

Hazard study of medium-voltage switchgear with SF₆ alternative gas in electrical room

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Abstract: This study presents the risks generated by the use of the alternative gases to SF₆ for people working on medium voltage electrical equipment or close to these apparatus and the precautions to be taken in order to ensure the safety of people. The acute toxicity of fluoronitrile and fluoroketone being more important than the SF₆, more precautions must be taken in order to ensure the safety of people in case of gas leakage. On the other hand, the level of toxicity of HFO1234zeE is similar to SF₆ and precautions to be taken are then same as for SF₆.

1 Introduction

SF₆ has been widely used since the 1950s in high- and medium-voltage (MV) electrical equipment as insulating and/or breaking medium without any issue regarding toxicity, flammability etc. Its by-products can be very toxic in case of numerous breaking operations but their concentrations are low thanks to the ability of SF₆ to recombine itself and to the presence of molecular sieve. Despite its interesting properties, this gas contributes to the greenhouse effect and, for this reason, some alternative candidates were identified to replace it: fluoroketone (C₅F₁₀O), fluoronitrile (C₄F₇N), trifluoroiodomethane (CF₃I), hydrofluoroolefin (HFO1234zeE: C₃H₂F₄) etc. CF₃I was the first serious candidate to replace SF₆. It was studied for several years by Nguyen [1] showing a great behaviour of this gas mixed with CO₂ in dielectric and arc quenching applications. The oxidation of materials due to the presence of iodine and the fact that CF₃I is potentially mutagenic showed the limits of this fluorinated gas which is not currently considered as 'good' candidate to replace SF₆. Since 2012, many publications were written on fluoroketone (CAS N°: 756-12-7) [2–4], fluoronitrile (CAS N°: 42532-60-5) [5–7], trifluoroiodomethane (CAS N°: 2314-97-8) and hydrofluoroolefin (CAS N°: 1645-83-6) [8–10]. The publications deal with the electrical characteristics of these gases and electrical equipment filled with these gases, or deal with the methods of validation [11, 12]. They do not mention the safety risks generated by the use of these gases for people working on these electrical equipment, close to these apparatus or in the surrounding area.

Thus, in order to answer to the questions of safety of people potentially in contact with one of these gases or with their by-products, studies were conducted at independent laboratories specialized in toxicology and prevention of industrial risks. This paper presents the safety risks relative to MV switchgear with SF₆ alternative gas in electrical rooms such as testing laboratories, manufacturing plants and electrical substations within public building coming from toxicity aspects determined by experimentation on animals. It presents the methods for the experimental characterization of gas toxicity, the determination of the gas concentration in the surroundings of a potential leakage, risks assessment and precautions to be taken to ensure people safety. Then, it shows an example of safety risks for MV electrical switchgear filled with SF₆ and new gases.

2 The method

2.1 Gas analysis

The gas or gas mixture is analysed by Fourier transform infrared spectroscopy (FTIR), gas chromatography-mass spectrometry (GC-MS) and fluorine-19 nuclear magnetic resonance (19F-NMR) spectroscopy to identify the pure gas, its impurities and the possible by-products, and the products that can appear after further reactions. A measurement of the total acidity of the gas is also performed. The analysis devices must be suitable to the gases potentially present in the gas mixture. Indeed, for instance, a non-suitable GC-MS column does not enable the detection of perfluoroisobutene (PFIB) which is a very toxic gas. That is why the analysis of gases cannot be sufficient to determine the toxicity of the mixture of gases and tests on animals are then necessary.

2.2 Determination of the LC50 toxicity and carcinogenic, mutagenic and reprotoxic (CMR) characteristics

The toxicity is assessed by the determination of LC50 on mice and CMR tests on nematodes.

The acute toxicity of the gas is determined by the assessment of the LC50 (50% lethal concentration means that the concentration of a chemical in air or a chemical in water causes the death of 50% [one-half] of a group of test animals within a specified time) according to the No. 403 guideline of Organisation for Economic Co-operation and Development (OECD) with a minimum of three concentrations.

Groups of five male and five female 'SWISS CD1' mice aged 8–14 weeks are adapted to accommodation and test device during 5 days. For each gas concentration, a group of five males and five females are exposed for 4 h to a mix of breathable air and gas. After exposure, every day the laboratory measures the weight of the mice and does a clinical examination and calculates the rate of mortality. Following the death of an animal or after the end of 14 or 28 days period of observation, an autopsy is done. The liver, kidneys and lungs are observed. Biochemical analyses (transaminase, creatinine, alcalin phosphatase and urea) are performed after having sampled blood by intracardiac way. In

parallel, two groups of male and female mice are exposed to breathable air as control sample.

The test organism *Caenorhabditis elegans* (Maupas, N2 var Bristol) is a non-parasitic free living bacterivorous nematode that is primarily found in terrestrial soils. This model organism gives several advantages. *C. elegans* is a well-studied organism that allows quantitative observations [13]. It is easy to cultivate, fully transparent for microscopic observations, with a tiny size (1 mm) and presents a fixed number of cells (959). Moreover, *C. elegans* shows a short average duration of life with both a fast development and a big fertility (one adult can yield 300–350 descendants). *C. elegans* can breed in either aqueous or solid medium. An interesting particularity for toxicity assessment and also very useful because fluorinated gases are not water soluble. It is believed that the Ames test (in vitro test with *Escherichia coli* bacteria) is performed in aqueous media. Moreover, bacteria and human are evolutionary well distant. As a consequence, the Ames test is not suitable for gases studies. The *C. elegans* model allowed us to study toxicity, mutagenicity and cancerogenicity of new gases. To define toxicity of gases, nematodes are exposed to gases and their survival is monitored during 7 days. To determine potential mutagenicity of gases, nematodes were submitted to gases and their progeny counted and observed (malformations, abnormal phenotypes, abnormal number of male etc.). A mutant strain of nematode (*glp-1*) was used for a first evaluation of the cancerogenicity of these gases.

2.3 Assessment of an 'estimated short-term exposure limit' of the gas mixture

There are no occupational exposure levels available neither for the studied gas mixtures nor for most of their compounds. To estimate exposure limits to workers, an empirical method has been proposed. It consists in trying to find a typical ratio between LC50% (on rats or mice) and the existing French occupational exposure levels like French VLEP 'valeurs limites d'exposition professionnelle' or VLCT 'valeurs limites court terme' (corresponding to American TLV-TWA 'threshold limit value-time weighted average' or TLVSTEL 'short-term exposure limit') from a range of well-documented substances structurally comparable to compounds found in gas mixture (mostly fluorinated and cyanide compounds) and for which similar toxicity mechanisms are expected. As the exposure situations of interest are mostly short-term exposures due to accidental emissions of gases, we focus on the ratio between LC50% and French VLCT instead of VLEP. It appears from the analysis that there is a large variability of the ratio LC50%-4 h/VLCT from one substance to another: depending on the selected substances, the ratio appears to vary from 5 to 30. Therefore, it is not statistically sound to determine a single generic value for that ratio. This variability may be partly explained by the fact that methods to determine TLV also introduce nontoxicological criteria according to the socioeconomic context. Nevertheless, in order to help decision making, a potential protective ratio of 30 is chosen in this study to get 'estimated short-term exposure limits' for gas mixtures whose LC50%-4 h is known. As an example, this means that for a mixture mostly composed of fluorinated and cyanide compounds (except carbon oxides and inert gases) with LC50%-4 h = 3000 ppm, the estimated short-term exposure limit' is $3000/30 = 100$ ppm.

It is important to keep in mind that this approach has no toxicological or statistical rigorous base. It should be seen as a tool for decision making and not as a toxicologically sound method to determine occupational exposure limits.

2.4 Calculation of the gas concentration in the electrical room

Numerical simulations of accidental gas releases have been performed to estimate the resulting concentration levels in the surrounding ambient air. DNV-GL's software PHAST (v7.11) was used. This widely used software is dedicated to simulate the

effects of hazardous phenomena for industrial safety concerns like aerial dispersion of toxic gases. The implemented models can simulate turbulent jets, passive or dense gas dispersion and other mechanisms. Yet, as implemented models are based on simplified assumptions and equations, no obstacle effect could be simulated. Therefore, in this study, aerial dispersion is simulated without any walls or congested area in the building.

The evolution of gas concentration as a function of the distance from the release point is calculated, depending on initial pressure and gas volume in the electrical equipment, assuming passive behaviour of the gas. Based on a series of calculations, generic curves have been built. The results are illustrated in Figs. 1 and 2, for two internal pressure values and volumes from 15 to 300 l.

2.5 Assessment of risks for people in case of a gas leakage

Concentration fields estimated in Section 2.4 and 'estimated short-term limits' determined by the approach described in Section 2.3 enable the delimitation of safety areas in the surrounding of an equipment containing gas, by considering that there is a risk for people whenever the local concentration becomes higher than the 'estimated short-term limit'. This approach enables to elaborate safety plans for collective or individual protection and risk prevention.

It should be kept in mind that the 'estimated short-term limits' suggested here could not be used for other purpose than accidental short-term exposure, as they are deduced from short-term acute toxicity exposure levels (LC50%-4 h). Possible CMR effects due to repeated exposure are not taken into account.

2.6 Precautions to be taken to ensure people safety

Protection and prevention precautions can be taken for the safety of workers and people surrounding the area.

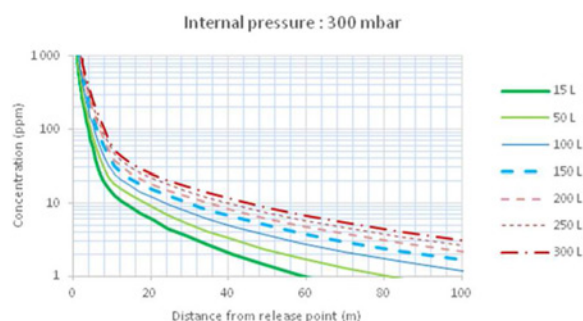


Fig. 1 Gas concentration versus distance from release point, for volumes from 15 to 300 l and an internal pressure of 300 mbar relative in the equipment

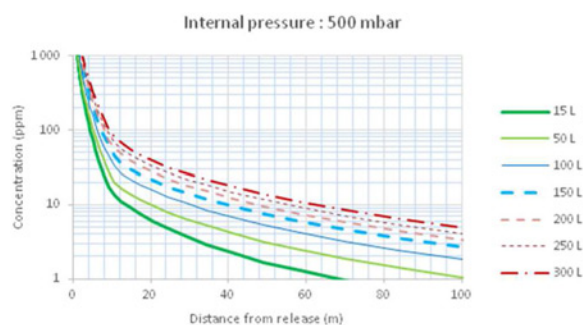


Fig. 2 Gas concentration versus distance from release point, for volumes from 15 to 300 l and an internal pressure of 500 mbar relative in the equipment

The main safety principles are the following:

- Giving clear information to people (dangers in the vicinity of the equipment, safety perimeters, safety instructions and recommendations etc.).
- Controlling the access to delimited safety areas.
- Training operators, safety clearance.
- Using appropriate gas sensors for leakage detection.
- Extracting/channelling gas leakages to a safe location.
- Providing suited individual protection equipment when necessary (gas mask, self-contained breathing apparatus etc.).

Collective prevention and protection precautions should be given priority over individual protection device.

3 Application to MV electrical equipment

This chapter aims to define the risks for people present in electrical rooms such as testing laboratories, manufacturing plants, and electrical substations within public building from characteristics of fluorinated gases known as potential candidates to the replacement of SF₆ in MV equipment. These risks due to gases, which could be used as dielectric medium or dielectric and arc quenching medium, are compared with SF₆ (Table 1).

3.1 Determination of pure gas toxicity

LC50 and CMR tests are performed according to Section 2.2. To see if there is a severe mortality of mice after the 14 days observation period, a second test is performed with a period of observation of 28 days (Table 2).

3.2 Determination of the gas mixture

For certain fluorinated gases the boiling point is too high to be used alone. It is then necessary to mix it with one or several buffer gases such as N₂, dry air, CO₂, CO₂ + O₂. A mix with a common gas will lead to a lower value of LC50 by dilution. This value could be measured by tests on animals or calculated in case of a dilution with air. The CMR characteristics of the mix remain the same by definition (because mutagenic, carcinogenic and reprotoxic effects are non-threshold effects unless otherwise specified).

Table 1 List of potential pure fluorinated candidates alternative to SF₆

Pure gas	CAS number	Supplier	Purity according supplier, %
sulphur hexafluoride SF ₆	2551-62-4	Inventec or Solvay	<99,9
fluoroketone C ₅ F ₁₀ O	756-12-7	Apollo Scientific	98
hydrofluoroolefin HFO1234zeE	1645-83-6	Inventec	99
fluoronitrile C ₄ F ₇ N	42532-60-5	P&M Invest – fluorine1	99,8

Table 2 Results of tests of toxicity performed on mice and C-elegans nematodes to assess the dangerousness of the pure gas

Pure gas	LC50 (4 h) according to MSDS, %	LC50 (4 h) on mice after 28 day	Main manifestation on mice	Results from C.elegans tests
SF ₆	>60	>60%	none	Not CMR
C ₅ F ₁₀ O	>1,9	will be defined	will be defined	Will be defined
HFO1234zeE	>21	>21%	none	Not CMR
C ₄ F ₇ N	<1	will be defined	will be defined	Will be defined

Table 3 Definition of the gas mixture for a minimum temperature of operating of –15°C

Pure gas or gas mixture defined (at 20°C) to operate at –15°C	SF6	C5F10O (0,18 b) + dry air	HFO 1234zeE	C4F7N (0,75 b) + dry air, %
LC50 4H (14 days) according to MSDS	>60%	>14.4%	>21%	<1.73
estimated short-term exposure limit	>2%v	>0.48%	>0.7%v	<0.06

Table 3 gives the values of LC50 (4 h) calculated from the results of the table and the values of the ‘estimated short-term exposure limit’ (according to assessment method of Section 2.3 for an MV equipment filled with 1.3 bar abs of ‘gas’).

The LC50 4 h of a –15°C mix (concentrations of gases are the same from high temperature down to –15°C) based on fluoronitrile is <2%, a value currently defined to be a limit of acceptable toxicity [7].

Table 4 Evaluation of a safety perimeter in case of an accidental release of pure gas mixture and definition of the precautions

Gas mixture for an application at –15°C	LC50 (4 h) calculated, %	Estimated short-term exposure limit, %	Distance of safety (D _s), m	Precautions
SF ₆ (1.3 bar abs)	>60	>2	<0.3	none
C ₅ F ₁₀ O (0.18 bar) + dry air (1.12 bar)	>14.4	>0.48	≈1	safety perimeter, local ventilation, gas detector and alarm system
HFO1234zeE (1.3 bar)	>21	>0.7	≈0.5	none
C ₄ F ₇ N (0.75 bar) + dry air (0.55 bar)	<1.73	<0.06	≈4	safety perimeter, local ventilation, gas detector and alarm system

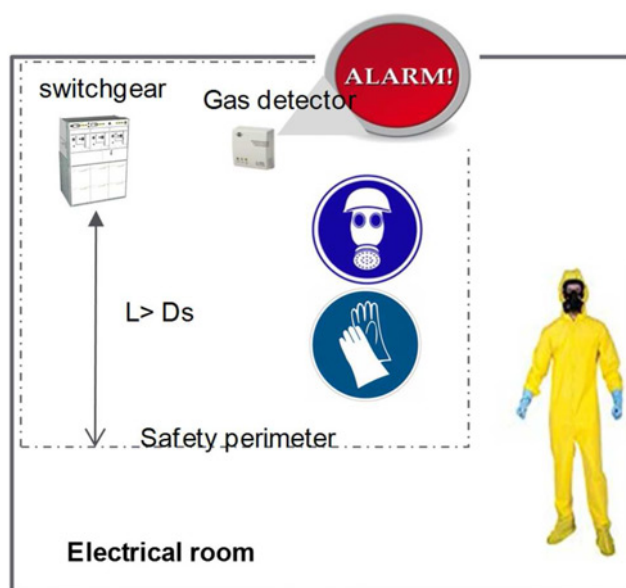


Fig. 3 Representation of an electrical room with the safety perimeter around the electrical switchgear

Table 5 Evaluation of a safety perimeter in case of an accidental release of gases after breaking and definition of the precautions

Gas mixture after breaking	LC50 (4 h)	Estimated short-term exposure limits	Distance of safety (D_s)	Precautions
fluorinated gas + dry air (mix – 15°C)	0.2%	0.0067%	≈10 m	Carry self-contained breathing apparatus + gloves + detector and alarm system

3.3 Gas concentration field around the apparatus

According to the method presented in Section 3.4, the decrease in gas concentration from the leaking point to a few tens of metres in the vicinity of the equipment can be determined.

3.4 Evaluation of risks for people

Different scenarios are studied in order to assess the risks for people in the case of severe leakage. A safety distance (D_s) is determined. Inside this safety perimeter, precautions are necessary to prevent all accidents.

Example 1: Release of overpressure from a GIS (250 l, $P_{\text{initial}} = 1.3$ bar abs, breaking by vacuum interrupter: assumption: no by-product) in a substation. The leakage is assumed to last 60 s. Table 4 shows the precautions to be taken to ensure the safety of people in case of gas leakage. In the absence of gas detector and alarm system, people must carry gas mask or self-contained breathing apparatus inside the safety perimeter (Fig. 3).

Example 2: Release from an AIS (20 l, $P_{\text{initial}} = 1.5$ bar abs, breaking in gas: assumption: LC50 (4 h) = 0.2%) in a substation; the leakage is assumed to last 10 s. Table 5 shows the precautions to be taken to ensure the safety of people in case of gas leakage.

In case of leakage, the risks of acute intoxication for people close to the electrical equipment without individual safety protection are very high when the gas ensures the arc quenching.

In the case of an accidental release of pure gas (leakage due to a defective pipe, bottle or connections) during the filling, the topping-up or refilling steps, the safety distance may be quite high and people inside this safety perimeter must carry suitable personal protective equipment (gas mask, gloves etc.)

When the gas is used for arc quenching, the by-products and their concentration depend on the materials in the breaking chamber and current and arc voltage values. Some of these by-products can be very toxic and it is then necessary that people inside the safety perimeter carry self-contained breathing apparatus

4 Conclusion

These studies demonstrate that some fluorinated gases are able to substitute SF₆ for dielectric and arc quenching performances have, when they are pure, a high acute toxicity. The acute toxicity of pure C₄F₇N is high. This gas can be considered as toxic according to Hodge and Sterner scale. The CMR characteristics of this gas are not entirely known. The acute toxicity of C₅F₁₀O is lower than C₄F₇N and the gas is considered as 'not toxic' according to Hodge and Sterner scale. The CMR characteristics of this gas are not entirely known either. Contrary to both previous gases, the same tests performed on HFO1234zeE demonstrate a low acute toxicity

of this gas, similar to SF₆. In addition, HFO1234zeE is not carcinogenic, mutagenic or reprotoxic as SF₆.

In the case of accidental release of fluoroketone or fluoronitrile gases, the calculation of the gas dispersion inside an electrical room and the criteria usually retained to assess industrial risks show that there is a significant risk for people who could be exposed to these pure gases or in mixture with a buffer gas like air or CO₂. The risk is still higher when people breathe the by-products of these gases used for arc quenching.

Preventive and protective precautions for the safety of the people are proposed: safety perimeter, containment, ventilation, collective or individual protective equipment, gas detection, alarm system, gas extractions etc. These precautions can be taken for the testing laboratories and the manufacturing plants. Additional precaution should be taken if the fluorinated gas is reported as CMR.

Regarding HFO1234zeE, because its toxicity is well known and very low contrary to fluoroketone and fluoronitrile and is of the same order as SF₆, the safety measures to be taken are identical to SF₆.

Even if the environmental impact is a key parameter to consider, replacing a non-toxic and greenhouse gas like SF₆ (which has an impact once released in atmosphere) by a more toxic gas with a lower environmental impact is largely questionable for MV switchgear applications.

5 References

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