COMPARISON OF ALTERNATIVES TO SF_6 REGARDING EHS AND END OF LIFE

Christophe PREVE
Schneider Electric – France
christophe.preve@schneider-electric.com

Daniel PICCOZ
Piccoz SASU – France
piccoz@orange.fr

Romain MALADEN
Schneider Electric – France
romain.maladen@schneider-electric.com

ABSTRACT

This paper proposes a complete overview of environmental and health parameters to consider during qualification of a new gas, gives an inventory of existing and missing data and makes recommendations for its handling and end-of life management.

INTRODUCTION

Because of its very high Global Warming Potential (GWP) and the potential creation of toxic by-products in some cases, SF_6 has to be recovered at the end of life of equipment according to the European regulation EU 517/2014. For medium voltage switchgear this action is particularly critical to implement due to the large number of locations of MV substations throughout any European countries. Recovery, transportation and recycling have also an environmental impact that should be assessed.

Several SF_6 alternative gases with much lower GWP have been investigated during the recent years [1]. Their physical properties such as dielectric strength, electric arc breaking capability, saturation vapor pressure curves and material compatibility are now well documented, but other aspects must also absolutely be considered before using these gases in a large scale for the next decades. Among them a complete environmental and toxicity assessment is mandatory to validate these new gases and then to avoid replacing a concern by another one.

Three alternative gases or gas mixtures are investigated using these criteria: HFO1234zeE (CAS 29118-24-9), mixture of fluoronitrile C_4F_7N (CAS 42532-60-5) with air and mixture of fluoroketone $C_5F_{10}O$ (CAS 756-12-7) with air. More details about possible gas mixtures compositions for MV applications are given in the table 1.

	Gas mixture		
Fluorinated gas	HFO1234zE 1,300 bar	C5F10O 0,250 bar	C4F7N 0,740 bar
Buffer gas	-	Air 1,050 bar	Air 0,560 bar
Minimum operating temperature	-15°C	-5°C	-15°C

Table 1: Considered gas mixtures

ENVIRONMENTAL IMPACT

Global warming

The Global Warming Potential (GWP) is an index to evaluate the relative contribution to global warming of the emission of 1kg of greenhouse gases compared to the emission of 1kg of carbon dioxide (CO_2) during a specified period which is in general 100 years. It assesses the potential warming of a greenhouse gas based on its lifetime in the atmosphere and its ability to absorb infrared radiation.

Several methods to evaluate this parameter exist, the latest one being described in the fifth assessment report proposed by the Intergovernmental Panel on Climate Change (IPCC) in 2014 is used as reference in this paper.

This environmental impact is probably the most known because of numerous scientific papers and regulations published in the recent years in the scope of the global warming concern.

C_4F_7N and $C_5F_{10}O$ are brand new gases and they are not listed in the fifth IPCC assessment report. Therefore, they are not yet mentioned by any of current Global Warming regulations including EU 517/2014, but it may happen in the future.

Regarding the end of life and to simplify the recycling process, the temptation is high to release in atmosphere all the alternative gases or gas mixtures because, as presented in table 2, they have a much lower GWP, and then low (Fluoronitrile) or negligible (Fluoroketone, HFO) impact on climate change.

	SF6	HFO1234zeE	C5F10O	C4F7N
GWP (100-yr ITH, IPCC AR5)	23500	<1	< 1	2100
Atmospheric lifetime (years)	3200	0,05	0,04	30

Table 2: Global warming impact

Other environmental impacts

However, and even if the main environmental concern to tackle is mainly driven by the reduction of global warming impact since the protocol of Kyoto in 1997, it must be kept in mind that global warming is just one environmental impact among many others.
Indeed, and even if numerous Life Cycle Assessment (LCA) methods exist, the following environmental impacts are generally considered:

- climate change (global warming)
- destruction of ozone layer
- acidification (water and soils)
- eutrophication
- formation of photooxidants (smog)
- reaching abiotic resources
- reaching biotic resources
- land use
- eco-toxicological impact
- toxicological impact (in humans)

It is then imperative to consider all environmental impacts when validating SF_6 alternatives in order to avoid any possible future regulation evolution in the coming years and then search again alternative solution to the alternative solution! Because of past environmental concerns such as the hole in the ozone layer in the eighties, some of them like Ozone Depletion Potential, appear to be obvious to be considered but most of the other impacts are not regulated and then less known but not necessarily less impacting for the environment.

Decomposition in the atmosphere

As seen in the table 2, all considered fluorinated alternative candidates to replace SF_6 have a much lower GWP, which is also linked to their very limited lifetime in the atmosphere: a few days for HFO1234zeE and Fluoroketone $C_5F_{10}O$ and 30 years for Fluoronitrile C_4F_7N. From a chemical point of view, this very short lifetime of new candidates in the atmosphere is due to their low chemical stability brought by the presence of a multiple bond in their structure. Keeping in mind that GWP is calculated over a long period, typically 100 years, a molecule that does not exist anymore in the atmosphere after a few days cannot have a high GWP.

However, once this fact is considered, the question that should come just after is: what become with the broken molecular chains of the initial molecules when they decompose into the atmosphere?
Regarding the branched perfluoroketone $C_5F_{10}O$ and as illustrated in the figure 1, D. Jackson et al. demonstrated [2] that its decomposition in the air is done according to a radical mechanism initiated by the light energy. The main element of degradation obtained is trifluoroacetic acid (TFA). There is also the appearance of a perfluorocarboxylic acid: i-PFBA. A release of ozone as well as hydrofluoric acid is also observed. The half-life of this reaction is around 1 to 2 weeks.

After its production in the atmosphere, TFA is rapidly partitioned into water droplets and falls down on land and oceans via wet precipitation (rain, snow and fog).
TFA is of particular concern as it is a persistent toxic pollutant [3] and it is assumed that no degradation of TFA is likely to occur in the environment [4].
TFA is classified as "Harmful to aquatic life with long-lasting effects" in its material safety datasheet. In addition, as TFA is a strong acid, it readily forms trifluoroacetate salts with minerals in soils and surface waters. Among them, ECHA (2017) mentions that sodium trifluoroacetate is known to be very toxic to aquatic life with long lasting effects.

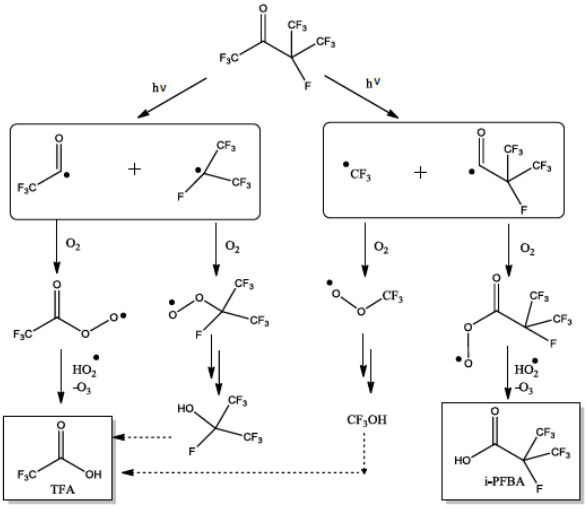

Figure 1: Atmospheric decomposition path of C5FK

For HFO1234ze(E), its REACH registration dossier states that it is degraded in the atmosphere by a hydroxyl radical initiated oxidation that finally leads to the formation of trifluoroacetaldehyde (CF_3CHO) and formyl fluoride (HC(O)F), a decomposition path (Figure 2) illustrating this degradation is proposed by Javardi et al [5].

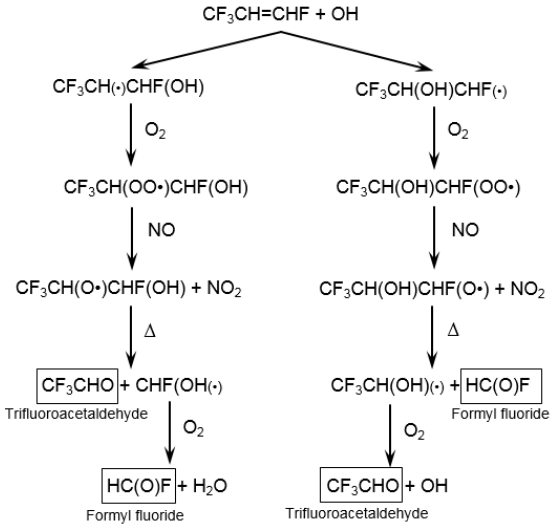

Figure 2: Main atmospheric decomposition path of HFO1234zeE

These atmospheric degradation paths illustrate that several final by-products are generated by the potential alternatives to SF_6 for MV switchgear. Obviously, the environmental impact of these by-products must then be considered. For some of them, such as TFA, environmental hazards are clearly identified. For the other ones, a lack of available data does not allow to conclude on their real environmental effect, reason why, by precautionary principle, any release in the atmosphere should be avoided.

HEALTH AND SAFETY

New gases

In addition to technical performances and environmental impacts, toxicity of alternative gases is a key input to consider during their validation process. Some toxicity properties such as acute toxicity, which describes the adverse effects resulting from a single exposure to a high concentration of a substance or by opposition, the chronic toxicity, which represents the development of adverse effects as a result of long term exposure to low concentration of a contaminant are generally well documented in the literature making possible a direct comparison of the new candidates with SF_6.

As illustration, the graph below compares short time toxicity of the main identified pure fluorinated alternative gases to SF_6 [6].

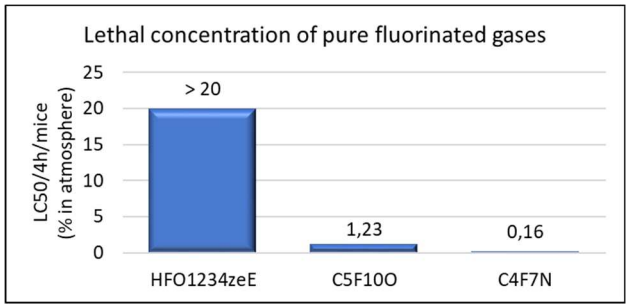

Figure 3: Lethal concentration of pure fluorinated gases

In a second time, as illustrated in figure 4, a toxicity estimation of the gas mixtures that may be used for MV application was done.

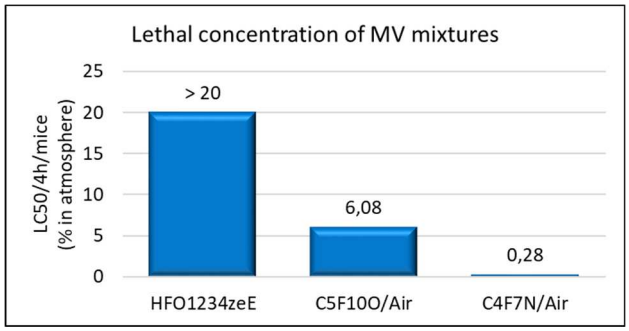

Figure 4: Lethal concentration killing 50% of gas mixtures

In parallel to these basic information, carcinogenic, mutagenic and reprotoxic (CMR) effects of the new candidates must also absolutely be well known in order to guarantee the long-term health of people, such as operators or users, who potentially may be exposed to these gases. Taking the example of the European REACH regulation ((EC) No 1907/2006), many different mutagenicity tests are proposed depending on imported quantities. The table 3 below summarizes mutagenicity tests that must be considered depending on the yearly imported quantities of a chemical in the European Union. It shows the situation for SF_6 and alternative gases. For alternative gases, annex IX should be considered (quantity > 100t and < 1 000t) in order to not take the risk that a gas is accepted for pilots and after rejected for mass application. It is important to note that depending on some results all tests are not always requested but the point must be covered.

	Annex			
	VII > 1 t	VIII > 10 t	IX > 100 t	X > 1000 t
	C5F10O C4F7N		HFO 1234ze	SF6
In vitro gene mutation study in bacteria (Ames)	X	X	X	X
In vitro cytogenicity study in mammalian cells or in vitro micronucleus study		X	X	X
In vitro gene mutation study in mammalian cells, if a negative result in Annex VII		X	X	X
In vivo somatic cell genotoxicity			X	X
Second in vivo somatic cell test				X
Potential for germ cell mutagenicity			X	X

Table 3: Mutagenicity requirements according REACH regulation and situation of SF_6 and alternative gases

This table illustrates that the gap between available data is huge between the SF_6 or HFO1234zeE and other candidates such as $C_5F_{10}O$ or C_4F_7N for which very limited mutagenicity information are available.

More disturbing, the in vitro Ames test that is the only one required for limited quantities (less than 10 tons/year) is subject to numerous debates and uncertainties in the scientific community. That is probably the reason why it must be completed by complementary tests for higher quantities whether its result is positive or negative. Among other ones, the main drawbacks published in the literature are those listed below:

- Validity of the correlation between mutagenicity results obtained on bacteria and the intensity of the carcinogenic effect on higher organisms
- Do not detect carcinogens that do not produce lesions on DNA (eg: hormone)

- Do not detect carcinogens acting on the number and chromosome distribution
- Excessive "Simplification" (eg metabolism ...)

For instance, Kirkland et al. [7] published many concrete examples for which Ames and in-vivo tests are contradictory: in some cases, Ames is positive (mutagenic) and in-vivo tests are negative (not mutagenic) and in the contrary, in many other cases, Ames gives negative results while the tested chemicals are known to be mutagenic for humans.

Gases used as arc quenching media

Due to their complex composition (molecules made of at least 9 atoms and 3 different elements) and the presence of a multiple bond in their structure, the new investigated molecules are significantly less stable than SF_6. When subjected to electrical arc, they may generate many different by-products that decompose without recombining themselves into the initial molecule as it happens with SF_6. For this reason, the current breaking involving electrical arc whose temperature exceeds 10.000 K clearly appears as non-pertinent for medium voltage switchgear made of compact cubicles with very limited amount of alternative gas used. It is better to use a combination of vacuum interrupters and sealed insulating alternative gases used as dielectric medium.
As example, breaking tests performed in a conventional load break switch lead to a strong gas decomposition. Despite the tank volume can be questionable (11 litres), the fluorinated gas decomposition rate is very close to published data [8], demonstrating that it mainly depends on the arc energy and not on the arcing chamber of the breaker. Both studies also confirm that low global warming fluorinated gases do not recombine after arcing.

	Test parameters	Number of operations	F-gas consumption (%)	Decomposition rate (mol/MJ)
$C_5F_{10}O$ Air	315A 13 kV	68	42	0,1
C_4F_7N Air	630A 24 kV	100	50	0,3

Table 4: Gas decomposition during breaking tests

In addition, acute toxicity measurements were done on mice with gas samples coming from the tested load break switches and compared with results obtained on pure mixtures. LC50/4h measurements, which represents the sampled gas concentration in air that causes the death of 50% of a group of test animals during an exposition of 4h or during the 14 days after, showed a significant increase of gas toxicity during breaking tests.

	LC50/4h (ppm_v) on mice		
	Pure gas	Mixture before test	Mixture after test
0,25 bar $C_5F_{10}O$ 1,05 bar Air	≈ 12300 1000000	≈ 60800	≈ 2000
0,74 bar C_4F_7N 0,56 bar Air	≈ 1600 1000000	≈ 2800	< 200

Table 5: Gas toxicity comparison

Moreover, the observation of the switchgear after tests showed the presence of solid and liquid by-products which are not present with SF_6 and that polluted the area close to electrical contacts.

Figure 5: Pollution in the contact area with $C_5F_{10}O$ and air gas mixture

END OF LIFE MANAGEMENT

Due to the numerous remaining uncertainties regarding the real overall toxicity and environmental concerns of fluorinated alternative gases to SF_6, it seems mandatory that, as it is done today with SF_6, all these new gases (or mixtures) will have to be recovered and recycled at their end of life.
For gases or mixtures of gases that will be classified as not toxic after the complete toxicity assessment and coming from switchgear where breaking operations are done in vacuum interrupters, a risk assessment still have to be done to determine if they have to be handled as used SF_6 or as inert gases.
In all other cases, the gases will have to be considered as toxic and/or corrosive and adequate precautions will have to be taken: bottles with yellow shoulders, “toxic” label, and respect of transportation rules as defined for example in the ADR, the European regulation dealing with the carriage of dangerous goods by road …

CONCLUSION

This paper illustrates that SF_6 alternative gases have reduced GWP but it does not mean they can be released in the atmosphere at the end of life. Their rapid decomposition will also have an environmental impact. Manufacturers and users should have in mind that the handling of these gases may be regulated in the future and they could not avoid the same end of life cost management as SF_6.
For some of them, (Fluoroketone and Fluoronitrile) the

end of life management may be heavier as their impact on human health are not yet fully known. For example, in Europe, they are at the beginning of REACH process and CMR risks are not yet evaluated. In addition, used as breaking medium, these gases produce a lot of toxic by-products after breaking. High precautions shall be taken for the recovery of the gas and its transportation considering the very high level of their toxicity.
The most preferable solution is to use natural gas, such air, for dielectric medium combined with Vacuum technology for current interruption. Another alternative solution is to use a proven safe gas, such as HFO1234ze, as dielectric medium in association with vacuum interrupters. Its recovery at end of life will not need specific precaution.

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