Review

Ecological Replacements of Ozone-Depleting Substances

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Abstract

Halogenated aliphatic hydrocarbons have appeared in the natural environment in steadily increasing amounts over several decades as a consequence of their growing use, chiefly as refrigerant, foam blowing agent and solvent, prompted by their unique properties and low cost. It is recognised that anthropogenic emissions of the above compounds, which are referred to as ozone-depleting substances (ODS's), are partly responsible for depletion of the stratospheric ozone layer and the so-called greenhouse effect.

The photodecomposition of halogenomethanes in the stratosphere produces significant amounts of chlorine atoms, leading to the decay of atmospheric ozone, which allows increased levels of biologically damaging UV radiation to reach the Earth's surface.

The discovery of the above phenomenon has initiated efforts towards the withdrawal of ODS.

Nowadays, it is accepted that fully halogenated chlorofluorocarbons (CFC's) are the main source of the chlorine that is eroding Earth's protecting ozone, and their role is of great global concern.

In spite of the fact production CFCs has been banned since 01.01.1995 and their use prohibited since 01.01.1996, the depletion of stratospheric ozone will continue because large amounts of these class compounds are still in use. Therefore, the recovery and subsequent destruction of the CFCs still in use is a logical next step, in particular the conversion of the CFC's into useful products is a challenging task.

At present CFCs are being replaced by hydrochlorofluorocarbons (HCFC's) and in perspective by hydrofluorocarbons (HFC's), before better replacements are found. The environmental impact of CFC replacements is considered in terms of their ozone depletion potential (ODP), global warming potential (GWP) and ability to form noxious degradation products.

Keywords: alternatives to ozone depleting substances (ODS's)

Introduction

In 1785, eleven years after the discovery of oxygen by J. Priestley, M. van Marum noticed a peculiar smell in the vicinity of working electrical machines, which he called the smell of "electrical matter" [1]. Additionally he observed that this "electric matter" may react with mercury. In 1801 W. Cruickshank also mentioned that a similar odour is produced near the anode when acidic water solution is electrolysed [2]. Later, C.W. Schonbein noticed that the odour developed during the electrolysis of acidic water and that appearing during the working of an electrical machine is similar [3]. He claimed that this smell must be due to the formation of a definite substance to which he gave the name "ozone" (Greek οξων means "to smell").

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It was thought for some time that ordinary oxygen was a compound composed of negative and positive oxygen. The former was called by C.F. Schonbein ozone and symbolised by +, and the later ontozone symbolised by Θ [2, 3]. Numerous studies of ozone undertaken by C.F. Schonbein have proved that this gas is a condensed form of oxygen, which can be described by the formula O_3 while ordinary oxygen is symbolised by O_2 [3].

The existence of ozone in the troposphere was established by chemical means in 1858 by A. Houzeau [4]. Subsequent spectroscopic studies in the visible and ultraviolet regions showed, as early as 1881, that ozone is present at a higher mixing ratio in the upper atmosphere than near the ground [5].

In the early part of the 20th century a study by G.M.B. Dobson [6], who constructed the first spectrophotometer for determination of ozone, had shown that concentration of ozone in the atmosphere shows a characteristic vertical and horizontal distribution. Additionally, annual latitudinal variations and fluctuation caused by changes in meteorological conditions were observed [7-10]. Most of the Earth's atmospheric ozone (about 90%) is found in the stratosphere where it reaches a maximum mixing ratio of about 10 ppm at an altitude of 25-30 km. The total column integrated ozone (that is the total amount of O_3 integrated from the surface of the Earth to the top of the atmosphere) is usually expressed in terms of Dobson Units (DU). It represents the thickness, expressed in units of hundredths of a millimetre, that the ozone column would occupy at standard temperature (273K) and pressure (1013,25 hPa). 1 Dobson (DU) = 10^{-3}atmx mm $\equiv 2.69 \times 10^{16}$ molecule x cm^{-3} [9, 10].

At present it is well known that ozone O_3 is one of the forms of elemental oxygen and an essential atmospheric trace substance. This triatomic ozone molecule is non-linear, with the O-O-O bond angle of 117°. It is a highly unstable, highly reactive, diamagnetic and poison gas. In the liquid form it has dark-blue colour (b.p. -112°C), due to intense absorption of red light $(\lambda = 557$ and 602 nm), whereas in the solid state it is dark-violet (m.p. -193°C) [11, 12]. The total amount of ozone in the atmosphere makes 6×10^{-5} of the total mass of the atmosphere [7, 8].

P. Crutzen [13] and H.S. Johnston [14] had originally suggested that release of trace amounts of gases of anthropogenic origin to the atmosphere might initiate a chain reaction leading to disturbances in the qualitative composition of the atmosphere [15].

In 1971 J. Lovelock [16] was first to identify in the stratosphere the presence of trichlorofluorometanu by means of a gas chromatograph with an electron capture detector he constructed. The above fact marked the beginning of extensive scientific and political controversy over the fate of the ubiquitous chemicals. In 1974 F.S. Rowland and M.J. Molina [17], issued the first warning that chlorine from halogenated aliphatic hydrocarbons could destroy ozone in the stratosphere through the catalytic cycle involving chlorine. They pointed out that the main process responsible for CFC removal was photolysis induced by solar radiation in the middle stratosphere along with such processes as oxidation or dissolution in raindrops [18].

In 1985 the world was alarmed by J.C. Farman, B.G. Gardiner and J.D. Shanklin [19] about the disappearance of ozone in the stratosphere. Results of atmospheric measurements made at Halley Bay (76°S), Antarctica by means of ground-based spectrophotometers showed that the total amount of ozone in a vertical column extending upward from the instrument has decreased. They also postulated that the observed ozone decrease was caused by reactions involving chlorine in the catalytic cycle [20]. Additionally they reported that since 1968 the ozone column in October had a downtrend [19], which has been supported later by data obtained from the NASA satellite Nimbus-7 [21-23]. Measurements of CCl_2F_2 by UARS's Cryogenic Limb Area Etalon Spectrometer indicate high levels of this compound reaching the stratosphere. The amount of CCl_2F_2 begins to decrease above 20 km as the molecules are broken apart by UV radiation. Simultaneous measurement of HCl and HF show the levels these halogenoorganic compounds decomposition products rise to heights where they undergo photolysis [23-31].

The most prominent instance of ozone layer destruction is the so-called "Antarctic ozone hole" which has shown up in recent years. This phenomenon is manifested by the appearance of a severely depleted stratospheric ozone layer, even up to 50% during the Antarctic's late winter and early spring, over the polar region [23]. Starting from the 1990s the ozone hole appears every year in September and October. The ozone depletion in the stratosphere lasts longer and covers a larger area [21-22]. Although over the North Pole ozone depletion has not been so drastic, this phenomenon has been observed and the rate of ozone decrease reaches a few percent per decade [10]. According to D. Hoffman maximum ozone depletion is observed between 14 and 22 km in altitude, indicating that ozone decay occurs at the altitude of maximum ozone concentration [9, 10, 32].

Critics of the concept presented by M.J. Molina and F.S. Rowland [17] claiming that the chlorine that evolved from halogenocarbons catalyses ozone depletion, argue that CFC molecules are too "heavy" to rise into the stratosphere [33]. Even if they did, the sceptics argue, the amounts of chlorine from CFC's carried into the stratosphere are small when compared with natural sources of chlorine such as seawater and volcanic exhalation. The National Aeronautics and Space Administration's Upper Atmosphere Research Satellite (UARS) data refute these claims [34, 35]. Satellite measurements have confirmed the presence of this species in both the Arctic and Antarctic atmosphere [9, 10, 36, 37].

In the ice cap core whose age has been estimated from ^{14}C isotope level as about a thousand years, so before any considerable anthropogenic pressure, the presence of various halocarbons (e.g.. 5ppt CCl_2F_2, 120ppt CH_2Cl_2) was detected [29]. It has been estimated that in the periods of warming up of the Earth climate about 15 millions tons of halocarbons have evaporated from the oceans to the atmosphere, which is a huge amount when compared with the products of anthropogenic pressure [38]. The opponents of the hypothesis put forward by M.J. Molina and F.S. Rowland [17] suggest that the depletion of the ozone layer is to a much greater extent due to climatic changes than the release of halocarbons of anthropogenic origin to the atmosphere [33]. Moreover,

it has been established that the effect of space programmes (rocket launches in particular) on the decay of stratospheric ozone is considerable [10, 14, 39].

ODS's *[ozone depleting substances)* is a general abbreviation for halogen-containing air pollutants with the potential to damage stratospheric ozone. Amongst this group of compounds chlorofluorocarbons (CFC's), often known by their trade name Freons, are identified as major contributors with the greatest potential for damage to the ozone layer [9,10, 32, 40]. It has been estimated that from among ODS's found in the troposphere CH_3C1, CCl_3F, CCl_2F_2, CCl_2FCClF_2 $CHClF_2$, $CHCl_3$ and CCl_4 occur in the greatest concentrations, close to 87% of the total anthropogenic emission of chlorine into the atmosphere [41-43].

The earliest identified natural source of gas halogenated compounds was evaporation of sea salt from the oceans [44-48]. Later it was found that all monomethyl halogen compounds have their natural sources [49-54]. They are mainly the products of biochemical processes taking place in the oceans; among these compounds CH_3CI is dominant. A powerful source of these compounds are also the products of biomass combustion (e.g. equatorial forest fires). The group of known halocarbons of natural origin comprises over 2000 compounds including Freons, till recently classified as xenobiotics [45-47]. Freons have been detected in the gases exhaled by volcano Santiaguito in Guatemala and by many volcanoes on Kamczatka [46, 52, 55]. In the gases emitted by volcanoes the most common were CCl_3F (CFC-11), CCl_2F_2 (CFC-12), $CHClF_2$ (HCFC-22) and CC_2FCClF_2 (CFC-113), whose concentrations vary in the range 0.4-160 ppb [46].

A wide range of applications of halocarbon compounds has stimulated increasing demand for their production. It has been estimated that over 500 compounds representing this group have been applied as final products or substrates in numerous syntheses [45]. A conse-

quence of this widespread use is the fact that halocarbon compounds have penetrated all elements of the biosphere and many of them, e.g. dichloro-difenylo-trichloroetan (DDT), polyhalogenated biphenyl PCB) or polyhalogenated triphenyl (PCT), have permanently polluted the natural environment [48, 51, 52, 56, 57].

According to statistical data concerning the most often used compounds of this kind, known as Freons: CCI3F (CFC-11) and CCl_2F_2 (CFC-12), in the years 1950-1975 their production increased in geometrical sequence (see Fig. 1) [9, 32, 58].

Over the same time these volatile compounds were released to a very large extent to the atmosphere. For example their combined worldwide production in 1977 was estimated at the level of 700,000 tonnes. It has been estimated that over 600,000 tonnes were released to the atmosphere [10, 32]. The results published in 1988 by NASA provided experimental evidence of thinning of the ozone layer at a location outside Antarctica [24].

The global importance of stratospheric ozone depletion was recognised by the United Nations Organisation which initiated the United Nations Environmental Program (UNEP)), aimed at international Cupertino to curb the release of ODS's [9, 59, 60]. In September 1987 an international conference on the subject was held in Montreal, at which representatives of over 120 countries signed the obligation to phase out ODS's, in the so-called Montreal Protocol [61-64]. The signatories of this document, Poland included, have gradually decreased the use of halocarbons from the group of Freons (commonly used as refrigerant) and Halons (effective fire extinguishers). In parallel, environmental-friendly cooling and fire extinguishing media [9, 58-64] have replaced Freons and Halons.

In spite of the phase out the depletion of ozone will continue, because large amounts of these compounds are still in use and the emission of these compounds will unavoidably continue [10, 65-70]. As accumulation rates of ODS's (mainly CFC's) in the troposphere begin to fall in accordance with international agreements, the concentration of several replacement compounds, such as hydrofluorocarbons (HCFC's), have increased rapidly in recent years [42, 71-75]. It has been established that by early 1995 anthropogenic chlorine loading due to release of CH_3CCl_3, CCl_4, CCl_2FCClF_2, CCl_3F, CCl_2F_2, and $CHClF_2$ to the atmosphere has decreased by 0.02 +/- O.Olppb since 1992 [76].

Both CI and Br atoms cannot account for all the ozone loss in the lower stratosphere observed by balloons and satellites. A better match for the observed ozone depletion is obtained by including iodine reactions in computer models of atmospheric chemistry indicating that this neglected element may play a significant role in ongoing changes in the ozone layer [11, 77-80].

Fig. 1. The increase of the size of world production of chlorofluorocarbons in kilotons in the years 1940-2000, on the example CCl3F (CFC-11) and CCl,F2 (CFC-12) (Adapted from ref. 58).

Natural Processes of Formation and Destruction of Ozone in the Atmosphere

A peculiarity of ozone is that O_3 molecules are both formed and partly destroyed in the atmosphere. The first quantitatively correct mechanism of formation and decay of ozone in the Earth's atmosphere was proposed in 1930
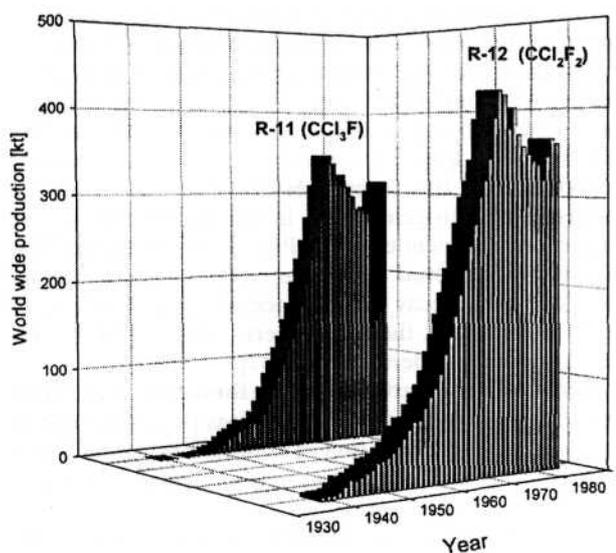
by S. Chapman [8, 81]. According to this concept, the ozone is formed in the upper atmosphere above 30 km in altitude when solar ultraviolet radiation is adsorbed by molecular oxygen, breaking the molecular bond and yielding two free atoms:

$$O_2 + h\nu \to O + O \qquad (1)$$

A free oxygen atom can then combine with an oxygen molecule to form ozone. This photodissociation is followed by a secondary thermal reaction (2) leading to O_3 formation:

$$O_2 + O + M \to O_3 + M \qquad (2)$$
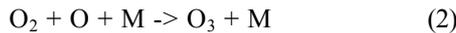
where M is a third neutral body such as an oxygen or nitrogen molecule. The formation of atomic oxygen in the primary reaction (1) is brought about by ultraviolet radiation (UV-C) with wavelengths $\lambda < 242$ nm in the upper atmosphere. Ozone itself undergoes photodissociation as a result of strong absorbing ultraviolet radiation (UV-B) in the band of 240-320 nm with maximum absorption at 255 nm. The photochemical reaction associated with this absorption also leads to the decay of ozone (3):

$$O_3 + h\nu \to O_2 + O \qquad (3)$$

Additionally, this absorption prevents solar radiation with wavelengths shorter than 290 nm from reaching the earth's surface. Absorption by ozone of most (99%) of the solar radiation (UV-C) in the 210-312nm region results in its conversion into infrared radiation. This accounts for the maximum temperature at an altitude of about 50 km, near the top of the stratosphere [10].

As follows from the above, ozone plays an important role in control of the ultraviolet radiation and heat balance of the Earth's stratosphere [9]. A further, non-photochemical reaction (4) controlling the destruction of ozone in the upper atmosphere is:

$$O_3 + O \to 2O_2{}^* \qquad (4)$$

where the resulting oxygen molecules are in an excited * electronic state. Theoretical considerations suggest that the net O_3 concentration should be proportional to the square root of the O_2 photolysis rate [9, 10, 58].

According to the scheme of ozone generation proposed by S. Chapman, its greatest concentration should occur at the latitude of 15-50 km, in the part of the stratosphere known as the ozone layer or ozonosphere [81]. Results of the measurements of ozone concentration have proved this prediction to be correct, but the actual concentration was much lower than predicted, which indicates that some significant processes leading to ozone decomposition have been neglected (see Fig. 2).

In 1971 P. Crutzen [13] pointed to the possibility of a catalytic process in which the concentrations of O and NO_2 do not change, whereas ozone undergoes conversion to mlecular oxygen:
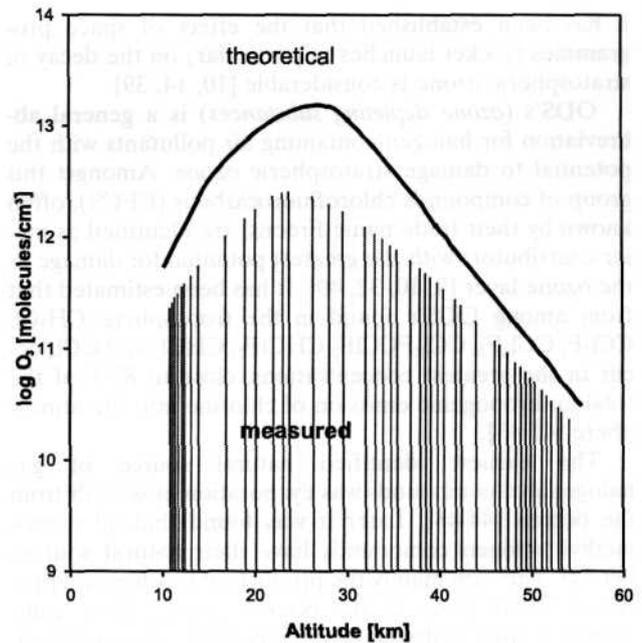
$$NO + O_3 \to NO_2 + O_2 \qquad (5)$$

$$NO_2 + O \to NO + O_2 \qquad (6)$$

Fig. 2. The vertical profile concentration of ozone expressed as log [O_3] molecules in 1 cm³ of air at different altitudes: a) calculated, b) measured (Adapted from ref. 32).

The atomic oxygen needed for regeneration of the NO molecule (6) appears as a result of the photochemical decay (3). The main source of NO and NO_2 in the atmosphere is the interaction of N_2O and solar radiation with wavelength of $\lambda \leq 337$ nm [7, 66]. It was shown by experiments carried out by C.C. Delwiche [82] that N_2O could be released from soil through bacterial denitrification (7):

$$NO_3{}^- + 2H_2 + H^+ \to 0.5\,N_2O + 2.5\,H_2O \qquad (7)$$

In 1978 Bremer and Blackmer [83] demonstrated that the activity of man is also a source of atmospheric N_2O, which is produced by bacterial denitrification processes of fertiliser -derived nitrate and ammonia. Earlier P. Crutzen [15] and H.S. Johnston [14] stated that supersonic aircraft flying in the stratosphere could emit NO and NO_2 in a quantity sufficient to alter the chemical composition of this layer. Results of the study of the chemistry of nitrogen oxides in the Earth atmosphere carried out independently by P. Cruitzen [84] and H.S. Johnston [85] proved that these compounds are responsible for ozone decay taking place at altitudes above 30 km. Unfortunately, the atmospheric chemistry of N_2O is still very poorly understood [86, 87].

A net balance between ozone formation and ozone destruction as well as other ozone loss processes lead to a quasi-steady concentration of atmospheric ozone that is the greatest in the lower atmosphere, between about 15 and 30 km of altitude [88].

As accumulation rates of ODS's (mainly CFC's) in the troposphere begin to fall in accordance with international agreements, the concentration several replacement compounds, such as the hydrofluorocarbons (HCFC's) have increased rapidly in recent years [42, 72-76, 89]. It has

been established that by the early 1995 anthropogenic chlorine loading due to releasing to the atmosphere CH_3CCl_3, CCl_4, CCl_2FCClF_2, CCl_3F, CCl_2F_2, and $CHClF_2$ has decreased by 0.02+/-0.01 ppb since 1992 [76, 90].

Development and Pphysicochemical Properties ofCFC's

Dichlorodifluoromethane, $CI2F2$, was for the first time synthesised by a Belgian chemist Swartsa at the end of the 19th century. However, it could not find practical use for many years [45]. In 1928 an American chemist, T. Migdley, working for DuPont chemicals, predicted that this compound might be a useful cooling medium [91]. Dichlorodifluoromethane (CCl_2F_2) has been manufactured since the 1930's by consortiums of DuPont and General Motors [9, 10, 32, 58]. It was introduced originally as the cooling medium in refrigerators, relacing the highly toxic and odorous SO_2, CH_3Cl_3 and NH_3, which had hitherto been used for this purpose. The recognition of the properties of CCl_2F_2 prompted fast development of refrigeration technologies. This compound is insoluble in water, chemically and thermally notably stable, non-flammable, non-explosive, non corrosive, non-toxic, volatile in ambient air, has a low thermal conductivity and surface tension as well as an appropriate boiling point [9, 32, 58]. Because CCl_2F_2 as well as other ODS molecules are transparent from 230 nm through the visible wavelengths, they are effectively protected below 25 km in altitude by the stratospheric ozone layer that shields Earth's surface from UV radiation [7, 9, 10]. Moreover, ODS's were easy and inexpensive to produce [9, 58].

The chemical inertness and high volatility which make this material suitable for technological use also mean that they remain in the atmosphere for a long time. Removal processes of CFC's are balanced by their steady-state emission. The later include reaction with OH radicals, photolysis in the stratosphere, uptake by oceans, destruction at the land surface as well as precipitation (washout). The atmospheric residence time (live time) is defined as the time from the moment a given compound enters the atmosphere to take part in the above processes till it is removed from it. The above definition we may write in the following form:

$$\tau = \frac{A}{|dA/dt|} \qquad (8)$$

where τ is the residence time (or lifetime) of a given compound A in the atmosphere, [A] its atmospheric concentration, and dA/dt can be either the rate of supply or the rate of removal of A from the atmosphere [9, 10, 58]. Atmospheric residence times of the halocarbons vary considerably depending on their mechanisms of removal, ranging from days to several centuries [92-97].

The troposphere residence time of a given compound determined by the reaction with the OH radicals is:

$$\tau = \frac{1}{K_{OH}[OH]_{av}} \qquad (9)$$

where K_{OH} is the reaction constant of a reaction of a given molecule with OH radical, and $[OH]_{av.}$ is a tropospheric OH concentration [9].

Soon after the introduction of CCl_2F_2, a large group of CFC's appeared, commonly referred to as Freons (see Table 1) [9, 10, 58, 77].

The Use of ODS's

Ozone depleting substances (ODS's) have important uses in modern society as the working fluids in refrigerators and air-conditioners and as the blowing agents for plastic foams and industrial solvents. In these applications their properties are paramount. Initially CCl_3F was used as a cooling medium in refrigerators while CCl_2F_2 in air-conditioners both stationary (rooms) and mobile (cars and other vehicles) ones [32, 45, 98]. The popularity of Freons has increased thanks to R. Abplanalp, who was the first to use CCl_2F_2 as propellants in spray cans containing deodorants and hair spray [32, 58]. Later they were widely applied in technological sprays of paints, varnishes and pharmaceuticals (e.g. CF_3CClF_2, CF_2ClBr, CF_3Br) [9, 45, 58]. Intense development of technology has extended the use of halocarbons, e.g. in medicine for sterilisation of surgical instruments (CCl_2FCClF_2), and as blowing agents in the fabrication of flexible and rigid foams ($CCl3F$, CCl_2F_2, CCl_2FCClF_2) used for thermal insulation in building engineering. The compounds being excellent cleaning and fat removing agents have been commonly applied in the electronics industry (CCl_2FCClF_2, $CClF_2CClF_2$) and as industrial solvents (CCL_4, $CHCl_3$, CH_3CCl_3, CH_2Cl_2, C_2Cl_4) [9, 10, 45, 58].

Another group of halocarbon compounds very interesting from the application point of view includes the bromo-analogues, which are in commercial use as fire extinguishers under the name Halons. They reveal low toxicity, low conductivity and low amount of residues left after fire suppression. They also show high heat capacity, so decrease the temperature of the flames and reduce the rate of combustion [34, 45, 96, 101,102]. Halons are also non-conducting and non-corrosive. Moreover, Halons are highly effective in chemical and physical fire smothering. Generally, fire-extinguishing agents are divided into two groups; the first comprises physical acting agents such as water CO_2 and inert gas blends, which operate primarily by heat absorption. The second including Halons is regarded as chemical action agents because they operate by removing free radicals from flames and combustion systems [9, 101, 102].

The major commercial Halons widely used in commercial and military application for fire suppression are $CBrF_3$ and $CBrClF_2$ [9, 10, 32, 58]. These compounds are used to protect valuable electronics, in oil and gas production and on civilian aircraft. They are also used by the military for extinguishing fires and suppressing explosions in fixed-wing aircraft, helicopters, ships, and armoured vehicles [17]. Additionally, CH_3Br is widely used in agriculture as a space fumigant [9, 32, 19, 103, 104].

Recently, there have been an increasing number of suggestions that global warming can lead to ozone depletion over the Arctic thanks to a mechanism which has

not been taken into consideration. The authors claim that an increase of the concentration of hotgases can lead to a warming up of the tropopause over the quatorial region causing an increase in the rate of water transportation to the stratosphere. The increased level of water vapour in the stratosphere would lead to development of the polar stratospheric clouds (PSC) on whose surface the processes of ozone decay take place [105-108]. The above suggestion is an important argument supporting the criticism of the hypothesis of M. Molina and F.S. Rowland [17].

Nomenclature of ODS's

The large number of halocarbon compounds and the diversity of their applications have aroused the need for their code notation. The American Society of Heating and Refrigeration Engineering proposed the somewhat arcane system of coding of these compounds in 1957 [9]. Generally a coding system is used to replace the chemical names CFC's *(chlorofluorocarbons)* and FCKW *(Fluor-chlorkohlenwasserstoffe),* which contains an abbreviation, followed by a 2-4 digits number code combined with vari-

ous small Latin letters. The abbreviations used in this coding system are CFC (chlorofluorocarbons; molecular compounds consisting of chlorine, fluorine and carbon, but no hydrogen), HCFC (hydrochlorofluorocarbons; whose molecules contain, hydrogen, chlorine, fluorine and carbon) and HFC (hydrofluorocarbons; whose molecules contain hydrogen, fluorine and carbon but no chlorine). Occasionally, they may be replaced by a more general abbreviation such as R (refrigerant) or trademark, such as Freons (DuPont, General Motors), Frigen (Hoechst), Kalt-RON (Kali-Chemie), Forane (Elf Atochem), Arcton (ICI) [9, 10, 32, 58].

In the above-mentioned code system the first digit from the right is the number of fluorine atoms, the second is the number of hydrogen atoms plus one, the third is a number of carbon atoms minus one. The number of chlorine atoms in Freon molecules is found as a difference between the total number of atoms in the molecule and the sum of fluorine and hydrogen atoms. A letter behind the code number indicates that it is an isomer [9, 10, 32, 58, 45]. The presence of the letter *a* denotes a compound of an asymmetric arrangement of halide substituents (e.g.. R-132a ($CHCl_2$-CHF_2)), whereas the letter *b* describes compounds of higher symmetry

Table 1. Effect of a number of ozone depleting substances (ODS's) on stratospheric ozone (ODP), global warming (GWP, HGWP) and their practical usage.

Chemical formula, abbreviation and coding number	Residence time[1] (Yr.)	Ozone depletion potential[2] (ODP)	Halocarbon global warming potential[3] (HGWP)	Global warming potential[1] (GWP) (Time horizon)			Application[4]
				20	100	500	
CCl_3F (CFC-11)	55 ± 5	1.0*	1.0*	5000	4000	1400	a, b, c, d
CCl_2F_2 (CFC-12)	102	0.82	3.2	7900	8500	4700	a, b, c
$C_2Cl_3F_3$ (CFC-113)	85	0.90	1.4	5000	5000	2300	a, b, f
$C_2Cl_2F_4$ (CFC-114)	300	0.85	3.9	6900	9300	8300	a, b, c, f
C_2ClF_5 (CFC-115)	1700	0.40	7.5	6200	9300	13000	a, b
$CClBrF_2$ (Halon-1211)	36	5.1	–	–	–	16000	a, b, c
$CBrF_3$ (Halon-1301)	65	12.0	3.3	6200	5600	2200	a, b, c
CCl_4 (R-10)	42	1.2		2000	1400	500	d, h
$CHCl_3$	0.55	–	–	15	5	1	d, h
CH_2Cl_2	0.41	–	–	28	9	3	d, i
$C_2H_3Cl_3$ (R-140a)	5.4 ± 0.6	0.12	0.1	360	110	35	d, f
CH_3Br	0.7	0.64					i
Azeotrope – R-500 (73.8 wt.% CFC-12; 26.2 wt.% HFC-152a)	–	0.7	2.4	–	–	–	a
Azeotrope – R-502 (48.8 wt.% HCFC-22; 51.2 wt.% CFC-115)	–	0.2	5.6	–	–	–	a

[1] Expressed relative to CO_2 as the reference substances, IPCC (1995) [10,70].
[2] WMO (1994), [34].
[3] Relative to a reference value of 1.0 for CCl_3F [97].
[4] (a) - cooling medium; (b) - aerosol propellant; (c) - blowing agent; (d) - solvent; (e) - for fire suppression and explosive protection; (f) - cleaning agent, (g) - air conditioner; (h) - substrate for manufacture halocarbon compounds; (i) - agricultural and space fumigant, food packing, industry.
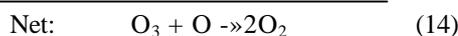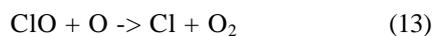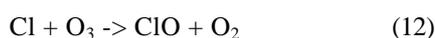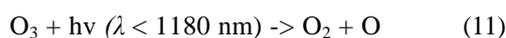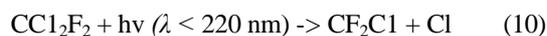* by definition [97].

(e.g. R-132b ($CCIF_2$-CH_2CI)). When the halocarbon compound is cyclic, a capital C is placed before the number (e.g. R-C318 (octafluorocyclobutane, C_4F_8)).

To decode the name of a given Freon a number 90 should be added to the number after the letter code. We obtain then a three-digit number in which the first, second and third are the number of carbon, hydrogen and fluorine atoms in the molecule, respectively. The number of the chlorine atoms present in the molecule results from the stoichiometry and existence of the double bonds [58]. Occasionally, a more general abbreviation such as R *{refrigerant)* or a trademark, such as Freon, may be used.

For bromine-containing halogenocarbons, the so-called halons, another system is used. The abbreviation used in the case of halons is a letter H or R and to the code are introduced additionally letter B and a digit indicating the number of bromine atoms in the molecule (e.g. R-13B1 (CF_3Br)). Additionally a trademark, such as Halon may also be used [32]. The code number consists then of four digits of which the first, second, third and fourth correspond to the number of carbon, fluorine, chlorine and bromine atoms, respectively (e.g.CF_2QBr, Halon-1211) [58].

Environmental Impact of ODS's

Although halogenoorganic compounds are quite inert in the lower atmosphere they undergo photodecomposition high-energy UV radiation in the stratosphere, whose energy is enough to break their very strong C-Cl bonds through such chain reactions (equations (11)-(14)) as:

$$CC1_2F_2 + hv\ (\lambda < 220\ nm) \rightarrow CF_2C1 + Cl \qquad (10)$$

$$O_3 + hv\ (\lambda < 1180\ nm) \rightarrow O_2 + O \qquad (11)$$

$$Cl + O_3 \rightarrow ClO + O_2 \qquad (12)$$

$$ClO + O \rightarrow Cl + O_2 \qquad (13)$$

$$\text{Net:} \qquad O_3 + O \rightarrow 2O_2 \qquad (14)$$

thereby releasing Cl atoms, which react with ozone, destroying it and producing CIO (reaction (13) [7, 17, 9, 26, 10].

The depletion of ozone molecules in the stratosphere would disturb the delicate natural balance between the process of ozone formation and destruction. Additionally these phenomena produce a new atmospheric situation with a substantially depleted ozone layer [9, 22, 23, 65, 69].
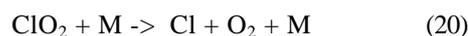
The concept presented above by M. Molina and F.S. Sherwood was modified several times because the rate of ozone decay was much faster than that obtained by different model calculation [7, 17]. Thus it has been shown by R.K.R. Vupputuri [109] that the resultant product of reaction (13), ClO may react with NO_2 to stabilise ozone decay by the Cl-ClO cycle in the midstratosphere:
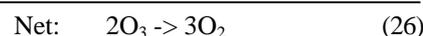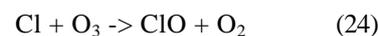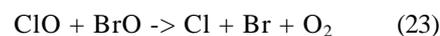
$$ClO + NO_2 + M \rightarrow ClONO_2 + M \qquad (15)$$

$$Cl + NO_2 + M \rightarrow ClNO_2 + M \qquad (16)$$

Additionally C.J. Howard and K.M. Evenson [110] demonstrated that the reaction:

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (17)$$
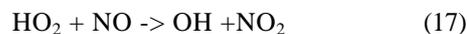
was much faster than previous measurements had indicated. In view of that a search for a mechanism of the reactions leading to the release of chlorine atoms from such molecules as HCl, $ClONO_2$ and $ClNO_2$, has started [7, 9]. It has been known on the basis of satellite data that the Antarctic winter stratosphere is a region of extensive cloud formation, which suggested that these polar stratospheric clouds might provide surfaces for heterogeneous chemical reactions [77, 111]. In 1986 a relationship was observed between the rate of ozone decay and the occurrence of the aerosols forming these polar stratospheric clouds (PSC) [10, 32, 111]. It was found that during the polar night on the surface of the clouds of the atmospheric aerosols identified as microcrystals of H_2O, HCl or HNO_3-$3H_2O$, the reactions leading to liberation of Cl_2 from such compounds as HC1 and $ClONO_2$ take place [110-113]. Additionally, M. Molina and F.S. Rowland [17, 181] discovered that in the conditions of the polar vortex the molecules of ClO undergo dimerisation (16). It is assumed that at least 95% of the chemically catalysed ozone loss can be attributed to ClO dimer mechanism (reactions (18)-(22) and BrO mechanism (reactions (23)-(26)):

$$ClO + ClO + M \rightarrow C1_2O_2 + M \qquad (18)$$

$$C1_2O_2 + hv \rightarrow Cl + C1O_2 \qquad (19)$$

$$ClO_2 + M \rightarrow Cl + O_2 + M \qquad (20)$$

$$2(C1 + O_3) \rightarrow 2(C1O + O_2) \qquad (21)$$

$$\text{Net:} \qquad 2O_3 \rightarrow 3O_2 \qquad (22)$$

and

$$ClO + BrO \rightarrow Cl + Br + O_2 \qquad (23)$$

$$Cl + O_3 \rightarrow ClO + O_2 \qquad (24)$$

$$Br + O_3 \rightarrow Br\ O + O_2 \qquad (25)$$

$$\text{Net:} \qquad 2O_3 \rightarrow 3O_2 \qquad (26)$$

Furthermore, it has been estimated that about 75% of the ozone loss results from reactions involving the ClO dimer and most of the remaining ozone is destroyed in reaction involving bromine [7, 9, 112]. The odd chlorine chain (Cl, ClO) can be compared with the odd nitrogen chain (NO, NO_2), which is believed to be immediately involved in the regulation of the present level of O_3 in the atmosphere [10, 32, 58].

As follows from the above evidence, the mechanism of formation and destruction of stratospheric ozone is complex and has been only partly explained, because not all factors leading to its decay have been recognised. It has been estimated that one chlorine atom acting as a catalyst in the reaction of ozone decay is able to cause the destruction of 100,000 ozone molecules [58]. In the case of Halons, which are bromine analogues of Freons, the problem is more complex because in the stratosphere they undergo photolysis to release free bromine atoms, Br:

$$\text{e.g. } CF_3Br + h\nu \; (\lambda < 220 \text{ nm}) \rightarrow CF_3 + Br \quad (27)$$

whose potential of ozone decay is about 20 times greater than that of Cl [32].

The decay of ozone by free atoms of halogens involves intermediate XO radicals (where: X= OH, NO, CI, Br, whereas XO= HO_2, HO_2, NO_2, ClO, BrO), which should be observed if chlorine is in fact responsible for the ozone destruction:
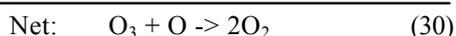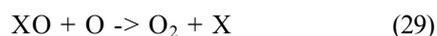
$$O_3 + X \rightarrow O_2 + XO \qquad (28)$$

$$XO + O \rightarrow O_2 + X \qquad (29)$$

$$\text{Net:} \quad O_3 + O \rightarrow 2O_2 \qquad (30)$$

Satellite measurements have confirmed the presence of this species in both the Arctic and Antarctic atmospheres during periods of severe ozone depletion [10, 51, 111, 113, 114].

The same extreme chemical stability that makes halogenated hydrocarbons non-toxic enables them to persist for years in the atmosphere and to enter the stratosphere. They reach the stratosphere through the tropopause by slow diffusion or through tropopause gaps [10, 24, 32, 58]. As mentioned earlier these substances, non-reactive under tropospheric conditions are photochemically destroyed in the stratosphere to form chlorine atoms, which leads to ozone decay by the Cl-ClO cycle [10, 70, 77, 93].

The time of a given halocarbon presence in the atmosphere is determined by its chemical composition and may range from a few months to a few hundred years [9, 10].

It has been estimated that in 1945 the mean global concentration of chlorine in the atmosphere was about lppm, which makes 25% of all chlorine of anthropogenic origin, whereas in 1995 these values increased to 3.5 and 85%, respectively [43, 76, 90, 94, 115].

Stratospheric ozone constitutes a natural shield-protecting mankind from excess ultra-violet (UV) radiation. UV radiation is believed to cause an increased risk of skin cancer and possibly also a suppression of the human immune system [10, 70].

Iodine atoms readily attack ozone, but carbon iodine bonds are so easily photolysed by sunlight that not much of CF_3J released at ground level would ever reach the stratosphere [80, 113]. Besides, researchers note the huge volume of natural iodocarbons produced by marine life

dwarfs (given off by the oceans to the stratosphere). Any potential industrial emission of CF_3J would probably amount to just 1 to 3% of natural emission [46, 47, 116].

The contribution of HFC degradation products to stratospheric ozone loss, increasing radiative forcing and pollution of aqueous environment has been recently assessed [10, 117]. All the degradation products were all found to be in trace amounts, although there is concern over the fate and toxicity of long-lived degradation products such as trifluoroacetic acid, TEA [118].

Increased intensities of ground level ultraviolet radiation caused by stratospheric ozone destruction (depletion) would have some significant adverse consequences [10, 58]. The UV-B radiation of the wavelengths in the range 280-320 nm is necessary to sustain life and its lack or deficiency is responsible for a number of conditions like avitaminosis and rickets. However, a too high dose of this radiation also leads to harmful effects [119, 123-127].

The effects of most concern to humans are the elevated occurrence of skin cancer in individuals exposed to UV-B radiation, particularly near midday [122-125]. This spectral range is harmful because it can be adsorbed in the tail of the absorption band of DNA ($\lambda_{max} \approx 260\text{-}280$ nm). It is postulated that under the influence UV-B radiation the function of DNA changes leading to improper transfer of the genetic code during cell division. This can result in uncontrolled cell division leading to skin cancer. People with light complexions lack protective melanin, which absorbs UV-B radiation and are especially susceptible to the effects of radiation. The most common type of skin cancer resulting from UV exposure is squamous cell carcinoma, which causes lesions that are readily removed and which has little tendency to spread (methastasises) [126-128]. Readily methastasised malignant melanoma caused by human exposure to UV-B radiation is often fatal. Fortunately, this form of skin cancer is relatively uncommon [122, 129]. It can also result in an increased incidence of cataracts [129]

Other negative effects of too high irradiation would be on plants including crops used for food and destruction of microscopic plants that are the basis of the world's seas (phitoplancton) [130-133]. Too high doses of UV-B irradiation inhibit the process of photosynthesis and hence slow down the growth of vegetation. However, some evidence has been provided that in periods of the most intense UV irradiation the phitoplancton in the Arctic waters is the most abundant [133].

Assessment of the harmful effect of compounds belonging to the group of ODS's is performed with the aid of a few indices. It is obviously important, for control and legislation, to estimate a chlorine loading potential (CLP) and bromine loading potential (BLP) of different natural and anthropogenic origin halocarbons to the atmosphere. These potentials are effectively increased with the tropospheric load of the relevant halogen brought about by the release of a fixed mass of the halocarbon, measured relative to the loading of the same amount of a reference compound, which is always CCl_3F (CFC-11) from the Earth surface [10]. In the terms of residence times, i, and relative molecular masses, M, CLP is given by the equation:

$$CLP = \frac{M_{CFC\text{-}11}}{M_x} \times \frac{n}{3} \times \frac{\tau_x}{\tau_{CFC\text{-}11}} \qquad (31)$$

where n is the number of chlorine atoms in a given compound X, which is compared with the three chlorine atoms in CCl_3F (CFC-11) as the reference substance.

The ozone depleting potential (ODP) is a measure of the integrated ozone destroying capacity of a particular compound relative to that of CCl_3F (CFC-11). It is related to the amount of chlorine in a given compound and its atmospheric residence time. ODP is usually defined as the total steady-state ozone destruction by a given compound, vertically integrated over the stratosphere, per mass $CFCl_3$ (CFC-11).

$$ODP = \frac{\Delta O_{3(x)}}{\Delta O_{3(CFC\text{-}11)}} \qquad (32)$$

Numerical models [134, 135] and semi-empirical approaches [10, 40, 66, 70, 77, 92, 93, 99, 134-137] have been employed to evaluate ODP's. In ODP calculation it is assumed that attack by OH radicals removes both HCFC's and HFC's, which give no long-lived products that could transport chlorine to the stratosphere [10]. Its value for some halocarbons may vary upwards or downwards in the future, as the models are refined and new kinetic data become available [10, 70, 97].

Generally, the Global Warming Potential (GWP) is the radiative forcing (increase in earthwards infra-red radiative flux) due to emission of a unit mass of a given compound, divided by the radiate forcing due to emission of the same mass of a reference compound [9, 10, 138-143]. The above factor depends on the strength with which a given species absorbs infrared radiation and the spectral location of its absorbing wavelengths as well as the residence time of species in the atmosphere [144]. Additionally, it is necessary to specify the time period over which the radiative effects of the compound (e.g. CCl_3F, CFC-11) are to be considered [10, 70]. On the basis of the residence time of a given halocarbon compound in the atmosphere, the Halocarbon Global Warming Potential (HGWP) as radiate forcing indices relative to a reference value of 1.0 for CCl_3F (CFC-11) is also used [70, 97]. This assessment assumes a pulse emission and an infinite integration time horizon (ITH), which is mathematically equivalent to a steady-state calculation, thus the HGWP can be calculated as:

$$HGWP = \frac{\int_0^{t_f} Q_A[A(t)]dt}{\int_0^{t_f} Q_R[R(t)]dt} \qquad (33)$$

where t_f is the time horizon, Q_A is the radiative forcing resulting from lkg increase of a given compound A, $[A(t)]$ is the time decay of a pulse of compound A, and Q_R and $[R(t)]$ are the quantities comparable with those characterising the reference compounds [70].

The value GWP may also be expressed relative to CO2 as a reference substance. For instance GWP of CCl_3F (CFC-11) is approximately 1300 times greater than that of CO_2 [9, 10, 70, 97, 99]. In GWP calculations it is assumed that the oxidation products are short-lived in comparison with the parent halocarbon, so that once a halocarbon molecule has reacted with OH radicals there is no further contribution to radiate forcing. Tables 1 and 2 list these values for selected halocarbons.

Moreover, an index describing the direct and indirect impact of a given cooling agent on the hothouse effect has been introduced under the name of total equivalent warming impact (TEWI). The indirect effect is related to the use of electric energy needed to supply a given refrigerator [9, 10]. The relative contribution of CFC's to man-induced GWP is estimated to be about 25% [32, 70, 143]. A relatively high contribution of halocarbons, occurring in trace amounts in the atmosphere is due to their strong absorption of infrared radiation. In extreme cases the value of radiative forcing indices is very large and may reach even 50,000 (e.g. CF_4) [9, 10, 70].

Identification and Quantification of ODS's in Atmosphere

In order to monitor the amount of ozone in the stratosphere, projects were undertaken to determine the concentration of ozone in the stratosphere [10, 70, 76]. Global release of hothouse gases has been estimated from the AGAGE (Advanced Global Atmosphere Experiment), GAGE (Global Atmosphere Gases Experiments), and ALE (Atmospheric Lifetime Experiment) [11, 35, 76, 145, 146].

The halocarbons from the group of Freons taking part in the processes of the stratospheric ozone destruction, occur in the atmosphere in concentrations from ppt to ppb [70, 73]. Particular attention is paid to monitoring of CCl_3F (CFC-11) and CCl_2F_2 (CFC-12), because these compounds are mainly responsible for observed stratospheric ozone depletion. According to recent measurements, the concentrations of these compounds in the troposphere are 0.35 ppb and 0.55 ppb, respectively [51, 73, 77, 135, 147-150].

It should be noted that a measurement of the ozone concentration in the stratosphere is difficult because of the height of the stratosphere, small concentration of ozone (order ppbs), and large natural seasonal and daily fluctuations of its concentration. The large fluctuations in the ozone concentration are related to atmospheric circulation [151]. The measurements indicate that globally averaged atmospheric concentration of CCl_3F (CFC-11) maximised at 265 ppt at the and of 1999, but there has been a significant decrease since that time, whereas the rate of decrease of Cl_2F_2 (CFC-12) content has been currently reduced to 7 ppt/ per year [9, 10, 70].

Relative to CFC's, HCFC's are difficult to detect in the background atmosphere by conventional electron-capture-gas chromatography (GC-ECD) because of their lower concentration and weaker ECD response. Gas chromatography spectroscopy (GC-MS) is a more suitable technique and usually a highly sensitive GC-MS instrument has been set up to make measurements of a variety of trace gases in the background atmosphere [9, 42, 73, 76, 152]. Results of atmospheric

measurements using GC-MS show that the concentration of $C_2H_2F_4$ (HCFC-134a)-the most frequently used replacement of CFC's- has increased rapidly in the background atmosphere [41, 43, 71, 74, 75, 77, 90, 95, 98, 103, 153].

It is now known that accumulation rates of some CFC's in the background troposphere are beginning to slow in response to reduced global emissions [10, 70, 72]. Additionally, it is to be expected that concentrations of their replacement compounds (e.g. HCFC's and HFC's) will increase rapidly over the next few years [10, 70, 99].

Legal Solutions Concerning of ODS's

In response to the hypothesis presented by M. Molina and F.S. Rowland [17, 18] and growing evidence on the ozone depletion caused by ODS's, the large-scale industrial production and use of CFC's have been rapidly phased out [61-64, 156]. The first to be replaced were the Freons used as spraying agents in cosmetic aerosols, according to the resolution banning their use and production issued by the Environmental Protection Agency (EPA) in 1979. As the next step the halocarbons used in technical aerosols, plastic foams, refrigerators and

Table 2. Effect of a number CFC replacements (HCFC's and HFC's) on the environment and their practical usage.

Chemical formula, abbreviation and coding number	Residence time[1] (Yr.)	Ozone depletion potential[2] (ODP)	Global warming potential[3] (HGWP)	Global warming potential[1] (GWP) (Time horizon)			Application[4]
				20	100	500	
$CHClF_2$ (HCFC-22)	13.3	0.04	0.37	4300	1700	520	a, b, c, d, g, i
$C_2HCl_2F_3$ (HCFC-123)	1.4	0.14	0.02	300	93	29	a, b, c
C_2H_4ClF (HCFC-124)	5.9	0.03	0.02	1500	480	150	a, c
$C_2H_3Cl_2F$ (HCFC-141b)	9.4	0.1	0.09	1800	630	200	b, c
$C_2H_3ClF_2$ (HCFC-142b)	19.5	0.05	0.36	4200	2000	630	b
$C_3HCl_2F_5$ (HCFC-225ca)	2.5	0.02		550	170	52	a
CO_2	200	0	0.00076			1.0*	a, i
CH_2F_2 (HFC-32)	6.0	0	0.094	1800	580	180	a
CH_2F_4 (HFC-134a)	14	0	0.26	3300	1300	420	a, b, c, g
C_2HF_5 (HFC-125)	36.0	0	0.58	4800	3200	1100	a
$C_2H_2F_4$ (HFC-134)	11.9	0	0.24	3100	1200	370	a
$C_2H_4F_2$ (HFC-152a)	1.5	0	0.03	460	140	44	b
$C_2H_3F_3$ (HFC-143)	3.5	0	0.04	950	290	90	c
$C_2H_3F_3$ (HFC-143a)	55	0	0.74	5200	4400	1600	a
Azeotrope – R-407C (23 wt.% HFC-32; 25 wt.% HFC-125 52 wt.% HFC-23)	–	4.54	0	–	–	–	a, g
Azeotrope – R-404A (44 wt.% HFC-125; 4 wt.% HFC-134a; 50 wt.% HFC-143a)	–	0	0.94	–	–	–	a, g
Azeotrope – R-507 (50wt.% HFC-125; 50 wt.% HFC-143a)	–	0	0.99	–	–	–	a, g
Azeotrope – R-409A (60wt.% HCFC-22; 25 wt.% HCFC-124; 15 wt.% CFC-142b)	–	0.05	0.316	–	–	–	a, g

[1] Expressed relative to CO_2 as the reference substances, IPCC (1995) [10,70].

[2] WMO (1994), [34].

[3] Relative to a reference value of 1,0 for CCl_3F [97].

[4] (a) - cooling medium; (b) - aerosol propellant; (c) - blowing agent; (d) - solvent; (e) - for fire suppression and explosive protection; (f) - cleaning agent, (g) - air conditioner; (h) - substrate for manufacture halocarbon compounds; (i) - agricultural and space fumigant, food packing, industry.
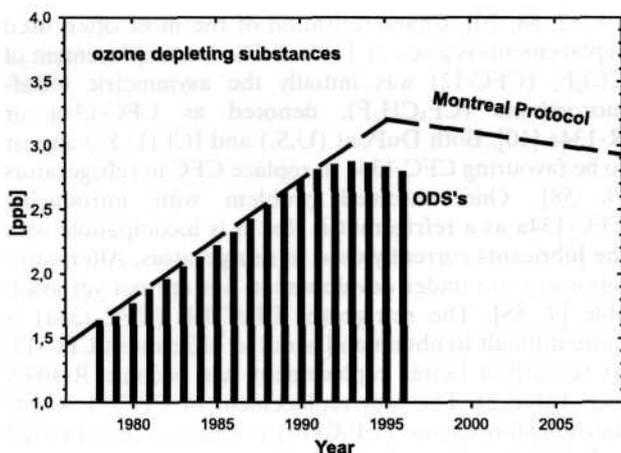
* by definition [97].

Fig. 3. Predicted changes in concentration of ozone depleting substances (ODP's) in the period 1980-2010 (Adapted from ref. 152).

air-conditioners have been gradually phased out. A few exceptions left are the halocarbons used for medical purposes like aerosol drugs, food products containing $CClF_2CF_3$ (R-115), products used by the army and some used in the electronics and aerospace industries [9, 10, 32, 58, 70].

The gravity of the stratospheric ozone depletion was recognised by the United Nations, which initiated the United Nations Environmental Programme (UNEP) aiming at the coordination of international cooperation on restriction of ODS use. In March 1985, in the "Convention for the Protection of the Ozone Layer" in Vienna, an international approach to scientific research was agreed upon [10, 70, 157, 158]. Two years later more than 35 countries signed an international agreement, the so-called Montreal Protocol on Substances that Deplete the Ozone Layer [6, 63]. This Protocol gradually restricts production of combined group of chlorinated compounds. In particular those concentrations measured by GAGE/AGAGE show that they contribute the most to global atmospheric chlorine input. The phase out of some ODS production has stimulated development of their substitutes. International consensus on the need to restrict CFC emissions emerged with the discovery that the loss of Antarctic stratosphere ozone correlated precisely with the increase in the concentration of stratospheric chlorine [9, 10, 32, 58, 70, 157].

Environmental Protection Agency (EPA) regulations imposed in accordance with the 1986 Montreal Protocol curtailed the production of ODS's (mainly CFC's) in the USA starting from 1989 [9, 10]. Major revisions to the original protocol have been introduced in Colorado Springs (1988), Helsinki (1989), London (1990), Geneva (1991), Copenhagen (1992), and Kyoto (1997) [9, 10, 58, 64, 70]. They concerned mainly the timing of the introduction of restriction of the use of such ODS's as $CCl_2=CHCl$, CCl_4, CH_3Br and hydrochlorofluorocarbons treated as temporary replacements of the compounds from the group of CFC's. As a result of the Montreal Protocol and its subsequent above-mentioned modifica-

tion, the global production of halogenocarbons has declined dramatically since 1990 [73, 159, 160-162].

The rapidly growing consequences of halocarbons released to the atmosphere have induced developed nations to introduce a ban on Freon production sooner than formerly assumed that is from 01.01.1995 and on their use - on 01.01.1996. The list of banned halocarbons from the group of ODS's included CCl_2F_2, CCl_3F, $CCl_2F\text{-}CClF_2$, $CClF_2\text{-}CClF_2$, $CClF_2\text{-}CF_3$, Halon-1211, 1301 and 2402, CCl_4, trichloroethane (CCl_3CH_3) [32, 58, 70, 160]. It has been estimated that Freons made up about 95% of all substances from this group. Moreover, the countries of the European Union have started the phase out of HCFC's, initially widely used as replacements of CFC's, which will be banned from 2010 [9, 70]. For the developed countries HCFC consumption was frozen at its contemporary level in 1996 and successive reductions are required from 2004 onwards that will lead to complete phase out by 2030 [10, 153].

According to the results of a model study, a 10-year postponement of the introduction of the Montreal Protocol resolutions, could soon cause a twofold increase of chlorine in the stratosphere and the global stratospheric ozone depletion would increase by 10%. Moreover, the regeneration of the Antarctic ozone hole would not take place in 2040, but 50-100 years later [9, 10, 58, 70, 161].

Substitutes for ODS's and Their Properties

The research for substances which could replace the most widely used, ODS's such as CCl_3F (CFC-11) and CCl_2F_2 (CFC-12) started with an investigation of the thermodynamical, physical and chemical properties of a number of aliphatic fluoroderivatives of organic compounds containing up to three carbon atoms in the molecule (C_1 - C_3), from the point of view of their potential use as cooling media [36, 140, 144, 153, 163, 164].

Amongst numerous requirements for CFC alternatives there are chemical and thermal stability and smallish or zero value of the ODP factor (which means that it
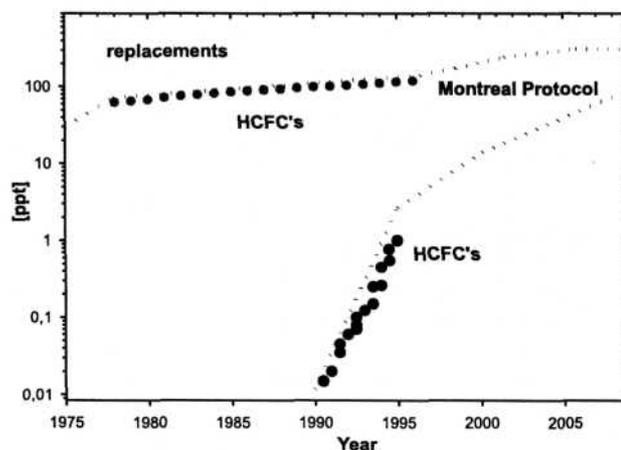

Fig. 4. Predicted changes in concentration of CFC replacements (HCFC's and HFC's) in the period 1985-2010 (Adapted from ref. 152).

should have a short tropospheric residence time). Additionally they should have an as low as possible GWP, suitable thermodynamical properties such a boiling point or heat vaporisation, relatively short residence time in the atmosphere, very low acute and subtonic inhalation toxicity, should not be toxicant or mutagenic [10, 58, 70].

Two classes of halocarbons have received particular attention as replacements for CFC's: hydrofluorochlorocarbons (HCFC's) and hydrofluorocarbons (HFC's) [166]. Like CFC's, they are volatile and insoluble in water and contain at least one-H atom per molecule. Each molecule of theses classes of compounds has an H-C bond susceptible to attack initiated by OH and OH_2, the naturally occurring radicals in the troposphere, thereby eliminating the compound with its potential to produce ozone depleting CI atoms before it reaches the stratosphere [10, 32, 58, 70, 157, 167]. The presence of hydrogen in the molecule makes most of them undergo decomposition in the lower atmosphere. Some of the chloromethane compounds are transported to the stratosphere and degraded there by reaction with hydroxyl radicals, free oxygen atoms and by photolysis [97, 99]. As a consequence they have considerably low or even zero values of ODP's. In the case of HCFC's, reduction of ozone damage (by 90-95% of the original CFC level) is observed, whereas HFC's (values ODP's = 0) does not affect chlorine loading. In addition, the above compound groups show considerably lower values of GWP than the CFC's (compare data given in Table 1 and Table 2) [9, 10, 77].

Although their performance is generally inferior to that of CFC's, various HCFC's and HFC's compounds are already in use. Of the alternative compounds mentioned above, the HCFC's in particular are seen only as transitional substances, whereas the HFC's are long-term alternatives. In the future, both groups are scheduled for phase-out by the Montreal Protocol [10, 58, 70]. Additionally, the production of CFC replacements has proven more complex and more expensive [9].

It was observed that low ozone depletion potential (ODP) correlates with short tropospheric residence time (τ), which means that the compound is destroyed in the troposphere, as mentioned above, before migrating to the stratosphere [9, 10, 58, 70]. The troposphere residence time of hydrohalocarbons depends upon a number of factors [168, 172]. Amongst them are: the number of hydrogen atoms in the molecule, which is particularly important because the C-H bond is vulnerable to attack by OH and HO_2 radicals, the number of carbon atoms, number of fluorine and chlorine atoms in the molecule [172].

In 1991 Du Pont began marketing CFC replacements for refrigeration applications under the trade name SUVA, CHF_2Cl (HCFC-22) replaced CCl_2F_2 (CFC-12) in industrial, transport and refrigeration units and its ODP value makes just 5% of that of CFC-12 [9].

The need to replace CFC's by various halogenoorganic compounds of new generation, characterised by relatively short residence time, zero or very small CLP and ODP, acceptable value of GWP (HGWP) and no harmful interaction of products of their decomposition on the natural environment has substantially stimulated development of such compounds. A large number of producers has offered a wide range of CFC replacements [9,

10, 32, 58, 70]. Characterisation of the most often used replacements is given in Table 2. The best replacement of CCl_2F_2 (CFC-12) was initially the asymmetric tetrafluoroethane (CF_3CH_2F), denoted as CFC-134a or R-134a [10]. Both DuPont (U.S.) and ICI (U.K.) appear to be favouring CFC-134a to replace CFC in refrigerators [9, 58]. One unsolved problem with introducing CFC-134a as a refrigerant is that it is incompatible with the lubricants currently used in refrigerators. Alternative lubricants are under development, but are not yet available [9, 58]. The refrigerant CF_3CH_2F (CFC-134a) is more difficult to obtain and is not as efficient as CFC-12, so recently a better replacement has become R-409A (see Table 2). The best replacement of CFC-11 is trifluorodichloroethane (CF_3CHCl_2), denoted as CFC-123 or R-123, but this replacement is less effective because its molecule contains only two chlorine atoms [99, 100].

The initially proposed replacements of CFC's did not as good thermodynamics properties as CFC's, as manifested by lower efficiency of refrigerators, greater use of electric power and louder motors. On top of that these replacements showed significant aggressive effect towards metals, seals and anticorrosion coatings. A mixture of these compounds with oil, filling the refrigerator motor at the presence of trace amounts of water led to corrosion of copper, which was commonly used in construction of small refrigerating units [10, 32, 58]. Consequently, the industry has been forced to look for and apply new construction materials [9, 32].

In stationary refrigeration units, such CFC's as CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), CFC-113 (CCl_2FCClF_2) and CFC-114 ($CClF_2CClF_2$) have been replaced by HCFC-123 ($C_2HCl_2F_3$) and HFC-134a (CF_3CH_2F) [9, 32, 58, 70]. In a number of domestic, commercial and automotive applications, HCFC-124a (C_2HClF_4), as well as HCFC-22 are effective but are not able to maintain a temperature below -9,5°C. Introducing motors with a two-stage compression system [9, 99, 159], has solved this problem.

An examination of boiling points suggests the following compounds as possible replacements for CFC-12 (CCl_2F_2) as a refrigerant: CFC-134a (CF_3CH_2F, b.p. -26°C), CFC-152a (CH_3CHF_2, b.p. -25°C), CFC-115 (CF_3CF_2Cl, b.p. -38°C), and CFC-22 (CHF_2Cl, b.p. -41°C). Of these, the fully halogenated compound CF_3CF_2Cl (CFC-115) shows an ozone depleting ability comparable to that of CCl_2F_2 CF-12. Although CH_3CHF_2 (CFC-152a) is flammable, it can be used as a "drop in" replacement for CFC-12. CFC-22 is already in service in air-conditioners and as a replacement for CFC-11 in some blown foam [9, 58, 70, 177]. From among the most often used replacements of refrigerants, HFC-32 (CH_2F_2) is favoured because of its lower GWP [9, 10]. As mentioned above, the physical and chemical properties of the replacements proposed proved more or less different from those of CFC's [9,10,58, 70]. An effective approach to this problem was the use of mixtures of halocarbon compounds characterised by greater refrigerating efficiency and a lower ODP than those of individual compounds [9, 58, 70, 173-175].

For example CFC-12 (Cl_2F_2) is also substituted with a mixture or less environmentally damaging refrigerant chlorodifluoroethane (about 15%wt. to about 40%wt.);

tetrafluoroethane and compatible lubricating oil (60-80%wt. hydrotreated light naphthalene distillate), and 10-20%wt. acrylic polymers for air-cooling systems [174].

It has been established that a fluorinated oxetane having the structure cyclo-$CF_2CH_2CF_2O$- as well as cyclo-CF_2CFHCF_2O- is an environmentally safer replacement refrigerant for CFC-12 (CCl_2F_2) [175]. Azeotropic mixture of HCFC-22 ($CHClF_2$, 48.8%wt.) and CFC-115 (C_2ClF_5, 51.2%wt.) denoted as CFC-502 could be used in low- and medium temperature refrigerating units. After the necessary changes in construction of refrigerating units, at present different ecologically safe individual hydrocarbons or their mixtures are used as cooling media. The most popular ones are propane (C_3H_8), butane (C_4H_{10}), iso-butane (($CH_3)_3CH$), pentane (C_5H_{12}), n-pen-tane (C_5H_{12}), cyclohexane (C_6H_{12}), and cyclopentane (C_5H_{10}) [9, 10, 32, 58].

In the process of production of plastic foams or insulating layered boards the use of CO_2 or pentane is recommended instead of a blowing CFC agent [9]. Successful use of water, alcohols, diluted CFC's or HFC's has been also reported for this purpose. At present the use of foam-blowing agents such as: CF_3CHCl_2 (HCFC-123), CH_3CFCl_2 (HCFC-141b), or mixtures of $C_2H_2F_4$ (HFC-134a) and $C_2H_3F_3$ (HFC-143a) is considered, instead of CCl_2F_2 (CFC-12) [58, 157]. The compound $CHClF_2$ (HCFC-22) is already being used in this application; its use is growing rapidly (about 10% per year). Either CF_3CHCl_2 (HCFC-123) or blend of $C_2HCl_2F_3$ (HCFC-123) and CH_3CFCl_2 (HCFC-141b) are possible candidates to replace CFC-11 in foam blowing applications in polyurethane and other rigid foams [157].

Both $C_2HCl_2F_3$ (HCFC-123) and CCF_3CHFCl (HCFC-124) can replace CCl_3F (CFC-11), for instance in production of the rigid foam CCl_2F_2 (CFC-12) [97, 152].

For use as cleaning agents in the electronics industry the recommended replacements of CFC's are perfluoropolyethers which, unfortunately, show too high GWP values [176]. The problem of a replacement for $C_2Cl_3F_3$ (HCFC-113) as a cleaning agent remains only partly solved. In this application, CFC's are used because of their low surface tension and low viscosity. These properties allow them to penetrate into tiny crevices, which would not be wetted by a solvent like water. $C_2H_2F_2Cl_2$ (HCFC-132b) looked to be a promising substitute, but failed toxicity testing. Du Pont is recommending a blend of $CHClF_2$ (HCFC-22) and methanol for this application; thereby reducing the ozone depleting potential by more than 95% if the same volume of each solvent were used [9, 10, 157, 178].

For use as a carrying agent in aerosols, likewise in refrigerating units, CFC-11 and CFC-12 are replaced by different hydrocarbons, including pentane, n-butane and isobutane, which are cheap and safe for the tropospheric ozone. Unfortunately, they are dangerous in certain applications and expensive to store. Moreover, when they are released into the atmosphere in the presence of sufficiently high concentrations of NO_X, they undergo physicochemical conversion leading to the appearance of photochemical smog [9, 10, 70]. Their considerable flammability is reduced by the addition of methylene chloride as a flame-suppressing agent [32, 58, 157].

Attempts have been made to use CO_2 as a carrying agent in aerosols, but this was characterised by poor atomising properties and variable pressure on use, which meant that sometimes the container could not have been emptied [157].

At present the aerosol carrying agents are some HCHC's like $CHClF_2$ (HCFC-22), CH_3CF_2Cl (HCFC-142b) or HFC's like as CHF_2CF_3) (HFC-125), CH_3CHF_2 (HFC-152a), $C_2H_2F_4$ (HFC-134a) being less damaging replacements for CCl_3F (CFC-11) and CCl_2F_2 (CFC-12). Moreover, different azeotropic mixtures of these compounds such as $CHClF_2$ (HCFC-22, 40% vol.) and CH_3CClF_2 (HCFC-142b, 60% vol.), showing similar properties as CCl_2F_2 (CFC-12) are used. The above replacements are usually mixed with up to 50% by weight of water in order to lower their flammability [9, 32].

Environmental Impact of ODS's Replacements

A matter of current significant concern is to define the environmental impact of ODS replacements which, released by man into the environment, reside in the atmosphere where they are oxidised into a wide variety of noxious and toxic degradation products [9, 10, 99, 100].

The atmospheric chemistry of commercially important ODS replacements is an important consideration in their use and is usually well established [178-181].

To define the environmental impact of ODS replacements, their residence time (i), chlorine and/or bromine loading potential (respectively CLP or BLP), ozone depleting potential (ODP), global warming potential (expressed as GWP or HGWP) must be assessed [9, 10, 70, 186]. Moreover, biodegradability of the degradation products in aqueous solutions, their noxious (e.g. mutagenic) and toxic properties, as well as their contribution to the acidity of rainwater should also be considered [9, 32, 58, 97, 157]. This assessment requires a detailed knowledge of the atmospheric chemistry of halocarbons [178-181]. Finally, concerns have been raised that the tropospheric chemistry of these ODS replacements have received insufficient study prior to the decision to go ahead with production [9, 70, 157].

The breakdown of ODS's in the troposphere, mainly commercially important HCFC's and HFC's, is initiated by OH radicals and proceeds via various free radical carbon-containing intermediates and carbonyl species [9, 10, 70]. Reaction rates with OH radicals determine the atmospheric residence times of all HCFC's and HFC's, which range from about one to 250 years (see Table 1 and 2) [93, 96, 135].

The sequences of gas phase reactions that follow from the initial attack of OH radicals on the parent halocarbon, which give rise to a wide variety of products are sufficiently rapid. In this case heterogeneous and aqueous processes play no role [9, 70]. For the variability of ODS replacements, the question is whether the rate of removal of any degradation product is slow when compared to the OH reaction limited residence time of the parent compounds [97, 99, 100]. The degradation products existing in gas phase are removed via reaction of
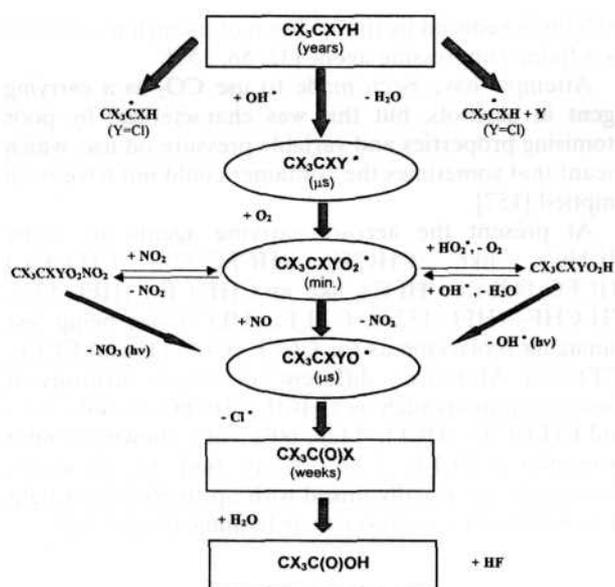
Fig. 5. A generalised scheme of the tropospheric degradation mechanism of CFC replacements (HCFC's and HFC's), where XY = F, CI, Br of H atoms, transient radical intermediates are enclosed in ellipses, products with less transitory existence are given in boxes, the order of magnitude of the residence time estimates is indicated in parenthesis (Adapted from ref. 168).

photolysis that is slow enough (days or longer) that heterogeneous deposition processing to the Earth's surface might be significant [10, 70, 100].

The removal processes include wet deposition via rainout (following uptake into tropospheric clouds), a dry deposition to the earth's surface, principally to the oceans. The rate of these processes is largely determined by the species chemistry in aqueous solutions [99].

Generally, the atmosphere concentrations of the degradation products of halogenated organic compounds are extremely small («ppb). Currently there are no known adverse environmental impacts associated with compounds at such low concentrations [70, 100, 157]. The generalised scheme for gas-phase oxidation mechanism of halogenated organic compounds, CX_3CXY (XY = F, CI, Br, or H atoms) is shown in Fig. 5.

As indicated above, the hydrohalocarbons (HFC's) contain no chlorine and have zero or near zero depletion potentials (ODP's) and are seen as long-term alternatives to CFC's [135]. Of the HCF class compounds, CF_3CFH_2 (CFC-134a), which contains no chlorine and so does not have the ozone depletion potential associated with the well-established chlorine catalytic cycle, is the top contender to replace CCl_2F_2 (CFC-12) [10, 70, 157]. The main atmospheric loss process for the above compound is reaction with OH radicals present in the troposphere, supplemented by oxidation and photolysis in the stratosphere [182-185]. Initial attack by OH radical consists of H-abstraction in the case of the above compound to yield a haloalkyl radical (CF_3CFH) that adds an O_2 molecule to form a haloalkyl peroxy radical (CF_3CFHO_2) [70]:

$$CF_3CH_2F + OH \rightarrow CF_3CFH + H_2O \qquad (34)$$

$$CF_3CFH + O_2 \rightarrow CF_3CFHO_2 \qquad (35)$$

In the next step of degradation, the peroxy radicals undergo a gas phase reaction with NO to give alkoxy radicals (CF_3CFHO):

$$CF_3CFHO_2 + NO \rightarrow CF_3CFHO + NO_2 \qquad (36)$$

The atmospheric fate of these radicals is either decomposition (37) or reaction with O_2 (38):

$$CF_3CFHO \rightarrow CF_3 + HC(O)F \qquad (37)$$

$$CF_3CFHO + O_2 \rightarrow CF_3C(O)F + HO_2 \qquad (38)$$

It has been established that HC(O)H is a major oxidation product (a yield of 70% in molar terms) of CF_3CFH_2 (HFC-134a) [99,100]. Next, HC(O)F is expected to either undergo a gas-phase reaction with OH radicals to give FCO radicals or be incorporated into (cloud, rain and sea) water where it undergoes rapid hydrolysis to HF and HCOOH, or both [10,145, 182]. Reaction of OH radicals with HC(O)F is of negligible atmospheric importance [100]. Similarly, photolysis of HC(O)F is expected to be unimportant because of the high C-F bond dissociation energy [100, 184].

The peroxy radicals derived from HCFC's and HFC's may also react with NO_2 and HO_2 to give peroxynitrates (RO_2NO_2) and hydroperoxides (ROOH) [10, 184]. Although they can be formed during degradation of CFC replacements, they are not thought to play a significant role in atmospheric chemistry and are probably rather short-lived intermediates (see Fig. 5) [97, 100].

Recently there has been some speculation regarding the possibility of an impact of HFC's on the stratosphere ozone by virtue of their degradation into CF_3O_X, and FCO_X while the FO_X radical could participate in the catalytic destruction cycles [10, 70, 182, 184]. **This fluorine-containing hydrohalocarbon species can undergo a series of reactions that results in production with CF_3 group species.** This species can act as intermediate in stratospheric ozone destruction [9, 97, 99]:

$$CF_3O + O_3 \rightarrow CF_3OO + O_2 \qquad (39)$$

$$CF_3COO + O_2 \rightarrow CF_3O + 2O_2 \qquad (40)$$

It has been estimated that the concentration of all degradation products is small, although there is concern over the fate and toxicity of such degradation products as trifluoroacetic acid, (TFA), $CF_3C(O)F$, which undergo hydrolysis [10, 70, 187].

$$CF_3C(O)F + H_2O \rightarrow CF_3C(O)OH + HF \qquad (41)$$

It should be noted that none from among the degradation products of CFC's replacements currently in use, could be considered noxious or toxic [9, 101, 86, 187].

Hydrochlorofluorocarbons (HCFC's) having shorter atmospheric residence time, have been proposed as interim (transitional substances) CFC replacement compounds. Despite their shorter lifetimes they still have the potential to transport chlorine to the stratosphere, and there is concern that their substantial use could soon add

Fig. 6. Logo of environmentally friendly CFC replacements.

significantly to the peak atmospheric chlorine burden and prolong the period of high chlorine levels. As HCFC's contribute significantly to stratospheric chlorine loading, their production has been restricted and they are planned to be completely phased out by 2020 under the current (Vienna 95) version of the Montreal Protocol. Photolysis of $CF_3C(O)Cl$ gives CF_3, CO and Cl. In addition, trace amounts (< 1%) of CH_3Cl have been reported [10, 186, 187]. There are no known HCFC's oxidation products that transport significant amounts of chlorine to the stratosphere [186]. Generally, any HCFC's present in surface or ground waters would have little tendency to portion onto biota or soil and usually represents a low potential for passive bioacumulation [117, 118, 186].

In addition, both HCFC's and CFC's strongly absorb infrared radiation and prevent its escape from the enclosure but their relatively short residence time reduce their radiation absorption activity [10, 70]. Generally they show considerably lower values of global warming potential (see Table 1 and 2) in comparison to CFC [58, 157].

Utility of Waste ODS's

Introduction of the ban on production and use of chlorofluorocarbons (CFC's) according to the terms of the Montreal Protocol, has created another important problem of dealing with an estimated amount of 2.5 mln tons of halocarbons stored at that time [9, 188, 189]. Moreover, hard to estimate amounts of these compounds are currently in the working and not-working old types of refrigerators [157, 189]. An inventory of the ODS's still in use shows that about 90% of the banked ODS's are Cl_3F (CFC-11) and CCl_2F_2 (CFC-12). Additionally, as mentioned above, the compounds belonging to the class of HCFC's (hydrochlorofluorocarbons), which as short-term replacement are gradually being replaced mainly by HFC's (hydrofluorocarbons) being the long-term replacement [9, 10, 189].

It is important to prevent the ODS's that are still in use from being emitted into the atmosphere. Concerns for the storage of large quantities of waste ODS's and the need for development of a technique of their destruction should receive more attention Thus, recovery and subsequent destruction of these compounds still in use is a logical next step to control future emissions [9, 10, 32, 58, 70, 157]. Long-term storage of gas waste ODS-impressed cylinders is not a solution [9, 10, 178, 190-193]. Recycling of used CFC refrigerants was introduced in 1986-1987. In many countries networks have been organised to recover, recycle, and reclaim the used ODS's

[9, 58, 157]. After collection by dealers, the essential processing steps are mechanical purification and distillation. Although the recycling has led to a limitation of the size of production of ODS's, this solution is not satisfactory as it leads to a delay of conversion or destruction of these compounds. Successful recycling depends on the will of the user and organisation of the recovery and recycling network. Available technology permits the CFC's recovery with a yield of about 98% and the recovery of CFC's from the foam polymers used in refrigerants as a thermoinsulting material with a yield of 94%. Prior to reuse, the compounds have to be purified in order to remove particles of metal, acids, lubricants and condensed vapours and gases [9, 58, 157]. The long-term storage of waste ODS's that are contaminated with oil mixture and acids is a problem. Mixed ODS's that cannot be recycled or reclaimed will also become waste. Refrigerant mixtures that cannot be separated by distillation are subjected to secondary recycling in the process developed by Hoechst [9, 188]. The refrigerants are cracked in a thermal reactor (Hoechst Reactor Cracking Process) and HF and HCl are recovered from outlet gas [192]. It is obvious that recycling of ODS's will stop when new technologies and equipment are developed to use alternative substances.

Transformation or/and destruction of ODS's is one of the world's goals for virtual elimination of discharges of persistent noxious and toxic substances into the environment.

A number of ODS techniques have been proposed, including incineration [194-196], catalytic oxidation [197-199], catalytic hydrolysis [200], hydrogenolysis [188, 201-211], pyrolysis [192, 212, 213], plasma destruction [214, 215], mineralisation [216], biodegradation [217, 218], electrochemical reduction and oxidation [219], as well as high energy radiation [220-222]. However, conversion of CFC's into useful and environmentally friendly chemicals is a better option then the above-mentioned destruction technologies with their associated consumption of energy and waste of principle valuable chemicals, e.g. difluoromethane (HFC-32).

From these techniques the most important and commercially available are: incineration, the "Reactor Cracking Process" of Hoechst and catalytic hydrogenolysis [9, 166, 188].

The use of halons amount can also be reduced by minimizing waste and by improving fire protection.

The development of the catalyst and processes for the conversion of CCl_2F_2 into CH_2F_2 would make it possible to convert the majority of the CFC's in use (CCl_3F and CCl_2F_2) into valuable, ozone friendly products (CH_2F_2) [9, 102, 157, 167, 223].

Summary

As follows from the above-discussed evidence, the release of compounds containing halogen atoms (X = Cl, F Br, I) into the atmosphere enhances the global threat to the natural environment caused by destruction of the stratospheric ozone and intensification of the hothouse effect.

Global Atmospheric Gases Experiment Advanced

(GAGE) (GAGE/AGAGE) observations of halocarbons indicate that global concentrations of CFC's and HCFC's reached a maximum and currently decayed slightly, the concentration of their replacements has slowly increased, e.g. HCFC's (see Fig. 3 and 4) [71, 72, 74-76, 71, 72, 226-228]. The knowledge of the concentration changes of tropospheric chlorine is important for future levels of stratospheric ozone destruction. Monitoring of halocarbon concentration is also significant regarding the effect of the global warming potential [9, 70].

Until the environment-friendly replacements are found, halon reserves or less efficient alternatives (HCFC's and HFC's), unfortunately, must be used.

Recently, much attention has been paid to ammonia, a compound well known and used for over 100 years in cooling technology, denoted as R-717. It is potentially a compound of common future use. Contrary to the currently used CFC replacements (i.e. the compounds from the groups HFC's and HFC's or their azeotropic mixtures), ammonia are characterised by better thermodynamical parameters. For example, it shows almost twice greater efficiency of cooling than e.g. R-404a or R-22. It is a naturally occurring substance undergoing in the atmosphere a conversion to nitrogen and not inducing a decay of stratospheric ozone. It is easy to localise its leak because of a characteristic smell, which is a natural alarm system. It is also much cheaper than other CFC replacements.

The questions related to its corrosive properties have been much reduced thanks to the new materials for construction of refrigerators. The only still unsolved problem related to the use of ammonia is its relatively high potential for hothouse effect generation [9, 10, 70].

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