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An Assessment of Eco-friendly Gases for Electrical Insulation to Replace the Most Potent Industrial Greenhouse Gas SF_6

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Abstract

Gases for electrical insulation are essential for the operation of electric power equipment. This review gives a brief history of gaseous insulation that involved the emergence of the most potent industrial greenhouse gas known today, namely sulfur hexafluoride. SF_6 opened up the way to space-saving equipment for the transmission and distribution of electrical energy. Its ever-rising usage in the electrical grid also played a decisive role in the continuous increase of atmospheric SF_6 abundance over the last decades. This Review broadly covers the environmental concerns related to SF_6 emissions and assesses the last generation of eco-friendly replacement gases. They offer great potential to reduce greenhouse gas emissions from electrical equipment but at the same time involve technical trade-offs. The rumours of one or the other being superior seem premature, in particular due to the lack of dielectric, environmental and chemical information for these relatively novel compounds and their dissociation products during operation.

1 Introduction

Today's transmission and distribution of electric power in densely populated areas is significantly and increasingly dependant upon space-saving electric power components. Equipment manufacturers address the challenges of both the electric and thermal stress onto the compact components mainly with sophisticated equipment design and special materials including solid, liquid, gaseous and vacuum insulation.[1] In principle, all types of electrical insulation media can achieve elevated voltage and current ratings of equipment, along with compound-specific trade-offs such as the equipment weight, outer dimensions, durability, flexibility, safety, maintenance effort, production costs, or environmental issues. The choice of the actual insulation medium is additionally influenced by historical developments, political instruments and social factors.

The applications of gaseous insulation - often containing components other than air and above atmospheric pressure - aim to avoid discharges in compact apparatuses.[2–10] The use of gases as electrical insulator in medium and high voltage equipment has many advantages over liquid and solid insulation such as relatively low weight, low costs, simple manufacturing process of equipment, full recovery of insulation performance after partial discharge and the ability of insulating moving parts. In transformers, bushings and gas insulated transmission lines (GIL) the insulation gas solely serves as an electrical insulator, whereas in high voltage circuit breakers of air-insulated switchgear or substations (AIS) and gas insulated switchgear (GIS) the gas must comply with both electrical insulation and - if no vacuum interrupters are used - current interruption. GIS can be installed in densely populated areas and therefore support network topologies with lower power losses. As shown in several life cycle assessment studies, this can potentially lead to an overall reduced CO_2 footprint in comparison to AIS.[11,12]

In particular for high voltage applications, SF_6 has been the electrical industry's favored insulation and arc quenching medium for half a century.[13,14] For very cold regions, SF_6 must be mixed with a more volatile carrier gas such as N_2 or tetrafluoromethane CF_4 to avoid

liquefaction.[15] GILs, typically filled with 20% of SF_6 in nitrogen, can be an alternative to cables, if the installation of overhead transmission lines is challenging due to space limitations or lack of public acceptance.[7,16,17] In radar systems of military reconnaissance planes, including the Airborne Warning And Control System (AWACS), SF_6 operates as an electrical insulating medium in the hollow conductors of the antenna.[18] In particle accelerators, e.g. in the waveguide of linear accelerators for medical radiotherapy, SF_6 is used to prevent sparking and provide cooling for the dielectric load.[8] In Resistive Place Chambers (RPC), which are e.g. used as particle detectors in all large experiments of the Large Hadron Collider (LHC),[9] SF_6 is used very diluted ($\leq 1\%$) due to its desired quenching effect on streamer discharges.[10]

After being classified as one of the greenhouse gases in the Kyoto protocol, regulative measures for the SF_6 usage have been implemented in various industries. The electrical industry as the largest contributor to reported SF_6 emissions[19–24] has been excluded from any SF_6 ban so far. In the short term, emissions have been reduced by voluntary commitments of the electrical industry by minimizing the use and leakage rates from electrical equipment, improving gas handling and recycling concepts.[25,26] In the long term, gradually reducing the quantities of greenhouse gases that can be placed on the market has been identified for other industries as the most effective way of reducing emissions.[27] For a phase-out of SF_6 from electrical power equipment, a replacement gas with acceptable environmental impact would be beneficial.

2 Brief history of gaseous insulation

In the very early beginnings of gaseous dielectrics, the focus has been on compounds other than SF_6. In pioneering experiments that he reported to the Royal academy of Sciences of the Austro-Hungarian Empire in 1889, K. Natterer first noticed the high electric strength of some substances, such as CCl_4, $CHCl_3$ or $SiCl_4$, relative to that of air or nitrogen.[28] He applied high-voltage pulses generated by an induction coil to the vapor of more than 50 different

substances. There is no evidence that Natterer's discoveries aimed on technological advances by potentially using gases of high electric strength in electrical equipment. Only decades later, the usefulness of these compounds as electrical insulation media were recognized in the United States. In the early 1930s, R.G. Herb noticed that the maximum obtainable voltage of a pressurized-air insulated Van de Graaff generator is significantly increased by using CCl_4.[29] Moreover, he found together with M.T. Rodine that when adding CCl_4 to air the electric strength rises more rapidly in the region of low CCl_4-concentration than at high concentrations. This effect, known as *synergism*, is generally a quality criteria also for the last generation of insulation gases.

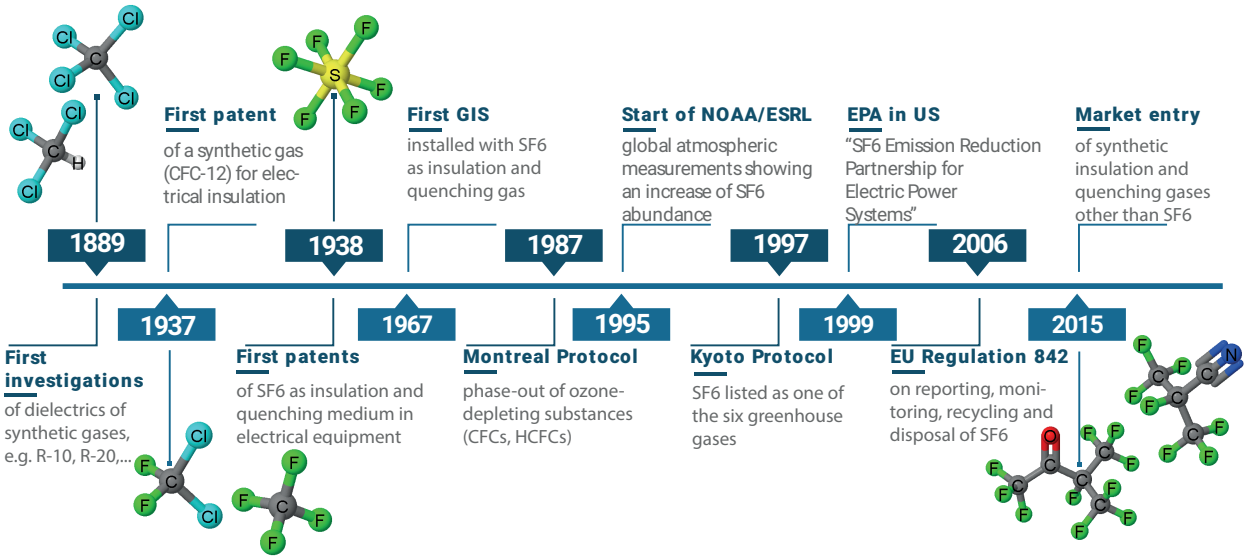

Figure 1: Timeline regarding substances used for electrical insulation and crucial events concerning the use and the development of insulation gases.

In the same years, E. E. Charlton and F. S. Cooper found that halocarbons generally have higher electric strength than nitrogen,[2] and in particular proposed CCl_2F_2, also known as the refrigerant CFC-12, which is non-toxic, non-corrosive and chemically stable, for the use in high voltage transformers.[3] Fifty years later the phase-out of CFC-12 was decided within the Montreal Protocol due its role in ozone depletion. Furthermore, E. E. Charlton and F. S. Cooper investigated tetrafluoromethane CF_4, which is used until today in admixture with SF_6 in polar regions.

Besides highly chlorinated compounds, K. Natterer run into another gas of high electric strength containing the cyano (-CN) functional group, namely cyanogen (C_2N_2). The electric strength of this toxic inorganic compound, was determined with more accurate experimental methods to be around 2 times the one of nitrogen.[30] With some detours over straight-chain nitriles, such as CF_3CN, C_2F_5CN or C_3F_7CN,[6,31] that have toxicities higher than would be considered acceptable for insulation purposes, the (-CN) group recently reappeared in the branched nitrile $(CF_3)_2CFCN$ (or C_4F_7N), which is a last generation insulation gas of "acceptable toxicity".[32]

Shortly after being patented as gaseous fire extinguishing substance,[33] SF_6 was for the first time patented as an insulation medium by F. S. Cooper from the American producer General Electric[34] and as an arc quenching media by V. Grosse from the German producer AEG in 1938.[35] In his patent, V. Grosse already explained that its exceptional ability of quenching arcs is due to its high heat capacity and its dissociation during arcing and the subsequent recombination of the dissociation products.

In the 1930-40s dielectric properties of various potential insulation gases including SF_6 were experimentally determined.[2,3,29,36–39] It has been speculated upon the reasons for their relatively high electric strength that crucial factors are the large molecular weight, complexity and electron affinity, since they affect the interaction between free electrons and gas molecules. More elementary studies by F. M. Penning pointed out that the development of an electron avalanche is suppressed in gases of small first Townsend coefficient (nowadays known as effective ionization coefficient), which quantifies the electron multiplication in an electron avalanche by electron impact.[40] The picture of an electron avalanche as the source of the electric breakdown led H. Raether, J. M. Meek and L. B. Loeb to identify the first Townsend coefficient as the principal controlling factor in the breakdown voltage of a gap in given geometrical conditions and particularly at high pressures.[41–43] Small Townsend coefficients should consequently result in relatively high breakdown voltages. Exactly this was experimentally observed in SF_6 and other halogenated gases by B. Hochberg and E. Sand-

berg.[39] They further speculated that the small Townsend coefficient for halogenated gases resulted from the inefficient production of new electrons by impact ionization or from the higher electron energy losses in inelastic non-ionizing collisions with these rather complex molecules in comparison to oxygen or nitrogen. However, other complex molecules such as hydrocarbons did not show such a high electric strength. It was not until the 1950s, supported by mass spectrometer studies,[44,45] that the halogenated molecules' ability to effectively attach free electrons has become generally recognized to be responsible for the small first Townsend coefficient and the high electric strength of halogenated gases.[46,47] It was found that negative ions are created by the two-body process of dissociative attachment such as in CCl_4,[47] SF_6[47,48] and Trifluoroiodomethane CF_3I,[30] or by the three-body process of electron attachment where a dissociation process does not occur.[48,49]

From all halogenated substances, SF_6 turned out to be the best insulation gas in terms of stability, toxicity and liquefaction temperature, although other gases revealed higher electric strengths. The industrial production of SF_6 began in the 1950s with the first commercial SF_6 circuit breakers in the United States.[20] With the market introduction of GIS in the late 1960s in Europe, companies began the move away from oil towards SF_6, and the use of SF_6 as an arc quenching and insulation medium became widespread. On the transmission level, AIS were more and more replaced by GIS. Also on the distribution level AIS have been gradually replaced by GIS, the latter being more compact, reliable and safe in operation.

In the late 1970s/early 1980s, a search for alternative gases superior to SF_6 was initiated by Westinghouse Electric Corporation,[4] General Electric[6] and Oak Ridge National Laboratory.[5] The goal of the systematic investigation was to find a gas or gas mixture that has lower production costs, lower boiling point, and an electric strength that is higher and less sensitive to surface roughness and particles. Ozone-depleting substances such as CFC-12 as well as strong greenhouse gases such as perfluorocarbons (PFCs)[50] or CF_3SF_5 with a GWP (100-year) of 17400[24] were considered. Even though compounds were not selected with respect to their environmental impact, no gas that would result in technical and economic

advantages to the electrical industry could be identified.

In the late 1980s, environmental concerns related to anthropogenic emissions of halogenated compounds arose for the first time with the discovery of large losses of total ozone in the Antarctic ozone layer.[51] This led to the formation of the Montreal Protocol which resulted in the phase-out of chlorofluorocarbons (CFCs) and later hydrochlorofluorocarbons (HCFCs), which were used at the time as refrigerants, blowing agents and aerosols. The healing of the Antarctic ozone layer due to emission reductions of CFCs has meanwhile been proven.[52] The electrical industry was not affected by political measures or bans since SF_6 is not ozone-depleting. However, the classification of SF_6 as a greenhouse gas by the United Nations Framework Convention on Climate Change in 1992 and later by the Kyoto Protocol affected also the use of SF_6. As a consequence, policy makers and environmental agencies increasingly expressed concern about the climate impact of this extremely strong greenhouse gas. This initiated new attempts to replace SF_6 by alternatives with lower global warming potential.[53,54] In 1999, the United states environmental protection agency (EPA) initiated the "SF_6 Emission Reduction Partnership for Electric Power Systems" based on a voluntary partnership with the members of the U.S. electric power industry[26] and in 2009 classified SF_6 as "a threat to the health and welfare of current and future generations due to their effects on world climate" under section 202(a) of the Clean Air Act. In 2006 the EU Regulation No. 842/2006[55] was put into force by the European Parliament and the Council, replaced in 2014 by the EU Regulation No. 517/2014.[27] This regulation makes, among other things, provision to the European commission for an assessment of SF_6 replacements in new medium voltage secondary switchgear no later than 2020 and for other applications, including high voltage equipment, no later than 2022. In 2012, the Australian government applied an equivalent carbon tax on synthetic greenhouse gases including SF_6, which was repealed in 2014.[56]

In parallel to the increasing number of regulative measures, the resumption of research activities in SF_6 replacements resulted in the development of equipment filled with the atmospheric gases CO_2, N_2 and O_2[57,58] and mixtures of these gases with synthetic compounds

of significantly lower GWP than SF_6.[59–62] The overall performance of some of these alternatives come very close to the one of SF_6, although some trade-offs such as larger equipment size, higher filling pressures, slightly thicker walls of vessels or higher minimum operating temperatures are necessary.[63]

3 Climate impact of SF_6

Anthropogenic emissions of extremely long-lived and potent greenhouse gases might irreversibly change the climate on millennium timescales.[24,64] SF_6 has a very pronounced absorption band exactly at an infrared frequency where the earth's atmosphere is relatively transparent and therefore absorbs upward radiance 42000 times more effectively than CO_2 (compare radiative efficiencies in table 2). The IPCC currently reports an atmospheric lifetime of 3200 years and a GWP value of 23500 (100 years time horizon),[24] assuming photolysis of SF_6 by UV radiation as the main removal process. However, the most recent estimate of the atmospheric lifetime of SF_6 is 850 years (uncertainty range from 850-1400 years), with electron attachment being identified as the main removal process.[65] This reduced lifetime yields a GWP value of ~ 22500.

3.1 SF_6 abundance and climate response

Pre-industrial atmospheric SF_6 abundance has been less than 6.4 ppq (parts per quadrillion) as known from measurements of air trapped in Antarctic firn.[66] Today, SF_6 abundance is three orders of magnitude higher. This is known with high precision due to sampling programs that measure background atmospheric concentrations of SF_6 and other trace species using gas chromatographs, as shown in figure 2(a). The NOAA/ESRL program starting 1995[67] and the AGAGE program starting 2001[68] show that SF_6 concentrations globally increase and are nearly equal over the northern and southern hemisphere.

The equilibrium global mean surface temperature response $\Delta T = \lambda \cdot RF$ due to the

radiative forcing of SF_6 ($RF = RE \cdot [SF_6]$) is shown in 2(b), with the equilibrium climate sensitivity parameter being $\lambda = (1.5\,°C - 4.5\,°C)/3.7\ Wm^{-2}$.[24] The transient temperature rise might be - in comparison to the equilibrium temperature response - time-delayed by the heat capacity of the earth climate system and the timescale for heat transport into the deep ocean.[24,69] The current equilibrium warming due to SF_6 is 0.004 °C, with a clear tendency to increase.

Emissions scenarios by 2100 have been given in the Fifth Assessment Report of the IPCC (table AII 4.4[24]). Table 1 summarizes the reported projections to 2030, 2050 and 2100 for SF_6 emissions and abundance[24] as well as the corresponding ΔT. The worst case emissions scenario in this report (A2) assumes a continuously increasing population and regionally oriented economic development, and would yield $\Delta T \sim 0.03\,°C$ due to SF_6 in 2100. In view of the Paris Agreement within the UNFCCC of keeping the increase in global average temperature to well below 2 °C, under the A2 scenario a SF_6 emission cut today could contribute 1.5% of this goal.

Table 1: SF_6 emissions, abundance and equilibrium temperature rise due to SF_6 radiative forcing for the best (RCP2.6) and worst (A2) emissions scenario.

year	emissions (Gg/yr)	abundance (ppt)	ΔT m(°C)
2030	2-12	10-15	5-7
2050	1-16	11-26	5-12
2100	<1-25	11-65	5-30

3.2 SF_6 emissions: top-down versus bottom-up estimates

The accumulation of SF_6 in the troposphere is a direct measure of its global emissions, since SF_6 is a long-lived compound and uniformly distributed throughout the troposphere with mixing times in the order of a year.[23,71] Emissions obtained from atmospheric measurements are referred to as *top-down* emissions. Top-down methods for calculating the SF_6 emissions on regional scales, e.g. on the country level, require precise atmospheric measurements and

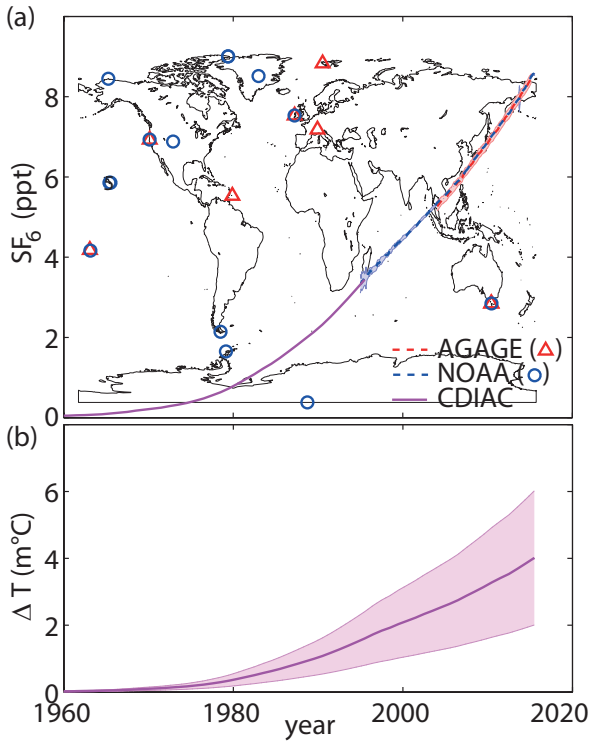

Figure 2: **(a)** Mean global atmospheric SF_6 abundance in parts-per-trillion (ppt) derived from indicated locations of the measurement stations from the NOAA/ESRL Global Monitoring Division[67] and the AGAGE.[68] The CDIAC data[70] is based on the the NOAA/ESRL data from 1995 and estimates of Maiss et al.[20] for the period 1953-1994. The shading represents 1-sigma uncertainties. **(b)** Equilibrium warming due to SF_6 radiative forcing using the SF_6 concentrations from CDIAC and the climate sensitivity parameters 1.5 °C/3.7 Wm^{-2} (lower bound) and 4.5 °C/3.7 Wm^{-2} (upper bound).[24]

reliable atmospheric transport models.[22,71–75] In this case, it is possible to geographically resolve the sites of emission sources, such as manufacturing sites of SF_6-filled equipment or densely populated regions,[71–74] as has been shown e.g. for New York City.[72]

Bottom-up emission estimates are either based on reported emissions, e.g. by Annex I countries to the United Nations Framework Convention on Climate Change (UNFCCC), or based on inventories such as the Emissions Database for Global Atmospheric Research (EDGAR),[76] where emissions are calculated based on production, sales and usage information. At this date, detailed documentation describing the methods of obtaining the SF_6 data in EDGARv4.2[76] and its uncertainties are not published. The extent to which top-down estimates are used for EDGAR is not entirely clear, even though EDGAR is supposed to be independent from published top-down data. For EDGARv4.0 emission data, an uncertainty of about 10% for the period 1970-1995, increasing to 15% at 2005 has been estimated by Rigby et al.[22]

Top-down methods provide a way to validate bottom-up emissions estimates. A comprehensive picture of global and regional SF_6 emissions should therefore consist of both estimation methods.[77] Figure 3(a) shows that top-down global emissions are in agreement with the bottom-up estimates from EDGARv4.2 but significantly exceed reported emissions to UNFCCC. In addition, top-down global emissions have increased over the last decades, whereas reported emissions have decreased. Whereas in the US and the EU total reported emission have decreased over the last years (as shown in figure 3(b)), there has been a strong emission increase in China after the year 2000, mainly due to the increasing number of SF_6-filled distribution and transmission equipment for China's growing energy demand.[78] However, the discrepancy cannot be explained solely by the increasing emissions from non-reporting parties according to various studies and higher emissions than reported by countries are suggested.[22,23,79] For example, Ottinger et al.[80] found that SF_6 emissions from the US in the year 2012, reported under EPA's greenhouse gas reporting program, consumption based on reports from users accounted for only 59% of the consumption based on reports from

suppliers.

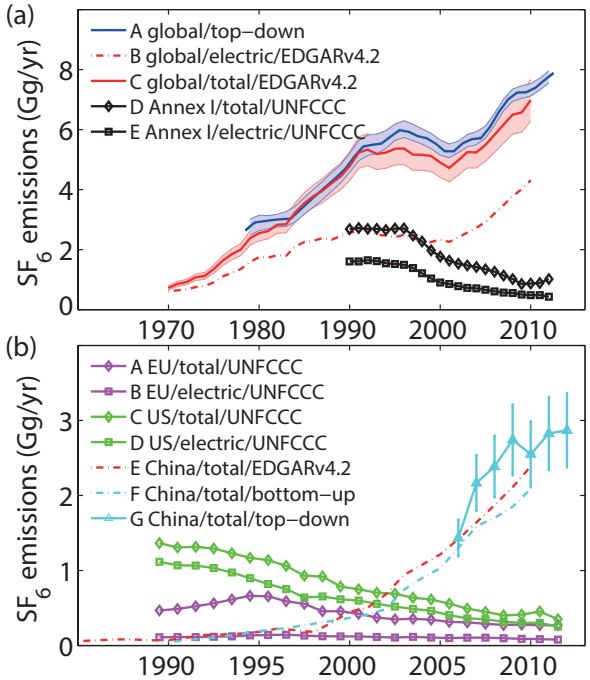

Figure 3: Comparison of annual SF_6 emissions from top-down and bottom-up estimates. Shading and error bars, representing 1-sigma uncertainties. **(a)** Global emissions. A: top-down.[81] B and C: EDGARv4.2 for electrical industry and all sectors.[76] D and E: total reported for all categories and for electrical equipment (2.F.8) from Annex I parties. **(b)** EU, US and China. A-D: total reported from all sectors as well as for electrical equipment (2.F.8) from EU and US. E-G: China total emissions from EDGARv4.2,[76] bottom-up[78] and top-down estimates.[75]

At this date, reliable top-down data for longer time spans are missing in most national greenhouse gas inventories, except for the United Kingdom[82] and Switzerland.[83] Both countries aim to verify their SF_6 inventories with continuous measurements at Mace Head (in Ireland) and the high-Alpine site of Jungfraujoch (in Switzerland), respectively. Reported SF_6 emissions from these countries show relatively good agreement (within the uncertainties) to the top-down emissions as shown in figure 4.

3.3 SF_6 emissions from the electrical industry

Since the 1970s to date, the electrical industry is globally the main consumer of SF_6 and the largest contributor to reported SF_6 emissions of all industries[19–24] and is in the order

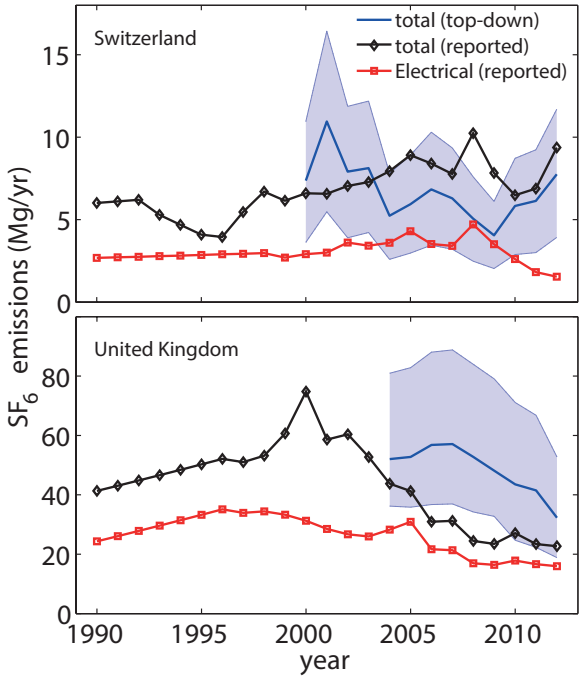

Figure 4: SF_6 emissions reported to UNFCCC and estimates for Switzerland from measurements at Jungfraujoch[83] and for the United Kingdom from measurements at Mace Head (Ireland).[82] Shading and error bars, representing 1-sigma uncertainties.

magnitude of $\sim 10^3$ tons/year, see also figure 3(a). The total mass of banked SF_6 worldwide in electrical equipment is increasing and is in the order of magnitude of $\sim 10^5$ tons.[84,85] The IPCC reported that "approximately 80% of SF_6 sales go to power utilities and electrical equipment manufacturers".[86] Reported global SF_6 emissions from the electrical industry decreased in the recorded period 1990-2012 due to initiated emissions-reducing measures. However, since other industries also implemented emissions-reducing measures,[27] the relative contribution of the electrical industry to SF_6 emissions did not show a clear tendency to decrease and the total emissions from Annex I parties vary between $\sim 40-60\%$ in reporting countries within the recorded period.

On the regional level, the relative contribution to SF_6 emissions from the electrical industry can vary strongly between countries. In the period 1990-2012, SF_6 emissions reported from the electrical equipment sector are $\sim 20-30\%$ in the EU and $\sim 70-80\%$ in the US of total SF_6 emissions, see figure 3(b). In those countries that try to verify their national SF_6

inventories with top-down emissions (see figure 4), the relative contribution of the reported emissions from the electrical industry to total reported SF_6 emissions was $\sim 16\%$ (Switzerland) and $\sim 70\%$ (UK) at the last year of the inventory 2012. In China, the electrical equipment sector is estimated to be responsible for $\sim 70\%$ of total SF_6 emissions.[78]

Most emissions from AWACS planes occur during the pressure-balancing process. When the plane ascends, SF_6 is directly released to the atmosphere to maintain the desired pressure difference between the system and the outside air. When the plane descends, SF_6 is filled into the system from an SF_6 container on board. Emissions from system leakage can also occur during other phases of flight or during time on the ground. The IPCC provides an annual emission estimate of 740($\pm$100) kg SF_6 per plane.[18] With the number of planes worldwide in the order of hundred, this would yield annual SF_6 emissions in the order of hundred(s) tonnes. In the United Kingdom, SF_6 emissions from AWACS, particle accelerators and tracer testing was estimated to 15% of the total emissions.[80]

In electric power equipment a fraction of the banked SF_6 is emitted until the end-of-life up to ~ 40 years. The actual amount of emitted SF_6 strongly depends on emission-reducing measures taken during production and testing of equipment, installation, use phase, disposal at the end-of-file and recycling and destruction of the SF_6 gas. Reducing SF_6 emissions during the equipment's life cycle has been the strategy adopted by many established manufacturers after the climate impact of SF_6 became relevant. Therefore, emissions per GIS unit have decreased in the recent past (see details in Supporting Information S1-S3). Countries where the SF_6 gas-collection infrastructure is well-developed, emissions at the disposal phase have been significantly reduced. Currently, in Europe reclaiming and reuse of SF_6 from electrical equipment is widely implemented,[25,87] whereas there is almost no recovery of SF_6 in e.g. China.[78] Strictly speaking, GIS are not banking SF_6 but rather delaying the emission of SF_6: an annual emission factor of e.g. $\gamma \sim 1\%$ from equipment corresponds to the entire release of the banked SF_6 quantity within $\gamma^{-1} \sim 100$ years ($\gg 850$ years lifetime).

4 Last generation of insulation gases

Compounds that are already widely-used as gaseous insulation in electrical equipment are SF_6, CF_4, CO_2, N_2, O_2. CO_2 is e.g. used as an insulation and quenching gas in circuit breakers.[63] Several novel gases for electrical insulation have been introduced within the last years, driven by the objective of replacing SF_6 by a low-GWP compound. They put focus on atmospheric gases at higher pressure,[57,58] on fluorinated gases of extremely low GWP enabling compact equipment[59,60] (e.g. $C_5F_{10}O$), or on fluorinated gases enabling compact equipment and low operating temperatures[61] (C_4F_7N). The alternative compounds - and in particular their mixtures - have GWPs much lower than SF_6 (see table 2) and zero or close to zero ODPs. Some compounds are already used in products and pilot installations (dry air, $C_5F_{10}O$, C_4F_7N) and several other compounds have been proposed (HFCs, CF_3I, $C_6F_{12}O$). Since all of the synthetic compounds are less volatile than SF_6 (see Supporting Information S4), they are admixed to atmospheric gases. It is incomplete to compare insulation gases as given in table 2. The comparison is more challenging for mixtures due to the additional degree of freedom of mixing two or more compounds in arbitrary mole fractions. A complete comparison of different insulation gases should include information on the synergism of the electric strength as well as the dew point of the mixture, which defines the minimum operating temperature of equipment.[88]

Hydrofluorocarbons HFCs in particular replace PFCs as refrigerants. The main atmospheric removal mechanism for the HFCs is through reaction with hydroxyl radicals.[89] The atmospheric lifetime of HFCs depends on their reactivity towards hydroxyl radicals and ranges from 2.1 days for CH_2 =CHF to 242 years for $CF_2CH_2CF_3$.[24] For unsaturated HFCs such as fluorinated alkenes (olefins), alkynes and aromatics this reaction is much more efficient than for saturated HFCs leading to much shorter lifetimes.[89] A subclass of HFCs, the hydrofluoroolefins HFOs, were proposed as refrigerants to replace the HFC-134a and are also considered as insulation gases, in particular HFO-1234ze(E).[90–92] Although HFO-1234yf has a higher vapor pressure than HFO-1234ze(E) it is not considered for electrical insulation due

to its relatively high flammability.[93] The class of fluorinated oxiranes have been investigated and generally have high electric strength.[94,95] However, their GWP is in general similar to PFCs.

CF_3I was introduced as replacement for the ozone-depleting substance CF_3Br as gaseous fire suppression agent and as inert gas in aircraft fuel tanks. It is also used for plasma etching in semiconductor manufacturing. The ODP of CF_3I is in the range of 0.006-0.017,[96–98] and in Europe it is subject to reporting under the EU Regulation No. 1005/2009.[99] CF_3I was found to be a cardiac sensitizer at concentration in air above 0.4%,[100] and objections were raised to its use. Its electric strength is slightly higher and its vapor pressure significantly lower than of SF_6.[101,102] Therefore, CF_3I is mixed e.g. with CO_2 or N_2.[101,103] CF_3I undergoes strong photolysis due to its weak C-I bond that is broken by UV radiation within days.[96] CF_3I also decomposes in electrical equipment under electrical arc and discharges, leading to iodine deposition and as a consequence reduced insulation performance.[104,105] In arcing chambers, where the iodine deposition is particularly strong, iodine might be removed from the gas flow during switching operations by adsorption materials, such as organic liquids, organic solids or carbon filters.[103,106]

The branched nitrile, C_4F_7N (2,3,3,3-tetrafluoro-2-(trifluoromethyl)-2-propanenitrile, known by the trade name Novec-4710) has been introduced as admixture to CO_2 with mole fractions from $\sim 4 - 10\%$ with lower temperature limits from $-5\,°C$- for the 10% mixture- down to $-30\,°C$ for the 4% mixture.[61,107,108] CO_2 is used since it shows good synergism with C_4F_7N and since CO_2 has better arc quenching capabilities than N_2. The materials compatibility of C_4F_7N is different from that observed with SF_6.[109] A pilot installation exists of 420 kV gas insulated busbars in a substation in UK down to $-25\,°C$. Furthermore, 145 kV gas insulated substations are planned in several European countries, and several 245 kV current transformers down to $-30\,°C$ are planned in Germany.[61]

The ketones $C_5F_{10}O$ (1,1,1,3,4,4,4-heptafluoro-3-(trifluoromethyl)-2-butanone, known by the trade name Novec-5110) and $C_6F_{12}O$ (1,1,1,2,2,4,5,5,5-Nonafluoro-4-(trifluoromethyl)-3-

pentanone, known by the trade names Novec-612, Novec-649 and Novec-1230) have been proposed as electrical insulation gases in binary mixtures with technical air or CO_2.[110–112] The presence of O_2 in the mixture might reduce soot deposits and harmful by-products like CO.[113] $C_6F_{12}O$ is also used as fire protection fluid, as an alternative to SF_6 in cover gases for molten magnesium and as the working fluid in Organic Rankine Cycle applications due to its short lifetime and zero ODP.[114] Both $C_5F_{10}O$ and $C_6F_{12}O$ degenerate via rupture of the bond between the (C=O) functional group and the α carbons by UV radiation.[114–116] In order to reach lower minimum temperatures, the $C_5F_{10}O$ has been chosen in preference to $C_6F_{12}O$. Similar to C_4F_7N, the materials compatibility of $C_5F_{10}O$ is different from that observed with SF_6.[117] At this date, medium voltage GIS with mixtures of $\sim 7-14\%$ $C_5F_{10}O$ in air are commercially available with minimum operating temperatures down to $-25\,^{\circ}$C. In high voltage GIS, $C_5F_{10}O$ is admixed in mole fractions of $\sim 6\%$ to O_2 and CO_2. A pilot installation with a minimum operating temperature of $+5\,^{\circ}$C is in operation since 2015.[59,118]

Table 2: Properties of pure compounds used or considered for electrical insulation

Chemical Formula	GWP [(1)] 100-year	lifetime [(2)] (years)	RE [(3)] $Wm^{-2}ppb^{-1}$	Boiling [(4)] Point (°C)	$(E/N)_{crit}$ [(5)] rel. to SF_6	Acute toxicity [(6)] LC50 (ppm)
SF_6	22500	850	0.575	-64 [(7)]	1	
CF_4	6630	50000	0.09	-128	0.4	
Atmospheric gases						
CO_2	1		$1.37 \cdot 10^{-5}$	-78.5	0.23	
N_2				-196	0.38	
O_2				-183	0.33	
Fluorinated ketones						
$C_5F_{10}O$	< 1	0.044		26.9	1.5-2.0	20 000
$C_6F_{12}O$	1	0.014	0.50	49	2.7	> 100000
Fluorinated nitriles						
C_4F_7N	1490	22	0.217	-4.7	2	10 000-20 000
Hydrofluorocarbons HFCs						
HFC-1234ze(E)	< 1	0.045	0.04	-19.2	0.85	> 207000
HFC-1234ze(Z)	< 1	0.027	0.02	9.6	-	
HFC-1234yf	< 1	0.029	0.02	-29.3	-	400 000
Others						
CF_3I	0.4	0.005	0.23	-21.8	1.2	160 000

[(1)] Global warming potential from references:.[24,62,65,114,117,119] The GWP calculation assumes that the compound is well-mixed throughout the troposphere. Short lived compounds do not meet this condition and therefore the calculated GWP value is overestimated. [(2)] Atmospheric lifetime from references:[24,62,65,96,114,117] [(3)] Radiative efficiency from references:[24,62,96,114,117,120] [(4)] Boiling point from references:[109,117,121,121–127]

[(5)] For the gases lacking data of the critical field strength ($C_5F_{10}O$, $C_6F_{12}O$, C_4F_7N and HFC-1234ze(E)) and for N_2 ($\alpha - \eta$ always positive), the electric strength determined from breakdown experiments is shown. References:[61,91,101,109,111,117,128–130] [(6)] 4 hour rodent (rat) LC50 (lethal concentration at 50% mortality) from references[93,109,117,131,132] [(7)] sublimation point

5 Assessment of SF_6 replacements

At this date, requirements on insulation gases listed by producers and utilities cover dielectric, thermal, environmental, chemical, thermodynamic and financial aspects. The ideal insulation gas would be a compound with minimum environmental impact that withstands electric fields associated to the highest voltage levels and meets safety, risk and toxicity standards in equipment that operates under all foreseeable conditions from arctic to tropic. It should be low-cost gas of high reliability and long durability, be chemically stable inside equipment, in particular not flammable and compatible with materials in electrical and service equipment. In addition, its degradation products within the troposphere and within the equipment should be harmless to the atmosphere, aquatic systems, farmland, biodiversity and human health. Neither experimental nor computational systematic searches for direct SF_6 replacements in electrical equipment found compounds than can be used as pure gases and no compound stands out above all the others in being the ideal gas that is superior with respect to all requirements.[4,6,54,133]

The desired compound properties are often in conflict with each other. I. Maximum voltage levels versus minimum ambient temperatures: increasing the molecular size typically leads to a higher electric strength and at the same time decreased vapor pressure.[130,133] II. Maximum voltage levels versus minimum environmental impact: the radiative efficiency of a molecule enters linearly into semi-empirical electric strength estimations[134] and into the GWP definition.[24] III. Flammability versus atmospheric lifetime: increasing the number of hydrogen atoms in HFCs generally decreases the atmospheric lifetime but increases the flammability. Therefore, low-fluorinated saturated HFCs are often relatively short-lived but flammable in contrast to very long-lived but non-flammable PFCs. IV. The advantage of SF_6 being chemically inert inside equipment, is accompanied by the disadvantage of its long atmospheric lifetime: on the one hand, unstable molecules inside equipment accelerate the aging process (and thus increase maintenance costs) due to reactions with materials such as gaskets, by-products formation under partial discharge and undesired decomposition on

solid insulators or electrodes. On the other hand, designing fluorinated compounds with short atmospheric lifetimes is the best method to ensure low GWP - rather than searching for compounds with small radiative efficiency - and is the strategy adopted by many industries to screen for the best molecule for an application.[89,135] However, substances with very short lifetimes (in the order of days or week) might contribute to smog formation and the decomposition products could affect aquatic ecosystems.[136,137] For compounds considered for electrical insulation the physical removal processes via rainout, ocean uptake and scavenging by aerosols are negligible due to the typically low water solubility and high vapor pressure. However, aquatic systems could be potentially negatively affected by the rainout of certain atmospheric degradation products. For example, one photo-dissociation product of the ketone $C_6F_{12}O$ is COF_2.[116] In contact with rain, clouds or seawater COF_2 will undergo hydrolysis to form hydrogen fluoride, whereas $CF_3C(O)F$ will form trifluoroacetic acid.[116,138] Similarly, the new-generation refrigerant HFC-1234yf forms trifluoroacetic acid that in turn is removed by rainout and potentially accumulates in water bodies as trifluoroacetate. However, a risk evaluation of HFC-1234yf as alternative refrigerant for North America predicted concentrations of trifluoroacetate to remain below levels that could impair water quality.[136,139] This must be seen in relation to the comparatively small quantities needed in the electrical industry.

The full global warming impact of electrical equipment is not entirely reflected by the direct GWP of the gas components. A comparison of different insulation gases in equipment should consist of their CO_2 equivalents rather than their GWPs. In general, manufacturers calculate the overall CO_2 equivalent environmental impact of equipment by means of life cycle assessments including gas leakage, materials, transport, Joule losses, maintenance and recycling.[58,118,140] For example, air - a zero-GWP insulation gas - can reach the breakdown voltage of most synthetic gases only at significantly larger gap distances or higher filling pressures. Therefore, larger equipment or thicker walls of vessels are required, resulting in more material use for aluminum or steel. The leakage rate through gaskets varies between

different gas species and materials. However, leakage rates from equipment using alternative gases do not significantly differ from SF_6 equipment, if compatible gasket materials are used. For example, for equipment using CO_2/C_4F_7N mixtures, EPDM rubber of the SF_6 equipment is replaced by halogenated butyl rubber.[141] Life cycle assessments of recently announced products resulted in $30 - 70\%$ reduction of the CO_2 equivalent compared to the equivalent SF_6 products.[58,118,142]

The energy consumption for the production of a compound is not included in its direct GWP. Highly fluorinated compounds are synthesized by different techniques[143] that typically have one thing in common: they rely on elementary fluorine. The latter is produced by the energy-intensive electrolysis of hydrogen fluoride $2\ HF \rightarrow H_2 + F_2$. The electricity consumption for this electrolysis is 14-17 kWh/kg F_2[144] and is e.g. responsible for more than 95% of the power consumption for the SF_6 production.[145] The subsequent fluorination of sulfur to produce SF_6 is exothermic and therefore a low energy consumption can be assumed.[144] EPA's emission factor of 0.7 kg CO_2-equivalents per kWh electricity[146] from 2012, yields $\sim 7 - 9$ kg CO_2-equivalents for the production of 1 kg SF_6 and will be in the same order of magnitude for other compounds that are synthesized by fluorination with elementary fluorine. Thus, the CO_2-equivalents related to production are negligible for a strong greenhouse gas such as SF_6 and only significant when comparing gases of GWP $\lesssim 10$.

By-products that are formed during operation of equipment or in the atmosphere are often neglected in the environmental assessment since their concentrations are generally much lower than of the compound itself. In atmospheric gases by-product formation is typically limited to ozone production and not a problematic issue for health or environment. Most fluorinated compounds, including $C_5F_{10}O$ and CF_3I, form the stable by-product CF_4 in electrical equipment under arcing conditions.[113,147–149] CF_4 is an extremely long-lived greenhouse gas with much higher GWP than the original compounds. It is also formed in SF_6 near to organic materials such as polymeric spacers under partial discharge conditions.[150] Toxic by-products formation under discharge or arcing conditions might involve risks to the

health of anyone in the immediate surroundings of electrical equipment filled with SF_6[151–154] or alternative gases.[148,155] Often the assumption is made that the formation rates of by-product is linearly correlated with the energy input of the partial discharge, sparking or the arc. However, formation rates depend on many parameters such as current, voltage, gas pressure and purity, materials of electrodes and spacers, humidity and the sampling technique used for the analysis.[150] As a consequence, a quantitative comparison of by-product formation rates in different insulation gases for different setups is difficult. Therefore, the prediction of by-product concentrations in a specific setup, based on the values obtained from another setup and different conditions, might strongly deviate from the actual concentrations.

6 Challenges and Perspectives

Today, the idea of an SF_6-free transmission and distribution system is inconceivable for most system operators and engineers. However, the early beginnings of gaseous insulation evolved synthetic gases other than SF_6. With the rapidly increasing success of the "superior" SF_6 gas in the electrical industry, these "inferior" gases, mostly CFCs, became extinct. SF_6 use enabled the installation of space-saving GIS in urban areas. No city could ever again sustain its energy demands if it returned to air insulated substations. In the 1960s, engineers were unable to fathom the consequences of the increased usage of the extremely potent greenhouse gas SF_6. As a consequence of climate policies, the technical improvements made with SF_6 became a millstone around the neck of the electrical industry. Whichever direction the road led, there was no going back to the old technologies.

Eco-friendly replacement gases could resolve this dilemma. In short, SF_6 outperforms all alternative gases due to its combination of good dielectric, liquefaction and heat transport properties. Therefore, no drop-in replacements for all SF_6-filled apparatus exist at this date, and maybe none will be found in the foreseeable future. In addition, drop-in replacements to replace SF_6 in presently installed equipment without any modifications appear unlikely

for reasons of compatibility between gas and solid materials. Furthermore, arc quenching applications and very cold weather regions are particular challenging for all alternative gases. However, alternative gases might serve as drop-in replacements in indoor or outdoor equipment in moderate climate regions.

Nevertheless, more material use for slightly larger equipment or higher gas pressures and thus thicker walls can compensate for the deficits of alternative gases. Despite the increased material use, life cycle assessments conducted by manufacturers show that solutions with alternative gases drastically reduce the net greenhouse gas emissions in comparison to the SF_6-filled counterparts. In general, more research efforts are needed since detailed information on the dielectric properties and long-term durability of alternative gas mixtures are lacking. In addition, the full environmental and health impact of the compounds and their possible dissociation products in the atmosphere is not entirely clear.

At this date, the majority of equipment manufacturers and system operators are aware of the climate impact of SF_6. However, they often emphasize the relatively small contribution of SF_6 emissions to global warming or the disproportionate high abatement costs, claiming that investment into reducing CO_2 emissions should be of primary interest.[156–158] Even though substantial cuts in CO_2 emissions are essential to reduce global warming, cuts in non-CO_2 greenhouse gas emissions would be a relatively quick way of contributing to this goal.[24,64] Also the contribution of the electrical industry to total SF_6 emissions is controversially discussed, mainly due to the unknown emissions from military applications. Therefore, following the model of the UK and Switzerland of tracing down the SF_6 emission sources on a country level to find consistency between top-down and bottom-up emission estimates would be beneficial.

On the medium voltage level, various SF_6-free switchgear using vacuum circuit breaker and air, solid or liquid insulation are commercially available since many years. However, SF_6 insulated switchgear being a mass product is generally cheaper than other technologies and there is a lack of economic incentives for users to purchase SF_6-free switchgear. Decisions by users are not solely made on the basis of the costs and benefits, but also on intuitive think-

ing.[159] Many system operators are biased towards the status quo. They avoid for example vacuum circuit breakers or solid insulation because of bad experience in the past, when these technologies were more prone to failure. Furthermore, users request that alternatives have to comply to the incumbent SF_6 technologies and they set the tolerance for trade-offs (e.g. outer dimensions of equipment) generally very low. Not only does this lead to a delayed introduction on the market, but it also limits the range of possible alternatives. Certainly, policy makers should also "listen carefully to new entrants and often small innovative firms ... since most lobby networks are dominated by large incumbent firms".[160] It is important that policy decisions contain technological differentiation between different fields of application, such as medium versus high voltage or insulation versus arc quenching. A climate impact assessment should consider that gases and their by-products in closed electrical equipment are not directly emitted. Still, abating SF_6 has the potential for significant greenhouse gas emission reductions over the entire life cycle. Ad hoc policy initiatives that may increase insecurity for the manufacturers, engineers and other actors should be avoided and rather be replaced by long-term policies - possibly changing over time - to stimulate the development of new technologies.[160] Such iterative decision-making strategies could adjust the pathway during implementation according to new information gained e.g. from pilot installations of alternative technologies.

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Supporting Information Available

Additional information on SF_6 emissions at SF_6 production, equipment production and at use phase of equipment. Vapor pressure curves of pure compounds used or considered for electrical insulation are provided.

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