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Review

Recent Development of Two Alternative Gases to SF_6 for High Voltage Electrical Power Applications †

John Owens [1,*], Ang Xiao [1], Jason Bonk [1], Michael DeLorme [1] and Agnes Zhang [2]

[1] 3M Company, Saint Paul, MN 55144-1000, USA; axiao3@mmm.com (A.X.); jbonk@mmm.com (J.B.); mdelorme@mmm.com (M.D.)
[2] 3M China Ltd., Shanghai 200336, China; azhang11@mmm.com
* Correspondence: jgowens@mmm.com
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Abstract: For many years, SF_6 has been the preferred dielectric medium in electrical power applications, particularly in high voltage gas-insulated equipment. However, with the recognition that SF_6 has an extremely long atmospheric lifetime and very high global warming potential, governments have pursued emission reductions from gas-filled equipment. The electrical power industry has responded to this environmental challenge applying SF_6-free technologies to an expanding range of applications which have traditionally used SF_6, including gas-insulated switchgear, gas-insulated circuit breakers and gas-insulated lines or bus bars. Some of these SF_6-free solutions include gas mixtures containing fluorinated compounds that have low climate impact, among them, a fluoronitrile and a fluoroketone developed as 3M™ Novec™ 4710 Insulating Gas and 3M™ Novec™ 5110 Insulating Gas, respectively. Both fluoronitrile and fluoroketone mixtures are successfully used in gas-insulated equipment currently operating on the grid where they reduce greenhouse gas emissions by more than 99% versus SF_6. This paper reviews these leading components of alternative-gas mixtures with updates on the performance, safety and environmental profiles in electrical power applications.

Keywords: sulfur hexafluoride; SF_6; insulation; dielectric medium; SF_6-free; SF_6-alternative; fluoroketone; fluoronitrile

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1. Introduction

Sulfur hexafluoride, SF_6, has been a critical component in high voltage applications for several decades with the installed base of gas-filled equipment continuing to grow. Its combination of chemical, electrical, and physical properties has made SF_6 the preferred dielectric medium in gas-insulated switchgear (GIS), gas circuit breakers (GCB) and gas insulated lines (GIL). While much of the equipment operating on the electrical grid today depends upon the use of SF_6, the industry has been searching for an alternative due to environmental concerns over the properties of this highly stable insulating gas. A long atmospheric lifetime of 3200 years results in a global warming potential (GWP) for SF_6 of 23,500, making it the most potent greenhouse gas identified to date.

Identification of viable alternatives to SF_6 is complicated by the unique combination of properties required in dielectric applications. Unfortunately, the very properties that make SF_6 an ideal insulating gas, namely chemical inertness, are the same properties that make it exceptionally long lived in the atmosphere. Therefore, any replacement of SF_6 as an insulating gas must implicitly have some form of reactivity to facilitate degradation in the atmosphere and overcome the environmental concerns. The materials also need to be nonflammable and low enough in toxicity to allow for safe handling using practices similar to those currently used within the industry. Alternatives certainly need to have very high dielectric strength, providing performance as close to SF_6 as possible. Since the gas-filled equipment will be used in a variety of conditions, the materials must remain gaseous over the expected operating temperatures of these systems. The dielectric medium must also be stable over the working life of this equipment without contributing to corrosion or other adverse effects on the device. Most importantly, to be sustainable alternatives, new compounds need to have acceptable combinations of environmental properties, including no ozone depletion potential and significantly reduce the greenhouse gas emissions from these applications compared to SF_6, since this is the principal reason for transitioning to new technology.

Two compounds, a fluoronitrile and a fluoroketone, were found to combine the requisite properties for electric power applications. They both have been shown to function as a key dielectric component in insulating gas mixtures while providing significantly lower climate impact. As a result, the electric power industry has begun implementing SF_6-alternative gas mixtures based upon these compounds over the last several years [1–4]. The fluoronitrile and fluoroketone are recognized within the electric power industry as 3M™ Novec™ 4710 Insulating Gas and 3M™ Novec™ 5110 Insulating Gas, respectively [5]. In some publications they are referred to as C4-FN or C5-FK or even simply C4 or C5. For the duration of this paper, these compounds will be identified as Novec 5110 gas and Novec 4710 gas. This paper is a review of these components in SF_6-alternative gas mixtures covering material properties and performance in dielectric applications as well as safety and environmental considerations.

2. Performance in Dielectric Applications

2.1. Properties of Pure Novec Insulating Gases

The Novec Insulating Gases exhibit several physical properties that are similar to SF_6. They are highly fluorinated, nonflammable, high density gases with extremely low freezing points and excellent dielectric properties. At any given pressure, the pure Novec gases display dielectric breakdown voltages that are superior to that of SF_6 as shown in Figure 1. Table 1 provides a summary of these key physical properties. It also lists the environmental attributes of each gas. Like SF_6, the Novec Insulating Gases are non-ozone depleting since they do not affect stratospheric ozone leading to an ozone depletion potential (ODP) of zero. However, their measurably shorter atmospheric lifetimes lead to significantly lower GWPs. As will be shown below, the shorter atmospheric lifetimes are also the key attribute that enables substantial reductions in the overall greenhouse gas (GHG) emissions resulting from gas-insulated equipment using these alternatives.

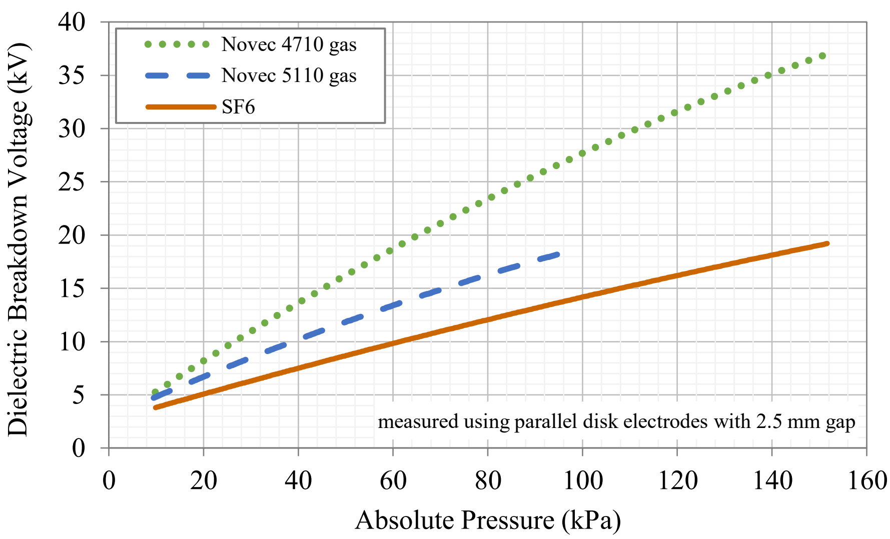

Figure 1. Dielectric breakdown voltage of pure gases [5].

Table 1. Alternative gas properties compared to SF_6 [5].

Property at 1 Bar, 25 °C	Sulfur Hexafluoride	Novec 4710	Novec 5110
Chemical Formula	SF_6	$(CF_3)_2CFCN$	$(CF_3)_2CFC(O)CF_3$
Molecular Weight	146	195	266
Boiling Point (°C)	−63.9 [a]	−5	27
Vapor Pressure (kPa)	2372	297	94
Freezing Point (°C)	−50.8	−118	−110
Flash Point (°C)	none	none	none
Gas Density (kg/m^3)	5.9	7.9	10.7
Thermal Conductivity (W/m·K)	0.013	0.025	0.004
Breakdown Voltage (kV) 2.5 mm gap with parallel electrodes	14.0	27.5	18.4 [b]
Atmospheric Lifetime (year)	3200	30	0.04 (15 days)
Ozone Depletion Potential	zero	zero	zero
GWP (100-year ITH)	23,500	2100	<1

[a] Sublimation Point, [b] at saturation.

2.2. Properties of Gas Mixtures

Due to their higher boiling points and corresponding lower vapor pressures, the Novec gases are used in gaseous mixtures rather than as pure materials. Dilution in gaseous mixtures allows the equipment to operate at temperatures well below the boiling points of these materials without condensation. Once gases form a homogeneous mixture, they do not physically separate unless liquefied by cooling below the condensation temperature or compressed to very high pressures. Similarly, although gas density will vary with height in a vertical column, the mixture does not separate over time with the higher molecular weight components concentrating at lower elevations. Figure 2 shows the change in gas density as a function of height in a column of gas for several gases. The pressure exerted by the column of gas above any point creates a greater density compared to higher elevations. Thus, the density of a gas decreases at higher elevations. Larger variations occur as the molecular weight of the gas increases since the greater mass produces higher pressures at the lower elevations. However, the concentrations of individual components in a gas mixture do not change with height. The pressure exerted by the column of gas mixture above a molecule of any component is the same, resulting from the density of the gas mixture above it rather than any individual pure gas. As a result, all components of a mixture are exposed to the same gravitational force and pressure. Therefore, no driving force is created to cause a separation. A similar conclusion was reached in the 1982 EPRI Report EL-2620 [6]: "In the absence of condensation, a gas mixture will not separate into its component gases over a short or long period of time even when the molecular weights of the component gases are markedly different." Accordingly, gas separation has not been observed experimentally [5–7]. For example, a gas mixture containing Novec 4710 gas and CO_2 was stored in a 2-m vertical tube at −15 °C for 6 months with no change in composition detected over the height of the tube [7].

Table 2 shows a comparison of representative gas mixtures that are used in high voltage systems relative to pure SF_6. The dielectric breakdown voltage of a gas mixture varies with the concentration of Novec gas as well as the total pressure of the mixture. As shown in Figure 3, it is possible to compensate for the lower dielectric strength of a dilute gas mixture by increasing the total gas pressure used within the system. In fact, that is the strategy often employed by manufacturers of gas-insulated equipment. Numerous systems using Novec gas mixtures are currently operating on the grid, including installations of GIS, GCB and GIL. These systems have been designed to deliver performance comparable to similarly rated SF_6 equipment, [8,9].

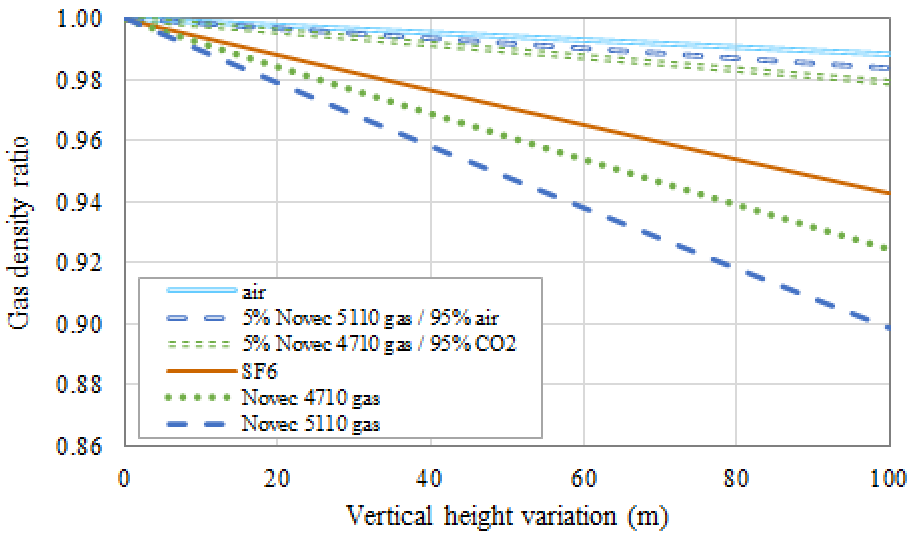

Figure 2. Variation in gas density as a function of gas column height. Gas mixtures are described in Table 2.

Table 2. Gas mixture properties compared to SF_6.

Gas Formulation (mole%)	100% SF_6	5% Novec 4710/95% CO_2	5% Novec 5110/95% Air
Typical GIS Pressure (bar)	4	6	6.5
Gas Density @ 25 °C (kg/m^3)	24.75	12.48	10.67
Condensation temperature (°C)	−38	−27	0
Dielectric breakdown voltage relative to SF_6	—	~1	~1

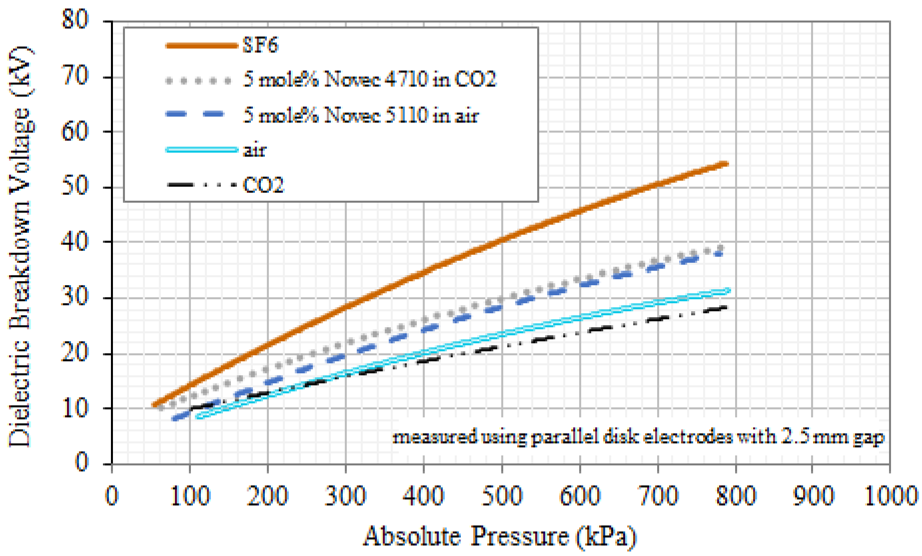

Figure 3. Dielectric breakdown voltage of gas mixtures compared to pure SF_6.

3. Safety Considerations

A key aspect for use of any SF_6-alternative technology is the ability to use it safely within gas-filled equipment. Personnel may come into contact with an insulating gas through handling during initial filling and maintenance of the equipment, leakage during normal operation and when decommissioning the system. The safety of Novec Insulating Gases has been evaluated through a series of toxicological studies [10,11]. These 3M-sponsored studies were approved by the laboratories' Institutional Animal Care and

Use Committees and animal care complied with all applicable national and local regulations. All toxicological studies that followed OECD guidelines (Organization for Economic Co-operation and Development) were performed under GLP conditions (Good Laboratory Practice). Both gases demonstrated low acute toxicity hazard as reflected in their Globally Harmonized System (GHS) classification of Category 4 or higher. Both Novec gases also presented a low hazard profile in repeat-dose inhalation toxicity studies where irritant-associated effects were noted in tissues at the portal of entry (nose and mouth), the respiratory and gastrointestinal tracts, at the highest exposure concentrations. In addition, both gases have demonstrated no genotoxicity potential where Novec 4710 gas was found to be not mutagenic in both in vitro and in vivo assays and Novec 5110 gas was shown to be not mutagenic in an in vitro genotoxicity assay. While Novec 5110 gas has not yet been evaluated in an in vivo study the next nearest homologue (an analogous fluoroketone with chain length one carbon longer) has been shown to be not mutagenic through in vivo tests. Thus, based on all available data the weight of evidence indicates that the both Novec Insulating Gases would not be classified as CMR hazards (carcinogenicity, mutagenicity, reproductive toxicity).

As an additional step, the assessment of the available data and associated hazard classification recommendation for Novec 4710 gas was confirmed and validated in an independent, third-party assessment [12]. This technical assessment confirmed that "Based on the available data, no self-classification for the CMR hazard categories is currently warranted or anticipated in the future." A summary of the key results for both Novec gases is shown in Table 3.

Table 3. Key toxicological results on pure Novec Insulating Gases.

Novec 4710 Gas	Novec 5110 Gas
Low acute inhalation toxicity (4-h LC_{50} > 10,000, <15,000 ppmv)	Low acute inhalation toxicity (4-h LC_{50} > 148, <213 mg/L) [1]
Low repeated-dose inhalation toxicity (based upon 28-day study)	Low repeated-dose inhalation toxicity (based upon 28-day study)
Negative for in vivo genotoxicity using both micronucleus and Comet assays	Not mutagenic in bacterial reverse mutation assays
Negative for reproductive and developmental toxicity	Expected to be negative for reproductive and developmental toxicity based upon read across from next nearest homologue

[1] Defined as a liquid under Globally Harmonized System based upon vapor pressure.

Considering the results from the full range of studies, the 3M Medical Department established occupational exposure limits (OEL) of 65 ppm and 225 ppmv (8-h time weighted averages) for Novec 4710 gas and Novec 5110 gas, respectively. Small releases of insulating gases can occur during filling, maintenance, and decommissioning operations when gas-tight connections are sealed and unsealed. However, airborne concentrations measured during gas transfer operations are normally less than 10 ppmv [5]. Workplace airborne SF_6 concentrations observed in indoor gas-insulated switchgear applications are typically below 1 ppmv [13]. As a result, the OELs stated above provide a sufficient margin of safety in these applications and the observed airborne concentrations of Novec Insulating Gases described above are well below the action level of $\frac{1}{2}$ the OEL as defined by US Occupational Safety and Health Administration (OSHA). On this basis, risk analyses have established that gas mixtures containing the Novec Insulating Gases are safe to handle in gas-filled equipment under all expected operational conditions [1,2].

Independent groups have also conducted toxicological tests [14–16] with Novec 4710 gas using non-OECD test protocols. Variation in test parameters such as the animal species, exposure time and the condition of the gas will provide significantly different results. As a result, OECD and international standards such as GHS have standardized hazard testing criteria, requiring test methods that are scientifically sound and validated according to international procedures in order to provide information relevant to a human health assessment while minimizing the need for animal testing. The results from tests conducted using non-standard protocols have led to some confusion over the toxicological profile for the Novec gases.

The data reported by Li and colleagues [14] for acute inhalation tests conducted in the rat over a 4-h time interval found an LC_{50} value of 15,000–20,000 ppmv, which is consistent with the LC_{50} value discussed above. Additional tests were conducted at high concentrations over a time interval of 24-h. Such an exceptionally long test period is far beyond the 4-h exposure required for acute inhalation testing that is used for GHS classification of a chemical and does not aid in performing a human health risk assessment. The alleged effects on various organs systems observed in the 24-h exposure were actually a result of pulmonary edema-induced hypoxia (insufficient oxygen reaching the internal organs) and not a direct response of the test material on these organs. The 3M-sponsored, 28-day inhalation toxicity study referenced above found the respiratory tract to be the target organ, exhibiting signs of an irritant-like effect, but no histopathological changes were noted in other organ systems. Overall, the results in the paper are consistent with the LC_{50} values published to date and do not contradict the recommended 65 ppmv occupational exposure limit.

Preve and colleagues [15] have repeatedly cited toxicological data developed outside of the recommended and validated testing protocols. The acute inhalation LC_{50} data used in their publications were derived using different animal models (mouse). The OECD protocols for acute inhalation toxicity (OECD 403, 433 and 436) all state that the preferred test species is the rat as it has been previously been demonstrated that mice are often more sensitive in acute inhalation studies than other mammals, a factor which complicates the use of data generated in mice for risk assessment purposes [17]. Similarly, the discussions in these papers regarding mutagenicity aspects appear to overlook both the available data on the Novec gases as well as the recommendations for the use of read-across techniques encouraged by regulatory bodies such as the European Chemicals Agency (ECHA). As a result, the data generated in those studies do not augment the information for a human health risk assessment.

Zhang and colleagues published the results from a series of inhalation toxicity studies conducted in the mouse [16]. As expected, the results demonstrated the higher sensitivity of the mouse in acute inhalation studies compared to the rat but again did not demonstrate any additional relevance for a human health risk assessment. While the authors stated that there is still much work to be conducted on the toxicity of C4 nitrile and a need for an occupational exposure level, this assessment clearly does not reflect the significant amount of data readily available on this material which includes GLP-conducted acute, sub-chronic, developmental and reproductive, and genetic toxicity studies. Based upon these studies, 3M has developed an occupational exposure limit of 65 ppm which is published on the 3M safety data sheets and product literature.

Additional considerations apply when handling any insulting gas after arcing events. In the case of electrical arcing in equipment containing SF_6, high-toxicity decomposition byproducts such as HF, S_2F_{10} and SO_2 can be generated. These byproducts are highly hazardous and pose a potential toxicity risk to those exposed. Depending on the nature of the arcing event, the Novec gas mixtures may also undergo some degree of decomposition. Even though testing demonstrated that arced Novec gas mixtures can be less hazardous than arced SF_6 mixtures [1,2], similar precautions should be taken when handling such gas mixtures. Employees performing maintenance procedures on electrical switches containing arced SF_6 are required to use proper handling procedures and wear personal protective equipment. Similar precautions should be taken with arced Novec gas mixtures.

4. Environmental Considerations

4.1. Global Warming Potentials

One metric for analyzing the potential environmental impact of SF_6 alternatives is a comparison of the global warming potential (GWP) for the gases used within the different technologies. The GWP is an index that provides a relative measure of the possible climate impact of a compound which acts as a greenhouse gas in the atmosphere. It effectively calculates the amount of energy absorbed by a compound over a period of time relative to that of a reference compound, CO_2. The GWP as defined by the Intergovernmental Panel on Climate Change (IPCC) [18] is calculated as the integrated radiative forcing due to the release of 1 kg of that compound relative to the warming due to 1 kg of CO_2 over the same time interval (the integration time horizon (*ITH*)), as shown in Equation (1):

$$\mathrm{GWP}_i = \frac{\int_0^{ITH} R_i C_{i_0} \exp\left(\frac{-t}{\tau_i}\right) dt}{\int_0^{ITH} R_{CO_2} C_{CO_2}(t) dt} \tag{1}$$

where R is the radiative forcing per unit mass of a compound (the change in the flux of radiation through the atmosphere due to the infrared (IR) absorbance of the compound), C is the atmospheric concentration of a compound, τ is the atmospheric lifetime of a compound, t is time and i is the compound of interest. The commonly accepted *ITH* is 100 years.

Only two variables in the GWP calculation are affected by the physical characteristics of the compound—the radiative forcing due to IR absorbance and the atmospheric lifetime. All fluorinated compounds absorb IR energy in the "window" at 8 to 12 μm which is largely transparent in the natural atmosphere. This IR absorbance, coupled with a long atmospheric lifetime, results in a high GWP for many perfluorinated compounds such as SF_6.

The most effective approach to producing a lower GWP alternative is to develop a compound with a significantly shorter atmospheric lifetime. For highly fluorinated compounds this means synthesizing a molecule containing functionality or structural features that allow it to decompose more readily in the natural atmosphere. This is precisely the approach that was taken with the Novec Insulating Gases. Novec 5110 gas incorporates a carbonyl group that undergoes direct photolysis when exposed to sunlight in the lower atmosphere leading to a GWP value of less than 1 [19]. Novec 4710 gas contains a nitrile group that reacts with hydroxyl radicals in a process similar to the degradation mechanism for most organic compounds that enter the lower atmosphere. Multiple studies have reported an atmospheric lifetime and GWP value for Novec 4710 gas. At first glance, these values may appear to vary considerably. However, as the review below demonstrates, the results are consistent within recognized experimental uncertainty.

The initial studies were performed in the 3M Environmental Laboratory to investigate the atmospheric lifetime of Novec 4710 gas. A series of experiments measured the rate of degradation for Novec 4710 gas due to reaction with hydroxyl radicals relative to methane or pentafluoroethane as a reference compound. Hydroxyl radicals were generated via photolysis of ozone in the presence of water vapor. Concentrations of the reactants were measured continuously by Fourier transform infrared spectroscopy (FTIR) using a 10-m pathlength within a 5.7 L gas cell maintained at 300 K. Additionally, gas samples were analyzed by gas chromatography with mass spectrometry during one of the experiments to confirm the concentrations of Novec 4710 gas. The average atmospheric lifetime calculated from four separate experiments was 30 years for Novec 4710 gas [20].

The radiative efficiency for Novec 4710 gas was calculated at 0.225 $Wm^{-2}ppbv^{-1}$ using the method of Pinnock et al. [21] with an IR cross-section measured using 0.5 cm^{-1} resolution. This radiative efficiency value takes into account the necessary stratospheric temperature adjustments and atmospheric lifetime corrections. The radiative efficiency combined with a 30-year lifetime results in a GWP of 2100 using the IPCC calculation method [18].

A study published by Sulbaek Andersen and colleagues conducted smog chamber experiments to investigate the atmospheric fate of Novec 4710 gas [22]. Experiments were performed within a 101 L photoreactor maintained at 296 K. Hydroxyl radicals were generated by photolysis of ozone in the presence of hydrogen gas. The atmospheric lifetime was determined from these experiments to be approximately 22 years. Combining this lifetime with the radiative efficiency they measured at 0.217 $Wm^{-2}ppbv^{-1}$ using an FTIR resolution of 0.25 cm^{-1} resulted in a GWP value reported as 1490. The lifetime reported in this study was calculated using the measured reaction rate constant and an average hydroxyl radical concentration in the atmosphere. For compounds considered to be well-mixed in the atmosphere (i.e., lifetimes more than a few months), it is more common to calculate the lifetime relative to a reference compound such as methyl chloroform since there is a comprehensive analysis of its abundance in the atmosphere as well as its rate of emission and removal. The atmospheric lifetime calculated from this method is 32 years, resulting in a GWP of 2090.

Another series of experiments were conducted by Blázquez and colleagues in which they examined the temperature dependence of the reaction of hydroxyl radical with Novec 4710 gas [23]. Hydroxyl radicals were produced by photolysis of HNO_3. Measurements were made from 278 to 358 K. A linear equation (in the form of the Arrhenius equation) was fit to these kinetic data. The atmospheric lifetime was reported as 47 years using kinetics extrapolated to 272 K. The radiative efficiency was measured in this study to be 0.279 $Wm^{-2}ppbv^{-1}$ using a 1 cm^{-1} spectral resolution. These data combined to report a GWP value of 3646. While the lower temperature for the kinetic calculations is more representative of the average tropospheric temperature, a comparison of values across all studies requires data to be compared from equivalent conditions. The kinetic data measured at 298 K in this study results in an atmospheric lifetime of 31 years. Calculation of the GWP using this lifetime and the above radiative efficiency produces a value of 2620.

While there is variability in the GWP values resulting from these independent studies, the values are well within the uncertainty reported by IPCC of ±35% [18] as shown in Figure 4. The average lifetime and GWP values from the 3 studies are 31 years and 2260, respectively, which agree well with the original values report by 3M. On this basis, 3M continues to report the lifetime and GWP values derived from their internal studies of 30 years and 2100, respectively.

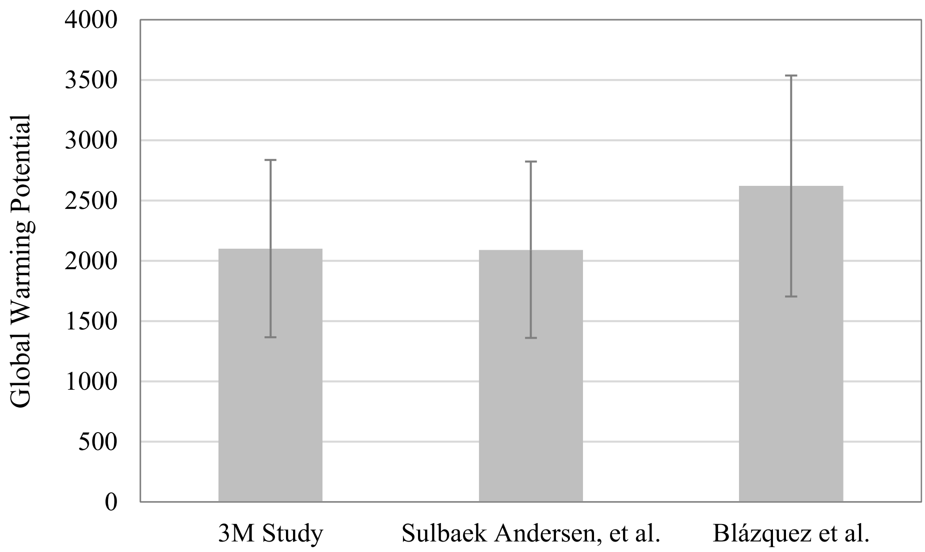

Figure 4. GWP values for Novec 4710 gas with uncertainty cited by IPCC.

The GWP for a gas mixture is calculated using the GWP value for each individual component multiplied by its weight fraction in the mixture according to Equation (2):

$$\mathrm{GWP}_{mixture} = \sum_i \mathrm{x}_i \, \mathrm{GWP}_i \quad (2)$$

where x_i and GWP_i are the weight fraction and GWP of component *i*, respectively.

4.2. Greenhouse Gas Emissions

A comparison of GWP values for representative gas mixtures used as alternatives to SF_6 is shown in Table 4. However, this type of comparison only provides a partial assessment of the environmental impact from insulating gas technologies. The mass of gas released, even from the same volumetric leakage rate, can be significantly different due to the considerably different gas densities. Table 4 also shows the GHG emission reductions achieved by the alternative-gas mixtures are even lower than would have been apparent through a simple comparison of GWPs.

Table 4. Initial climate performance of alternative-gas mixtures compared to SF_6.

Gas Formulation (mole%)	100% SF_6	5% Novec 4710/95% CO_2	5% Novec 5110/95% Air
Pressure (bar)	4	6	6.5
GWP of gas mixture	23,500	398	<1
GWP reduction vs SF_6	—	98.3%	>99.9%
GHG content (kg CO_2e/m^3)	553,929	4969	3.5
GHG emission reduction from discrete emission relative to SF_6	—	99.1%	>99.9%

Another disadvantage to assessing the climate impact of gases solely through comparison of GWP values is the inherent limitations within the GWP calculation itself. It is important to note that the commonly recognized GWP for a substance is calculated over a 100-year ITH. This ITH is a compromise between shorter-term and longer-term effects [18]. However, this means that the full climate impact of a very long-lived gas, such as SF_6, is not fully accounted for in the GWP calculation. Figure 5 displays a plot of the quantity of gas remaining in the atmosphere following a 1 kg release. A compound such as Novec 4710 gas with an atmospheric lifetime of 30 years is expected to be essentially fully degraded within the GWP calculation timeframe. Contrast that with SF_6 which, due to its atmospheric lifetime of 3200 years, remains in the atmosphere far longer than the 100-year ITH. As a result, only a fraction of its potential impact on climate change is included in the GWP calculation.

Installations of gas-filled electric power equipment are expected to remain in use for decades with low level emissions occurring throughout this time due to leakage. Many regions require reporting of these GHG emissions on an annual basis, even though, as shown in Figure 5, a portion of the gas leaked in any year can remain in the atmosphere for far longer. An assessment of the cumulative GHG emissions would account for not only the mass of gas emitted annually but also the amount of the gas that accumulates in the environment during its use. Both factors can have a measurable influence on the overall climate impact of a technology.

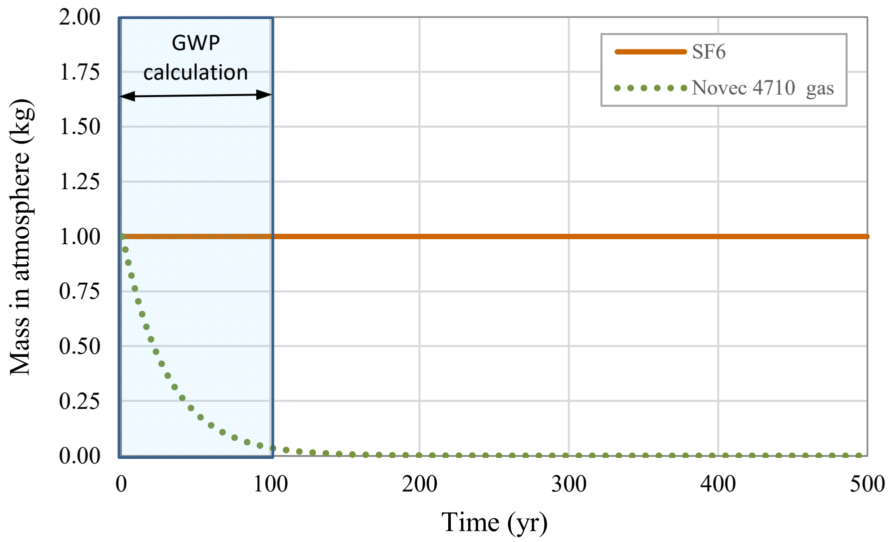

Figure 5. Residence time of insulating gas in the atmosphere, assuming 1 kg release of each compound at time zero.

Figure 6 compares the cumulative GHG emissions that would occur due to leakage of insulating gas over a 40-year lifetime of an installed base of gas-filled equipment. The comparison assumes volumetric emissions from the equipment equivalent to 1 T/year of SF_6 over that lifetime. The calculations are carried out for 100 years corresponding to the timeframe used in GWP assessments in order to illustrate the limitation of relying on the GWP parameter alone. Results for alternative-gas mixtures with GWPs of 398 and 1 are plotted along with SF_6. Comparison of the GWPs for these mixtures to SF_6 suggests that these alternatives represent a 98.3% and >99.9% improvement, respectively. Additionally, if the different gas densities are factored into the calculation, the reduction in GHG emissions improves to 99.1% and >99.9%, respectively, as shown in Table 4. However, the shorter atmospheric lifetimes of the alternative gases mean that both materials degrade much more rapidly over time compared to SF_6, preventing measurable accumulation of these alternatives in the environment. This limits the cumulative GHG emissions from the alternative-gas insulation technologies. When calculated over a 100-year timeframe both gas mixtures reduce GHG emissions by more than 99.9%, regardless of the GWP of the alternative-gas mixture.

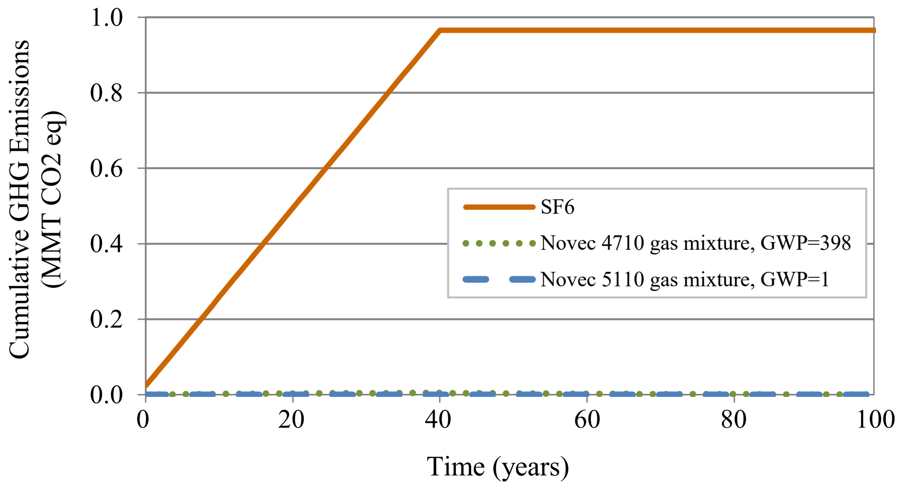

Figure 6. Cumulative greenhouse gas emissions, assuming emission equivalent to 1T/yr of SF_6 for 40 years of operation.

A lifecycle assessment (LCA) comparing the climate impacts of these alternative-gas technologies came to similar conclusions [24]. The analysis compared 145 kV GIS bays operating with the alternative-gas mixtures to identical equipment designed for SF_6 throughout the gas-use phases of the equipment lifecycle (filling, operation, decommissioning). The LCA demonstrated that the alternative-gas technologies result in large reductions of the carbon footprint of these applications with a climate impact that is negligible compared to SF_6, confirming the results of the GHG calculations shown above.

5. Conclusions

Gas mixtures containing a fluoroketone or a fluoronitrile, Novec™ 5110 Insulating Gas and Novec™ 4710 Insulating Gas, respectively, are being implemented as low climate-impact alternatives to SF_6. When used at higher pressure, these gas mixtures can deliver dielectric performance comparable to SF_6 in high voltage systems. The safety of Novec gases has been evaluated through a series of toxicological studies which demonstrate that the hazard profiles of the gas mixtures containing these materials are safe to handle in gas-filled equipment. Both alternative gases have significantly lower GWPs than SF_6. Moreover, their shorter atmospheric lifetimes prevent measurable accumulation of these gases in the atmosphere. This results in substantial reduction (>99.9%) in GHG emissions over the expected working life of equipment using these alternatives, irrespective of the GWP for the individual gas mixture components. As a result, these advanced materials enable insulation technologies that can make a meaningful contribution to reducing the environmental impact of high voltage applications. Therefore, limiting alternative-gas technologies based on GWP alone could be counterproductive to the goal of reducing the climate impact from electric power applications. In fact, the European Commission report in 2020 stated "In specific sites where the voltage rate must be maintained and space is restricted, such as substations at power plants or in urban areas, currently designs based on fluoronitriles may be the only viable alternative to SF_6 based switchgear" [25]. Gas insulated equipment containing Novec 4710 gas mixtures first started operating on the grid in 2017, while equipment containing Novec 5110 gas mixtures first started operating on the grid in 2015. More than 100 equipment bays containing alternative gas mixtures have now been installed by multiple utilities located primarily in Europe with recent installations in Asia and North America.

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Institutional Review Board Statement: The 3M-sponsored toxicological studies were approved by the laboratories' Institutional Animal Care and Use Committees and animal care complied with all applicable national and local regulations. All toxicological studies that followed OECD guidelines were performed under good laboratory practice conditions.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this review are available from 3M or in the European Chemicals Agency database at https://echa.europa.eu/information-on-chemicals (accessed on 14 August 2021) under EC reference numbers 690-995-3 and 806-451-7.

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References

1. Hyrenbach, M.; Paul, T.; Owens, J. Environmental and safety aspects of AirPlus insulated GIS. *CIRED Open Access Proc. J.* **2017**, *1*, 132–135. [CrossRef]
2. Kieffel, Y.; Biquez, F.; Vigouroux, D.; Ponchon, P.; Schlernitzauer, A.; Magous, R.; Cros, G.; Owens, J. Characteristics of g^3—An alternative to SF_6. *CIRED Open Access Proc. J.* **2017**, *1*, 54–57. [CrossRef]

3. Kieffel, Y.; Irwin, T.; Ponchon, P.; Owens, J. Green Gas to Replace SF_6 in Electrical Grids. *IEEE Power Energy Mag.* **2016**, *14*, 32–39. [CrossRef]
4. Cigré. *Technical Brochure 802—Application of Non-SF6 Gases or Gas-Mixtures in Medium and High Voltage Gas-Insulated Switchgear*; Cigré: Paris, France, 2020.
5. Xiao, A.; Owens, J.; Bonk, J.; Zhang, A.; Wang, C.; Tu, Y. Environmentally Friendly Insulating Gases as SF_6 Alternatives for Power Utilities. In Proceedings of the ICEMPE 2019—2nd International Conference on Electrical Materials and Power Equipment, Guangzhou, China, 7–10 April 2019; pp. 42–48.
6. Wooton, R.E.; Kegelman, M.R. *Gases Superior to SF_6 for Insulation and Interruption*; Report EL-2620; Electric Power Research Institute (EPRI): Washington, DC, USA, 1982.
7. Pohlink, K.; Meyer, F.; Kieffel, Y.; Biquez, F.; Ponchon, P.; Owens, J.; Van San, R. *Characteristics of Fluoronitrile/CO_2 Mixture—An Alternative to SF_6*; Cigré: Paris, France, 2016; Paper D1-204.
8. Stoller, P.; Hengstler, J.; Doiron, C.; Scheel, S.; Simka, P.; Müller, P. *Environmental Aspects of High Voltage Gas Insulated Switchgear That Uses Alternatives to SFf_6 and Monitoring and Long-Term Performance of a Pilot Installation*; Cigré: Paris, France, 2018; Paper D1-202.
9. Laruelle, E.; Maksoud, L.; Kieffel, Y.; Lüscher, R.; Ficheux, A. *SF_6 Alternative—What to Learn from the High Voltage Experience*; Cigré: Madrid, Spain, 2019; Paper 0028.
10. *Material Toxicity Summary Sheet, 3M™ Novec™ 4710 Insulating Gas*; 3M Company: St. Paul, MN, USA, 2019.
11. *Material Toxicity Summary Sheet, 3M™ Novec™ 5110 Insulating Gas*; 3M Company: St. Paul, MN, USA, 2019.
12. Ramboll US Consulting, Inc. Global Product Safety and Stewardship Practice, "CMR Self Classification". Available online: https://bit.ly/2LQHkEO (accessed on 14 August 2021).
13. Castonguay, J. In-situ measurements of SF_6 leak rates in indoor gas-insulated switchgears (GIS). In *Gaseous Dielectrics IX*; Christophorou, L., Olthoff, J., Eds.; Kluwer Academic/Plenum Publishers: New York, NY, USA, 2001; pp. 549–554.
14. Li, Y.; Zhang, X.; Zhang, J.; Xiao, S.; Xie, B.; Chen, D.; Gao, Y.; Tang, J. Assessment on the toxicity and application risk of C4F7N: A new SF_6 alternative gas. *J. Hazard. Mater.* **2019**, *368*, 653–660. [CrossRef] [PubMed]
15. Preve, C.; Maladen, R.; Piccoz, D. *Innovative SF_6 Free Load Break Switch with Shunt Vacuum Interruption (SVI) Technology*; Cigré: Paris, France, 2020; Paper A3-116.
16. Zhang, X.; Fanchao, Y.; Li, Y.; Tian, S.; Xie, B.; Gao, Y.; Xiao, S. Acute toxicity and health effect of perfluoroisobutyronitrile on mice: A promising substitute gas-insulating medium to SF_6. *J. Environ. Sci. Health Part A* **2020**, *14*, 1646–1658. [CrossRef]
17. Ten Berge, W.F.; Zwart, A.; Appelman, L.M. Concentration-time mortality response relationship of irritant and systemically acting vapors and gases. *J. Hazard. Mater.* **1986**, *13*, 301–309. [CrossRef]
18. IPCC. *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*; Stocker, T.F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S.K., Boschung, J., Nauels, A., Xia, Y., Bex, V., Midgley, P.M., Eds.; Cambridge University Press: Cambridge, UK; New York, NY, USA, 2013.
19. Ren, Y.; Bernard, F.; Daële, V.; Mellouki, A. Atmospheric fate and impact of perfluorinated butanone and pentanone. *Environ. Sci. Technol.* **2019**, *53*, 8862–8871. [CrossRef]
20. 3M Company. *Internal Report No. E11-0512*; 3M Environmental Laboratory: St. Paul, MN, USA, 2015.
21. Pinnock, S.; Hurley, M.D.; Shine, K.P.; Wallington, T.J.; Smyth, T.J. Radiative forcing of climate by hydrochlorofluorocarbons and hydrofluorocarbons. *J. Geophys. Res.* **1995**, *100*, 23227–23238. [CrossRef]
22. Sulbaek Andsersen, M.; Kyte, M.; Andersen, S.T.; Neilsen, C.J.; Nielsen, O.J. Atmospheric chemistry of $(CF_3)_2CFCN$: A replacement compound for the most potent industrial greenhouse gas, SF_6. *Environ. Sci. Technol.* **2017**, *51*, 1321–1329. [CrossRef] [PubMed]
23. Blázquez, S.; Antiñolo, M.; Nielsen, O.J.; Albaladejo, J.; Jiménez, E. Reaction kinetics of $(CF_3)_2CFCN$ with OH radicals as a function of temperature (278–358 K): A good replacement for greenhouse SF_6. *Chem. Phys. Lett.* **2017**, *687*, 297–302. [CrossRef]
24. Billen, P.; Maes, B.; Larraín, M.; Braet, J. Replacing SF_6 in Electrical Gas-Insulated Switchgear: Technological Alternatives and Potential Life Cycle Greenhouse Gas Savings in an EU-28 perspective. *Energies* **2020**, *13*, 1807. [CrossRef]
25. European Commission Report C(2020) 6635. REPORT FROM THE COMMISSION: Assessing the Availability of Alternatives to Fluorinated Greenhouse Gases in Switchgear and Related Equipment, Including Medium-Voltage Secondary Switchgear. Available online: https://ec.europa.eu/clima/sites/clima/files/news/docs/c_2020_6635_en.pdf (accessed on 14 August 2021).