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HOF

Information sheet about refrigerants

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Thermal energy only flows from hot to cold. Thus, a heat sink is needed to cool the process. The heat sink can be generated by a refrigeration machine. This requires energy as well as a refrigerant. Many of the refrigerants being used (fluorinated refrigerants) are harmful to the environment and are internationally regulated (Montreal protocol or EU F-GasV).

This information sheet summarizes the most important aspects regarding the selection and availability of refrigerants and some recommendations are made.

The impact and challenge of refrigeration

In Germany, about 14% of the total electrical energy is used for cooling processes [1]. The resulting emissions have a significant impact on our climate and are referred to as indirect CO_2 emissions. Direct emissions from refrigeration machines are caused by leaks and the resulting release of refrigerants. Refrigerants is also released during maintenance, filling and disposal of the system.

Refrigerants have different effects on the environment. The first generation of chemical refrigerants (CFC – chlorofluorocarbons) led to the destruction of the ozone layer (ODP – Ozone depletion potential), while the subsequent substitute refrigerants (HFC - partly fluorinated hydrocarbons and PFC - fully fluorinated hydrocarbons) have a high global warming potential (GWP). The GWP-value of a refrigerant defines its global warming potential in relation to CO_2 (Known also as CO_2 equivalent).

CO_2 has a normalized GWP of 1, which means that the GWP-value indicates by how many times the refrigerants have a stronger impact on the greenhouse effect compared to CO_2. GWP is always related to a time horizon and describes the impact on global warming in the given period of time. For currently valid regulations, such as in Europe, the F-Gases regulation is referred to a GWP_{100} and therefore describes what impact a greenhouse gas will have in a time horizon of 100 years. From the latest IPCC publication, it appears that the next 10-20 years will determine whether or not the international climate agreement will be met. A consideration of the GWP20 is therefore relevant for climate policy, but not legally binding. For this, as mentioned, the GWP100 applies. Newly introduced low-GWP refrigerants (HFO – hydrofluoroolefin) have a low atmospheric lifetime and lead to persistent degradation products (PFAS/TFA) when they are decomposed in the atmosphere. This leads to a long term and more local pollution of the environment and a potential health risk (e.g., liver damage) for humans. Current water treatment processes cannot remove these substances. For the treatment, energy-intensive processes (e.g., reverse osmosis) are required. The most used refrigerants, their GWP and their atmospheric lifetime can be seen in Table 1.

In terms of environmental regulations, in the coming years many refrigeration systems will no longer meet the legal requirements.

Sources: See source list on last page

Table 1: The most used refrigerants and their GWP_{20} / GWP_{100}. [2]

Group	Refrigerant	Atmospheric lifetime	GWP – 100 years	GWP – 20 years	Composition
HFC	R134a	14 years	1430	3830	Pure substance
HFC-mixture	R404A	Up to 52 years	3920	4314	44% R125, 52% R143a, 4% R134a
HFC	R23	270 years	14800	12000	Pure substance
HFO	R1234yf	10-12 days	3	-	Pure substance
HFO/ HFC mixture	R452B	Up to 32.6 years	698	-	67% R32, 7% R125, 26% R1234yf
HFO/ HFC mixture	R449A	Up to 32.6 years	1282	-	24.3% R32, 24.7% R125, 25.3% R1234yf, 25.7% R134a

F-Gas regulation - Reduction of GWP value

The EU F-Gases Regulation (Regulation (EU) No. 517/2014), which came into force in 2015, has the goal of reducing CO2 equivalents from fluorinated greenhouse gases to around 21% by 2030. To achieve this, the total amount of CO2 equivalents, fluorinated greenhouse gases, allowed on the market will be gradually reduced (see Figure 1). The baseline is 183.1 million tons (100%) [3], which corresponds to the average amount of CO_2 equivalents placed on the European market between 2009 and 2012. In order to balance this value, Germany would have to completely abandon road transport for 1.25 years or stop using the agricultural sector for 2.7 years (status 2020) [3].

For refrigeration systems with a charge of >40 tons of CO_2 equivalent, which are operated with a refrigerant with a GWP higher then 2500, are prohibited by the article 13 since 1.1.2020. Exceptions are made for systems with a useful temperature below -50 °C and for maintenance and servicing with recycled refrigerants. From 2030, recycled refrigerants may also not be used for systems with application temperatures >-50 °C. A revision of the F-Gases Regulation was finally proposed in 2022 [4].

Sources: See source list on last page

One of the proposed changes is to increase the emission reduction goals for the period 2021 to 2030. CO_2 equivalents are now to be reduced to 5% [4] by 2030 instead of 21%.

These tightening are expected to take effect in the next few years.

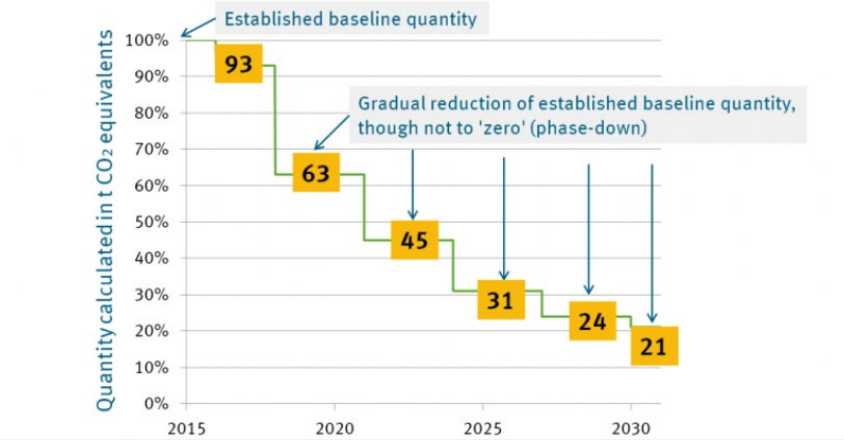

Figure 1: HFC refrigerant phase-down to 2030 to date
(Source: Federal Environment Agency, Germany)

F-Gas Regulation - Price Development

Supply and demand determine the price in a free market economy. Due to regulations and the associated limited availability of refrigerants on the market, lead to an increase in the price of GWP refrigerants. The first restriction on the maximum of CO_2 equivalents to be placed on the market in 2017, resulted in a significant increase in the price of the refrigerants. Since 2018, the high price increase of refrigerants has led to the emergence of an illegal market of GWP refrigerants which has formed within the EU. As a result of this and the additional stockpiling of refrigerants and according to the Eco Research Report, there was an oversupply of refrigerants in the third quarter of 2019. Which led to a reduction in the price of refrigerants (Figure 2).

The recent Eco-Recherche report shows a price increase in the high GWP refrigerants R134a, R404A and R410A (average price increase of 24%, 17%, and 15%, compared to Q1/2021) and mixtures of HFCs and HFOs (R448A, R452A, and R449A by 13%, 5%, and 4%).

[Source: Monitoring of refrigerant prices against the background of Regulation (EU) No 517/2014 Q1/2022]

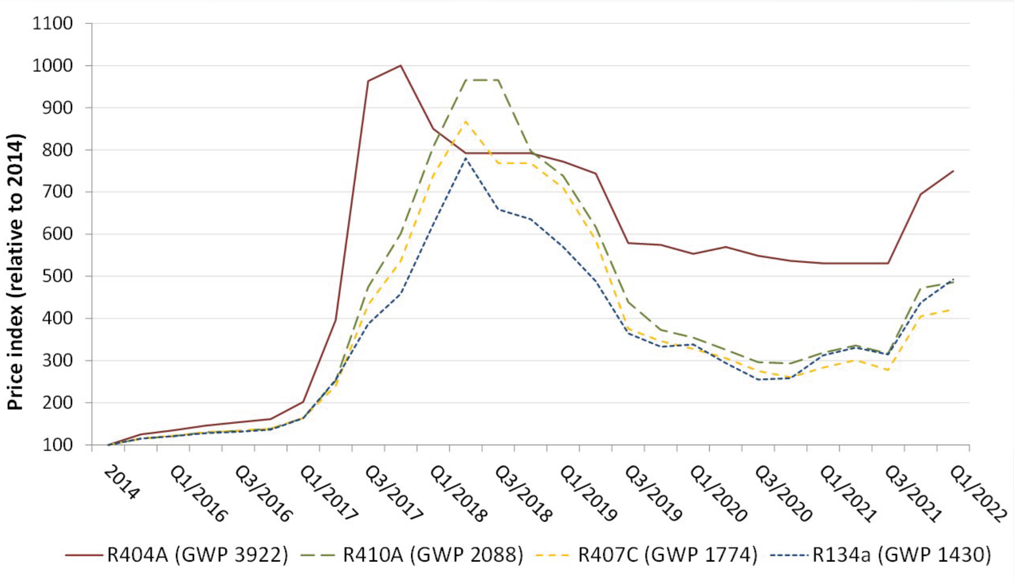

Figure 2: Price development of different HFCs refrigerants between 2014 and 2021

The illegal trade complicates the goal of meeting the F-Gas Regulation. Achieving the goals will require an accelerated shift to natural refrigerants and the elimination of illegal trade.

In the United States, the task force was established in 2021 to investigate any attempt to illegally import or manufacture of F-gases [5]. The task force announced a few months ago (March2022) that over the past ten weeks, it had prevented illegal HFC shipments amounting to about 530,000 tons of CO_2 emissions prevented. This is roughly equivalent to the CO_2 emissions of 100,000 households in one year.

The previous regulations in the EU have not been able to prevent illegal trading of the F-gases. To control the illegal trade in refrigerants, the customs authorities of the EU countries must be equipped with the right tools.

New generations of chemical refrigerants

HFOs (hydrofluoroolefins) are refrigerants of the 4th generation. Compared to HFCs (partly fluorinated hydrocarbons), HFOs have a low GWP value, and the industry considers them as an alternative.

The replacement of the climate-harmful refrigerant R-134a (GWP-1430), which is used for car-air- conditioning with HFO-1234yf (GWP < 3) is underway. HFO-1234yf has a short atmospheric lifetime of 10-12 days and decomposes to 100% to trifluoroacetic acid. Compared to R134a, with an atmospheric lifetime of 14 years and which decays to 7-20% TFA, the conversion results in higher and more localized TFA emissions.

TFA belongs to the group of the short chain perfluorocarboxylic acids (scPFCAs), which are persistent in the environment and highly mobile in the water cycle. Today's drinking water treatment plants are not capable of filtering out TFA, leaving humans directly exposed to accumulated TFA in drinking water. The current measurements of TFA in drinking water are below the drinking water guidance value for TFA. However, an increase in concentrations of up to 13 times has already been observed in Switzerland compared to the year 2000. The health risks, particularly exposure to low levels over extended periods of time of TFA, have not been conclusively researched.

In a study (Umwelt Bundesamt, 2020), an increase in ALT (alanine aminotransferase) concentration was observed with increasing TFA concentration. An elevated ALT concentration is a sign of liver damage, since destroyed liver cells release these enzymes.

Similar symptoms occur with the administration of halogenated inhalation anesthetics, such as the administration of halothane. Due to the oxidation of halothane, TFA is formed in the body, and after administration, an increase in the ALT concentration is recorded and decreases after the administration is stopped.

The same characteristic is seen with the direct addition of TFA in drinking water can be seen from the UBA study. Before chemicals are introduced into the environment, it must be proven to be harmless to both humans as well as for the environment. It is only a question of time before there are negative effects on humans and the environment will occur. More detailed information on this topic HFO/TFA can be found in our HFO/TFA-Report [6].

Sources: See source list on last page

Energy efficiency

The goal of energy efficiency measures is to reduce the total energy demand of processes by reducing the quantitative and qualitative losses that occur during the conversion, transport or storage of energy. Refrigeration systems require more drive energy (at constant heat sink and a constant cooling capacity) the lower the useful temperatures are. The ratio of the cooling capacity and the drive power is described as the refrigeration coefficient of performance.

In typical refrigeration systems for air conditioning the coefficient of performance is in the order of 3. In other words, for 1 kW drive power, a refrigeration system provides 3 kW cooling capacity for air conditioning. The maximum coefficient of performance which can be achieved with a lossless, reversible process is described by the coefficient of performance of a Carnot process. This is purely dependent on the ambient temperature (heat sink) and the useful temperature (heat source). The lower the temperature is required, the lower is also the coefficient of performance of a refrigeration machine.

Different refrigeration processes have different efficiencies depending on the temperature. Compression refrigeration systems (2-stage-booster systems or cascades) are more efficient in comparison with cold-air refrigeration up to useful temperatures of -50 °C. Below temperatures of -70 °C, cold air refrigeration has the highest efficiency. Liquid nitrogen is frequently used for cooling processes. This process differs in principle in having a refrigerant (nitrogen) that is consumed and has already been generated in an air separation plant at temperatures of -196 °C.

The generation of liquid nitrogen at -196 °C requires significantly more energy than the generation of process temperatures of -80 °C with a refrigeration plant. The use of nitrogen at high useful temperatures leads to high nitrogen consumption and high energy costs, which are generally not included in the balance sheet of the manufacturing company. Therefore, the choice of refrigeration technology requires knowledge of the sensible areas of application for the different refrigeration technologies. More on the topic of energy efficiency can be found in our freely available ULT report.

Natural refrigerants

Natural refrigerants have gained popularity over the last decades and technological developments in this regard are making very good progress. They are competitive and even more efficient than chemical refrigerants. Natural refrigerants can replace the high GWP refrigerants currently used on the market. For example, CO_2 heat pumps (GWP = 1) are used for water treatment at home or as booster systems for commercial refrigeration. Furthermore, propane (GWP = 3) is used for chillers. Ammonia (GWP = 0) is a refrigerant with good thermodynamic properties and is used in industry due to its high efficiency.

To reach low temperatures (e.g., freeze drying) refrigerants like R404A (GWP 3922), R410A (GWP 2088) or R507A (GWP 3985) are used. The global warming potentials (GWP) of these refrigerants are regulated by the F-Gases Regulation, which means that the refrigerants will be banned in the future, or their use will be so severely restricted that they will only be available at very high prices. In order not to be affected by these problems, it is worthwhile to switch to natural, environmentally friendly and safe technologies at an early stage. Refrigeration with air as a natural refrigerant has become established in recent years in various areas, including freeze-drying, and is considered a forward-looking technology for a fail-safe, efficient and environmentally friendly process.

Natural refrigerants are cost-efficient, available in unlimited quantities and can already cover almost all refrigeration applications. With a very low GWP and high energy efficiency, the use of natural refrigerants is highly recommended.

Sources: See source list on last page

Significance for the operators

Most refrigeration systems for cryogenic technology are regulated by the EU F-Gases Regulation due to the refrigerants used (e.g., R404A, R410A, R499A, R23). Currently, high GWP refrigerants are allowed through the exemption of Article 13 of Regulation F-Gases until at least 2030.

Due to climate policy targets, operators will face further restrictions on the use of high GWP refrigeration systems in the coming years. Among other things, the -50 °C exception for the use of high GWP refrigerants is increasingly criticized and possible phase-downs are proposed. To continue to ensure production reliability, strategic decisions must be made at an early stage. However, investments must also be made in future-proof technologies. Those who currently invest in new systems and retrofits with a high GWP (e.g., R452A) run the risk of no longer being able to operate their systems from 2030 onwards, as either maintenance is prohibited, or the availability of the refrigerants decreases strongly and the costs for maintenance increase considerably. In the meantime, solutions using natural refrigerants will be future-proof technologies, since on the one hand these are environmentally friendly and efficient and are also free of all regulations.

For applications below -50 °C, cold-air refrigeration and cascade systems with flammable refrigerants have become established and are already being safely used in many applications. Besides the new plants, the consideration of existing plants must also be included. Many plants can be equipped with a retrofit of the refrigeration side without changing the actual process.

An early action is essential, because as soon as further restrictions are imposed, all plant operators will be affected, and they will take action at the same time.

Criterion:	2 Stage Freon	Liquid Nitrogen	Burnable cascade	Air Refrigeration
Future-proof	X	0	+	+
Reliable	0	+	0	+
Operation costs	0	-	0	+
Maintenance	-	0	-	+
Efficiency	0	-	0	0
Safety-effort	+	-	-	+
Space	+	+	-	-
First invest	+	+	0	-

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