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The Influence of Modern Refrigerants on Environmental Protection

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Abstract: The aim of reviewing information was characterizing in the labor factor using in refrigeration technology is and their impact on the environment. The development of the refrigeration industry occurred thanks to progress towards coolants. The most important aspect of using of refrigerators is their impact on health and human life, and atmosphere. By caring for health, the European Union achieves legal rights. Research on thermodynamic factors pose a wide field of work for many scientists and are the most popular, new information, that can be used in practice.

Keywords: refrigerant, protection, environment, GWP, ODP

1. Introduction

The beginnings of refrigeration can be seen in ancient Egypt and India, where drinking water was cooled several thousand years ago in porous, clay jugs.

In ancient China, during the summer season, to cool drinks, people used snow and water ice collected in the winter. It was stored in well-protected pits. In the reign of Alexander the Great, the above method was used to cool wine for legionnaires, and at Nero's feasts. Drinks were also served chilled as indicated. Francis Bacon (1561-1621) assessed as first the importance of cooling to maintain perishable products in good condition. In Italy was very popular method of cooling water by dissolving saltpetre in it, and to obtain even lower temperatures – a mixture of saltpetre and snow. The above-described methods of cooling were based on the use of appropriate properties and physical processes carried out in a natural way. The scientific foundations of refrigeration began to emerge at the turn of the 18th and 19th centuries. Josepf Black defined the concept of the heat of vaporization and developed the basics of calorimetry Gay-Lussac and Dolton investigated the phenomena of gas cooling during their expansion. Faraday liquefied some gases (e.g. chlorine). Sadi Carnot studied thermodynamic processes and transformations, developed the science of ideal and irreversible processes, and carried out an analysis of thermodynamic cycles enabling the reception of heat at the expense of providing mechanical work. The discovery and definition of many concepts and physical laws made it possible to make the first technical attempts to describe the issue of cooling processes and the construction of industrial refrigerators – cooling devices. The first attempts to build mechanical air and vapour chillers as well as sorption chillers were made around the mid-19th century. Dr Garricka from Florida, initiated air chillers. The air chillers were developed and produced by Bell-Coleman, Lightfoot, Leicester. Allan, Windhausen produced significant capacities for those times. Vapour coolers were created in parallel with the air ones. In 1830 Jacob Perkins patented a refrigerator with a solution corresponding to the modern one, with a working medium – ethyl ether. The initiative and design work of David Boyle from Chicago and Karol Linde from Munich resulted in the replacement of ether with ammonia. Some, especially positive, thermodynamic properties of ammonia as a refrigerant caused the refrigeration system with this refrigerant to displace others for many years.

In the same period (1859), Ferdynand Carre constructed an absorption refrigerator that was extremely carefully and well thought out, the basic idea of which has survived to this day. The transport of food products (meat, fruit) from overseas countries (South America, Australia, New Zealand) to Europe had a significant impact on the development of refrigeration. A distinguished pioneer in this field is Ch. Tellier, who was the first to implement the idea of transporting perishable food products by ocean vessels, adapting the ship "Le Frigorifique" and then "Le Paraquay". The development of land refrigeration was mainly based on the ammonia (approx 90%), partly on carbon dioxide (carbonic anhydride approx 10%) and to a small extent on sulfur dioxide (sulfur anhydride approx 1%) (Kuprianoff et al. 2014, Niebergall 1959, Stefanowski 1949).

Nowadays, they strive for energy efficiency, miniaturization, and being eco on every level of life also in the field of refrigerants, new solutions are used to allow the most economical steps to improve efficiency (Abas et al. 2018, Antunes et al. 2016).

2. Research

The refrigerants used in a cooling device for heat transport should meet certain specific requirements, the most important of which are:

1. Pressures used in refrigeration should not be too high, not exceeding those used in other fields of technology, but not lower than the atmospheric pressure, so that any leaks result in harmful suction of air and moisture from the outside;

2. The heat of evaporation (evaporation enthalpy) should be as high as possible, and the specific volume of vapors as small as possible, so that the dimensions of the refrigerator are not excessively large;
3. The refrigerants must not react chemically and may not have a harmful effect on the elements of machines and other technical devices or on their surroundings;
4. The production price, cost, and ease of purchasing factors should correspond to economic conditions;
5. Refrigerants and their products resulting from their decomposition (caused by e.g. too high temperature, moisture content) should not affect on the environment.

In the area of large on-ground cooling towers, ammonia is most used due to its ease of production (e.g. in the production of fertilizers for agriculture or by hydrogen and nitrogen synthesis), not very high vapor pressure in the cooling device (maximum approx 13 MPa), the possibility of using iron-based materials, high, practically unlimited solubility in water, easy to identify presence in the air due to the characteristic smell (0.001% by volume can be detected by smell).

The basic disadvantages of ammonia as a refrigerant include its harmful effect on human health when its content in the air exceeds 0.1% by volume.

Carbonic acid anhydride is also used in refrigeration. This fluid when used in refrigeration, makes the devices relatively small, due to high operating pressures and a small volume of vapors. Carbon dioxide is an odorless and does not chemically interact with metals and refrigerants, but for humans, air containing more than 5% by volume becomes suffocating. There are several methods of obtaining carbon dioxide relatively easily, so its availability does not pose any problems. On the other hand, a negative property of carbon dioxide is its very high, maximum pressure of up to about 100 bar and a low critical point (about 3 MPa, at a temperature of +35°C and a pressure lower than 5.28 MPa) it may solidify – freeze. High pressures and low cooling (evaporation) efficiency have limited its use.

Sulfuric anhydride – sulfur dioxide SO_2 has found little use, because of a low content in the air (about 0.01%) it has a choking effect and irritates the respiratory system. The liquefied oil shows oily properties, so the friction elements of the compressors do not require the use of lubricants, which would, however, be aggressive. In the presence of moisture, it becomes aggressive towards metals.

Methyl chloride CH_3Cl, when inhaled in larger amounts, has a stunning effect – similar to the action of alcohol, it is flammable, has a weak chemical effect on metals and breaks down greases and oils.

Sulfur dioxide and methyl chloride have been used sporadically in refrigeration, mostly in small refrigerators, especially household refrigerators, as well as in gastronomic refrigeration.

Extremely intensive development of refrigeration at the beginning of the 20th century in transport, especially sea transport, led to the search for a refrigerant that is safer than ammonia, especially in shipbuilding, the use of which in the face of the threat of a sea disaster or other major failure has become problematic for ship crews. This search was directed to the compounds of carbon, chlorine, fluorine and hydrogen, the so-called freons.

The first, used from around the 1930s, was deufluoride chloromethane (CF_2Cl_2), known as freon 12. It is a colorless gas with no odor heavier than air, non-poisonous, non-flammable, aggressive to metals in the presence of moisture. HCl and HC – extremely dangerous, gases – choking on the body through the respiratory tract.

The introduction of freon 12 as a refrigerant increased the operational safety of ship refrigeration equipment, however, it did not meet the demand for refrigerants in a wide range, especially in terms of efficiency. The search for more universal agents resulted in the development and production of new agents with a wide range of applications including various mixtures, which continues to this day. The new refrigerants, however, are mostly based on components characteristic of freons, but more stable and containing much less chlorine and fluorine.

The gigantic development of refrigeration, including the production of refrigerants, has led to the need to analyze the harmfulness of their impact and introduce mechanisms limiting their use.

As a result of the destructive impact of CFC and HCFC refrigerants on the natural environment, in particular the destruction of the ozone layer and the intensification of the greenhouse effect, radical measures were taken to eliminate halogen derivatives from common use. The first international agreement to protect the ozone layer was the Vienna Convention adopted on March 22, 1985. Next international agreement to protect the environment was the Montreal Protocol, which entered into force on September 16, 1987. Since the entry into force of the Montreal Protocol, the production and consumption of ozone-depleting substances (CFCs, HCFCs, halons) has fallen by more than 97 percent (https://www.schiessl.pl/pl/czynniki-chlodnicze). Its implementation was adopted by the Council of the European Union and ratification by the Sejm of the Republic of Poland of the Act on Substances that Deplete the Ozone Layer of April 20, 2004. These documents define the principles of using substances harmful to the ozone layer in the operation of equipment, and introduced a ban on the widespread use of CFC agents (R11, R12) and from 01.01.2010 R22 freon in newly designed cooling devices.

On the basis of the new Act of May 15, 2015 on substances that deplete the ozone layer and some fluorinated greenhouse gases – Journal of Laws of 2015, item 881 and the Regulation of the Minister of Development of January 11, 2016 on leakages in refrigeration, air conditioning and heat pumps as well as the fire protection system containing controlled substances or harmful fluorinated greenhouse gases (Journal of Laws of 2016, item 89), it is required to check the tightness in accordance with the schedule temporarily.

The above provisions triggered an increased search for substitutes for the above-mentioned prohibited substances, which had to meet a number of chemical, physical, physiological, temperature, ecological, economic and safety criteria.

The necessity to withdraw the refrigerants identified as dangerous resulted in replacement with pro-ecological agents (e.g. R401A, R407C, R410A), including those of natural origin (NH_3, CO_2, propane).

The R134a refrigerant has become the most popular substitute for R12 in recent years, despite its indisputable thermodynamic advantages, but this refrigerant is characterized by a very high greenhouse effect (GWP134a = 1430). This property influenced the decision to withdraw from use and operation with the Directive of the European Parliament and the Council of Europe in 2006 EG in all newly manufactured refrigeration devices and MAC (Mobile Air Conditioning) systems the use of fluorinated greenhouse gases for which the GWP is greater than 150. So it was proposed to withdraw the R134a refrigerant from car air conditioning systems in all new models from January 2011, while from January 2017, the use of R134a was banned in all newly manufactured cars.

This refrigerant has been replaced by a new, environmentally friendly refrigerant from the HFO group currently used.

The use of freons in EU countries is covered by the Regulation of the European Parliament and of the Council of Europe (EC No. 517/2014 of April 16, 2014) on certain so-called fluorinated greenhouse gases. The limitation and elimination of harmful gas emissions to the atmosphere is an important issue in refrigeration technology. Each EU regulation is a stimulus for national law and is the basis for the development of national internal regulations. The European Parliament has created a strict situation defining the methods of dealing with substances that deplete the ozone layer – CFC chlorofluorocarbons, HCFC hydrochlorofluorocarbons as well as substances contributing to the greenhouse effect – the so-called F-gases – HFC hydrofluorocarbons.

A positive results of the application of the above-mentioned measures are signals of a slow recovery of the ozone layer in the atmosphere.

The Prozon Foundation in Poland works to protect the ozone layer, which protects the Earth from harmful UV-B solar radiation. Prozon supports the reduction of the consumption and emissions of ozone-destroying substances, CFCs and HCFCs (https://prozon.org.pl/index.php).

Now the most commonly used synthetic HFC and HFO refrigerants. Many of them are modern. These are factors with the global warming potential of GWP less than 1500, 750 or even 150. From January 2020, it is forbidden to replenish the losses of R404A, R507 or R23 refrigerants. The ban also applies to direct substitutes for R22 – i.e. R419A, R422A, R422D and MO89. The ban has several exceptions, e.g. it does not apply to military equipment and devices for freezing products at -50°C (http://www.rynekinstalacyjny.pl/artykul/id3695, czynniki-chlodnicze-legislacja-dzis-i-jutro?gal=1).

3. Results of research

In addition to the production and appropriate selection of new and new refrigerants, a serious problem is obtaining information about their thermodynamic properties, including heat transfer. An additional difficulty is obtaining this information in multiphase processes: evaporation and condensation. It requires a lot of painstaking work that is carried out by specialized research centers around the world. The great complexity of the heat transfer processes of such substances makes it impossible to conduct effective theoretical research, which forces us to carry out experimental works, and therefore practical ones, requiring the construction of complex, costly research and measurement stands that greatly increase costs and time-consuming. Hence, few scientific centers undertake the above-mentioned research. One of them is the Koszalin University of Technology, where such research is successfully carried out at the Department of Heat and Cooling Technology – currently the Department of Energy. These studies concern obtaining the values of the heat transfer coefficients of new pro-ecological refrigerants entering into service:

1. Heat transfer coefficients during evaporation in tube, mini-channel and plate heat exchangers,
2. Heat transfer coefficients in tubular heat exchangers and long coils during condensation processes,
3. Heat transfer coefficients of refrigerants in the area of superheated of compressed vapors,
4. Research on the flow resistance of refrigerants during evaporation, condensation in tubular exchangers and mini channels,
5. Research on the possibility of extending the use of various refrigerants.

Fig. 1 shows the ecological indicator set for the selected refrigerants.

Fig. 2 shows for new small refrigeration equipment commercial and industrial and air conditioning and safety groups according to EN 378.

Refrigerants group	Refrigerants type	Temperature of boiling [K] (p = 1013 hPa)	Ecological indicators ODP	Ecological indicators GWP	Vitality in the atmosphere [years]
CFC	R11	296,9	1,00	4750	45
	R12	243,4	1,00	10900	100
	R113	320,7	1,00	6130	85
	R114	276,7	1,00	10000	300
	R115	233,9	0,44	7370	1700
	R502	227,6	0,25	4657	876
HCFC	R22	232,3	0,05	1810	12
	R401A	240,1	0,03	1182	8,5
	R402A	223,95	0,03	2788	22,2
HFC	R134a	247,1	0,00	1200	15,5
	R23	191,1	0,00	14800	270
	R152a	249,1	0,00	124	1,4
	R404A	226,4	0,00	3922	40,4
	R407A	227,4	0,00	2107	18,2
HC	R50	111,7	0,00	25	12
	R170	184,6	0,00	5,5	12
	RC270	241,7	0,00	1,8	
	R290	231,0	0,00	3	12
	R600	272,7	0,00	4	12
	R600a	261,4	0,00	3	12
	R601	309,2	0,00	4	0,08
	R601b	282,7	0,00	4	12
	R1150	169,4	0,00	3,7	12
	R1270	225,5	0,00	1,8	12
Natural	R717	239,8	0,00	0	0,02
	R718	373,1	0,00	0,2	0,03
	R744	194,8	0,00	1	29 300
	R744A	184,7	0,17	298	114

Fig. 1. Ecological factors of chosen refrigerants-compare (Białko B. 2019)

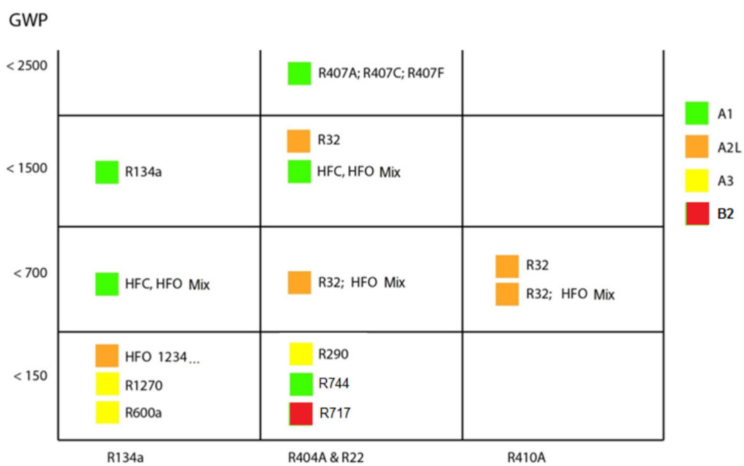

Fig. 2. Replacements for new small refrigeration equipment (for R134a), commercial and industrial (for R404A) and air conditioning (for R410A) – safety groups according to EN 378: A – non-toxic, B – toxic, 1 – non-flammable, 2L-slightly flammable, 2 – medium flammable, 3 – flammable (Danfoss drawing) (Targański W.)

TEWI – Total Equivalent Warming Impact.

$$TEWI = GWP\ L\ n + GWP\ m\ (1\text{-}f) + n\ E\ z$$

Ingredients this impact are (Zakrzewski, B. 2014):
GWP – refrigerant capacity factor to global warming with reference to the CO_2,
L – emission factor to air [kg/year],
n – operation time [years],
m – filling installation of refrigerant [kg],
f – dimensionless number of assessment the degree of recovery [-],
E – energy consumption by the device during the year, ($E = n \cdot tr$),
z – CO_2 emissions per unit of energy conversion [kg CO_2/kWh],
n – power of heat pump [kW],
tr – annual working time [h].

Legislation has been developed on ozone-depleting substances and on certain fluorinated greenhouse gases. EU regulations must also be respected by our country. Legal regulations are the provisions of the European Union treaty on which the regulations in the individual EU member states are based. There have been many directives, regulations and journals of laws which regulate the provisions in this matter (Commission Regulation (EU)… 2015, Journal of Laws… 2018, Commission Regulation (EU)… 2016/2281). Fig. 3 present a process of reducing internal greenhouse gasses in UE.

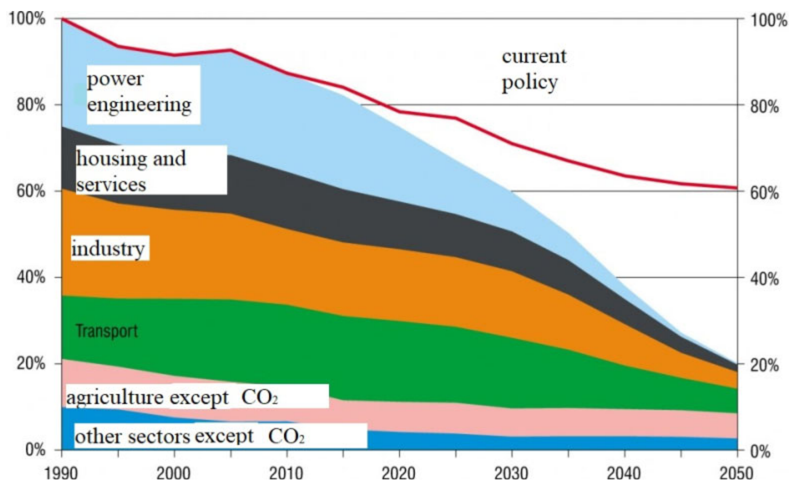

Fig. 3. The process of reducing internal greenhouse gasses in UE (100% = 1990)
Source: http://www.rynekinstalacyjny.pl/artykul/id3695,czynniki-chlodnicze-legislacja-dzis-i-jutro?gal=1

Fig. 4. present a global refrigerant standards and codes.

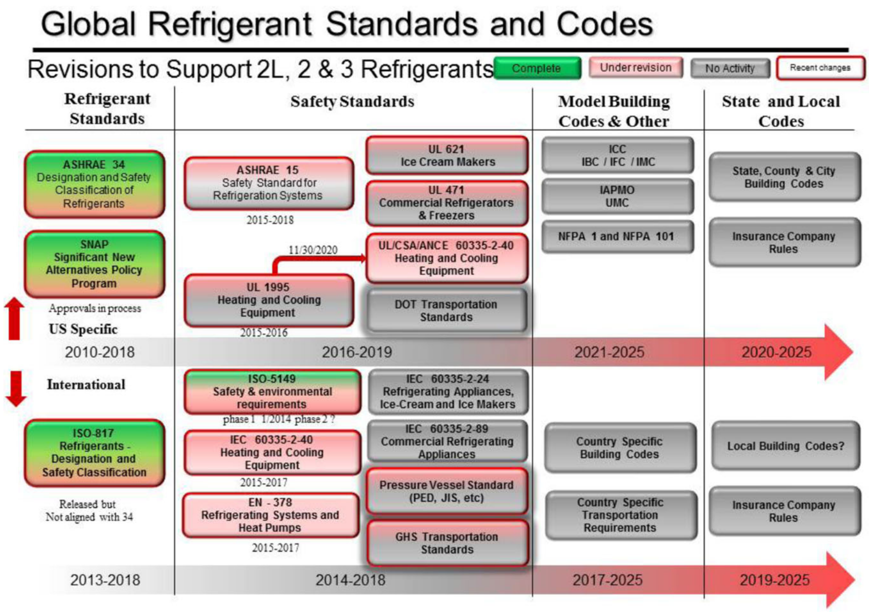

Fig. 4. Global refrigerant standards and codes
Source: Carrier Engineering Newsletter Vol. 3, Issue 2, Carrier Corporation 2015, New Refrigerants Impact Standards and Codes. Available: www.carrier.com/commercial

Compared to the 1990s, industrial countries should reduce greenhouse gas emissions by as much as 95% by 2050. There are 6 sectors spread over the years and with an increasing percentage of HFC reduction. The European Commission implements the Low Carbon Economy Roadmap, a low-carbon economy. They are withdrawn from the use of substances that destroy the ozone layer (i.e. CFC and HCFC freons). All this to protect our life and planet (http://www.rynekinstalacyjny.pl/artykul/id3695,czynniki-chlodnicze-legislacja-dzis-i-jutro?gal=1).

4. Conclusion

When using refrigerants, safety is the first priority! Of course, it is best if the GWP potential indicator is as low as possible and the ODP potential indicator is zero. However, factors with low GWP are usually highly flammable, while factors with a high energy content can be toxic (https://prozon.org.pl/index.php). It is a matter of the appropriate selection of priorities and a compromise between thermodynamic indicators and ecology.

From the beginning of its existence, refrigeration technology has set specific and very complex and excessive requirements regarding the construction, material engineering, durability of both individual elements (compressors, heat exchangers, evaporators, coolers, condensers, subcoolers, safety and automation elements and systems) as well as appropriate, certain permanent entire systems, sometimes operating in variable, often extreme environmental conditions, especially in relation to the function of the need to secure food storage, including all types of transport (land, sea and air), as well as ensuring appropriate climatic conditions, both in general and specialized systems, (medical facilities, in recent years even in space).

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