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 fluoroacetone 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, among others, 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, among others, SF₆ has been typically replaced by alternative gases in the past decades. However, new gases are currently studied for their potential to replace SF₆.

2 The method

2.1 Gas analysis

The gas mixture is analysed by Fourier transform infrared spectroscopy (FTIR), gas chromatography-mass spectrometry (GC-MS) and fluorne-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-suited CG-MS column does not enable the detection of perfluorosobutene (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) 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 specific 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 males and five females ‘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, alkaline 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 bacteriovorous 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 carbonyl 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 toxics 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](image1)

![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](image2)
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. 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 1 List of potential pure fluorinated candidates alternative to SF₆

| Pure gas                  | CAS number | Supplier           | Purity according supplier, % |
|---------------------------|------------|--------------------|------------------------------|
| sulphur hexafluoride      | 2551-62-4  | Inventec or Solvay | <99,9                        |
| SF₆                       | 756-12-7   | Scientific         | 98                           |
| fluoroketone C₅F₁₀O       | 1645-83-6  | Invenetc           | 99                           |
| hydrofluoroolefin HFO1234zeE | 42532-60-5 | P&M Invest         | 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 |
|----------|--------------------------------|---------------------------------|---------------------------|-----------------------------|
| SF₆      | >60                            | >60% will be defined            | will be defined           | Not CMR Will be defined     |
| C₅F₁₀O   | >1,9                           | >21% will be defined            | will be defined           | Not CMR Will be defined     |
| HFO1234zeE | >21                           | >21% will be defined            | will be defined           | Not CMR Will be defined     |
| C₅F₁₀N   | <1                             | <1 will be defined              | will be defined           | Will be defined             |

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 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 | HFO1234zeE | C₅F₁₀N |
|---------------------------------------------------------------|-----|--------|------------|--------|
| LC₅₀ 4H (14 days) according to MSDS estimated short-term exposure limit | >60% | >14.4% | >21% | <0.7v |
| Safety perimeter, local ventilation, gas detector and alarm system | none | ≥1 | none | ≥4 |

**Fig. 3** Representation of an electrical room with the safety perimeter around the electrical switchgear.
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 \( (D_e) \) 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 SF\(_6\) for dielectric and arc quenching performances have, when they are pure, a high acute toxicity. The acute toxicity of pure C\(_4\)F\(_7\)N 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 C\(_4\)F\(_7\)N 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 SF\(_6\). In addition, HFO1234zeE is not carcinogenic, mutagenic or reprotoxic as SF\(_6\).

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 CO\(_2\). 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 SF\(_6\), the safety measures to be taken are identical to SF\(_6\).

Even if the environmental impact is a key parameter to consider, replacing a non-toxic and greenhouse gas like SF\(_6\) (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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