

Avoiding Fluorinated Greenhouse Gases

Prospects for Phasing Out

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by

Katja Becken

Dr. Daniel de Graaf

Dr. Cornelia Elsner

Gabriele Hoffmann

Dr. Franziska Krüger

Kerstin Martens

Dr. Wolfgang Plehn

Dr. Rolf Sartorius

German Federal Environment
Agency (Umweltbundesamt)

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06844 Dessau-Roßlau
Germany
Phone: +49-340-2103-0
Fax: +49-340-2103 2285
Email: info@umweltbundesamt.de
Internet: <http://www.umweltbundesamt.de>
<http://fuer-mensch-und-umwelt.de/>

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Katja Becken, Dr. Wolfgang Plehn

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Foreword

Fluorinated greenhouse gases (F-gases) are 100 to 24,000 times more harmful to the climate than CO₂. The contribution of fluorinated greenhouse gases to global warming is projected to triple from nearly 2% to around 6% of total greenhouse gas emissions by the year 2050. This is revealed by global projections prepared for the Federal Environment Agency in a scenario where no new measures are taken. The need for action is evident. F-gases are mostly used in similar ways to the CFCs and halons used in the past, which are responsible for the destruction of the ozone layer in the stratosphere. For this reason the international community of states has been engaged for over a year in negotiations about the inclusion of a number of fluorinated greenhouse gases in the Montreal Protocol – the international environmental agreement on the protection of the ozone layer. There is therefore a great need for up-to-date scientific information about the climate-friendly and innovative alternatives to F-gases. This is the purpose of the present report.

In 2050, some 80% of F-gas emissions will derive from stationary and mobile refrigeration and air-conditioning applications. These are emissions that can be prevented by using climate-friendly natural refrigerants in the future: Manufacturers are successfully using hydrocarbons in household appliances, and for a few years now the same has been true of laboratory appliances. In supermarkets and discount stores, a growing number of practical examples are showing that halogen-free refrigerants such as CO₂ or hydrocarbons can not only provide the necessary refrigeration, but can also make a significant contribution to saving energy thanks to good energy efficiency and waste heat recovery. Similar innovative developments can also be found in the mobile air-conditioning sector. For modern vehicles with fuel-saving technology and for electric cars, scientists and development engineers regard CO₂ as a suitable refrigerant for air-conditioning systems, partly because it is not flammable, and partly because the air-conditioning systems can also be used “in reverse” as a heat pump. The Berlin public transport system (*Berliner Verkehrsbetriebe – BVG*) have been leading the way by testing city buses with this refrigerant since 2010. Since 2009, the Federal Environment Agency itself has been running one of its cars with a CO₂ air-conditioning system, and experience to date is good. This and other “phase-out paths” are described in this report. The industry has developed numerous climate-friendly solutions. Now it is time for users, businesses, public transport companies and the car industry to make use of these innovative technologies in practice. This report is our contribution to the discussion about measures at European and international level.

Jochen Flasbarth

President of the Federal Environment Agency, Dessau-Roßlau, November 2010

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Introduction

Climate protection has become increasingly important since the Rio Conference in 1992 with the signing of the Framework Convention on Climate Change (FCCC). In Article 2 of the Framework Convention on Climate Change, the Parties to this Convention set themselves the target of achieving “stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system. Such a level should be achieved within a time frame sufficient to allow ecosystems to adapt naturally to climate change, to ensure that food production is not threatened and to enable economic development to proceed in a sustainable manner.” [KRK 1992]. To achieve this target there was a need for further elaboration. To this end Conferences of the Parties (COPs) have been held regularly. The Kyoto Protocol [Kyoto-Protokoll 1997] which was adopted in December 1997 must be regarded as the most important result of these conferences. In it, the industrialised countries promised – for the first time – to make a binding reduction in their greenhouse gas emissions. Whereas the industrialised countries undertook to make an average reduction of 5.2%, the European Union committed itself to the target, which was binding under international law following the ratification of the Protocol, of reducing greenhouse gas emissions by a total of 8% compared with 1990 during the period 2008 - 2012. Under the burden-sharing arrangements of the European Union, Germany undertook to reduce emissions by 21%. The first commitment period of the Kyoto Protocol ends in 2012. Against this background the Parties are currently negotiating a new international climate change convention for the period after 2012. The UN Climate Conference in Copenhagen in December 2009 was intended to agree at least the key points of this follow-up convention, but did not succeed. The German government has set itself the target of achieving a 40-percent reduction in greenhouse gas emissions by 2020, compared with the base year 1990. This target remains valid regardless of any follow-up convention.

In addition to the classic greenhouse gases carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O), the fluorinated greenhouse gases HFC, PFC and SF₆¹ were included in the Kyoto Protocol in 2007 in view of their global warming potential, which in some cases is extremely high.

In 2000 the German government first included fluorinated greenhouse gases in its climate protection programme as a separate module [Klimaschutzprogramm 2000]. In 2002 the Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU) produced a key point paper (“Implementation of the National Climate Protection Programme

¹ HFC: hydrofluorocarbons, PFC: perfluorocarbons, SF₆: sulphur hexafluoride

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in the field of fluorinated greenhouse gases”). This discussed the predicted development in emissions of fluorinated greenhouse gases, identified necessary fields of action and indicated ways of reducing emissions [EckpPapier 2002]. From 28 to 30 January 2003 and from 12 to 14 February 2003 the suggestions were discussed with interested parties at a hearing in Bonn [Anhörung 2003]. These discussions were an important basis for the first edition of this report.

In the context of the European Climate Change Programme (ECCP), the European Commission (COM), representatives of industry, Member States and non-governmental organisations discussed possible EU-wide measures to reduce emissions of fluorinated greenhouse gases [ECCP 2000]. On this basis, the European Parliament and the Council Rat issued in 2006 *Regulation (EC) 842/2006 on certain fluorinated greenhouse gases* [KOM 2006] and *Directive 2006/40/EC relating to emissions from air conditioning systems in motor vehicles and amending Council Directive 70/156/EEC* [KOM 2006a].

Transposition of the two pieces of legislation into German law was by means of the Chemicals Climate Protection Ordinance (*Chemikalien-Klimaschutzverordnung*) [ChemKlimaschutzV 2008] and announcement in the *Verkehrsblatt* 2006 [Verkehrsblatt 2006].

In view of the high global warming potential of fluorinated gases, their emission reduction commitments under the EU burden-sharing arrangements and expectations of a disproportionate rise in emissions of these gases, some European states planned or adopted emission reduction measures, including prohibition of use, to varying extents even before the EU. This applies in particular to Denmark, Austria and Switzerland [Danish EPA 2001; HFKW-FKW-SF₆-VO 2002; StoV 2003].

Whereas the classic greenhouse gases are mostly released as undesirable by-products, e.g. in the combustion of fossil fuels, fluorinated greenhouse gases are largely produced deliberately and used in products such as refrigerants, blowing agents, fire extinguishers, propellant gas etc. Reducing emissions of these substances therefore calls not only for technological measures, but also for targeted use of substitute substances or alternative technologies.

Purpose and structure of report

A considerable need for information on the subject of “fluorinated greenhouse gases” exists among commercial users of products and systems containing fluorine gas, the general public – as private users of products which may contain fluorinated gases – and non-governmental organisations, research establishments etc. This relates to fluorinated greenhouse gases as a group of substances and to potential alternative substances and technologies. The aim of this report is to fill this need for information. It is also intended to serve as an updated situation report for decision makers. In addition to policy makers at EU, federal, regional and local level, decision makers in research and industry are also potential addressees for information.

Part A of the report provides a brief presentation of the fluorinated gases group. A description of their properties and their environmental impacts is followed by an outline of the emissions situation. Part B gives an account of the individual areas of application and the state of the relevant technology. There are also other applications which are not dealt with in this report because of their very minor importance with regard to emissions of fluorinated gases. The conclusions following each sub-chapter assess – as far as possible – whether the use of halogen-free substances or processes is technically and economically possible and ecologically desirable.

The basis for the report published in 2004 was the wide range of discussions about the key point paper on fluorinated greenhouse gases held with interested parties by the Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU) and the Federal Environment Agency (UBA). These centred round the discussions held in Bonn from 28 to 30 January and 12 to 14 February 2003. The information made available there has since been supplemented by further discussions or analysis of the literature. In 2010 the report was updated on the basis of this new information.

This report described the technical situation regarding the use of fluorinated gases in the individual applications and contrasts this with technical measures to reduce emissions of these substances. This includes descriptions of substitute substances and processes that manage without using fluorinated greenhouse gases or are based on fluorinated greenhouse gases with a lower GWP, and descriptions of other technological measures. Emission reduction measures already taken under regulatory law or in voluntary undertakings are described in the individual chapters.

Part A General Part

1 Properties and environmental impacts of fluorinated gases

1.1 *Structure, nomenclature and physico-chemical properties*

Following the Kyoto Protocol, the term “fluorinated greenhouse gases” is used collectively for the group of hydrofluorocarbons (HFC), the group of perfluorocarbons (PFC), and sulphur hexafluoride (SF_6). From a chemical point of view there are other groups of substances, e.g. the fluorinated ethers and nitrogen trifluoride (NF_3), which ought to be classified as fluorinated gases. At present these substances are not included in the Kyoto Protocol, but the possibility is being discussed. Even within the substance group of HFCs and PFCs there are individual substances that are not covered by the Kyoto Protocol, because the relevant reports by the Intergovernmental Panel on Climate Change (IPCC) do not attribute any greenhouse gas potential to them and they are not subject to the reporting requirements laid down in the Kyoto Protocol.

The term perfluorinated hydrocarbons and also perfluorocarbons, is a collective term for a large number of low-molecular aliphatic (open-chain) or alicyclic (ring-shaped, non-aromatic) hydrocarbons in which the hydrogen atoms are completely replaced by fluorine atoms. However, if the molecule also contains hydrogen atoms, these substances are subsumed under the collective term hydrofluorocarbons. It is a feature common to all the substances in these two groups that they do not contain any elements other than carbon, fluorine and possibly hydrogen. The most important HFCs and PFCs are derived from methane (CH_4), ethane (C_2H_6) and propane (C_3H_8).

The various substances are usually referred to by their code number. This frequently starts with an “R” for refrigerant. The codes are three-digit numbers. They are assigned in accordance with the following scheme:

- 1st digit: Number of carbon atoms in molecule, minus one (a “0” is suppressed),
- 2nd digit: Number of hydrogen atoms, plus one,
- 3rd digit: Number of fluorine atoms. Lower-case letters after the number indicate the substitution site.

Example: 134a = $\text{C}_2\text{H}_2\text{F}_4$ or $\text{CF}_3\text{-CH}_2\text{F}$.

- Preparations (blends, mixtures) of HFCs and PFCs are also assigned codes, but these are not derived from the number of atoms. Here a distinction is made between the 400 series and the 500 series. The classification of the mixtures is based on their

Part A – General Part

refrigeration-relevant properties: 400 series = zeotropic mixtures and 500 series = azeotropic mixtures.

A detailed description can be found in DIN 8960 [DIN 1998].

Compared with the relevant halogen-free hydrocarbons, partially and perfluorinated hydrocarbons are much more stable from a chemical and thermal point of view. Perfluorocarbons are among the most stable organic compounds that exist. They only start to decompose at temperatures above 800°C. Both PFCs and most HFCs are not combustible or not readily combustible. Examples of exceptions are HFC-152a, HFC-365mfc and HFC-1234yf (HFO-1234yf) [Harnisch *et al* 2003, Sicherheitsdatenblatt 2008]. In the event of a fire, decomposition products such as hydrogen fluoride or carbonyl fluoride may be formed. Some of these are toxic. HFCs are practically insoluble in water. PFCs are not readily miscible, even with other solvents.

Unlike the HFCs and PFCs, sulphur hexafluoride is not a collective term, but an individual substance. It is a colourless, practically inter gas with high dielectric breakdown resistance and great thermal stability. SF₆ only decomposes at very high temperatures or under the influence of electric arcs. This gives rise to low-fluorinated degradation products, some of which are toxic.

Nitrogen trifluoride (NF₃) is also an individual substance. The Parties are negotiating on its inclusion in the Kyoto Protocol in view of its increasing climate relevance (increasing use, high GWP). NF₃ is a chemically indifferent colourless gas with a musty smell. It does not react with water at room temperature and, unlike ammonia, possesses virtually no basic properties.

The main physico-chemical properties and the maximum workplace concentration in Germany (*MAK*) of the most important fluorinated gases in terms of quantity can be seen in Table 1.1.

Table 1.1: Physico-chemical properties and maximum workplace concentrations (*MAK*) of selected fluorinated gases [DFG 2009; Air Liquide 2009; NICNAS 1999; DesMarteau, Beyerlein 1996; DuPont 2002]

Compound Code	Formula	Molecular weight in g/mol	Melting point in °C	Boiling point in °C	Vapour pressure at 20°C in bar	MAK limit [DFG 2009]	
						in ml/m ³	in mg/m ³
HFC-23	CHF ₃	70	-155	-82.2	41.6	1,000*	
HFC-32	CH ₂ F ₂	52	-136	-52	13.8		
HFC-43-10mee	C ₅ H ₂ F ₁₀	252	-83.7	55	0.25		
HFC-125	C ₂ HF ₅	120	-103	-48.5	12.1	1,000*	
HFC-134a	CH ₂ FCF ₃	102	-101	-26	5.7	1,000	4,200
HFC-152a	C ₂ H ₄ F ₂	67	-117	-25	5.1	1,000*	1,910*
HFC-143a	C ₂ H ₃ F ₃	84	-111	-47.6	11.1		
HFC-227ea	C ₃ HF ₇	170	-131	-16.4	4		
HFC-236fa	C ₃ H ₂ F ₆	151	-94.2	-1.1	2.5 (25°C)	1,000*	
HFC-245ca	C ₃ H ₃ F ₅	134	-73.4	25			
Sulphur hexafluoride	SF ₆	146	-50.8	-63.8	21	1,000	6,100
Nitrogen trifluoride	NF ₃	71	-206.8	-129			
FC-14	CF ₄	88	-184	-128			
FC-116	C ₂ F ₆	138	-101	-78			
FC-218	C ₃ F ₈	188	-183	-36.7	7.7		

*: Internal workplace concentration guide figure, DuPont® [DuPont 2002]

1.2 Global production, use and emission forecast

Production

In 2007 nine internationally operating companies notified their production quantities of fluorinated hydrocarbons (HCFC, HFC) to AFEAS (Alternative Fluorocarbons Environmental Acceptability Study). The production quantity notified came to 209,059 t. This is an increase of 6% on 2006. To this must be added the quantities of HFCs produced in China and India, which are not notified to AFEAS. AFEAS estimates that the production quantity notified to AFEAS accounts for about 60% of total worldwide production [AFEAS 2008].

Production capacity in the European Union for HFC-134a was estimated by IPCC [2005] at 40,000 t for 2003 (worldwide 185,000 t). Other substances produced in the EU in 2003 were HFC-143a, HFC-125 and HFC-32, plus HFC-365mfc. There were three companies. SF₆ was also produced.

Fluorinated hydrocarbons can be produced by a variety of processes. In view of the extreme exothermic reaction, direct fluorination of hydrocarbons with elementary fluorine is not practical. The main production routes for fluorinated hydrocarbons are electrochemical fluorination of hydrocarbons, addition of hydrogen fluoride to multiple bonds (e.g. olefins), or catalytic Cl/F exchange of chlorinated hydrocarbons by means of hydrogen fluoride or metal fluorides. PFCs are also produced by means of indirect fluorination with fluorinating agents (e.g. CoF₃) [Kirk-Othmar 1994; Ullmann's 1988].

Sulphur hexafluoride was first produced by burning sulphur in a fluorine atmosphere. Its technical production subsequently used a similar method: Liquid sulphur is converted with elementary fluorine at 300°C in a cooled reactor and the reaction gases are then purified [Ullmann's 1976]. If previously produced SF₆Cl is pyrolysed instead of sulphur, no elementary fluorine is needed. Furthermore, electrochemical processes are patented [Ullmann's 1988].

Development from CFCs to HFCs

HFCs and to some extent PFCs are used in many applications that formerly used chlorofluorocarbons or hydrochlorofluorocarbons (CFCs or HCFCs) and halons. Both CFCs and halons are ozone depleting substances (ODS). Today they are subject to an international phasing-out scenario under the Montreal Protocol on Substances that Deplete the Ozone Layer dating from 1987 [Montreal Protocol 2000] and its successor conventions. In 1991 Germany made a start on completely phasing out CFCs and halons under the *CFC-Halon Prohibition Ordinance* [FCKW-Verordnung 1991]. This process was completed – apart from a few exceptions – in the late 1990s. It was not until 2006 that the *Ozone Layer Chemicals Ordinance* (*Chemikalien-Ozonschichtverordnung*) [ChemOzonschichtV 2006] replaced the *CFC-Halon Prohibition Ordinance* (*FCKW-Halon-Verbots-Verordnung*).

The European legislation in force since 1 January 2010 is *Regulation (EC) No 1005/2009 of 16 September 2009 on substances that deplete the ozone layer* [EG-Verordnung 2009]. This has superseded earlier regulations, such as *Regulation (EC) No 3093/94* of 15 December 1994 [EG-Verordnung 1994] and *Regulation (EC) No 2037/2000* of 29 June 2000 [EG-Verordnung 2000].

In view of their incombustibility and technical properties, ozone depleting substances (ODS) were used on a large scale in many areas of application. With few exceptions, the halons also included in the Montreal Protocol were used solely as fire extinguishing agents.

Once the ozone depleting potential (ODP) of these substances was discovered, the search for possible substitutes began. Initially the research effort concentrated on substances that were chemically very similar. Via HCFCs the road led to the chlorine-free alternatives: perfluorocarbons and hydrofluorocarbons.

Due to the development of HFCs and PFCs as substitutes for ODS, the areas of application are also largely similar. In certain areas, HFCs in particular have contributed to rapid phasing-out of ozone-depleting substances. In many applications, however, halogen-free substances succeeded from the start in becoming established as substitutes for ODS, for example as solvents and cleaners, refrigerants, fire extinguishing agents, and in many areas of foam production. In some cases, it is only in recent years that processes and products based on the use of halogen-free substances have reached a technological level that permits their broad use. This is true, for example, of the use of CO₂ as a refrigerant. Today these technologies can replace the processes and products with fluorinated gases that were necessary in the intervening period, while in other areas of application this process is already virtually complete.

Following the increase in emissions of fluorinated greenhouse gases as a result of the ban on CFCs and HCFCs, the European Community issued *Regulation (EC) 842/2006 of 17 May 2006 on certain fluorinated greenhouse gases* (F-gas Regulation [KOM 2006]). Among other things, the F-Gas Regulation prohibits the use of PFCs, HFCs and SF₆ in certain products, e.g. in sound-insulating windows, footwear, tyres and fire extinguishers. The operation of stationary refrigeration systems, air-conditioning systems and heat pumps containing fluorinated greenhouse gases is subject among other things to regular leakage checks and certification of personnel and facilities that run their systems in a professional manner. In Germany the F-Gas Regulation was supplemented by passing the *Ordinance on protecting the climate against changes due to inputs of certain fluorinated greenhouse gases* (Chemikalien-Klimaschutzverordnung [ChemKlimschutzV 2008]). By laying down limit values for specific refrigerant losses from “stationary applications” (refrigeration and air-conditioning systems), this goes far beyond the EU Regulation.

In parallel with the F-Gas Regulation, *Directive 2006/40/EC of the European Parliament and of the Council of 17 May 2006 relating to emissions from air conditioning systems in vehicles and amending Council Directive 70/156/EEC* entered into force. It initially applies to air-conditioning systems in passenger cars and small commercial vehicles that are designed to contain fluorinated greenhouse gases with a GWP in excess of 150. The Directive prescribes

leakage tests on such air-conditioning systems and bans them from 2011 in new car models, and from 2017 onwards in all newly built cars (see Chapter 3.3.7).

Areas of application and use

The areas of application for fluorinated greenhouse gases are many and various, and go beyond those of ozone-depleting substances. A basic distinction can be made between use in largely enclosed cycles (e.g. as refrigerant), in open applications (e.g. as propellant gas) and as process gas (e.g. semiconductor manufacture). The type of application is crucial to the amount and timing of the emissions. For this reason it is important with fluorinated greenhouse gases to distinguish between the amounts input/used and the amounts actually emitted in a year. The quantity input/used means the total quantity which is used or input to produce or service a product and which may remain present in this product as refrigerant or expanding gas or may be consumed directly, e.g. as etching gas or tracer gas.

HFC

The areas of application for HFCs are primarily

- stationary and mobile refrigeration and air-conditioning applications (as refrigerant),
- insulating materials/foam plastics (as blowing agent) and
- aerosols (as propellant gas).

Other applications/emission sources exist

- in the production of HCFCs (formation of HFC-23 as by-product),
- in semiconductor production (as etching gas),
- as fire extinguishing agent, and
- as a solvent.

Today the main emission sources are the production of HCFCs, where HFCs are formed as an unwanted by-product, and the use of HFCs as refrigerants. Whereas in 2005 some 44% (246 megatonnes CO_{2eq}) of worldwide emissions were due to HCFC manufacture, about 43% (240 megatonnes CO_{2eq}) of HFC emissions were due to their use as refrigerants in stationary and mobile cooling systems (refrigeration and air-conditioning). Some 67% (160 megatonnes CO_{2eq}) of these refrigerant emissions were due to commercial refrigeration systems [Schwarz, Gschrey 2009].

PFC

In 2005 some 68 megatonnes CO_{2eq} of PFC were emitted into the atmosphere. This corresponds to 9% of total F-gas emissions. The biggest emission sources for PFCs are the aluminium and semiconductor industries. The aluminium industry is unlike the other PFC emission sources in that it does not deliberately use PFCs; these are formed during the production process [Schwarz, Gschrey 2009].

PFCs are used on a targeted basis

- in semiconductor production (as etching gas),
- in circuit board production (as etching gas),
- in refrigeration systems (as refrigerant).

SF₆

SF₆ is not one of the substitute substances for ODS, and has been in use since the late 1960s. This gas, with the highest GWP, accounted for emissions of 140 megatonnes CO_{2eq} in 2005, some 18% of global F-gas emissions. Today the biggest sources of SF₆ are electrical equipment and the magnesium and semiconductor industries [Schwarz, Gschrey 2009].

The wide range of application areas for SF₆ comprise

- in electrical equipment (as insulating gas and arc-quenching gas),
- in aluminium foundries (as cleaning gas),
- in magnesium foundries (as cover gas),
- in semiconductor production (as etching gas),
- in high-voltage electronic devices (electron microscopes, x-ray equipment etc.),
- in car tyres (as filling gas),
- in noise-insulating windows (as insulating gas),
- in the production of photovoltaic cells (as etching gas),
- in the production of optical fibres (for fluorine doping),
- as tracer gas, and
- as leak detection gas.

In global terms, fluorinated greenhouse gases currently account for about 1-2% of all emissions of climate-relevant gases. This is roughly the same as the share due to air transport. However, forecasts commissioned by the UBA show that in a “business-as-usual” scenario this share will rise to 5.9% (4019 megatonnes CO₂ equivalent) by 2050 [Schwarz, Gschrey 2009]. Some forecasts prepared in cooperation with manufacturers of fluorinated greenhouse gases expect the share to be even larger [Velders et al. 2009].

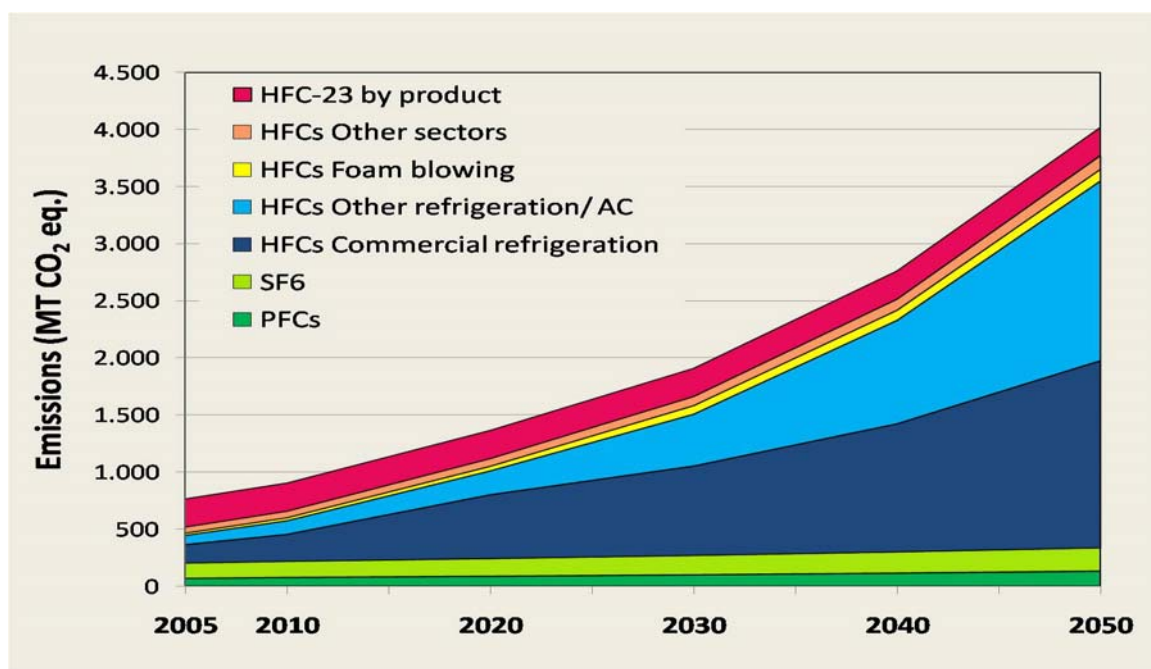


Figure 1.1: Global forecasts of fluorinated greenhouse gas emissions in the main fields of application in megatonnes CO₂ equivalent (“business-as-usual scenario”) [Schwarz, Gschrey 2009].

Eighty percent (3211 megatonnes CO₂ equivalent) of F-gas emissions in 2050 result from HFC emissions from stationary and mobile refrigeration and air-conditioning applications. The share due to PFC emissions in 2050 is around 3% (133 megatonnes CO₂ equivalent), and approximately 5% (206 megatonnes CO₂ equivalent) of F-gas emissions result from the use of SF₆. Figure 1.1 provides an overview of the predicted worldwide development of emissions of HFCs, PFCs and SF₆ up to the year 2050 (“business-as-usual scenario”). HFC emissions are shown separately for the main areas of application – commercial refrigeration, other refrigeration and air-conditioning applications, foam manufacture and emissions of HFC-23 from production of HCFCs [Schwarz, Gschrey 2009].

1.3 Environmental impacts (focus on climate)

HFCs, SF₆ and NF₃ are largely produced deliberately and used in systems and products. Emissions occur primarily during use of the substances and disposal of systems and products. PFCs also occur as an unwanted by-product in the production of primary aluminium (see Chapter 1.2). The concentrations of the individual HFCs, PFCs and SF₆ in the atmosphere are in the parts-per-trillion (ppt) range. However, because of their relatively long – in the case of PFCs and SF₆ extremely long – life in the atmosphere they generally display an increasing trend. The concentration of some substances has increased sharply in recent years (see Fig. 1.2). The biological effectiveness of the fluorinated compounds is slight, and harmful effects only occur at very high concentrations. In view of the very low concentrations of fluorinated gases in the atmosphere (in which these substances remain), neither human nor eco-toxicological aspects are an issue.

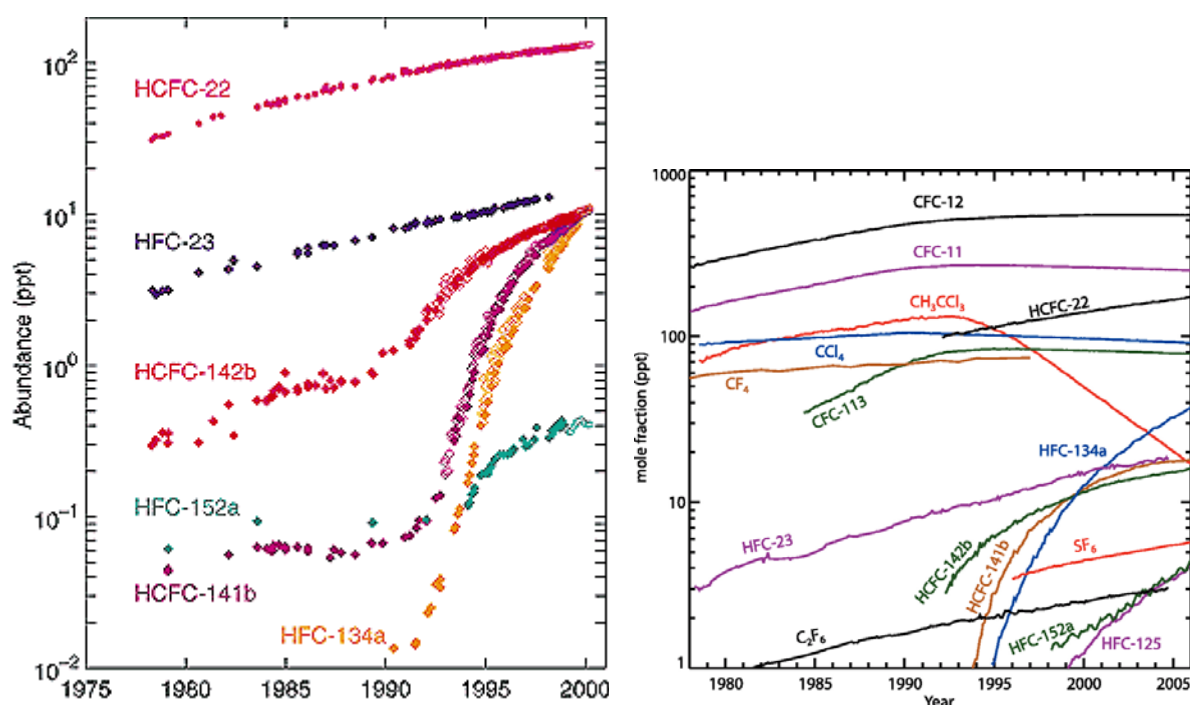


Figure 1.2: Concentrations of long-lasting greenhouse gases in the atmosphere [IPCC 2001, IPCC 2007].

The ecological impacts of fluorinated greenhouse gases were the subject of investigation in the UBA research project “Risks and Benefits of Fluorinated Greenhouse Gases in Processes and Products under Special Consideration of the Properties Intrinsic to the Substance” [Harnisch *et al* 2003]. The findings from that report have been incorporated in the following remarks.

1.3.1 Degradation in the atmosphere / sinks and persistence

It is characteristic of HFCs that, unlike PFCs, their molecules still contain hydrogen atoms which can be abstracted by reacting with hydroxyl radicals (OH radicals, “atmospheric detergents”) (H-abstraction). This primary step is decisive for the speed of degradation. It thus determines the life of the substance. Further degradation takes place relatively quickly – by radical reaction via various intermediate products or reaction channels – to hydrogen fluoride (HF) and trifluoroacetic acid (CF_3COOH , TFA) as principal degradation products. Other sinks such as photolysis, adsorption and leaching do not play a role.

In the case of PFCs and SF_6 there is no possibility of H-abstraction. These molecules are therefore extremely resistant and are degraded by photolytic means, not in the troposphere or the stratosphere, but in the mesosphere. This process takes place after very long delays due to transport and is, moreover, very slow. This explains the great persistence of these compounds.

Both hydrogen fluoride and trifluoroacetic acid dissolve readily in water and are therefore eliminated from the atmosphere by precipitation. However, the extent to which the fluoride content of precipitation and waters is due to decomposition of HFCs is only very limited. The concentration of hydrogen fluoride or fluoride from HFCs that is present globally in rain results in concentrations that are five orders of magnitude below the relevant damage

thresholds for land plants [Harnisch *et al* 2003]. In the past, a number of different industrial processes (combustion of certain types of coal, aluminium production etc.) have caused damage to plants and grazing animals in Germany and the EU. Thanks to the stringent air quality control requirements this is no longer the case in this country. In other parts of the world, however, fluoride emissions from the combustion of poor-quality coal are a factor of serious human and eco-toxicological relevance.

TFA is a caustic substance which still forms highly caustic mixtures with water even when diluted. To a certain extent, TFA contributes to the acidification of waters and has a phytotoxic effect, though only at higher concentrations than currently observed [Harnisch *et al* 2003]. TFA is very stable and can accumulate in the environment. An estimate of TFA concentrations for Japan assuming the large-scale use of HFC-1234yf as a new refrigerant comes to the conclusion that in closed aquatic systems the gap between the calculated concentration in surface waters and the effective threshold (NOAEL) for aquatic eco-toxicity is not wide enough [Kajihara 2010].

“Whereas the geochemistry of fluoride has been quite well understood for some time now, considerable uncertainties continue to exist regarding the occurrence and the sources and sinks of trifluoroacetic acid” [Tromp *et al* 1995: from Harnisch *et al* 2003; Frank *et al* 1996: from *et al* 2003]. Only a small proportion of the concentrations of trifluoroacetic acid found in waters is attributable to degradation of HFCs. The origin of the main quantity is unknown and is still the subject of research.

1.3.2 Decomposition of stratospheric ozone

None of the fluorinated gases considered here contain chlorine or bromine or iodine in the molecule. They are therefore not in a position to degrade ozone catalytically. Their ozone destruction potential is therefore very small (see [Harnisch *et al* 2003]).

There is occasional scientific discussion of the possibility that the CF₃ group might also be capable of degrading ozone to a small extent. No concrete findings are available to date. However, compared with the ozone depletion potential of the ODS already in the atmosphere this would be of very minor importance.

1.3.3 Contribution to photochemical oxidant formation

The degradability of HFCs means that ozone is formed in the troposphere through the formation of peroxides and oxidation from NO to NO₂. In keeping with their long residence time in the atmosphere compared with NMVOC (non-methane volatile organic compounds), this process takes place very slowly. For this reason it does not contribute to the peak values that occur during summer heat periods (summer smog), but only to the global background. This contribution is very small, however. It is largely in line with the ratio of several hundred million tonnes of anthropogenic and biogenic NMVOCs to several hundred thousand tonnes of HFCs per year.

PFCs and SF₆ are not degraded in the troposphere and do not contribute to ozone formation.

1.3.4 Contribution to global climate change

Most of the fluorinated compounds show relatively strong absorption in an infrared (IR) range of the spectrum where other components of the atmosphere do not display any IR absorption (“atmospheric window” [WMO 1995]). Increasing the concentration of these substances in the atmosphere therefore results in an almost unchecked increase in absorption. In conjunction with an atmospheric life that is moderately long (e.g. 1.4 years for HFC-152a) to extremely long (e.g. 50,000 years for CF₄), this means that most of the fluorinated compounds have a strong greenhouse effect. Here SF₆ takes first place among the greenhouse gases.

The greenhouse effect is usually characterised by the global warming potential (GWP), which considers the effectiveness of the relevant gases compared with the reference substance CO₂ (GWP = 1) over a period which is usually 20, 100 or 500 years. In the interests of comparability, the international community of states agreed in 1997 on a standard of 100 years (GWP₁₀₀) in the context of the Framework Convention on Climate Change and the Kyoto Protocol. The global warming potential of the most important fluorinated gases varies from 140 to 7,000 for HFCs and from 6,000 to 9,000 for PFCs. SF₆ has a GWP₁₀₀ of 23,900. This means that nearly all fluorinated greenhouse gases must be classified as substances with a high GWP (see Section 1.4).

Another measure of climate impact, which does not have a time horizon, is radiative forcing. This indicates how strongly the radiation balance would be affected if the atmospheric concentration of the substance were increased by one part-per-billion (ppb). The global warming potential and radiative forcing figures for all greenhouse gases covered by the Kyoto Protocol and commonly used mixtures of substances are shown in Table 1.2 together with their atmospheric lifetimes. Table 1.3 shows these figures for other compounds containing fluorine that are potential candidates for inclusion in a follow-up convention.

Fluorinated greenhouse gases contribute to global climate change, not only directly, but also indirectly through the energy consumption involved in their use. For example, the specific energy consumption for the production of fluorinated greenhouse gases is considerably greater than for alternative refrigerants [Harnisch *et al* 2003].

Table 1.2: Overview of global warming potential, radiative forcing and atmospheric lifetime for the greenhouse gases covered by the Kyoto Protocol and selected mixtures of substances [IPCC 2007a]

Compound/ Code	Formula	Atmospheric lifetime in years	Radiative forcing in W/m ²	Global Warming Potential (GWP)			
				20 yrs	100 yrs	500 yrs	100 yrs ²
Carbon dioxide	CO ₂	variable	0.000014	1	1	1	1
Methane	CH ₄	12	0.00037	72	25	7.6	21
Nitrous oxide	N ₂ O	114	0.00303	289	298	153	310
HFC-23	CHF ₃	270	0.19	12,000	14,800	12,200	11,700
HFC-32	CH ₂ F ₂	4.9	0.11	2,330	675	205	650
HFC-41	CH ₃ F	2.4	0.02	323	92	28	150
HFC-43-10mcc	C ₅ H ₂ F ₁₀	15.9	0.40	4,140	1,640	500	1,300
HFC-125	C ₂ HF ₅	29	0.23	6,350	3,500	1,100	2,800
HFC-134	C ₂ H ₂ F ₄	9.6	0.18	3,400	1,100	335	1,000
HFC-134a	CH ₂ FCF ₃	14	0.16	3,830	1,430	435	1,300
HFC-143	C ₂ H ₃ F ₃	3.5	0.13	1,240	353	107	300
HFC-143a	C ₂ H ₃ F ₃	52	0.13	5,890	4,470	1,590	3,800
HFC-152a	C ₂ H ₄ F ₂	1.4	0.09	437	124	38	140
HFC-227ea	C ₃ HF ₇	34.2	0.26	5,310	3,220	1,040	2,900
HFC-236fa	C ₃ H ₂ F ₆	240	0.28	8,100	9,810	7,660	6,300
HFC-245ca	C ₃ H ₃ F ₅	6.2	0.23	2,340	693	211	560
Sulphur hexafluoride	SF ₆	3,200	0.52	16,300	22,800	32,600	23,900
FC-14	CF ₄	50,000	0.10	5,210	7,390	11,200	6,500
FC-116	C ₂ F ₆	10,000	0.26	8,630	12,200	18,200	9,200
FC-218	C ₃ F ₈	2,600	0.26	6,310	8,830	12,500	7,000
FC-318	c-C ₄ F ₈	3,200	0.32	7,310	10,300	14,700	8,700
FC-3-1-10	C ₄ F ₁₀	2,600	0.33	6,330	8,860	12,500	7,000
FC-4-1-12	C ₅ F ₁₂	4,100	0.41	6,510	9,160	13,300	7,500
FC-5-1-14	C ₆ F ₁₄	3,200	0.49	6,600	9,300	13,300	7,400
HFC-404A	mixture				3,922		3,260
HFC-407C	mixture				1,774		1,526
HFC-410A	mixture				2,088		1,725
HFC-417A	mixture				2,346		1,955
HFC-437A	mixture				1.805		1.567

² GWP figures recognised by the Parties and valid until 2012 for the first commitment period of the Kyoto Protocol [IPCC 1995]

Compound/ Code	Formula	Atmospheric lifetime in years	Radiative forcing in W/m ²	Global Warming Potential (GWP)			
				20 yrs	100 yrs	500 yrs	100 yrs ²
HFC-507	mixture				3.985		3.300

Table 1.3: Overview of global warming potential, radiative forcing and atmospheric lifetime for selected newer substances [IPCC 2007a]

Compound/ Code	Formula	Atmospheric lifetime in years	Radiative forcing in W/m ²	Global Warming Potential (GWP)		
				20 yrs	100 yrs	500 yrs
HFC-152	C ₂ H ₄ F ₂	0.6	0.09	187	53	16
HFC-161	C ₂ H ₅ F	0.3	0.03	43	12	3.7
HFC-236cb	C ₃ H ₂ F ₆	13.6	0.23	3,630	1,340	407
HFC-236ea	C ₃ H ₂ F ₆	10.7	0.30	4,090	1,370	418
HFC-245fa	C ₃ H ₃ F ₅	7.6	0.28	3,380	1,030	314
HFC-365mfc	C ₄ H ₃ F ₅	8.6	0.21	2,520	794	241
Nitrogen trifluoride	NF ₃	740	0.21	12,300	17,200	20,700
Trifluoromethyl- sulphur pentafluoride	SF ₅ CF ₃	800	0.57	13,200	17,700	21,200
FC-216	c-C ₃ F ₆	>1,000	0.42	12,700	>17,340	21,800
FC-9-1-18	C ₁₀ F ₁₈	>1,000	0.56	>5,500	>7,500	>9,500
HFE-143a	CH ₃ OCF ₃	4.3	0.27	2,630	756	230
HFE-227ea	C ₂ HF ₄ OCF ₃	11	0.40	4,540	1,540	468
HFE-236fa	C ₂ H ₂ F ₃ OCF ₃	3.7	0.34	1,710	487	148

The GWP figures shown in the right-hand column of Table 1.2 are those recognised by the Parties to the Framework Convention on Climate Change. No GWP figure has yet been defined for the newer substances listed in Table 1.3. Different GWP figures may be quoted in other publications because of the models used there. More recent data are the result of improved spectroscopic data and changes in the figures for atmospheric lifetime.

Conclusions

Of all the properties of fluorinated compounds, the contribution to global climate change is by far the most important from an environmental point of view. Even if their share of the additional greenhouse effect to date is small, the problem is very important in view of the great growth potential in the context of CFC/HCFC substitution and the growing need for refrigeration and air-conditioning, especially in developing and emerging countries. It must also be borne in mind that an emission reduction of 100% is frequently possible through measures relating to fluorinated gases – e.g. by substitution. In the case of classic greenhouse gases this is not usually possible. For example, the emission reductions possible for the greenhouse gas CO₂ by taking individual measures are of similar order to the potential emission reductions for the fluorinated gases.

Since both direct and indirect effects play a role, emission reduction measures should always take account of the total contribution to the greenhouse effect, which is characterised by the **Total Equivalent Warming Impact (TEWI)** figure (see Chapter 3.3). In such considerations it is also important to take account of the risks that arise from the persistence of the fluorinated gases. In cases of doubt, and assuming there are no other ecological or safety disadvantages, preference should be given to halogen-free substances or processes.

1.4 *Overview of possible substitute substances*

In virtually all fields of application, fluorinated greenhouse gases compete with other substances. It is not possible to give a full overview here of all the substances and/or substance groups that can technically be used. The most important are given here by way of example: carbon dioxide, hydrocarbons, ammonia, dimethyl ether and nitrogen. All the substances mentioned are relevant to refrigeration and air-conditioning systems, and some to the foam and aerosol industries and as solvents and fire extinguishing agents. Apart from the other substances of relevance in specialised areas (e.g. fluorinated ether, nitrogen), air and “vacuum” are also important “substitutes”. For a few years now, producers of fluorinated greenhouse gases have also been announcing a new generation of these substances, known as HFOs. The most prominent candidate is HFC-1234yf (HFO 1234yf), which is being discussed as a refrigerant for mobile refrigeration systems (see Section 3.3.7). What all substitutes mentioned so far have in common is their low GWP₁₀₀. They have a GWP₁₀₀ of less than 20. This classification is based on a system proposed by the UBA which uses existing limits:

Low GWP ₁₀₀ :	GWP ₁₀₀ < 20
Medium GWP ₁₀₀ :	20 ≤ GWP ₁₀₀ ≤ 150
High GWP ₁₀₀ :	GWP ₁₀₀ > 150

Using substitutes usually involves making changes in the process. Sometimes new equipment and processes are developed for the use of substitutes. These new developments frequently involve technological advances that permit energy savings or improved performance.

One example is the CO₂ air-conditioning system for mobile applications: It cools more efficiently and in winter it can be used as a heat pump that produces heat even when the motor is cold, thereby saving energy and improving safety.

As long ago as 1989 the Federal Environment Agency took a close look at the substitutes issue in connection with the debate about phasing out the use of ozone-depleting substances. Some of the substances under discussion at the time are no longer of any importance today. But the majority of substances are still relevant today, some of them also as potential substitutes for fluorinated greenhouse gases.

The overview in this chapter is largely based on the UBA's findings dating from 1989 [UBA 1989]. There has been no change in the basic assessment of these substances by the UBA. The material is supplemented by new information. A more detailed assessment of the ecological and technical properties of possible substitutes and HFCs can be found in the study "Risks and Benefits of Fluorinated Greenhouse Gases in Processes and Products under Special Consideration of the Properties Intrinsic to the Substance", which was commissioned by the Federal Environment Agency [Harnisch *et al* 2003].

All substitutes considered for the various fields of application have either a very low GWP₁₀₀ or none at all. In most cases they have other properties that have to be taken into account in connection with their use. These include in particular their combustibility, their toxicity or – in the case of CO₂ as refrigerant – the high pressures occurring during their use. In view of the significance of the properties "combustibility" and "toxicity", Table 1.3 shows the explosion limits and maximum workplace concentrations of potential halogen-free substitutes. A number of HFCs are included in the table for comparison.

Table 1.3: Explosion and German maximum workplace concentrations (MAK) of selected halogen-free substances and some HFCs [DFG 2009; Harnisch *et al* 2003; UBA 1989]

Compound/ Code	Formula	Lower explosion limit in %	Upper explosion limit in %	MAK (max. workplace conc.) [DFG 2009]	
				in ml/m ³	in mg/m ³
Carbon dioxide	CO ₂	-	-	5,000	9,100
Propane	C ₃ H ₈	2.1	9.5	1,000	1,800
Butane	C ₄ H ₁₀	1.5	27	1,000	2,400
c-pentane	C ₅ H ₁₀	1.4	9.4	1,000	3,000
n-pentane	C ₅ H ₁₂	1.3	8.0	1,000	3,000
Ammonia	NH ₃	16	28	20	14
Nitrogen	N ₂	-	-		
Dimethyl ether	(CH ₃) ₂ O	2.7	32	1,000	1,900
HFC-152a	C ₂ H ₄ F ₂	3.8	21.5	1,000*	1,910*
HFC-134a	CH ₂ FCF ₃	-	-	1,000	4,200

*: Internal workplace concentration guide figure, DuPont® [DuPont 2002]

1.4.1 Carbon dioxide (CO₂)

Carbon dioxide is formed in particular in the complete combustion of fossil fuels. It is used as a compressed gas in spray cans, in foam manufacturing, as a fire extinguishing agent and as a refrigerant. As a refrigerant it has the code R 744. Because it occurs in nature it counts as a natural refrigerant.

Its concentration in air is about 0.037%. This CO₂ originates from a wide variety of deposits and processes. These include volcanoes, combustion of fossil fuels, forest fires, flue gas from chemical production, and gas and oil refining etc. [eurammon 2002].

Carbon dioxide is an important greenhouse gas; a large proportion of the man-made greenhouse effect can be attributed to rising CO₂ emissions from combustion of fossil fuels.

CO₂ used as a refrigerant or expanding gas does not require special production. Technical CO₂ obtained from natural sources or from process waste gases is used. This can be used without having any impact on the climate, since it would have entered the atmosphere in any case. Thus any emissions do not place an additional burden on the climate.

CO₂ is a non-combustible, non-toxic, odourless, non-caustic and chemically stable (quasi inert) gas which is not dangerous to water. The gas liquefied under pressure is heavier than air. Skin contact with liquid or solid CO₂ or cold pipes can cause “cold burns” [Carbo 2002]. Carbon dioxide may displace air, so high concentrations can cause a danger of suffocation. Concentrations of 10 to 20% upwards in breathing air are life-threatening [Hommel 1987:

from UBA 1989]. Carbon dioxide has a MAK (maximum workplace concentration) of 5,000 ppm (or 0.5%) [DFG 2009].

1.4.2 Hydrocarbons

Propane / Butane

A mixture of propane, iso-butane and butane is one of the most important substitute propellant gases in spray cans. As individual substances, these hydrocarbons are also used as refrigerants, for example in household refrigerators and commercial refrigerated cabinets and small refrigeration systems. In these applications they are known by the codes R 600a (iso-butane) and R 290 (propane). Because they occur in nature, hydrocarbons are also among the natural refrigerants. The GWP₁₀₀ of both substances is less than five. Thanks to special purification, these hydrocarbons are almost odourless. Both the individual substances and their mixtures are highly flammable (see Table 1.3). As gases, the mixtures are not toxic, but in large quantities they have a narcotic effect [UBA 1989]. A maximum workplace concentration (MAK) figure for Germany of 1,000 ppm has been defined for propane and butane [DFG 2009].

Pentane

Pentane is available as an alternative blowing agent for the manufacturing of foams. The GWP₁₀₀ of pentane is less than five. Like propane/butane it is a highly flammable hydrocarbon. Its vapours are highly flammable, and it forms explosive mixtures with air (see Table 1.3). This property creates a need for increased safety measures when using this gas. There are health risks if the vapours are breathed in high concentrations. It has a narcotic effect and may cause irregular heartbeat. Contact with the liquid causes irritation of eyes and skin [Hommel 1987: from UBA 1989]. Pentane has an occupational exposure (MAK) figure of 1,000 ppm [DFG 2009].

1.4.3 Ammonia (NH₃)

Ammonia is involved in the natural nitrogen cycle. In nature it is formed primarily during the degradation of organic materials containing nitrogen, e.g. in the decomposition of proteins. For example, metabolic processes in humans give rise to about 17 mg ammonia per day which is emitted by the body.

For more than 100 years, ammonia has been used for numerous commercial and industrial refrigeration applications. Special features of this substance are its very good thermodynamic properties and its low price [Hoechst 1988: from UBA 1989]. As a refrigerant it has the code R 717. Ammonia has no global warming potential, and as a natural substance it also belongs to the category of natural refrigerants.

The colourless gas has a pungent smell and a highly irritant effect; its odour threshold is as low as 5 ppm. Escaped liquid partially evaporates to form cold mist (see Table 1.3). Ammonia is flammable, toxic if inhaled, and causes caustic burns. Although ammonia involves a risk of ignition, this is only the case under particular boundary conditions in limited fields. Ammonia itself is not readily combustible; without any heat input, the flame goes out immediately [Hommel 1987: from UBA 1989].

When used as a refrigerant, ammonia only escapes into the environment if not used properly, and as a rule only part of the system contents – usually a small part – is released. Ammonia dissolves readily in water. It is highly toxic to aquatic organisms and is therefore classified as dangerous to water. In view of the risk of groundwater contamination, it should be prevented from entering the soil.

The irritant effect of ammonia can range up to serious caustic burns (concentrations in excess of 700 ppm) to eyes, airways and lungs and also the skin. Inhalation of highly concentrated gas (upwards of 3.5 g/m^3) may result in sudden death. Contact with the liquid causes severe frostbite. In the agricultural sector, elevated ammonia concentrations result in damage to plants [UBA 1989]. The German maximum workplace concentration (*MAK*) for ammonia is 20 ppm [DFG 2009].

1.4.4 Dimethyl ether (DME)

After propane/butane, DME is the most important alternative propellant gas in spray cans. It is occasionally used as a refrigerant in refrigeration systems. After special purification it is almost odourless. As a liquid propellant gas it has special solvent properties. Because of its oxygen content it has a lower energy content than propane or butane. Unlike propane and butane, DME is soluble in water [DuPont 1989c: from UBA 1989] and slightly dangerous to water. According to existing information [Lucht 1985: from UBA 1989], DME is virtually non-toxic on acute inhalation in the kind of concentrations that are used in spray cans; in high concentrations, DME has a narcotic effect. DME is a highly flammable gas. The 2003 MAK list shows a figure of 1,000 ppm for dimethyl ether [DFG 2009].

1.4.5 Nitrogen (N_2)

Nitrogen is a natural component of the atmosphere (about 80% in the lower layers of the atmosphere) and is obtained by liquefying air followed by distillation or pressure swing absorption. Nitrogen is used as a compressed gas in spray cans, as a fire extinguishing agent, and as an inflation gas for car tyres. Its use does not cause environmental damage. Nitrogen is a non-combustible gas. Rapid transition to the gas phase can result in displacement of air (especially in rooms), which means there is a danger of suffocation in special cases [UBA 1989].

1.4.6 Hydrofluoro alkenes

Chemically speaking, hydrofluoro alkenes belong to the hydrofluorocarbons (HFCs). In view of their low global warming potential, they are often referred to by manufacturers as “low-GWP refrigerants” or “fourth-generation refrigerants”. To distinguish them from the HFCs covered by the Kyoto Protocol, manufacturers also use the code HFO. A combustible substance in this group, HFC-1234yf, is currently being investigated primarily for use in car air-conditioning systems (see Chapter 3.3.7). It has yet to be launched on the market.

The pros and cons of using these new substances need to be considered carefully. The low global warming potential of hydrofluoro alkenes comes at the expense of greater instability and reactivity of the substances. Important considerations for operators of refrigeration and air-conditioning systems include very good refrigeration performance, system safety and

refrigerant stability, system life and, last but not least, refrigerant costs. There is a considerable need for research and development here.

Release of hydrofluoro alkenes as a result of leakages leads to additional input of persistent degradation products into the environment (see Chapter 1.3.1). Hydrofluoro alkenes are complicated to produce, and production outside Europe involves shipment over long distances. To date there has been no large-scale production of HFC-1234yf.

Solutions using natural refrigerants already exist for the proposed fields of application of hydrofluoro alkenes.

1.4.7 Summary

Halogen-free organic compounds such as propane, butane, pentane, dimethyl ether etc. received a more favourable toxicological rating than chlorinated hydrocarbons in [UBA 1989]. This also stated:

“Propane, butane, pentane and DME have a very high MAK figure of 1,000 ppm. Provided health and safety regulations are observed, there is no reason to expect health risks to employees. Since all these substances are combustible, they are usually present contained in enclosed or encapsulated explosion-proofed systems only. [...]

From a toxicological point of view there can be no doubt that carbon dioxide and nitrogen [...], as natural components of the atmosphere, should be given priority in their potential fields of application. Given proper handling, ammonia is also an acceptable substitute substance for refrigeration purposes.

Any assessment of a substitute substance with a view to use in a particular process must cover the following criteria, which are not necessarily listed in order of importance:

- ozone depletion potential*
- global warming potential of substance*
- global warming potential of process (energy consumption)*
- toxicity*
- ecological suitability*
- occupational safety”*

The Federal Environment Agency also weighted the importance of substitutes. In view of their low relevance at the time, fluorinated gases were disregarded. Other substances included in the weighting no longer have any relevance in connection with this report. The substances of relevance for this report were weighted as follows:

1. carbon dioxide, nitrogen,
2. propane, butane, dimethyl ether, pentane.

To date there has been no change in the assessment criteria or in the fundamental statements. It is not possible to pass an overall judgement on the substitutes compared with fluorinated gases. The wide range of influencing factors (indirect greenhouse gas emissions, health and safety etc.) make it necessary to assess each case in the context of the application in question.

This means that because of their high global warming potential and their persistence, fluorinated gases should be dispensed with where the use of halogen-free substances and/or processes is possible from a technical and safety point of view and does not result in environmentally harmful situations.

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2 Emission trends in Germany

Total emissions of fluorinated greenhouse gases in Germany have more than doubled since 1995. However, emissions of HFCs, PFCs and SF₆ have developed very differently: HFC emissions in Germany have risen sharply since 1995¹. By contrast, the increase in emissions of PFCs has been halted. Annual PFC emissions since the mid 1990s actually display a steady downward trend. Emissions of SF₆ reached a minimum of 4.2 million tonnes CO₂ equivalent in 2002, but have been increasing again since then.

The high climate impact of PFCs and SF₆ in particular has prompted various producers and users to take steps to reduce emissions. Awareness of the harmful effects of these gases on the climate has also been heightened by the critical discussion in the EU and a number of Member States.

Although absolute emissions (in tonnes (t)) of all fluorinated greenhouse gases more than doubled between 1995 and 2007 (1995: 3250 t; 2007: 7300 t), emissions in terms of CO₂ equivalent rose by only 1.8 million tonnes CO₂ equivalent (1995: 15.4 million t CO₂ equivalent; 2007: 17.2 million t CO₂ eq.) because of the very much greater GWP of PFCs and SF₆ compared with HFCs.

As already described in the section on *areas of application and use* in Chapter 1.2, the way the fluorinated greenhouse gases are used is crucial to the amount and timing of the emissions. Whereas emissions and input quantity are identical in the case of open applications, large amounts remain in storage in closed applications (stocks). It is from these annually increasing stocks that the substances are partially or wholly emitted during the entire use phase and during disposal. A distinction is therefore made between actual and potential emissions when reporting on fluorinated greenhouse gases. Unless explicitly stated otherwise, the figures given here are always actual emissions. These are made up of emissions from production, stock/use, process and/or disposal. By contrast, the potential emissions, in other words the maximum emissions possible in a year for closed applications correspond roughly to the average stocks for a year. For simplicity's sake, actual and potential emissions for a year can usually be considered equal in the case of open applications. One special case is emissions from foams: Since fluorinated greenhouse gases have only been in use for a few years, only a small stock has built up. Since the emissions attributed to the production process are in some cases high (they form part of actual emissions), actual emissions may be higher than potential emissions (stock). Other examples of special cases are found in the

¹ In 1990 there was no deliberate production / use of HFCs. The emissions attributed to 1990 are solely the result of the HCFC-22 production process, in which HFC-23 is formed as a by-product.

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semiconductor industry (see Chapter 8) and the aluminium industry (where emissions occur during the manufacturing process).

For applications where stocks are building up and/or have built up, the following Tables 2.1 to 2.6 for the year 2007 include, in addition to actual emissions, a final column showing the potential emissions as well (average annual stock).

HFC

In the case of HFCs in particular, the Federal Environment Agency expects emissions to continue rising if no further measures are taken. The reason for this is as follows: HFCs are used primarily as substitutes for the ozone-depleting CFCs and HCFCs which have been phased out internationally since the early 1990s. Despite extensive successes, it will be a few years before the final discontinuation of ozone-depleting substances in Germany and the EU takes place. For example, the sale of virgin HCFC refrigerant R 22 is prohibited with effect from 1 January 2010; existing systems may only be topped up with non-virgin R 22. Since many systems have been converted to HFC refrigerants and only some have been replaced by HFC-free systems, it may be assumed that emissions of HFCs from refrigeration systems will show a sharp increase in the next few years, because the R 22 stocks in refrigeration systems in the EU are put at 130,000 tonnes [Stahl 2009]. Although CFCs and HCFCs were replaced by halogen-free alternatives in nearly all areas of application, the HFC emissions resulting from their use rose by a factor of about 3 between 1995 and 2007 (see Table 2.1); this is more than a fivefold increase in terms of CO₂ equivalents (see Table 2.2).

In the case of HFCs in particular, it is also clear that the increasing use of these substances is resulting in a gradual build-up of large stocks, especially in refrigeration and air-conditioning systems, and in the long term in thermal insulation material as well. This is especially evident from the example of car air-conditioning systems: The additional annual quantity of HFC-134a simply for filling new car air-conditioning systems for the German market went up from 1,450 t in 1995 to 3,900 t in 2007, as a result of the larger proportion of cars being fitted with air-conditioning systems. In 2007 the cumulative stocks of HFCs in car air-conditioning systems in Germany were as high as 22,400 t. This quantity corresponds to 29 million t CO₂ equivalent (see Table 2.1 and 2.2).

Table 2.1: Trend in HFC emissions in Germany from 1995 to 2007 in tonnes [BReg 2009, Schwarz 2009]

Emission source	HFC emissions in t (rounded)						
	1995	2000	2002	2004	2006	2007	2007*
Stationary refrigeration / air-conditioning	70	850	1,100	1,600	2,000	2,100	21,500
of which: commercial refrigeration only	55	600	800	1,100	1,350	1,300	10,400
Mobile refrigeration / air-conditioning	170	1,200	1,600	2,100	2,700	2,900	25,300
of which: only cars	130	1,000	1,400	1,800	2,300	2,500	22,400
one component foam (OCF)	1,800	1,500	800	600	400	500	-
PUR foam products	0	90	100	250	170	190	2,800
XPS foams	0	0	2,000	1,500	1,000	900	1,800
Metered dose inhalers	0	80	200	190	205	210	-
Miscellaneous	660	380	300	360	225	200	-
Total	2,700	4,100	6,100	6,600	6,700	7,000	51,400

*: Potential emissions (average annual stock)

Table 2.2: Trend in HFC emissions in Germany from 1995 to 2007 in million CO₂ equivalent [BReg 2009, Schwarz 2009]

Emission source	HFC emissions in million t CO ₂ equivalent (rounded)						
	1995	2000	2002	2004	2006	2007	2007*
Stationary refrigeration / air-conditioning	0.2	2.0	2.7	3.8	4.9	5.1	51
of which: commercial refrigeration only	0.1	1.5	2.0	2.7	3.4	3.5	28
Mobile refrigeration / air-conditioning	0.2	1.6	2.2	2.9	3.6	3.9	34
of which: only cars	0.2	1.3	1.8	2.4	3.0	3.2	29
one component foam (OCF)	1.5	1.1	0.5	0.6	0.4	0.6	-
PUR foam products	0	0.1	0.1	0.25	0.2	0.2	3.1
XPS foams	0	0	0.9	0.7	0.6	0.6	
Metered dose inhalers	0	0.2	0.3	0.3	0.3	0.3	-
Miscellaneous	4.6	1.5	2.1	0.9	0.6	0.5	-
Total	6.5	6.5	8.8	9.4	10.6	11.2	

*: Potential emissions (average annual stock)

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PFC

Emissions of PFCs are only partly due to their deliberate use. Since 1990 the biggest single source of PFC emissions has, despite substantial reductions, been primary aluminium production with nearly 40%. As can be seen in Table 2.3 and Table 2.4, total PFC emissions have fallen by about 80% since 1990, both in tonnes and in CO₂ equivalents. This is due to the extensive modernisation measures taken in aluminium production in particular, which have resulted in a drastic reduction in specific PFC emissions per tonne of aluminium produced [BReg 2009].

Table 2.3: Trend in PFC emissions in Germany from 1990 to 2007 in tonnes [BReg 2009, Schwarz 2009]

Emission source	PFC emissions in t (rounded)							
	1990	1995	2000	2002	2004	2006	2007	2007*
Aluminium production	350	230	53	64	66	28	29	-
Semiconductor production	15	23	43	33	33	31	24	-
Printed circuit board production	3	2	2	2	2	2	2	-
Refrigeration	0	1	11	13	15	18	17	73
Total	368	256	109	112	116	79	74	73

*: Potential emissions (average annual stock)

Table 2.4: Trend in PFC emissions in Germany from 1990 to 2007 in million CO₂ equivalent [BReg 2009, Schwarz 2009]

Emission source	PFC emissions in million t CO ₂ equivalent (rounded)							
	1990	1995	2000	2002	2004	2006	2007	2007*
Aluminium production	2.3	1.6	0.36	0.43	0.45	0.19	0.19	-
Semiconductor production	0.12	0.18	0.33	0.3	0.25	0.24	0.18	-
Printed circuit board production	0.02	0.01	0.01	0.01	0.01	0.01	0.01	-
Refrigeration	0	0.01	0.08	0.10	0.11	0.13	0.125	0.6
Total	2.5	1.8	0.8	0.85	0.8	0.6	0.5	0.6

*: Potential emissions (average annual stock)

SF₆

SF₆ is used in a large number of applications, in some cases on a very small scale. The development of SF₆ emissions is shown in Table 2.5 and Table 2.6. At present the biggest sources of SF₆ in Germany are emissions from aluminium foundries and the disposal of sound-insulating windows. As a result of a drastic decline in the use of SF₆ in sound-insulating windows and car tyres, the sharp rise in emissions since 1990 was first brought to a halt and subsequently reversed. All in all, SF₆ emissions fell by 40% between 1995 and 2002. However, SF₆ emissions have been rising again since 2002 and, primarily because of the “open” disposal of old window panes some 25 years after manufacture, they will probably continue rising until 2020. Also SF₆ has been in use on a fairly large scale since 2007, to clean the reaction chambers in the production process for thin film silicon modules. Consequently there was a sharp rise in SF₆ emissions in the solar technology sector in 2007 [BReg 2009].

Table 2.5: Trend in SF₆ emissions in Germany from 1990 to 2007 in tonnes [BReg 2009, Schwarz 2009]

Emission source	SF ₆ emissions in t (rounded)							
	1990	1995	2000	2002	2004	2006	2007	2007*
Cast aluminium / trace gas	1	1	14.5	35.5	46	85.5	84	-
Sound-insulating windows	69	108	52	46	54	61	67	1.950
Solar technology / optical fibres	0	0	0	0.4	1.5	4.7	20.3	-
Electrical switchgear	23	27.3	16.9	15.7	16.3	14.4	15.8	1770
Magnesium foundries	7.4	7.7	13.4	16.1	24.9	24.1	15.2	-
T&D components	no data	16.7	26.6	23.3	16.0	12.4	9.9	no data
Particle accelerators	5.2	4.5	5.0	4.9	4.9	4.9	4.9	74
Car tyres	65	110	50	9	4	2.5	2	6
Semiconductor production	3.7	2	2.4	2.4	3.4	1.3	1.2	-
Miscellaneous	11	26	32	24	21	20	13	no data
Total	200	300	210	180	190	230	230	-

*: Potential emissions (average annual stock)

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Table 2.6: Trend in SF₆ emissions in Germany from 1990 to 2007 in million CO₂ equivalents [BReg 2009, Schwarz 2009]

Emission source	SF ₆ emissions in million t CO ₂ equivalents (rounded)							
	1990	1995	2000	2002	2004	2006	2007	2007*
Cast aluminium / trace gas	0.02	0.02	0.35	0.85	1.10	2.04	2.00	-
Sound-insulating windows	1.65	2.58	1.24	1.10	1.29	1.46	1.60	47
Solar technology / optical fibres	0	0	0	0.01	0.04	0.11	0.49	-
Electrical switchgear	0.55	0.65	0.40	0.38	0.39	0.34	0.38	42
Magnesium foundries	0.18	0.18	0.32	0.38	0.60	0.58	0.36	-
T&D components	no data	0.4	0.64	0.56	0.38	0.30	0.24	no data
Particle accelerators	0.12	0.11	0.12	0.12	0.12	0.12	0.12	1.8
Car tyres	1.55	2.63	1.20	0.22	0.96	0.06	0.05	0.14
Semiconductor production	0.09	0.05	0.06	0.06	0.08	0.03	0.03	-
Miscellaneous	0.26	0.62	0.76	0.57	0.50	0.48	0.31	no data
Total	4.8	7.2	5.0	4.3	4.5	5.5	5.5	-

*: Potential emissions (average annual stock)

Projections commissioned by the Federal Environment Agency on emissions of **HFCs, PFCs and SF₆** for Germany for the period up to 2050 show that measures already adopted and in force to reduce F-gas emissions will have a considerable influence on future emission trends. Given complete implementation of *Regulation (EC) No 842/2006*, *Directive 2006/40/EC* and the national *Chemicals Climate Protection Ordinance (Chemikalien-Klimaschutzverordnung)* including compliance with the maximum leakage rates specified therein (“with-measures scenario”, variant a), emissions of fluorinated greenhouse gases can be expected to fall to 7.9 million tonnes CO₂ equivalent by 2030. From 2030 onwards, emissions are likely to rise again to 9 million tonnes CO₂ equivalent in 2050 in spite of the measures adopted [Schwarz, Gschrey 2010].

On the basis of the assumptions of a “with-measures scenario, variant a”², **HFC** emissions will fall by about 45% to 6.2 million tonnes CO₂ equivalent between 2007 and 2030. After 2030, this scenario shows emissions rising again to 7.4 million tonnes CO₂ equivalent by 2050. For comparison: latest estimates indicate that without the measures taken since 1998, consumption-induced HFC emissions would rise to nearly 17 million tonnes CO₂ equivalent by 2050. On the other hand, further emissions could be prevented by adopting additional measures. A “with-further-measures scenario” includes those measures which are technically

² The Federal Environment Agency’s “with-measures scenario”, variant a, takes account of the implementation of all legislation passed up to 2009 (*Regulation (EC) No 842/2006*, *Directive 2006/40/EC* and the national *Chemicals Climate Protection Ordinance*).

possible today, but have not yet been implemented politically. These include, for example, substituting HFCs in all types of vehicles with refrigerants with a GWP of less than 150, using only natural refrigerants in stationary refrigeration and air-condition systems, and dispensing with the use of HFC in the manufacture of PUR and XPS foam products. Compared with the “with-measures scenario”, these additional measures would make it possible to save as much as 5.7 million tonnes CO₂ equivalent in 2030, and about 7.2 million tonnes CO₂ equivalent in 2050 [Schwarz, Gschrey 2010].

The “with-measures scenario, variant a” for SF₆ shows SF₆ emissions falling to 4.2 million tonnes CO₂ equivalent by 2030, and as low as 0.8 million tonnes CO₂ equivalent by 2050. The reasons for this sharp drop in emissions include the following: since 2008 the use of SF₆ has been prohibited in large magnesium die-casting production facilities (annual quantity of SF₆ used greater than 850 kg). Also, emissions from sound-insulating windows will cease after about 2035, since windows filled with F-gases may not be placed on the market in the EU with effect from 2008. The predicted decline in SF₆ emissions in the field of solar technology is due to the fact that production facilities constructed in Germany from 2008 onwards use NF₃ for chamber cleaning, a gas with a high GWP which is not yet subject to reporting requirements [Schwarz, Gschrey 2010].

Without the legal provisions outlined above, F-gas emissions in Germany could be expected to show a further rise in the next few decades to a total of nearly 20 million tonnes CO₂ equivalent by 2050 (“business-as-usual scenario”). The share of total emissions due to fluorinated greenhouse gases would, as described in the global forecasts (see Chapter 1), rise sharply in Germany as well.

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Part B Application areas and processes: Use, emissions and alternatives

3 HFCs and PFCs as refrigerants in refrigeration and air-conditioning systems

3.1 *Overview of possible types of refrigeration*

At this point we can only give a very general overview. For further information, see the relevant specialist literature. For example, a detailed overview can be found in Cube *et al* 1997 or Jungnickel *et al* 1990.

A basic distinction can be made between refrigeration systems with mechanical power and those with thermal power.

3.1.1 *Refrigeration systems with mechanical power*

Refrigeration systems with mechanical power are vapour compression systems (compressor systems). Such systems are used throughout almost the entire spectrum of applications of refrigeration and air-conditioning technology. Their detailed design, especially the compressor type, depends in particular on the performance required. The systems are filled with a refrigerant which passes through the various components of the system (compressor, condenser, expansion valve, evaporator), changing its physical state in the process: First of all, the refrigerant is compressed from evaporation pressure to condenser pressure by the compressor, with input of work (W). Then the refrigerant is liquefied in the condenser and gives off the heat flow Q . This is followed by expansion of the refrigerant from condenser pressure to evaporation pressure, and the evaporation of the refrigerant, taking in the heat flow. Figure 3.1 gives a schematic diagram of the refrigerant cycle.

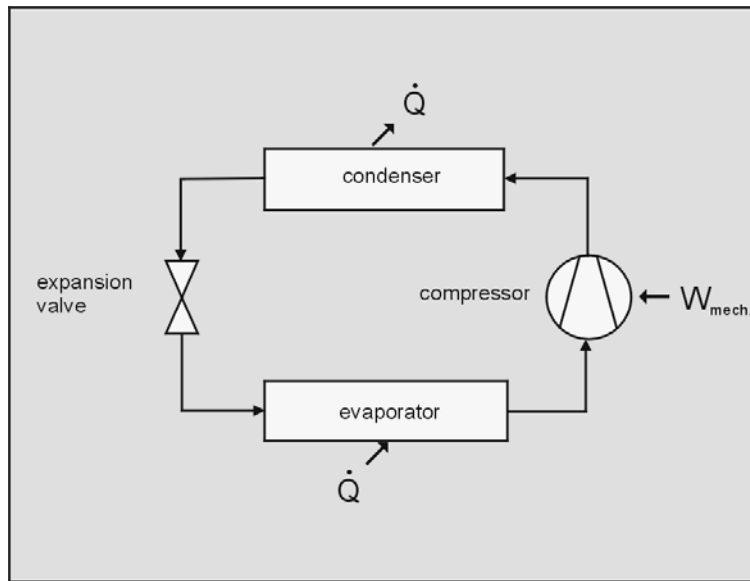


Fig. 3.1: Schematic diagram of refrigerant cycle of a vapour compression refrigeration system. After: [Grage, Pareidt 2000].

In simplified terms, the evaluation criterion for the cycle process is the ratio of effort (work/energy input) to benefits (refrigeration capacity): the coefficient of performance (COP).

Refrigeration systems by compressor type: reciprocating, screw, scroll or turbo compressors. They may be designed as open, semi-hermetic or hermetic compressors [Grage, Pareidt 2000]. Whereas the case of a hermetic compressor is welded, semi-hermetic compressors have removable assembly flaps. These permit repairs to the compressor. Both types have neither a shaft nor a shaft seal passing to the outside. In an open compressor, by contrast, the driven shaft passes through the case (DIN EN 378 [DIN 2008]). Only hermetic compressors are described as “permanently closed”, because of their welded case. Unlike semi-hermetic and open compressors, their use gives rise to very small refrigerant losses. However, other components/joints (refrigerant pipes, offtake points etc.) usually play a more important role in the refrigerant losses of an entire system – especially in large direct evaporation systems (see Harnisch *et al* 2008).

In reciprocating compressors, compression and displacement is by means of reciprocating pistons running in enclosed cylinders. Valves connect these alternately with the suction and pressure pipes of the compressor. Here again, a distinction can be made between hermetic (fully welded case, for low refrigerating capacity) and semi-hermetic motor compressors (for medium capacity), and also open compressors (high capacity). Reciprocating compressors are used for a wide range of applications. They are also suitable for part-load operation.

Screw compressors operate with rotary movements only. Their characteristic features are a minimum of moving parts, robustness, compactness, great reliability (short service intervals) and long life. The screw compressor draws the gas for compression into the working chamber, which is then closed and reduced in size to compress the gas (displacement principle).

Scroll compressors have a very simple design. The type of compression (also displacement principle) means that the noise level created by the compressor is very low. Their fields of application are mainly in air-conditioning. They can achieve very high coefficients of performance [Grage, Pareidt 2000].

Turbo compressors (centrifugal compressors) are not displacement machines, but fluid flow machines. Turbo refrigerating units (liquid chilling packages, cold-water units with turbo compressors) are built as compact systems for a wide performance range and used mainly in air-conditioning (of buildings) and for process units with cold-water or brine circulation [FKW 1998a]. They are often used in cases where high refrigeration performance is needed with frequent part-load operation, because compared with screw compressors their energy efficiency is greater under part-load conditions [Axima 2003b]. Other advantages of turbo compressors over reciprocating compressors (in high performance ranges) are their smaller size and simpler structure. These aspects mean they take up less space and are less prone to faults (simpler servicing). At high discharge rates their efficiency is no less than reciprocating compressor systems [FKW 1998a].

Turbo compressors, like centrifugal pumps, work on the dynamic principle. In other words they generate the static pressure by converting kinetic energy into static pressure energy. Their power transmission element is impellers rotating at high speed. Depending on the impeller design, a distinction is made between radial compressors and axial compressors. Turbo compressors with a radial impeller are suitable for medium gas flow rates. They supply a uniform, oil-free flow of pressurised gas. If several impellers in succession are mounted on a drive shaft, it is possible to achieve medium and very high pressures. Turbo compressors with axial impellers deliver very high flow volumes of up to 1,000,000 m³/h. They are used in natural gas liquefaction plants in the chemical industry [Grage, Pareidt 2000].

3.1.2 *Refrigeration systems with thermal power*

Refrigeration systems with thermal power are supplied with a “heating energy flow” as their driving force. One advantage is that this heating energy flow can be taken from thermal energy that is otherwise not very usable (waste heat, waste steam, hot water, solar energy). Energy assessment of refrigeration systems with thermal power is by means of the heat ratio (as the “efficiency” of refrigeration systems with thermal power). The equipment required, especially in the case of absorption refrigeration systems, is more complicated than for refrigeration systems with mechanical power. But absorption refrigeration systems have virtually no moving parts. Wear is therefore low, and service life high despite low maintenance requirements.

A distinction is made between absorption, adsorption and steam jet refrigeration systems.

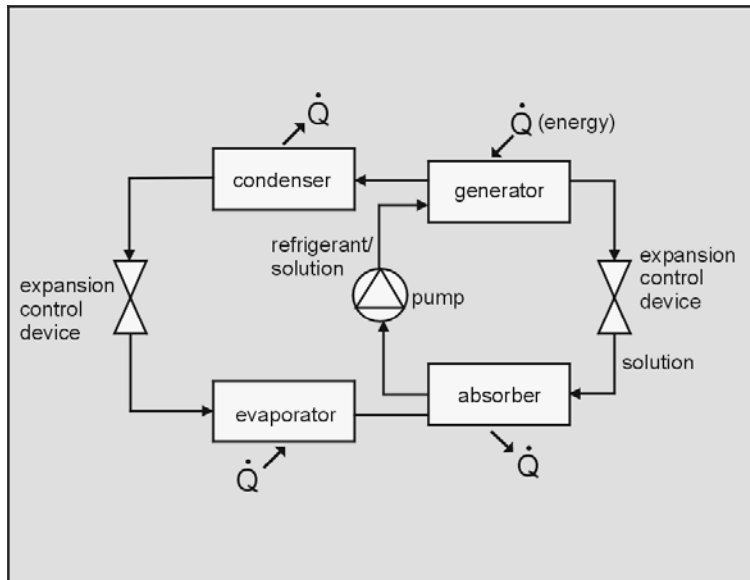


Fig. 3.2: Schematic diagram of refrigerant cycle in an absorption refrigeration system.
After: [Grage, Pareidt 2000].

Using an absorption refrigeration system is the best-known and most widespread means of thermal refrigeration. Here liquids / gases are taken up at low temperature and low pressure and delivered at high temperature and high pressure. Absorption systems have a compressor which operates not mechanically, but thermally. The refrigerant cycle outlined in Figure 3.2 is, apart from the compressor, identical to the cycle in a mechanical system – which here comprises an absorber, a pump (for the fluid (solution)), the boiler and the throttle valve.

In the thermal compressor, the evaporated refrigerant first enters the absorber, where it is absorbed by the fluid (solution). The resulting heat of solution has to be removed from the absorber. The fluid (solution) containing the refrigerant passes through a pump which brings it to a higher pressure level. Then heat is input into the boiler, which boils off the refrigerant from the fluid (solution). The boiled-off refrigerant vapour arrives at the condenser, from where it passes through the circuit to the evaporator. The solution from which the refrigerant has been boiled off passes through the throttle valve and back into the absorber.

The operating materials used are water / lithium bromide (air-conditioning, water cooling) or ammonia / water [Grage, Pareidt 2000].

Refrigeration is also possible by means of adsorption refrigeration systems with solid sorbent material. Figure 3.3 shows a schematic diagram of this thermally powered refrigeration system.

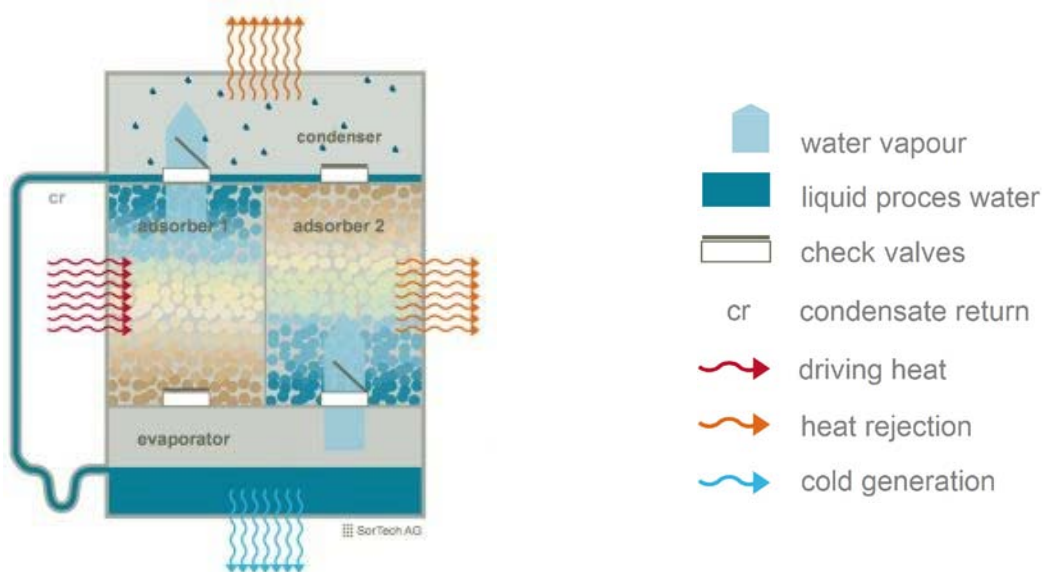


Fig. 3.3: Schematic diagram of refrigerant cycle in an adsorption refrigeration system. After: [SorTech AG 2009].

Such systems use silica gel as sorbent material, for example, and water as refrigerant. The process is discontinuous and takes place in two periods. The refrigerant (steam) is adsorbed on the surface of the sorbent material. This releases heat of combination. As the deposition increases, the heat of combination tends towards zero. The evaporation of the refrigerant removes heat of evaporation from the surroundings. Desorption (second period) and pressure generation for condensation take place at very low drive temperatures, making this technology particularly suitable for the use of solar energy [Jacob 2002]. Quasi continuous refrigeration can be achieved by operating several units staggered in time [Hesse *et al* 1992]. Continuous operation is also possible by using liquid sorption systems. A further advantage of this system is the buffer effect of the adsorbent substance. If refrigeration requirements are continuous, but there is no solar energy available at the time (clouds combined with sultry heat), the “used” solution can be temporarily stored for subsequent regeneration.

Other refrigeration processes are the steam jet refrigeration system and the DEC process (desiccative and evaporative cooling). The structure of a steam jet refrigeration system is identical to that of a compressor system. The mechanical compressor is simply replaced by a steam injection unit. These two processes are not described in any detail here.

3.2 *Use and emissions*

HFCs and to a small extent PFCs are used in refrigeration and air-conditioning systems as substitutes for the now banned CFCs and HCFCs. In some areas the use of fluorinated greenhouse gases has made it possible to phase out the ozone-depleting substances rapidly.

Today the use of fluorinated greenhouse gases in stationary and mobile refrigeration and air-conditioning is the main source (78%) of HFC emissions in Germany, totalling 8.7 million t CO₂ equivalent (5,000 t). In 2007, some 37% of these refrigerant emissions were due to car air-conditioning systems, which emitted about 3.2 million t CO₂ equivalent (2,500 t). 40% of refrigerant emissions were due to commercial refrigeration systems, which emitted nearly 3.5 million t CO₂ equivalent (1,325 t) of HFCs in 2007.

Figure 3.4 shows for 2007 the distribution of HFC emissions among the various applications in the refrigeration and air-conditioning sector in Germany (red columns). A total of nearly 5,000 t HFCs and 17 t PFCs were emitted from refrigeration and air-conditioning systems. With a total of around 2,800 t, mobile air-conditioning systems – and here car air-conditioning systems in particular – accounted for the largest share (55%) of HFC emissions. 27% (about 1,300 t) of the emissions were due to commercial refrigeration systems, 10% (nearly 500 t) to industrial refrigeration systems, 6% (about 280 t) to stationary air-conditioning systems, and 3% (134 t) to transport refrigeration systems. As well as the emissions, Figure 3.4 also shows the quantity of HFCs used to produce refrigeration and air-conditioning products for the German market in 2007 (blue columns). Here too the share due to mobile air-conditioning systems was largest, at around 4,400 t, followed by commercial refrigeration systems (1,000 t), industrial refrigeration systems (500 t), stationary air-conditioning (300 t) and transport systems (46 t). The total quantity used for production (6,300 t) is the annual HFC input in 2007. The annual increase in stocks is this annual HFC input less the HFC quantity from decommissioning of HFC systems and units which are subsequently disposed of or exported. This results in a figure of about 47,000 t for the HFC stocks in refrigeration and air-conditioning systems in Germany in 2007 [BReg 2009].

Apart from the individual substance HFC-134a, stationary refrigeration and air-conditioning systems, like mobile refrigeration systems, mainly use mixtures containing HFC such as R-404A.

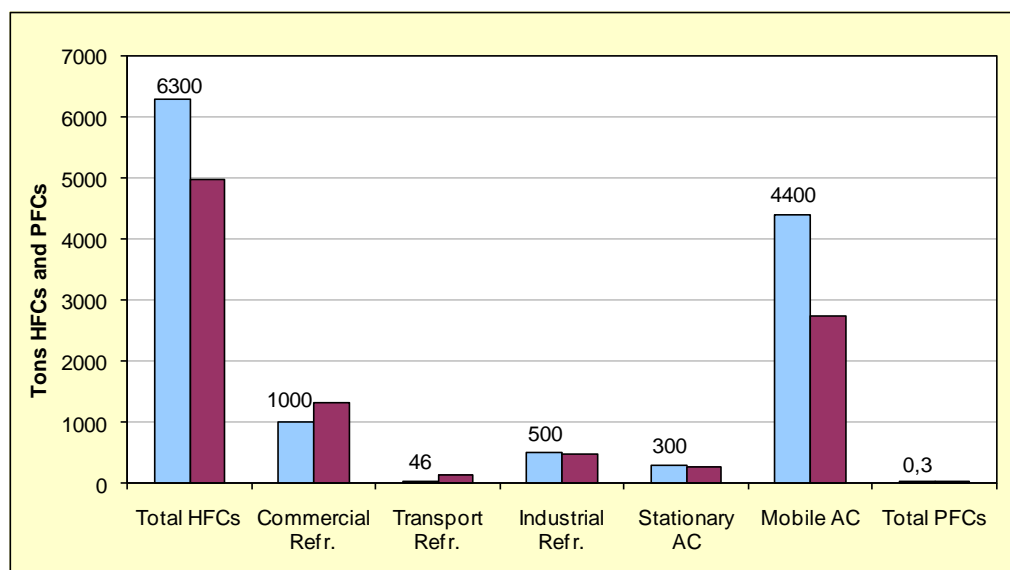


Fig. 3.4: HFC stock increase (blue columns) and HFC emissions (red columns) in refrigeration / air-conditioning systems in Germany in 2007 (figures in tonnes, rounded). Data from: [BReg 2009].

As already described in general terms in Chapter 2, HFC emissions result from the production, application (use) and disposal of refrigeration systems and products. Emissions due to production are of secondary importance. Since 2002, emissions arising from disposal have been included in the emission data for Germany and have been exerting an increasingly strong influence on total emissions by the refrigeration and air-conditioning sector since then. However, not all products containing HFCs are disposed of in Germany; many old units are exported to other countries after use. Examples of the products typically exported include household refrigerators, trailers, tour coaches and cars. According to international greenhouse gas reporting requirements, the emissions arising from disposal as scrap in the receiving countries do not form part of the German emissions balance. This is significant when one considers that the export rate for passenger cars deregistered in Germany was more than 80% in 2006 [Daten zur Umwelt 2008].

Recent emission forecasts show that in future a sharp rise in HFC emissions can be expected in the field of stationary air-conditioning applications in particular. Measures already adopted to reduce F-gas emissions under German and European legislation will ensure, among other things, that emissions from car air-conditioning systems, which will initially continue to increase until 2020, will be making little contribution to total HFC emissions by 2050. But the contribution by air-conditioning systems in other mobile applications (trucks, buses, rail vehicles, ships) will remain at a constant high level [Schwarz, Gschrey 2010]. The emissions from commercial refrigeration systems forecast for 2050 are halved compared with 2007, especially because the “with-measures scenario” assumes compliance with the statutory specific refrigerant losses. Figure 3.5 shows a forecast for the year 2050 (“with-measures

scenario”, variant a, see Chapter 2) indicating the quantities and breakdown of HFC emissions in the refrigeration/air-conditioning sector.

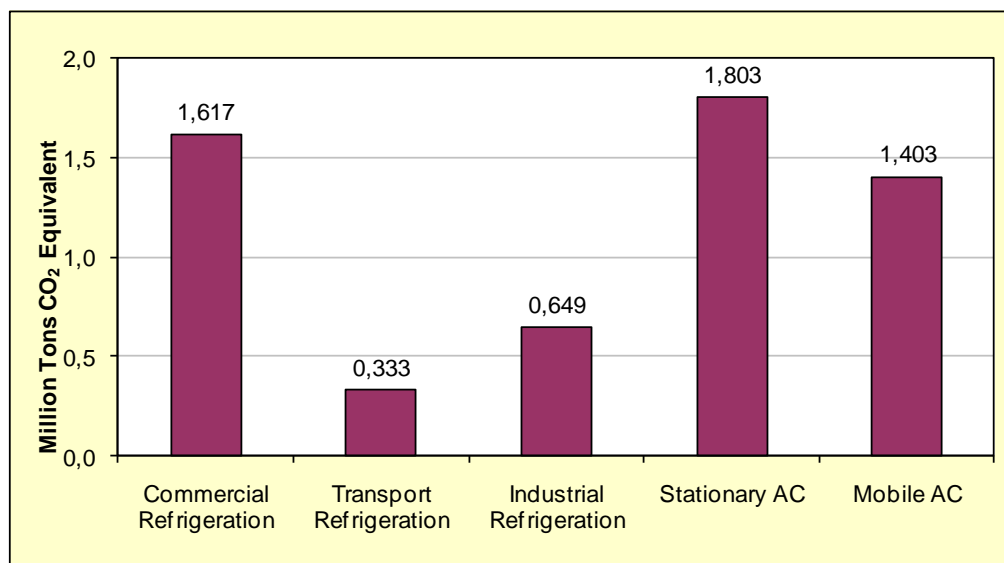


Fig. 3.5: Predicted HFC emissions in the refrigeration/air-conditioning sector in Germany for 2050, in million t CO₂ equivalent (“with-measures scenario”, variant a). Data from: [Schwarz, Gschrey 2010].

Most PFCs have a very much higher global warming potential than HFCs. That is another reason why PFCs are only used in special applications in the refrigeration / air-conditioning sector, particularly for generating very low temperatures. They are also components of refrigerant blends that have been developed as drop-in substitutes for CFCs and HCFCs.

3.3 *Application areas and reduction options*

This chapter gives a detailed description of the various refrigeration and air-conditioning applications. For each individual application, it briefly outlines the technical situation regarding the use of fluorinated gases. It also takes a look at their role as CFC substitutes. This is followed by a description of technical measures to minimise the use of these substances.

Basically, HFCs are currently still in use in nearly all stationary and mobile refrigeration and air-conditioning applications. In the European Union, however, decisions have been taken and laid down in binding legislation to replace them with less climate-relevant substances in a number of applications (see below).

Measures to reduce HFC and – less commonly – PFC emissions can be classified in terms of two fundamentally different approaches:

1. Measures that seek to minimise emissions of these substances during production, operation and disposal of systems or units.
2. Measures aimed at replacing them with halogen-free substances or processes.

The first category can basically be applied to all stationary and mobile refrigeration and air-conditioning applications. The most important individual measures in this category include:

- keep installation/production emissions as low as possible,
- take technical measures to improve leakage prevention over the entire life cycle of the system,
- ensure leakage prevention by means of regular inspection and maintenance measures, and
- keep disposal emissions as low as possible.

Measures falling between the two categories are:

- select fluorinated gases with the lowest possible global warming potential, and
- reduce the quantity of refrigerant used in the system.

Since the individual measures mentioned above are not specific to one or more individual applications, they are not listed afresh as potential emission reduction measures in the following chapters. Only in individual cases is it useful to draw attention to them again and describe them in more specific terms.

Some of the measures mentioned have already been laid down by the Ministry for the Environment, Nature Conservation and Nuclear Safety and the European Commission in the form of binding legislation [KOM 2006; KOM 2006a; ChemKlimschutzV 2008]; others are still being discussed at political level or implemented on a voluntary basis. The measures specific to individual applications are dealt with in the relevant sub-sections. The general legally binding measures laid down for stationary systems in the refrigeration and air-conditioning sector include the limit values in force since 1 August 2008 for specific refrigerant losses in normal operation (emission rate = regular emissions). In 2003 manufacturers expected that it would be possible to reduce emission rates for new systems from 5-10% (in individual cases 20%) to around 2% within five years [Bock 2003; Linde 2003]. The preconditions mentioned were regular leakage tests with suitable equipment, and systems without hidden joints (leakage points) [Bock 2003]. VDMA-Specification 24243-1 [VDMA 2005] dated August 2005 also recommended low levels of permissible refrigerant losses. With the entry into force of the Chemicals Climate Protection Ordinance [ChemKlimaschutzV 2008] on 1 August 2008, the legislature prescribed correspondingly low emission rates for systems containing HFCs as refrigerant and erected at the operation site after 30 June 2008:

- | | |
|---|------------|
| • Refrigerant charge less than 10 kilograms | 3 percent; |
| • Refrigerant charge between 10 and 100 kilograms | 2 percent; |
| • Refrigerant charge more than 100 kilograms | 1 percent. |

For self-contained packaged units with a refrigerant charge of at least three kilograms the limit value for specific refrigerant losses in normal operation is 1 percent.

Limit values also apply with effect from 1 July 2011 to systems erected at the operation site before 30 June 2008.

The next few years will show whether these limit values can be achieved in practice.

The following chapters primarily describe measures aimed at replacement with alternative substances or processes. As a rule, these measures can only be used for new systems.

Many applications already use “natural refrigerants” such as hydrocarbons, water, ammonia or CO₂. The list of “natural refrigerants” can be extended to include the operating materials air and helium for cold-gas processes in which the refrigerant always remains in the gaseous state despite very low temperatures.

These natural refrigerants could basically be used for all refrigeration and air-conditioning applications. It must however be remembered that using these refrigerants sometimes involves higher capital outlay and, where hydrocarbons, CO₂ or ammonia are used, greater safety requirements (flammability, high pressures, toxicity). The much-discussed possibility of energy efficiency deficits has only been confirmed in a few exceptional cases.

There are some applications in which ammonia (e.g. industrial systems) or hydrocarbons (e.g. plug-in commercial systems, household refrigerators) are becoming or have already become established. CO₂ has become increasingly important as a refrigerant in recent years and today it is hard to imagine refrigeration and air-conditioning without it.

When assessing whether the use of halogen-free refrigerants in the individual applications is ecologically beneficial, it is not considered necessary to take an eco-balance approach. For such an approach it would be necessary to include not only the impacts of the refrigerants on all relevant environmental compartments, but also the effects on these environmental compartments that result from the provision of energy and the consumption of materials (incl. production). However, the main environmental impacts arising from refrigeration systems result from their energy consumption and their emissions of the refrigerant used. Both basically have impacts on the climate, if one disregards the use of chlorinated, ozone-depleting refrigerants. A concept that has become established for comparing negative climate impacts of products and processes is **Total Equivalent Warming Impact (TEWI)**.

TEWI is a calculated figure for the overall contribution a “system” makes to the greenhouse effect. As set out in DIN EN 378-1, it describes the total indirect emissions by a system as a result of its energy consumption and the direct emissions due to refrigerant losses.

The Federal Environment Agency has not performed calculations of its own for this report. All TEWI figures¹ used for calculations are taken from the literature or are figures determined by experts at the request of the Federal Environment Agency. Where no TEWI figures are available for individual applications, a qualitative statement is made for each field of application to indicate the energy efficiency situation for the system described. If the use of halogen-free refrigerants as replacements for halogenated refrigerants is not accompanied by a drop in energy efficiency, it may be assumed that their use reduces the overall negative

¹ Where available, LCCP (Life Cycle Climate Performance) figures have been included in individual assessments.

impacts on the climate. Where more detailed information is available, a concrete comparison is made, including both direct and indirect contributions.

Where possible, the description of the technical possibilities in refrigerant selection or the choice of refrigeration supply is supplemented by a description of the economic framework conditions. Attention is also drawn to safety issues and/or problems. The conclusions following each sub-chapter assess whether the use of halogen-free substances in the individual applications areas is technically and economically possible and ecologically desirable.

3.3.1 *Household and laboratory appliances (refrigerators and freezers, tumble dryers)*

This section is primarily concerned with small refrigerators and freezers of the kind found in millions of households. It also describes refrigerator and freezer units developed specifically for laboratories, since the refrigerant situation here is different from that of household appliances. It does not consider other laboratory applications which also contain (fluorinated) refrigerants. In addition to refrigerators and freezers there is also another common appliance which contains refrigerant: the tumble dryer with integrated heat pump. These appliances are also described briefly.

Today refrigerators and freezers are found in almost every household in Germany, and also in many offices and other areas. Manufacturers around the world produce more than 100 million appliances a year, and the number of existing appliances is put at 1,500 to 1,800 million [UNEP 2009]. The appliances available on the market vary in size and equipment. As a rule the insulating material used is polyurethane (PUR), and refrigeration is by means of hermetic, permanently enclosed systems (compressor systems).

Also on the market, in addition to the appliances used largely in households, are refrigerators and freezers developed specifically for laboratories. These have to comply with special requirements compared with household appliances. Examples include exact temperature control, rapid cooling to target temperature, explosion protection etc.

Heat-pump tumble dryers have only been on the European market for a few years. Their market share is growing steadily, and the figure for Germany in 2008 was just under 6% [EEDAL 2009]. Compared with conventional tumble dryers, the capital cost of appliances with integrated heat pumps is higher, but they offer energy-saving potential of up to 50%, so the total cost of heat-pump tumble dryers over their entire life cycle is lower [EEDAL 2009a]. The refrigerant in heat-pump tumble dryers, mostly HFC-407C, but also HFC-134a, HFC-410A and HFC-152a, is contained in a hermetically sealed system. Refrigerant charges range from 300 g to 600 g.

Until the early 1990s, CFC-12 was used as a refrigerant in household and laboratory appliances working on the compression principle, and CFC-11 was used as a blowing agent for the manufacture of thermal insulation materials. For a short time manufacturers used HCFC-141b as a blowing agent instead of CFC-11 because of its lower ODP. Since the ban on CFCs, they have used HFCs and halogen-free refrigerants and blowing agents.

Approximately 63% of all household refrigerators and freezers produced worldwide still use HFC-134a, while about 1-2% use HFC-152a and HCFC-22. However, experts estimate that by 2020 some 75% of household appliances will be using hydrocarbons as refrigerant. Every household appliance contains between 50 g and 250 g of refrigerant [UNEP 2009]. Like CFCs, HFC-134a is not combustible. There is therefore no need for explosion-proofing measures during production or in the product. Laboratory appliances usually contain HFC-134a and HFC-404A.

In Germany, household refrigerators and freezers are not important as a source of HFC emissions. Only very few appliances using HFCs are on the market (see further below). They are nevertheless included in this report because of their fundamental importance and because of the use of HFC in other countries. Although existing laboratory appliances mostly contain HFC as refrigerant, their significance as a source of HFC emissions is fairly low because of their relatively small numbers, small refrigerant charges and good disposal facilities.

Reduction options

In Germany, the complete changeover of conventional compressor systems in the household appliances sector to CFC-free refrigerants took place in 1993/94. After using the refrigerant HFC-134a for a short period, all German manufacturers went over to using the hydrocarbon R 600a (iso-butane). Since the mid 1990s (1993/1994), pentane or cyclopentane (c-pentane) have been used as a blowing agent for insulation materials. No appliances containing HFCs are produced in Germany [BSH 2003].

The technical design of the appliances underwent changes, at least in detail, with the introduction of hydrocarbons as the new refrigerant. For example, it was necessary to cater for the flammability of hydrocarbons. Moreover, the stricter requirements for the energy efficiency of refrigeration systems also resulted in product modifications (improved compressors, reduced heat transfer losses, better insulation etc.) [UNEP 2003]. Modern appliances with hydrocarbons as refrigerant and blowing agent satisfy the requirements of energy efficiency classes A+ and A++.

Over a period of more than 15 years, appliances with hydrocarbon refrigerants have demonstrated their safety and their economic and environmental viability. No system-related technical problems are known [UNEP 2006]. Safety concerns nevertheless continue to be discussed from time to time in other European countries; in some countries outside Europe, the use of combustible refrigerants is a problem because of existing national regulations. This also applies to quantities of less than 150 g hydrocarbon per appliance [BSH 2003]. This situation could change, at least in the USA, because in May 2010 the Environmental Protection Agency (US-EPA) proposed under the U.S. Significant New Alternatives Policy (SNAP) that isobutane and propane be listed as acceptable alternatives to CFCs in household and commercial refrigeration appliances (up to 150 g). The hydrocarbon technology was successfully introduced some years ago in other countries, especially China and India.

No publications exist on the costs arising in practice from the changeover to hydrocarbons. Basically, additional costs arise from safety precautions needed for the transport and storage of hydrocarbons, explosion protection measures needed at the production site (especially

capital cost), and necessary modifications to the product design (development work) and the components used. Other significant cost aspects are disposal, energy consumption and the refrigerant. With regard to disposal and refrigerant costs, the use of hydrocarbons results in a reduction; there is no significant change with regard to energy consumption.

Apart from appliances with compressor systems, there are isolated appliances on the market with other technologies, so-called “not-in-kind technologies”. According to UNEP [UNEP 2006], these include absorption systems mostly using ammonia/water (see Chapter 3.1.2), appliances using the Stirling process, thermoacoustic and thermomagnetic appliances, and appliances using the transcritical CO₂ process. Some of these technologies have also become state of the art. In terms of costs and specific energy consumption, however, these “not-in-kind technologies” are still not competitive for mass production by comparison with compressor systems [UNEP 2006]. Nevertheless, absorption appliances in particular are used primarily in the hotel and camping sectors because of their quiet operation. But their numbers are very small compared with appliances using compressor systems [UNEP 2003].

Some appliances, especially those produced in former East Germany, were insulated with expanded polystyrene instead of PUR insulating material. No halogenated substances are used in the production of expanded polystyrene. These appliances are an exception, however. In view of the poorer energy efficiency of the appliances with expanded polystyrene, the manufacturers did not pursue this technology any further.

Until 2008, laboratory appliances were only available with HFC. Since then, various European manufacturers have put appliances with halogen-free hydrocarbons on the market, which means that – according to information from the suppliers – the entire product range is now available with these refrigerants. These appliances are notable for their high energy efficiency and hence lower operating costs, and do not cost any more to buy [Gram 2010; MSL 2010].

To date, no heat-pump tumble dryers with natural refrigerants are available on the market, but tests have been performed with hydrocarbons, CO₂ and water. The use of hydrocarbons, e.g. propane, looks very promising because it permits further energy savings compared with present-day dryers using HFC. One objective of the development work with hydrocarbons is to reduce the refrigerant charge below 150 g [EuP Lot 16; Siemens 2009].

Conclusions

Even before 1993/94, German manufacturers put CFC-free and HFC-free refrigerators and freezers on the market. Today such appliances are manufactured in various European countries, and also worldwide. They have demonstrated their economic and environmental viability. Other European and non-European manufacturers (e.g. manufacturers in the USA) continue to use HFC-134a as refrigerant and in the insulating material. Some of these appliances are also available in Germany.

For a few years now, HFC-free refrigerators and freezers complying with the special requirements for laboratory use have been available on the market. Their energy efficiency is very high, and they do not cost any more to buy.

In the case of tumble dryers with integrated heat pumps, the use of natural refrigerants, especially hydrocarbons, would seem to be possible and to make sense from an economic and environmental point of view. Further research is necessary to develop such appliances.

There is no need to use HFCs either as a refrigerant or as a blowing agent. When buying an appliance, therefore, the choice can and should go in favour of HFC-free products with high energy efficiency.

A large proportion of end-of-life appliances still contain CFCs, and in some cases HFCs. In the course of disposal, these substances must be recovered and destroyed with a minimum of emissions.

3.3.2 *Commercial refrigeration systems*

Commercial refrigeration systems are used to keep products fresh or frozen, especially food. They are installed in the retail food trade (in supermarkets, discount stores, butchers, bakers etc.), in cafés and restaurants, market gardens, catering facilities (hotel, canteen etc.) and other sectors. Many versions can be distinguished depending on the field and purpose of the application.

A basic distinction can be made between centralised and decentralised systems.

In centralised systems, several refrigeration points (appliances) are served by a single refrigeration system. These are usually multi-compressor refrigeration systems (see Chapter 3.3.2.3), in which several compressors connected in parallel are combined to form a refrigeration unit. Whereas the refrigeration points are located in the salesroom, the actual refrigeration system (compressor) is usually installed in a separate room (machine room). “Distributed systems” are an exception. Here one or more compressors are bundled together with a (mostly water-cooled) condenser as sound-insulated units and installed in the immediate vicinity of the cooling points, usually in the salesroom. Typical areas of application for multi-compressor systems include supermarkets and hypermarkets. Centralised systems may also include condensing units which are set up as factory-made units at a central location in smallish supermarkets.

Decentralised systems (appliances) may be executed as

- industrially prefabricated compact units with integrated compressor and condenser (e.g. plug-in chilled cabinets, vending machines, see Chapter 3.3.2.1) or
- individual systems with an external condensing unit (see Chapter 3.3.2.2).

Unlike the compact units mentioned earlier with hermetically sealed condensers, the compressor and condenser in decentralised individual systems are installed separately from the cooling points. These systems require on-site assembly. Their cooling capacity ranges up to about 20 kW. Typical areas of application include butchers (meat counters) [UNEP 2003]. In practice, it is commonly the case that two or more of the technologies mentioned are installed in retail food stores [Harnisch *et al* 2003; UNEP 2006].

The various types of centralised and decentralised systems differ in flexibility, size, refrigerant charge and cooling capacity, and also in their specific energy consumption (by reference to a “unit of refrigerated product”). Thus the specific energy consumption figures for the condensing units of individual systems are usually higher than for multi-compressor systems [UNEP 2006]. Compact units (plug-in appliances) use even more specific energy than individual systems [Harnisch *et al* 2008]. On the other hand, plug-in appliances are particularly flexible and are particularly suitable for small shops (e.g. kiosks), where there is no sense in installing a centralised system. Measurements on American supermarket systems reveal that especially by minimising suction-side losses it is possible to reduce the energy consumption of “distributed systems” by 5-8% compared with HFC direct evaporation systems [Kauffeld 2007]. In view of the numerous influencing factors, other sources do not make any clear statements about energy efficiency [UNEP 2006].

The refrigerants used well into the 1990s were usually CFCs, especially CFC-12, and HCFC-22, and the CFC-containing blend R 502, which today are replaced by HFC-134a (for R 12) and HFC blends (R 404A, R 407C, R 507A) [UNEP 2003].

In 2007 about 1,000 t of HFCs was used in the production of new systems as a refrigerant for commercial refrigeration. Emissions in the same year came to about 1,300 t (3.5 million t CO₂ equivalent) [BReg 2009]. This means that on the basis of CO₂ equivalent, commercial refrigeration systems are the biggest source of HFC emissions from refrigeration and air-conditioning applications. See Figure 3.4, Table 2.1 and Table 2.2.

3.3.2.1 Plug-in appliances

In this report the term “plug-in appliances” means appliances which are delivered to the end consumer as a ready-to-use, (series-produced) industrial product and only need to be connected to a power supply (outlet). All components of the refrigeration unit (compressor, evaporator, expansion device and condenser) and the cooling point are integrated in the appliance.

This means that household appliances and mobile air-conditioning units are also covered by this definition, but these are dealt with separately in Chapter 3.3.1 and Chapter 3.3.5.1.

The special characteristic of “plug-in appliances” is that no on-site assembly is needed and that as a rule the refrigerant is contained in a hermetically sealed system (compressor refrigeration system). The refrigerant charges, and also the applications, may however vary considerably between the different appliances.

Typical examples of “plug-in appliances” are refrigerators, freezers and chilled display cabinets in the food sector, and also commercial refrigerators and soft drink vending machines. Possible locations range from supermarkets to kiosks, from platforms to service stations. The total number of such appliances is growing [UNEP 2003; UNEP 2006].

The quantity of refrigerant used in plug-in appliances ranges from less than 150 g to about 500 g [Danfoss 2003a]. Quantities of up to 1.5 kg are possible [FKW 1998b]. The refrigerants used today are HFCs (HFC-134a, or for lower temperatures R 404A or R 507A); these

replaced CFCs in the mid 1990s [UNEP 2003]. Regarding insulation, the same remarks apply as for household appliances.

Because of their hermetic design, emissions from the individual appliances are low. Annual leakage rates are around 1.5%. Thus regular emissions from plug-in appliances account for about 1% of the stock emissions due to commercial refrigeration as a whole [Schwarz 2005]. Of greater importance – in relation to the individual appliance – are the emissions on disposal, since it is not possible to recover the refrigerant completely. However, the relevance of this application can be seen from the growing numbers in particular. In 2008, according to estimates by the Refrigeration Research Council [Forschungsrat 2009], there were some 385,000 plug-in refrigeration appliances installed in Germany in supermarkets alone.

Reduction options

Manufacturers are increasingly using hydrocarbons (R 600a, R 290 and blends) or CO₂ as halogen-free refrigerants [UNEP 2006].

Today, using hydrocarbons is regarded as state of the art. Thousands of freezers and vending machines using hydrocarbons are installed around the world [UNEP 2006; Harnisch *et al* 2008]. This is due partly to the efforts of a number of component and appliance manufacturers to dispense entirely with the use of HFCs, but also to the users of these appliances [e.g. Coca-Cola 2000; Coca-Cola 2008; McDonald's 2003; Unilever 2010]. These efforts are also fostered by the decisions in some EU countries to phase out HFCs. The use of hydrocarbons in plug-in appliances is still a subject of controversy, however, as these usually have larger refrigerant charges than household refrigerators, for example. Some European manufacturers have appliances with charges of up to 1 kg in their range [UNEP 2010]. In Germany, quantities of up to 150 g as refrigerant are currently regarded as an acceptable limit, and charges of up to 500 g are considered possible from a safety point of view [TÜV Süd 2003a]. Other countries inside and outside Europe regard even this as critical. In the USA, for example, there has so far been a basic objection to even small quantities of flammable refrigerants because of the product liability laws prevailing there and the extremely high damages in the event of loss or injury (however improbable). Nevertheless, under the U.S. Significant New Alternatives Policy Program (SNAP) the Environmental Protection Agency (US-EPA) proposed in May 2010 that isobutane and propane be listed as acceptable alternatives to CFCs in household appliances and plug-in commercial appliances (up to 150 g).

Development work on the use of hydrocarbons in plug-in appliances is currently exploring various avenues: On the one hand attempts are being made to reduce the refrigerant charge needed by optimising systems. Furthermore, efforts are constantly being made to increase the quantities of flammable refrigerants laid down or recommended in standards, wherever this seems possible from a safety point of view. To date such efforts have not met with any success.

The energy consumption of deep-freeze cabinets with hydrocarbons (R 600a and R 290) is 10-15% lower than for comparable units with HFCs [Harnisch *et al* 2008: from Jürgensen 2004]. For bottle coolers with hydrocarbons the figure is as much as 30% lower. The capital

cost is about the same (bottle coolers) or up to 15% higher (deep-freeze cabinets), but operating costs are some 10-30% lower [Harnisch *et al* 2008].

According to UNEP [UNEP 2006], one manufacturer started commercial marketing of CO₂-based freezers (for ice cream) in 2006. Its market share continues to be small [UNEP 2010]. A small number of companies have decided to use CO₂ as refrigerant for vending machines as well and have installed several thousand units. According to tests by the DTI (Danish Technological Institute), these units are better than or equivalent to HFC appliances at ambient temperatures below 32°C [UNEP 2006; UNEP 2010]. Others sources speak of both lower and higher consumption figures [Harnisch *et al* 2008]. At present, bottle coolers and freezers with CO₂ are still considerably more expensive than comparable appliances with HFC or hydrocarbons. In 2003, however, Danfoss [Danfoss 2003b] did not expect series-production CO₂ compressors to have any cost disadvantages compared with HFC compressors.

In addition to using halogen-free refrigerants, some manufacturers are trying out the use of “not-in-kind technologies” for plug-in appliances. These include the Stirling technology, which manufacturers have introduced to the market in transport cool boxes and vending machines (e.g. for cans). The energy efficiency of these appliances is similar to that of HFC appliances [UNEP 2006].

Conclusions

In plug-in appliances with refrigerant charges of less than 150 g, the use of hydrocarbons is already state of the art. In these appliances, hydrocarbons can replace HFCs.

In future, if the permitted quantity of combustible refrigerant can be increased without additional safety risks and if they represent acceptable alternatives in other countries, hydrocarbons can make an even greater contribution to reducing the use and emission of climate-relevant substances.

The development of CO₂ compressors specially for plug-in appliances (units with low refrigeration capacity) is a great step forward. Thus in new installations, HFC can be replaced by either hydrocarbons or CO₂.

Thanks to their good energy efficiency, appliances without HFC can make a contribution to reducing greenhouse gas emissions.

3.3.2.2 Condensing unit systems

Condensing unit systems are installed in butchers (meat counters), restaurants (bars), and also in supermarkets. In these installations the condensing unit is located outside the salesroom. Cooling capacity ranges from several 100 W to about 20 kW [UNEP 2006; FKW 1998b].

The refrigerant is added on site once the unit has been installed. Unlike the “appliances” described above, the refrigerant is not contained in a permanently hermetically sealed circuit; every installation contains connections, some of them detachable. Depending on the cooling capacity, hermetic and semi-hermetic compressors are used (see Chapter 3.1.1).

Today, condensing units mostly use HFCs. It is only in older units that HCFC-22 is still used.

In view of their construction, the annual leakages from these units amounting to 5-10% of the refrigeration charge [Schwarz 2005] are larger than for plug-in units, but smaller than for centralised systems. On the basis of available data, Schwarz [Schwarz 2003b] estimates the share of emissions at less than 20% of emissions by the commercial refrigeration sector, despite the large number of units.

Reduction options

Because of the smaller cooling capacities of around 2 kW needed for this field of application (bakeries, butchers etc.), it is not possible to use ammonia. The compressors necessary for this capacity range are not on the market and, according to manufacturers, will not be available in future either [e.g. Danfoss 2003b]. However, one company has proposed a new system design for the applications discussed here which covers the necessary refrigeration capacities. This is a small, two-stage cascade system using ammonia and CO₂ [UNEP 2010].

Although the use of hydrocarbons is technically possible, at present it is not usually implemented in individual units for safety reasons. Compared with plug-in units, which mostly manage with small quantities of refrigerant, these systems use well over 500 g of refrigerant, e.g. in a butcher's condensing unit [Danfoss 2003a; TÜV Süd 2003a]. According to UNEP, however, condensing units with hydrocarbons are in fact found in countries with strict regulations about fluorinated greenhouse gases UNEP [UNEP 2010].

To date no manufacturer has developed compressors and/or units with CO₂ as refrigerant [UNEP 2010]. However, in view of the development of low-capacity CO₂ compressors for plug-in units, the possibility of using CO₂ for this application in the future cannot be ruled out.

Conclusions

Some halogen-free solutions are available for condensing unit systems as well, but have yet to prove their suitability in practice.

Hydrocarbons can be used in systems with small refrigerant charges. Whether hydrocarbons will in future be used for this application in more countries, undoubtedly depends on decisions taken in connection with other areas. For example, increasing the permitted quantity of flammable refrigerants in units could provide a stimulus.

At present, CO₂ is not yet used in condensing unit systems. But here too one can expect to see dynamic developments which will depend heavily on developments in other fields of application.

In addition to the ongoing development of systems using natural refrigerants, the current objective should continue to be technical optimisation (reducing emissions, refrigerant charges and energy consumption).

3.3.2.3 Centralised systems (supermarket refrigeration)

Centralised systems (see also Chapter 3.3.2) differ in the choice of refrigerant, the type of cold distribution, and the type of condenser cooling. They are designed as direct or indirect (dual-circuit, secondary circuit) systems. In the more widespread direct systems (direct evaporation) the refrigerant is fed direct to the cooling points (= loads, e.g. chilled cabinets). Here the multi-compressor refrigeration system and the cooling points are connected by branched pipework systems in which the refrigerant circulates. In indirect systems the cold is transmitted to the cooling points via a secondary refrigerant of liquid (e.g. propylene glycol), melting (ice slurry) or evaporating type (usually CO₂), while the primary refrigerant is confined to the refrigeration unit. One variant is the “distributed system”, in which one or more compressors are bundled together with a (mostly water-cooled) condenser as sound-insulated units and installed in the immediate vicinity of the cooling points, usually in the salesroom. Such systems are common in the USA in particular [Kauffeld 2007; UNEP 2006]. An overview of 16 different types of centralised systems can be found in Harnisch *et al* [Harnisch *et al* 2008].

Most centralised systems have separate parts for the low-temperature range (LT: product temperature approx. -18°C, evaporation temperature from -35 to -40°C) and the medium temperature range (MT: product temperature approx. 0 to +8°C, evaporation temperature -15 to +1°C). In some cases different refrigerants are used for the two temperature ranges. The refrigeration capacity of centralised systems ranges from 20 kW to > 1 MW [UNEP 2003; UNEP 2006].

Centralised systems are installed in parts with the aid of detachable connections. In indirect systems the actual refrigeration unit may be of very compact design and it is possible to use factory-made units. The refrigerant is added on site after the unit has been installed. Refrigerant charges vary greatly depending on refrigeration capacity and system type. For a normal direct-evaporation compound system in a supermarket, FKW [FKW 1998b] quotes a charge of 300 kg, though it points out that there is a wide range of variation. It should also be noted that supermarkets in Germany tend to be small by comparison with other countries [Harnisch *et al* 2003]². Indirect systems contain considerable smaller refrigerant charges (see section on “Reduction options”).

In 2008 there were nearly 36,000 centralised refrigeration systems installed in German supermarkets with a sales area of more than 400 m² [Forschungsrat 2009]. These systems and most newly installed systems usually take the form of direct-evaporation centralised systems using HFCs only (mainly R 404A and/or R 134a). Indirect systems with HFCs are rare [Harnisch *et al* 2003].

The annual emission rates for these systems are high, at up to 15% of the refrigerant charge in old systems [Schwarz 2005]. New systems have lower emission rates (see below). In the

² UNEP [2006] quotes refrigerant charges of 800-2000 kg for large supermarket systems.

commercial refrigeration field, centralised systems have the greatest relevance with regard to HFC emissions.

Reduction options

Hydrocarbons, CO₂ and ammonia are used as refrigerants in different concepts. Such systems are installed in several European countries and have become state of the art. By 2009, several hundred CO₂ cascade systems (CO₂ in the LT stage, mostly HFC in the MT stage), some 300 CO₂ direct-evaporation systems (MT and LT), approx. 80 ammonia, 20 propene and 4 propane refrigeration systems had been installed in supermarkets throughout Europe by various manufacturers [Harnisch *et al* 2008]. As a result of decisions by two discounters and several supermarket chains to step up their use of natural refrigerants or switch to them entirely, the number of systems in Germany has shown a further increase since then.

Hydrocarbons and ammonia

Hydrocarbons and ammonia are ideal refrigerants from a thermodynamic point of view. Because they are flammable and/or toxic, however, their use in areas frequented by the public is limited: it is necessary to use a secondary circuit (indirect system) for such applications. In this case the primary refrigerant is confined to the primary circuit, which is usually located in a separate room (machine room) or outside the building. The spatial separation of refrigerant and (sales) rooms accessed by the public ensures safety even in the event of a leak (accident) [TÜV Süd 2003a].

Indirect systems have a number of advantages over direct-evaporation systems, which is why large numbers of them are used in certain countries (e.g. Switzerland, Luxembourg and North America). The advantages listed by Kauffeld [Kauffeld 2007] include the following:

- use of factory-made primary refrigeration units with high quality standards and low leakage potential,
- smaller fluid quantities in the refrigeration systems, with much smaller refrigerant-circuit volumes,
- especially easy heat recovery in cases where the condenser heat is dissipated to the ambient air via a separate water-glycol circuit,
- more constant air temperature and humidity in sales cabinets (lower weight loss in unpackaged goods at higher relative humidity),
- fewer defrost cycles and hence lower energy consumption for defrosting,
- longer compressor life and/or less frequent actuation of compressor, since the secondary refrigerant performs a certain storage function, and
- possibility of using plastic pipes and fittings (which are usually less expensive).

Up to 2010, there were very few indirect refrigeration systems in Germany and hence little experience in this field. This could change in future as a result of the decision by the Lidl chain to equip all new Lidl stores with a new refrigeration concept from 2010 onwards. In its new stores, Lidl is using integrated systems with hydrocarbons which meet the stores' entire heating and refrigeration requirements. This not only avoids climate-relevant HFC refrigerant emissions, but also reduces CO₂ emissions due to energy consumption [Lidl 2010].

The necessary safety precautions and their design as dual-circuit systems increase the capital cost of systems using hydrocarbons or ammonia [Axima 2003a; Bock 2003]. Additional heat exchangers and a pump are needed for the secondary circuit. In theory, as well as increasing the capital cost, this also leads to higher power consumption by the system. In practise it transpires that the power consumption of secondary-circuit systems in the normal temperature range tends to be similar to or less than that of direct-evaporation systems, whereas secondary-circuit systems for the low temperature range may have a higher power consumption. Lidl expects a considerable reduction in overall costs for the new stores equipped with indirect systems, since the extra capital cost of the refrigeration system will be more than offset by a significant reduction in operating costs. According to information in the literature and from users, the energy consumption of indirect ammonia and hydrocarbon systems (MT + LT) is about 5-20% higher, but manufacturers claim that it can be reduced to the same level in (more expensive) next-generation systems. The capital cost of indirect systems is about 0-35% higher, but the operating costs (incl. maintenance) are usually lower [e.g. see Harnisch *et al* 2008]. This information relates to standard systems and does not include innovative concepts (e.g. integrated system).

Exact calculations of the energy efficiency of centralised systems are difficult, since the energy consumption is influenced by many factors – including external ones; there is no standardised method of classification/measurement. Determination of the power consumption of individual cabinets is relatively easy and can be carried out on the basis of European standards (e.g. DIN EN ISO 23953-2 [DIN 2006]). To determine energy efficiency, however, it is first necessary to define a reference quantity (e.g. content, inspection opening, chilled shelf area), the choice of which has a considerable influence on the result. In some cases, comparisons of energy consumption figures from largely identical supermarket refrigeration systems show that the range of variation of energy requirements is much larger than the stated differences [ILK 2003a].

Even on the basis of unfavourable consumption figures, dual-circuit systems with halogen-free alternatives come out well when TEWI is considered. Since TEWI – as described in the introduction to Chapter 3.3 – is made up of the indirect (energy consumption) and direct (refrigerant) emissions, the result depends not only on energy consumption, but also on the assumed emission rate and hence on the system's loss rate (incl. manufacturing emissions, regular emissions (= emission rate), accident-induced emissions). For emission rates of 10% (\triangleq 11.65% loss rate), 5% (\triangleq 6.15% loss rate), and even – with one exception – 2% (\triangleq 2.65% loss rate), Harnisch *et al* [Harnisch *et al* 2008] found higher (= less favourable) values of TEWI for HFC direct-evaporation systems than for indirect systems.

Recent calculations of specific abatement costs (cost per tonne of CO₂ equivalent avoided) have been published by Harnisch *et al* [Harnisch *et al* 2008]. The authors have based their calculations on the additional cost compared with an R 404A reference system, and have included the capital cost and the energy and full maintenance costs. Since these costs vary

depending on the system standard and the legal requirements for maintenance and leakage tests, the authors have defined and calculated three scenarios. On balance, they arrive in one case at negative specific abatement costs³, and otherwise at specific abatement costs of up to several hundred €/t CO₂ equivalent. For details of the underlying assumptions and the results, the reader is referred to the source study.

Carbon dioxide (CO₂)

For some years now, systems have existed with CO₂ as an (evaporating) secondary refrigerant (on the lines of an indirect system, see above), CO₂ cascade systems, and transcritical CO₂ direct expansion systems. In the case of CO₂ cascade systems and transcritical CO₂ direct expansion systems, CO₂ is used as a primary, not a secondary, refrigerant. Indirect systems and CO₂ cascade systems that make subcritical use of CO₂ for the low-temperature range require a separate refrigerant for normal cooling. However, a separate refrigerant is also needed for CO₂ direct expansion systems (low-temperature and normal cooling) that are cascaded with another refrigeration system to liquefy the CO₂. Other possible refrigerants include HFCs, ammonia or hydrocarbons.

CO₂ cascade systems for low-temperature applications have long since graduated from the pilot phase and can now be regarded as standard systems. In the chilled cabinet sector (LT, high-pressure side of system) the use of CO₂ is technically more difficult because of the high pressures (up to 120 bar). One requirement for the implementation of such systems was availability of the necessary components for these pressure levels. Although all components were available by the end of 2008, some of them did not exist as (inexpensive) series products. Initially, centralised systems with CO₂ as refrigerant for the normal temperature range, with supercritical operation and high pressures, had been installed by manufacturers as pilot systems only. Manufacturers were planning to start series production as soon as larger numbers of systems were installed from 2008 to 2010 [Brouwers 2007; Tillner-Roth 2008 in: Harnisch *et al* 2008]. This is in line with the decision by ALDI SÜD to equip all new stores with CO₂OLtecTM CO₂ refrigeration systems by Carrier [Presseportal 2009]. Other operators have also installed transcritical CO₂ systems in the meantime.

As long ago as the German Refrigeration and Air Conditioning Conference 2007 (*Deutsche Kälte-Klima-Tagung*) in Hanover, the refrigeration journal KK [KK 2008b] summarised the state of development of CO₂ refrigeration systems as follows: “CO₂ as a refrigerant has demonstrated its suitability in the low-temperature stages of cascade systems and is being used extensively and to advantage. It is gaining ground as a universal refrigerant, and that includes transcritical uses for normal refrigeration. There is good reason to expect that the numerous prototype installations in supermarkets with systems making exclusive use of CO₂ will soon become the standard solution for both temperature levels.”

³ Assumption: high standard of requirements for reference system. Comparative system: small indirect hydrocarbon system (NT only).

Although cascades theoretically have disadvantages from an energy point of view, practical experience has shown that they can compete in energy terms in supermarkets [Linde 2003; Haaf, Heinbokel 2002; Sienel 2007 in: Harnisch *et al* 2008; Harnisch *et al* 2008]. Some publications actually confirm a lower energy consumption than for comparable single-stage HFC systems [Rees 2007 *et al*, in Harnisch *et al* 2008]. For example, the cascade exchanger can be run at very small temperature differences of 2 to 3 Kelvin. Any energy disadvantages on the high-pressure side can be offset by a gain on the low-pressure side. Because of the higher pressure level with CO₂, this gain results from the lower relative pressure losses from the very long pipework systems commonly found in supermarkets. The repeated small pressure losses that occur with HFC-404A are virtually non-existent in the case of CO₂. The heat transfer figures are significantly better. Today CO₂ cascade systems are installed around the world. For example, CO₂-ammonia cascade systems are installed in supermarkets in South Africa. This project, implemented by GTZ Proklima and funded by the German Environment Ministry as part of the Climate Initiative, resulted in energy requirement savings of up to 30% compared with the old R-22 systems [GTZ 2010].

Various manufacturers have performed comparative measurements on the energy consumption of transcritical CO₂ direct-evaporation systems and HFC standard systems. A good overview of the results and of ways and means of improving energy efficiency can be found in Harnisch *et al* [Harnisch *et al* 2008]. On balance, it can be said that the energy consumption of present-day CO₂ direct-evaporation systems is at least equivalent to HFC standard systems, and that the potential for improvement has yet to be fully exploited. Similar inexpensive measures for other refrigerants would meet with less success [KK 2005].

According to recent TEWI calculations by Harnisch *et al* [Harnisch *et al* 2008], transcritical CO₂ direct-evaporation systems have significantly lower annual emissions of greenhouse gases than HFC direct evaporation systems (reference system: R 404A). For the cascade systems in view, the results are more differentiated: whereas cascades with natural refrigerants or R 134a have lower greenhouse gas emissions in the MT stage, greenhouse gas emissions by the R 404A/744 reference system are slightly higher. This is due to the underlying assumption in the calculations that the HFC refrigerant charges are larger. Figure 3.6 shows an excerpt from the information on annual greenhouse gas emissions per metre of cabinet length for hypermarkets. To ensure that the results are comparable, all variants are calculated without heat recovery. Heat recovery is basically possible for all types of systems. This has an influence on the level of greenhouse gas emissions, but not on the ranking order of the design variants in Fig. 3.6. Transcritical CO₂ direct-evaporation systems also have the advantage of making the waste heat available at a higher temperature level, which means it can also be used to heat process water.

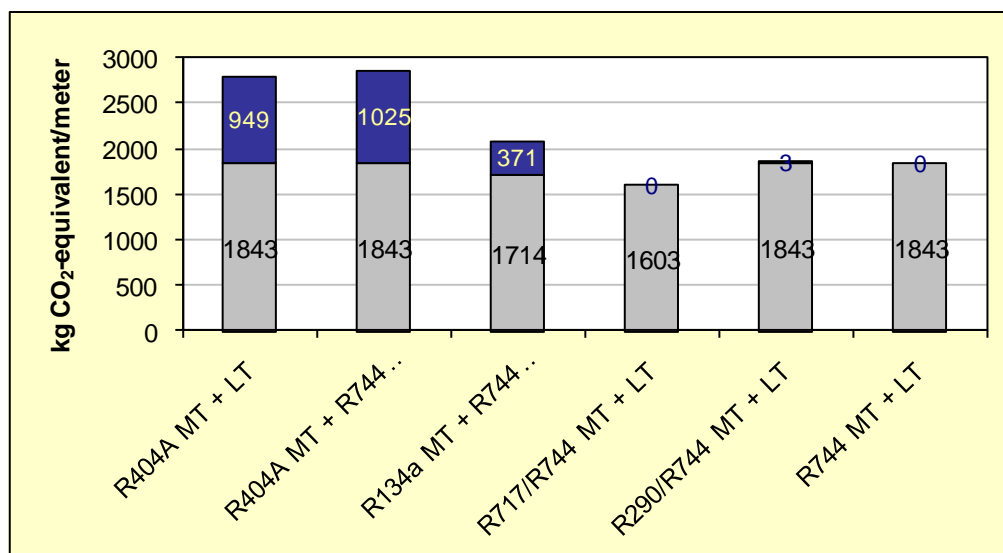


Fig. 3.6: Annual greenhouse gas emissions per metre of cabinet length for hypermarkets, with various design variants (emission rate 10%, loss rate 11.65 %) [after Harnisch *et al* 2008].

Today the capital cost of cascade systems with CO₂ for freezer applications is similar to that of HFC direct-evaporation systems. The costs may however work out higher depending on cascade design. These differences in costs are due on the one hand to higher component costs for the CO₂ system, and on the other to lower costs resulting from the smaller dimensions of the pipework system and compressors. The level of operating and servicing costs (full maintenance costs) for the HFC system depends among other things on the statutory requirements for servicing and leakage testing. Taking the current statutory requirements as a basis, these costs are likely to be considerably higher for HFC systems than for cascade systems with natural refrigerants.

In 2007 the cost of transcritical CO₂ systems was about 30% higher than the cost of direct-evaporation HFC standard systems, because they were one-off models containing non-series components. Experts take the view that in the short to medium term (from the start of series production of these systems) the additional costs can be reduced to 20% [Expertenkreis 2007]. At the same time the experts expect the cost of standard HFC systems to increase by about 15% in connection with compliance with the statutory emission rates. Thus assuming rigorous enforcement of the legal requirements, the cost of the two system types will move closer together.

For CO₂ systems as well, Harnisch *et al* [Harnisch *et al* 2008] have published up-to-date calculations of specific abatement costs (costs per tonne of CO₂ equivalent avoided) (see also section on “Hydrocarbons and ammonia”). The range of results is due to the very broad spectrum of assumptions made: for CO₂ cascade systems the authors arrive at specific abatement costs of -156 to +105 €/per tonne of CO₂ equivalent, for transcritical CO₂ systems the figures are -172 to +178 €/per tonne of CO₂ equivalent. The low and/or negative specific abatement costs must be taken as a basis for future decisions (see Table 3.1), as only these are based on the assumption of rigorous enforcement of the existing requirements for HFC

systems. For details of the underlying assumption and the results, the reader is referred to the source study.

Table 3.1: Specific abatement costs in €/per tonne of CO₂ equivalent for CO₂ centralised systems (cascade and transcritical direct-evaporation systems) compared with an R404A direct-evaporation system with an emission rate of 2% per annum (\triangleq 2.65% loss rate) [after Harnisch *et al* 2008]

Model technology	Additional capital costs [€]	Additional annual costs [€]	Abatement costs [€/tonne CO ₂]
Reference system R404A	-	-	-
R134a MT + R744 LT (hypermarket)	3,958	-1,500	99.-
R717/R744 MT + LT (hypermarket)	5,980	-6,750	-18.-
R290/R744 MT + LT (hypermarket)	62	-3,250	-156.-
Dir. 744 MT (discounter)	432	-1,400	-172.-
Dir. 744 MT (hypermarket)	2,281	-1,950	16.-
Dir. 744 MT (self-service dept. store)	4,932	-4,000	10.-

Reduced HFC refrigerant charges

In some countries, such as Sweden, indirect systems are also used to achieve marked reductions in the total quantity of HFCs used compared with direct-evaporation systems [UNEP 2003; Harnisch *et al* 2003]. These systems frequently permit substantial reductions in refrigerant emissions thanks to the possibility of using factory-made units and the smaller refrigerant charge.

In addition to indirect systems, “distributed systems” (see above) can help to reduce refrigerant charges. The refrigerant charges of distributed systems may be up to 75% smaller than in direct-evaporation systems [UNEP 2006]. Other sources speak of 30-50% reductions in refrigerant charge [Kauffeld 2007].

Another possibility for reducing refrigerant charges in HFC systems is to use microchannel profiles in heat exchangers, which at the same time brings improvements in efficiency [Kauffeld 2007].

Conclusions

Centralised systems are the biggest source of HFC emissions in the commercial refrigeration sector. In 2007 this sector was responsible for 31% of all HFC emissions (38% of emissions by the refrigeration/air-conditioning sector) (see Fig. 3.4 and Table 2.1). Emission reduction measures in this field are therefore particularly important.

In considering measures, a distinction must be made between existing and new systems.

New systems

Of all the measures possible, preference should clearly be given to installing HFC-free systems in the interests of climate protection.

Systems without HFCs are already state of the art, which means that in most cases it is possible to use halogen-free refrigerants. This represents a 100% reduction in HFC refrigerant charges and hence in HFC emissions. In view of the more favourable TEWI of HFC-free systems, this measure yields the largest reductions in climate-relevant emissions. Furthermore, additional optimisation potential can be assumed to exist for a number of systems that have only been on the market for a few years.

In the case of new buildings, HFC-free systems can be included at the planning stage. Where new refrigeration systems are installed in existing buildings, it may be necessary to convert the utility rooms.

In many cases the installation of HFC-free systems still involves higher capital expenditure. However, experts expect to see a narrowing of the costs gap for many of the possible technologies in the near future. Whether the costs are indeed higher is something that in any case has to be investigated in the individual situation, since contradictory examples are to be found in practice. It should also be remembered that owing to the strict statutory requirements for leakage prevention which are in force today, using HFCs makes it necessary to plan for higher capital expenditure and also higher maintenance costs.

If it is not possible to install an HFC-free refrigeration system, the most effective way of reducing regular refrigerant emissions is to reduce the refrigerant charge and improve leak prevention.

The refrigerant charge can be reduced by means of technical measures and by optimising system design (refrigeration capacity). The most effective solution, however, is to install indirect systems. This also confines the refrigerant to a small, easily inspected space.

Existing systems

Reductions in refrigerant emissions in existing systems are usually only possible by means of technical measures to improve leak prevention and by regular leakage checks of the kind now prescribed by law. Depending on the condition of the system, this may involve considerable human and technical resources and may result in a marked increase in operating costs.

In the worst case it may therefore be necessary to replace the system (see “New systems”) in order to reduce existing emissions and running costs.

3.3.3 *Industrial refrigeration (industrial systems, coldstores, food processing etc.)*

Depending on the definition, “industrial refrigeration” may be taken to cover a variety of applications. The present report uses this term to cover the following fields, but does not consider all of them in detail:

- food production / processing,
- chemical and pharmaceutical industries,
- oil, gas and plastics industries,

- coldstores,
- sports and leisure facilities,
- agriculture,
- metal industry and
- large-scale heat pumps.

Until CFCs were developed, CO₂ and especially ammonia were the standard refrigerants for industrial refrigeration. Whereas ammonia maintained its position in many applications, especially larger ones, CO₂ disappeared from the market for a long time. Some years ago, however, CO₂ made a successful comeback on the industrial refrigeration scene and has become increasingly well established until the present day. The use of hydrocarbons is of minor importance.

As well as compressor systems, the industrial sector also used absorption systems. The use of adsorption is also possible. The two technologies, which may represent suitable substitutes for compressor systems depending on the application, are described briefly in Chapter 3.3.1 (fundamentals) and Chapter 3.3.5.2 (application) and are not considered any further here.

CFCs and HCFCs were used in many industrial applications, where they have been and are being replaced partly by PFCs and HFCs, especially R 404A [KK 2009a], and frequently by halogen-free refrigerants.

In 2007 about 500 t of HFCs were used as refrigerants for the production of new systems in industrial refrigeration. Emissions in 2007 came to some 470 t HFCs and 0.8 t PFCs (together 0.9 million t CO₂ equivalent) (see also Figure 3.4). Total industrial sector stocks in 2007 amounted to about 5,000 t [BReg 2009]. Industrial refrigeration accounts for about 8% of HFC emissions in the refrigeration/air-conditioning sector. This means that despite the large number of installations and often large refrigerant charges it is of relatively minor importance. This is due in particular to the already large proportion of halogen-free refrigerants in this sector. However, the quantities of HFCs or PFCs per system, which are usually large, may result in very considerable emissions from individual systems. As a rule, estimates of sectoral HFC emissions are rough or non-existent (see Chapters 3.3.3.1 to 3.3.3.7).

3.3.3.1 Food processing

The term “food industry” is used here to cover all industries that process foods. As well as dairies and breweries, this includes slaughterhouses, large bakeries, coffee roasting operations and chocolate factories. Here the refrigeration capacity installed is mostly larger than in the applications described above, and may range up to several megawatts (MW).

Today the food processing industry largely uses ammonia and CO₂ as refrigerants for new systems. In many cases, however, existing systems still contain R 22. The use of R 22 in new systems has been banned in Germany since 1 January 2000. While CFCs were used until they were banned in the mid 1990s, they were only of minor importance even then [UNEP 2003; UBA 1989; FKW 1998b]. Despite the ban on the sale of virgin R 22 scheduled for 2010, little has been done to convert existing R 22 systems. Surveys conducted in France in 2006

revealed that about half of all refrigeration systems in the food processing sector contain R 22. Experts [KK 2009b] believe that these figures can be applied to Germany as well, and that an estimated 4,000 t of R 22 is present in such systems. Conversions, like some new systems, mostly use HFC mixtures as refrigerant [FKW 1998b; FKW 2001].

Although refrigeration in the food processing sector plays an important role in the field of industrial refrigeration, energy considerations have resulted in most major installations going over to using ammonia, or in recent years CO₂ as well. In 2001, HFC emissions arising from refrigeration in the food processing sector came to nearly 120 t [Schwarz 2003b].

Reduction options

In individual cases natural refrigerants such as CO₂ and ammonia can also be considered for conversion of CFC / HCFC systems [UNEP 2003; Gebhardt 2000; Gebhardt 2002b]. As a rule, however, this causes problems because of incompatible materials or high pressures [Witt 2009].

“For new systems, natural refrigerants have always been used for preference in industrial refrigeration for reasons of energy efficiency alone – ammonia is acknowledged to be the most economical refrigerant of all” [Witt 2009]. Thus ammonia is the usual refrigerant in the food industry as well. It is particularly suitable for industrial purposes above –35°C. In the industrial context it is also possible to use direct refrigeration systems with ammonia. In the refrigeration capacity range required here, ammonia systems are energy-efficient and inexpensive. Thanks to their energy efficiency, ammonia systems also contribute to reducing total greenhouse gas emissions.

Apart from pure ammonia, a mixture of ammonia and dimethyl ether (DME) has also been used in refrigeration systems in the food industry for some years now. This blend, known as R 723, has a very low global warming potential of 8. One example of its application in food processing is found at Südbayerische Fleischwaren GmbH. Two R 723 multi-compressor systems with a capacity of 150 kW each were installed at their factory in Obertraubling, near Regensburg [KK 2009a].

For some years now, CO₂ has again been used increasingly in new systems, either as refrigerant in the lower stage of cascade systems, or as secondary refrigerant. According to manufacturers, the use of CO₂ in transcritical refrigeration systems is currently not being pursued for industrial refrigeration, partly for energy efficiency reasons [Danfoss 2007]. However, UNEP [UNEP 2009] lists CO₂ as a refrigerant for transcritical industrial applications as well, so it remains to be seen how industrial systems with CO₂ as refrigerant develop.

In some cases CO₂ is used to reduce the quantity of ammonia present in these systems, which are often very large, thereby simplifying authorisation procedures [Axima 2003a; Danfoss 2010]. This trend has been observed for nearly ten years in the case of very large systems in particular, not only at European level, but also worldwide.

It is not the size of the system, but the temperature that is crucial for the use of CO₂ as a refrigerant. CO₂ is very suitable for temperatures below –35°C. In this temperature range, CO₂

systems have economic and other advantages. For example because the high volumetric refrigeration capacity of CO₂ makes it possible to build compact systems (system components). Its good availability combined with a low price also reduces costs. CO₂ refrigeration systems also have a positive impact on product quality: Where CO₂ cascade systems are used for shock freezing fish, the greater efficiency of the system makes it possible to freeze the fish faster and at lower temperatures. This improves its quality. This process also consumes less energy than when using other refrigerants [Danfoss 2007]. Possible refrigerants for the high-pressure side in CO₂ cascade systems - apart from HFCs (e.g. R 410A or R 507) - are especially ammonia and also, for thermodynamic reasons, halogen-free hydrocarbons.

CO₂ is very attractive as a secondary refrigerant in applications with low and medium temperatures (up to 0°C) [Danfoss 2007]. Systems with CO₂ as a secondary refrigerant have been implemented, as have two-stage CO₂/ammonia cascade systems in the deep-freeze range (down to about -50°C), e.g. for frosters (freezers for bakery products and other foods) [eurammon 2002, KK 2006b], freeze-drying [Selmer 2001; Gebhardt 1999] and breweries [KK 2006b].

Another means of providing refrigeration without using HFCs (or using smaller quantities) is to use ice slurry (as secondary refrigerant) in combination with a (halogen-free) primary refrigerant. Ice slurry can be used, for example, in the meat industry, breweries and fruit and vegetable processing. According to one supplier, the higher fluid temperature and the resulting higher evaporation temperature compared with direct evaporation or operating with brine make it possible to reduce operating costs thanks to lower energy consumption [Integral 2003]. However, this does not apply specifically to the use of ice slurry in combination with a halogen-free refrigerant.

The energy efficiency of systems with natural refrigerants is undisputed in industrial refrigeration. For example, practical experience in cost calculations for funding applications repeatedly show that, because of their greater efficiency, systems with natural refrigerants are up to 40% lower than the TEWI figures for conventional systems [KK 2009a].

Information about abatement costs based on CO₂ equivalent dates from 2000 and earlier. This was based on the state of technology at the time. It does not take account of the very economical use of CO₂ as a refrigerant. At 2.7 €/per tonne of CO₂ equivalent for total HFC substitution in new systems [Harnisch, Hendriks 2000] and 20-30 € per tonne of CO₂ equivalent – combined with reduced HFC input and a significant reduction (of up to 3%) in annual HFC leakage rates – in the remaining HFC systems [March 1998], the calculated abatement costs are nevertheless low compared with the estimated costs of a straight reduction in emissions from HFC systems (62 € per tonne CO₂ equivalent [Harnisch, Hendriks 2000]). Particularly because of the continued developments in the field of natural refrigerants over the last ten years, these cost estimates – despite all uncertainties – permit the conclusion that replacement of HFC is economically possible and should be preferred to technical emission reduction measures from an economic point of view as well.

The economic and energy-related assessment of CO₂ systems, and especially CO₂ cascades (LT), has already been the subject of several studies reported in the literature. As a rule, they

are compared with ammonia systems, since HFC systems are not of any great significance in this field of application. On balance, CO₂/ammonia systems are considered to be cost-effective and energy-efficient [e.g. Gebhardt 2002a; Gebhardt 2002b; Roth, König 2002].

In addition to compressor refrigeration systems, to which the above remarks refer, the food industry sometimes uses absorption systems, which basically manage without HFCs. The reader is referred to Chapter 3.1.2.

Conclusions

Whereas a few years ago the standard refrigerants in the food industry were R 22 and ammonia, since the ban on R 22 this has only been true of ammonia and increasingly of CO₂ as a low-temperature refrigerant. Ammonia systems are notable for their high cost-effectiveness and great energy efficiency. CO₂/ammonia systems have also demonstrated their cost-effectiveness and are now state of the art.

HFCs are negligible as refrigerants in the food industry and are not necessary. This is due to their lower cost-effectiveness in this field of application.

When considering cost, the capital expenditure and operating costs must always be included. In individual cases, it may only emerge at this point that HFC-free systems are the better alternative in the long term.

3.3.3.2 Chemical and pharmaceutical industries

In the chemical and pharmaceutical industries there are a wide range of processes which require refrigeration. In most cases ammonia is used, or sometimes halogen-free or halogenated hydrocarbons. CO₂ is of no importance to date.

It is only in exceptional cases that the use of halogen-free refrigerants is not economic. In such cases CFCs such as R 13 or R 503, or brominated refrigerants such as R 13B1, were used until they were banned. As a rule these are very specialised applications with special conditions. One example is chlorine liquefaction plants. Today HFCs or PFCs are mostly used as CFC substitutes in these systems – which were previously filled with CFCs.

When considering whether halogen-free refrigerants are available, it is first of all necessary to distinguish whether existing systems are to be converted or completely replaced. For example, in the case of total replacement (new system) it is often possible to do without PFCs and HFCs. Since these are on the whole specialised applications, this field will not be discussed in depth here.

No information is available about refrigerant emissions in this specific sector of industry. The special problems associated with PFCs are discussed again in Chapter 3.3.8.

Turbo refrigeration systems

The industry sometimes uses process systems with cold-water or brine circulation. In view of the generally high refrigeration capacities, turbo (centrifugal) compressors are employed. In industrial applications, turbo compressors are also used in direct systems. In addition to the

technical information provided in Chapter 3.1.1, the following general points can be made about these turbo compressors:

Turbo refrigeration systems deliver large flow volumes and are thus suitable for refrigerants with low volumetric refrigeration capacities. They need a refrigerant with a high molecular weight, and until the ban on CFCs they were therefore run mainly on these refrigerants, as a rule R 11. Since the ban on CFCs, the refrigerant used in new systems has mostly been HFC-134a [FKW 1998a; Grage, Pareidt 2000]. Occasionally HFC-245fa is used, or HCFC-123 is still in use outside the EU [UNEP 2009].

In new systems, water (R 718) can be used as a refrigerant. First pilot systems have been created with water as refrigerant. Under a joint research project supported by the Federal Ministry of Education and Research, work is currently in progress on the development of a third generation of this R 718 turbo chillers [ILK 2010]. One implemented example of a turbo system with water as refrigerant is the turbo process system at DaimlerChrysler in Düsseldorf. Since turbo compressors are mainly found in high-capacity chillers (water chillers) used for air-conditioning, the possibility of using water as refrigerant is described in more detail in Chapter 3.3.5.2 (air-conditioning of buildings).

As far as is known, halogen-free hydrocarbons are used only in systems in the petrochemical industry, where hazardous and, in particular, explosive substances are handled on a routine basis [UNEP 2006; UNEP 2009].

In view of its low molecular weight, ammonia is not suitable for turbo refrigeration systems. In the construction of new systems, however, multi-stage ammonia systems, which are highly energy-efficient, are theoretically a technically feasible alternative to HFC turbo systems. Such systems are not implemented, however, because of the very high costs involved in multi-stage ammonia systems [Axima 2003b].

Conclusions

The use of halogen-free refrigerants is state of the art in the chemical and pharmaceutical industry, apart from certain specialised applications.

If there are technical reasons – e.g. in existing systems – why it is not possible to do without fluorinated refrigerants, the use of PFCs should be avoided because of their very high global warming potential. Moreover, in view of the large refrigerant charges that are usual in these systems, particularly effective measures must be taken to minimise emissions of the fluorinated refrigerants.

As yet it is not possible to do without HFCs in turbo chillers. Water as refrigerant is very promising and trendsetting, but for cost reasons it cannot be used everywhere at the present time. When drawing up plans, however, one should always consider whether the use of turbo systems is absolutely essential, or whether it might make economic and ecological (energy-efficient) sense to use other technologies without HFCs.

3.3.3.3. Coldstores

Most foods, and also pharmaceutical products or blood plasma, for example, need to be kept cool during processing, transport and storage. Within this chain, coldstores (refrigerated and freezer warehouses) are used to store frozen products (product temperature $\leq -18^{\circ}\text{C}$) or chilled products (product temperature $> 0^{\circ}\text{C}$), nearly 90% of which are foods. Initial storage of raw materials and/or finished products takes place at the manufacturer/processor. From there the finished products are sent – sometimes via intermediate stores (carriers' warehouses) to central warehouses, where they remain until shipped to the point of sale, e.g. supermarkets. Supermarkets themselves have their own storage facilities. As well as large central (regional) warehouses, the trade in Germany operates smaller trade warehouses which are usually closer to the point of sale [Meurer, Schwarz 2002].

The average size of coldstores ranges from 45,000 to 75,000 m³ [VDKL 2009a]. According to a survey by the German Association of Coldstores and Refrigeration Logistics Companies [VDKL 2009], there were more than 750 coldstores in Germany in 2009 with a total storage space of 21.6 million m³ or 4.5 million Euro-pallets. The survey covered not only commercial coldstores run by VDKL member companies, but also in-plant coldstores. The total capacity of the 239 commercial VDKL coldstores (approx. 80% of all coldstore operators are VDKL members) amounted to about 12.6 million m³ [VDKL 2009].

Until the 1990s, a small number of high-capacity systems (> 1 MW for deep-freeze applications) using the refrigerant R 22 (HCFC) were built for coldstores. In Germany, however, R 22 has been banned in new systems since 1 January 2000. HFCs have not acquired any importance as substitute refrigerants in this capacity range. For cost reasons alone they are not normally used [DKV 2003].

Today HFC systems are effectively found only in smaller trade/transshipment warehouses not exceeding 50,000 m³ in size [VDKL 2010]. These systems have a refrigeration capacity of less than 500 kW. In this capacity range the capital costs of HFC systems are often lower, because there are many series-production components available. This also improves the spare parts availability situation [VDKL 2003]. Other considerations include a simpler and speedier construction permit procedure and a broader and usually cheaper range of services [VDKL 2010]. One disadvantage is that there is rarely any energy optimisation and adaptation to specific conditions [DKV 2003]. No comparative information is available on overall costs (capital and operating costs).

A statistical survey by the VDKL [VDKL 2009a] of 246 coldstores with 554 refrigeration systems revealed that over 80% of the refrigeration volume is cooled using ammonia, about 16% with HFCs (mainly R 404A, R 134a), nearly 2% with R 22, and less than 1% with CO₂. In 2001 these applications emitted about 7 t of HFCs [Schwarz 2003b]. With a share of about 4% of industrial refrigeration, coldstores are not of any great importance with regard to HFC emissions. This is due in particular to the already large proportion of halogen-free refrigerants in this sector.

Reduction options

In large coldstores, which are mostly operated using refrigeration systems with a capacity of over 1 MW, ammonia is already the standard refrigerant used. Since these are premises without any public traffic, the great majority are ammonia systems with direct evaporation. In isolated cases, ammonia/CO₂ cascades have been in use for some years now as an alternative with favourable energy properties [UNEP 2003; Meurer, Schwarz 2002]. The quantity of ammonia installed in these systems is considerably smaller, with the result that the immission control authorisation procedure required for ammonia quantities of 3 t or more is not necessary [UNEP 2003; Axima 2003a]. Nevertheless, these systems have not succeeded in becoming established, partly because of the higher capital costs compared with ammonia systems [VDKL 2010]. The VDMA specification (draft) 24247-3 [VDMA 2009] basically recommends ammonia or an ammonia-CO₂ cascade for new coldstores. Coldstores with straight CO₂ systems are the exception in Germany and very rarely found [VDKL 2010]. UNEP [UNEP 2009] reports that in 2008 a chilling and freezer warehouse with a transcritical CO₂ refrigeration system was built in Denmark. As well as the necessary refrigeration capacity (1,500 kW), this system also supplies heat (1,200 kW) which is fed into a local heating system. In this form CO₂ is judged to be very cost-effective.

From a technical point of view there are no major problems involved in building ammonia systems or ammonia/CO₂ cascades for capacities of 500 kW or less. In view of the necessary safety precautions and the permits required, there is a need for long-term planning here. This planning input, the higher capital cost (up to 30% more) and a rather thin service network have so far prevented the use of this environmentally sound technology [VDKL 2010; DKV 2003; Peilnsteiner, Truszkiewicz 2002].

In the case of larger ammonia systems, the higher capital costs are offset by lower operating costs: compared with a normal HFC system, ammonia systems have any energy advantage of

some 15-20% [VDKL 2003; DKV 2003]. Since the refrigeration system is responsible for more than 70% of the energy consumption of a coldstore [VDKL 2009a], this permits a substantial reduction in energy costs. Refrigerant costs are also lower for ammonia systems [VDKL 2003; DKV 2003]. In practice, however, energy efficiency - or even operating costs in general - are quite often rated less important than capital cost [Peilnsteiner, Truskiewicz 2002].

For fairly small systems (ammonia or ammonia/CO₂) the operating cost savings in the first few years are usually smaller than the extra capital cost compared with an HFC system. In the final analysis the depreciation period is the crucial factor for this cost comparison.

The high energy efficiency of ammonia systems is due to the favourable thermodynamic properties of ammonia. The TEWI figures for ammonia systems are therefore favourable. Because of the greater heat of evaporation, it is also possible to select smaller-bore pipes than for HFCs [Peilnsteiner, Truskiewicz 2002], which in turn has a positive effect on capital cost.

Unlike HFC systems, an ammonia system is built for the individual site. Components are produced in relatively small numbers. Material-related and production-related aspects also result in higher costs. For example, the fact that ammonia is not compatible with copper means that ammonia systems cannot use the copper pipes that are otherwise normal in refrigeration systems. For the reasons mentioned, such systems are on the whole more expensive to buy [DKV 2003], but of high quality.

In other countries, e.g. the Netherlands, one also finds smaller coldstores (with refrigeration capacities of around 350 kW or even lower) using highly energy-efficient ammonia/CO₂ cascades [Axima 2003a]. However, their construction has usually been facilitated by state assistance programmes [VDKL 2010]. From a technical point of view it would also be possible to build systems with a capacity of around 100 kW and a good coefficient of performance (COP). To date, such systems have not been implemented for cost reasons (capital cost) [Axima 2003a]. Selection of the necessary refrigeration components also becomes more difficult as the refrigeration capacity of the system decreases [VDKL 2010].

No information is available about specific abatement costs in relation to CO₂ equivalent. This is due to the fact that cost studies usually look at the entire field of industrial refrigeration and are not broken down by individual sectors.

Conclusions

Ammonia is the standard refrigerant in coldstores with refrigeration systems with a capacity exceeding 1 MW. In this capacity range the use of HFCs does not make technical or economic sense.

Refrigeration systems with ammonia or ammonia/CO₂ are state of the art in smaller coldstores as well (< 50,000 m³, system capacity < 500 kW). It is already technically possible to build ammonia systems with capacities of as little as 100 kW. Nevertheless, smaller coldstores in Germany have not so far used ammonia or ammonia/CO₂ systems, but only HFC systems. The reasons given are the higher capital cost and extra planning and authorisation work for ammonia systems. This disregards the fact that the energy efficiency of systems with natural refrigerants is very high and their operating costs are usually lower.

3.3.3.4 Sports and leisure facilities

Apart from small refrigeration appliances and systems of the kind also found in other fields of application, refrigeration in this sector in Germany is only needed on a large scale for ice rinks and – to a lesser extent – for indoor ski centres. Ice rinks may have stationary or mobile refrigeration systems. The refrigeration systems here are needed to create and maintain the ice. In Germany there are currently more than 200 indoor and open-air ice rinks. These are mostly operated without HFC refrigeration systems. There are six indoor ski centres in Germany at present (2010). Here the refrigeration system is responsible for cooling the inside of the building and the snow and for supplying cold water for the snow cannons. Artificial snow is produced not only for indoor ski centres, but also for sporting events, festivals/events, film shoots etc. Mobile systems are used for this purpose.

Artificial ice rinks

In the past, the refrigerants used have been ammonia and also R 22 (HCFC), which is now banned for new systems. Today HFCs (R 404A) are also used [Reiner 2003]. In addition there are now a number of ice rinks in Germany where CO₂ is used as a secondary refrigerant. Here too, ammonia is the primary refrigerant [Cofely 2009].

The level of HFC emissions resulting from the creation of artificial ice is not known. In view of the extensive use of ammonia, however, these emissions can be assumed to be a relatively small percentage of total emissions.

Indoor ski centres / mobile snowmaking systems

The first indoor ski centres in Germany were not built until 2001, in other words after the ban on CFCs and HCFCs for new systems. As a result, these refrigerants are not used in the refrigeration systems installed there. The refrigeration systems installed at indoor ski centres in Germany are mostly ammonia systems; but the use of HFCs is not ruled out. For example, mobile snowmaking systems which can also be used in indoor ski centres contain the HFC blend R 404A [Schnee- und Eistechnik 2009].

Reduction options

Ammonia is the usual refrigerant in this field of application [Reiner 2003]. It can be used either as a directly evaporated refrigerant or in conjunction with an (evaporating) secondary refrigerant (e.g. brine, CO₂).

Where refrigerants are used in direct-evaporation systems, steps must be taken to ensure that the refrigerant cannot find its way into public areas (indoor ice rink) [BGV 1997]. For safety reasons, indirect systems are used in many cases today. The secondary refrigerant used is either glycol or CO₂. Another possibility is to use ice slurry [Integral 2003].

Using CO₂ has advantages from an energy point of view. Admittedly the CO₂/ammonia system needs about 8-10% more energy than a direct ammonia system, but an ammonia/brine system needs about 40% more energy than a direct ammonia system [Lindborg 2000]. Moreover, more uniform secondary refrigerant temperatures are possible with CO₂, bringing improvements in the surface quality of the ice rink [eurammon 2002].

We do not have any information on cost comparisons. Since ammonia is usually used as the refrigerant, it may be assumed that these systems are cost-effective.

Conclusions

The use of CFCs as a refrigerant is neither technically nor economically necessary for ice rinks and indoor ski centres. Ammonia, ammonia/brine, ammonia/CO₂ and possibly ammonia/ice slurry offer available halogen-free alternatives that can already be described as standard refrigerants for these applications. This is also true of mobile ice rinks.

3.3.3.5 Metal industry (foundries, smelting plants etc.)

In addition to standard refrigeration appliances and systems, the metal industry uses crane air-conditioning units developed specially for this industry, and these have to work reliably at the prevailing extreme ambient temperatures of up to 90°C. In 2005 Schwarz [Schwarz 2005] assumed the existence of about 1,000 systems on the basis of manufacturers' information. No more recent estimates exist. The refrigerant charge, which depends on refrigeration capacity, varies from 2.5 to over 20 kg [Axima 2003b; FKW 1998a; Schwarz 2005; FrigorTec 2007].

In view of their thermodynamic properties, CFC-114 and the brominated refrigerant R 12B1 are used in this application [FKW 1998a]. Both refrigerants have been banned from use in new systems since the 1990s and their use is now prohibited in existing systems as well. Initially HCFCs were considered as drop-in substitutes for existing systems [FKW 1998a]. In the meantime, HCFCs have also been used in new systems. In view of their remaining ozone depletion potential, however, these were not a suitable long-term alternative and are now banned for new systems as well.

Today manufacturers are therefore using HFC-227ea, HFC-236fa and HFC-134a for new systems; the use of R 227ea and especially R 134a is confined to lower ambient temperatures. Manufacturers' figures for the permissible ambient temperature for R 227ea vary between

75°C [FrigorTec 2007], 80°C [Weisshaar 2009] and 85°C [Wende 2008; Axima 2003b]. HFC-134a is used up to comparatively low ambient temperatures of 60°C [Wende 2008; Weisshaar 2009] or 65°C [FrigorTec 2007].

Since only rough estimates of the number of systems in Germany are available and there are great variations in refrigeration charge, the level of annual emissions from crane air-conditioning systems in Germany is not known.

Reduction options

In addition to HCFCs, it was also theoretically possible to use hydrocarbons (e.g. iso-butane) as a drop-in substitute for existing systems. In practice, as far as is known, no systems have been converted to use hydrocarbons, because of safety considerations and the high cost of the necessary safety measures [FKW 1998a].

Apart from hydrocarbons, the use of CO₂ is also conceivable. This, however, results in poor energy efficiency [Axima 2003b]. Although further research work has been done, it has not so far led to a marketable product. In addition to the poor energy efficiency, the high pressures resulting from the high ambient temperatures present a challenge.

Conclusions

In view of their thermodynamic and material properties, hydrocarbons are suitable for use as halogen-free refrigerants for air-conditioning of crane cabins, but they have not been used because of the special safety requirements and the resulting additional costs. It is not possible to say yet whether it will make sense to use CO₂ in future; this also depends on decisions in other fields of application (automobile industry).

It should be noted that HFC-236fa has a much greater GWP₁₀₀ (6,300) than HFC-227ea (GWP₁₀₀ = 2,900, see Table 1.2). Where technically possible, HFC-227ea should be used – if it continues to be necessary to use HFCs in the future.

3.3.3.6 Large-scale industrial heat pumps

High-capacity (large-scale) heat pumps are frequently used in industry or in specialised applications such as district heating/cooling and for heating and dehumidifying swimming baths. These heat pumps have capacities of 500 kW or more and are often powered by gas engines, but can alternatively use the heat from district heating systems or from the wastewater from sewage works. Capacities of 3.5 to 5 MW are usual; in individual cases the capacity may range up to 28 MW. On the whole this is a small number of highly specialised systems.

Contrary to earlier information [Anhörung 2003], large heat pumps are no longer exclusively equipped with turbo compressors. For example, high-temperature heat pumps are available with a heating capacity of 0.5 to 4 megawatts which reach inlet temperatures of 80°C. These use CO₂, not the refrigerant R 134a which used to be standard for this size of system. As a result of the heat transfer in the supercritical range, the heat pump has a much higher coefficient of performance than a system using R 134a [Wobst *et al* 2008]. A screw

compressor is used to compress the CO₂. In 2010 the same manufacturer is likely to put on the market a heat pump which works with a turbo compressor and achieves a heat output of up to 8 MW with an inlet temperature of 130°C [Thermea 2009].

Reduction options (HFC-free process)

By contrast with the HFC R 134a that is used in the subcritical state in most of the systems realised, CO₂ on the heat utilisation side of heat pumps is in the supercritical state. As a result it is not liquefied during heat transfer, but only cooled, thereby changing the temperature of the gas. The substance flow to be heated (water) can be adapted to this change, making it possible to minimise the exergetic losses [Wobst et al 2008]. Thus in heat pumps using CO₂, not only direct emissions (leaks, accidents), but also indirect emissions are lower than in systems using HFCs, thanks to improved energy efficiency. For economic reasons too, CO₂ is to be preferred to R 134a in this application, since it needs less energy for the same capacity and thus reduces operating costs (compressor power consumption).

High-capacity heat pumps (>3 MW) which can be used to generate heat or cold as desired are implemented using ammonia as refrigerant. One example is a system in Mülligen, Switzerland, which supplies the local mail distribution centre with heat or cold as necessary. Here a large proportion of the energy needed for heating is recovered from the waste heat from the building's air-conditioning system and the wastewater from a nearby sewage works. During cold production, by contrast, the wastewater is used for recooling [KI 2008c]. The compressors used for the two-stage ammonia system (4.3 MW refrigeration capacity) are reciprocating piston compressors or high-pressure reciprocating piston compressors (heat pump operation).

In 2009 the firm of Thermea won a first prize (BMU sponsorship award: Climate protection with climate technology) in the category "Highly efficient refrigeration systems with halogen-free refrigerants" for a series of industrial high-temperature heat pumps in the capacity ranges 50 to 100 kW and 1,000 to 4,000 kW using the natural refrigerant CO₂ [BMU 2009].

Conclusions

In view of the considerable advances made in the development of industrial heat pumps with natural refrigerants, it is possible to dispense with systems using HFCs. The advantage of HFC-free systems lies not only in the substitution of the refrigerant, but also in the much improved energy yield of CO₂ systems in heat-pump mode. The resulting additional capital costs are thus more than made good by reduced operating costs. If operators still want to avoid the capital costs despite the short payback period, there is the possibility of "heat contracting", which is offered by system manufacturers [Thermea 2009].

3.3.3.7 Miscellaneous applications

There are numerous fields of application in industry for (turbo) process refrigeration systems and chillers (water chillers). For example, chillers are used for cooling laser cutting machines in the automobile industry and also in medical technology (e.g. computer tomography or

magnetic resonance tomography) [KKW, HEA 2003; Grasso 2003a]. For various fields of application in the capacity range 20 kW upwards, chillers using ammonia as refrigerant are available as completely finished products.

Power plant systems (e.g. nuclear power plants) require large refrigeration systems (turbo refrigeration units) which have to meet very specialised requirements (earthquake tests etc.). There are no halogen-free solutions on the market yet for this application [Axima 2003a].

It is not necessary to discuss the individual applications in this report, because the remarks on chillers/turbo systems in Chapters 3.1.1 (turbo compressors, technical execution), 3.3.3.2 (turbo compressors, refrigerants) and 3.3.5.2 (chillers and turbo compressors, water as refrigerant) are essentially transferable.

3.3.4 *Transport refrigeration*

Transportation of deep-frozen or chilled products, mostly food, is increasing worldwide. Products are transported by road, rail and water. The means of transport used are refrigerated vehicles, semi-trailers, intermodal containers (combined road/rail transport), containers for international shipment (e.g. by container ships) and refrigerated ships

This chapter deals with the refrigeration systems only; insulation issues can be found in Chapter 4.

Alongside vehicle air-conditioning, transport refrigeration is one of the relevant applications with regard to energy consumption and greenhouse gas emissions arising from artificially generated cold. There is a considerable potential for savings here, in terms of both energy and refrigerants.

In 2007 transport refrigeration systems (vehicles, refrigerated containers) in Germany were filled with around 950 tonnes of hydrofluorocarbons (HFCs). Total emissions from these systems in 2007 came to around 155 t HFC, thus accounting for 3.5% of the HFC emissions in the refrigeration/air-conditioning sector.

Road vehicles

Worldwide freight transport performance by road came to 16 trillion (10^{12}) tonne-kilometres in 2005, and growth rates of 2.5% per year are expected until 2030. In Europe the annual freight performance is about 50 billion (10^9) tonne-kilometres. A fleet of 650,000 refrigerated vehicles is available for this purpose [UNEP 2006]. In Germany there were some 55,500 refrigerated trucks registered in 2007 and 44,500 trailers with refrigeration units [KBA 2009].

Transport refrigeration systems have to ensure reliable refrigeration at ambient temperatures ranging from -40°C to $+40^{\circ}\text{C}$; in some cases it is also necessary to cool down the transported goods. There are international requirements on the refrigeration capacity for the transport of perishable food (ATP Agreement, see Glossary); the internal and external dimensions of the vehicles are standardised [FRIGOBLOCK 2003].

The refrigeration units contain 2-15 kg of refrigerant. Refrigerated vehicles with 6-15 kg of refrigerant are used for long-distance transport; these are trucks, trailers and semi-trailers with autonomous transport refrigeration units [Peilnsteiner, Truszkiewitz 2002]. Smaller vehicles

(distribution vehicles) with charges of around 2 kg of refrigerant take care of local distribution of chilled products and to some extent deep-frozen products. Many vehicles are used for both chilled products and deep-frozen products.

Traditionally CFC-12, CFC-502 and HCFC-22 have been used as refrigerants in refrigerated vehicles [UNEP 2003]. CFCs are now banned in Europe by Regulation (EC) No. 1005/2009 on the basis of the Montreal Protocol [Montreal Protocol 2000]. Under existing regulations HCFC-22, which is permitted as a substitute in some countries, is banned for use in new vehicles in Germany. Today hydrofluorocarbons (HFCs) are used as refrigerants in new vehicles. The blends R 404A and R 410A (especially in Germany) are used for long-distance vehicles carrying chilled and deep-frozen products, and HFC-134a is used for chilled products [FRIGOBLOCK 2003; Öko-Recherche 2003; Thermo King 2003a].

HFC emissions from refrigerated vehicles in 2007 came to about 86 t [Schwarz 2009a]. Emissions on disposal of many long-distance vehicles do not take place in Germany, since the vehicles are sold to purchasers in other countries before being scrapped. Distribution vehicles containing R 134a are mostly disposed of within Germany. Refrigerated containers

Refrigerated containers are used in international transport of goods by road, rail and ship. They may have integrated or external transport refrigeration units [Peilnsteiner, Truszkiewicz 2002]. Today the usual containers, the *Integrated Reefer Containers*, are equipped with an integrated refrigeration unit. Containers without their own refrigeration unit, so-called *porthole containers*, are rare [Kauffeld, Christensen 1998]. Until the ban on CFCs the refrigerant of choice for refrigerated containers was CFC-12. It was replaced by HFC-134a, the blend HFC-404A and also HCFC-22. Annual worldwide production totals about 100,000 containers; today they use HFC-134a and the blend HFC-R404A for refrigeration [UNEP 2003; Wild 2008]. In the meantime the entire production of marine containers has been shifted to China [Wild 2008].

In 2007 the German share of HFC emissions from container refrigeration units came to about 51 t; some of these emissions took place outside Germany [Schwarz 2003b; Schwarz 2009].

Ships

Refrigerants are present in the refrigeration and/or air-conditioning systems of factory ships as used for fishing, refrigerated ships for transporting goods that require cooling, other cargo vessels, research vessels, navy vessels and passenger ships. This chapter on “Transport refrigeration” discusses ships’ refrigeration systems only; ships’ air-conditioning systems are discussed in Chapter 3.3.7.

There are no longer any refrigerated vessels operating under the German flag [Öko-Recherche 2003]. Older refrigerated vessels use direct-evaporation systems to generate their cold. These systems contain 3-5 t of refrigerant. As in other transport refrigeration sectors, they originally

used CFC-12; after the ban on CFCs⁴ this was frequently replaced by HCFC-22. Owing to the restrictions on this refrigerant, HFC blends of the 400 series are used [UNEP 2003]. Today hardly any refrigerated vessel is built with direct-evaporation systems; instead, refrigerated containers with their own refrigeration units are used (see section on *Refrigerated containers*). Since refrigerated containers only need a power connection, they can be transported on most freight vessels.

Older deep-sea fishing vessels (factory ships) used ammonia or the refrigerant R 22. HFCs did not gain acceptance as substitute refrigerants for factory ships and are only used in a few isolated cases [Schwarz 2003b].

All other refrigeration systems on “vessels” – from ferries to research vessels – mostly use HFCs. Air-conditioning applications commonly use R 134a, refrigeration systems (food stores etc.) use R 404A or R 407C. In some cases the R 134a that is already used for air-conditioning is also used for refrigeration purposes. Although it is more efficient to use R 404A for low-temperature refrigeration, R 407C is also used as a sole refrigerant for chilling and low-temperature refrigeration. The refrigeration capacity needed is considerably lower than that required on factory ships.

Estimates indicate that HFC emissions (refrigeration and air-conditioning) from ships belonging to the EU-27 states amount to 241 t, of which 38 t come from refrigeration [BiPRO 2008].

Aircraft

A maximum of 20% of aircraft use small quantities of fluorinated refrigerants for cooling food; the refrigerant charge per compact unit is 0.5 kg, with leakage rates of <0.1% per annum; cooling in aircraft is normally by means of dry ice [Schwarz 2007].

Reduction options

Road vehicles

Possible halogen-free refrigerants for road vehicles are hydrocarbons and carbon dioxide (CO₂; R 744).

In the 1990s, one manufacturer of transport refrigeration systems equipped a refrigerated vehicle with a demonstration system using hydrocarbons. This system was used for several years by a food retailer chain and proved to be suitable from an energy point of view. However, economic operation of such systems has not been possible to date under the prevailing legal conditions (safety requirements and standards for hydrocarbons) [FRIGOBLOCK 2003, 2009]. A refrigeration system for “multi-temp operation” (i.e. vehicles

⁴ Annex VI to the *International Convention on the Prevention of Pollution from Ships* (MARPOL 73/78) also contains rules on the use of ozone-depleting substances on ships [MARPOL 1997]. These are of no significance for Germany and the EU because of the more stringent regulations in force here (see Chapter 1.2).

for both chilling and deep freezing) using the natural refrigerant propene was shown at the IAA 2010. A safety concept was prepared by the technical inspection authority TÜV, and field tests with refrigerated vehicles are planned [FRIGOBLOCK 2010].

The use of CO₂ as refrigerant in refrigeration systems for food distribution (chilling and deep-freezing) has been demonstrated in a multi-year prototype test in a research project at a discounter (Aldi). The test results for the mobile refrigeration system developed by Konvekta AG show that using CO₂ as a refrigerant for this application in temperate climate zones (e.g. in Germany) is an environmentally sound alternative to the use of HFCs [DBU 2003]. Its extension to a two-stage system could lead to further efficiency improvements for transport refrigeration, especially where temperatures in the refrigerated compartment are low and ambient temperatures are high [DBU 2009]. Another new development is a transport refrigeration system on the basis of CO₂ as refrigerant for chilled products. The system is of two-stage design. No measurements have been published yet, and two-stage systems for generating low temperatures are planned. First a field test of the system in chilled product distribution is planned. It will be installed in a newly developed semi-trailer based on carbon fibre material, which has yet to be tested in operation [IAA 2010].

Refrigeration systems in vehicles around the world are still filled with R 404A. Apart from reducing the greenhouse gas contribution of the refrigerant, one of the most important issues is the energy consumption of the transport refrigerant system.

In an overall assessment (TEWI), one manufacturer of transport refrigeration systems came to the conclusion that the environmental impact caused by the use of hydrocarbons at higher temperatures (evaporation temperatures from 0 to -10°C) is lower than when using the blend HFC-410A. The global warming potential of HFC-410A is even lower than that of the blend HFC-404A [FRIGOBLOCK 2003].

The introduction of CO₂ as a refrigerant in transport refrigeration for chilled and deep-frozen product distribution also depends on developments in the field of air-conditioning systems for cars. Suppliers of transport refrigeration systems would welcome broad use of CO₂ systems in the market. One reason is that CO₂ could, as sole refrigerant in the transport sector, cover the entire range of chilled and deep-frozen product distribution. This would eliminate the additional costs arising from the need to use more than one HFC refrigerant [Konvekta 2003].

Konvekta [2002] produced an initial cost comparison. In this, an R 134a series-production system was compared with a fictitious CO₂ system ready for series production. The study makes a first estimate of the costs. Depending on the calculations, the authors arrive at total costs which are 16 to 34% higher for the CO₂ system if it goes into series production. These must be set against non-quantifiable cost reductions in the fields of maintenance, refrigerant and disposal [Konvekta 2002]. Despite the extra capital cost, the use of CO₂ as refrigerant is justified because of the associated advantages (ready worldwide availability of refrigerant, lower adverse effects on the environment, simpler disposal, reduced operating costs etc.) [DBU 2003].

CO₂ is also used as a “refrigerant for consumption”. Liquefied CO₂ passes from a vacuum-insulated stainless-steel tank into a heat exchanger in the vehicle body and cools the

refrigerated compartment. Direct spraying into the refrigerated compartment was abandoned, especially for health and safety reasons. The system does not have a power unit or a compressor, but the technical equipment in the refrigerated compartment is the same as with a usual refrigeration system. All the gasified CO₂ is released into the atmosphere. This open CO₂ cooling system is more suitable for chilled product distribution. Stationary CO₂ tanks with liquefied CO₂ need to be kept for refilling the CO₂ containers on the vehicle. The manufacturer sees advantages for this technology, which has so far been used mainly in Sweden, in lower noise levels and lower maintenance costs due to the simple design of the system [Thermo King 2003b]. For longer distances, a combination with a refrigeration system using conventional diesel power is possible [Peilnsteiner, Truskiewitz 2002]. There is as yet no full life-cycle assessment which might confirm the advantages of systems with CO₂ as a consumable refrigerant compared with optimised compressor systems.

Refrigerated containers

Due to their flammability, the use of hydrocarbons or ammonia in refrigerated containers is not permitted under the international rules for shipping (IMO regulations). The use of CO₂ was tested some years ago in various projects promoted by the Danish environmental authority. Those taking part included component manufacturers, refrigeration system manufacturers and users [Kauffeld, Christensen 1998]. In addition to hitherto unsolved technical issues, there are also logistical problems to be solved when using CO₂. For example, before their widespread use, it must be ensured that a reserve unit is available in every port [Bock 2003; VDR 2003]. Since the containers are now only made in China, and containers are used internationally, there is a need for international measures for conversion to CO₂ as refrigerant.

Ships

Up to the present, the refrigeration systems of deep-sea fishing vessels (factory ships, trawlers) have used HCFC-22 and also ammonia for the large refrigeration capacities needed. In new vessels, HCFC-22 is not replaced by HFC, but by ammonia or ammonia/CO₂ [Schwarz 2003b; Lindborg 2003; Lund 2003].

Ammonia refrigeration systems are also used on refrigerated vessels [Grasso 2003b]. Today, only a few vessels with an integrated refrigeration system are built.

Germanischer Lloyd (a German ship classification company) has issued special guidelines on ammonia. Compliance with these safety requirements makes ammonia-based refrigeration systems more expensive [Grasso 2003b]. In factory ships with large refrigeration capacities the higher capital costs can compensate for the lower operating costs.

Otherwise there are only a small number of vessels with ammonia refrigeration systems. One example is the Greenpeace ship *Esperanza*. One of the world's largest vessels for shock-freezing of fish has a cascade refrigeration system using ammonia and CO₂. Another example of the use of natural refrigerants in ships is a special crude oil transport and processing vessel with a 5 MW refrigeration system using propane as refrigerant [eurammon 2007].

In the German eco-label UZ 110 “Environment-conscious ship operation” [UZ 110] the eco-label jury laid down requirements for environmentally sound ship operation. One of the requirements relates to the refrigerants used: they must not possess any ozone depletion potential. This rules out the use of CFCs and HCFCs. Since HFCs cannot be replaced by environmentally sounder substances in all applications in ships, HFCs are permitted as refrigerants, but must not exceed a GWP₁₀₀ value of 1,650. The eco-label UZ 141 “Eco-friendly ship design” has adopted this requirement [UZ 141]. UZ 110 has been under revision since 2009 and will in future lay down the use of the refrigerants ammonia and/or CO₂ as an optional measure.

Conclusions

Road vehicles

Prototypes of CO₂ transport refrigeration systems have already been developed for deep-frozen and chilled product distribution and have passed practical tests. Optimisation with regard to energy efficiency is desirable. The use of CO₂ systems in transport refrigeration (refrigerated vehicles, especially chilled product distribution) also depends on developments in the car air-conditioning sector (see Chapter 3.3.7.1). If a positive trend towards CO₂ for cars emerges, the development of efficient, inexpensive CO₂-based system will be possible for refrigerated vehicles as well in the medium to long-term.

Other systems on the basis of natural refrigerants have been tested. When using flammable natural refrigerants in particular there are safety issues to consider and limiting standards to check.

CO₂ as a refrigerant for consumption in chilled product distribution is used primarily in Sweden. A comprehensive life-cycle assessment is not available.

In the introductory phase the new technologies involve additional costs. Supporting measures are therefore needed for their introduction to the market.

Refrigerated containers

CO₂ has been tested as a refrigerant for refrigerated containers. There are still technical and logistical problems to be solved, and development work is still in progress. If CO₂ as a refrigerant is introduced on a widespread basis in other sectors, it will be possible to simplify the logistical issues in this sector. This could give a boost to CO₂ for container refrigeration. Since refrigerated containers are transported worldwide and are now only made in China, the use of CO₂ as refrigerant will have to be promoted and agreed at international level.

Ships

In factory ships and refrigerated vessels, refrigeration using ammonia and/or ammonia/CO₂ systems is no problem.

Other vessels which only require smaller refrigeration capacities, e.g. for cooling provisions, use HFCs as refrigerants. The possibility of refrigeration using halogen-free refrigerants needs to be investigated on a case-by-case basis. There are already examples in which the use of HFCs has been dispensed with completely. Basically the possibilities do not differ from those in other fields of application. The special regulations for ship refrigeration systems need to be taken into account.

In future, operators using HFCs will be required to take measures to reduce emissions and should choose a refrigerant with a low global warming potential.

3.3.5 *Air-conditioning of rooms and buildings*

Until a few years ago, air-conditioning of rooms or buildings in Germany was confined to a small number of uses. Air-conditioned buildings included luxury hotels, production facilities with special temperature and humidity requirements, or rooms with special heat loads (e.g. computer rooms). With the rise in the standard of living, people's expectations with regard to comfort in living and work rooms have increased. As a result, the degree of air-conditioning has increased in many fields of activity. Temperature and humidity are frequently controlled by means of air-conditioning systems, and this involves the use of refrigerants.

This chapter makes a distinction between room air-conditioners with cooling capacities between 1 and 50 kW (max. 100 kW) and air-conditioning of rooms and buildings by means of larger-capacity air-conditioning systems. Split and multi-split air-conditioning units are dealt with in Chapter 3.3.5.1, and chillers, which are used for capacities of as little as 5 kW upwards, in Chapter 3.3.5.2.

In 2002, room and building air-conditioning was the source of about 120 t of HFC emissions [BReg 2004]. Room air-conditioners alone emitted about 5 t in 2001 [Schwarz 2003b]. The stock of HFCs in this field of application in 2002 was about 2,300 t [BReg 2004].

3.3.5.1 Room air-conditioners

Various types of equipment are grouped under the heading of room air-conditioners. Depending on the type of unit, the air in the room may be cooled, dehumidified or heated. The great majority of units produced in Japan, for example, are "reversible" and hence suitable for heating as well. Known as "heat-pump air-conditioners", these appliances must however be distinguished from the heat pumps commonly used for heating purposes in Germany (see Chapter 3.7).

A basic distinction can be made between units with an exhaust air hose (mobile room air-conditioners) and units with an external component (split units). Split units with an external component circulate the room air and use a refrigerant to extract the heat from it. Hose units remove the waste heat from the condenser to the outside via an exhaust hose and at the same time draw warm outside air into the room to be cooled. The cooling effect of such units is therefore very low.

Mobile room air-conditioners are used where there is a need for fast and flexible solutions. They are only suitable for short-term use (e.g. to bridge short periods of heat) and not for continuous use. Typical areas of application include living and work rooms [Stiebel Eltron 2003a]. The cooling capacity of these units ranges from 1 to 5 kW.

There are also compact air-conditioning units (window-mounted room air-conditioner) with a hermetically sealed compact refrigeration circuit in the range 1.5 to 9 kW, and split room air-conditioners – usually stationary – up to about 15 kW. The latter are systems consisting of a factory-made internal unit (evaporator) and a factory-made external unit (compressor-condenser unit) which are joined together on site to form a single system with connecting refrigerant pipes.

In an article in the magazine “test”, published by the consumer test foundation *Stiftung Warentest*, the authors say the following about the test results for several single-split and mobile air-conditioning units with a capacity of 2 to 4 kW: “From an environmental point of view, air-conditioners cannot be recommended because of their power consumption. Intelligent heat protection with sources of shade is better.” And also: “Improve [...] the building’s heat protection. If you prevent too much sunlight from entering the building in the first place, there is no risk of extreme overheating. In many cases an external roller blind can work wonders” [test 2008].

In capacity ranges up to about 50 kW (max. up to 100 kW) one finds stationary multi-split room air-conditioners consisting of several internal units connected to a single external unit [Daikin 2003]. Multi-split units are usually described as VRF units (VRF: variable refrigerant flow). By installing multiple VRF room air-conditioners it is also possible to serve larger buildings. This technology is then in competition with the centralised systems usually employed for air-conditioning of buildings. Centralised systems and the possibilities they offer for using halogen-free refrigerants are described in Chapter 3.3.5.2.

Stationary air-conditioners can be very quiet and are suitable for continuous operation. The internal and external parts of these systems are usually connected by copper pipes. The range of applications is broader than for mobile units: offices, living accommodation, technical rooms, wine cellars etc. [Stiebel Eltron 2003a].

Units with an internal and an external part (split units) can be implemented as mobile units. In this case the two parts are usually joined by a permanent “umbilical cord”, enabling the small external unit to be placed on the window-sill or balcony [Fachinstitut Gebäude-Klima 2003].

The great majority of units on the market in Germany are produced in Asia, and a few in other European countries [Daikin 2003].

In the past the refrigerants used were initially CFCs and HCFCs, most recently R 22 in particular, but these are now banned for new systems in the EU. The substitutes used are mainly HFC blends such as R 407C and R 410A, but also hydrocarbons (R 290/propane) [TÜV Süd 2003a; Daikin 2003; Delonghi 2009]. In the year 2000, units already produced using R 22 were converted to the HFC blend R 417A, because they were no longer allowed to be sold in Germany with R 22 [Rhodia 2000].

Split air-conditioners are also sold in department stores, building material/DIY stores and to some extent in supermarkets. This raises problems in connection with refrigerant emissions, especially in cases of improper use. Unlike “plug-in units” (mobile room air-conditioners), these units require expert installation. In many cases, however, this is not clear to the buyer, or only becomes clear after reading the instructions. Incorrectly installed units must be expected to cause increased refrigerant leaks, sometimes resulting in total loss.

HFC emissions in 2008 came to 321 t, or 64 times the figure for 2001 [Schwarz 2009b]. This is mainly due to the fact that since the final ban on R 22 in 2000, most of the appliances coming onto the market have used HFCs. The estimate of emission rates is based on the assumption that the units are installed correctly.

Reduction options

In the case of split units where the internal parts are in living or office areas, there is a direct connection to these rooms. This causes problems with the use of halogen-free refrigerants such as hydrocarbons [Daikin 2003].

Some European manufacturers nevertheless use hydrocarbons (R 290) as well, especially for mobile room air-conditioners (R 290) [TÜV Süd 2003a; Daikin 2003; Delonghi 2009]. There are also isolated cases on the market of split air-conditioners using hydrocarbons [Delonghi 2009]. These air-conditioners have a refrigerant charge of between < 500 g and 1,000 g [TÜV Süd 2003a]. As an approximation, one can generally work on the basis of 0.25 kg of refrigerant per kW of cooling capacity (or 0.15 kg per kW in the case of hydrocarbons) [UNEP 2003]. The German development aid agency (*Gesellschaft für Technische Zusammenarbeit – GTZ*), in cooperation with the Chinese manufacturer Gree, has developed a split air-conditioner using propane as refrigerant. This has a maximum charge of 330 g and a capacity of between 2.7 and 3.5 kW depending on the size of the unit. The units have a COP of at least 3.5, which is well in excess of the European requirements for energy efficiency class A. In the event of a leak the compressor stops running to avoid high temperatures, but the fan continues, thereby diluting the escaping refrigerant and preventing the formation of combustible concentrations. Acoustic and visual warnings indicate leaks. Series production is to start in 2010 [Hasse 2009]. Other manufacturers are also about to launch single-split systems using hydrocarbons [Hydrocarbons21 2010].

UNEP [UNEP 2003] reports that a number of organisations have made risk assessments which come to the conclusion that the use of hydrocarbons tends to reduce the fire or explosion risk. The risk is proportional to the refrigerant charge.

However, widespread use of hydrocarbons presupposes recognised standards and rules for their use even in cases of low risk. From an energy point of view, the use of hydrocarbons (propane) must be considered favourable [UNEP 2003; Calor 2002].

Although the use of CO₂ in the air-conditioning/comfort sector has so far been adjudged technically difficult and unfavourable from an energy point of view [Daikin 2003], the first prototype of a VRF air-conditioning system with CO₂ as refrigerant has recently been unveiled [Daikin 2009; CCI 2008]. This is designed so that it can be run with CO₂ or the HFC blend R 410A as desired. For the variant with CO₂, a special compressor (swing compressor)

and a new heat exchanger and valve technology were developed to achieve the high condensation pressures of up to 123 bar. However, delivery of the first series systems is not expected before 2012. In view of the heat pumps with CO₂ as refrigerant that have recently come onto the market (see Chapter 3.3.6), it can however be assumed that further advances will be achieved in future and a growing number of manufacturers will offer similar split systems.

Compared with compact units, the refrigerant charge in VRF units (greater cooling capacity) is large. In view of the design of these systems (one external unit and multiple internal units, resulting in numerous connections), the risk of refrigerant leaks is also greater, not least because of the total length of piping required, which may add up to a few hundred metres or as much as several kilometres [KI 2008b]. The leakage rate is around 5-15% [Jakob 2009]. In most cases it is possible to opt for alternative air-conditioning solutions with smaller refrigerant charges and lower refrigerant emissions. Possible examples include chillers with ammonia (see Chapter 3.3.5.2).

Another possibility for reducing emissions in this field of applications as well is technical and/or organisation measures. This includes ensuring installation by specialist personnel.

Conclusions

In the case of room air-conditioners, it is necessary to distinguish between mobile compact units and (usually stationary) split and multi-split (VRF) systems.

In mobile units where refrigerant charges can be kept below 500 g, it is possible to use halogen-free refrigerants (hydrocarbons) even having regard to safety aspects. Especially in the field of standardisation there is a need to establish better requirements/conditions for safe larger-scale use of hydrocarbons in appropriate areas.

Only in the case of split or multi-split systems is it still not possible to do without HFCs entirely. But there are also isolated (fairly small) split systems on the market which use propane. An alternative to installing multiple VRF air-conditioning units with large total HFC charges is the installation of a centralised air-conditioning system (see Chapter 3.3.5.2).

At present there is no reason to expect widespread use of CO₂, although it remains to be seen how things develop in this field in future.

In the case of units intended for direct sale to final consumers, a clearly visible indication of the need for installation by a specialist enterprise should be provided where necessary.

3.3.5.2 Building air-conditioning / chillers

Although building air-conditioning is generally taken to mean air-conditioning of an entire building, this chapter also deals – where similar systems are used – with air-conditioning of parts of buildings (room air-conditioning), e.g. doctors' surgeries, salesrooms etc. (Multi-)split air-conditioners, which are also used for these applications, are described in Chapter 3.3.5.1.

Today a wide range of system solutions are conceivable for air-conditioning of buildings. Except where additional systems are dispensed with entirely in view of constructional measures, compressor, absorption or adsorption systems may be used (see also Chapter 3.1). In new buildings, the two latter system types in particular now tend to be coupled with energy supplies from renewable sources (solar collectors, geothermal systems etc.) [Wolkenhauer 2002].

Despite the numerous systems possible today, the great majority of air-conditioning solutions continue to use compressor refrigeration systems. These make use of direct evaporation and liquid chilling packages (cold-water units, water chillers), often with turbo compressors. Below about 1,000 kW, chillers without turbo compressors are used. As mentioned above, other refrigeration technologies are used in some cases, e.g. water-lithium bromide (LiBr) or ammonia-water absorbers and adsorption refrigeration systems [TÜV Süd 2003a; Wolkenhauer 2002].

This report does not discuss the various solutions for conditioning the air in buildings without using air-conditioning systems and for saving energy, e.g. waste heat recovery, although the choice of refrigeration system is closely connected with the choice of overall solution and energy supply. These complex interactions must however be taken into account when designing and operating the system as a whole.

Chillers

Water chillers are used to cool water or another secondary refrigerant; air-conditioning takes place via a distribution circuit. Chillers are differentiated by their cooling capacity or compressor type, for example. Turbo compressors are frequently used for cooling capacities of 700 kW or more. Alternatively, it is possible to use multiple chillers with screw compressors to achieve very large cooling capacities.

Chillers for building air-conditioning have cooling capacities ranging from about 30 kW (in individual cases, e.g. doctors' surgeries, 5 kW upwards) to about 30 MW, or sometimes even more. The systems may use air cooling or water cooling. The operating costs (water price versus energy price, maintenance costs), and also the installation of a water-cooling system (water tower) are higher than for the air-cooled version. From an energy point of view, water cooling is to be preferred because of its lower – in some cases considerably lower – energy consumption [Anhörung 2003].

Chillers (HFCs)

On the German market, chillers up to a refrigeration capacity of about 100 kW are available as industrially produced products (mostly from abroad) which are ready for connection (reciprocating and scroll compressors, see Chapter 3.1). These chillers have refrigerant charges of 1 to 50 kg and are largely made of copper. This means that ammonia cannot be used in them. These systems only require a water connection to be provided on site. Today they are almost exclusively operated with HFCs (e.g. 407C) [KKW, HEA 2003]. In the past the main refrigerant used was R 22 [FKW 1998b]. Apart from air-conditioning applications, these systems are also used in industry, medicine and to some extent in trade applications [KKW, HEA 2003].

HFCs such as R 134a or R 407C are also often used in higher capacity ranges, up to about 900 kW [KKW, HEA 2003, Clivet 2009].

In particular, turbo cold-water units used for capacities of 250 kW or more [Axima 2009] were operated almost entirely with CFC-11 until the ban on CFCs. Today R 11 is replaced in new installations by HFC-134a [FKW 1998a]. See Chapter 3.1.1 (turbo compressors, technical design) and 3.3.3.2 (turbo compressors, refrigerants).

Reduction options

As described above, there are numerous system solutions for air-conditioning buildings; these range up as far as the constructional measures not considered here, which make it possible to dispense (almost) completely with additional cooling. In the following description of reduction options, various technologies are distinguished.

Chillers (HFC-free)

It is technically possible to use any refrigerant in chillers [Axima 2003a; KKW, HEA 2003].

The use of halogen-free refrigerants such as hydrocarbons or ammonia once again raises the question of liability [KKW, HEA 2003]. Unlike hydrocarbons, which are relatively new in refrigeration engineering and where uncertainties exist about the technical requirements (standards etc.) and case law, ammonia is a technology that has been tested and recognised for many years. Here manufacturers regard the liability issue as less problematic [Axima 2003a; Grasso 2003a].

Ammonia

Today there are already chillers with ammonia for refrigeration capacities of around 30 kW or more (air-conditioning of small buildings) [Behnert, König 2003; KI 2008a]. During the phasing-out of CFCs in the early to mid 1990s, compact, ready-to-connect chillers with ammonia were first put on the market in increasing numbers. This trend was interrupted by the sale of chillers with HFCs, which are sometimes cheaper in terms of capital cost, but usually have higher energy consumption and hence higher operating costs. Today substantial reductions can be made in ammonia charges for water-cooled, ready-to-connect chillers. Charges of < 3 kg/100 kW have been implemented [Axima 2003b; Behnert, König 2003].

Larger chillers of the kind commonly used in industry are often run with ammonia [KKW, HEA 2003; Grasso 2009]. Chillers (screw compressors, refrigeration capacity about 0.2 MW upwards) offer a technically sound solution without HFCs for air-conditioning of larger buildings in particular. Both in Germany and in other countries, many ammonia chillers have been implemented for air-conditioning of large buildings [Anhörung 2003; Grasso 2003b]. For example, the complex of buildings at the Ostbahnhof station in Berlin, which consists of shopping mall, hotel and office buildings, is air-conditioned by means of four compact chillers with a total capacity of 1,600 kW [eurammon 2009].

When selecting a refrigerant it is important to take account of the installation conditions. It goes without saying that existing rules, e.g. those forbidding the installation of ammonia systems in places frequented by the public, must be observed. It is always necessary to check whether installation in a separate machine room is possible, whether a high-rise block/hotel is

to be air-conditioned, where the system is or can be located in the basement (= machine room) or on the roof or inside the building (floor for technical services), and how much public traffic there is. In view of the flexibility of water pipe systems, the installation site for smaller units can be decided with relative freedom. When planning new buildings, however, it is also possible to determine installation sites that permit the use of ammonia [Axima 2003a].

An energy consumption comparison based on COP figures and published by eurammon [eurammon 1998] shows that ammonia chillers (500 kW, screw compressor) consume less power than R 134a systems. This means that energy costs are usually considerably lower when using ammonia as refrigerant.

By contrast, the capital cost of ammonia systems is higher than for HFC systems, though it is not possible to generalise about the precise differences in costs. They depend on the individual requirements and the individual design [Anhörung 2003]. Thus an overall profitability calculation is necessary for assessing the economics of ammonia and HFCs as refrigerants.

Hydrocarbons

Chillers with hydrocarbons have been in use in the petrochemical industry for many years now [UNEP 2003]. According to UNEP [UNEP 2003], European manufacturers have been offering chillers (air or water cooling) with hydrocarbons for the air-conditioning sector (air-conditioning of buildings) since 1997/98. The refrigerants used are R 1270 (propylene), R 290 (propane) and R 290/R 170 blends (propane/ethane), in charges of between 3 and 34 kg. The capacities quoted range from 20 kW to 1,265 kW [Earthcare 2009], though the possible capacity depends on the desired temperature range. The energy efficiency is comparable to chillers with R 134a [UNEP 2003].

The installation of hydrocarbon chillers is basically subject to the same principles as described for ammonia (see above). Explosion protection measures are also necessary. This and the smaller numbers produced to date make chillers with hydrocarbon refrigerants rather more expensive [UNEP 2003].

In building air-conditioning systems with large cooling capacities, the use of hydrocarbons has hitherto been ruled out by the large refrigerant charges required [Axima 2003a; Grasso 2003a]. A number of examples in the United Kingdom, however, make it clear that externally installed R 290 chillers are an alternative to HFC systems in air-conditioning [Earthcare 2010].

Ammonia / dimethyl ether (DME)

The refrigerant R 723, an azeotropic blend consisting of 60% ammonia and 40% dimethyl ether, is firmly established on the market as an environmentally sound and efficient alternative to refrigerants containing HFCs. Systems with a capacity of 10 kW upwards are available for various applications, including air-conditioning of buildings [KI 2008a]. Huber [2003] reported on initial experience with a water chiller for cooling production of plastic parts. He put the additional cost compared with HFC systems at about 10%. Components for systems with fairly small capacity are still being manufactured in relatively small numbers,

which increases the capital cost of such systems by about 20-30% compared with HFC [Frigopol 2009]. This extra cost is offset by the greater energy efficiency of ammonia/DME systems, which reduces ongoing energy costs by 25-30% and ensures a short payback period (2-3 years) for the additional capital cost.

CO₂

As in the case of VRF systems, the use of CO₂ as a refrigerant in larger centralised systems was regarded as out of the question until a few years ago because of the temperatures required in air-conditioning (climate range). This was also due to the fact that components for the relevant pressures were neither available, nor were they expected to be developed in the medium term [KKW, HEA 2003]. The latter point stemmed from the fact that the energy efficiency levels that were possible with CO₂ in the air-condition field were not considered good enough to compete with HFC systems [UNEP 2003]. Despite these obstacles, an air-conditioning system for office buildings was recently unveiled, covering a capacity range of between 50 and about 340 kW. As this is a direct-evaporation system, it does not need an additional water circuit with the associated pumps. Its energy efficiency therefore exceeds that of conventional HFC systems by 10-20%. The installation costs can also be expected to be lower [R744 2009]. See also Chapter 3.3.2.3.

Costs

Studies of abatement costs in terms of CO₂ equivalent are only available from the year 2000. Harnisch and Hendriks [Harnisch, Hendriks 2000] quote 49 € and 173 € per tonne of CO₂ for the EU as average abatement costs for stationary air-conditioning with chillers. The first estimate is for replacement of HFCs by halogen-free refrigerants, the second is for the reduction in HFC emission rates. Thus Harnisch and Hendriks [Harnisch, Hendriks 2000] rate the replacement of HFC refrigerant considerably more cost-effective than other measures to reduce HFC emissions. Compared with other CO₂ reduction measures, the abatement costs for HFC substitution in this application, on the basis of CO₂ equivalent, are in the middle to upper range. Here too the figures should be regarded as rough estimates only, based on a large number of assumptions. For details of the underlying assumptions, the reader is referred to the source study.

Turbo refrigeration systems with water (R 718) as refrigerant

Water is also used as a refrigerant in turbo refrigeration systems (see Chapter 3.1.1 and Chapter 3.3.3.2). The advantages of water as a refrigerant are above all its unrestricted availability, its low price, its ease of handling and its lack of toxicity [ILK 2003b]. Until now, only isolated systems in Germany have been run with water. One example is the air-conditioning system of *Gläserne Manufaktur Dresden* (VW). Under a joint research project supported by the Federal Ministry of Education and Research, work is currently in progress on the development of a third generation of this R 718 turbo cold-water unit [ILK 2010]. The refrigeration capacities start at 400 kW. One disadvantage is that when using water it is basically necessary to work in the under-pressure range, and that the specific volume of water vapour is very large. Very large flow rates (50 m³/s) are required; the compressors are very large [ILK 2003a]. In energy terms the systems are comparable to or better than other systems

[ILK 2003b]. Operating costs are lower than for HFC systems, but the capital costs are appreciably higher than the cost of comparable systems using HFC as refrigerant. This is largely due to the fact that the systems are manufactured more or less on a one-off basis. At refrigeration capacities below 400 kW the price differences would be even larger [ILK 2003a].

Absorption refrigeration systems (HFC-free)

Another possibility for HFC-free air-conditioning is based on the use of absorption refrigeration systems. Large numbers of absorption systems are installed for air-conditioning of buildings as well. Various pairs of substances can be used as working fluids (refrigerant and solvent), but today only two of these are employed in practical refrigeration systems: water/lithium bromide and ammonia/water. Capacities range from 10 kW [Wiemken 2009] to 17.5 MW [UNEP 2003], thereby covering the needs of smaller buildings and detached houses. The capital cost of absorber systems is higher than for mechanically driven refrigeration systems.

As a thermally powered refrigeration system, an absorber refrigeration system can be supplied with thermal energy that could otherwise hardly be used economically, e.g. heat from district heating networks or a solar power system. As heat sinks, absorber systems (and heat pumps, see 3) relieve the load on district heating networks in summer, when there are hardly any takers for heat. Since no compressor is needed to compress the refrigerant, absorber systems use far less electrical energy than compressor refrigeration systems. Thermal air-conditioning systems (absorption and adsorption) save primary energy if the annual energy requirements of a sorption refrigeration system in terms of primary energy (heat and electric auxiliary drives) are smaller than the primary energy requirements of compressor system. They also make a substantial contribution to smoothing out peak power demand on hot summer days when large quantities of power are needed for air-conditioners based on the compression principle. This technology thus avoids or totally eliminates greenhouse gas emissions from two sources, power generation and refrigerants.

From an economic point of view, the use of absorber technology pays off particularly if a favourable heat source (waste heat) is available. Absorber refrigeration systems use a simple, robust and very low-maintenance technology. At the Massachusetts Institute of Technology (MIT) in Boston, USA, an absorption chiller has taken care of cooling since the late 1930s.

It is also possible to use water, the environmentally sound refrigerant [Grage, Pareidt 2000]. Many buildings in Germany are air-conditioned with the aid of absorber systems.

Adsorption refrigeration systems (HFC-free)

Like absorber systems, adsorption systems basically work without HFCs. They run on low-temperature heat and are particularly suitable for utilising solar energy or waste heat – even comparatively low-temperature waste heat. As already mentioned, one great advantage when using solar energy is the simultaneous timing of peak cooling demand in summer and the solar energy needed to power the system. Compared with compressor systems, they can be operated on a favourable energy basis if the annual solar or waste heat coverage and the energy efficiency ratio (EER) are sufficiently large [Schölkopf 2008]. Adsorption cooling

systems are state of the art and have increasingly been used for air-conditioning of buildings in recent years. The working fluids used are the couples silica gel/water and zeolite/water. In the solar information centre in Freiburg, a liquid sorption pilot system using LiCl/water provides air-conditioning for 310 m² of office space [Wiemken 2009]. Liquid sorption systems have the advantage that part of the solar energy can be stored in the form of regenerated adsorbent, thereby making it possible to smooth out fluctuations in solar radiation despite continuous refrigeration requirements. Adsorption cooling systems are of simple construction and are very reliable. In terms of capital cost, however, they are more expensive than compressor systems. Several systems are installed in Germany. The Federal Environment Agency's new building in Dessau has an adsorption system with a cooling capacity of around 70 kW. General technical information can be found in Chapter 3.1.2.

Conclusions

Air-conditioning of buildings using refrigeration systems without HFC has been implemented in many projects and is state of the art. The following options are available:

1. Absorption refrigeration systems,
2. Adsorption refrigeration systems,
3. Chillers with ammonia as refrigerant for refrigeration capacities of about 20 kW upwards,
4. Chillers with hydrocarbons as refrigerant for refrigeration capacities of about 20 kW to 1,200 kW, and
5. Turbo refrigeration systems using water as refrigerant.

The choice between compressor and absorption or adsorption refrigeration systems will depend to a large extent on the overall concept, including the heat and energy sources available.

If a chiller is selected as the appropriate technical solution, the choice of compressor (reciprocating, screw or turbo compressor) will depend on the refrigeration capacity required. HFC-free solutions are available for capacities of 20 kW upwards.

The capital cost of ammonia chillers is rather higher than for the widely used HFC technologies. In most cases this additional cost can be offset by reduced operating costs (reduced energy consumption etc.). Thus the use of ammonia is often advantageous even from an entirely economic point of view, but a detailed assessment is only possible on the basis of an overall profitability calculation. In ecological terms the use of ammonia is clearly favourable compared with HFCs.

Turbo refrigeration systems with water as refrigerant – although they have not yet become established because of their small numbers to date and the higher capital cost compared with HFC systems – are an interesting a future-oriented technology from an ecological point of view, because in terms of energy efficiency they are equivalent or even better, and because each individual system can replace a very large quantity of HFCs (refrigerant).

If absorption or adsorption refrigeration systems are chosen, it is possible to power them with energy that is otherwise difficult to put to economic use. Both types of systems are of simple construction and are very reliable. Whereas the capital cost is higher than for mechanical refrigeration systems, savings on operating costs are possible. A broad spectrum of absorption refrigeration systems is available (10 kW up to several MW).

3.3.6 *Heat pumps (domestic heat pumps)*

Heat pumps (heat pump systems and units) can produce heat capacities at widely varying levels. This chapter looks at heat pumps that deliver up to 50 kW heating capacity (domestic heat pumps). These heat pumps are used as heating system heat pumps for heating and cooling of small buildings (detached or semi-detached houses) or for heating domestic water (domestic water heat pumps). If several houses are connected together, heating capacities of 100 kW may be necessary [Stiebel Eltron 2003]. Heat pumps with larger capacities of around 500 kW upwards are considered in Chapter 3.3.3.6.

Whereas a mere 400 heat pumps for heating purposes were installed in Germany in 1990 [Laue 2000], by 2001 the figure was as high as 10,100 [Frey 2003]. In the following five years the installation of heat pumps showed a further sharp increase, sometimes making substantial leaps. For example, 18,500 systems were installed in 2005, and in the following year this figure more than doubled to nearly 44,000 systems. According to the Federal Heat Pump Association (*Bundesverband Wärmepumpen – BWP*), 62,500 systems were installed in 2008 [BWP 2009]. There has thus been an almost continuous increase since the early 1990s. The previous record sales figure of more than 20,000 around 1980 in the wake of the oil price shock has thus been more than doubled several times since 2006. By 2009 the share of heat pumps as a heating system for new buildings (detached houses) in Germany was as high as 25% [BWP 2010]. In other European countries too, the heat pump market has displayed impressive sales growth. In France, for example, some 135,000 systems were installed in 2008 [KK 2009], an increase of 180% on the year before.

In the capacity range required here, current practice is almost exclusively to use electrically powered heat pumps working on the compression principle. Heat pumps powered by gas engines are available for larger units (heating capacity >100 kW). Today lower-capacity gas heat pumps are also available, but hardly for capacities below 20 kW [ASUE 2008]. This segment continues to be dominated by electrically powered heat pumps.

The heat sources are groundwater (in rare cases surface water), ambient air or the soil. In 2008 some 48% of all newly installed heat pumps were equipped with horizontal flat-plate collectors or vertical ground probes for utilising heat from the soil (brine/water heat pump), while 44.9% derived their heat from the ambient air. Only 7.1% used groundwater as a heat source [BWP 2009].

The heat from the energy source used (ground heat) is first transferred to a secondary refrigerant circulating in the collectors/probes (dual-circuit system principle, see also Chapter 3.3.2). A few years ago, however, direct-evaporation systems entered the discussion: here the refrigerant itself circulates through the many metres of collector, e.g. plastic-coated

copper pipes or plastic pipes. For the same capacity, these systems need roughly twice as much refrigerant as dual-circuit systems, but are more energy-efficient [Klima:aktiv 2007]. This is due to the fact that, unlike dual-circuit systems, direct-evaporation systems work without the additional heat transfer (intermediate heat exchanger) and the brine pump for the ground collectors. Where they use natural refrigerants such as propane, such systems are clearly superior from a climate protection point of view to those using HFC.

Despite these advantages, direct-evaporation systems are not undisputed. Apart from the larger quantity of refrigerant required in direct-evaporation systems, some experts take a critical view of the increased leakage risk [KKW, HEA 2003]. In spite of the theoretically superior design compared with dual-circuit systems, comparative measurements by a test laboratory in Vienna have shown that in practice it is not possible to detect any difference in the energy measurements. In some cases the brine systems actually displayed energy advantages [Anhörung 2003].

For a long time the blend R 502 was the standard refrigerant in heat pumps. Because of its CFC content it was first of all replaced by HCFC-22 [FKW 1998b]. From about 1997/98 manufacturers increasingly started to use HFCs as so-called “safety refrigerants” [Stiebel Eltron 2003]. The HFC blends used are R 407C, R 410A, R 404A and R 417A and the pure substance R 134a. The latter is frequently used in domestic water heat pumps.

HFC emissions from domestic heat pump applications in 2007 amounted to about 8.5 t, and the total stock stood at 570 t. This means that emissions more than quadrupled compared with about 2 t in 2002 (HFC stock about 90 t) [Schwarz 2005; Schwarz 2009a]. In view of the fast-growing sales there is reason to fear that this trend will continue in the next few years.

Reduction options

Even before the use of HFCs, from about 1992/1993, manufacturers mostly replaced HCFC-22 with flammable hydrocarbons, e.g. propane (R 290) or propene (R 1270) [Stiebel Eltron 2003; Laue 1999]. Safety aspects connected with the use of flammable refrigerants were controllable [Bock 2003; Stiebel Eltron 2003; Hautech 2002].

However, the introduction of HFCs hardly brought any further advances in the development of heat pumps using hydrocarbons. No technical/energy optimisation took place [Stiebel Eltron 2003; HEA 2003].

The reasons for discontinuing development work on systems with hydrocarbons were many and varied. Manufacturers repeatedly cite the prevailing standards and the lack of binding legal regulations for the use of flammable refrigerants [Bock 2003; Stiebel Eltron 2003; ASERCOM 2003; Carrier 2003]. Relevant standards in this sector, e.g. DIN EN 378 [DIN 2008], do not permit the use of flammable refrigerants below ground level in quantities exceeding 1 kg.

However, heat pumps – except those for very small heating capacities – normally contain more than 1 kg of refrigerant, and it is not usual to install such systems above ground level. In fact, heat pumps for heating purposes are generally located in the basement below ground level.

According to DIN EN 378, it is possible to use larger quantities of flammable refrigerant in heat pumps if certain safety measures are complied with (mechanically ventilated housing). Other standards, such as DIN 7003 (draft) [DIN 1995b], also permit the use of larger quantities provided certain safety precautions are installed. However, European standards are observed primarily for product liability reasons. Future European standards could also permit the use of larger quantities.

The situation is different for domestic water heat pumps. Here refrigerant charges of less than 150 g are state of the art, and suitable units are on the market [Stiebel Eltron, 2009]. With this small refrigerant charge the use of flammable refrigerants such as propane does not cause any problems (e.g. under IEC 60335, Part 40) [Stiebel Eltron 2003; IEC 2003].

Another reason quoted by heat pump manufacturers in addition to the standards situation is the unwillingness of component manufacturers, e.g. makers of fully hermetic compressors in the USA and France, to give their products clearance for the use of flammable refrigerants [Bock 2003; Stiebel Eltron 2003; Laue 1999]. Around 1998, for example, the component supply industry abruptly stopped clearance of components for use with hydrocarbons. The reason given was the high product liability risk in the event of loss or injury [Anhörung 2003].

On behalf of the Swiss Federal Office for Energy (*Schweizer Bundesamt für Energie*), Wolfer *et al* [Wolfer *et al* 1999] produced a study which investigated risks, product liability and criminal law issues in connection with the use of ammonia and hydrocarbons as refrigerants. For the study scenario “heat pump in detached house” the authors come to the conclusion that *“the risks of using ammonia or propane are acceptable for heat pump owners and are lower than for conventional gas-fired heating systems”*.

Regarding the question of product liability and criminal liability of the manufacturer or fitter, the authors come to the conclusion that *“the use of ammonia or hydrocarbons cannot be described as incorrect, because there are good ecological reasons for using them instead of ozone-depleting or climate-relevant substances. The state of the art must however be achieved.”* The study indicates what measures need to be taken to avoid being held liable in the event of an accident.

The study – as the authors expressly point out – is based on Swiss legislation. The authors are nevertheless of the opinion that it ought to be possible to apply the conclusions to other European legal systems as well.

Kruse and Heidelck [Kruse, Heidelck 2002] point out that *“while an accident caused by flammable refrigerants can never be ruled out completely, the safety risk is virtually negligible given proper installation and operation”*.

In spite of the difficulties mentioned, heat pumps with capacities of up to 20 kW (for room heating and water heating) with hydrocarbons as refrigerant are still available on the market [Buderus 2009]. Systems with two compressors can even achieve capacities of over 25 kW [Dimplex 2009]. The problem of flammability of propane, for example, is overcome by locating the heat pump including evaporator out of doors (air/water heat pump), which means that in the event of a leak or accident the risk arising from the refrigerant is at least

considerably reduced [Acalor 2009; Dimplex 2009, Klima:aktiv 2007]. Installations below ground level are fitted with a gas warning device. If refrigerant escapes, the warning device starts a fan which sends the gas outside, thereby preventing the formation of a potentially explosive air/propane mixture [Acalor 2009a]. Some systems are designed as direct-evaporation systems, enabling them to achieve high energy efficiency and correspondingly high coefficients of performance [Klima:aktiv 2007].

As well as hydrocarbons as refrigerants, the use of CO₂ as a refrigerant in household heat pump applications, especially domestic water heat pumps, is possible and already established. Domestic water heat pumps using CO₂ have already been available on the Japanese market for some years now [Kruse, Heidelck 2002], and CO₂ heat pumps for heating and hot-water are now available in Germany as well [KK 2008a]. A CO₂-air/water heat pump with a heating capacity of up to 9 kW has been available on the German market since 2008 for heating and hot water in new and existing buildings [Kaut, Sanyo 2008]. For the minimum-energy and passive house sector, a 2 kW heat pump using CO₂ as refrigerant is due to be launched shortly. This meets the entire heat requirements of a detached house with a floor area of 145 m² (hot water and heating), while achieving a much better annual coefficient of performance than a system using R 134a [Kosowski *et al* 2008]. In spring 2009 a pilot heat pump system with CO₂ ground heat pipe and CO₂ as refrigerant started operating at the Research Centre for Refrigeration and Heat Pumps (*Forschungs-zentrum für Kältetechnik und Wärmepumpen GmbH*) [FKW 2009].

Although ammonia has not so far been used in household heat pumps operating on the compressor principle and has been rated as being of no practical relevance [Stiebel Eltron 2003; Laue 1999], a study within the EU SHERPHA project demonstrated that a heat pump with ammonia is not only basically possible, but in terms of efficiency is capable of surpassing conventional systems with HFC [Palm 2008]. The study makes it clear that the limiting factor here is not so much thermodynamic or technical considerations, but rather the fact that there are hardly any components on the market that are designed for ammonia in this capacity range (around 10 kW). For example, only one manufacturer offers a semi-hermetic compressor suitable for this refrigerant. This “separating hood compressor”, in which the motor winding is not in contact with the refrigerant, is used in industrial processes where aggressive gases have to be compressed. This design has hardly been used to date in refrigeration engineering, however. Existing open compressors are hardly suitable for household heat pumps because of the risk of leaks and the toxicity of ammonia. Other components such as heat exchangers and throttle valves are also either not available at all or only to a limited extent. It has nevertheless proved possible to design a prototype heat pump using ammonia which has a refrigerant charge of only 100 g and achieves coefficients of performance in excess of 4 [Palm 2008].

The situation is different for absorption heat pumps, which are marketed with ammonia (the substance couple ammonia/water). The fundamentals of the absorption principle are described in Chapter 3.1.2. Today absorption heat pumps are only available for heating capacities of between 16 and 40 kW, which means they can only be considered for multi-family houses or commercial establishments. However, the start of series production of an absorption heat

pump in the range from 4 to 10 kW is scheduled for the end of 2011, and this will be suitable for single-family houses [FAZ 2010]. Absorption heat pumps have few moving parts and are therefore very quiet [ASUE 2002].

Another alternative to heat pumps working on the compression principle is adsorption heat pumps. Chapter 3.1.2 describes the fundamentals of the adsorption principle with solid sorption materials. Since 2010 one manufacturer has been offering a gas-powered adsorption heat pump using the system water (refrigerant) and zeolite (sorbent) which has a heating capacity of up to 10 kW [Vaillant 2010]. Another manufacturer has already successfully field-tested zeolite heat pumps and plans to launch them at the end of 2012 [FAZ 2010]. There are also plans to develop units with greater heating capacities.

The differences in the energy efficiency of heat pumps depending on their power source and heat source and their impact on CO₂ emission savings cannot be dealt with in this report on fluorinated greenhouse gases, as a wide range of factors need to be considered. Examples of relevant overviews include Laue [Laue 2000], Leven *et al* [Leven *et al* 2001] and ASUE [ASUE 2002]. In a comparative study of electric heat pumps and conventional and renewable heating technologies, the Federal Environment Agency has already determined and assessed the environmental balance of this type of system [UBA 2008]. Although today heat pumps are regarded as a mature technology, ongoing improvements mean that one can expect further increases in the efficiency of these applications in the future [Löffler 2008].

It must be stressed that in addition to the refrigerant issue, the question of energy efficiency has gained considerably in importance. Since the heat pump's successful entry into the market, manufacturers of heat pumps and components have succeeded in making improvements in this field. Manufacturers claim that thanks to the input of development work, today's heat pumps with HFC refrigerant charges achieve better coefficients of performance than units which were built in the mid 1990s and which used hydrocarbons (mostly propane). On the one hand this is not surprising, because any further development also results, among other things, in improved energy efficiency. On the other hand, manufacturer's information is frequently at variance with the actual figures measured for systems already installed. First-time purchases of heat pumps are supported, as in the case of solar collector and biomass systems, by the Federal Environment Ministry (BMU) under the "Guidelines on support for measures for the use of renewable energy sources in the heating market", in cooperation with the Federal Office of Economics and Export Control (*Bundesamt für Wirtschaft und Ausfuhrkontrolle – BAFA*), in the context of the German government's market incentives programme [BAFA 2009]. The same applies to heat pumps powered by gas engines. The main criterion for a system's eligibility for support is its annual coefficient of performance, which is to be determined in accordance with VDI Guideline 4650. However, the latest findings of a field study conducted by the Fraunhofer Institute for Solar Energy Systems indicate that the annual coefficients of performance calculated before installation are rarely achieved in practice [Morhart 2009]. It remains to be seen whether the revised version of the Guideline will bring any improvement in advance calculation of the annual coefficient of performance. Another point that needs to be improved is the fact that the refrigerant used does not play any part in the assessment of eligibility. This would however be a crucial point

in helping natural refrigerants (e.g. propane, CO₂), which are of virtually no climate relevance compared with HFCs, to finally make a breakthrough in the field of heat pump applications and replace climate-relevant refrigerants. This would seem to be an urgent necessity, especially in view of rising sales figures and the associated growth of HFC emissions.

Conclusions

For low-capacity heat pumps (up to 20 kW) and correspondingly small refrigerant charges, eco-friendlier alternatives are available today in the form of hydrocarbons (propane) and CO₂. This means that in this application it is already possible to avoid the use of HFCs entirely. This applies in particular to domestic water heat pumps. Units for this field are available at slightly higher prices (additional cost of housing ventilation comes to about 1.5% of total costs).

Many experts regard hydrocarbons as refrigerants with very good thermodynamic properties combined with acceptable risks for use in heat pumps. Many manufacturers have nevertheless stopped further technical development work on these heat pumps, including energy optimisation, and are now concentrating entirely on HFCs. One possible way of making the use of propane more attractive for manufacturers would be to ensure that heat pumps with natural refrigerants receive greater support than HFC systems under the German government's market incentives programme.

In the capacity range from about 16 to 40 kW (e.g. for multi-family houses and commercial purposes), not only compressor heat pumps are available, but also absorption heat pumps which do not contain any halogenated refrigerants. Development work has already started on absorption heat pumps for single-family houses (capacity range from 4 to 10 kW). The start of series production is planned for 2011 [FAZ 2010].

Adsorption heat pumps having a heating capacity of up to 10 kW (for single-family houses) and using water as refrigerant are already available on the German market. Work is in progress on the development of heat pumps with greater heating capacities.

3.3.7 Vehicle air-conditioning

Mobile air-conditioning systems (MAC) are vehicle air-conditioning systems in cars, trucks or commercial vehicles, buses (long-distance coaches, city buses), rail vehicles, aircraft⁵ and ships. Both refrigerant consumption and refrigerant emissions are dominated by car systems. 89% of HFC emissions from mobile air-conditioning systems originate from car air-conditioning systems [Schwarz 2010].

⁵ Cooling in aircraft is generally done by means of the ambient air. Fluorocarbons are only used for air-conditioning in helicopters and in low-altitude aircraft. The total refrigerant charge in these systems in the European Union amounts to 6.7 t; an assumed emission rate of 5% would result in emissions of 336 kg a year [Schwarz 2007].

All MACs in vehicles built before 1991 contained the CFC dichloromethane (R 12) as refrigerant [SAE 2001]. The ban on R 12 in mobile air-conditioning systems with a charge below 5 kg was imposed in 1995. Since then, mobile air-conditioning systems have almost exclusively used the HFC refrigerant tetrafluoroethane (R 134a). Exceptions are a small number of converted R 12 air-conditioning systems that were filled with the drop-in refrigerant R 413A (88% R 134a, PFC-218 (9%) and R 600a (isobutane)) instead of R 134a [Schwarz, Leisewitz 1999].

As a rule, air-conditioners for road vehicles are not hermetically sealed systems: their compressors are mechanically driven by a shaft powered by the vehicle engine and are exposed to the vibrations of the engine.⁶ The refrigerant flows through flexible pipes (hoses) to the other refrigeration circuit components which are fixed to the vehicle frame. Hoses with better diffusion resistance and better seals made it possible to reduce losses in normal operation from the R 134a systems by about 50% compared with CFC systems [Schwarz, Leisewitz 1999; Nonnenmann 1995]. Two thirds of the total greenhouse gas emissions caused by the operation of vehicle air-conditioners are due to direct emissions of the refrigerant (R 134a), and one third to indirect emissions from the fuel consumption needed to power the air-conditioning system [COM 2003].

Air-conditioning systems have long been standard equipment for vehicles on the Japanese and North American markets [Holdack-Janssen 1996]⁷. In recent years the percentage of new vehicles fitted with air-conditioners (MAC rate) increased sharply in Germany and Europe as well. In Germany, for example, as many as 96% of all cars newly registered in 2008 were fitted with air-conditioning, being the average of 98% of German models and 92% of imported cars (see Table 3.1) [Schwarz 2010].

3.3.7.1 Car air-conditioning systems

Statutory provisions

EU Directive 2006/40/EC relating to emissions from air-conditioning systems in vehicles (known as the MAC⁸ Directive) entered into force on 4 July 2006. The directive applies to small passenger motor vehicles with at least four wheels and a maximum of 8 seats plus driver (vehicle category M1) and to motor vehicles designed and built for transporting goods and having at least four wheels and a maximum permitted total weight of up to 3.5 tonnes, whereby the vehicle weight must not exceed 1.305 tonnes (vehicle category N1, class 1)⁹.

⁶ Individual hybrid vehicle types have electrically powered compressors which are not powered by an engine-driven shaft.

⁷ As early as 1994 some 98% of all cars in Japan had air-conditioning, and in the USA the figure was over 90%. By comparison, in the same year only 20% of vehicles in Europe had air-conditioners.

⁸ MAC – Mobile Air Conditioning

⁹ Directive 2007/46/EC of the European Parliament and of the Council of 5 September 2007 establishing a framework for the approval of motor vehicles and their trailers, and of systems, components and separate technical units intended for such vehicles, as amended in 2008 by Commission Regulation (EG) No.

Category M1 includes mainly cars and minibuses, but also special vehicles such as motorhomes, ambulances and hearses, and armoured or wheelchair-adapted vehicles. Category N1, class 1, includes small commercial vehicles such as vans, but also special vehicles such as caravans.

With effect from 1 January 2011, EU Directive 2006/40/EC prohibits air-conditioning systems in vehicles of category M1 and N1, class 1, which contain as refrigerant fluorinated greenhouse gases with a global warming potential higher than 150. The deadlines are staggered.

As from 1 January 2011, the Member States shall not issue EC type-approval or national type-approval for new vehicle types with such air-conditioning systems. Retrofitting is also banned. With effect from 1 January 2017, newly built vehicles having a type approval issued before 1 January 2011 and having air-conditioning systems containing refrigerants with a GWP higher than 150 may no longer be sold or registered. Retrofitting of such air-conditioning systems to any vehicle is also prohibited.

The regulation also includes provisions on leak testing. Air-conditioning systems with a single evaporator may not release more than 40g per annum, and systems with two evaporators may not release more than 60g per annum, of fluorinated greenhouse gases with a GWP in excess of 150. Leak testing has to be applied to new car types since 21 June 2008, and since 21 June 2009 to all new cars with R 134a systems¹⁰.

Refrigerant quantities and emissions

In 1995 only a quarter of all new cars were air-conditioned. Today nearly all new cars in Germany are equipped with air-conditioning. In 2008, about 96% of new cars in Germany were fitted with mobile air-conditioning, and nearly three quarters (73%) of all cars registered in Germany had air-conditioning [Schwarz 2004; Schwarz 2010].

Until 2017 air-conditioning systems in new cars are allowed to be filled with HFC-134a (R 134a). Despite the small average refrigerant charge of less than 0.7 kg per system, the annual new input of R 134a for initial filling of car air-conditioning systems for the German market has risen as a result of the large number of new air-conditioning systems. In 1995 the figure was 1,400 t, by 2008 it had already reached 3,800 t of R 134a (see Table 3.2). There was also a further increase in the total quantity of R 134a refrigerant in car air-conditioning systems. In 2008 the quantity of R 134a in car air-conditioning systems in German totalled 23,645 t, which corresponds to about 31 million t CO₂ equivalent [Schwarz 2010].

1060/2008. The limit on vehicle weight (class 1) in category N1 follows from the current version of Directive 70/220/EEC.

¹⁰ The Commission supplemented the leakage limit requirements by a harmonised leakage measurement procedure for type approvals in Article 7 of Regulation (EC) No. 706/2007 of 21 June 2007, in conjunction with Annex II.

From 1995 to 2008, annual refrigerant emissions rose from 133 t to 2,700 t. These quantities represent a steadily increasing contribution to the greenhouse effect, from 0.17 million t in 1995 to 3.5 million t CO₂ equivalent in 2008 (see Table 3.1). Today more than a third of all HFC emissions are due to car air-conditioning systems [Schwarz 2010]. Given continued use of R 134a, annual emissions of this refrigerant could be expected to reach 3,500 t by 2020 [Schwarz 2003a].

Refrigerant emissions occur during filling, as a result of gradual diffusion through the seals of the system, during servicing (opening and evacuating the circuit), as a result of irregular events such as damage to the system due to accidents, flying stones etc., and during final disposal of air-conditioning systems [Schwarz 2001; Schwarz 2005]. Emissions during filling are quoted as 2%. During operation an average of about 10% of the refrigerant per year escapes into the atmosphere (7% regular losses and 3% irregular losses), while estimates of emissions per service range from a few grams up to 10%. Losses on disposal are assumed to be 30% [Schwarz 2005]. Disposal of cars with air-conditioning systems retrofitted with R 134a began in 2002; from 2005 onwards, the first model years that contained R 134a as their initial charge were scrapped [Schwarz 2010].

Today a large proportion of cars taken off the road leave Germany before being scrapped (e.g. export to eastern countries and Africa) [Buchert, Hagelüken 2003]. Only a few of these vehicles end up in countries where regulated disposal of the refrigerant is guaranteed. There is no reliable information about the fate of the vehicles and hence about emissions, servicing and refrigerant disposal. It is therefore likely that a large proportion of the refrigerant (R 134a) in the air-conditioning systems of these vehicles is ultimately emitted into the atmosphere.

Table 3.2: Car air-conditioning systems in Germany – HFC-134a refrigerant charges and emissions from 1995-2008 [BReg 2004; Schwarz 2004; Schwarz 2003a; Schwarz 2010; Schwarz 2010a]

	1995	1998	2000	2002	2004	2006	2008
Initial charge of R 134a (new vehicle manufacture incl. export vehicles) (t)	1,446	3,345	3,486	3,473	3,623	3,779	3,806
Quantity of R 134a in cars in Germany (t)	1,680	6,523	10,782	14,783	18,537	21,846	23,645
R 134a emissions from air-conditioning systems (t)	133	561	984	1,401	1,817	2,292	2,696
R 134a emissions from air-conditioning systems (million t CO ₂ equivalent)	0.17	0.73	1.3	1.8	2.4	3.0	3.5
Percentage of new cars fitted with A/C ¹¹	25%	62%	80%	87%	93%	96%	96%

Car refrigerant circuit

The air-conditioning system removes heat from the interior of the car and discharges it to the outside. The refrigerant circuit of an R 134a car air-conditioning system consists of the following components: compressor, condenser, drier/accumulator, expansion valve, evaporator, hoses and pipes and control equipment. All the components are joined to form a closed circuit (see Figure 3.7). The air-conditioner works on the principle of a compressor refrigeration system (see Chapter 3.1.1). If the engine is running and the air-conditioning is switched on, the compressor draws in cold gaseous refrigerant from the evaporator and compresses it, causing it to heat up, and forces it into the condenser (high-pressure side). The compressed hot gas is cooled by the external air flowing past (external airstream or additional fan). Once the pressure-dependent dew point is reached, the refrigerant condenses. It is then collected in the accumulator, and any moisture and impurities are removed in the drier. The liquid refrigerant under high pressure flows through the expansion valve and is injected into the evaporator (low-pressure side). Here it expands and evaporates. The necessary heat of evaporation is extracted from the air flowing past the evaporator fins, and this cools the passenger cabin of the car.

¹¹ Air-conditioned vehicles as percentage of all new registrations for the year in Germany.

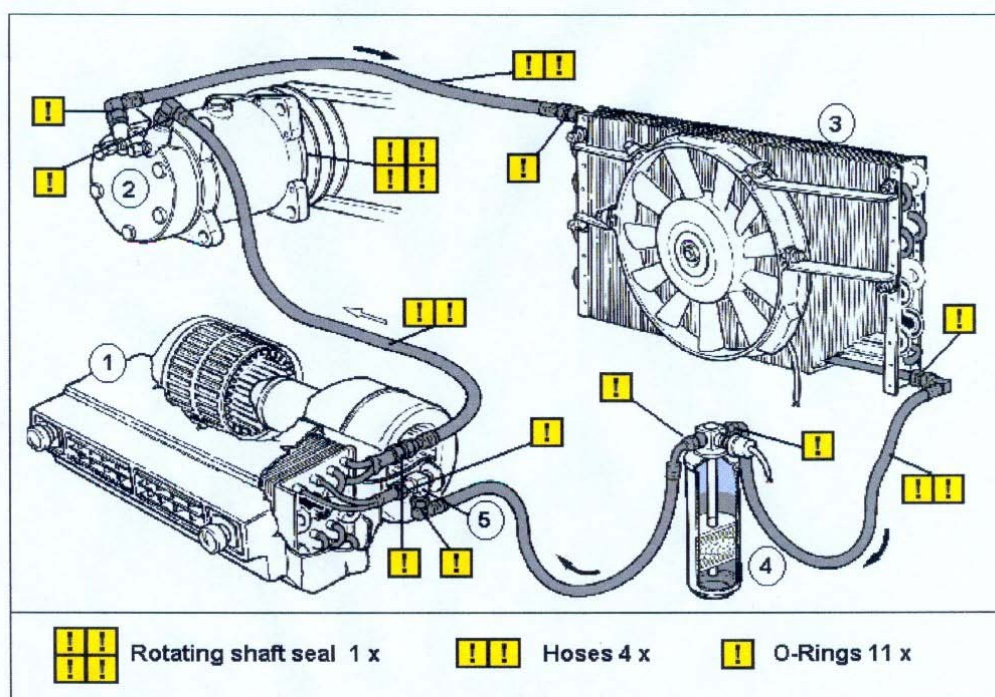


Fig. 3.7: The R 134a refrigerant circuit in a car.
The number of exclamation marks (!) indicates the importance of individual leak sites. Refrigeration circuit: 1: evaporator, 2: compressor, 3: condenser, 4: accumulator/drier, 5: expansion valve. From: [WAECO 2000, modified after Schwarz 2001].

The average refrigerant charge in Germany for newly registered cars with factory-fitted air-conditioning fell from 900 g in 1995 to 625 g in 2008 [Schwarz 2004; Schwarz 2010a]. The main leakage sites for refrigerant in the context of normal depletion (approx. 50 g per annum) are the compressor shaft seal, the hose system and the sealing rings (O-rings) (see Figure 3.7) [Schwarz 2001].

Reduction options

With effect from 1 January 2011, air-conditioning systems in new types of cars and small commercial vehicles must contain a refrigerant with a GWP not exceeding 150. Possible alternative refrigerants are discussed below.

CO₂ (R 744)

In the 1990s, German car manufacturers and the component supply industry had already identified CO₂ as the most suitable refrigerant for vehicle air-conditioning systems. The deciding factors here were its thermodynamic properties, its negligible contribution to the anthropogenic greenhouse effect (GWP_{CO₂} = 1) and its physical properties “non-flammable” and “non-toxic”. CO₂ is generated as a by-product in the chemical industry (see Chapter 1.4.1). However, the use of CO₂ in car air-conditioning systems makes it necessary to develop a completely new system with new components for the refrigerant circuit. This differs from a conventional R 134a air-conditioner in being designed for higher pressures of

up to 135 bar and having an additional internal heat exchanger. This heat exchanger is needed because at temperatures above 31°C CO₂ air-conditioning systems work with supercritical heat discharge [Parsch, Brunsch 2002]. It is also necessary to take precautions to prevent dangerous concentrations of CO₂ inside the vehicle's passenger cabin (see Chapter 1.4.1).

The advantages of using CO₂ as a refrigerant in cars is that there is no need for a second circuit as in the case of flammable refrigerants, and that no precautions against ignition are needed because CO₂ is itself a fire-extinguishing agent. Also there is no need to redesign the entire car, because it is possible to use the space hitherto occupied by the R 134a system. In fact the CO₂ air-conditioning system actually requires less space than an R 134a unit [Parsch 2002].

Compared with R 134a and R 152a, a CO₂ system permits faster cooling and faster heating of the passenger cabin. The better refrigeration capacity and hence better cooling bring gains in comfort for the customer and improvements in safety, thanks to faster demisting of steamed-up windows. Tests of the air-conditioners and in vehicles demonstrate the high efficiency of CO₂ as a refrigerant in car air-conditioning systems [Wieschollek, Heckt 2007; Wolf 2007; Neksa *et al* 2007; Graz 2009].

Calculations of life-cycle climate performance (LCCP) for car air-conditioning circuits with different components show that CO₂ is a refrigerant with advantages [Hafner *et al* 2004; Wolf 2007].

In 2002, Toyota, with assistance from Denso, placed the first commercial mobile car air-conditioning system using carbon dioxide on the market in Japan and California [COM 2003]. Since all the components are available today, the CO₂ air-conditioner for cars is ready for series production [Riegel 2007; Parsch 2007; Neksa 2007]. Several major car manufacturers and suppliers in Europe, USA and Japan equipped test vehicles with CO₂ air-conditioners, often in joint programmes [Mager 2003; Wertenbach 2005; Riegel 2007; Morgenstern 2008; SAE 2009].

As well as their cooling function in summer, CO₂ air-conditioning systems can be used in winter as heat pumps for faster heating of the passenger cabin, making it possible to do without other conventional but less efficient supplementary heating systems. Instead of technical implementation of the heat pump function of CO₂ air-conditioning systems, another system, the *hot gas cycle*, was tested. This technology, which has a slightly lower capital cost, can also replace a conventional supplementary heater. Supplementary heating will in future be needed for many vehicles, especially hybrid or all-electric vehicles, because the waste heat of a highly efficient engine or electric motor is not enough to supply adequate heat [VDA 2004; Heinle *et al* 2003; Heckt 2004]. The IAA 2010 saw the unveiling of a newly developed innovative heating/cooling module with CO₂ as refrigerant, which can also be used for electric cars [ixetic 2010].

HFC-152a (R 152a)

Some manufacturers (especially from the USA) considered using the fluorinated greenhouse gas 1,1-difluoroethane (R 152a) instead of R 134a. With a GWP₁₀₀ of 140, R 152a has a considerably lower global warming potential than HFC-134a (GWP₁₀₀ = 1,300). Since the

thermodynamic properties of the two substances are very similar, it would largely be possible to use the existing technology. However, R 152a – like hydrocarbons – is flammable (from 3.9 to 20.4% by volume), and its auto-ignition temperature is 455°C. It belongs to refrigerant safety group A2 [DIN 2008]. In the event of a fire R 152a, as a fluorinated substance, releases toxic hydrogen fluoride (HF). The other safety limits “practical limit”¹² and ATEL/ODL¹³ determined for the refrigerant R 152a on the basis of toxicity data and quoted in standards are lower than for R 134a and CO₂ [DIN 2008].

In 2008 the US Environmental Protection Agency (EPA) approved the refrigerant R 152a as an alternative substitute for R 12 and issued directions for its use in mobile air-conditioning systems. The air-conditioning systems must be designed so that passengers in the passenger cabin are not exposed to concentrations of R 152a exceeding 3.7% by volume for more than 15 seconds, even in the event of leakages [EPA 2008].

As early as 1990, safety concerns had resulted in German car manufacturers ruling out R 152a as a substitute for the CFC R 12. To solve the safety problems it is necessary to install magnetic valves before and after the evaporator or to install a second heat exchanger in conjunction with a second circuit. Some experts have fundamental doubts whether all safety problems can be solved at reasonable cost [Mager 2005]. The measures described for solving the safety problems would reduce energy efficiency and increase the cost, size and weight of the system. Further costs arise because the production and service personnel would have to be trained in handling a flammable refrigerant.

Hydrocarbons

Hydrocarbons such as propane and butane have proved successful as refrigerants in numerous applications. Since they have no ozone depletion potential and their global warming potential is very low, they are also recommended, e.g. by non-governmental organisations, for use in mobile air-conditioning systems. Retrofit demonstration projects have been run in Australia and the USA, for example with blends of 60% propane and 40% isobutane [COM 2003; Maclaine-cross 2004]. In the Philippines, the use of hydrocarbons to refill R 12 car air-conditioners is permitted [Hydrocarbons21 2010].

However, the fact that hydrocarbons are readily flammable represents a risk for car passengers. Their use in car air-conditioning systems is therefore banned in the United States, for example [EPA 2003]. Car manufacturers around the world will normally only consider the use of hydrocarbons in vehicle air-conditioning systems if the refrigerant can be kept hermetically sealed in the engine compartment by using a second circuit.

¹² Maximum concentration in an area frequented by personnel that does not require any acute escape measures.

¹³ ATEL: Limit value for the time that persons may be exposed to acute toxicity [kg/m³] / ODL: oxygen deficit limit [kg/m³].

New fluorinated substitute refrigerants

Since 2006 the chemical industry has put forward and then rejected in quick succession a wide range of substitute refrigerants with a global warming potential of less than 150. To date the HFC R 1234yf has been pursued further.

HFKW-1234yf – R 1234yf

The chemical name of the substance with the designation R 1234yf is 2,3,3,3-tetrafluoropropene, and its empirical formula is $\text{CF}_3\text{CF}=\text{CH}_2$. Tetrafluoropropene belongs to the hydrofluoroalkene group. A large proportion of the manufacturing patents for R 1234yf are held by Honeywell or DuPont [Patente 2010]. In January 2010 Honeywell announced that a European Patent, which Dupont could share in, had been granted for the use of R 1234yf in air-conditioning systems [Chemie.DE 2010, EP 2010]. Honeywell has applied to the European Patent Office (EPO) for further patents for the production of R 1234yf [Wang 2009; Chiu 2010; Nair 2008]. Other chemicals manufacturers have also applied for patents for the production of R 1234yf or for refrigerant blends using R 1234yf [Elsheikh 2009; Rached 2010], as have manufacturers of air-conditioning systems outside Europe [Lim 2009].

R 1234yf has a GWP_{100} of 4, and its ODP is 0. Its atmospheric lifetime is 11 days [Nielsen *et al* 2007; Papadimitrou *et al* 2008]. The degradation products correspond to those of R 134a [Yau 2008]. Examples of R 134a degradation products include $\text{HC}(\text{O})\text{F}$ and $-\text{CF}_3$ - radicals at the Earth's surface and $\text{CF}_3\text{C}(\text{O})\text{F}$ in the tropopause¹⁴ [Tuazon, Atkinson 1993; Hurley UBA. 2008]. Trifluoroacetic acid (CF_3COOH) is also being discussed as a degradation product [Kajihara 2010; Luecken 2010] (see also Chapter 1.3.1).

The occupational exposure limit for R 1234yf for 8 hours (TWA value)¹⁵ is quoted by Honeywell as 400 ppm and by DuPont as 500 ppm [Honeywell 2008; DuPont 2009]. AIHA has fixed a TWA-limit of 500 ppm¹⁶ [AIHA 2010].

R 1234yf is extremely flammable: its lower explosion limit is 6.2% by volume, and its upper explosion limit 12.3% by volume [Dupont 2009; Honeywell 2008]. Using common European measurement procedures, the upper explosion limit of R 1234yf was found to be higher, at 14.4% by volume in air [BAM 2010]. According to the CLP Regulation [GHS 2008] the substance R 1234yf must be labelled “H220: Extremely flammable gas”. The self-ignition temperature of R 1234yf is 405°C (for comparison: propane 470°C). R 1234yf has a density four times higher than air. Therefore it can accumulate at ground level and form explosive mixtures there. In practical tests with settings close to application conditions, the Federal

¹⁴ Tropopause: Atmospheric layer with an upper limit at a height of about 10-15 km, above which the much less turbulent stratosphere begins.

¹⁵ TWA (Time Weighted Average) corresponds to the German maximum workplace concentration (MAK) and workplace limits (AGW).

¹⁶ For comparison: The TWA of R 134a is 1,000 ppm [AIHA 2010].

Institute for Materials Research and Testing (BAM) confirmed the formation of explosive gas mixtures and toxic hydrogen fluoride (HF) in connection with the use of R 1234yf. In the event of a fire or explosion, concentrations above 90 ppm HF were measured in the passenger cabin. Even without an explosion or fire, moreover, hydrogen fluoride forms on hot surfaces such as are commonly found in engine compartments.

In view of its flammability and the formation of hydrogen fluoride the car industry needs to systematically analyse various scenarios before using and handling R 1234yf, and to carry out a comprehensive risk analysis. Adequate safety precautions must be taken when using this refrigerant [BAM 2010; UBA 2010a]. Examples of these include rigorous shielding of hot surfaces and the installation of an automatic extinguishing system in the engine compartment, measures to prevent hydrogen fluoride entering the passenger cabin in dangerous situations, measures to prevent sparking in the event of an accident (including cutting off the power supply), and informing and training rescue personnel.

In 2009 a working group of the SAE (Society of Automobile Engineers) made a safety study of R 1234yf [SAE 2009]. Since the data on which this study was based have not been published, it is not possible to follow the results.

According to DuPont and Honeywell, the performance of car air-conditioners using R 1234yf is comparable to that of R 134a systems [Yau 2008; Spatz 2009; Sorg 2009]. This is however a comparison of systems with different degrees of optimisation. Although the thermodynamic properties of R 1234yf are similar to those of R 134a, on the basis of the refrigeration diagram it is not possible to identify any advantages regarding the energy consumption of R 1234yf compared with the existing refrigerant R 134a. On the contrary, the refrigeration capacity of R 1234yf is 8-10% [Petitjean 2010] or 10-15% [Eusitice 2010] lower than that of R 134a. Investigations by the component supplier Visteon revealed that the capacity of R 1234yf was up to 10% lower than that of R 134a in an identical air-conditioning system [Wieschollek 2009]. To achieve the same performance as the conventional R 134a system, the R 1234yf system needs to be optimised [Petitjean 2010; Eustice 2010]. However if the R 134a systems were optimised, R 134a would once again display better performance than R 1234yf.

R 1234yf systems need new refrigeration oils and additives to stabilise the refrigerant/oil mixtures. R 1234yf is very sensitive to moisture and air [Seeton 2010; Grimm 2010; Dixon 2010]. All components of the refrigeration circuit must be tested for compatibility with the refrigerant/oil/additive system that has yet to be developed. The miscibility of R 1234yf with the refrigerant oil at higher temperatures still needs to be improved. Refrigerant oil manufacturers and refrigeration research institutes expect the development of suitable oils and additives for R 1234yf to be much more complicated than for R 134a. In the end, only a suboptimal solution will be possible with regard to the necessary material and refrigeration properties of R 1234yf [Grimm 2010; Dixon 2010].

Production impurities in the refrigerant R 1234yf can considerably reduce the stability of the refrigerant/oil/additive system and of the refrigeration circuit components and seals [Grimm 2010]. The individual manufacturer's specifications for R 1234yf must be described very precisely and documented batch by batch. Moreover, one of the constituents of R 1234yf is

the toxic substance 1,2,3,3,3-pentafluoropropene (1225ye), the concentration of which should be limited to a maximum of 150 ppm. The concentration of other contaminating compounds in R 1234yf, which can affect the stability and life of the oil, must not exceed 0.5%. The composition of the impurities varies depending on the production process for R 1234yf [Low, Schwennesen 2009; Seeton 2010].

R 1234yf cannot simply be dropped into the old R 134a system. For example, it is necessary to replace plastic materials such as seals and hoses. Therefore, the substance cannot be regarded as a drop-in solution.

The production technology for R 1234yf is not yet operating on an industrial scale. DuPont plans to start commercial deliveries to the car industry in the fourth quarter of 2011. A plant for global-scale production is to follow later [Seeton 2010]. No precise information is available to date either on the costs of the refrigerant R 1234yf itself or on the cost of the relevant system technology. The refrigerant costs quoted are 10 to 20 times those of R 134a [Sorg 2009; Eustice 2010].

Other refrigerants under discussion

In 2009 a chemicals manufacturer announced a new blend of fluorinated substances, but this will not be available on the market until 2014 at the earliest [Low 2009; Low, Schwennesen 2009]. It contains HFC-1243zf, HFC-32 and HFC-134a, but its exact composition has not yet been disclosed. Its global warming potential is said to be in the region of 150. This blend too is flammable. It is however said to have better energy properties than R 134a and R 1234yf [Low 2009; Low, Schwennesen 2009; UNEP 2010].

Conclusions

In Germany, as in other countries, the trend towards fitting new vehicles with air-conditioning systems as standard equipment has led to a massive increase in both direct greenhouse gas emissions – due to the refrigerant R 134a – and indirect emissions – through the resulting higher fuel consumption.

One short-term measure for reducing refrigerant emissions is the introduction of R 134a technology with reduced leakage rates. Owing to the growth in the total number of air-conditioning systems in all sectors, however, total emissions will continue to rise in the years ahead. But it is hardly possible to monitor emissions throughout the life of a car. This applies in particular to the recovery of refrigerant from end-of-life vehicles, which are frequently sold abroad before being scrapped.

In 2006 the European Commission, in fulfilling its obligations under the Kyoto Protocol, issued binding legal provisions aimed at reducing emissions from air-conditioning systems in cars and small commercial vehicles. The phase out of R 134a in air-conditioning systems in cars and small commercial vehicles throughout Europe starts in 2011. In the opinion of the Federal Environment Agency the refrigerants R 152a and R 1234yf, which have similar thermodynamic properties but a much lower global warming potential than R 134a, are not suitable alternatives either from an ecological or from a technical point of view. Moreover, the second circuit that seems likely to be necessary for safety reasons, or other comparable safety measures, make its cost-effectiveness questionable.

Years ago, German car manufacturers rejected R 152a and hydrocarbons as suitable refrigerants for car air-conditioning systems.

Until the end of 2008 the research activities of German car manufacturers were focused on CO₂. The leading car and component manufacturers developed mobile air-conditioning systems for the climate-neutral refrigerant CO₂. In Japan and California the first commercial products were on the market as early as 2002. At present the cost of an individual system is still higher than for the conventional R 134a technology. Improvements to a number of components and series production will however bring considerable reductions in the extra cost compared with an R 134a system. CO₂ mobile air-conditioning systems are ready for series production. Tests with CO₂ mobile air-conditioners installed in vehicles have demonstrated their efficiency.

Since 2006 the chemical industry has developed several new refrigerants; of these, R 1234yf has been pursued further. In view of its flammability and its chemical instability, the use of R 1234yf involves risks and additional pollution of the environment. Satisfactory answers have yet to be found to fundamental issues such as suitable refrigeration oils and long-term stability.

Taking all aspects into account, CO₂ is clearly the best refrigerant currently available.

3.3.7.2 Other mobile air-conditioning systems

In 2008, emissions of the HFC refrigerant R 134a by the following applications totalled: trucks 151 t, buses 94 t, agricultural machinery 60 t, rail vehicles 14 t and air-conditioning units in ships 23 t [Schwarz 2010].

Buses (long-distance coaches, interurban buses, city buses)

In Germany today, 100% of all new long-distance coaches delivered are equipped with air-conditioning. In the case of interurban buses, which are used for regional services on weekdays and for tourist traffic at weekends, about 73% of vehicles are delivered with air-conditioning systems. To create incentives to use public transport, city buses are also increasingly being equipped with air-conditioning. Whereas in 1993 only 5% of new city buses had air-conditioning, the figure rose to 40% in 2002 and reached 64% by 2008. The refrigerant used is almost exclusively R 134a [Schwarz 2004; Schwarz 2010; Schwarz 2010a]. For years now, air-conditioning systems in buses have continued to use the vapour-compression process. In most cases they use standard refrigeration components. Different concepts are employed for air-conditioning these vehicles: whereas long-distance coaches are usually equipped with more or less complex split air-conditioning systems¹⁷, in the case of city and interurban buses there has from the start been a trend to equipping them with simpler and hence cheaper roof-mounted compact systems. With the exception of the evaporator, these combine all components necessary for air-conditioning in a single unit. The compressor, which is frequently power-controlled, receives its power direct from the vehicle engine via a V-belt and an electromagnetic clutch [Mayer 1997]. Since the introduction of the refrigerant R 134a (from about 1995 onwards), the systems have generally used fixed pipes, the only flexible hose connection being to the compressor.

The refrigeration capacity is between 12 and 30 kW (split systems) or between 18 and 24 kW (roof-mounted compact systems) [Mayer 1998]. The systems are designed in such a way that in the cooling mode they can maintain a temperature difference of 2-3 Kelvin below ambient temperature in the case of city and interurban buses, or 5-8 Kelvin in the case of long-distance coaches. Controllable fresh-air operation (up to 100%) is generally standard. In addition, nearly all systems are fitted with water-cooled heating registers, which permits heating of the vehicle as well [Mayer 1997].

The average annual leakage rate of new bus air-conditioning systems is 13.3% of refrigerant for long-distance coaches and 13.7% for scheduled-service buses, according to a study on behalf of the European Commission [Schwarz 2007b].

In the bus sector there are two possibilities for minimising emissions and reducing costs. One is to use a liquid chilling package that can also be operated with natural refrigerants (e.g. propane, CO₂), the other is to use the natural refrigerant CO₂ (R 744) in the usual bus air-

¹⁷ Several evaporators inside the bus and an evaporator for the driver's seat ensure the right temperature.

conditioner types (roof-mounted system) [Mayer 1998; Kirsamer 1999; in Schwarz, Leisewitz 1999; Sonnekalb 2002].

Compact air-conditioning system with secondary circuit (liquid chilling package)

The heart of the liquid chilling package is the so-called “energy station” at the back of the bus, a compact assembly consisting of a plate evaporator, standard condenser, all necessary valve groups, the water equalising tank, and the auxiliary heating system. In the passenger compartment, water heat exchangers are used instead of evaporators [Mayer 1998].

Unlike the roof-mounted system driven by the rear engine, with more than 10 kg of circulating refrigerant, the primary circuit needs only a few kilograms of refrigerant. In this way the refrigerant charge was reduced from 12 kg to 7 kg in a quarter of all long-distance coaches [Schwarz 2004]. The small assembly as supplied to the bus manufacturer is fully pre-assembled, tested and filled with refrigerant. As well as the marked reduction in refrigerant charge, low leakage rates, better control convenience and reduced maintenance result in considerable cost savings for the bus manufacturer combined with improvements in performance. The result is even more favourable if the system is installed outside the passenger compartment and natural refrigerants such as propane or CO₂ are used in the primary circuit.

Roof-mounted air-conditioning system with CO₂

In 1996 the first bus worldwide with an air-conditioning system based on CO₂ went into public transport in Bad Hersfeld. One year later a second bus was put into regular service. The long-term test in city traffic – more than 2,000 operating hours – showed that the CO₂ air-conditioning system developed by Konvekta AG, with commercially available open compressors, worked well and was very reliable. Comparative measurements on a city bus that was identical apart from the refrigerant used (with the necessary modifications) revealed no differences with regard to refrigeration capacity, efficiency and dynamic behaviour. Konvekta AG, one of the market leaders in the bus air-conditioner sector, continued to optimise the CO₂ system. Today several city buses are equipped with CO₂ air-conditioning systems. Since mid 2009 the BVG has been running a city bus with a CO₂ system, and six more buses went into service in mid 2010 [BVG 2010]. Saar-Pfalz-Bus, a subsidiary of Deutsche Bahn, has one vehicle in service with a CO₂ system, and it is due to be joined by five more [BReg 2010]. Instead of 10 kg of R 134a, the system needs only 5-6 kg of CO₂ as refrigerant. By converting from R 134a to CO₂ it is possible to save about 30% of the direct and indirect greenhouse gas emissions. A reduction in the cost of CO₂ systems can be expected if the air-conditioning systems are installed by the bus manufacturers themselves, in which case the cost would be about 20% above the price for present-day R 134a systems. As a result of the reduction in operating and maintenance costs, the payback period for a CO₂ system works out at only 4 to 5 years [Sonnekalb 2002; Sonnekalb 2003; Konvekta 2010].

A concept for a compact roof-mounted system with a 24-volt electrically powered R 744 refrigerant compressor has also been proposed for city buses [Rindsfüßer 2008]. All refrigeration components are included in the assembly, the air management system is modified, and the air-conditioner is fitted in the emergency exit opening which is not needed

in city services. The system is hermetically sealed to a very large extent, which reduces maintenance work. To date the concept has not been introduced, partly because of the lack of suitable R 744 components.

Combination of cooling and heating

A new possibility for buses is to use an air-conditioning system with a heat-pump function, which improves the efficiency compared with conventional heating systems using burners or electric heaters. Tests have already been carried out and documented [Sonnekalb 2009]. In summer 2010 a city bus will be equipped with a CO₂ air-conditioning system with heat-pump function [Konvekta 2010].

Truck cabs and other drivers' cabs

The technical development of air-conditioners for trucks cabs or drivers' cabs on utility vehicles (such as construction or agricultural vehicles) is closely connected with developments in the car and bus sectors. When phasing out CFCs, the manufacturers developed, with a slight time-lag, modified solutions for specialised applications in trucks and utility vehicles, using the same technology as for cars. The means that in the case of trucks and utility vehicles any phase-out of R 134a and introduction of CO₂ systems, which is technically possible, is not likely to take place until this has been done for cars, once the necessary technologies have proved successful and the components are available on the market at affordable prices.

With the growing demands on drivers with regard to concentration and reaction capacity, the percentage of new vehicles fitted with air-conditioning systems has increased in recent years. In 2008, 45% of small commercial vehicles (< 1.5 t), 43% for medium-sized and 85% of large commercial vehicles (> 7.5 t) were equipped with air-conditioning [Schwarz 2010; Schwarz 2010a]. The refrigerant charges are between 700 g and 1,450 g, i.e. an average of around 1 kg, and are thus slightly larger than in cars [Schwarz 2004; Schwarz 2007a]. The average annual leakage rate, taking account of irregular emissions, is put at 11% of the refrigerant charge [Schwarz 2007a].

Rail vehicles

Air-conditioning in the railway sector has a long tradition. Until the 1990s, mainly long-distance trains in Germany were equipped with air-conditioning systems. Today air-conditioning is usual in local trains, suburban trains and new trams even in regions with a temperate climate. In underground trains in Germany, only the driver's cab has been air-conditioned to date. The local transport sector uses air-conditioning systems that have proved successful in buses. Today's air-conditioners are preferably executed as compact systems and combine a number of functions: cooling, ventilation, heating and - in high-speed trains - pressure protection. The units and/or components can be located in the roof, under the floor or inside the vehicle structure [Adolph 1998].

The cooling or heating capacity of the individual system depends on the ambient thermal conditions and the requirements for passenger comfort, the insulation of the vehicle, the passenger load, i.e. the number of passengers, the ratio of external to internal air, and the

electrical consumer load in the air-conditioned zone, such as lighting, fan motors or control devices [Adolph 1998].

In Central Europe the refrigeration capacity needed for about 70 passengers per railway carriage is about 25-35 kW, of which about 10 kW is required for dehumidification. Drivers' cabs and power cars need a refrigeration capacity of about 5-10 kW because of the higher fresh-air rate required, the large windscreens used in many cases, and the waste heat from numerous additional electrical control devices [Adolph 1998]. Heat insulation is generally good in trains, whereas the level of insulation in buses and trams has fallen because of the light-weight design and large windows.

After the phase-out of the CFC refrigerants R 12 (in Germany) and R 22 (southern Europe), which were used in the early phases of railway air-conditioning, only R 134a is now used in Germany. In southern Europe the HFC blend R 407C¹⁸ is also used.

Air-conditioning systems in railway passenger cars of local or long-distance trains and ICE (high-speed) trailers contain an average of 18 kg of refrigerant, commuter trains 10 kg and driver's cabs and power cars 2.2 kg [Schwarz 2004]. After 1995 the total quantity of R 134a in railway air-conditioning systems displayed a nearly tenfold increase to reach 224 t in 2008 [Schwarz 2010]. Hermetic or semi-hermetic systems are generally used for air-conditioning in trains. The annual emission rate of new railcar air-conditioning systems is estimated at 5%. Units with open compressors driven directly by the diesel engine, known as diesel-driven multiple units (DMU), have an annual emission rate of 10% [Schwarz 2007]. The emission rates of converted older systems are about 25% higher [Schwarz 2004]. Emissions from railcars are on the increase: in 1995 they stood at 2 t, and by 2008 they had reached 14 t [Schwarz 2010]. Deutsche Bahn AG has a total of 10,500 passenger compartment air-conditioners, 95% of which use the refrigerant R 134a [BReg 2010].

In 1989 the Danish railways installed an indirect cooling system with a primary refrigerant circuit and a secondary water circuit in 150 passenger cars of the IC/3 "Rubber Nose" series. Instead of 12 kg of refrigerant for a single direct circuit, this needs only 6 kg [Schwarz 2007].

An innovative solution is found in the trains of the ICE 3 series of Deutsche Bahn AG, which are cooled with cold air, a technology used for aircraft. In summer 2003 problems were encountered during operation of the first generation of AC systems, which were then modified and improved. The trains of the second ICE 3 series were equipped with different cold-air systems, which work without any technical problems and are very service-friendly. A total of 504 air-cooled systems for passenger cell air-conditioning are in service, i.e. 5% of all systems [BReg 2010]. DB has yet to conduct an overall review of the air-cooled systems. However, calculations indicate that the air-cooled systems can make sense from an energy point of view, for example in high-speed trains operating in middle latitudes [Aigner 2007, Liebherr 2010]. One advantage for servicing is that there is no handling of R 134a. On the

¹⁸ The HFC blend R 407C consists of R 32 (23%), R 125 (25%) and R 134a (52%).

other hand, the latest trains in this series have gone back to conventional R 134a air-conditioning systems [Wüst 2010]. However, the latest air-cooled systems optimised for trains, on show at Innotrans 2010, indicate that air-cooled systems continue to be available for future applications [Liebherr 2010].

In summer 2010 there were a number of failures in air-conditioning systems on ICE 2 trains. These were R 134a systems. DB has not yet taken any decisions on future air-conditioning systems for the new trains of the ICX series; the railway company is calling for an environmentally sound, non-flammable and non-toxic refrigerant that is approved for the lifetime of the vehicle [BReg 2010].

When choosing a new refrigerant for rail vehicles, it is necessary to satisfy a wide range of requirements and carry out trials to ensure that these are met, e.g. with regard to fire precautions, maintenance, operating costs, environmental impacts or availability [BReg 2010]. Moreover, railway air-conditioning systems have to be developed separately, or at least adapted, for the various climate zones and types of trains.

CO₂ air-conditioning systems could be an alternative to R 134a systems for use in trains. In this context it is important to target a lower overall contribution to the greenhouse effect (TEWI), something which is basically feasible from a technical point of view with CO₂. Most components needed to build CO₂ air-conditioning systems for railcars are now available on the market. The estimated lead time for the first new trains with CO₂ systems is in the region of 2-3 years.

Deutsche Bahn AG is planning to equip a diesel trainset with a prototype CO₂ system based on CO₂ air-conditioning technology for buses (see section on buses). Test operation is to start in 2011 [Konvekta 2010; BReg 2010]. The CO₂ system is about 20% more expensive than an R 134a system. Thanks to savings on maintenance and energy consumption, the payback period for a CO₂ air-conditioning system is about 5 years [Konvekta 2010].

Prototypes of compact electrically driven CO₂ air-conditioning systems for electric and diesel-electric rail vehicles such as trams and local trains have undergone long-term tests (10,000 hours) in a climate test rig, which means that first vehicles could now be equipped for test operation [Konvekta 2010; Presetschnik 2008 and 2010].

An electrically driven CO₂ under-floor unit has been undergoing tests in the Czech Republic since 2007 [Presetschnik 2008].

In general, the energy consumption of railway air-conditioning systems needs to be determined on a project-specific basis; it depends on the individual system concept and on the operating and ambient conditions. Measurements of the annual energy consumption of a CO₂ prototype system for passenger cars revealed that consumption was 52% lower than for a conventional R 134a system and 12% lower than for an optimised R 134a system [Aigner 2007; Morgenstern, Ebinger 2008].

A new means of optimising heat management in trains is offered by a combination of the functions cooling in summer and heating in winter with the refrigerant CO₂. Tests have been performed in a climate test rig and in buses [Presetschnik 2008 and 2010; Sonnekalb 2009;

Hafner 2010]. Computer simulations indicate that by implementing heat-pump heating with CO₂ as refrigerant, energy consumption could be reduced by up to 78% compared with electric heating, depending on the climatic situation [Hafner 2010].

Ships

All 353 sea-going ships (cargo vessels) under the German flag with a gross registered tonnage (GRT) of more than 100 are air-conditioned, as are 16 passenger ships and 1 cruise liner. After brief tests with the refrigerant R 407C, conversion to R 134a took place from 1996 onwards. The HCFC R-22 was still used up to the end of 1998. Average refrigerant charges are 100 kg in new cargo vessels, 250 kg in passenger ships and 500 kg in naval vessels. Cruise liners each have an air-conditioning system with about 1,000 kg of refrigerant [Schwarz 2004].

By contrast, the more than 1,300 cargo vessels and tankers in the inland waterway sector are basically not air-conditioned. They use household appliances to cool provisions on board. However, new passenger vessels are air-conditioned throughout, using R 134a since 1997. Cabins ships need an average of about 250 kg and day cruisers about 100 kg of refrigerant [Schwarz 2004].

As a rule they use water chillers, i.e. water and not refrigerant circulates through long pipes [Schwarz 2004]. Ship air-conditioning systems are relatively prone to leaks. Systems with direct evaporation of the refrigerant (as in cargo vessels) emit 40% per year, indirect systems (as in passenger ships) 20% of the refrigerant charge [Schwarz 2007].

Conclusions

Since the technical development of air-conditioning systems for trucks and utility vehicle cabs is closely connected with developments in the car sector, the reader is referred to the conclusions in Chapter 3.3.7.1 (Car air-conditioning systems) for the basic technical means of reducing greenhouse gas emissions in this sector. Phasing-out of the refrigerant R 134a should be targeted in the above mentioned sectors as well. The use of flammable refrigerants such as hydrocarbons, HFC-152a or new flammable refrigerants in the hydrofluoroalkene group is difficult to imagine because of the large refrigerant charges required in these applications by comparison with car air-conditioners. At most, systems with a secondary circuit might be an exception here. But then these could contain hydrocarbons instead, and the use of R-152a or other fluorinated refrigerants would not be necessary. In view of this and other aspects it would be desirable - as in the car sector – to give preference to the climate-neutral refrigerant CO₂.

After years of trials with test vehicles, several city buses have been in daily service since 2010 with CO₂-based air-conditioning systems. The systems used in the rail sector are similar to those in the bus sector. Long-term tests with CO₂ systems have proved successful. A start could be made on their commercial introduction. In view of the special importance of rail vehicles for local public transport systems and the fact that rail vehicles are extremely durable goods with difficult constructional issues and special requirements with regard to availability, support should be provided for projects in this

sector in particular. The air-conditioning requirements should be calculated as precisely as possible, since mobile air-conditioning systems need energy and also increase the weight to be transported. For example, air-conditioning of the passenger compartments in underground trains could largely be dispensed with in Germany.

The manufacturers concerned draw attention to the fact that timely creation of a clear framework by the state authorities could stimulate the desired innovations. For this reason the EU regulations which at present impose bans relating to cars and small commercial vehicles only, should be supplemented by rules and deadlines for all other vehicles.

3.3.8 *Other applications/ use of PFC*

In addition to the specific fields of application already mentioned, there are many other areas where refrigeration is necessary. In some cases compliance with highly specialised requirements is needed. This applies, for example, to a number of medical and laboratory applications. On the other hand, standard refrigeration appliances are also used in laboratories and hospitals. For most refrigeration and air-conditioning applications, therefore, the reader is referred to the descriptions in the preceding sections. In particular, reference is made to the remarks about refrigeration units and systems in commercial refrigeration in Chapter 3.3.2 and on chillers in Chapter 3.3.5.2.

This report does not discuss the refrigeration requirements associated with special needs in the above-mentioned and other fields. However, since perfluorocarbons (PFCs) are used in a number of medical applications, e.g. refrigeration for cold chambers (very low temperatures) for the treatment of skin diseases¹⁹, this section takes a fresh look at the special problems associated with these substances. In view of their very high global warming potential (see Table 1.2), PFC emissions make a bigger contribution than HFC emissions to the anthropogenic greenhouse effect²⁰. Before using PFCs, therefore, it is important to investigate the suitability of substances with less impact on the climate. If it proves necessary to use PFCs, efforts should be made to minimise the quantities used and the emissions, and suitable measures taken to ensure this.

Another field of applications for fluorinated greenhouse gases that is not discussed in the preceding chapters is their use as an organic working fluid in ORC processes. ORC processes are used when electricity is generated from geothermal or solar heat sources, or when waste heat from industrial processes is utilised and the heat transformed into usable energy. Using organic working fluids instead of water vapour makes it possible to select the optimum working fluids for specific individual applications.

¹⁹ In this application, possible alternatives include refrigeration systems powered by the Stirling principle and cold gas processes.

²⁰ One exception here is emissions of HFC-23, which has a GWP₁₀₀ of 11,700.

In addition to pure hydrocarbons such as isopentane (e.g. Landau geothermal power plant), the working fluids used include HFC-245fa, HFC-134a and other fluorinated greenhouse gases. The decision in favour of a particular fluid depends on many factors, such as the temperature range of the heat source [Heberle *et al* 2009; BINE 2007]. Nevertheless, any decision on a working fluid must take into account not only its influence on the efficiency of the system, but also the global warming potential of the working fluid itself.

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Part B – Application areas and processes: use, emissions and alternatives

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Part B – Application areas and processes: use, emissions and alternatives

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4 HFCs as blowing agents for foam manufacture

German standard DIN 7726 defines ‘foams’ as a mass made up of open or closed cells whose raw density is lower than the raw density of its matrix [DIN 1982]. The matrix of the foam may consist of organic polymers (plastic foams) or inorganic materials (foamed concrete, foam glass). DIN 7726 classifies foams as rigid foam materials, semi-rigid foam materials, flexible foam materials, elastic foam materials, and elastomeric foam materials, depending on their resistance to deformation under a compressive load.

This section takes a closer look at foam plastics made from organic polymers, which can be divided into rigid foam, flexible foam and integral foam. DIN 7726 defines rigid foams as foam materials which, on deformation under compressive load, present a relatively high resistance: the compressive stress at 10% deformation (compressive strength according to DIN EN ISO 844 [DIN 2009c] is ≥ 80 kPa).

Technically, the most important base polymers for rigid foams are polystyrenes, polyurethanes and polyisocyanurates; also important to a certain extent are polyolefines, formaldehyde resins and polyvinylchloride. Characteristic properties of rigid foams are good insulating capacity, good moisture resistance and high mechanical strength.

On compression, flexible foams display relatively little resistance to deformation; according to DIN EN ISO 844 [DIN 2009c], the compressive stress at 10% compression is ≤ 15 kPa. In most applications the base polymers for flexible foams are polyurethanes.

German standard DIN 7726 defines integral foams as structural foams that are chemically homogeneous over their entire cross-section, but whose density continuously decreases from the outside to the inside. They are characterised by a soft or porous core and a virtually solid outer skin. Again, the most commonly used base polymer is polyurethane.

There are two ways to achieve a typical foam structure:

- By using a “chemical” blowing agent that forms directly during the polymerisation process. An example of this is the foaming process for polyurethane, where water or carboxylic acids present during the polyaddition process react with isocyanates to release CO_2 , which has a blowing and foaming effect.
- By adding a “physical” blowing agent: here substances or preparations are added as blowing agents which either evaporate from the liquid solution during the polymerisation process or decompose at a certain temperature to form gas (CO_2 , N_2). Examples of suitable physical blowing agents include volatile organic compounds such as pentane, but also CFCs, HCFCs or HFCs.

Using a physical blowing agent offers a number of advantages:

- No additional components enter the foam matrix.
- As it evaporates, the blowing agent cools down the exothermic polyaddition reactions during polyurethane foaming.
- If a suitable blowing agent is chosen, it can be used as a cell gas to improve the thermal insulating properties of the foam.

Owing to the above-mentioned advantages of physical blowing agents, they are often the preferred option in many applications. The following discussion therefore focuses on the use of physical blowing agents.

Emissions of HFCs as blowing agents for foam plastics and estimates of emission trends are described in detail in the general part of this report (see Part A, Chapter 1.3 and Chapter 2). Today the use of HFCs as blowing agents is responsible for about 17% of total HFC emissions in Germany (2008). This means that there has been a substantial drop since 2000/2002, which is due in particular to the reductions in the field of PUR caulking foams and XPS foams. HFC emissions from the manufacture and use of foams amount to 1.02 million t CO_{2eq}. They thus account for 9% of total HFC emissions in Germany (see Table 2.1 and Table 2.2).

Efforts to reduce the use of HFCs are being thwarted by the use of 2-chloropropane as a blowing agent for rigid phenolic resin foam panels. This substance damages the ozone layer, and its use is therefore a retrograde step within the process of phasing out CFCs and HCFCs. Although 2-chloropropane has only a slight ozone depletion potential (ODP) of 0.002 [UNEP 2006] and does not belong to the list of regulated ozone-depleting substances, products foamed with 2-chloropropane do not seem to offer any significant advantages in terms of thermal insulation properties that would justify the use of this substance. On the contrary, their thermal conductivity is actually higher than that of insulation panels containing HFCs [UNEP 2006]. 2-chloropropane has a highly narcotic effect, is very volatile and highly flammable [IFA 2010]. These properties call for extensive health and safety measures in foam production. The blowing agent also escapes from the closed-cell panels during finishing and cutting, and also during use. The remaining residues of this problematical cell gas are finally released on disposal, if not before. There is also the risk of irritant corrosive chlorine gases forming in the event of a fire. For environmental and health reasons, the use of 2-chloropropane as a blowing agent should be discontinued and preference should be given to blowing agents such as CO₂ or hydrocarbons.

4.1 Rigid foams for thermal insulation

An overview of the thermal insulation market in the building sector in Germany is provided by Figure 4.1 and Table 4.1. It should be noted that, for cartel-law reasons, the Thermal Insulation Industry Association (*Gesamtverband Dämmstoffindustrie – GDI*) no longer publishes such data, so the most recent figures available are for 2005.

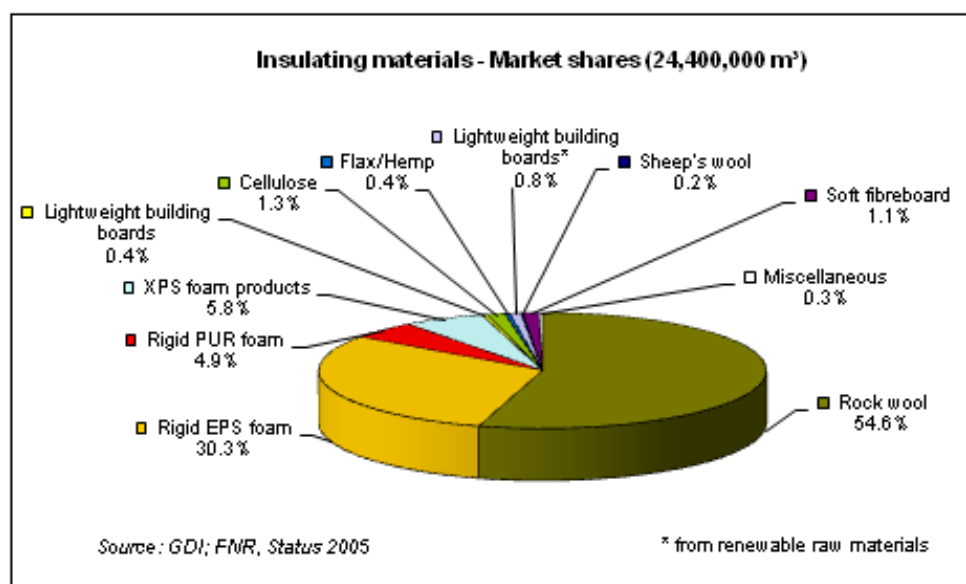


Fig. 4.1: Thermal insulation market in the building sector in Germany [GDI 2006].

Sales of thermal insulation materials in the building sector displayed rapid growth in the early 1990s and reached a peak in 1999. Since then they have fallen by about 31% [GDI 2006]. This decline was probably due to the economic situation and affected all insulating material groups considered by the GDI. Only XPS insulating materials (rigid foam made from extruded polystyrene) grew by 10% between 1999 and 2005.

Table 4.1: GDI building market statistics 1996 – 2005 [GDI 2006]

Product groups (figures in 1,000 m ³)	1996	1999	2000	2001	2002	2003	2004	2005
(1) Mineral wool insulating materials	18,980	21,300	19,980	16,770	15,840	15,572	14,574	13,320
(2) EPS rigid foam insulating materials	9,100	9,738	9,611	8,448	8,025	7,985	7,757	7,439
(3) PUR rigid foam insulating materials	1,365	1,588	1,572	1,484	1,389	1,428	1,398	1,198
(4) XPS rigid foam insulating materials	985	1,296	1,383	1,351	1,310	1,336	1,452	1,426
(5) Insulating lightweight building boards	310	260	240	206	176	159	132	95
Interim total	30,740	34,182	32,786	28,259	26,740	26,480	25,313	23,478
Rigid EPS foam insulating materials*	-170	-140	-129	-114	-102	-93	-72	-50
Insulating materials market**	30,570	34,042	32,657	28,145	26,638	26,387	25,241	23,428

* These quantities of EPS rigid foam insulating materials are processed in multi-layer building boards to DIN 1101. They are also included in Group 5 of these statistics and are therefore deducted from the total quantity [DIN 2000].

** These quantities of the product groups covered by GDI represent about 96% of the total building and construction market in the Federal Republic of Germany.

4.1.1 *Rigid XPS foam*

According to Bipro (2008), Germany's consumption of extruded polystyrene (XPS), also known for short as extruded foam, was nearly 1.9 million m³ in 2007. More than 80% of this figure went to the building and construction sector [Bipro 2008]. Owing to its closed cell structure, rigid XPS foam absorbs hardly any water even when in direct contact with it. It is rot-proof, very resistant to compression, but not UV resistant. The upper limit of the application temperature range is about 75°C.

Rigid XPS foam is produced in a continuous extrusion process: polystyrene pellets which do not contain a blowing agent are fed into an extruder, where they are melted. A blowing agent is then added and the mixture is continuously forced through a wide-slot nozzle. This results in a homogeneous closed-cell foam. The foamed extrudate that forms downstream of the nozzle can be produced in thicknesses between 20 mm and 200 mm (up to 320 mm with multi-layer bonding). After passing through a cooling zone, the foam undergoes mechanical processing to form panels and blocks with a variety of surface and edge properties. For example, the smooth skin resulting from the extrusion process is either left on the panels or removed by mechanical means on specialised panel types for better coupling in conjunction with concrete, mortar, building adhesives etc. Panels are also manufactured with special embossed surface patterns or rills.

In the building sector, rigid XPS foam is frequently used for external insulation in heavily stressed places in contact with the soil: below the floor slab of the building, and as insulation between the basement and the soil (“perimeter insulation”). Other areas of application are insulated roof membrane assemblies (single-shell, non-ventilated flat roof) or roofs with a shallow gradient. A special feature of the insulated roof membrane assembly is that the insulation layer, unlike that of conventional warm roofs, is on top of the roofing membrane. A special application is insulation of thermal bridges, which is becoming increasingly important.

In addition to the typical insulating material products for the building sector, rigid XPS foams are also used for specialised applications. These special products account for less than 10% of the European XPS insulation market, but cover a wide range of applications. No statistical data are available for these special products (types of application, quantities used) [Anhörung 2003]. They can be divided into the following categories:

- Panels and sandwich elements (with surface coverings made of steel, aluminium or wood);
- Building material in wet areas (for covering with tiles);
- Refrigerated vehicles, refrigerated containers, cold stores;
- Pipe insulation (in view of their maximum application temperature of approx. 75°C, rigid XPS foam materials are not suitable for insulating district heating pipes).

Until about 1989/1990, rigid XPS foam was produced using the CFC R-12 as blowing agent [UBA 1989]. In 1990 German manufacturers replaced R-12 with HCFCs. They used HCFC-142b or a blend of HCFC-142b and HCFC-22 [Schwarz, Leisewitz 1999]. Due to the ban on HCFCs ten years later it became necessary to replace these CFC-substitute blowing agents as well. Up to this time, no HFCs had been used in the production of rigid XPS foam. Even after that, some rigid XPS foam was produced without any fluorinated blowing agents at all; these products are used mainly in the building and construction sector. Other production processes use HFC-134a or HFC-152a as blowing agents [Harnisch *et al* 2003]. A figure of 893 t of HFC emissions from rigid XPS foam is quoted for Germany in 2007 [Schwarz 2009b]. Thus the production of rigid XPS foam insulating materials is the foam sector with the highest HFC emissions. The quantities of HFC-134a used have shown only a slight drop since 2001, whereas the use of HFC-152a was more than halved by 2007. However, this sharp drop has very little effect on climate-relevant emissions (2001: 0.8 million t CO_{2eq}, 2007: 0.6 million t CO_{2eq}), because HFC-152a has a relatively low global warming potential (140) [Schwarz 2009b].

As long ago as 1996 the biggest producers in Germany (BASF and Dow Chemical Deutschland) agreed, in a voluntary undertaking given to the Federal Environment Ministry, that by 30 June 1998 they would manufacture 80 percent of their insulation panels produced for the German market without using HCFCs and would switch their entire production to HCFC-free blowing agents by 1 January 2000. At the beginning of 1999 BASF AG switched its entire production for the building sector from HCFCs to halogen-free blowing agents (CO₂) [BASF 2010]. By contrast, Dow Chemical Deutschland did not comply with the phase-out deadlines and did not discontinue the use of ozone-depleting blowing agents until the end

of 2000. As an alternative, Dow Chemical uses HFC-134a as well as CO₂ [DOW 2010]. Today other manufacturers are offering, alongside HFC-free products, XPS insulating materials produced using CO₂ blended with HFC-152a or HFC-134a as blowing agents [Jackson 2010; URSA 2010].

Special products are mostly blown with blowing agents containing HFCs. Possible candidates here are HFC-152a and HFC-134a, either as single substances or in blends which may also contain CO₂ or organic blowing agents (ethanol) [Schwarz, Leisewitz 1999]:

- **HFC-152a:** The advantage of HFC-152a lies in its good solubility in the polystyrene melt, which results in a foam with a very fine and homogeneous cell structure. HFC-152a also offers the possibility that existing plant designed for HCFCs as blowing agent can be modified at relatively low expense to use the new blowing agent. Its technical disadvantage is its rapid diffusion out of the foam cells, which – according to various sources – results in its complete removal from the foam within a few weeks or within 2 years. As a result, HFC-152a does not permit any long-term improvement in heat insulation performance compared with XPS blown using CO₂. Since HFC-152a is flammable, its use calls for suitable operational safety measures in production. A further disadvantage is that the cost of HFC-152a is several times higher than that of CO₂.
- **HFC-134a:** Compared with HFC-152a, this blowing agent has the advantage that it is not flammable and that it remains in the product much longer, because its diffusion from the foam takes place almost as slowly as that of HCFC-142b. The half-life of a 100-mm thick panel is 76 years for HFC-134a and 84 years for HCFC-142b. Following the loss of 25% of the cell gas during the year of production, the annual emission rate works out at 0.66% for a panel thickness of 100 mm. One great disadvantage of HFC-134a is its high global warming potential. Unlike HFC-152a, HFC-134a does not dissolve readily in polystyrene, so the quality of the foam is limited with regard to cell structure and homogeneity. When used for rigid XPS foams, HFC-134a is therefore mostly combined with other blowing agents (HFC-152a, CO₂, ethanol). The manufacturers' main argument is an improvement in heat insulation performance as the primary objective of using HFC-134a, which is claimed to be advantageous in the long term because of the slower diffusion of the blowing agent out of the foam.

Reduction options

Some 80% of the rigid XPS foam materials produced in Germany today are foamed with CO₂ or a combination of CO₂ and organic blowing agents (approx. 2 to 3% ethanol) [Bipro 2008]. In the case of XPS, unlike rigid PUR foam, the CO₂ does not originate from a chemical reaction, but has to be added from outside like the other blowing agents. CO₂ is relatively difficult to handle as the blowing agent in an expansion plant and requires different technology from the HCFCs formerly used, because the production process is designed differently with regard to pressure. Fairly thin panels of up to 60 or 70 mm can be produced at low cost in small plants. For panel thicknesses of 80 mm or more, the technological effort

involved in modifying the plants is greater. However, the cost of converting the production plant is offset by the much lower cost of CO₂ compared with fluorinated blowing agents. XPS producers work on the basis that converting a plant costs in the region of 30 to 50% of the cost of a new plant [Anhörung 2003].

Using a combination of CO₂ with 2 to 3% of an organic blowing agent (ethanol), it is possible to produce the entire product range without any sacrifice in quality. Germany's largest manufacturer uses this approach [BASF 2010]. In addition to HFC-free XPS products, other manufacturers also offer XPS insulating materials using HFC-134a as blowing agent or CO₂ blended with HFC-152a [Dow 2010; Jackson 2010; URSA 2010]. HFC-152a, which is completely emitted during production, is employed here to create finer cell structures.

Before the introduction of the new European product standards¹ – in the case of rigid XPS foam this means DIN EN 13164 [DIN 2001a], replaced by DIN EN 13164 [DIN 2009a] – the standards for building products required the calculated heat conductivity for insulating materials for the construction sector to be stated in steps of 0.005 W/(m*K). This design value was specified in the form of a thermal conductivity group (TCG) (e.g. "TCG 035"). Since then the nominal thermal conductivity figure has been required to be specified in steps of 0.001 W/(m*K) or preferably 1 mW/(m*K).

According to manufacturers, the use of HFC-134a and HFC-152a is largely confined to specialised fields of application for rigid XPS foam, such as use in refrigerated vehicles and refrigerated containers or in panels and sandwich elements [Anhörung 2003]. But some manufacturers still offer XPS panels foamed with HFC for roof insulation, perimeter insulation or similar applications [Dow 2010; Gefinex 2010; URSA 2010]. For a technical point of view, it is possible to replace HFCs with HFC-free blowing agents not only in applications in the construction sector, but also in specialised applications. With the present state of the art, restrictions apply only to the lowest thermal conductivity levels (< TCG 035) in conjunction with greater panel thicknesses of 80 mm or more [Anhörung 2003]. An alternative here is to use CO₂-foamed multi-layer panels, which thanks to multi-layer bonding technology permit a panel thickness of up to 320 mm and heat transfer coefficients (U-Wert) of 0.15 W/(m²*K) [Bipro 2008]. Another possibility for such applications is to use vacuum insulation panels made from microporous silica or other rigid foam materials (e.g. HFC-free rigid PUR foam).

Another important aspect is the disposal of insulating materials foamed with HFC-134a. To permit environmentally sound waste management of rigid XPS foam products, they would have to be installed in a way that allows them to be removed separately and disposed of separately. Since controlled removal has not taken place in the construction sector in the past and cannot be expected in future either, it has to be assumed that the remaining HFC-134a left in the foam at the end of the period of use will undergo complete and uncontrolled release [Schwarz, Leisewitz 1999; Bipro 2008].

¹ The European product standards have been in force in Germany since 1.1.2004.

Conclusions

It is not necessary to use HFCs as blowing agents in rigid XPS foam for the construction sector. The entire product range can be produced with CO₂ as blowing agent or using a combination of CO₂ with 2 to 3% ethanol. Overall, the target should be a complete phase-out of HFCs in the production of rigid XPS foam.

All of the four manufacturers in Germany are already using CO₂ for their production (at least for a large proportion of their range), so the argument of high capital cost cannot be the decisive factor here.

Rigid XPS foam for thermal conductivities of less than TCG 035, which is produced for a small market segment of specialised applications, cannot be produced using CO₂ as blowing agent given the present state of the art. In this market segment one could conceivably replace rigid XPS foam with other products (such as HFC-free rigid PUR foam or vacuum insulation panels made from microporous silica).

4.1.2 *Rigid PUR foam*

Rigid PUR insulating materials are closed-cell, rigid plastic foams made of polyurethane (PUR). They have excellent thermal insulation performance. Factory-made rigid PUR foam insulating panels are standardised in accordance with DIN EN 13165 [DIN 2009b], and in Germany their quality is monitored by a quality monitoring association (*Überwachungsgemeinschaft Polyurethan-Hartschaum e.V. – ÜGPU*). The design figure for the thermal conductivity of PUR panels is commonly $\lambda(R) = 0.025, 0.028$ or $0.030 \text{ W/(m}\cdot\text{K)}$. Another property is their high compressive strength.

Rigid PUR foam is a thermosetting plastic, i.e. it does not melt even at high temperatures. The application temperature limits are -30°C to +90°C. Specialised products can be used even at lower or higher temperatures. For short periods rigid PUR foam can even withstand +250°C, a temperature which occurs during bonding with penetration grade bitumen.

In the building and construction industry, rigid PUR foam panels are mostly used to insulate flat roofs, saddle roofs, ceilings, floors – also in combination with under-floor heating systems – and walls. Another area of application is insulation for low-energy houses.

Rigid PUR foams are available in a variety of forms:

- appliance insulation foam (i.e. technical insulation for refrigeration appliances or hot-water storage tanks);
- flexible-faced laminates (rigid PUR foam composites with flexible surface skins made of aluminium, foil, paper or glass-fibre fleece);
- rigid slabstock (continuous production of rigid PUR foam, cut into panels, or discontinuous production of rigid PUR foam, used in blocks for various technical applications, and also in the building and construction industry);
- sandwich panels (predominantly with surface layers of steel);

- spray foams (e.g. foam that is poured or sprayed in situ for roof insulation);
- pipe insulation (e.g. for district heating systems).

Polyurethanes are formed using the polyisocyanate polyaddition process: Rigid PUR foams are produced with the aid of catalysts and blowing agents, through the chemical reaction of polyisocyanates with polyolene and/or by trimerisation of polyisocyanates. In the presence of special catalysts, isocyanates may also react with each other. This results in the formation of not only PUR, but also polyisocyanurate (PIR) structures in the matrix, which display improved flame retardant properties [Kapps, Buschkamp 2004; Buschkamp 2001]. The term “PUR” as used below is taken to mean all rigid polyurethane foams including PIR-modified products.

Rigid PUR foam can be foamed entirely with process-related CO₂. The reaction between water, which is present in small quantities in the polyol formulation, and isocyanate gives rise to CO₂, which is used as a “chemical” blowing agent. Since the CO₂ generally diffuses very quickly out of the foam cells it has formed, it does not contribute to the thermal insulation performance of the foam. In applications that require a high thermal insulation performance (low lambda (λ) figures), a “physical” blowing agent that stays in the foam cells is added to the process-related chemical blowing agent CO₂. In the past, CFC-11 was used as this physical blowing agent. Because the use of fully halogenated CFCs has been prohibited since 1 January 1995 under the CFC/Halon Prohibition Ordinance (*FCKW-Halon-Verbots-Verordnung*) [FCKW-Verordnung 1991], the halogen-free hydrocarbon pentane is now commonly used in Germany for the production of rigid PUR foam. There was no changeover from CFCs to HCFC-141b, which has also been prohibited as a foam blowing agent in the EU and Japan since January 2004 and in the USA since January 2003 [Hammond Suddards Edge 2002]. Instead, pentane has been joined since 2002 by the fluorinated blowing agents HFC-365mfc and HFC-227ea, and since 2004 by HFC-245fa, which at those times were technically competitive and commercially available [UNEP 2003]. However, their use is declining in favour of pentane [Bipro 2008]. HFC-134a, which served as a successor to HCFC-141b, has no longer been used in rigid PUR foams since 2004 [Bipro 2008; NIR 2010]. Pentane, like CFCs and HCFCs, remains in the foam cells and thereby makes a contribution to heat insulation. After the replacement of CFC-11 it was no longer possible to achieve the thermal conductivity level 020, i.e. $\lambda(R) = 0.020 \text{ W/(m}\cdot\text{K)}$, for rigid PUR foams – regardless of the blowing agent used.

For process reasons, the production of PUR foams involves higher blowing agent emissions. By contrast, the regular annual emissions from the finished product during the use phase are comparatively low. Table 4.2 shows the emission figures for HFC-134a (used in production of rigid PUR foams until 2004) and HFC-245fa/-365mfc, which were taken as a basis for emissions reporting in the National Inventory Report (NIR).

Table 4.2: Emission factors for rigid PUR foams [NIR 2010]

Emission factors for rigid PUR foams			
	Lifetime	Losses in first year (<i>Production emissions</i>)	Annual losses (<i>Losses during use</i>)
	[years]	[%]	[%]
HFC-134a applications	50	10	0,5
HFC-245fa/HFC-365mfc applications	50	15	1

Losses of HFC-134a during the use phase (stock emissions) are assumed to be 0.5% per annum. On disposal after 50 years' useful life, a calculated 65% of the blowing agent is still present in the foam. Corresponding calculations apply to the applications HFC-245fa or HFC-365mfc. As Table 4.2 shows, losses of these blowing agents in the first year (production emissions) average 15% depending on the type of application, and annual losses during use average out at 1%. This means that on end-of-life disposal, some 35% of the blowing agent is still present in the foam [NIR 2010; Schwarz 2009b].

In Europe there are different national building regulations, standards and authorisation procedures for the planning and construction of buildings. The start of the Single European Market saw an intensification of efforts to harmonise the standards and authorisation procedures for the construction sector, with the aim of awarding the CE mark for building materials and building products [Walter 2004].

The central property of a thermal insulation material is its thermal conductivity (heat transmission resistance). For a given thickness of rigid foam, the lower the thermal conductivity λ of the blowing agent and cell gas enclosed in the foam cells, the greater is the insulating performance. The values of λ for the blowing agent gases as such increase in steps of about 1.5 mW/(m*K) in the order CFC-11 (8.5 mW/(m*K)), HCFC-141b (10.1 mW/(m*K)), c(cyclo)-pentane (12.4 mW/(m*K)) and n-pentane (14 mW/(m*K)). However, the values of λ for the finished foam products – the calculated thermal conductivity – are influenced not only by the values of λ for the physical blowing agents, but also by a large number of other factors. Thermal insulation materials are long-lasting products which can be assumed to have a useful life of between 25 and 50 years. There is therefore a need for a realistic long-term figure for thermal conductivity that takes into account the effects of ageing [Walter 2004]. European standard DIN EN 13165 [DIN 2009b] for rigid PUR foam materials includes details of the methods for testing thermal conductivity. It provides for two ways of taking account of the impact of ageing in thermal conductivity:

- Fixed additions to the measured initial figure for thermal conductivity. The additions are defined for known and extensively researched products. Their use is tied to compliance with relevant conditions.

- Measurement of the “aged” thermal conductivity figure using a rapid method (storage at $70 \pm 2^\circ\text{C}$ for 175 ± 5 days plus an increase in this value by a predetermined safety allowance).

The thermal conductivity of the insulation products is stated as the nominal or design value. The design value (λ_D) is determined from the initial measured value, having regard to the statistical scatter of the measurements and the ageing allowance, and assigned to a category. The increments laid down are 1 mW/(m*K) steps. The design value also includes safety allowances and describes the thermal properties of the insulating material over the entire use phase [Endres, Kleser 2008].

Typical experimentally determined values for the calculated thermal conductivity of a rigid PUR foam with diffusion-resistant coating are 21 mW/(m*K) with HCFC-141b (banned in the EU since 2004), 23 mW/(m*K) for c-pentane and 24 mW/(m*K) for n-pentane as physical blowing agents.

According to the manufacturer, the value of λ for the blowing agent HFC-365mfc as a gas (10.6 mW/(m*K)) lies between the figures for HCFC-141b and c-pentane. The same is true of HFC-245fa. Rigid PUR foam produced with these blowing agents thus has a calculated thermal conductivity λ of about 22 mW/(m*K) [Bipro 2008]. In the final analysis, these differences between pentane and the HFCs are negligible, especially since the long-term pattern of thermal conductivity depends not only on the blowing agent used, but also on numerous other influences (bulk density, temperature, time of measurement, influence of water and moisture) [Endres, Kleser 2008].

The use of pentane requires explosion-proof processing plant and other technical modifications to the process technology compared with fluorinated blowing agents. The manufacturers of rigid PUR foam estimate that a changeover to pentane involves sizeable investments. Given large production throughput, however, this capital expenditure pays off very quickly thanks to the low cost of the blowing agent. The Foam Plastics Association (*Fachverband Schaumkunststoffe*) estimates that in the thermal insulation field the threshold above which it becomes economic for the plant operator to adopt pentane technology without subsidies and using its own resources is around 100 cubic metres of foam per working day [Anhörung 2003].

For the various applications of rigid PUR foams this leads to different consequences, for which there are often economic grounds in addition to the technical reasons. It is therefore necessary to consider the individual applications separately.

Flexible-faced laminates, insulation panels for use in construction sector

Insulation panels with TCG 020 have not been available since the prohibition of CFCs. PUR insulation panels for the construction sector are now predominantly foamed with n-pentane; the market share of these products in Germany is around 95% [Bipro 2008]. The reasons for the choice of blowing agent are largely economic; there is therefore no reason to expect developments leading to the use of new HFCs, as these HFCs are considerably more expensive than the blowing agents used to date.

HFC-365mfc and HFC-245fa are still used for specialised applications (stringent fire protection requirements during production or use and especially high demands with regard to thermal conductivity and low weight and/or small thickness of panels) for which HCFCs were used until the end of 2003. For economic reasons these applications also use blowing agent blends with CO₂, though these also contain HFCs (mostly HFC-365mfc). The argument of better insulation performance is not a justified reason for using HFCs as blowing agents in the future, however, they do not offer any relevant advantages over pentane.

Without using HCFC-141b, plain PUR insulation panels, i.e. rigid foam without a metallic surface layer, can no longer comply with building materials class B1 under DIN 4102-1 [DIN 1998] for maximum fire protection requirements. Even the use of blowing agents based on HFC-365mfc does not permit manufacture of rigid PUR foam complying with building materials class B1 [Anhörung 2003].

From a technical point of view, it is not necessary to use HFCs in PUR insulation panels. The changeover to halogen-free blowing agents is almost complete. Moreover, a PUR insulation panel foamed with pentane has a much better greenhouse gas balance than a PUR panel foamed with HFCs. This is true – on the basis of conservative assumptions – both for the case of an increase in the thickness of the insulating layer for the pentane-foamed insulation panel, and for the situation where the thickness of the insulating layer is kept constant and slightly more heat energy is used for the insulation panel foamed with pentane [Harnisch *et al* 2003].

Thus future use of HFCs represents a great setback for efforts to mitigate climate change, and appropriate measures should therefore be taken to prevent this.

Appliance insulation foam (insulation of refrigeration appliances, hot-water tanks etc.) and pipe insulation

HFCs are not used at all as blowing agents in the manufacture of PUR appliance insulation foams. Instead, CO₂ is used for hot-water tanks and pentane for household refrigeration appliances. For reasons of cost, it is unlikely that production will make a fresh switch to HFCs.

Rigid PUR foams are also used for thermal insulation of large pipes (district heating). The most important criterion for this application is the heat resistance of the foam. The thermal conductivity levels of pre-insulated pipes foamed with pentane are comparable to those of pipes foamed with HCFC-141b [Welte & Godthardt 2004]. Increased thermal insulation performance requirements can usually be met by increasing the thickness of the insulating layer. The blowing agents used in Germany are pentane (95%) and CO₂ (5%) [Bipro 2008].

When it comes to producing insulating materials for pipes in fields other than local and district heating (heating systems, sanitation, plant and pipeline construction), CO₂ is the most commonly used blowing agent. Although this results in a slight sacrifice in insulation performance, the manufacturing process is much cheaper than with HFCs, because CO₂ is formed during the process and does not have to be added separately. Apart from CO₂, pentane is also used as a blowing agent to a small extent. According to experts [Bipro 2008], HFCs are used for about 1% of pipe shell insulation. In particular, this is the case where there are

very high requirements regarding stability and compression resistance and also fire protection (buildings materials class 1, without using increased amounts of flame retardant), or where low thermal conductivity levels need to be ensured in confined spaces. It should be noted here, however, that there as far as compression resistance is concerned are no differences between CO₂, cyclopentane and HCFC-141b, which was used until 2004. The same applies to cyclopentane and HCFC-141b with regard to thermal conductivity [Welte & Godthardt 2004]. On this basis we can conclude that for these applications there are no technical arguments in favour of using HFCs, which have been used as a substitute for HCFC-141b since the latter was banned.

Sandwich panels, composites

Continuous production of PUR insulation panels with top and bottom surface coverings of inflexible metallic material is dominated by a few large manufacturers. The blowing agent used in Germany is almost entirely pentane, though small amounts of CO₂ are also used. The thermal insulation performance of pentane is comparable to that of the HFC candidates (HFC-245fa or blends which may contain not only HFC-365mfc but also HFC-227ea). Production of PIR systems is increasing, with the aim of improving fire protection properties. HFCs are however still being used for the production of sandwich or composite panels intended for export, in order to keep down the cost of meeting the fire protection requirements, which in some cases are very high (e.g. in France, United Kingdom) [Bipro 2008].

Discontinuous production of PUR insulation panels with a metallic surface layer is a batch production operation that is generally performed in small firms or on small plants. The sandwich elements are foamed mainly with pentane, but also with CO₂ or butane. In about 30% of batch-produced insulation panels (about 50,000 m³) the blowing agents used are HFC-245fa, HFC-365mfc and HFC-227ea [Bipro 2008]. From a technical point of view there are no problems with using pentane as a blowing agent in this process. The biggest manufacturer in Germany has switched its entire production to pentane. The arguments against such a changeover are mainly economic, because the use of pentane – especially in discontinuous production – makes it necessary to step up the precautions against explosions. The changeover involves high capital expenditure, which smaller firms in particular do not consider economically justified. This must be set against considerably lower consumption and relatively low blowing agent costs for the use of pentane.

All in all, there is no need from a technical point of view to use HFCs instead of pentane for continuous or discontinuous production of PUR insulation panels with a metallic surface layer.

Rigid slabstock

In most cases, rigid slabstock foam is produced in a continuous production process. While discontinuous production is technically possible, it is of minor importance and is not practised in Germany. The final product is not the foam block itself, but the more complex shapes or structures that are cut out of the block, such as mouldings or pipe shells. Rigid slabstock is also used for the production of panels with a thickness exceeding 180-200 mm [Anhörung 2003].

In economic terms, the production of slabstock is far less important than the production of flexible-faced laminates. It is also associated with higher emissions, because cutting the foam blocks destroys large numbers of foam cells and releases the blowing agent contained in them.

The use of pentane for slabstock is basically state of the art. Problems do however arise when maximum fire protection requirements have to be combined with low thermal conductivity and limited panel thickness. Although it is possible to meet high fire protection standards using CO₂, the thermal conductivity is relatively high at 0.04 W/(m*K). For this purpose, therefore, HFC-365mfc (0.022 W/(m*K)) is generally used in conjunction with CO₂. The proportion of slabstock containing HFCs is less than 5% [Bipro 2008]. For applications that involve particularly high fire protection requirements, a possible option is offered by alternative products such as foam glass.

In-situ PUR foam

In-situ polyurethane foams are sprayed or poured directly on site and are therefore exposed to many influences. When in-situ foams are applied to flat roofs, external walls or storage tanks, it is necessary to take account of substantial variations in temperature and humidity, which have a considerable influence on the quality of the foam.

The advantage of in-situ foam is that this process makes it possible to cover the surface of even complicated structures with a relatively uniform layer of foam. Another point is that there is no need to transport large volumes of foam, but only the raw materials and the foaming machine. The main applications of in-situ foams are cavity foaming and seamless insulation of components and sections. In the construction sector it is mainly used for insulation and refurbishment of flat roofs on existing buildings. Depending on the method, in-situ foam can be subdivided into in-situ spray foam (spray foam and roofing spray foam) or poured foam.

The percentages of HFCs used as blowing agents differ between sprayed and poured foam. In the sprayed foam segment, 100% of spray foams and 95% of roofing spray foams are foamed with HFCs. The remaining 5% use CO₂ as an alternative. In the poured foam segment, the proportion foamed using CO₂ is more than 95%. The remainder is produced using mixtures of HFC (as supporting gas) and CO₂. The HFCs of relevance to the foaming of in-situ foams are HFC-365mfc mixed with HFC-227ea and HFC-245fa [Bipro 2008].

Being highly flammable, the HFC-free blowing agent pentane is not an alternative. Since in-situ foams involve open application, safety considerations require the use of liquid blowing

agents that are not readily flammable [Schwarz, Leisewitz 1999]. Pentane is unsuitable for indoor foaming, because explosive concentrations can quickly build up in enclosed spaces. This problem does not exist with CO₂, which is thus available as an HFC-free blowing agent [Bipro 2008].

The use of in-situ spray foam is greatly affected by weather conditions. Since HFC-foamed spray foams are less sensitive in this respect and hence have less of a tendency to shrink, they are generally given preference over CO₂-foamed spray foams. However, these shrinking processes can be counteracted by using larger quantities of CO₂-driven foam. Technical measures can be taken to limit process fluctuations and the associated problems, making it unnecessary to use HFCs.

Using CO₂ as the blowing agent increases the risk of a deep-seated fire due to heat build-up resulting from the greater bulk density and the larger quantities of foam needed to achieve better thermal insulation. According to experts, however, deep-seated fires can be avoided by careful working [Bipro 2008].

There are also other insulating materials that offer alternatives (e.g. HFC-free PUR insulation panels, foam glass). In new buildings their use does not cause problems, but in existing buildings or when refurbishing flat roofs the use of alternative insulating systems frequently involves more work.

A life-cycle assessment prepared for in-situ PUR foam does not reveal any clear advantage for blowing agents containing HFCs [UBA 2002]. On the whole it is possible to do without in-situ PUR foam produced using blowing agents that contain HFCs, since alternative products or processes are known and have been tested in practice.

Refrigerated containers

On the basis of Regulation (EC) No. 2037/2000 [EG-Verordnung 2000] imports of refrigerated containers into the EU have been banned since 1 January 2004 if the material used was foamed with HCFC-141b and manufactured after 31.12.2003 [Wild 2008]. Since the entry into force of Regulation (EC) No. 1005/2009 of the European Parliament and of the Council of 16 September 2009 on substances that deplete the ozone layer [EG-Verordnung 2009] (revised version of Regulation (EC) No. 2037/2000), there has been a general ban on imports into the EU of refrigerated containers with insulation foamed using HCFC-141b.

Today refrigerated containers are made only in China. Here, however, HCFC-141b is not subject to controls until 2013, and a complete phase-out is not planned until 2030 [Wild 2008; WorldCargo News 2010]. Nevertheless, since the end of 2009 China has been starting to employ a technology using cyclopentane as the blowing agent. Thus it is now possible to obtain refrigerated containers from China that are free from HCFC-141b [WorldCargo News 2010].

Conclusions

On the whole, there is no need to use HFCs as blowing agents for rigid PUR foams. From a technical point of view, pentane or process-related CO₂ offer suitable alternative blowing agents which in the great majority of applications yield equivalent results. For the few exceptions where there are technical reasons for using HFCs, alternative products are available which are well established and tried and tested in practice. A new kind of insulation system for internal insulation of external walls offers a possible alternative. This consists of a combination of rock wool and aerogel. According to the manufacturer its heat conductivity is 0.019 W/(m*K) for an insulation thickness of 40 mm [Rockwool 2010].

4.2 Flexible PUR foams

Flexible foams differ from rigid foams in that they are easily deformed under pressure. In most applications the base polymers for flexible foams are polyurethanes. Flexible foams have a very broad spectrum of applications: this ranges from cushions, pillows and mattresses, through upholstery pads in the furniture and car sectors, to toys, sports equipment, sound-absorbing products or packaging material. Flexible foams are open-cell foams with a homogeneous structure, good resilience and also good sound-absorption properties.

Since as long ago as 1990, work has been in progress on developing and testing processes that make it possible to manufacture flexible PUR foams without using CFCs. One example is the VPF (Variable Pressure Foaming) process, the development of which was supported by the Federal Environment Ministry's investment programme for reducing environmental pollution. In this foaming process the atmospheric pressure in a completely closed production plant is reduced so far that the CO₂ formed by the reaction between isocyanate and water has sufficient power as a blowing agent to create flexible PUR foams with bulk densities of 11 kg/m³ upwards (from 10 kg/m³ to 70 kg/m³). There is no need to use additional physical blowing agents. Moreover, production under defined atmospheric conditions makes it possible to optimise the input of raw materials and improve the quality of the products. In the demonstration plant it proved possible to reduce the exhaust air stream, which in normal foaming processes was between 80,000 m³/h and 100,000 m³/h, to 6,000 m³/h.

Conclusions

Flexible PUR foams do not play any role in the discussion about HFCs: they are driven by process-related CO₂ from the reaction with water. Ever since the phase-out of CFCs, halogenated blowing agents for flexible foams have no longer been used in Germany, and there are no technical or other arguments for the use of HFCs.

4.3 Integral PUR foams

German standard DIN 7726 defines integral foams as structural foams that are chemically homogeneous over their entire cross-section, but whose density continuously decreases from the outside to the inside. Integral foams typically have a soft core and an almost solid surface layer with a compact, closed outer skin.

Integral PUR foams are manufactured by means of a foam moulding process known as RIM (**R**eaction **I**njection **M**oulding). In this process the reaction mixture for foaming is mixed under high pressure and fed in liquid form into cold moulds which it completely fills when the foaming reaction is finished. Thus the chemical reaction takes place in the mould. The selected temperature gradient from the centre of the mould to the outer wall leads to differential expansion of the blowing agent as it evaporates over the mould cross-section and hence to the density differences responsible for the structure of integral foams as described above. By choosing suitable reaction conditions it is possible to cover a wide range of hardnesses (rigid, semi-rigid and flexible integral foams).

Further developments or specialised variants of RIM are RRIM (**R**einforced **R**eaction **I**njection **M**oulding) and SRIM (**S**tructural **R**eaction **I**njection **M**oulding). In RRIM the liquid components are mixed with solids (e.g. glass spheres or synthetic mineral fibres). In the SRIM process, reinforcing mats (e.g. of glass fibre) are placed in the mould, and the result is cured to form a composite material. The reinforcements embedded in the structure of the material improve the mechanical properties of the plastic components.

Integral foams also have a wide range of applications:

- furniture manufacture (seat pads, moulded pads)
- automobile industry (seat pads, moulded pads; arm-rests, headrests, footrests; protective padding; gear-shift knobs, dashboards etc.,
- footwear, sports equipment (soles, shock-absorbing elements, protective padding),
- cases and toolbox mouldings,
- electrical appliances (especially rigid integral foams),
- mouldings in many other applications.

In integral PUR foams the focus is not so much on the insulating properties, but rather on the expansion behaviour of the blowing agent. Blowing agents with a low vapour pressure are ideal for good foam density results. The fluorinated blowing agents HFC-365mfc (also in blends with HFC-227ea), HFC-134a and HFC-245fa are therefore used for this purpose. However, the desired properties (break resistance, stability, long life) can also be achieved with pentane. Another possible blowing agent is process-related CO₂.

Reduction options

Since the ban on using CFCs, the blowing agents used for (rigid and semi-rigid) integral foams have been, in addition to pentane and process-related CO₂, the fluorinated agents HFC-365mfc (also in blends with HFC-227ea), HFC-245fa and HFC-134a. From a technical

point of view, it is possible to produce all required grades of integral foam using pentane or CO₂; the necessary technology is available [Anhörung 2003]. In Austria the use of fluorinated blowing agents for production of integral foams has been banned since July 2003 [Bipro 2008].

Conclusions

From a technical point of view, it is not necessary to use HFCs to produce rigid or semi-rigid integral foams.

The barrier to the use of pentane is an investment barrier, not a technical one: for economic reasons, the many small and medium enterprises that produce and process integral foams have difficulty in complying with the safety requirements for production using pentane. If economic considerations make it impossible or undesirable to use pentane, process-related CO₂ from the reaction with water is available as an alternative blowing agent.

4.4 Caulking foams

Workmen and DIY handymen use PUR caulking foam for a large number of applications, especially in interior finishing of buildings. The main applications include:

- filling spaces around doorframes and window frames,
- filling various cavities, and
- sealing roller shutter boxes [Schwarz, Leisewitz 1996].

The majority of caulking foams are one-component foams (OCF). They are applied either with a simple aerosol can or with a caulking gun attached to the can. Although this does not make any difference to the possible applications, working with a gun allows the foam to be applied more accurately. Expelling an one-component foam from the can requires a physical blowing agent. This does not, however, contribute to the insulating effect of the PUR foam. This blowing agent is largely emitted during application of the foam, and a small proportion remains in the foam for a maximum of one year [Schwarz, Leisewitz 1999; Harnisch, Schwarz 2003].

Alternatively, it is possible to use two-component foams. These do not need any extra blowing agent, but are expelled by the chemical reaction resulting from mixing the two components. However, they can only be considered a possibility if it is possible to use up the entire contents of the can rapidly in a single application. Otherwise the foam hardens in the can in a few minutes. It is basically possible to replace caulking foams with other materials and techniques. These are not considered in this report because of its focus on the blowing agent problem.

The market for PUR foam cans depends on the economic situation and is very dependent on imports and exports. Of roughly 20 million cans sold throughout Germany in 2002, some 13 to 14 million were imported, although domestic production came to 33 million [AKPU 2003a].

Since 1993 it has been possible to send spent PUR foam cans for recycling by P.D.R. (“Produkte Durch Recycling”)² in Thurnau. Since its establishment, P.D.R. has built up a nationwide collection and take-back system. Take-back is provided at no additional cost, since this is already included in the purchase price of the can [PDR 2003].

Since the total discontinuation of blowing agents containing chlorine, mixtures of – highly flammable – hydrocarbons (propane, butane, dimethyl ether) and – non-flammable or not readily flammable – HFCs (134a or 152a) have been used in Germany.

In 2007, HFC emissions from caulking foams totalled around 470 t. This means that emissions from this application were 65% down on the 2002 figure of 720 t. The share of total HFC emissions was around 6.7% [NIR 2009].

Reduction options

From 1993 onwards, under a voluntary agreement by central and west European producers, the proportion of highly flammable blowing agents was reduced to 50 g per 750-ml can (50-g rule). In 2002 this was extended to a 100-g rule [AKPU 2003b]. The foam cans contain a total of 16 to 18% by weight of blowing agent.

Since 4 July 2008, placing one-component foams on the market in the EU has been prohibited under Annex II to Regulation (EC) 842/2006 on certain fluorinated greenhouse gases (F-Gas Regulation) [EG-Verordnung 2006]. As these foams (caulking foam) are classed as “preparations”, the total value of the global warming potential is allowed to be up to 150. For this reason it continues to be permissible not only for the blowing agent to consist entirely of HFC-152a (GWP 140), but also for it to contain up to 11.5 percent by weight of HFC-134a (GWP 1300) if the other gases have no appreciable global warming potential. Furthermore, exceptions are permitted if these are necessary to ensure compliance with national safety standards (e.g. for fire protection). In Germany there is only one such exception, and this relates to underground coal-mining [Schwarz 2009a]. The marked reduction in HFC emissions from caulking foam can be seen as the result of this regulation.

In Germany, caulking foam has to meet the requirements of building materials class B2 according to DIN 4102-1, i.e. materials used in the building sector must be “regular fire protection grade” [DIN 1998]. This follows from the minimum requirements of the Model Construction Code (*Musterbauordnung – MBO*) or the Länder construction codes (LBOs) for materials for permanent use in building structures [DIBt 2003]. In the test for classification in building materials class B2, the specimens are stored for at least 14 days under normal climatic conditions before being subjected to a flame test. The material passes the test if the flame does not reach a 150-mm mark within 20 seconds in any of the five specimens (exposure to flame: 15 s). The test for classification in building materials class B1 (“flame resistant”) simulates the burning of an object in a room. The fire must have a low tendency to spread, and the heat given off must be limited (DIN 4102-1 [DIN 1998]). In general, however, caulking foams do not reach these and other higher fire protection grades because of the base

² “Products through recycling”. Formerly: “Polyurethan Dosen Recycling” (polyurethane can recycling)..

material polyurethane [DIBt 2003]. Class B3 comprises all flammable building materials that do not meet the requirements for either B1 or B2 (DIN 4102-1 [DIN 1998]).

DIN 4102-1 classifies the combustibility of the products – in this case the cured caulking foam – after two weeks [DIN 1998]. In relation to the lifetime of the foam, however, which is theoretically the same as that of the building, the improvement in fire protection that results from using HFCs can be regarded as slight, since all the blowing agent is emitted from the cured foam within a maximum of one year.

The all-purpose foams sold on the German market today are generally free from HFCs and meet the requirements of building materials class B2 [Schwarz 2009a]. Only the relatively new foam specifications “flame retardant foam”, “winter foam” and “mega foam”, which account for up to 20% of cans produced by individual manufacturers, contain (in some cases) the blowing agent HFC-134a. Fire protection foam and winter foam each have a market share of 1% in Germany, mega foam a share of 18%. Flame retardant foam in particular, because of the high flame retardant content needed to comply with building materials class B1, requires special blowing agent properties. However, under the Model Construction Code (MBO) and the Länder construction codes, this building materials class is not necessary, so flame retardant foams containing HFCs should be dispensed with for climate reasons.

Winter foam is no longer dependent on the former minimum temperatures (+5°C), but can still be used at -5 to -10°C. Mega foam means that it is possible to produce up to 60 litres or more of foam instead of the previous maximum of 45 litres without changing the size of the can, or the same amount of foam as before from a smaller can. This reduces the number of times that users have to change cans when working, or allows them to use smaller cans for working in places that are not easily accessible. In spite of the more stringent requirements for blowing agents in specialised foams, five of the seven suppliers of flame retardant foam and mega foam in Germany claim to offer these foams entirely without HFCs [Schwarz 2009a].

The minimum processing temperature is not usually of any relevance to the *Do-it-Yourself* sector. Here most applications are indoors or at higher outdoor temperatures. It is only in the professional sector, where cans are stored in contractors' sheds (even in the winter) and the product is used at low outdoor temperatures, that this aspect is of any importance at all [Henkel 2003].

Conclusions

There is no need to use HFCs as a blowing agent in caulking foams. The HFC-free all-purpose, flame retardant and mega foam products on the market are perfectly adequate for all fields of application; only in the exceptional case of underground coal-mining are other specialised foams with HFCs required. There is also the possibility of using two-component foams.

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5 HFCs as propellant gas in technical and other aerosols

Until the ozone-depleting effect of CFCs was discovered and the necessary steps were taken, the aerosol sector was the main consumer of this group of substances. CFCs were used in medicinal sprays (metered dose inhalers) or sprays for technical and non-technical applications. Sprays for technical applications also include caulking foams, which are dealt with in Chapter 4.4. In 1999, some 75% of sprays for mainly non-technical applications were used in the cosmetics or household sectors [Schwarz, Leisewitz 1999]. Today the propellant gases used in these sectors are almost exclusively propane, butane or dimethyl ether, and also – to a small extent – HFCs. There are also products on the market which have no propellant gas, such as pump sprays.

HFCs are used or have been used not only in medicinal sprays, but also in freezer sprays, compressed air sprays, insecticide sprays (pest control), lubricant sprays, hair sprays, defence sprays (pepper sprays), tank fillers/pressure compensating vessels in heating systems, pipe freezer sprays, horns, novelties (streamer sprays, snow sprays etc.) and drain cleaners [IG Sprühtechnik 2003].

Every year about 400 t of HFCs are used as propellant gas in aerosols. In 2007, two thirds went into medicinal aerosols [CRF 2009]. In 2003, about 2.2% of the HFC-134a used in Europe went into non-medicinal sprays [IG Sprühtechnik 2003].

In applications where HFCs are used as propellant gas, the emissions are the same as the amount used (“open application”). However, because of the extensive imports and exports of these products, the propellant gases are not necessarily emitted in the country where the products were produced. Figure 5.1 shows the breakdown of HFC emissions among the various fields of application for the year 2002. In total, aerosols were the third-largest HFC emission source in Germany in 2007, after stationary and mobile refrigeration systems and foam production [NIR 2009]. In view of the relatively late phase-out of CFCs, emissions arising from medicinal sprays have been rising slowly but steadily since 1995. In the case of medicinal sprays, the Federal Environment Agency expects a further rise in HFC emissions up to the year 2010 and beyond [Schwarz 2003a]).

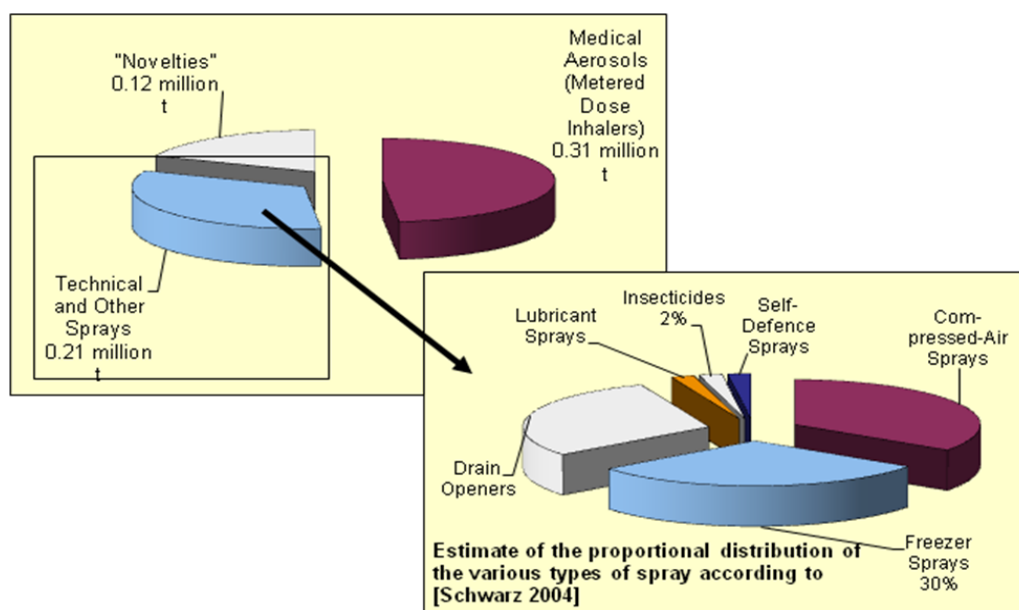


Fig. 5.1: HFC emissions in Germany from use as propellant gas in various sprays/aerosols in 2002, in million t CO₂ equivalent. Data from: [Schwarz 2004; BReg 2004].

The cost of hydrocarbons (or other halogen-free propellant gases) is basically lower than for HFCs. Replacing HFCs therefore results in cost savings. In many sectors – despite the necessary non-recurring capital expenditure on explosion control measures at the production location – this has resulted in widespread use of hydrocarbons, especially as propellant gas.

In all cost studies available for this field of applications, the authors arrive at negative CO₂ abatement costs, i.e. cost savings, in the event of HFC substitution. One of these sources is Harnisch and Schwarz [2003]. Since this fact applies to all the products described below, the costs are not considered separately in the following chapters. The only exception here is products in which HFCs cannot be completely replaced by halogen-free propellant gases such as hydrocarbons, e.g. medicinal sprays.

5.1 *Technical sprays*

The term “technical sprays” is used here for freezer sprays, compressed air sprays, lubricant sprays and pipe freezers). In individual cases HFC-134a or – less commonly – HFC-152a are used. For the emissions, see Figure 5.1.

5.1.1 *Freezer sprays and compressed air sprays*

Compressed air sprays are used to blow out dust in servicing work on electronic devices such as copiers, radio and television sets and other systems with sensitive electronics [IG Sprühtechnik 2003], and also in switchgear cabinets [Schwarz, Leisewitz 1999]. Instead of compressed air, these “compressed air sprays” frequently contain a compressed HFC [Zürich 2006].

Freezer sprays are used for testing purposes (fault localisation) on electronic systems/components [IG Sprühtechnik 2003]. Brief local chilling of live components makes it easier to identify faulty sites (e.g. in a television) than when the set is switched off [Schwarz, Leisewitz 1999]. In this field HFC-134a is used because it is not readily flammable. These products are mostly used by experts in a professional context [IG Sprühtechnik 2003].

Freezer sprays are also used outside the electronics industry. Apart from medicinal uses, they are also used for removing chewing gum, e.g. from bus and cinema seats [IG Sprühtechnik 2003]. Other fields of application are testing temperature sensors and brief cooling of components before soldering or assembly.

Freezer sprays are also used on an international scale for servicing refrigeration systems. In Europe their use is banned in the servicing, maintenance or filling of refrigeration systems, air-conditioning systems, heat pumps, fire protection systems or high-voltage switchgear systems. This ban applies to the servicing of mobile air-conditioning systems even if the fluorinated greenhouse gas is used partly to expel another substance from the spray can.

Reduction options

Where flammable substances like propane or butane are used, there is a possibility that the sparks that occur in such systems could cause a deflagration/explosion [IG Sprühtechnik 2003; Meeh 1998]. However, the industry also offers products with flammable gases. Nothing is known about serious accidents with propane/butane freezer sprays [Meeh 1998]. Today many manufacturers also offer freezer sprays using propane and butane for testing temperature sensors and cooling components before soldering or assembly [e.g. Tes 2010, Wek 2010].

In compressed air sprays it is also possible to use non-flammable compressed gases other than HFCs. In other applications where compressed but not liquefied gases are used as propellant gases, this may result in poorer output quality. This is not important for dust removal. Possible gases therefore include not only flammable hydrocarbons, but also air, CO₂ or nitrogen.

5.1.2 *Other technical sprays*

HFC-134a is also used in pipe freezer sprays. These products are used to freeze sections of pipes so that fitting work can be carried out on individual parts. Unlike the freezer sprays mentioned above, these are not test instruments. For cost reasons, HFCs are used here as refrigerants in an open application [TUNAP 2003].

Other gases, e.g. CO₂ (dry ice), can be used to freeze parts of systems. Suitable transportable systems are available on the market [UBA 2003b]. Cryogenic collars are also used.

Another field of application for HFCs in sprays is specialised lubricants for which high standards of application quality are required. Since these applications usually take place at high ambient temperatures, the product is required to be absolutely non-flammable [IG Sprühtechnik 2003]. As it is not possible to use other gases for safety or technical reasons, other application techniques would be needed to replace HFCs. According to IG Sprühtechnik [2003], these are not available at present and would first have to be developed.

Conclusions

In most cases, techniques other than the use of HFCs in technical sprays are available for producing compressed air or generating cold. In the case of pipe freezing in particular, transportable CO₂ systems and refrigeration systems are available. Thus it is possible to do without HFCs to a large extent; any exceptions should be substantiated on a case-by-case basis.

5.2 *Medicinal sprays*

Within the medicinal applications sector, HFCs are largely used in metered-dose inhalers (asthma sprays, MDIs). By contrast, most other medicinal sprays (foot sprays, skin sprays etc.) do not use HFCs. About 5-10% of the freezer sprays described in Chapter 5.1.1 are used for medicinal applications, e.g. for vitality testing of teeth in the dental sector [IG Sprühtechnik 2003].

Metered-dose inhalers are used in the treatment of respiratory disorders such as asthma and COPD (chronic obstructive pulmonary disease). Metered-dose inhalers make use of propellant gases to ensure finely distributed application of the active ingredient. Until 1996 these gases were always CFCs. Until 1998 about 400 t of CFCs were emitted by this application in Germany every year [Schwarz, Leisewitz 1999].

Under the rules on exceptions for important purposes, CFCs were still available for use in metered-dose inhalers in Europe in accordance with *Regulation (EC) No. 2037/2000* [EG-Verordnung 2000]. With effect from 1 January 2006 the German Federal Institute for Medicines and Medicinal Products (BfArM) stopped issuing special permits pursuant to Section 2 subsection 2 of the CFC/Halon Prohibition Ordinance (*FCKW-Halon-Verbots-Verordnung*) [FCKW-Verordnung 1991] for the use of CFCs in pharmaceutical products [BfArM 2005]. Germany was thus the first country to discontinue CFCs entirely in this sector.

Therapeutic products for asthma and COPD are divided into five classes of preparations, groups A to E. For preparations in classes A and B (e.g. Budesonid, Beclomethason, Dexamethason, Flunisolid, Fluticason and Triamcinolon), which account for some 80% of these medicines, CFCs have been phased out in Germany since the end of 2002. For classes C (active ingredient Nedocromil) to E (e.g. combination preparations) there was no adequate substitute at that time [BfArM 2003]. In the meantime, therapeutic alternatives exist for these medicines as well.

Reformulation of the numerous medicinal substances with HFCs instead of CFCs is a research-intensive and expensive process. In Germany the first metered-dose inhaler with HFCs as propellant gas came onto the market in 1996; it was followed by two each in 1997 and 1998, and another in 1999. All contained HFC-134a [Schwarz, Leisewitz 1999]. Even today, this is the only HFC used by German manufacturers in this field. Internationally, metered-dose inhalers with HFC-227ea are also on the market, but HFC-134a is favoured for medicinal aerosols [IG Sprühtechnik 2003]. For the emissions, see Figure 5.1.

Reduction options

Consideration has also been given to developing alternatives with halogen-free hydrocarbons as propellant gas, e.g. propane or iso-butane [Langen 1999]. As far as is known, however, this is no longer being pursued.

Powder inhalers (DPIs) offer an alternative without propellant gas for asthma and COPD therapy. Whereas the market share of these products in the Scandinavian countries was already as high as 80% some years ago [March 2000], the figure for Germany in 2003 was around 25%. Today nearly all manufacturers of metered-dose inhalers also produce DPIs. However, powder inhalation is not suitable for all groups of patients [BfArM 2003]. For example, metered-dose inhalers are preferred for the treatment of small children and elderly people. In some cases there are problems switching patients from one system to the other [IG Sprühtechnik 2003].

Changing the propellant gas basically involves high costs. As well as the complex research and development work, numerous tests are needed for approval of the “new medicinal product”. The same applies to the development of systems without propellant gas (DPIs). A number of estimates have been made of the costs and the specific CO₂ abatement costs. One example is the study by March [2000]. March [2000] estimates the specific abatement costs in the EU at more than 500 euros per tonne of CO₂. The cost estimates average 400 to 500 euros per tonne of CO₂, but there is some controversy about these figures [ECCP 2000; ECCP 2001]. These costs include the additional cost of the medicinal product (DPIs are usually more expensive than MDIs) and patient training (changeover) by a doctor. For Germany, March [2000] quotes a 38% increase in costs compared with MDIs. It is difficult to assess these cost estimates. This is partly because there are extreme variations in the situation in the individual countries, but also partly in view of the fact that today - unlike the year 2000 - nearly all manufacturers market DPIs as well as MDIs.

Another possible means of reducing emissions is recycling of MDIs after use. This would first involve building up a collection system, e.g. at chemists. This, however, would only avoid

emissions of the residual propellant gas still present in the MDI. This possibility has been rated “cost-effective” in the context of the measures discussed at European level [ECCP 2001].

Conclusions

Replacement of HFCs in metered-dose inhalers by halogen-free propellant gases is no longer being pursued by manufacturers. It is not possible to switch all patients to powder inhalers (DPIs). Moreover, DPIs are rather more expensive.

Nevertheless, data from other countries show that it is possible to achieve a large DPI share while continuing to ensure good patient care. Informing doctors and patients could help to increase the proportion of patients in Germany who are switched to DPIs or are provided with DPIs from the outset.

5.3 *Miscellaneous sprays*

Miscellaneous sprays, or non-technical sprays, are those sprays which cannot be classified in one of the two product groups described above. The greater part of this product group is accounted for by household and cosmetic sprays, but the group also includes “novelties”, i.e. party items such as streamer sprays, and artificial snow in spray cans. For the emissions, see Figure 5.1.

5.3.1 *Household and cosmetic sprays*

Typical aerosol applications found in the household and cosmetic sectors include spray deodorants, hair sprays, insecticide sprays, shoe sprays etc.

The products in these fields were classic applications for the use of CFCs. But as long ago as 1987 German aerosol manufacturers gave the German government an undertaking that they would make a substantial reduction in the quantities of CFCs used [UBA 1989]. Since 1991 the use of CFCs has been banned by the *CFC-Halon Prohibition Ordinance* [FCKW-Verordnung 1991]. Because the use of CFCs was phased out so early in Germany, aerosol manufacturers were at first unable to fall back on HFCs, which were not developed until later.

This is why the use of HFCs is only known in exceptional cases. For example, drain cleaners are a product also sold in the consumer sector which contains HFC-134a. Where drain cleaners use a propellant gas, this has to be a non-flammable, non-toxic gas, because the propellant gas can find its way into the sewer system and give rise to toxic or explosive mixtures of gases [IG Sprühtechnik 2003].

Reduction options

In the field of household and cosmetic products described here, manufacturers of products containing CFCs first developed and marketed replacements with halogen-free propellant gases (hydrocarbons) or products with alternative application techniques (pump sprays, roll-on deodorants etc.). Spray systems without a propellant gas (pump sprays) were not popular with consumers. Today, flammable products have become established in these products. As well as hydrocarbons, air has also been discussed as a propellant gas [Koch 1991].

Thus the question of reduction options only arises in very few cases today. In the drain cleaners segment there is no need to use products containing propellant gas. In this application, HFCs are not used to apply chemicals: their effect is solely due to the pressure they build up. Thus their effect is purely mechanical. Apart from chemical alternatives, which may cause problems for other reasons, a wide variety of other mechanical solutions are available.

Today, as described above, all common hair sprays, deodorants etc. contain only halogen-free hydrocarbons as propellant gases, or no hydrocarbons at all. This confirms that it is technically and economically possible to use propellant gases with a much lower climate impact.

Conclusions

It is not necessary to use HFCs in household or cosmetic sprays.

5.3.2 *Decorative sprays and party items*

This product group includes artificial snow sprays, paint sprays with glitter or metallic effects, artificial spiders' webs, snow, football and other horns, and streamer sprays.

HFCs, especially HFC-134a, were widely used propellant gases in this product sector because they are non-flammable. Using HFCs made it possible to dispense with explosion control measures in production. There was also no need for safety instructions on the products.

Since 4 July 2009, Regulation (EC) No. 842/2006 [KOM 2006] has forbidden the marketing of "novelty aerosols" with fluorinated propellant gases if they were made after 4 July 2009.

Item 40 of Annex XVII to the REACH Regulation (EG) No. 1907/2006 also bans the use of flammable propellant gases in products for decoration and entertainment purposes destined for the consumer sector. This ban on selling to private end consumers does not apply if the manufacturer has shown that there is no danger of ignition despite the content of flammable components [VIS 2008].

Since many products for decoration purposes not only go to the private sector, but are also used for commercial purposes, this rule is difficult for manufacturers to implement. For example, it would be necessary to make a distinction between decorative paint sprays with metallic sheen effects and paint sprays (metallic effect) for car repair purposes [IG Sprühtechnik 2003; Harnisch, Schwarz 2003]. The latter are produced in very large numbers and contain flammable hydrocarbons as propellant gases. What is more, the restriction only applies to a few countries in Europe. In the USA, where there are normally strict rules about the use of flammable substances, the use of flammable propellant gases is permitted in these products [Harnisch, Schwarz 2003].

Reduction options

As with other sprays, the use of flammable propellant gases (hydrocarbons) results in cost savings because of the high cost of HFCs [Harnisch, Schwarz 2003].

Conclusions

It is not necessary to use HFCs in decorative sprays. Products containing hydrocarbons are established on the market. At present, European rules in some cases prevent the use of hydrocarbons in products for private consumers.

Since the products referred to here as party items do not require total application or other qualities (see Chapters 5.3.4 and 5.3.5), it ought to be possible to use halogen-free non-flammable gases or alternative application techniques. The classical paper streamer is an obvious alternative.

5.3.3 Sound devices (signal horns)

Sound devices such as signal horns are needed for safety purposes particularly in shipping, but also in other sectors. Whereas sound devices are required by law on boats or ships to indicate manoeuvres and as fog or emergency signals etc., they are also put to uses other than those intended, e.g. at sporting events or parties [UBA 2003a; Goodmark 2003]. In Germany the use of signal horns in stadiums has long been banned for safety and noise abatement reasons [Harnisch, Schwarz 2003]. Signal horns for party purposes also belong to the category of “novelty aerosols” and have been prohibited throughout Europe by Regulation (EC) No. 842/2006 since 4 July 2009.

In the case of sound products, various devices are distinguished by their type and how they are powered. Under Section 4.01 of the Inland Waterways Code (*Binnenschiffahrtsstraßen-Ordnung – BinSchStrO*) [1998], mechanical sound devices are required for powered craft, excluding small craft¹. Technical requirements are laid down in the Inland Waterways Code and the Inland Waterways Inspection Code (*Binnenschiffahrtsuntersuchungsordnung – BinSchUO*) [1988]. The technical requirements include the sound-pressure level and the basic frequency. In the small craft sector, a further distinction is made between craft less than 20 m in length and craft of less than 12 m.

In the commercial shipping sector, electronic sound devices (electric compressor signal horns and automatic signal horns) are used in view of the on-board power supply and the requirements specified [BSH 2003; Befragung Fachhandel 2003]. In the leisure craft sector there is usually no power supply, so bells etc. or pressurised signal horns are used [Befragung Fachhandel 2003].

The sound devices required on craft exceeding 12 m must be approved [BinSchUO 1998; BSH 2003]. This is not the case with bells etc. or gas-powered sound devices (signal horns). Craft not exceeding 12 m are not subject to equipment requirements [BSH 2003].

Whereas pressurised-gas sound devices (e.g. signal horns) are available from about 6 euros upwards, prices of electronic sound devices are 30 euros or more [Befragung Fachhandel 2003].

¹ Small craft are defined in Section 1.01 of the Inland Waterways Code as craft with a body or hull less than 20 m in length. Exceptions should be noted. The reader is referred to the Inland Waterways Code.

Since craft not exceeding 12 m (leisure craft) are not subject to equipment requirements, bells etc. or compressed-gas sound devices tend to be used in this segment because of their relatively low price. One possibility is to use signal horns. These are powered by a liquefied gas and are connected to an interchangeable gas cartridge [Befragung Fachhandel 2003].

In most cases the gas contained in the product is not specified. Usually, therefore, neither the distributors nor the users of these signal horns know anything about the composition. Thus it is mostly impossible to distinguish between products that contain HFCs and products that do not. The information on the product is usually confined to “CFC-free”, “contains environmentally neutral gas” or “contains non-flammable gas”. As a rule it is HFC-134a [UBA 2003a]. Some manufacturers consider the use of HFC-134a to be necessary to guarantee proper functioning [IG Sprühtechnik 2003; Harnisch, Schwarz 2003].

Reduction options

The use of gas signal horns on craft less than 12 m in length is permitted, but not required. Usually – for visual reasons alone – other sound devices are used, e.g. ship’s bells. It is however possible to do without devices altogether. Under the Inland Waterways Code, it is also permissible to strike metal on metal (e.g. metal bar on railing).

According to distributors of the gas cartridges needed for gas-powered signal horns, there are also products without HFCs on the market [Befragung Fachhandel 2003].

The products should be labelled clearly to enable distributors and users to recognise the environmental relevance of the propellant gases and to choose between the various products. The labelling information about the pressurised gas suggests to the customer that the product is environmentally sound.

Conclusions

It is possible to do without HFCs in sound devices.

The use of signal horns is not permitted on craft with a length exceeding 12 m. On craft of less than 12 m their use is possible, but not required. Other sound devices can be used and are widespread.

It is not necessary to use HFCs in gas signal horns. This is especially true in view of the fact that gas signal horns are mainly used for purposes other than those intended (parties, major events), where they are now prohibited.

5.3.4 *Pepper sprays*

HFC-134a is also used in defence sprays (pepper sprays) of the kind used by the police and KFOR troops. Technical rules require products in this sector to be absolutely non-combustible. Moreover, a defined spray range must be ensured, and the product must be ready for use at all times (as long as there is active substance in the can). According to the manufacturers, technical compliance with these two criteria can only be guaranteed at present by using HFCs (134a). HFC-134a as a propellant gas has pressure in reserve and ensures

adequate pressure. This cannot be ensured by other non-flammable gases such as nitrogen [IG Sprühtechnik 2003].

5.3.5 *Insecticides, pesticides etc.*

Insecticide sprays (approved pesticides) used as stock protection agents are available on the market. The main field of application is the food industry. Also, insecticide sprays containing HFCs are used by pest control personnel, e.g. for fumigating rooms. These are “permanent sprayers” with an automatic spray mechanism which are placed in the rooms. Insecticide sprays are also used in sensitive areas, e.g. aircraft, to prevent the entry of malaria or other diseases. HFCs are not used in insecticide sprays for household use [IG Sprühtechnik 2003].

HFC-propelled products cost 5 to 8 times as much as HFC-free products. In the opinion of the manufacturers and distributors, this ensures that the products are only used in applications where HFCs are absolutely essential for safety reasons [IG Sprühtechnik 2003].

CO₂ could conceivably be used as a replacement for HFCs. However, CO₂ does not deliver the necessary application quality or the fine spatial distribution of the active ingredient [Anhörung 2003].

In view of their flammability, hydrocarbons have not been used to date. Furthermore, the active ingredients (including solvents) in spray aerosols are formulated such that as far as possible they are non-flammable [Anhörung 2003].

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6 HFCs as fire extinguishing agents

In the 1970s and 1980s, halons (fluorochlorobromocarbons) were increasingly used as fire extinguishing agents. Using halons for fire-fighting and the protection of buildings and equipment offered a number of advantages, for example:

- good extinguishing effectiveness,
- extinguishing concentrations that are on the whole toxicologically safe for humans (e.g. making it possible to extinguish burning clothing on the wearer),
- no release time required,
- extinguishing medium not electrically conductive,
- residue-free extinguishing agent.

There were however various practical disadvantages in addition to their ozone depletion and global warming potential:

- formation of aggressive and toxic decomposition products in the event of fire,
- cannot extinguish ember-forming fires,
- very short warning times needed to prevent embers forming.

The high ozone depletion potential of this group of substances resulted in Germany introducing the CFC/Halon Prohibition Ordinance (*FCKW-Halon-Verbots-Verordnung*) [FCKW-Verordnung 1991], which prohibited the production and use of halons as extinguishing agents with effect from 1992. With the exception of a small number of “critical uses”, it was found possible to replace halons in the majority of applications within a short time. Today only military and civil aviation and a very few other applications are regarded as critical. A full list of all critical uses can be found in *Regulation (EC) No. 1005/2009 of the European Parliament and of the Council of 16 September 2009 on substances that deplete the ozone layer* [EG-Verordnung 2009]. The use of halons in all fields other than the critical ones has been prohibited within the EU since 1 January 2004.

Shipping (existing vessels) also counts in part as a critical use. Since 1 January 2004, however, halons have only been permitted in naval vessels for the protection of spaces occupied by personnel and engine compartments and on commercially used cargo ships to protect normally occupied rooms [EG-Verordnung 2000, EG-Verordnung 2009, EG-Verordnung 2010]. According to Pleß and Seliger [2003], it is evident from publications that while alternatives are also available for halons on existing vessels, they are frequently not used for reasons of cost.

In addition to the environmentally friendly extinguishing agents described in the section on *Reduction options*, a number of HFCs and PFCs have been tested as fire-extinguishing agents in other countries. In Europe, fluorocarbons for use in fixed fire-extinguishing systems and hand-held extinguishers have been banned since 4 July 2007 [EG-Verordnung 2006]. HFCs are used in many countries. Some of them have very high global warming potential. Moreover, they form toxic decomposition products when exposed to fire. Apart from HFCs, manufacturers have developed other halogenated compounds, for example the fluoroketone nonafluoro-4-(trifluoromethyl)-3-pentanone, also known as Novec1230 or FK 5-1-12, for use as fire-extinguishing agents.

Stationary fire-extinguishing systems

The requirements for stationary fire-extinguishing systems and the agents used in them are as follows [Pleß, Seliger 2003]:

- acts as genuine volume extinguisher, flooding all parts of the enclosed space,
- minimal extinguishing concentration in enclosed volume,
- minimal space requirements for storage of extinguishing agent,
- little pressure equalisation during flooding of room with extinguishing agent,
- extinguishing agent can be fed in over quite long distances,
- no chemical side-effects due to irritant, corrosive or solvent effects of gases or vapours,
- no corrosive effects during fire or afterwards,
- no acute toxic effects,
- no long-term toxic effects,
- no impacts on the environment either from the compound itself, or from its decomposition products resulting from fire or natural degradation,
- low working pressures for storage of extinguishing agent stocks and the overall system,
- tightness of the seals or joints used,
- low cost of extinguishing agent.

A large number of fluorocarbons and various mixtures with HFCs are under discussion at international level [HTOC 2007]. The fluorocarbons mentioned in Table 6.1 are used in Germany for stationary fire-extinguishing systems. Like other extinguishing agents, fluorocarbons cannot meet all the specified requirements.

Table 6.1: HFCs in stationary fire-extinguishing systems in Germany

Code	Name	GWP ₁₀₀ [WMO 2006]
HFC-227ea	1,1,1,2,3,3,3-heptafluoropropane	3,220
HFC-236fa	1,1,1,3,3,3-hexafluoropropane	9,810
HFC-23	trifluoromethane	14,760

It should be noted that where chemical (fluorinated) extinguishing agents are used, they decompose during the extinguishing process to form reactive compounds for negative catalysis of the combustion reaction. This can give rise to a number of acute toxic compounds. If extinguishment is not successful and a fire develops, a large proportion of the HFCs used decomposes to form hydrogen fluoride and carbonyl fluoride. In such cases, the high concentrations of decomposition products would greatly impede fire-fighting by mobile fire brigade personnel (indoor fire-fighting), or even render it impossible [Pleß, Seliger 2003].

Hand-held and mobile fire extinguishers

Fluorinated extinguishing agents have also been developed for hand-held and mobile extinguishers. In Germany, such hand-held extinguishers are sometimes used in powered recreational craft and racing craft. These extinguishing agents are also used to protect specialised military vehicles. As a rule, water, powder, foam or carbon dioxide hand-held extinguishers satisfy all normal extinguishing requirements.

Table 6.2: HFCs for hand-held and mobile fire extinguishers

Code	Name	GWP ₁₀₀ [WMO 2006]
HFC-227ea	1,1,1,2,3,3,3-heptafluoropropane	3,220
HFC-236fa	1,1,1,3,3,3-hexafluoropropane	9,810

Extinguishing agent situation in Germany

In the past, only approved fire-extinguishing agents were allowed to be marketed and used in Germany. As a result, little use was made of HFCs at first. In 1997, HFC-227ea was the first HFC agent to be licensed in Germany. When participating in the licensing procedure, the Federal Environment Agency advocated the use of HFC-227ea with the reservation that “*FM 200 [...] should only be used where no environmentally sounder alternatives are available and where it is still absolutely essential to use halons within the meaning of the ‘essential-use’ definition in the CFC/Halon Prohibition Ordinance. As a basic rule, test flooding should be dispensed with.*” [UBA 1996]. HFC-236fa and HFC-23 followed in 2001 and 2002. During the approval procedure, the Federal Environment Agency had advocated the use of HFC-236fa with the same reservation as for HFC-227ea. The Federal Environment Agency added “*that approval of this substance in Germany should be for a limited period and should be confined to the use of fire extinguishers in the interior of tanks and in armoured civilian vehicles*” [UBA 2000]. There is no need for HFC-23, nor is this substance acceptable as an

extinguishing agent from an environmental point of view. The Federal Environment Agency therefore recommended that it should not be approved.

Today all three HFCs are used in Germany, mainly in stationary fire-extinguishing systems. Emissions in 2007 came to about 2,100 kg, or nearly 10 kt CO₂ equivalent [NIR 2009]. The total quantity installed in fire-extinguishing systems in 2007 was 258 t [NIR 2009].

Reduction options

In 1992, directly after the ban on halons in Germany, the competent authorities issued special permits for only a handful of halon applications, because substitution was possible in all other applications. In a large number of applications, fire-protection systems were converted to halogen-free agents and techniques. Examples include carbon dioxide, sprinkler and inert gas systems and improved early warning systems. Hand-held extinguishers are once again making increased use of powder, water, foam and carbon dioxide. Selected fields of application are considered separately later.

According to the manufacturers fluoroketone, which is mentioned above and which – like carbon dioxide (CO₂) – has a global warming potential of 1, is suitable for flooding, sprinkler and explosion suppression systems and for hand-held extinguishers [3M 2009].

According to Pleß and Seliger [2003], the struggle to maximise market shares has an unfavourable effect on the choice of the ideal extinguishing agent for an application. The advantages of HFC extinguishing agents are often stressed, and the disadvantages remain unmentioned. It is hardly possible for the user to take objective decisions on the basis of the information available. To change this situation, Pleß and Seliger suggest that the extinguishing agent manufacturer's safety data sheet under the Technical Rules for Hazardous Substances 220 (TRGS 220 [TRGS 220 2009]) should be made a compulsory part of the tender documents for chemical extinguishing agents capable of forming harmful or toxic compounds during the extinguishing process, and for extinguishing agents with toxic properties.

Stationary fire-extinguishing systems

Examples of halogen-free extinguishing agents for stationary fire-extinguishing systems include water mist systems and inert gases. Both function as volume extinguishers, i.e. they exert their extinguishing effect in the flames and stop the combustion reaction by binding radicals, producing a shock reaction or absorbing energy [Pleß, Seliger 2003].

Water mist systems work with a fine water mist having a droplet diameter of less than 200 µm. The extinguishing mechanism is based on the aspects [HTOC 1997]:

- cooling the gas phase,
- displacing the oxygen,
- wetting and cooling the surfaces.

The performance of water mist systems depends greatly on their ability to create droplets of very small diameter (10-100 µm) and to distribute the necessary quantities of water over the entire extinguishing area. The extinguishing effect is also influenced by the geometry of the

water jet and the area to be protected. For this reason the suitability of water mist systems must always be considered in connection with the technology of the system. Water mist cannot be assessed as an extinguishing agent alone [HTOC 1997]. For example, water mist systems are used to protect machine rooms, emergency generators, computer rooms, hotels, offices, underground railways and historic buildings. They have proved very effective and are currently also being tested for use as a replacement for halons in critical applications.

Inert gases are available in a variety of mixtures (see Table 6.3). As opposed to fluorinated fire extinguishing agents, they have no global warming potential. The main difference is that they do not undergo thermal decomposition. This means that greater concentrations are needed for extinguishing purposes. On the other hand, they do not form any corrosive by-products that are harmful to health. Inert gases are used to protect computer centres and control rooms, for example.

Table 6.3: Inert gases for stationary fire-extinguishing systems [HTOC 2007]

Name	IG-541	IG-55	IG-01	IG-100
Trade name	Inergen	Argonite	Argotec	NN 100
Chemical composition				
• Nitrogen	52%	50%		100%
• Argon	40%	50%	100%	
• Carbon dioxide	8%			

An extinguishing agent containing halogens, the fluoroketone Novec1230 or FK 5-1-12, is also available on the market. In view of its non-existent ozone depletion potential and its very low GWP₁₀₀ of 1, this substance is, from an environmental point of view, a suitable alternative to the halons and also to HFCs. In fire situations NovecTM 1230, like HFCs, can form decomposition products that are toxic to humans [Tolksdorf 2003].

However, unlike halogen-free extinguishing agents already available on the market such as Inergen, water, water mist or CO₂, the use of NovecTM 1230 results in an anthropogenic input of fluorine into the environment in the form of fluorocarbons, fluorinated organic acids and hydrogen fluoride (HF). Although the inputs due to NovecTM 1230 are probably very small, NovecTM 1230 should not be used for existing systems without halogenated extinguishing agents or for applications where halogen-free extinguishing agents have proved successful.

Selected applications

A detailed description of the fire-extinguishing possibilities in the applications selected here and other fields can be found in Pleß and Seliger [2003] and elsewhere. We therefore provide only a brief overview here.

Computer centres, computer rooms, control rooms

Computer centres, control rooms and similar applications are usually equipped with stationary fire-extinguishing systems. In Germany, halons were often replaced by a combination of early fire detection and the extinguishing gases nitrogen and argon. HFCs are rarely used in

Germany. Special mini extinguishing systems using nitrogen, argon or carbon dioxide as extinguishing agents have been developed for server cabinets [bvfa].

Inert gases are favoured for this field of application in Denmark too, as they do not form any corrosive decomposition products [Pedersen *et al* 1995]. One example is the use of Inergen in the control centre of the Danish Railways. In this case one requirement for the extinguishing system was that it had to be possible for personnel to remain in the control centre even after the extinguishing system had been triggered [Pedersen *et al* 1995].

Event facilities, airports

Sprinkler systems are installed in a large number of buildings in Germany that are frequented by the public. In addition to the extinguishing system, numerous constructional and organisational fire protection measures ensure comprehensive safety. Examples include Düsseldorf Airport, the Nuremberg Trade Fair and the Allianz Arena in Munich [bvfa].

Explosion suppression

In the past, halons have been used for explosion suppression in areas such as aerosol-filled rooms, grain silos, paper industry or milk powder production. The main alternatives used are powder and water-based systems [UNEP 2002].

Libraries, museums

Libraries and museums always have hand-held fire extinguishers for fighting incipient fires. The extinguishing agent used here is CO₂. One problem in such places is timely detection of fires during the night. Without fire detection precautions, it is a long time before such fires are discovered. Libraries and museums are often in historic buildings. So the fire may spread particularly fast because of the construction of the building and the materials used. The best-known example is the fire in the Anna-Amalia Library in Weimar in 2004. Today the Anna-Amalia Library is equipped with a fine-spray extinguishing system.

As well as sprinkler systems, stationary extinguishing systems may also take the form of CO₂ or inert gas systems [Pleß, Seliger 2003]. CO₂ has the advantage that reliable extinguishing of ember fires is also possible if the extinguishing concentration is adequate. One disadvantage is the fact that a sufficiently long warning period is needed to ensure that all personnel have left the zone that is to be flooded.

Archives

Fire protection concepts tailored to individual requirements and combining constructional measures with hand-held fire extinguishers and automatic extinguishing systems can usually provide comprehensive protection for archives with the aid of halogen-free substances. One possibility is controlled delivery of nitrogen to reduce the oxygen concentration in the air. This rules out the risk of an open fire. At the same time, the reduction in the oxygen concentration can slow down the ageing process in old documents. Access to areas protected by active fire protection systems remains possible [bvfa].

Hand-held and mobile extinguishers

Hand-held fire extinguishers and mobile extinguishing equipment mainly use the traditional extinguishing agents such as water, water mist, foam, carbon dioxide and powder. It is not necessary to use HFCs. The only possible exceptions are mobile extinguishing systems for the interior of tanks, armoured civilian vehicles, and aircraft.

Conclusions

Today halons can be replaced by alternative extinguishing agents in nearly all fields of application. The only exceptions are military applications and aviation.

HFCs and PFCs are not necessary for hand-held extinguishers or mobile extinguishing equipment. The usual agents here are carbon dioxide, foam and powder.

None of the extinguishing agents described in this chapter can satisfy all the requirements for stationary fire-extinguishing systems. However, past experience has shown that halogen-free fire-extinguishing agents can be used for virtually all applications. Today, use of these agents is state of the art. Problems of substitution exist only in some applications in the aviation sector.

HFCs should only be used as extinguishing agents in cases where there are no environmentally friendly alternatives available and their use is absolutely essential to protect human life and health. Each individual case requires careful scrutiny as to whether the use of HFCs as extinguishing agents is justified or not. Marked improvements in fire protection are possible simply by ensuring good constructional planning and a good fire protection concept (early warning systems etc.).

Users must be supplied in suitable form with full information about the properties of chemical extinguishing agents, including those properties that are relevant to the environment.

If halogenated substances are used in special cases, steps must be taken to minimise emissions during the installation and use phases by ensuring continuous inspection of the systems. It must also be guaranteed that on reaching the end of its maximum life, the extinguishing agent will be either recycled or properly disposed of. Moreover, substances with the lowest possible GWP should be selected.

A halogen-containing extinguishing agent with a very low GWP is available on the market as NovecTM 1230 (FK 5-1-12). From an environmental point of view, this substance is a suitable alternative to halons and to HFCs. NovecTM 1230 should not be used for existing systems without halogenated extinguishing agents or for applications where halogen-free extinguishing agents have proved successful.

Substances with a very high GWP should not be used in any circumstances. These include PFCs, which are already prohibited in the EU, and HFC-23.

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7 HFCs as solvents

Solvents are applied in many fields. This chapter discusses the possibility of using HFCs as solvents for surface cleaning in commercial and industrial installations. It does not include dry cleaning, because HFCs are not used for dry-cleaning.

Industrial applications of solvents include in particular the surface cleaning of metals, glass and gemstones. Surface cleaning is mostly concerned with degreasing and drying. It frequently takes place between individual manufacturing or treatment stages (e.g. before surface coating, before bonding of materials etc.) and at the end of production processes. Examples of important branches of industry / users of solvents in surface cleaning systems include the metal-working industry, the optical industry, precision engineering, aerospace industry and medical technology [Schwarz, Leisewitz 1994; Harnisch, Schwarz 2003; UNEP 2003].

In some areas, the quality requirements for surface cleaning are extremely high. Sensitive surfaces and the need for complete and residue-free removal of grease, dust and moisture from very small objects with complex geometrical shapes make great demands on the solvents and/or cleaning processes. At the same time the cost of installing and operating the system, including the energy costs of drying processes, should be low [Schwarz, Leisewitz 1994; Harnisch, Schwarz 2003].

In principle, organic solvents are well suited to cleaning surfaces. For many years the solvents used were mainly chlorinated hydrocarbons and CFCs [Schwarz, Leisewitz 1994; UNEP 2003]. CFCs were used because of their non-flammability, their inert character in relation to materials, their low toxicity and their good capacity for dissolving oils and fats. Until the ban on CFCs was imposed, the main product used was CFC-113. Other CFCs were rarely used [UBA 1989].

Suitable substitutes for CFCs are low-solvent/no-solvent processes and chlorine-free solvents. In view of their ODP, HCFCs and n-propylbromide (n-PB) are not alternatives. HCFCs are not used in Germany. No cases are known where n-PB is used.

HFCs are widely used around the world. Especially for precision cleaning, solvent manufacturers in the USA have developed new, non-flammable fluorinated compounds to replace CFC-113, HCFC-141b and 1,1,1-trichlorethane which have been banned there since 1996. The product most widely marketed in the USA is HFC-43-10mee = $C_5H_2F_{10}$ (sold in the USA since June 1995, in Europe since 1996). Other HFCs available are HFC-365mfc [Schwarz, Leisewitz 1999; Solvay 2009], HFC-245fa and HFC-c447ef on their own or in blends [UNEP 2006].

Part B – Application areas and processes: consumption, emissions and alternatives

In Germany the emissions resulting from use of HFCs as solvents in surface cleaning are negligible because of existing national regulations (see section on *Reduction options*). In view of their relevance in other countries, however, this report provides a brief overview of this potential field of application.

Reduction options

In Germany the use of not only CFCs, but also HFCs and PFCs, as solvents has been prohibited since 1993 under the Second Federal Immission Control Ordinance [BImSchV 1990]. The amendment adopted in 2001 in connection with the transposition of the European *VOC Solvents Directive* [1999] does not lift this ban. Under the Second Federal Immission Control Ordinance (2. BImSchV), which was renamed *Ordinance on controlling emissions of volatile halogenated organic compounds* in the course of adaptation to EC law, “*the only volatile halocarbons that may be used in the operation of installations are tetrachloroethene, trichloroethene or dichloromethane in technically pure form*”. However, the new provisions allow special permits on application; these are tied to strict requirements: According to Section 17 “*the competent authority may on application by the operator also permit the use of volatile fluorocarbons in technically pure form or blended with trans-1,2-dichloroethene for high-quality applications in surface treatment installations, especially in the cleaning of electronic components, the manufacture of precision components or the production of instrumentation and control systems, provided that in the individual case there is no reason to expect harmful environmental effects or climate impacts and if the state of the art is such that no other fluorocarbons can be used for such applications*”. This special provision has been used only once to date.

In addition to HFCs, manufacturers have also developed hydrofluoroethers (HFEs) as a special substitute for CFCs [UNEP 2006, 3M 2009]. In some cases these have been used as drop-in substances, i.e. these substances made it possible to continue using existing CFC systems [Schwarz, Leisewitz 1999].

Because of their ether bond in the molecule, HFEs have a shorter atmospheric lifetime than HFCs. Therefore their GWP is usually lower than for HFCs. However, with a GWP₁₀₀ of 30 to 500 their GWP₁₀₀ is still far higher than the GWP of halogen-free hydrocarbons. Today HFEs are used in specialised applications, mostly in blends or co-solvent processes [UNEP 2003; IPCC/TEAP 2005, 3M 2009]. The chemical industry is increasingly offering HFEs in aerosol containers for the electronics industry. No data are available on this field of applications in Germany.

Owing to the early phase-out of CFCs as solvents in Germany and the bans imposed by the Second Federal Immission Control Ordinance, the selection and use of substitute substances has taken a different course than in countries that made the phase-out later. At the time the HFCs and HFEs were developed, for example, water-based cleaners, semi-aqueous processes, changes in production methods to eliminate the need for cleaning, and halogen-free organic solvents (de-aromatised aliphatic hydrocarbons, solvents based on alcohol/glycoether) had already become established in Germany [Schwarz, Leisewitz 1994; Harnisch, Schwarz 2003]. As a result, HFEs were of minor importance in Germany compared with other countries. As

volatile halogenated organic compounds, HFEs fall within the scope of the revised Second Federal Immission Control Ordinance and are subject to the strict technical requirements defined there. Under this ordinance, HFCs like HFC-43-10mee were not allowed to be used in Germany at the time they came onto the market.

Instead of using chlorine-free organic or water-based solvents, one could also consider using low-solvent/no-solvent processes. One example of a no-solvent process is plasma cleaning [3M 2000; UNEP 2003].

In view of the special situation in Germany, this report does not describe the possible uses or the advantages and disadvantage of the various processes. For example, any overall comparison of the various processes must also take account of differences in energy consumption. A good description can be found in [UNEP 2003].

Conclusions

While fluorinated CFC-substitutes such as HFCs or HFEs were being developed, halogen-free solvents and processes or manufacturing techniques without cleaning processes were in Germany already accepted and in use. Although the use of HFEs and in exceptional cases also HFCs is still allowed, this possibility is not used in Germany (with one exception). This leads to the conclusion that the use of fluorinated solvents is not strictly necessary.

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8 HFCs, PFCs and SF₆ as etching gases

Fluorinated gases (HFCs, PFCs, SF₆ and NF₃) are suitable fluorine suppliers for etching processes (plasma etching, plasma processes). PFCs are primarily used for etching purposes. Etching processes are used in the semiconductor industry, circuit board manufacture and the photovoltaic industry. The semiconductor industry plays a dominant role here as far as quantities used and emissions are concerned.

Unlike most of the uses of fluorinated gases described above, this use as etching gas results in their conversion or decomposition. However, the quantities used are not necessarily a measure of the emissions. On the contrary, a wide variety of factors are relevant here, such as process management, exhaust-gas cleaning, type of process and type of gas used etc.

When it comes to PFC emissions, the semiconductor industry is the second-largest source after the aluminium industry. In the case of HFC and SF₆ emissions, however, it is relatively unimportant compared with other sources. For example, annual HFC emissions by the semiconductor industry are around 0.02 million t CO₂ equivalent. There have been only slight variations over the last five years (see Fig. 8.1). And annual SF₆ emissions, which are currently in the region of 0.03 million t CO₂ equivalent, have been halved since 2004. The same is true of PFC emissions. From a peak of 0.33 million t in 2000 they had fallen to 0.14 million t by 2008. The emission reductions can be attributed not only to the drop in production, but also to emission reduction measures [Infineon 2009].

According to current estimates, PFC emissions from printed circuit board manufacture have remained virtually unchanged since 1995 at around 0.02 million t CO₂ equivalent. Not all manufacturers have started using plasma processes in PCB manufacture. With advances in technical development and growing requirements for printed circuit boards, this could change in the years ahead. As a result, emissions in this sector could rise if no emission reduction measures are taken. Figure 8.1 shows how emissions developed during the period 1995 to 2008.

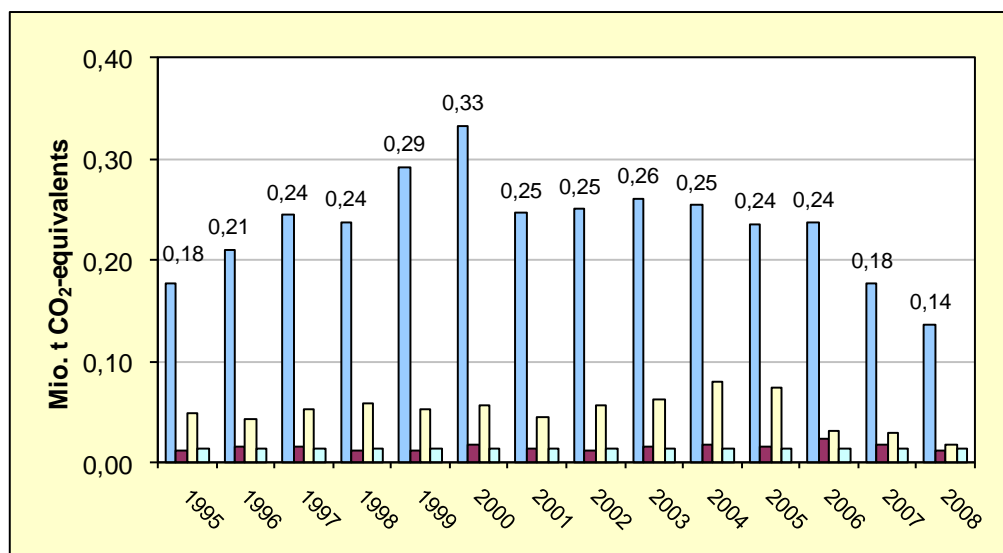


Fig. 8.1: Emissions of fluorinated gases by the semiconductor industry (left to right: PFCs, HFCs, SF₆) and from PCB manufacture (right column) in Germany, in million t CO₂ equivalent. Data from: [Schwarz 2009; ZVEI 2009].

8.1 Semiconductor industry

Today, products from the semiconductor industry are found in virtually all sectors. Examples include mobile communication, computers, safety and chip card technology, and automobile and industrial electronics. The semiconductor industry produces electronic components which, among other things, help to reduce power consumption, e.g. in computer mains units or in car engine control systems.

HFCs, PFCs and SF₆ are needed by the semiconductor industry for producing “wafers”, the modules of high-purity silicon which form the basis for all semiconductor components. F-gases are largely used in two fields: plasma etching (etching gases) and chamber cleaning (cleaning gases). From a chemo-physical point of view, these are both etching processes.

Fluorine ions and radicals are needed for etching silicon (wafer production). Initially the semiconductor industry used hydrofluoric acid for this purpose. The etching process serves to structure the surface of the silicon. In recent years there have been major changes in the nature of the structures. In the past the structures were relatively coarse, but today their width has been reduced to only 0.15 µm. This feature width can no longer be achieved with hydrofluoric acid. This led to the use of fluorinated gases. These are first “cracked” in a prechamber to release the fluorine [Infineon 2003]. Thus PFCs are already partly converted during the etching process. These conversion and recombination processes result in a large number of gases in the chamber and in the exhaust air. For example, the conversion of the PFCs C₂F₆ and C₃F₈ in the plasma results in the formation of non-negligible quantities of CF₄ as a by-product [Schwarz, Leisewitz 1999].

The choice of PFCs in plasma etching depends on the desired structure. Each PFC is closely keyed to the individual process [Infineon 2003], because not only the fluorine content is important, but also the carbon content. Both have an influence of the formation of C-F-

polymers, which in turn influence the etching process [Beu *et al* 1998]. In general, there have been major technological advances in wafer production and in the etching processes. This has to be borne in mind in the search for substitutes and emission reduction measures. SF₆ is used only in older installations (4-inch and 6-inch installations¹) or for specialised etching operations.

Wafers with various dielectric (silicon) and metallic films are produced by the Chemical Vapour Deposition (CVD) method. During deposition of the films from the gas phase, some of the material is not deposited on the wafer, but in the CVD chambers. To prevent these films peeling off in the subsequent process and giving rise to impurities on the wafer, the chambers are cleaned in accordance with fixed cycles. Fluorinated gases are again used to clean the chambers, and these also undergo conversion as in the etching process proper. Unlike plasma etching, however, chamber cleaning – which is itself basically an etching process – does not have any great influence on the product. This means there is more scope when selecting the gases to be used. As a result there are more possible substitutes [Infineon 2003].

Reduction options

The driving force behind emission reductions in the semiconductor industry, apart from possible cost reductions, is targets set by the industry itself: In April 1999 the World Semiconductor Council (WSC) declared that it would make a 10% reduction in greenhouse gas emissions from semiconductor production by 2010, compared with the base year 1995 [WSC 1999]. In view of a growth rate of 15%², this corresponds to a reduction in the region of 90-95% [Infineon 2003]. At both European and national level, the relevant semiconductor manufacturers are seeking to achieve equivalent targets. The voluntary undertaking of 2004 by the semiconductor manufacturers with production locations in Germany must also be seen in this context. On the lines of the undertakings given at supra-national level, these producers undertook to reduce absolute greenhouse gas emissions by at least 8% compared with the base year 1995 [ZVEI 2005]. According to the emission data recorded by the Components Association within the Central Association of the Electrical Engineering and Electronics Industry (ZVEI), this target was exceeded as early as 2007 with a reduction of 13.4% [ZVEI 2008]. This emission trend is due partly to the fact that wafer production has in fact not grown as fast as the forecasts, and partly to the newly installed exhaust-gas cleaning systems (see below).

Despite these successes, intensive work is continuing on research into new etching gases and processes as an emission reduction option. The leading role here is played by the international research association SEMATECH (Semiconductor Manufacturing Technology). Many semiconductor manufacturers are members of this association. The results of this research work are presented on the Internet, and also at conferences.

¹ The figures in inches relate to the size of the wafers. Wafer sizes have continuously increased from 4 inches (100 mm) to 12 inches (300 mm).

² This growth rate can be calculated statistically from the growth rates of the last 40 years. In view of the slower growth in recent years, this figure should now be corrected to about 10-12%.

Part B – Application areas and processes: consumption, emissions and alternatives

The research activities can be divided into four basic fields:

- alternative chemicals,
- process optimisation,
- recycling and
- exhaust-gas cleaning / end-of-pipe technologies.

The search for less environmentally harmful alternative chemicals has top priority among current research activities. The main focus of the search is on gases with a lower GWP and higher degradation in the process. Satisfying these criteria is made more difficult by the fact that a high degree of fluorination in a stable compound does basically not feature a lower GWP.

New gases for etching processes are being developed and tested in combination with new chamber generations. This means they cannot be used for existing chambers; conversion is not feasible [Infineon 2003].

At first NF_3 was considered as a possible substitute for sub-processes (chamber cleaning). According to the state of knowledge at the time, this was to be 98% destroyed even without subsequent exhaust-gas cleaning (see text below). In well managed etching processes, as much as 99.9% of the NF_3 used is destroyed, but complex cleaning is necessary to ensure that the scrubber water from the downstream exhaust-gas cleaning system is freed from dissolved HF, heavy metals and sand. Furthermore, only about 60% of all flue gas is treated by exhaust-gas cleaning systems [ZVEI, 2007], which means that a substantial proportion of NF_3 escapes into the atmosphere from badly managed etching processes. In spite of this problem there was a continuous increase in the use, and hence emissions, of NF_3 until 2005, but in recent years the figure has been brought down again nearly to the base level of 1995 [ZVEI 2008]. Factors responsible for this development are the lower level of plant utilisation, and also investment by the manufacturers in process optimisation (remote plasma clean) and flue-gas cleaning systems. The remote plasma clean method converts some 99.9% of the NF_3 employed, whereas the rate for HFC gases is only around 95% [Chen *et al* 2003].

ClF_3 was discussed in Japan as a possible substitute. This is a rocket fuel additive and a highly explosive hazardous chemical. Its use is rejected in Europe and the USA for safety reasons [Infineon 2003].

A few years ago, C_3F_8 was announced for chamber cleaning, initially as a possible alternative to C_2F_6 . Today C_3F_8 is already in use in the semiconductor industry. The quantities used first of all showed continuous growth after its introduction in 1997, but have remained more or less constant for the past few years. According to the manufacturer, C_3F_8 can reduce costs by up to 60% thanks to smaller input quantities while simultaneously reducing PFC emissions. Furthermore, C_3F_8 can be used as a drop-in substitute in existing C_2F_6 systems [3M 2003a]. One disadvantage mentioned is that CF_4 forms as a by-product. As long ago as 1998, C_3F_8 was therefore classed as an interim solution [Beu *et al* 1998].

Other new substances under discussion were $\text{C}_4\text{F}_8\text{O}$ (3M), C_4F_9 (Dupont) and many other chemicals, including various HFCs and CF_3I [Beu *et al* 1998; 3M 2003b]. In spite of

promising tests in Europe and Germany, which the manufacturers claimed permitted a 90% emission reduction compared with optimised PFC processes, none of these chemicals became established here in Germany [3M 2003b; ZVEI 2008].

Apart from finding substitutes for substances, process optimisation is another option for reducing emissions of greenhouse gases. Intensive work is in progress in this field. Process optimisation in the semiconductor industry aims to reduce the input of chemicals by stepping up conversion rates. This means reduced raw materials costs and disposal costs, accompanied by a reduction in emissions. Thus process optimisation usually leads to a reduction in adverse environmental impacts combined with a reduction in costs [Infineon 2003]. Research into process optimisation has so far focused on chamber cleaning processes. This is connected with the less stringent requirements for the etching processes that take place during chamber cleaning. In individual cases, process optimisation can result in emission reductions of 10-50%. For example, intensive research has been carried out into C₂F₆ as a cleaning gas [Beu *et al* 1998].

As well as process optimisation, work is in progress on recycling concepts. Membrane processes and/or cryogenic separation techniques are under development [Vartanian *et al* 2000]. Recycling concepts be applied to both exhaust gases and cleaning processes. Information from semiconductor manufacturers indicates that a pilot plant for PFC recycling which was tested in the USA in this connection (Texas Instruments) did not meet with any success. The main problem here was that one is basically dealing with mixtures of gases which are very difficult to separate [Infineon 2003].

At present, emission reduction techniques are focusing largely on exhaust-gas cleaning [Infineon 2003]. Like recycling concepts, these can be applied to exhaust gases from both etching and cleaning processes. PFCs are already partly converted during the etching/cleaning process. To a large extent (85-99%) they can then be destroyed in the downstream exhaust-gas cleaning process. Exhaust-gas cleaning systems are currently state of the art. On the other hand not all installations are equipped with efficient exhaust-gas cleaning systems. In 1997 the figure was 30% of all German production locations [Schwarz, Leisewitz 1999], and by 2007 the proportion had – as mentioned – increased to 60% [ZVEI 2007]. Some manufacturers have already reached the maximum equipment level, which means that 95-98% of the gases produced are cleaned [Infineon 2009]. A distinction can be made between local point-of-use (POU) technologies and end-of-pipe (EOP) technologies for several chambers or entire production sites [Beu *et al* 1998]. The cost of exhaust-gas cleaning systems ranges from 60,000 to 200,000 euros plus installation costs. These can be between 5,000 and 30,000 euros. Operators quote operating costs of around 18,000 euros. All costs depend on the throughput and the type of plant [Infineon 2003]. As a general rule it is true to say that exhaust-gas cleaning costs more than primary measures [Beu *et al* 1998]. Thermal processes are the most expensive of all exhaust-gas cleaning processes [Infineon 2003]. Vartanian *et al* [2000] compared the costs of thermal processes (EOP) and plasma processes (POU). They arrive at capital costs of \$25,000-\$50,000 per chamber for the tried-and-tested thermal process and \$20,000-\$25,000 per chamber for the relatively new plasma process. Annual operating costs were around \$10,000-\$25,000 and \$500-\$1,000.

The industry takes the view that in future a wide range of emission reduction measures will continue to exist in parallel. In most cases new developments will only be adopted for new factories or plant extensions [Infineon 2003].

Conclusions

The targets first defined in the 1999 declaration by the WSC and adopted by German semiconductor manufacturers in a voluntary follow-up undertaking can only be achieved by implementing efficient measures. Emission reduction measures are:

1. alternative chemicals / gases,
2. process optimisation,
3. recycling and exhaust-gas cleaning (end-of-pipe technologies).

The development of alternative and less environmentally hazardous chemicals is the best and most far-sighted solution and has therefore top priority. Process optimisation consists in important supplementary measures which usually result in cost savings as well. End-of-pipe technologies make sense wherever primary measures are not possible or where they complement primary measures. This applies to existing plants in particular. Generally speaking, new gases for etching processes can only be used for new chambers, whereas other measures can also be implemented in existing plants.

Some of the alternative chemicals developed by the chemical industry in cooperation with plant manufacturers have produced good results in pilot plants, and in some cases they are already being used for production-scale operations. In view of these alternatives, in combination with process optimisation and the other measures described, the semiconductor industry can be expected to meet its targets.

In order to achieve these targets there is a need for systematic implementation of research results when setting up new production capacity or modernising existing facilities, and for equipping existing production locations with downstream exhaust-gas cleaning systems or implementing other suitable measures.

8.2 *Thin-film solar modules and flat-screen production*

The Chemical Vapour Deposition (CVD) method is used in the manufacture of thin-film solar modules, as in the production of multilayer wafers. Here the silicon is deposited on a glass disk from the gas phase, and the CVD chambers have to be cleaned just as in semiconductor manufacture. To this end SF_6 and, increasingly, NF_3 are used. The latter ensures faster chamber cleaning compared to SF_6 and is therefore more suitable for the production process. For this reason it can be assumed that in future NF_3 will tend to be used for cleaning purposes rather than SF_6 . Although the manufacturers producing thin-film solar modules in Germany have equipped their production facilities with exhaust-gas cleaning plants, some 3-5% of the cleaning gas used escapes into the atmosphere because systems are overloaded or not functioning properly. This is the result of incorrect dimensioning of these systems, which

were first installed in semiconductor production where they were designed for much smaller quantities of gas [Sollmann 2008].

Another process in which the CVD method is used for coating glass surfaces is the production of flat-screen displays (liquid crystal displays, LCD) and LCD television sets. As in the production processes described above, chamber cleaning is necessary here as well. In this field NF₃ is the main source of fluorine. According to the ZVEI, there is no significant production capacity in Germany for LCD flat-screen displays or LCD television sets [ZVEI 2010].

Reduction options

The simplest solution is first of all to design exhaust-gas cleaning systems to deal with the greenhouse gas quantities actually occurring, and to ensure trouble-free operation, e.g. by redundant design of exhaust-gas cleaning systems.

One alternative to fluorinated greenhouse gases is to use fluorine gas (F₂). Because of its corrosive properties and its toxicity, however, this is not supplied and used in compressed-gas cylinders, but is produced from hydrogen fluoride (HF) in an on-site chemical process. This method, known as the on-site fluorine process, is already used in the production of flat-screen displays [Toshiba 2006]. In combination with suitable exhaust-gas cleaning technologies, this process offers great potential for achieving sizeable reductions in emissions of fluorinated greenhouse gases in this and related fields of application. The technology is already in use in Germany. Since using elementary fluorine can halve the cleaning time and thereby shorten the entire production process by 10%, this alternative is also more cost-effective than the chamber cleaning processes used to date [Linde 2010].

As an alternative to the CVD technology, thin-film solar module production is also possible by means of electron-beam evaporation, which permits targeted coating. This method does not need the complicated process of chamber cleaning, and the deposition rates of 20 nm/s are also significantly higher than with the CVD process (0.5-2 nm/s) [Becker *et al* 2008]. To date, however, this technology has been confined to laboratory scale, and has not yet been implemented on a large scale in production operations.

Conclusions

The use of fluorinated greenhouse gases is no longer necessary in large new installations. In existing systems, process management can be optimised to achieve marked reductions in emissions of fluorinated greenhouse gases. Emission minimisation is ensured by redundant design of exhaust-gas cleaning systems.

8.3 Printed circuit board manufacture

In printed circuit board (PCB) manufacture, etching processes are used to clean and/or prepare surfaces for subsequent deposition of copper films (metallisation), e.g. to remove (desmear) the unwanted products formed from the epoxy resin after hole drilling, and for etching back (e.g. epoxy resin) to create a larger surface. If plasma processes are used for

etching, CF₄ mixed with oxygen is used as the etching gas [Schwarz, Leisewitz 1999; ZVEI 2002]. Depending on the application, the CF₄ concentration is between 5 and 15% [plasonic 2003].

Another example of an application for plasma processes is plasma drilling of flexible circuit boards [iaf].

Reduction options

Although plasma processes are widely used in semiconductor production, not all manufacturers are using them yet for printed circuit board production [plasonic 2003]. Many manufacturers, especially in Europe, continue to use wet-chemical methods. For desmearing purposes the base material is swelled with solvent and then etched with a hot permanganate solution and neutralised [anonym; EPA]. Other methods exist, but are hardly used today. Inorganic acids can be used for etchback processes [anon.].

Compared with liquid cleaning methods (wet-chemical processes), plasma processes do not leave behind any corrosive residues on the components. Consistent quality is guaranteed (because there are no fluctuating bath concentrations) [iaf]. Some printed circuit board materials do not permit the use of wet-chemical processes. According to the ZVEI [2002], for example, the dry plasma process has to be used to remove drilling smears on Teflon and on polyimide in combination with acrylic resin adhesives. Also, cleaning of microvias (micro drill holes) in flexible PCBs is hardly possible with wet-chemical processes because of their very small diameter [plasonic 2003]. For this reason post-laser plasma cleaning is performed, as the name suggests, with the aid of plasma processes [ZVEI 2002].

Using plasma processes eliminates the need for the entire wet-chemical process. According to various statements [anon.; EPA; ZVEI 2002] this results in reductions in operating costs, water consumption and waste volume. Plasma processes are rated more environmentally sound than wet-chemical processes. In view of this, the US EPA supports a changeover from wet-chemical to plasma processes.

To date no new etching gases with less environmental impact have been developed for printed circuit board manufacture.

Unlike the plasma processes described above (desmearing, etchback), plasma drilling of flexible circuit boards competes with laser drilling. The latter achieves such good quality that drilling with the plasma process is unlikely to become widespread [plasonic 2003].

According to plasonic [1999: in Schwarz, Leisewitz 1999], although alkali exhaust-gas scrubbers exist in PCB manufacture for intercepting the reaction products (e.g. HF), there are no systems capable of splitting the non-converted or recombined CF₄ in the exhaust gas. As a result, Schwarz [1999] estimates the CF₄ emissions in the process chamber exhaust gases at 85%, while plasonic [2003] puts the figure at up to 98% of the CF₄ gas input. To date there has been little change in the situation since 1999. Today, according to plasonic [2003], there are technologies available for downstream incineration (on the lines of the technology used in the semiconductor industry). However, implementing these technologies involves capital costs of around 200,000 euros. For comparison: Plant costs (plasma system) are also around

200,000 euros, and the cost of the downstream scrubber around 50,000 euros; downstream incineration does not render the scrubber superfluous.

Conclusions

Those technologies currently available for printed circuit board manufacture which do not use CF₄ cannot be used for all circuit boards (materials, types). Moreover, they are generally regarded as less environmentally sound. In view of the low relevance of these applications with regard to PFC emissions, a number of assessments have not been carried out. To date no alternative etching gases have been developed for printed circuit board manufacture.

Thus as things stand at present, this leaves mainly end-of-pipe technologies as a means of achieving emission reductions. In circuit board production, as in the semiconductor industry, using downstream splitters (incineration) is one technical means of reducing CF₄ emissions. This involves high costs, however. Against the background of the fairly low emissions, such a measure would in many cases be out of proportion. However, plasma processes will probably become increasingly established in PCB production. As a result, emissions of fluorinated gases will increase. The possibility of using a downstream incineration system should therefore be considered, at least for major production facilities. Also, the development of smaller and hence less expensive systems for small production plants should be encouraged.

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9 SF₆ as arc-quenching and insulating gas in electrical equipment

Electrical equipment (switchgear and controlgear, transformers) is used in electricity grids to distribute and transform power and to connect and disconnect power supply companies and industrial plants. Electrical equipment is used in all voltage ranges from low voltage (voltages of less than 1 kV) up to extra-high voltage. The voltage range above 1 kV is subdivided into medium voltage (1 to less than 52 kV), high voltage (52 kV upwards) and extra-high voltage (110 kV upwards). Electrical equipment using SF₆ is mainly operated by the power supply companies (public network operators).

Sulphur hexafluoride (SF₆) has been used worldwide as an arc-quenching and/or insulating medium in high-voltage electrical equipment (>52 to 380 kV) since the 1960s, and in the medium voltage range (1-52 kV) since about 10 years later. SF₆ replaced the media oil or air. SF₆ is also used for manufacturing components for gas-insulated indoor switchgear (instrument transformers and bushings) and high-voltage outdoor instrument transformers. SF₆ is not used in low-voltage equipment [ZVEI 2003].

The bulk of the SF₆ used in Germany – 915 t in 2008 – enters the “electrical equipment” sector [ZVEI 2009]. A large proportion of the systems produced in Germany are exported. This means that, except for the emissions during manufacture, SF₆ emissions from these systems are released at the point of use and are therefore not taken into account in German reporting of GHG emissions.

In 2008, electrical equipment in Germany for the voltage range above 1 kV contained around 1,860 t of SF₆. Some 60% of the SF₆ amount is used in high-voltage equipment. Conventional devices (high-voltage circuit-breakers, instrument transformers) account for 1/3 and gas-insulated switchgear (GIS) for about 2/3 of the SF₆ quantities in high-voltage equipment.

About 40% of the SF₆ quantities are used in medium-voltage equipment. Here ring-main units (RMUs) are a key application, with 2/3 of the SF₆ used in this sector. Small quantities are used in circuit breakers (up to 36 kV) and circuit-breaker systems [ZVEI 2004, 2009]. Figure 9.1 shows the quantities of SF₆ installed in Germany in 2008 in the various types of electrical equipment.

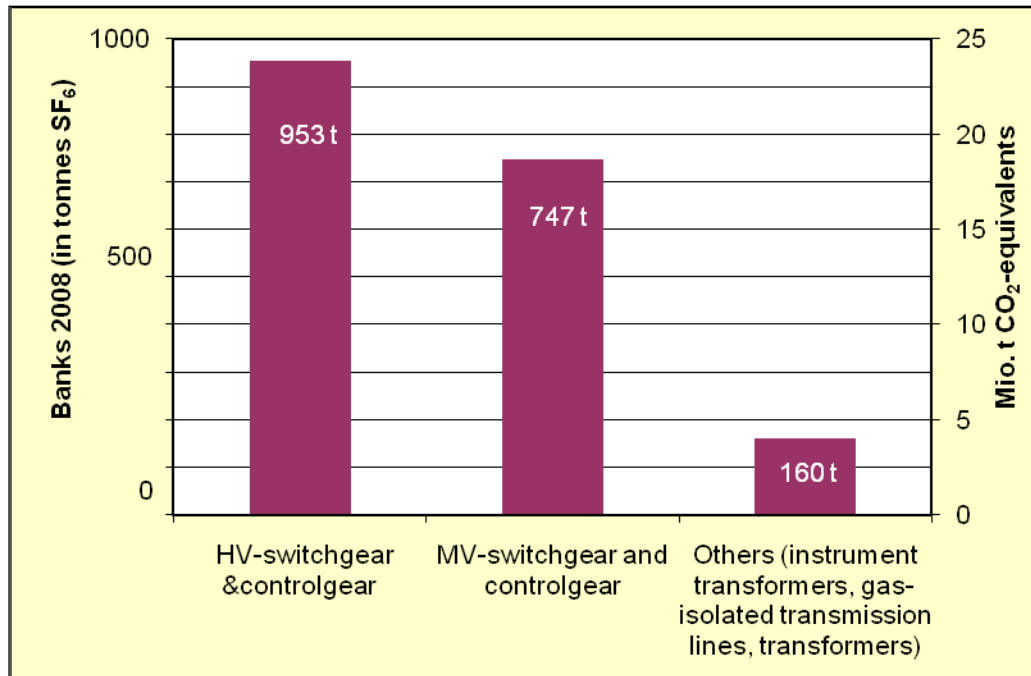


Figure 9.1: Quantities of SF₆ installed in electrical equipment in Germany in 2008, in tonnes [ZVEI 2009].

In 2008, emissions of SF₆ at manufacturers and operators of electrical equipment came to about 22.7 t [ZVEI 2009]. The network operators designed their survey of data on the high-voltage segment more efficiently; in order to determine emissions factors for such installations, they determine leakage from equipment in representative reference installations [Schwarz 2007]. The emissions trend since 1990 can be seen in Chapter 2 of this report.

A study on high and medium voltage equipment in Europe shows that life-cycle emissions of SF₆ have decreased since the mid 1990s; however, further reductions would be possible by 2020 if the measures were implemented throughout Europe [Ecofys 2005].

Switchgear containing SF₆ is subject to the European F-Gas Regulation. This requires that recovery of SF₆ from switchgear exceeding 1 kV must only be carried out by certified personnel, and specifies minimum requirements for the personnel that carries out recycling, reclamation and destruction. Switchgear containing SF₆ must be labelled.

Numerous international standards for switchgear and controlgear (like the IEC 62271-series standards at international level, and DIN EN 62271/VDE0671 in Germany) have been systematised and revised in recent years, with the result that the use of SF₆ in switchgear and controlgear is now possible on a standardised basis worldwide. In Germany the information supplied by the employers liability insurance association (*Berufsgenossenschaft*) on SF₆ switchgear and controlgear provides additional advice and recommendations for practical implementation of the rules on SF₆ [BGI 2008].

CIGRE (Conseil International des Grands Réseaux Electriques), the international forum for electrical power generation, transmission and distribution, has published guidelines on the handling and recycling of SF₆ [CIGRE 2003, 2005]. These CIGRE guides have been incorporated in a technical report by the IEC International Standards Committee and are available in German in the VDE's set of national standards.

These reports also refer to the poor tightness of certain older gas-insulated equipment, high-voltage systems in particular, which may lead to a high operational leakage rate of SF₆; therefore measures have to be taken to reduce these SF₆ emissions. With the aim of preventing SF₆ emissions, procedures are defined for safe, environmentally sound handling of SF₆ during initial assembly and installation, putting into operation, usual and exceptional operating situations, and end-of-life disposal of high-voltage switchgear and controlgear. They also deal with storage and transport of SF₆. Furthermore, they define procedures for handling possible decomposition products of SF₆ which may form under the influence of strong electric arcs [IEC 2007, IEC 2008].

In 2007, CIGRE published a new brochure "SF₆ Tightness Tests" for SF₆-insulated equipment > 1 kV. The aim is to define procedures and measurement methods at international level with a view to minimising operational leakage rates. A revised version is expected at the end of 2010.

The Intergovernmental Panel on Climate Change (IPCC) has developed two approved methodologies for calculating credits for SF₆ emission reduction during recovery/reclamation of SF₆ from electricity grids and for the recovery and reclamation of SF₆ after switchgear testing procedures [UNFCCC 2006, 2009]. As yet, no projects have been started under the UNFCCC. Projects would only be possible in countries where the recovery of SF₆ was not yet prescribed by law.

Switchgear and electrical equipment

Electrical equipment for power supply is found at the junctions of transmission and distribution networks in the public power supply sector and in industry. In these grids, switchgear is used to connect or disconnect grid subdivisions and/or consumer groups, for example. Major components of **switchgear** are circuit-breakers, switch-disconnectors and disconnectors. Switchgear may be executed as outdoor or indoor systems.

In medium-voltage networks, a distinction is made between primary and secondary distribution networks. **Primary distribution** includes medium-voltage switchgear with circuit-breakers, e.g. in transformer substations¹ or power plants, which transform the power from high to medium

¹ All high-voltage switchgear is made up of several switch bays. Each switch bay (usually six to ten per switchgear) has its separate circuit breaker, its separate busbar, its separate points of withdrawal, cable outlets etc. High-voltage switchgear is often located at the feed-in points from regional or supra-regional high-voltage lines to local medium-voltage networks. They are usually situated upstream of a power transformer which takes care of voltage reduction.

voltage. Apart from connecting and disconnecting operating power in sub-networks, switchgear must also be able to switch off within milliseconds any high short-circuit currents resulting from faults and problems on the circuit, and to quench any electric arcs that occur. The **secondary distribution network** comprises the distribution of the electrical energy at the medium-voltage level and the voltage reduction² from medium to low voltage. The equipment used is largely ring-main units and – to a small extent – combination of ring-main-units with switchgear with circuit-breakers [Schwarz, Leisewitz 1999; VDN 2002; Nelles, Tuttas 1998; Heuck, Dettmann 1999].

Typical electrical equipment containing SF₆ is described in a study for the EU [Ecofys 2005].

9.1 Switchgear in the voltage range 52-380 kV (high voltage)

Today there are, apart from very old installations, essentially two types of installation which are used in the high-voltage sector: SF₆-insulated high-voltage switchgear and air-insulated substations. Both types contain the greenhouse gas SF₆, though in very different quantities.

SF₆-insulated high-voltage switchgear (Gas Insulated Switchgear or GIS) is mainly installed indoors. All the components are combined in a sealed, metal-encapsulated system. The main reason for using SF₆ is its excellent insulating properties and its good quenching capacity for high-energy electric arcs. In a GIS, the distances between the live components can be kept up to ten times smaller than in the usual air-insulated substation [Schwarz, Leisewitz 1999; VDN 2002; Nelles, Tuttas 1998; Heuck, Dettmann 1999]. The area needed for a GIS is smaller than the area needed for an air-insulated substation by a factor of 10. The quantity of SF₆ in SF₆-insulated switchgear ranges from a few kilograms to 200 kg per gas compartment. Maintenance is required after 20-25 years [Ecofys 2005]. Since this is a “closed pressure system for gas”, operational leakage rates are less than 0.5% per annum [IEC 2007], and in practice even less. To this must be added any emissions due to maintenance. The non-recurring emissions on disposal are less than 2%. At present, annual emission rates of 0.7% are quoted for high-voltage switchgear, and this includes refilled quantities due to leakages and maintenance losses [ZVEI 2009].

Where space is at a premium, as in conurbations or industrial centres, GIS are increasingly being used as alternatives to the usual air-insulated substation [VDN 2002; RWE 2003]. However, GIS are also being installed on sites where space is not restricted [Anhörung 2003]. Operation of these installations must comply with the limit values of the 26th Ordinance for the Implementation of the Federal Immission Control Act (BImSchV) – Ordinance on electromagnetic fields – of 16.12.1996 (Sections 3 and 4) [26. BImSchV 1996]. In inner-city areas, this means that switch bays and high-voltage cables cannot always be implemented without problems.

On the outgoing or medium-voltage side of the transformer there is medium-voltage switchgear (10-30 kV) for connecting and disconnecting the lower-voltage network. The high-voltage switchgear, transformer and medium-voltage switchgear (switch gear with circuit-breakers) frequently form a single constructional unit, the transformer substation.

² The transformer substations handle the voltage reduction from medium to low voltage. In addition to the actual power transformer, these are equipped with ring-main units (RMUs).

Air-insulated substations are the traditional and most common type of high-voltage switchgear. In an air-insulated substation, the surrounding air insulates the live parts from each other. At the heart of outdoor control gear are **circuit-breakers**. They switch the current during normal operation, and in the event of a short-circuit they interrupt the rise in current by quenching the high-current electric arcs. Today, SF₆ is used for arc quenching. Older circuit-breakers were built with air or oil as insulation and quenching medium, but these are no longer state of the art. Minimum-oil circuit-breakers are still in use today, but are no longer manufactured [Schwarz, Leisewitz 1999; VDN 2002; Nelles, Tuttas 1998; Heuck, Dettmann 1999].

Vacuum, which is already used as an arc-quenching medium in circuit-breakers in the medium-voltage range, has been tested by manufacturers for the high-voltage range, but has not so far proved technically and economically feasible in the voltage ranges of 52 kV upwards which are usual in Germany [Siemens 2002]. In principle, other types of insulating media are available in the form of solids, liquids or combinations of the two. Today, however, gaseous insulating media are established on the market [Schwarz, Leisewitz 1999; VDN 2002; Nelles, Tuttas 1998; Heuck, Dettmann 1999].

The capital cost of air-insulated substations is lower than for GIS. Depending on the location, however, the higher capital cost of GIS may be offset by lower land prices.

An option that has been available for some years now is HIS – Highly Integrated Switchgear – which combines the benefits of conventional air-insulated technology with those of SF₆-insulated switchgear. HIS consists of metal-encapsulated, gas-insulated modules which can be combined with air-insulated switchgear components and are suitable for outdoor use. One advantage is their smaller space requirement (about half) compared with conventional air-insulated substations [Helbig 2000; Siemens 2010]. Since in HIS only the components circuit-breaker and disconnector are gas-insulated, the volume of SF₆ used is about 25 to 30% smaller than in GIS [VDE 2010].

Reduction options

Air-insulated substations contain less SF₆ than SF₆-insulated high-voltage switchgear. One means of reducing SF₆ consists in only using SF₆-insulated high-voltage control gear where this is actually necessary because of space constraints.

A comparative life cycle assessment of GIS and air-insulated substations was undertaken for Solvay by Solvay Management Support GmbH [Krähling, Krömer 1999]. The study compared systems that complied with the latest switchgear standards. Therefore, the SF₆ emissions of the switchgear systems investigated were low compared with older systems still in operation. However, no generally valid statements – taking into account the smaller size, the resulting greater flexibility and the smaller amount of materials used, etc. – can be made about the ecological advantages of GIS systems compared with air-insulated substations. Undoubtedly the most important findings are that from an ecological (climate-protection oriented) point of view there is a need to aim for low SF₆ emissions in manufacture, operation and disposal, and for an

optimised distribution network with minimised losses. To ensure that the second point is achieved, it may make sense to use GIS rather than air-insulated substations if it is not possible in an individual case to install an air-insulated substation at the location selected for network optimisation purposes. Where space is at a premium, however, highly integrated switchgear may be an alternative solution.

SF₆ emissions can be prevented not only by substitution, but also by measures during production and maintenance, equipment-related action (improved system tightness) and measures during disposal of GIS. In 1996 the ZVEI (German Electrical and Electronic Manufacturers' Association) and the VDEW (Association of German Electricity Supply Companies) issued a voluntary declaration on SF₆ to the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety [Erklärung 1996]. In this they make a commitment to avoid SF₆ emissions – wherever possible. Measures include a guaranteed leakage rate of less than 1%, recovery and reuse and, if appropriate, environmentally sound disposal. The SF₆ manufacturer, Solvay Deutschland, is included in the voluntary declaration. In 1997 the alliance of producers and operators gave a voluntary commitment to the German Federal Environment Ministry. In 2005 the voluntary commitment was extended to other applications in the field of power transmission and distribution, and supplemented by concrete reduction targets. By 2020, total annual emissions from all life cycles of control gear and switchgear are to be limited to 17 t (corresponding to 0.4 million t CO₂ equivalent) [SV 2005].

Conclusions

There is currently no alternative to SF₆ for circuit-breakers (> 52 kV) that complies with the state of the art and could thus replace SF₆. In the voltage range discussed here, the only scope for decisions for or against greater use of SF₆ is in the choice of switchgear. Since the entire system in a GIS is filled with SF₆, the quantities used and hence the emissions per system are comparatively large. Moreover, their leakage rates for existing and new systems average about 1% higher than medium-voltage systems (< 0.1% per annum for “hermetically sealed pressure systems for gas”, according to IEC62271-1). To this must be added non-recurring disposal losses of the order of less than 2%.

From an environmental point of view, GIS systems should only be used where they are necessary to maintain or create an optimised network (to minimise transmission losses) or, e.g. in industry, for power feed-in close to the consumer. This need should be checked on a case-by-case basis, having regard to suitable criteria. Emissions are to be avoided as far as possible in the use of SF₆. Air-insulated outdoor substations make a contribution to this.

9.2 *Switchgear in the voltage range > 1-52 kV (medium voltage)*

Ring-main units (RMUs) and switchgear with circuit-breakers are the switchgear used in the medium-voltage range. Both types are available on the market with air or SF₆ as arc-quenching

and/or insulating medium.

Where SF₆ is used, the switchgear – as in the case of high-voltage switchgear – takes the form of metal-encapsulated, hermetically sealed units. All components are combined in a sealed system and insulated from one another by SF₆ under slight over-pressure. Like high-voltage switchgear, they are also referred to as GIS. The units contain between 0.25 and 10 kg of SF₆ per gas compartment. They have a lifetime of 40 years [Ecofys 2005].

The circuit-breakers used in switchgear with circuit-breakers are mostly vacuum circuit-breakers; it is only in special cases that SF₆ circuit-breakers are used. These circuit-breakers are not produced in Germany, and are only used in special cases for technical reasons, e.g. for generator circuit-breakers in combination with air-insulated equipment [Driescher 2003].

Reduction options

Today, for technical reasons, vacuum is the main insulating medium in the circuit-breakers used in switchgear with circuit-breakers. Minimum-oil circuit-breakers are no longer available today [Driescher 2003]. From a technical point of view, there is no need to use SF₆ in circuit breakers.

Research is being carried out on mixtures containing SF₆ which could reduce the quantity of SF₆ in RMUs and switchgear with circuit-breakers, but they are not commercially available [RWE 2002].

A technology that has been in common use for years is air-insulated ring-main units and switch gear with circuit- breakers. Today metal-encapsulated, air-insulated units with over-pressure are also on the market, whereas air is normally used at normal pressure. One manufacturer offers hermetically sealed, air-insulated ring-main-units up to 24 kV. Like SF₆ units, they are completely sealed off from their surroundings and hence from adverse environmental impacts (salt-laden, corrosive air etc.) [Holec Holland 2003]. The technology is different from that of SF₆-insulated units.

The advantages and disadvantages of the two types of unit as described by manufacturers, distributors and operators of SF₆-insulated and air-insulated units cover a wide range. The main criteria cited for comparison are personnel safety (including toxic decomposition products of SF₆), security of supply, lifetime, total costs, resource consumption (including depletion of non-sealed land / space requirements), transmission losses, and emissions of environmentally harmful (including persistent) substances.

Assuming that annual SF₆ emissions per unit over an entire lifetime are less than 0.1% of the charge, and that the SF₆ charge is fully recovered on disposal (losses < 2% of charge), an examination and evaluation of the information available to the Federal Environment Agency leads to the conclusion that it is not possible to state unequivocally whether one type of unit is better than the other from an environmental point of view. No clear substantiation of the need for using SF₆ in the medium-voltage range was possible. Air-insulated units have the advantage that they do not contribute to building up the SF₆ reservoir (installed quantities) and make a smaller

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contribution to inputting persistent substances into the environment. Special conditions (e.g. very limited space available, extreme environmental influences) may create a need to use GIS units with SF₆ for specialised applications. Off-shore wind turbines are a new application using SF₆-insulated switchgear, partly for technical reasons (e.g. for voltages over 30 kV).

In view of the conflicting information and the difficulty of comparing the various environmental criteria, manufacturers and operators of SF₆-insulated units together with an SF₆ manufacturer prepared a life-cycle assessment of the GIS technology in the medium-voltage range. This compared air-insulated switchgear (AIS) with gas-insulated switchgear (GIS) in representative switchgear and grid designs; the study was confined to type approved switchgear. In addition to an average product mix, medium-voltage grids were analysed, using a voltage of 10 kV for simulation of urban areas and 20 kV for simulation of rural areas. A lifetime of 30 years was assumed for AIS, and 40 years for GIS. The SF₆ emission rates for GIS were taken as 0.14% per annum for production and operation, and 2% for end-of-life management [Solvay 2003].

The results show that using SF₆ has very little influence on the environmental impacts of medium-voltage switchgear. On the whole, the SF₆ switchgear (GIS) studied emerges rather better from this life-cycle assessment than the air-insulated switchgear (AIS) included in the comparison. Switchgear without SF₆ from small and medium companies was not included in the life-cycle assessment because of the conflicting data situation. The information value of the life-cycle assessment is therefore limited.

In a life-cycle assessment undertaken by an Italian manufacturer, the authors come to the conclusion that when comparing SF₆ switchgear, air-insulated units (standard) and compact air-insulated switchgear, the last group are the most environmentally sound variant [Petroni *et al* 2003]. It must however be borne in mind that the study assumed rather higher SF₆ leakage rates, which German manufacturers claim to be unrealistic. Another significant fact is that the study compared switchgear from the year 2000 (air) with units dating from 1990 (SF₆).

SF₆ emissions can be avoided in the medium-voltage range as well, not only by substitution, but also by measures during manufacture, maintenance and disposal. For this reason, the voluntary commitment by the German SF₆ producers and the manufacturers and operators of electrical equipment in excess of 1 kV [SV 2005] also includes switchgear in the medium-voltage range.

Conclusions

In the medium-voltage range, vacuum-insulated circuit-breakers are a suitable and widely used alternative to SF₆ switchgear.

Medium-voltage switchgear has low leakage rates of less than 0.1% per annum, so SF₆ emissions continue to be comparatively low despite the large quantities of SF₆ installed. Although large quantities of these units will be disposed of in the years ahead, the rise in emissions can be minimised by means of suitable measures which the industry has committed itself to implementing.

Considering this fact in conjunction with the results of the life-cycle assessment, there would seem to be no need for concrete action at present. However, in view of the high global warming potential, the persistence of SF₆, the alternative technologies available and the large quantities put into circulation this must not lead to uncontrolled use of SF₆. In the medium-voltage sector there is no fundamental technical need to use SF₆-insulated switchgear.

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10 SF₆ applications in the non-ferrous (NF) metal industry

10.1 SF₆ for use as cover gas (*magnesium processing*)

The magnesium industry has been using SF₆ as a cover gas since the mid 1970s. In 2008, a total of 719,000 tonnes of magnesium were produced worldwide, the main producer being China with 559,000 t [IMA 2010]. In Germany and the entire EU, only magnesium delivered as ingots is processed; magnesium is also recycled. This report does not therefore consider primary magnesium processing, in other words the production of ingots. SF₆ is however used in this processing stage as well to protect the molten magnesium [Harnisch, Schwarz 2003]. It is also kept available in the factories as a fire-extinguishing agent in case of magnesium fires [Öko-Recherche 2009].

In terms of technology, magnesium casting can be subdivided into high pressure die casting, permanent mould casting, sand casting and direct chill (DC) processes. Processing temperatures are between 630°C and 750°C for high pressure die casting, and between 730°C and 830°C for permanent mould, sand and direct chill (DC) casting. A tabular overview of casting types and typical temperature ranges can be found in the report [Öko-Recherche 2008]. Some types of magnesium casting are described in more detail in the report [Öko-Recherche 2009]. Most magnesium is processed using the cold-chamber or hot-chamber high pressure die casting process. A total of 30,600 t of magnesium was processed in Germany in 2006; some 29,800 t of this was high pressure die cast [GDM 2007].

Together with carrier gases (e.g. nitrogen, dry air or carbon dioxide), SF₆ is used as a cover gas in the melting and casting of magnesium and magnesium alloys. The cover gas helps a protective coating to form at the surface, which prevents the molten metal from oxidising and igniting. The SF₆ concentration is around 0.2-3% [Harnisch, Schwarz 2003].

Some of the SF₆ used is degraded in the process [Carli *et al* 1997; Bartos *et al* 2003, EPA 2004, 2007]. It is not possible to quantify the figure exactly, since the degree of decomposition depends on the particular casting process, the composition of the cover gas, the temperatures involved, the composition of the magnesium etc. According to the international emission reporting requirements, SF₆ consumption and emission are regarded as equivalent in this application. [Schwarz, Leisewitz 1999; IPCC 1996].

Since Article 8(1) of the European F-Gas Regulation prohibited the use of sulphur hexafluoride (SF₆) for magnesium die casting with effect from 1 January 2008 if the quantity of SF₆ used exceeds 850 kg per year, the amount of SF₆ used is declining. Whereas magnesium foundries in Germany emitted 28 t of SF₆ in 2005, the figure for 2008 was only 7.3 t [Schwarz 2009, 2010]. The emissions trend since 1995 can be seen in Chapter 2. In the

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majority of cases SF₆ was replaced with HFC-134a, producing a rise in emissions of HFC-134a. In 2008, emissions of HFC-134a totalled 15 t. When estimating emissions of HFC-134a from magnesium die casting, consumption is again taken to be equal to emissions, even though some decomposition of HFC-134a takes place in the cover gas. The new IPCC Guidelines published in 2006 refrained from quoting standard values for the emission factor, because the effective degree of decomposition depends on many factors such as temperature, concentration, mass flow and the carrier gas used.

An overview of the SF₆ emission situation in the magnesium industry in Europe can be found in a report on behalf of the European Commission [Öko-Recherche 2009].

The increasing criticism of SF₆ as a cover gas has already resulted in its voluntary replacement worldwide in the production and processing of magnesium [EPA 2008, IMA 2009]. Conversion of existing installations from SF₆ to SO₂, perfluoroketone or HFC-134a is supported by the opportunity to acquire certificates for emissions trading. Since 2008 there has been an IPCC-approved methodology for the calculation of credits which lays down additional conditions for the use of these alternative cover gases [UNFCCC 2008].

Reduction options

Since the 1970s there have been various technical improvements in the use of SF₆ which have led to substantial emission reductions. For example, specific SF₆ emissions per tonne of magnesium have been reduced from over 3 kg/t to between 0.4 and 1 kg/t in modern foundries [Harnisch, Schwarz 2003; Hydro Magnesium 2000, Öko-Recherche 2009].

Before the introduction of SF₆, sulphur dioxide (SO₂) was commonly used as the main cover gas component. The reason for using SF₆ was largely its non-toxic properties compared with SO₂. Up to the end of the 1960s, cover salts (eutectic mixtures of alkaline chlorides and alkaline earth chlorides) or sulphur were used to protect the molten metal [Ricketts *et al* 2003, Karger 2006b]. Adding very small quantities of beryllium (0.0005-0.00015% by weight) protects the melt from oxidation by forming a surface layer of magnesium and beryllium oxides, but also makes the material more brittle [Karger 2006b].

In principle, once the decision in favour of a particular cover gas is taken, both the foundry itself (e.g. protective measures when using SO₂) and the production process are geared to that gas [VW 2003a]. Conversion to other cover gases is possible, but requires alterations of varying extent depending on the old and new cover gases concerned; no real drop-in substitute exists as yet [Ricketts *et al* 2003; Öko-Recherche 2008]. As a basic principle, conversion to a different cover gas should involve as little interference as possible with the production process; consistently high product quality should be assured [VW 2003a].

SO₂

Several foundries still use SO₂ today; and for cost reasons, some newly built foundries have decided to use SO₂ [Harnisch, Schwarz 2003]. Some installations were converted to SO₂ in response to the ban on SF₆ [Öko-Recherche 2008]. The recycling sector also uses mainly SO₂, except for special alloys with high melting points [Öko-Recherche 2009].

Whereas in Germany, and also in France and in Italy, mainly SF₆ was used until 2008, casting in Austria and Denmark has traditionally been carried out under SO₂ [Harnisch, Schwarz 2003].

Due to the toxicity of SO₂ and the consequent additional health and safety requirements, and also because of the great GWP of SF₆ (GWP₁₀₀ = 23,900 [IPCC 1995]), magnesium processors and users and cover gas producers have initiated research programmes for evaluating alternatives [Australian Magnesium 2003a; 3M 2003; VW 2003b; VDG 2003; EPA 2004; EPA 2007; IMA 2009]. The driving force here was the automobile industry as the biggest customer for magnesium. The basis for this was provided by life-cycle assessments (LCAs) which showed that the CO₂ emission reduction contribution achieved in the vehicle sector by using lightweight components instead of steel (reduced fuel consumption) was more than offset by the SF₆ consumed in the production process (magnesium). However, the improvement in the climate balance of vehicles is a crucial reason for choosing lightweight magnesium components [VW 2003a; Australian Magnesium 2003a; Ricketts u. a. 2003; Hydro Magnesium 2000].

Since the mechanisms involved in the use of SF₆ as a cover gas were known, the search for alternatives largely focused on other fluorinated substances. These, however, were to have a lower GWP than SF₆ [Ricketts *et al* 2003]. Promising alternatives investigated in various plants in recent years have been HFC-134a and a perfluoroketone (C₂F₅C(O)CF(CF₃)₂, empirical formula C₆F₁₂O) [VW 2003a; Australian Magnesium 2003a; 3M 2003; Ricketts *et al* 2003; EPA 2004; EPA 2007]. Both substances – like SF₆ – are used in conjunction with carrier gases. Although other gases, such as BF₃, the hydrofluoroether C₄F₉OCH₃ and HFC-1234ze, have been or still are under discussion [Hillis 2002; EPA 2008], they have yet to achieve more than minor importance and are not discussed any further here.

HFC-134a

For years now, HFC-134a has been commercially marketed and used in many applications, especially as a refrigerant. It too is a greenhouse gas, with a global warming potential (GWP₁₀₀) of 1,300 [IPCC 1995]. Thus its GWP is considerably smaller than that of SF₆. Test results for a specific production site show that greenhouse gas emissions can be reduced by more than 95% (calculated as CO₂ equivalent) by converting to HFC-134a [VW 2003a, EPA 2007]. This is also quoted as an average value in Ricketts *et al* [2003]. The main reasons for this reduction are the smaller quantities used compared with SF₆ and at the same time the greater decomposition of HFC-134a. Tests in existing installations as well have shown that HFC-134a is a suitable cover gas for replacing SF₆. In many respects, such as sludge quantity and quality, it has actually proved superior to SF₆ [Ricketts u. a. 2003]. In 2003, first industrial-scale tests were conducted in Germany at various high pressure die casting plants [VW 2003a; Australian Magnesium 2003a]. Today HFC-134a as a cover gas is commercially available to all users [Australian Magnesium 2003b]. Suitability tests also proved positive for sand casting processes with low-melting alloys up to 730°C [Australian Magnesium 2004]. HFC-134a is not suitable for the temperatures above 730°C that are normally necessary for sand casting of magnesium alloys [Öko-Recherche 2008].

Perfluoroketone

Perfluoroketone, already mentioned above, has a GWP₁₀₀ of about 1. It is a new substance which has only been produced and used on a small scale to date. Extensive tests with perfluoroketone have been carried out in various countries. The producer of the ketone states that studies have shown it to offer advantages compared with HFC-134a, and that the production and availability of adequate quantities can be assured [3M 2003]. The concentration required in the carrier gas is around 0.01%, and is thus many times smaller than the necessary concentration of SF₆ [Milbrath 2002]. Recent studies have shown that perfluoroketone is already effective at concentrations as low as 0.00025 to 0.00035% [EPA 2008]. Questions relating to possible thermal decomposition products (PFCs, fluoro-olefins, TFA, HF, carbonyl fluoride), the GWP of such decomposition products, and workplace safety were examined [Ricketts *et al* 2003; Milbrath 2002]. Tests have shown that the formation of unwanted decomposition products can be almost entirely prevented by adding small quantities of oxygen and optimising the concentration of cover gas [Milbrath 2002]. In the meantime, perfluoroketone has been introduced in America as a substitute for SF₆ [EPA 2008]. In Europe, chemicals legislation currently prevents its being used as a cover gas [Öko-Recherche 2009]. Before it is used in Europe, the manufacturer must register the cover gas in accordance with European chemicals legislation [REACH 2006]. The producer is planning to register it with ECHA (Status 2010).

CO₂ snow

Another alternative is to cover the magnesium melt with CO₂ snow. CO₂ snow is induced in the furnace by spraying liquid CO₂ under high pressure through a nozzle. The CO₂ snow cools the melt surface, thereby reducing the evaporation rate of the magnesium. At the same time the CO₂ snow sublimates and expands, which displaces air from the surface of the melt surface [VDG 2003, Karger 2006a, b]. The process has been tested on a magnesium alloy in a high pressure die casting machine, where it has been shown to be basically technically feasible in the temperature range up to 700°C [Karger 2006b]. The disadvantages of gaseous CO₂, leading to the formation of carbon monoxide and elementary carbon, have not been observed with CO₂ snow. The use of CO₂ snow offers another alternative, though from a technical and economic point of view it will have to compete with the other new cover gases.

Costs

Basically, the cover gas producers and users surveyed all state that the alternative gases HFC-134a and perfluoroketone are less expensive than SF₆ [VW 2003a; Australian Magnesium 2003a; 3M 2003; Milbrath 2002]. SO₂ is also cheaper than SF₆: a source dating from 2008 works on the basis that the operating costs are between one fifth and one tenth of the cost of SF₆ [EPA 2008].

One aspect of great importance to users is the establishment of an optimised production process and the resulting consistently high product quality. Conversion can always involve – at least temporary – problems, which deter small foundries in particular despite the prospect of potential long-term economic advantages [VW 2003a; VW 2003b]. Ricketts *et al* [2003]

assume that conversion to perfluoroketone involves higher costs than converting to HFC-134a.

A very detailed cost comparison between SO₂ and SF₆ as cover gas and a description of the costs arising from conversion to SO₂ can be found in Harnisch and Schwarz [2003]. In simplified terms, the authors come to the conclusion that using SO₂ instead of SF₆ is more expensive in terms of capital cost. In view of the low running costs for SO₂, foundries can offset this additional capital cost in the long term depending on the quantity of magnesium they process. For smaller foundries, however, it is not economic to use SO₂ because of the very long periods involved, especially if an existing installation (SF₆) has to be converted to SO₂. A recent study on behalf of the EU shows the cost of converting to and operating with HFC-134a and SO₂ for smaller installations with an SF₆ consumption of less than 850 kg per annum [Öko-Recherche 2009]. The results vary. In many cases the changeover (conversion and operating costs) is more expensive than continuing to use SF₆. For some installations, however, total annual costs using SO₂ are lower than for SF₆. HFC-134a can generally be expected to result in higher costs than SO₂. This is mainly due to the fact that the patent holder currently (2010) charges a licence fee for HFC-134a.

Conclusions

As a basic principle, preference should be given to cover gases with the lowest possible GWP as substitutes for SF₆. Other aspects are also important, such as a reduction in input quantities, the degree of decomposition of the cover gas, the availability of suitable substitutes, and the technical feasibility of alternatives.

SO₂ is available for magnesium foundries (high pressure die casting) as a proven and cost-effective cover gas that has been tested over many years instead of SF₆. In view of its toxicity, however, special health and safety measures are needed when using SO₂.

Today SF₆ is prohibited in Germany and Europe in existing magnesium high pressure die casting installations with an annual consumption exceeding 850 kg, and has already been replaced. HFC-134a is the usual new cover gas in Germany. Emissions of greenhouse gases are reduced through the change from SF₆ to HFC-134a because of its lower GWP, the slightly lower consumption and its degradation to substances with no GWP. It is also possible to replace SF₆ with SO₂, and this has already been done.

Perfluoroketone is suitable for use as a cover gas and has a very low GWP. However, it cannot be used in Europe at present (2010) because it is not yet registered in accordance with chemicals legislation.

10.2 SF₆ as cleaning gas for secondary aluminium casting

Before being cast in moulds, aluminium melts are pretreated to remove the gases present in the melt (degassing), mainly hydrogen, but also to remove unwanted elements (cleaning). Degassing and cleaning serve to improve quality. Degassing is mostly effected by introducing the inert gases nitrogen and/or argon. Halogens (chlorine, fluorine etc.) are introduced for cleaning purposes. Whereas primary melts are usually cleaned by adding elementary chlorine

as a chemically reactive substance to the inert gases, because the purity requirements for primary aluminium are very high, it is generally sufficient to purge secondary aluminium melts with inert gases without any additive [Steinhäuser 1996: in Schwarz, Leisewitz 1999]. According to the NF Metals Industry Association [Wirtschaftsvereinigung Metalle 1995] the use of SF₆, which was normal in the USA at the time, did not become established in Germany because of workplace problems. This was reaffirmed to the UBA in 2002. Another reason mentioned was that SF₆ was unable to compete with the established media in terms of costs either.

A German manufacturer is the only one in Europe to use SF₆ for degassing and cleaning in the production of a special aluminium alloy. To date, the quantity of SF₆ used has grown every year. Measurements have shown that quantities of SF₆ are destroyed in the process. Whereas until 2008 some 3% of the SF₆ input escaped and 97% was destroyed in the process, the manufacturer showed in measurements on the converted installation in 2009 that the exhaust gas contained only 1.5% of the SF₆ input, i.e. 98.5% of the SF₆ was destroyed. The manufacturer intends to do without SF₆ in future and to replace it with another gas from 2015 onwards.

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11 SF₆ as filling gas in double-glazed soundproof windows

As long ago as the 1970s, single glazing in windows and glass facades was superseded by multi-pane insulating glass. And since 1975, manufacturers have been using SF₆ to improve the sound-insulating effect of the pane interspace. Since 4 July 2008 there has been a ban in place in the European Union on the distribution of windows containing SF₆ or other fluorinated greenhouse gases¹ [KOM 2006]. Even before this ban, manufacturers had reduced SF₆ quantities or dispensed with SF₆ entirely.

Although emissions of SF₆ from this application start during production and the use phase, the greater part of the emissions do not occur until disposal. The reader is referred to Chapter 2.

In Germany, the production of insulating panes is mostly decentralised, and takes place in small and medium establishments (about 400 manufacturers). The window panes have an average lifetime of about 25 years [Schwarz, Leisewitz 1999].

Noise can be a considerable nuisance. In recent years people have become increasingly aware of noise as a disturbing environmental influence. More and more importance is being attached to peaceful, undisturbed living as a major element in the quality of life. There are a number of acts, ordinances and guidelines that lay down limit values or facilitate active noise abatement in the planning process.

Crucial factors for the sound-insulating effect of a window are the glazing, the design of the frame, and minimised crack permeability. To improve sound insulation, the spaces between the panes in multi-pane windows are filled with gas.

In Germany, sound insulation of windows is divided into six classes under VDI guideline 2719 [1987]; classification is based on the weighted sound-reduction index [dB] [Fensterportal 2008]. Rules exist for calculating the sound-reduction index. A certificate from an approved testing station is required for assigning a window to a sound-insulation class.

Compared with glazing units filled with air or inert gas, SF₆ improves sound insulation in the “frequency range defined for construction purposes” by 2-5 dB [Anon 2001; Saß, Schuhmacher 2000]. However, an accurate assessment of the sound insulation actually achieved calls for a more detailed consideration.

¹ An exception was made for windows manufactured before this date. Distribution of windows for residential buildings had already been prohibited since 4 July 2007.

As a result of the special characteristics of the test procedure under DIN 52210-4² [DIN 1984] for sound insulation of building components, the rating of insulating glass panels filled with SF₆ is much too high for practical sound insulation against urban traffic noise [Schwarz, Leisewitz 1999]. The SF₆ or mixture of argon and SF₆ filling the space between the panes improves the sound-insulation of multi-pane insulating glass panels in the “frequency range defined for construction purposes” by 2-5 dB compared with air-filled insulating glass panels. Accordingly, the sound reduction factor R_w stated in the glazing unit’s test certificate is 2-5 dB higher, which is a good selling point [Anon 2001; Saß, Schuhmacher 2000]. However, this marked improvement in soundproofing at high frequencies contrasts with a deterioration in soundproofing at low frequencies. Urban traffic noise often has a large proportion of low frequencies. This is particularly true of streets with heavy truck traffic. Here the improvement in sound insulation in the high frequency range brings little or no advantage [Saß, Schuhmacher 2000; Isolar 2000].

The European standard which came into effect in Germany in 1996 as DIN EN ISO 717-1 takes account of this intrusion of low frequencies [DIN 2006]. It introduces “spectrum adaptation values”. Thanks to the resulting allowance for the frequency spectrum of urban traffic noise, the weighted sound reduction index (now R_w+C_{tr}) of the insulating-glass panels improves by only about 0 to 2 dB as a result of the SF₆ filling. Glazing units with an SF₆ component bring only about 1 dB improvement in the weighted sound-reduction factor of complete window systems [Saß, Schuhmacher 2000].

The improved sound insulation targeted with SF₆ is accompanied by a deterioration in thermal insulation properties. For this reason, manufacturers have already made several reductions in the SF₆ component in soundproof windows to ensure compliance with the Thermal Insulation Ordinance (*Wärmeschutzverordnung*) [1994], and have mostly used mixtures with argon [Anon 2001].

The discussion about the climate impacts of SF₆ initially resulted in a search for less environmentally harmful gases as substitutes with comparable sound-insulation properties. However, tests with special mixtures of gases did not yield satisfactory results, so this route was not pursued any further. Neither did it prove possible to furnish consistent evidence that using krypton had a positive effect on the sound-proofing properties of insulating glass panels [Hornischer 2002].

It is technically possible to achieve the improved sound insulation resulting from SF₆ by modifying the construction of the glass structures [Anon 2001]. In addition to soundproof window system designs such as double windows, other conceivable possibilities are thicker panes or soundproofing films [Hornischer 2002]. If particularly effective soundproofing is required for specialised applications, such modifications to window construction result in extra costs. The actual amount of the additional cost depends on the window construction chosen and, above all, on the noise-reduction factor that the window is to achieve. Whereas price differences are almost negligible below a noise-reduction factor of 40 dB, the additional

² Part 4 was withdrawn in 1997 and replaced by DIN EN ISO 717-1 [DIN 2006]. Other parts of the standard were withdrawn in 1998 and replaced by DIN EN ISO 140 [e.g. DIN 2005].

cost above 40 dB amounts to between €7 and €29 per m². The average additional cost as a percentage of total cost comes to about 17.8% (€10) in the range 37-45 dB per m² [Harnisch, Schwarz 2003]. For many applications it is possible simply to do without SF₆ – which does not involve any additional cost [BF 2003]. Calculations indicate that even where high noise-reduction factors are concerned, the reduced heating costs resulting from improved thermal insulation without SF₆ can more than offset the additional cost of a window without SF₆ [Harnisch, Schwarz 2003].

Recovery of the climate-relevant gas SF₆ as a means of emission reduction has not proved feasible, either from a technical or an economic point of view [Schwarz, Leisewitz 1999; Hornischer 2002]. This means that the gas which was input during production is emitted in its entirety.

Conclusions

Since 4 July 2008 there has been a ban in place in the European Union on distribution of windows containing SF₆ or other fluorinated greenhouse gases [KOM 2006].

Even without a filling of SF₆, it is possible to make insulating-glass panels with very good soundproofing properties. The additional cost is small. Moreover, using SF₆ in multi-pane insulating-glass windows reduces the thermal insulation of the glazing unit. Calculations show that the slight additional cost of good soundproofing without SF₆ can be offset by savings in heating costs.

Although it would be desirable to recover the nearly 2,000 t of SF₆ currently present in Germany in insulated glazing units that are already installed (figures: 2006), it cannot be regarded as practicable for technical/logistical and economic reasons.

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12 SF₆ as leakage detection and tracer gas

Even today, SF₆ is a tracer gas in common use for air current and gas diffusion measurements (urban climate studies, air exchange measurements in buildings etc.). SF₆ is suitable for this application because of its low background concentration, stability, low tendency to interact with materials, non-toxicity, non-flammability and ease of detection.

One of the best-known applications of SF₆ in this field is for measuring air exchange in buildings and interiors in accordance with DIN EN ISO 12569 (Thermal performance of building and materials - Determination of specific airflow rate in buildings - Tracer gas dilution method) [DIN 2001] and VDI Guideline 4300, Sheet 7 (Measurement of indoor air pollution - Determination of ventilation rate in interiors) [VDI 2001]. The methods are based on measuring the concentration of an introduced tracer gas as a function of time. The annexes to both standards list other tracer gases in addition to SF₆: helium (only DIN 2001), C₆F₆ (only VDI 2001), CO₂ or laughing gas. The use of SF₆ is not mandatory for any of the methods described.

SF₆ is also a commonly used tracer gas for urban climate studies, as shown by (*inter alia*) publications about studies in Trier/Ludwigshafen [Eggert 2000], Osnabrück [Weber, Kuttler 2003] and Freiburg [Matzarakis *et al* 2008]. For example, it is largely necessary to use visual tracers (e.g. smoke generators) or chemical tracers (e.g. SF₆) to detect cold air currents, as conventional wind measuring equipment is not accurate enough in the low wind range due to mechanical inertia (Barlag and Kuttler 2008). Accordingly, the draft version of VDI Guideline 3785 “Environmental meteorology - Methods and presentation of investigations relevant for planning urban climate” [VDI 2007] also recommends the tracer gas method for detecting air movements, cold air currents and odour distribution in low-wind situations. Apart from SF₆, it only mentions CF₄ as a possible tracer gas, although a footnote draws attention to the fact that “release of the tracer gases listed here (SF₆, CF₄) [should] be restricted to a minimum [...] in view of the fact that they are extremely strong and long-lived greenhouse gases, and that a ban on their use for certain applications is already in preparation. Other substances with a lower global warming potential should be used instead.” Using smoke generators has the disadvantage that they can only be detected visually and hence qualitatively, but cannot be detected quantitatively as well like chemical tracers (Kuttler and Düttemeyer 2003).

SF₆ is also used as a tracer gas in research and development work on measurement methods, for example. These applications are highly specialised (long-term atmospheric measurements, measurement of methane emissions by cattle, determination of circulation processes in lakes

etc.), and the quantities used are mostly small. This report therefore refrains from describing these applications.

The concentrations needed for the various measurements are mostly in the ppm range and have been reduced still further in recent years thanks to improved sensors. The quantity of SF₆ used as tracer gas in Germany has been decreasing for years and is currently well below 500 kg per annum [Schwarz 2010].

In 2007 the British Ministry of Defence performed tests on the spread of poisonous gases in the London underground tunnel system, in which SF₆ was also used as a test gas [BBC 2007]. Nothing is known about the quantities used.

Although SF₆ has in the past been used as a leak detection gas (test gas) for precise localisation of leakages, e.g. in water-bearing pipes of district heating systems, there are now no longer any indications of such uses. For this purpose, and for testing newly installed pipe sections, it is possible to use other gases such as helium or nitrogen/hydrogen mixtures, which are firmly established today. SF₆ has no advantages over these gases, but involves higher costs [Umsicht 2003].

There are also numerous applications for leak detection gases in apparatus construction or component manufacture. This includes the automobile components industry. As far as is known, SF₆ is not used here.

Conclusions

Using SF₆ as a leakage detection gas or test gas (pipe systems, apparatus construction etc.) does not make economic sense and is not ecologically justifiable. Other substances than SF₆ should be used for these purposes.

Its use as a tracer gas in the research sector must be seen in a different light. It may be assumed that other applications exist here in addition to those mentioned. Whereas the mostly highly specialised applications cover a wide range, the quantities used are negligible. Neither is there any reason, as things stand at present, to expect a significant rise in emissions in this sector. In the interests of avoiding emissions harmful to the environment, the potential environmental impacts should be taken into account when selecting substances, and the quantities used should be minimised.

Where SF₆ is listed in standards as a tracer gas for measurements, a note about its extremely high global warming potential should be included. Where alternatives exist, these should be pointed out and used for preference.

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13 SF₆ as filling gas in car tyres

In about the mid 1980s, tyre manufacturers first propagated the idea of using SF₆ instead of air as a filling gas for car tyres. This was followed by a steady increase in use and emissions of the gas (see Chapter 2). Since 4 July 2007 the use of SF₆ for this purpose has been prohibited in the European Union [KOM 2006], which means that until 2010 there will only be residual amounts present in tyres filled before this date and the stock will then be reduced to zero. On the other hand, sales of SF₆ for filling car tyres were already declining steadily before this ban came into force.

Because of the size of the SF₆ molecule, the gas diffuses from tyres more slowly than air. This was supposed to ensure long-lasting stable tyre pressure and hence safer driving, reduced tyre wear and lower fuel consumption.

Practical tests failed to confirm greater comfort (driving experience). Also, according to tyre manufacturers, the use of SF₆ did not relieve motorists of the need to keep checking their tyre pressures [UBA 1997]. This invalidated a crucial - apparent – benefit of SF₆ (adequate tyre pressure without constant checking). The advantages mentioned in addition to long-lasting tyre pressure are also invalidated, because they are not ensured by the use of SF₆ as such, but by adequate tyre pressure.

Given regular checks on tyre pressure, all the above objectives can be achieved without difficulty using air as the filling gas.

Some years ago, tyre manufacturers withdrew their recommendation about the use of SF₆ because of its climate relevance and the lack of practical confirmation of the benefits of this substance. However, customers continued to ask for SF₆ and obtained it from repair shops.

Gas and tyre manufacturers and car repair shops also offer another means of maintaining adequate tyre pressure over a longer period than is possible with air, namely the use of nitrogen (N₂) [Bundesverband Reifenhandel 2003; Weymann 1997]. Nitrogen is a major constituent of air and can be extracted from air. This gas does not possess any adverse environmental properties. According to system suppliers, when used as a filling gas it reduced pressure loss because of its diffusion properties and its “inertifying” effect [Weymann 1997]. But even here, pressure checking is essential. The tyres of aircraft and Formula 1 racing cars are filled with nitrogen [Weymann 1997]. The advantages of nitrogen over air are not undisputed, however [ÖAMTC 2003].

Conclusions

The use of SF₆ as a filling gas for car tyres has been banned in the European Union since 4 July 2007. Stabilisation of tyre pressures by using SF₆ had in any case proved irrelevant in practice and would also have been out of proportion to the resulting climate-relevant emissions. Compressed air or nitrogen are available as economical and environmentally sound alternatives.

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14 SF₆ and PFCs as shock-absorbing gas in shoes

In the 1970s [Greenpeace 1998] or 1990s [Harnisch, Schwarz 2003], a sports equipment manufacturer (Nike) started producing running shoes and indoor sports shoes with SF₆. Until 1997, annual worldwide consumption of SF₆ was around 280 t, each pair of shoes containing about 2-2.5 g [Greenpeace 1998; Harnisch, Schwarz 2003]. Since 1997 Nike has continuously reduced its input quantities [Harnisch, Schwarz 2003], and in 2003 it completely discontinued the use of SF₆.

As with car tyres, this application took advantage of the size of the SF₆ molecule. In the case of sports shoes, the aim was to keep the gas in the sole as long as possible. The idea of the gas in the sole was to act as a shock-absorber relieving the strain on the athlete's foot. For example, SF₆ was used in jogging or basketball shoes.

Between July 2003 and 4 July 2006, Nike completely replaced SF₆ with other gases that had a lower global warming potential. In some cases perfluoropropane (GWP₁₀₀ = 7,000) was used. The manufacturer's announcement that it would finally discontinue using gases with a high GWP in 2006 [Harnisch, Schwarz 2003] was taken up by the European Commission in Regulation (EC) No. 842/2006 [KOM 2006], which prohibited the use of fluorinated greenhouse gases for this application with effect from 4 July 2006.

Conclusions

The use of SF₆ is not necessary in this application and should be rejected on environmental grounds. It is therefore only logical that the use of fluorinated greenhouse gases in shoes has been banned in the European Union since 4 July 2006.

Literature used in Chapter 14

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15 Overview of substitution options and other means of emission reduction in the individual fields of application

Halogen-free alternatives can be used as substitutes for fluorinated greenhouse gases (HFCs, PFCs and SF₆) in nearly all fields of application. There are also a large number of other means of reducing emissions. Table 15.1 provides a summary of the substitution options described in Part B of this report and the other means of emission reduction. A number of important applications are then discussed specifically.

The applications (refrigerant, blowing agent, propellant gas, fire-extinguishing agent, solvent etc.) are listed in Table 15.1 in the same order as they are dealt with in the report. The column “F-Gases” lists the HFCs, PFCs and SF₆ used in each case. In some fields of application, substitution of substances is possible on a “drop-in” basis even in existing installations without appreciable technical modifications (substitution in existing systems). In most cases, however, significant alterations to the installations or their complete replacement are required. In the case of new installations/products, there is a wider range of substitution options. As a rule, the column “Substitution Options” (replacement substances/processes) lists fluorine-free substances and processes; in a few cases, however, HFCs etc. are also included if their use makes it possible to reduce the greenhouse gas contribution. In addition to substitute substances, other means of reducing emissions frequently exist in the form of alternative products and production processes that do not use substances with a global warming potential (replacement substances and replacement processes in new installations or products). The list is rounded off by other emission reduction measures for existing and new installations and products.

Table 15.1 is merely intended as a guide to the many substance replacement options. It is part of the report as a whole, and is only meaningful in the context of the additional information contained in the report.

Chap.	Function	F Gases	Substitution options ¹			Further emission reduction measures	
	Application		Replacement substances and processes			Existing systems/ disposal	New systems/ products
			Existing systems	New systems/products			
				in use	under test		
3	Refrigerants						
3.3.1	Household and laboratory appliances	HFCs: 134a, 404A		600a, absorber, not-in-kind	Not-in-kind	Low-emission disposal	
	Heat-pump tumble dryers	HFCs: 407C, 134a, 410A, 152a			Hydrocarbons, CO ₂ , water		
3.3.2	Refrigeration systems for commercial purposes	HFC: 134a, 404A, 407C, 507A	depends on individual case	290 and 600a (plug-in), CO ₂ (cascade), CO ₂ transcritical, NH ₃ (indirect), 1270 and 290 (indirect)	CO ₂ , NH ₃ /CO ₂ cascade (stand-alone systems)	Reduced charge, maintenance/ leak monitoring, low-emission disposal, system replacement	Hermetisation/ tightness, maintenance/ leak monitoring, low-emission disposal
3.3.3	Refrigeration systems for industrial purposes	HFCs: 134a, 404A, 407C, 507A, 236fa, 227ea, PFCs	depends on individual case	290, 600a, NH ₃ (with and without secondary refrigerant), NH ₃ /CO ₂ cascade, absorber, adsorber	CO ₂		
3.3.5	Stationary air-conditioning systems	HFCs: 134a, 407C	depends on individual case	Absorber, adsorber, H ₂ O, air-conditioning without mechanical refrigeration, NH ₃ , hydrocarbons, NH ₃ /DME	H ₂ O, air-conditioning without mechanical refrigeration		
3.3.4	Transport refrigeration systems	HFCs: 410A, 404A, 134a, 407C		CO ₂ , hydrocarbons, NH ₃ , NH ₃ /CO ₂	CO ₂ , hydrocarbons	Low-emission disposal, tightness	Reduced charge, hermetisation/ tightness, low-emission disposal
3.3.2	Cooling and air-conditioning units	HFCs: 407C, 410A, 417A		290, central system without HFCs	CO ₂		
3.3.5							
3.3.6	Heat pumps	HFCs: 407C, 410A, 404A, 417A, 134a		290, CO ₂ , adsorber, absorber			
3.3.7	Vehicle air-conditioning systems	HFCs: 134a (prohibited in future)	290	290, CO ₂	1234yf		

¹ Abbreviations for hydrocarbons: 600a: isobutane; 290: propane; 1270: propene

Other abbreviations: LT: low temperature; NT: normal temperature; Mon.: monitoring; Dis.: disposal; Tightness: improvement in tightness through technical measures

Chap.	Function	F Gases	Substitution options ¹			Further emission reduction measures	
	Application		Replacement substances and processes			Existing systems/ disposal	New systems/ products
			Existing systems	New systems/products			
				in use	under test		
4	Blowing agents						
4.1	Rigid foams for thermal insulation (XPS, PUR)	HFCs: 134a, 152a, 365mfc, 245fa, 227ea		CO ₂ , CO ₂ /ethanol, c-pentane, i-pentane, n-pentane, other insulating materials			
4.2	Flexible PUR foams			CO ₂			
4.3	Integral PUR foams	HFCs: 134a, 245fa 365mfc, 227ea		CO ₂ , pentane			
4.4	Caulking foams	HFCs: 134a, 152a (to some extent prohibited)		290, n-butane, DME, systems without blowing gas		Low-emission disposal	
5	Propellant gas						
5.1.1	Technical sprays: freezer sprays, compressed air sprays and other technical sprays	HFCs: 134a (to some extent prohibited)		290, 600a, N ₂ , CO ₂			
5.2	Medicinal sprays	HFCs: 134a, 227ea		Powder inhalers	600a		
5.3	Other sprays (except insecticides etc.)	HFCs: 134a (to some extent prohibited)		290, 600a, N ₂ , CO ₂ , products without propellant gas (e.g. pump sprays, paper streamers, mechanical sound devices)			
5.3.6	Insecticides, pesticides etc., not intended for household use	HFCs: 134a			CO ₂ , CO ₂ /formic acid ethyl ester		
6	Fire-extinguishing agents	HFCs: 227ea, 236fa, 23, plus others outside Germany		CO ₂ , N ₂ , argon, Inergen®, water mist, fluoroketone, foam, sprinklers, early warning systems etc.	Water mist, fluoroketone for new applications	Maintenance/ leak monitoring, low-emission disposal	Tightness, maintenance/ leak monitoring, low-emission disposal

Chap.	Function	F Gases	Substitution options ¹			Further emission reduction measures	
	Application		Replacement substances and processes			Existing systems/ disposal	New systems/ products
			Existing systems	New systems/products			
				in use	under test		
7	Solvents	HFCs: 43-10mee; outside Germany: various		halogen-free organic and water-based solvents, HFE, no cleaning, solvent-free cleaning		Technical measures	Technical measures
8	Etching gas						
8.1	Semiconductor industry	SF ₆ PFCs HFCs	(NF ₃)	Various substances depending on process, e.g. NF ₃ ,	Various substances depending on process, e.g. C ₄ F ₈ O	Exhaust-gas cleaning, process optimisation, (recycling)	Process optimisation, (recycling), exhaust-gas cleaning
8.2	Printed circuit board manufacture	PFCs		(wet-chemical processes), laser		Exhaust-gas cleaning, process optimisation, (recycling)	Exhaust-gas cleaning, process optimisation, (recycling)
9	Arc-quenching and insulating gas						
9.1	Switchgear 110-380 kV	SF ₆		Air	Vacuum (<80 kV, theoretically conceivable up to max. 145 kV)	Maintenance/ leak monitoring, low- emission disposal	Hermetisation/ tightness, maintenance/ leak monitoring, low-emission disposal
9.2	Switchgear > 1-36 kV	SF ₆		Air, vacuum			
10	Cover gas						
10.1	Magnesium processing	SF ₆ (to some extent prohibited) HFCs: 134a	SO ₂	SO ₂ , 134a as substitute for SF ₆ , fluoroketone	CO ₂	Process optimisation	Process optimisation
10	Cleaning gas						
10.2	Secondary aluminium casting	SF ₆	Inert gases + elem. halogens	Inert gases + elem. halogens			
11, 13	Filling gas						
13	Car tyres	SF ₆ (prohibited)		Air, N ₂			
11	Insulated glass panels	SF ₆ (prohibited)		Modified glazing structures		(Low-emission disposal)	

Chap.	Function	F Gases	Substitution options ¹			Further emission reduction measures	
	Application		Replacement substances and processes			Existing systems/ disposal	New systems/ products
			Existing systems	New systems/products			
				in use	under test		
12	Leakage detection and tracer gas	SF ₆ PFCs		He, N ₂ /H ₂ , Ar			
14	Shock-absorbing gas						
14	Shoes	SF ₆ , PFCs (prohibited)		Air, N ₂			

16 Abbreviations

Abbreviation	Meaning (German)	Meaning (English)
AFEAS		Alternative Fluorocarbons Environmental Acceptability Study
AG	Aktiengesellschaft	public limited company
ATP		see Glossary
BAFA	Bundesamt für Wirtschaft und Ausfuhrkontrolle	Federal Office of Economics and Export Control
BImSchG	Bundesimmissionsschutzgesetz	Federal Immission Control Act
BImSchV	Bundesimmissionsschutzverordnung	Federal Immission Control Ordinance
BMU	Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit	Federal Ministry for the Environment, Nature Conservation and Nuclear Safety
BWP	Bundesverband Wärmepumpe e.V.	Federal Heat Pump Association
CFCs		chlorofluorocarbons
CH ₄		methane
CO ₂		carbon dioxide
COM		European Commission
COP		coefficient of performance
COPD		chronic obstructive pulmonary disease
CVD		chemical vapour deposition
DB AG	Deutsche Bahn Aktiengesellschaft	German railway company
DBU	Deutsche Bundesstiftung Umwelt	German Federal Foundation for the Environment
DEC		desiccative and evaporative cooling
DG		Directorate-General
DIN	Deutsches Institut für Normung e. V.	German Institute for Standardisation
DIY		do-it-yourself
DKV	Deutscher Kälte- und Klimatechnischer Verein e.V.	German Refrigeration and Air Conditioning Association
DME		dimethylether

List of Abbreviations

Abbreviation	Meaning (German)	Meaning (English)
DPI		dry powder inhaler
DTI		Danish Technological Institute
ECCP		European Climate Change Programme
EOP		end-of-pipe
EPA		Environmental Protection Agency
EPS		expanded polystyrene
EU		European Union
FCCC, UNFCCC		(United Nations) Framework Convention on Climate Change
F-gases		fluorinated gases (HFKW, FKW, SF₆)
GDI	Gesamtverband Dämmstoffindustrie	Thermal Insulation Industry Association
GDR		German Democratic Republic
GHG		Greenhouse gas
GIS		gas insulated switchgear
GTZ	Gesellschaft für Technische Zusammenarbeit	German agency for technical cooperation
GWP		global warming potential
HCFCs		hydrochlorofluorocarbons
HCs		hydrocarbons
HF		hydrogen fluoride
HFCs		hydrofluorocarbons
HFE		hydrofluoroether
HFO		hydrofluoroolefin
HGV		heavy goods vehicle
HV		high voltage
IMO		International Maritime Organization
IPCC		Intergovernmental Panel on Climate Change

Abbreviation	Meaning (German)	Meaning (English)
IVPU	Industrieverband P olyurethan-Hartschaum e.V.	Rigid PUR Foam Association
KBA	K raftfahrt- B undesamt	Federal Motor Transport Authority
KFOR		Kosovo Force
LBO	L andes b auordnung	state building control regulations (<i>Land</i> = state = regional level)
LCA		l ife c ycle a ssessment
LT		l ow t emperature
LV		l ow v oltage
MAC		m obile a ir c onditioner
MAK	M aximale Arbeitsplatz k onzentration	maximum allowable workplace concentrations (used as workplace-related emission limit values in Germany)
MBO	M uster b auordnung	model building control regulations
MDI		m etered d ose i nhaler
MT		m edium t emperature
MV		m edium v oltage
N ₂		nitrogen
N ₂ O		nitrous oxide, laughing gas
NF ₃		nitrogen trifluoride
NH ₃		ammonia
NMVOC		n on- m ethane v olatile o rganic c ompounds
n-PB		n-propylbromide
ODP		o zone d epletion p otential
ODS		o zone- d epleting s ubstances
ORC		o rganic R ankine c ycle
P.D.R.	P rodukte D urch R ecycling	(products from recycling)
PFCs		p erfluorocarbon s
PIR		p olyisocyanurate

List of Abbreviations

Abbreviation	Meaning (German)	Meaning (English)
POU		p oint of u se
ppb		p arts p er b illion
ppm		p arts p er m illion
ppt		p arts p er t rillion
PUR		p oly u rethane
\dot{Q}		heat flow
R (e.g. R404A)		r efrigerant
RAL	Deutsches Institut für Gütesicherung und Kennzeichnung e.V. – <i>formerly:</i> Reichsausschuss für Lieferbedingungen	German Institute for Quality Assurance and Labelling
RIM		r ea ct ion i njection m oulding
RMU		r ing m ain u n i t
RRIM		r einforced r ea ct ion i njection m oulding
SEMATECH		Semiconductor Manufacturing Technology
SF ₆		sulphur hexafluoride
SNAP		S ignificant N ew A lternatives P olicy
SO ₂		sulphur dioxide
SRIM		s tructural r ea ct ion i njection m oulding
TEAP		T echnology and E conomic A ssessment P anel
TEWI		t otal e quivalent w arming i mpact
TFA		t ri f luoroacetic a cid
UBA	U mwelt b undesamt	F ederal E nvironment A gency (Germany)
ÜGPU	Ü berwachungsgemeinschaft P olyurethan-Hartschaum e.V.	Rigid PUR Foam Monitoring Association
UNEP		U nited N ations E nvironment P rogramme
USA		U nited S tates of A merica

Abbreviation	Meaning (German)	Meaning (English)
UZ	Umweltzeichen	Eco-label
VDA	Verband der Automobilindustrie e.V.	Automobile Manufacturers' Association
VDE	Verband der Elektrotechnik, Elektronik, Informationstechnik e.V.	Electrical Engineering, Electronics, and Information Technology Association
VDEW	Vereinigung Deutscher Elektrizitätswerke e.V.	Association of German Electricity Supply Companies
VDKL	Verband Deutscher Kühllhäuser und Kühllogistikunternehmen e.V.	German Refrigerated Warehouse and Logistics Association
VDMA	Verband Deutscher Maschinen- und Anlagenbau e.V.	German Engineering Federation
VOC		volatile organic compounds
W		work
WLG	Wärmeleitfähigkeitsgruppe	thermal conductivity group as defined by German Standard DIN 18164-1
WMO		World Meteorological Organization
WSC		World Semiconductor Council
XPS		extruded polystyrene
ZVEI	Zentralverband Elektrotechnik- und Elektronikindustrie e. V.	Central Association of the Electrical Engineering and Electronics Industry

17 Glossary

Term	Explanation
A+, A++	Energy efficiency classes
ATP Agreement	Agreement on the international carriage of perishable foodstuff and on the special equipment to be used for such carriage. See http://www.tuev-sued.de/anlagen_bau_industrietechnik/technikfelder/elektro-_und_gebaeudetechnik/kaelte-_klimatechnik_atp-pruefstelle
Azeotropic refrigerant	Azeotropic refrigerants evaporate and liquefy at constant temperatures. The boiling point of an azeotropic blend lies either above the highest or below the lowest boiling point of its single components.
Blend	Mixture of different types of refrigerants.
Cascade system	A cascade system consists of two or more separate cooling systems that are linked with each other. Heat is exchanged between the condenser of the one system and the evaporator of the other system. The advantage of such a system, as compared to a two-phase refrigeration unit, lies in the fact that each cycle can be operated with a different cooling agent depending on the respective temperature conditions.
Category M1	Vehicles used for the carriage of passengers, comprising not more than eight seats in addition to the driver's seat.
Category N1	Vehicles used for the carriage of goods, with a maximum mass not exceeding 3.5 t.
COP	The Coefficient of Performance (COP) describes the relationship between the performance of heating/cooling (output) and effective energy consumption (input). The COP primarily depends on the temperatures in the evaporator and condenser. The smaller the temperature difference, the higher the COP.
Drop-in refrigerant	Drop-in refrigerants allow the conversion of existing units without the need to replace parts or change oil. Please note: The term "drop-in" is sometimes applied to other applications.
Emission rate	The emission rate is the quotient of all emissions (including emissions during production, regular emissions and emissions due to accidental leakages) and the total filling quantity/total charge referring to one year.

Term	Explanation
End-of-pipe technology	<p>The term “end-of-pipe technology” describes techniques which reduce the environmental impact only at the end of the technological process, i.e. the pollutants are generated before they are reduced, controlled or eliminated, for example, from the waste gas, wastewater etc. Typical end-of-pipe technology includes flue gas cleaning, scrubbers and catalytic converters.</p> <p>The opposite of end-of-pipe technology is low-emission or emission-free technology.</p>
Exergy	<p>Energy is exergy plus anergy.</p> <p>Exergy is energy that can be converted into work.</p> <p>The term “exergy” helps to assess the practical usability of the different forms of energy. For example, the energy quality of electric power and heat is very different: The exergy level of heat is relatively low, because it is limited by thermodynamic efficiency. By contrast, electric power consists of 100% exergy.</p>
Explosion limit	<p>Upper and lower explosion limits are the highest and lowest concentrations of a flammable substance in a mix of gases, vapours, mist and/or dust, in which an explosion is no longer able to spread after ignition.</p>
F-Gas Regulation	<p>Regulation (EC) No. 842/2006 of the European Parliament and of the Council of 17 May 2006 on certain fluorinated greenhouse gases</p>
Flame retardant	<p>The group of flame retardants includes a variety of different chemical compounds. Most commonly used are polybrominated biphenyls (PBB), polybrominated diphenyl ethers (PBDE), tetrabromobisphenol-A (TBBA), chlorinated paraffins and antimony trioxide.</p> <p>Flame retardants are intended to lower the ignitability of flammable substances, and to prevent or retard a fire. They are most commonly used in the following sectors: wood, wooden materials, plastics and textiles.</p> <p>From a toxicological and eco-toxicological point of view, some of the flame retardants that are in use have significant adverse effects.</p>
Flammability	<p>The term “flammability” refers to how something burns after ignition, in particular to the speed and intensity of burning. A distinction is made between substances that are hard to ignite, substances with normal flammability, and highly flammable substances.</p>
GWP ₁₀₀	<p>Global warming potential of a substance over a 100-year period.</p>

Term	Explanation
Halon	Halon is an organic compound that contains bromine. They are derived from methane and ethane. In the past, halons were used in hand-held and stationary fire extinguishing systems. Like chlorofluorocarbons, halons belong to the group of ozone-depleting substances, but their ozone depletion potential is one to ten times higher.
Ignitability	The less energy (ignition heat) a flammable substance requires to reach its ignition temperature, the more easily it can be ignited.
Inergen®	Inergen® is a patented fire extinguishing agent consisting of nitrogen (52 vol.%), argon (40 vol.%) and carbon dioxide (8 vol.%).
Inert / inert gas	<p>The term “inert” means inactive, stable. The term “inert gas” thus describes gases which are characterised by very low chemical reactivity. Almost all noble gases belong to the group of inert gases.</p> <p>Inert gases are used, for example, as fire extinguishing agents. Inert gas extinguishers are based on the principle of oxygen displacement and are therefore very effective. They are residue-free and suitable for the protection of high-quality goods and equipment.</p>
Kyoto Protocol	The Kyoto Protocol was adopted by the Third Conference of the Parties of the Framework Convention on Climate Change in 1997. In the Kyoto Protocol, the industrialised countries committed themselves to reducing their overall emissions of the most relevant greenhouse gases by at least 5% below 1990 levels between 2008 and 2012. The individual countries have committed themselves to different emission reduction levels. Germany ratified the Protocol together with the other EU Member States in May 2002.
Leakage rate	The leakage rate is the quotient of all regular emissions and the total filling quantity/total charge referring to one year.
MARPOL	International Convention for the Prevention of Pollution from Ships (1973/78).
Mesosphere	The mesosphere is the atmospheric layer above the stratosphere. It starts at approximately 50 km above ground level and extends up to a height of approximately 80 km above ground level.

Term	Explanation
Montreal Protocol	The Montreal Protocol on Substances that Deplete the Ozone Layer is the most important international instrument for protecting the ozone layer. It was signed in September 1987 by 25 governments and the Commission of the European Union. In London (June 1990), Copenhagen (November 1992), Vienna (December 1995), Montreal (September 1997) and Peking (1999) it was amended. Additional measures were added and it was made more stringent. See www.unep.org/ozone/ .
NMVOC	NMVOC are volatile organic compounds (VOC) excluding methane (which is considered separately due to its specific characteristics)
Off-shore installation	Installation located away from the coast (in the sea).
OH radicals	After photolysis of ozone, when the newly formed O atoms react with H ₂ O, hydroxyl radicals (OH) are formed in the atmosphere ($O + H_2O \rightarrow 2 OH$). OH radicals have a strong tendency to form H ₂ O again and therefore react with hydrogen-containing compounds.
Plasma	Plasma is a completely or partly ionised, electrically conductive gas consisting of electrons and ions. Due to its characteristics, it differs considerably from gases, liquids or solids. The term “plasma” was created by Irving Langmuir (in 1928).
Plasma etching	Plasma etching is a dry etching process. Reactive atoms or ions (e.g. fluorine) generated through a gas discharge (mostly triggered by high voltage) transfer patterns into a substrate.
Plasma processes, plasma technologies	“Plasma processes” is a collective term for a number of industrial plasma applications such as etching processes in the production of semi-conductors and circuit boards, silicon precipitation for the production of solar cells, arc welding or melting.
ppb	parts per billion / mixing ratio of 1 : 10 ⁹
ppm	parts per million / mixing ratio of 1 : 10 ⁶
ppt	parts per trillion / mixing ratio of 1 : 10 ¹²
R 404A	Blend of R 125/143a/134a in the ratio 44:52:4
R 407C	Blend of R 32/125/134a in the ratio 23:25:52
R 410A	Blend of R 32/125 in the ratio 50:50
R 413A	Blend of R 134a/218/600a in the ratio 88:9:3
R 417A	Blend of R 125/134a/600 in the ratio 46.6:50:3.4
R 437A	Blend of R 125/134a/600/601 in the ratio 19.5:78.5:1.4:0.6

Term	Explanation
R 507	Blend of R 125/143a in the ratio 50:50
Refrigeration unit/ heat pump	<p>The operation of refrigeration units (and heat pumps) is based on refrigerants, which are generally run in a closed cycle. The evaporation of the liquid refrigerant generates cold. When pressure is elevated, and the temperature is lowered, the gas is liquefied again and heat is generated.</p> <p>Units which are mainly used for refrigeration are called refrigeration units. Units which are mainly used for heat generation are called heat pumps.</p>
Retrofit	The term “retrofit” means refrigerant replacement in an existing cooling system. As opposed to “drop-in”, the retrofit method requires several oil changes, some times even the remodelling of the entire system. It is therefore more cost-intensive in terms of labour and material.
Single-circuit system, direct evaporation system	In a single-circuit system, the low temperature is transferred directly from the refrigerant to the cooling points.
Stratosphere	The stratosphere is the atmospheric layer above the troposphere. It starts at approximately 12 km above ground level and extends up to a height of approximately 50 km above ground.
Transcritical	Owing to the low critical temperature of R-744 (CO ₂), namely 31.1°C, transcritical operating modes frequently occur in systems using this refrigerant. Supercritical CO ₂ is CO ₂ in a fluid state above its critical temperature and its critical pressure. In refrigeration systems, heat release takes place in the supercritical range above the critical temperature, resulting in higher system pressure than in conventional systems. A single-stage cycle process of this kind is known as a transcritical process.
Troposphere	The troposphere is the lowest layer of the atmosphere. It extends up to a height of approximately 12 km above ground level.
Two-circuit system, indirect system, secondary system, brine-based system	In a secondary system, the low temperature is transferred indirectly to the cooling point, i.e. via a heat transfer fluid/“secondary refrigerant” (e.g. brine, CO ₂).

Glossary

Term	Explanation
United Nations Framework Convention on Climate Change (UNFCCC)	The UN Framework Convention on Climate Change was adopted at the Earth Summit for Environment and Development held in Rio de Janeiro in 1992. Since then, it has been ratified by 186 countries. In 1994 the Convention came into force. It provides the framework for the negotiations on climate protection that take place at the Conferences of the Parties to the Convention on Climate Change. The Secretariat of the Framework Convention on Climate Change (UNFCCC Secretariat) is based in Bonn.
Wafer	The term “wafer” refers to a polished single-crystal silicon wafer used for chip production.
Zeotropic refrigerant	Zeotropic refrigerants evaporate and liquefy within a certain temperature range. This range is called “temperature glide”.