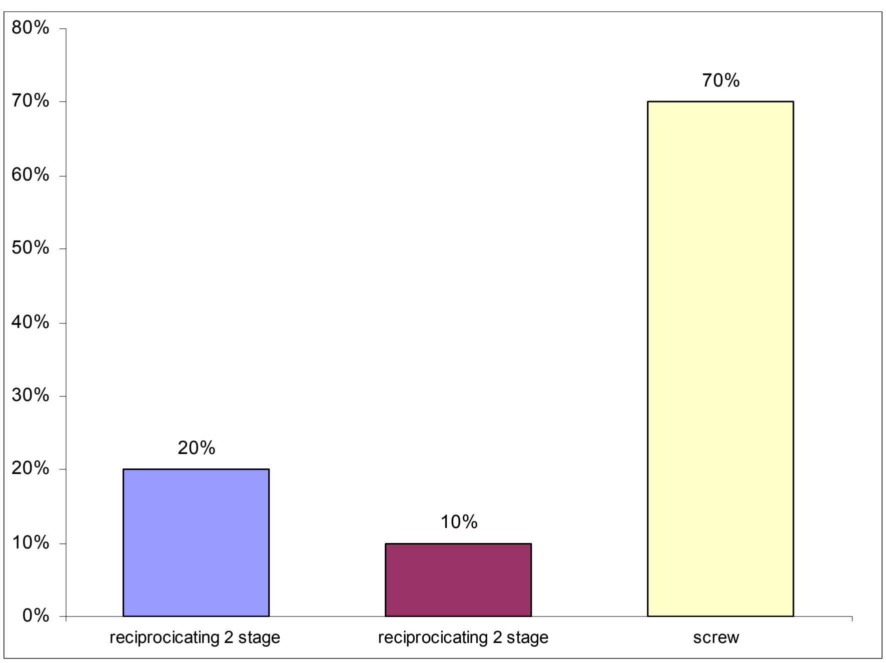

Fig. 4 Types of ammonia compressors used in Romania

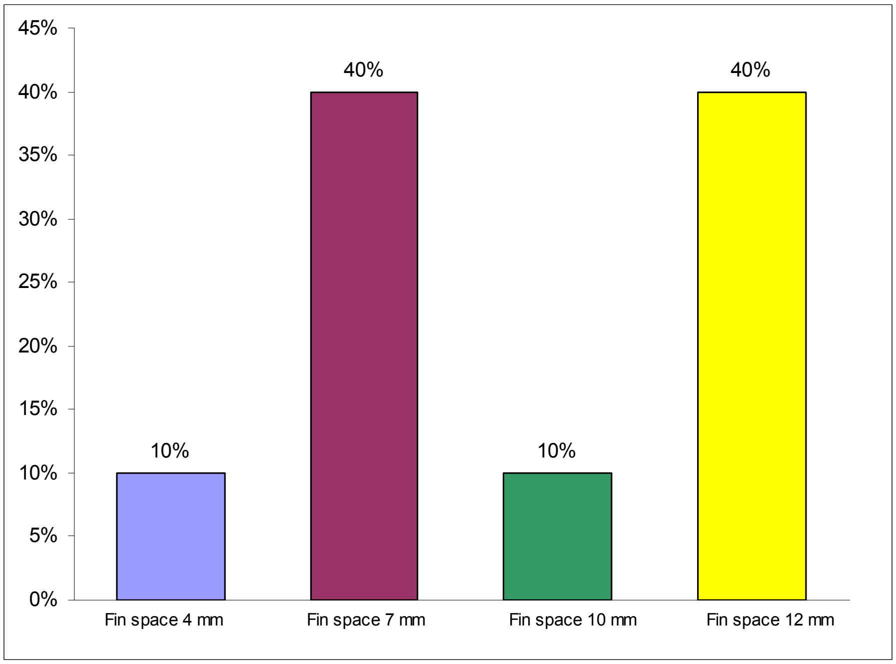

Fig. 5 Types of ammonia evaporators used in Romania

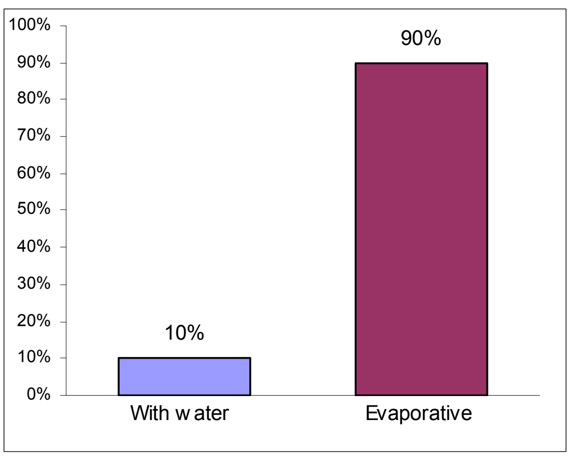

Fig. 6 Types of ammonia condensers used in Romania

5 Conclusions

Scientific research based on monocompound substances or mixtures, will lead to find adequate substitutes for cooling applications, that will be ecological (ODP = 0, low GWP), nonflammable and nonpoisonous, but also with favorable thermodynamic proprieties.

A possible solution is the use of inorganic refrigerants (NH_3, CO_2) and hydrocarbon refrigerants (propane, isobutene, ethylene, propylene) for industrial applications, in air-conditioning or food and household cooling. Because the hydrocarbon refrigerants presentes a high risk of flammability and explosion, this substances will not be often used as refrigerants comparative with CO_2 or NH_3.

On other advantage of these two substances represents the fact that they were used for a long time as refrigerants.

The European Partnership for Energy and Environment considers the HFC refrigerants as the best alternative for the refrigerant CFC and HCFC in most of the applications. The HFC refrigerants allowes the use energetically efficient applications, offering significant benefits comparing with the existent alternatives. In average over 80% of the gases with green house effect used in cooling equipments have the indirect emissions as sources. The high energy efficiency resulted by the use of HFC refrigerants balances in a great measure the global warming potential.

The replacement of some refrigerants with other nonpolluting influences the operating conditions of the cooling installations, by a rapid degradation of components made from elastomers [21] or plastic materials [6], or it is necessary to replace mineral oils with some other oils adequate to the new refrigerants. There are cases with more options for an alternative refrigerant and the problem is to choose the economical variant. Some problems of materials endurance and compatibility can be solved only during many testing, but the estimation of energetical performances and expenses that results by modification of operational characteristics when replacing the refrigerant can be solved with numerical modeling.

It is imposed a new conception in execution the refrigerating systems: it must be realized very tight, with refrigerants having a reduced atmospheric warming potential, but as possible efficient energetically.

References:

[1] Al Jeran, H.O. Khan, A.R. Intensity of ultraviolet as an indicator of ozone layer thickness in troposphere at gulf cooperation council, *WSEAS Transactions on Environment and Development*, no.1, vol. 5, 2009, pp. 34-43.

[2] ASHRAE, *Fundamentals Handbook*, American Society of Heating, Refrigerating and Air Conditioning Engineers, Atlanta, 2009.

[3] ASHRAE, Designation and safety classification of refrigerants, *ANSI&ASHRAE Standard 34*, 2004.

[4] Berglöf, K. Methods and potential for on-site performance validation of air-conditioning, refrigeration and heat pump systems, *IEA Conference*, Las Vegas, 2005.

[5] Cavallini, A. and Steinle, F. Natural working fluids in a historic perspective, *Fluides actifs naturels*, *Conference de l'IIF*, Gustav Lorentzen, Oslo, 1998, pp. 37-42.

[6] Cavestri, R.C. Compatibility of refrigerants and lubricants with engineering plastics, *Air-Conditioning and Refrigeration Technology Institute Report*, Arlington, 1993.

[7] Chicco, G. Mancarella, P. Models and indicators for energy and CO_2 emission assessment of electric chillers and direct-fired absorption chillers, *Proceedings of 5th WSEAS Int. Conference on Environment, Ecosystems and Development*, Tenerife, Spain, December 14-16, 2007, pp. 163-168.

[8] Dragos, G. V. Dragos, R. Use of CO_2 in non-polluting refrigerating systems, *Proceedings of the 28th Conference "Modern Science and Energy"*, Cluj-Napoca, 2009, pp. 149-157.

[9] Eiseman, B.J. Effect on elastomers of Freon compounds and other halohydrocarbons, *Refrigerating Engineering*, no. 12, 1949, pp. 1171.

[10] Gheorghe, F. Replacement of refrigerant R22 in the equipments for air-conditioning and associate problems, *Plumber Journal*, no. 4, 2002, pp. 8-9.

[11] Hera, D. Drughean, L. and Ivan, G. Confirmări şi incertitudini în strategia privind substituirea agenţilor frigorifici, *Conferinţa „Instalaţii pentru Construcţii şi Confortul Ambiental*", Timisoara, 18-19 Aprilie, 2002, pp. 340-353.

[12] Hera, D. Ivan, G. Pîrvan, A. Use of azeotropic and zeotropic blends as substitutes of the R22, *Proceedings of the 20th Conference "Modern Science and Energy"*, Cluj Napoca, 2001, pp. 120-126.

[13] Iyer, G.V. Mastorakis, N.E. Experimental investigations on eco-friendly refrigeration and air-conditioning systems, *Proceeedings of the 4th WSEAS Int. Conference on Fluid Machanics and Aerodynamics*, Elounda, Greece, August 21-23, 2006, pp. 445-450.

[14] Ravishankara, A.R. Turnipseed, A.A Jensen, N.R. Wareen, R.F. Do hydrofluorocarbons destroy stratospheric ozone? *Science*, no. 248, 1994, pp. 1217-1219.

[15] Ricardo, R.Q. Analysis of the behavior of ternary hydrocarbon mixture as substitutes of the CFC-12, *Proceedings of the 2th IASME/ WSEAS Int. Conference on Energy & Environment*, Portoroz, Slovenia, May 15-17, 2007, pp. 91-94.

[16] Stewart, R.B. Jacobsen, R.T. Penoncello, S.G. *ASHRAE Thermodynamic properties of refrigerants*, 1986.

[17] * * * *Proprietes thermodinamiques des fluides frigorigenes*, Dehon Service, 1977.

[18] * * * UNEP, *Handbook for the international treaties for the protection of the ozone layer*, United Nations Environment Programme, Nairobi, Kenya, 2003.

[19] * * * U.N. *Report of the refrigeration, air conditioning, and heat pumps technical options committee*, United Nations Environment Programme, Nairobi, Kenya, 1994.

[20] * * * MMGA, *Update of Country Programme for the Phaseout of Ozone Depleting Substances in Romania*, Bucharest, 2004.

[21] * * * http://www.arap.org/