EMISSION REDUCTIONS THROUGH USE OF SUSTAINABLE SF_6 ALTERNATIVES

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ABSTRACT

For decades, SF_6 has been a preferred dielectric gas used in many electrical power applications, including medium voltage gas-insulated equipment. However, SF_6 has an extremely long atmospheric lifetime and has been recognized as a potent greenhouse gas. As a result, governments have sought to reduce emissions from gas-filled equipment. The electrical power industry has demonstrated a willingness to respond to this environmental issue. Emission rates from gas-filled equipment have been reduced. Progress has been made but complete elimination of emissions will not occur until alternative technologies are implemented for SF_6 in electrical power applications.

The development of alternative insulating gases is quite challenging due to the complex combination of performance and safety properties required in electrical power applications. An insulating gas needs not only high dielectric strength but must also have good heat transfer properties and be nonflammable, thermally stable and low in toxicity. Today, an insulating gas must also have sustainable environmental properties, meaning, zero ozone depletion potential and a global warming potential significantly lower than SF_6.

Environmentally sustainable solutions that are both effective and low in climate impact are available for some of the applications which have traditionally used SF_6. Both a fluoroketone and a fluoronitrile have been successfully used in gas-insulated equipment currently operating on the grid. This paper will review these recently-implemented insulating gases with updates on the performance, safety and environmental profiles in electrical power applications.

INTRODUCTION

Sulfur hexafluoride (SF_6) has been widely used as an insulating gas medium in various gas insulated equipment (GIE) such as gas insulated switchgear (GIS) and gas insulated lines (GIL) due to its excellent insulation and arc extinguishing properties. Compared to other insulating media, SF_6 not only improves the insulation strength of equipment but also reduces equipment size. However, SF_6 is now known as an extremely strong greenhouse gas with a Global Warming Potential (GWP) of 23,500 times that of carbon dioxide. The atmospheric lifetime of SF_6 was initially reported as approximately 3,200 years. More recent calculations have indicated a lifetime in the range of 850 to 1278 years [1, 2]. The revised lifetimes result in a reduction in the GWP of at most 4% since the GWP is calculated over a 100-year time horizon. Therefore, SF_6 remains the highest GWP compound identified to date.

Research on insulating gases had continued even after the introduction of SF_6. This effort took on greater urgency after governments in various regions began to establish policies to limit SF_6 emissions beginning in the late 1990s with its inclusion in the Kyoto Protocol. Identification of a viable alternative to SF_6 is complicated by the unique combination of properties required in electric power applications. The material needs to be nonflammable and low enough in toxicity to allow for handling using practices similar to those currently used within the industry. An alternative compound needs to have very high dielectric strength, as close to the performance of SF_6 as possible. Since the electrical equipment will be used in a variety of ambient conditions, the material must remain gaseous over the expected operating range of the equipment, typically down to at least -30°C. 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. In addition, to be a sustainable alternative any new compound would need to have an acceptable combination of environmental properties, including no ozone depletion potential and a significantly lower global warming potential (GWP) compared to SF_6.

After years of research, two materials have shown the right balance of properties to function as an SF_6 alternative: one is C4 fluorinated nitrile, C_3F_7CN, and the other is C5 fluorinated ketone, $CF_3C(O)CF(CF_3)_2$. These new compounds, the structures of which are shown in Figure 1, are being commercialized under the tradenames 3M™ Novec™ 4710 Insulating Gas and 3M™ Novec™ 5110 Insulating Gas. The safety, insulating, physical and environmental properties of Novec 4710 and Novec 5110 Insulating Gases were studied by 3M [3]. The results showed Novec 4710 and Novec 5110 Insulating Gases are sustainable alternatives to SF_6 in many dielectric applications. Both fluoronitrile and fluoroketone have been successfully used in gas-insulated equipment currently operating on the grid [4-5].

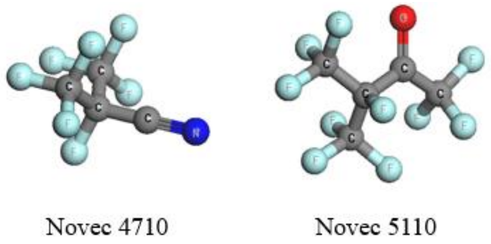
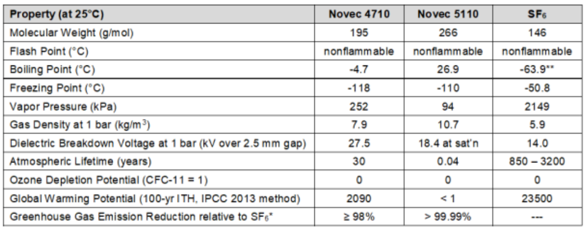


Figure 1. Molecular Structure of Novec 4710 and Novec 5110 Insulating Gases

PHYSICAL PROPERTIES

The physical properties of Novec 4710 and Novec 5110 Insulating Gases are shown in Table 1 in comparison to SF_6. A number of the properties of these materials are similar to SF_6. Novec 4710 and Novec 5110 gases are high density, nonflammable gases with very high dielectric strength.



Property (at 25°C)	Novec 4710	Novec 5110	SF_6
Molecular Weight (g/mol)	195	266	146
Flash Point (°C)	nonflammable	nonflammable	nonflammable
Boiling Point (°C)	-4.7	26.9	-63.9**
Freezing Point (°C)	-118	-110	-50.8
Vapor Pressure (kPa)	252	94	2149
Gas Density at 1 bar (kg/m^3)	7.9	10.7	5.9
Dielectric Breakdown Voltage at 1 bar (kV over 2.5 mm gap)	27.5	18.4 at sat'n	14.0
Atmospheric Lifetime (years)	30	0.04	850 – 3200
Ozone Depletion Potential (CFC-11 = 1)	0	0	0
Global Warming Potential (100-yr ITH, IPCC 2013 method)	2090	< 1	23500
Greenhouse Gas Emission Reduction relative to SF_6*	≥ 98%	> 99.99%	---

*calculation based on ≤10 volume% in gas mixture, **sublimation point

Table 1. Physical properties of Novec 5110 and Novec 4710 Insulating Gases compared to SF_6

The normal boiling point of Novec 4710 and Novec 5110 gases are much higher than that of SF_6, meaning these compounds have a much lower vapor pressure at any temperature. Nevertheless, Novec 4710 and Novec 5110 Insulating Gases are sufficiently volatile to form gaseous mixtures that can be used at temperatures well below their boiling points. Figure 2 displays the condensation curves for gas mixtures containing Novec 4710 and Novec 5110 Insulating Gases when mixed with dry air. As illustrated by these curves, gas mixtures with lower Novec 4710 and Novec 5110 gas concentrations can achieve relatively low condensation temperatures similar to pure SF_6.

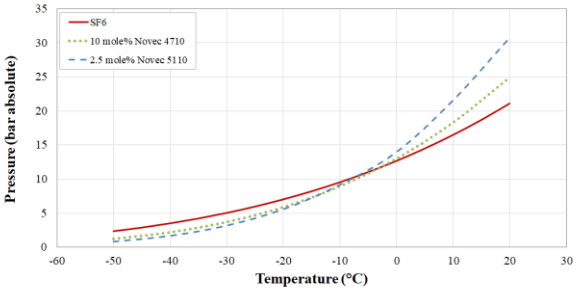


Figure 2. Condensation curves for gas mixtures containing Novec Insulating Gases compared to SF_6 vapor pressure

The potential for Novec 4710 and Novec 5110 Insulating Gases to impact the radiative balance in the atmosphere is limited by their significantly reduced atmospheric lifetimes relative to SF_6. The atmospheric lifetime of Novec 5110 and Novec 4710 gases are 0.04 years and 30 years, respectively, while that for SF_6 is as long as 3200 years. Using the IPCC 2013 calculation method [6], the Global Warming Potential (GWP) for Novec 4710 gas is 2090, and the GWP for Novec 5110 gas is less than 1. These are significantly lower than the SF_6 GWP of 23,500. The GWP for a gas mixture is calculated based upon the weight fraction of each component. When used in dilute gas mixtures as an alternative for SF_6, Novec 4710 and Novec 5110 Insulating Gases can enable significant reductions in greenhouse gas emissions. The combination of their lower GWP with reduced concentrations in gas mixtures and lower gas densities results in greenhouse gas emission reductions of as much as 99% when compared to the emissions from SF_6-filled equipment (assuming similar leak rates).

MOLECULAR ELECTROSTATIC POTENTIALS

The positive potential area of the molecular surface has a strong correlation with the arc-extinguishing performance of a dielectric medium [7]. It is of significant interest to run the similar correlation analysis on Novec 5110 and 4710 Insulating Gases. No method is currently available for calculating the molecular positive surface area. In this work, we developed a method for calculating the molecular positive surface area of Novec 5110 and Novec 4710 Insulating Gases for comparison with SF_6.

The positive surface area of a molecular surface can be calculated from the molecular electrostatic potential (ESP). The ESP at a given point p(x,y,z) in the vicinity of a molecule is the force acting on a positive test charge (a proton) located at p through the electrical charge cloud generated through the molecule's electrons and nuclei. Negative electrostatic potential corresponds to an attraction of the proton by the concentrated electron density in the molecule (from lone pairs, pi-bonds, etc.). Positive electrostatic potential corresponds to repulsion of the proton by the atomic nuclei in regions where low electron density exists and the nuclear charge is incompletely shielded. If the number of positive and negative ESP points on the molecular surface is calculated, one can estimate the size of positive and negative surface area from the fraction of ESP points in that category.

In order to calculate the number of ESP points and surface area of a molecule, a quantum mechanics (QM) calculation was applied to optimize the geometry of the system by using density functional theory (DFT) method at the B3LYP/6-311G* level of theory. Visualization of the ESP requires three more steps: 1. calculation of the outer envelope as defined through a constant value of electron density; 2. calculation of the ESP at a number of points including positive and negative ESP points around the molecule; 3. mapping of the ESP on the molecular surface using a color-coded scheme. The molecular geometry, number of ESP points, and visualization of ESP isosurface were calculated by molecular simulation tools Schrödinger Jaguar [8] on 3M's high-performance computation server.

To compare the differences of molecular electrostatic potential on the van der Waals surface, the potentials of SF_6, Novec 5110, and Novec 4710 were plotted using a molecular visualization program as shown in Figure 3. The plots demonstrate that Novec 5110 and Novec 4710 Insulating Gas molecules have higher maximum positive potential values than SF_6. This suggests that Novec 5110 and Novec 4710 should have stronger electron adsorption capacity than SF_6.

Table 2 summarizes the molecular surface area of SF_6, Novec 4710 and 5110 Insulating Gases. The positive surface area of the molecular surfaces for Novec 4710 and 5110 Insulating Gases are much larger than that of SF_6, explaining why in pure form these new materials can provide better insulating characteristics than SF_6. The higher positive surface area means stronger electron absorption capacity and potentially better arc-extinguishing performance. The negative surface region of the molecular surface does not appear relevant to the insulating characteristics of dielectric media.

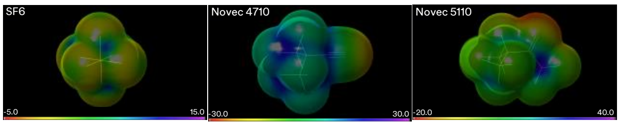


Figure 3. Electrostatic Potential Isosurface of SF_6 and Novec Insulating Gases

	SF_6	Novec 4710	Novec 5110
Number of surface points	3586	5500	6388
Number of positive ESP points	2157	4630	4859
Number of negative ESP points	1429	870	1529
Molecular surface area (Å^2)	101.9	152.6	179.1
Positive surface area (Å^2)	61.3	128.5	136.2
Negative surface area (Å^2)	40.6	24.1	42.9

Table 2. ESP and molecular surface area of SF_6, Novec 5110 and 4710 Insulating Gases

INSULATING CHARACTERISTICS

As shown in Table 1, the pure Novec 4710 and Novec 5110 Insulating Gases display dielectric breakdown strengths that are nearly twice that of SF_6, particularly at higher pressures. The data in Table 1 were measured on the pure gases using a method similar to that described in ASTM D877 using a 2.5 mm gap with parallel disk electrodes (i.e., a relatively uniform field).

In many cases, however, it is likely that Novec 4710 and Novec 5110 Insulating Gases will be used in gaseous mixtures rather than as a pure gas since gas-filled equipment installations are often designed to operate at temperatures well below the boiling point of these materials. As shown in Figure 4, when Novec 4710 and Novec 5110 Insulating Gases are mixed with air to form gaseous mixtures, the dielectric breakdown strength of the gas mixture increases at higher pressures and increased Novec Insulating Gases concentration. At the same pressure, the dielectric strength of Novec Insulating Gas mixtures is lower than pure SF_6. However, dilute mixtures containing the Novec Insulating Gases can be used at higher pressures to reach dielectric performance of SF_6. For example, as shown in Figure 4, at 3 bar pressure, the dielectric breakdown voltage of 2.5 mole% Novec 5110 and 10 mole% Novec 4710 is 20 kV and 24 kV, respectively, which is about 71% and 86% of dielectric strength of SF_6. In order to reach the same dielectric performance of SF_6, one needs to raise the pressure of the Novec 4710 gas mixture to 4 bar and the pressure of the Novec 5110 gas mixture to 5.2 bar.

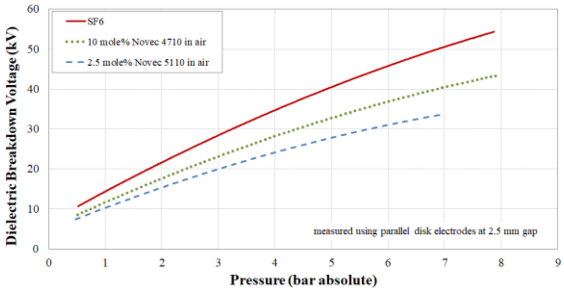


Figure 4. Dielectric breakdown voltage of Novec 4710/air and Novec 5110/air mixtures vs pure SF_6

HOMOGENEITY OF GAS MIXTURE

Concern has been raised over the possibility that a gas mixture could separate vertically over time with the higher molecular weight components concentrating at lower heights. The effect of height on the mixed gas homogeneity was calculated in this study. A simple expression for the change in gas pressure with height is shown below:

$$-dp = \rho \cdot g \cdot dh \qquad (1)$$

where p is pressure, g is the gravitational acceleration, h is height, and ρ is the gas density at height h.

Combining equation (1) with an expression of the ideal gas law for ρ gives:

$$\frac{dp}{p} = -\frac{M \cdot g}{R \cdot T} \cdot dh \qquad (2)$$

where T is temperature, R is the gas constant and M is the gas molecular weight. Through integration of (2) and rearrangement, one can get (3) and (4) below:

$$\frac{p}{p_0} = e^{-(h-h_0)/H} \qquad (3)$$

$$H = \frac{R \cdot T}{M \cdot g} \qquad (4)$$

where, h is the gas height, h_0 is the gas baseline height, p is gas pressure at height h, p_0 is the gas pressure at the baseline height h_0 and H, the scale height, is the vertical distance over which the density and pressure fall by a factor of 1/e.

Assuming SF_6, Novec 4710 or Novec 5110 Insulating Gases behave as ideal gases, then the ratio of the gas molecular density at height h vs. height h_0 is equal to the ratio of gas pressure, as shown in (5) below.

$$\frac{N}{N_0} = \frac{p}{p_0} = e^{-(h-h_0)/H} \qquad (5)$$

where. According to (5), one can calculate the influence of vertical height on the molecular density of pure gases CO_2, Novec 4710, and Novec 5110 as shown in Figure 5. Clearly, the density change with height of a lower molecular weight gas such as pure CO_2 is smaller than that of the pure Novec gases.

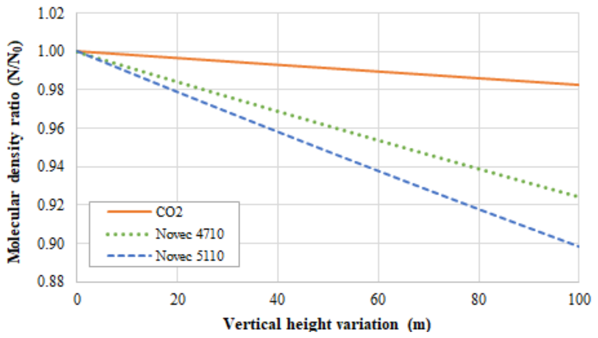


Figure 5. Molecular density ratio of pure gases as the function of vertical height

This difference in pure gas density as a function of height has led to the question of whether the mixtures containing the Novec Insulating Gases could separate vertically over time. Gas separation has not been observed experimentally. A gas mixture containing Novec 4710 gas and CO_2 was stored in a 2-meter vertical tube at -15°C for 6 months with no change in composition detected over the height of the tube [9]. This result can be explained theoretically if one applies the preceding analysis to a gas mixture.

From (6), for a mixture of gas A (e.g. Novec 4710 gas or Novec 5110 gas) and gas B (e.g. CO_2), the mixing ratio (ratio of the number of gas molecules) varies with height that can be expressed by (7).

$$\frac{N_A/N_B}{N_{A_0}/N_{B_0}} = \frac{N_A/N_{A_0}}{N_B/N_{B_0}} = e^{-(h-h_0)\cdot(\frac{1}{H_{AB}}-\frac{1}{H_{AB}})} \qquad (7)$$

$$H_{AB} = \frac{R\cdot T}{M_{AB}\cdot g} \qquad (8)$$

where, N_A is the gas A vol.% at height h, N_B is the gas B vol.% at height h, N_{A0} is the gas A vol.% at baseline height h_0, N_{B0} is the gas B vol.% at baseline height h_0.

H_{AB} is the scale height of gas mixture A and B which is dependent on M_{AB}, the average molecular weight of the gas mixture containing gas A and gas B. H_{AB} is therefore the same for both components and the exponential in (7) is equal to 1. Thus, N_A/N_B is equal to N_{A0}/N_{B0}, meaning a mixture of gas A and gas B does not change with height. This is because the pressure exerted by the column of gas mixture above any molecule of either A or B is the same, resulting from the density of the gas mixture rather than the density of any individual pure gas. A similar conclusion was reached in the 1982 EPRI Report EL-2620 [10]: "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."

It should be noted that when filling a device with two or more gases, the time required for complete inter-diffusion of the gases at room temperature and pressure can be quite long, possibly on the order of days, if not premixed when filling the device. Lower temperatures, higher pressures and the geometric complexity of the volume to be filled can all increase the time required for mixing. But once mixed, the gases do not separate unless exposed to temperatures below their dew point (condensation temperature).

TOXICOLOGICAL PROPERTIES AND EXPOSURE ASSESSMENT

The safety of Novec Insulating Gases has been evaluated through a series of toxicological tests [11, 12]. The compounds have demonstrated low toxicity in acute inhalation studies. The 4-hour rodent (rat) LC_{50} (lethal concentration at 50% mortality) is between 10,000 ppmv and 15,000 ppmv for Novec 4710 gas and 14,000 ppmv and 20,000 ppmv for Novec 5110 gas. Based on the results of a number of tests, including 28-day repeat dose inhalation studies, the Novec Insulating Gases were found to also be low in repeat dose inhalation. Both Novec gases were found to be not mutagenic in bacterial reverse mutation assays. Considering the results of all these tests, the 3M Medical Department has established 8-hour time weighted average (TWA) occupational exposure limits (OEL) of 65 ppmv and 225 ppmv for Novec 4710 gas and Novec 5110 gas, respectively.

The OEL is designed to represent conditions under which it is believe that nearly all workers may be repeatedly exposed over a working lifetime without adverse health effects. It is set to protect human health based on a worker's exposure to the material for eight hours a day, five days a week, 52 weeks a year, for an occupational lifetime typically assumed to be 30 years or more.

Workplace airborne SF_6 concentrations observed in indoor gas-insulated switchgear applications are 20 ppbv in summer, 60 ppbv in winter, and 200 ppbv during equipment maintenance [13]. Typical airborne concentrations measured during gas transfer operations have been measured at less than 10 ppmv. These concentrations are far below the occupational exposure limits of 65 ppmv for Novec 4710 gas and 225 ppmv for Novec 5110 gas providing a sufficient margin of safety in these applications.

Safety assessments have also been conducted to evaluate representative degradation products that could be formed in gas mixtures containing the Novec Insulating Gases. These assessments considered the by-products that have been identified under conditions of normal use as well as fault conditions. In each case, the hazards associated with the Novec Insulating Gas mixtures were no greater than those posed by used SF_6 which is currently operating in GIE today [14, 15].

CONCLUSIONS

Novec 4710 and Novec 5110 Insulating Gases are high dielectric strength compounds that are atmospherically much shorter lived than SF_6. The shorter atmospheric lifetimes result in much lower GWPs which leads to substantially reduced greenhouse gas emissions from gas-insulated, electric power equipment.

Gas mixtures with lower Novec 4710 and Novec 5110 Insulating Gas concentrations can achieve relatively low condensation temperatures approaching that of pure SF_6. These gas mixtures maintain relatively high dielectric breakdown voltages due to the high positive surface area and strong electron absorption capacity of the Novec Insulating Gas molecules.

In the absence of condensation, a gas mixture containing Novec 4710 or Novec 5110 Insulating Gas and inert gases such as air or CO_2 will not separate into its component gases over time based on height even though the molecular weights of the component gases are significantly different.

Based upon a range of toxicological studies, the 3M Medical Department established occupational exposure limits of 65 ppm (8-hour time weighted average) for Novec 4710 Insulating Gas and 225 ppm (8-hour time weighted average) for Novec 5110 Insulating Gas. These occupational exposure limits provide a sufficient margin of safety in the application of Novec Insulating Gases in power transmission and distribution industries.

In summary, this combination of safety, physical, and environmental properties make 3M Novec 4710 and Novec 5110 Insulating Gases sustainable alternatives to SF_6 in many dielectric gas applications.

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