DECOMPOSITION OF SF_6-FREE GAS MIXTURES BY ENERGY IMPACTS

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ABSTRACT

For in-door application of medium voltage gas insulated switchgear (MV GIS) it is essential to know the environmental, health and safety (EHS) risks caused by the release of the used gaseous dielectric, particularly after degradation due to the arc lightning that comes along with switching operations. SF_6-free and halogen-free gas mixtures that consist of natural gases (main components of ambient air, e.g. N_2, CO_2 and O_2) were tested at different voltage and current levels in this study. Decomposition products of the gas that occurred after switching operations were analyzed by means of Fourier-transform infrared absorption spectroscopy (FTIR) both qualitatively and quantitatively. Concentrations of carbon monoxide (CO) and nitrogen oxides (NO_x) have been detected in the gas samples.

In case of accidental gas release safety related exposure limits will not be exceeded.

INTRODUCTION

Sulphur hexafluoride (SF_6) is the ideal insulation gas currently applied for medium and high voltage gas insulated switchgear. It shows excellent dielectric insulation properties and switching behaviour. The only disadvantage of SF_6 is its high global warming potential (GWP), which has 23,500 times the potential of carbon dioxide (CO_2) [1]. The GWP of CO_2 equals 1. The search for viable SF_6 alternatives as insulation gas has started long time ago. This paper shows the influence of tests impacting energy on alternative gas mixtures of components of ambient air (e.g. N_2, CO_2 and O_2). Those do not contain fluorinated or other halogenated constituents and their GWP is between 0 and 1.

SCOPE

The formation of the following health and safety relevant substances was investigated quantitatively: carbon monoxide (CO), nitrous oxide (N_2O), nitrogen monoxide also known as nitric oxide (NO), nitrogen dioxide (NO_2), and ozone (O_3).

The formation of other substances e.g. higher nitrogen oxides (NO_3, N_2O_4, N_2O_5) and acids (HNO_2, HNO_3) was not expected and was neither observed.

The search for further substances was not explicitly intended however in case of detection of further components they were documented.

TEST CONDITIONS

Test Objects

Test objects are members of the Siemens medium voltage GIS product family. Two switch-disconnector panels have been used referred to as type A for 10kV and 12kV tests and type B for 24kV test.

Gas Mixture

As insulation gas exclusively components of ambient air are used. The gas mixtures are created from dry technical gases of defined purity.

The gaseous dielectric of type A panels is a mixture of nitrogen (N_2), carbon dioxide (CO_2), and oxygen (O_2)[1].

The gas mixture of type B test objects consists of nitrogen (N_2) and carbon dioxide (CO_2)[1].

Table 1: Test condition overview

No.	test object	gas filling	test condition	discharge count
#1	Type B0	N_2, CO_2	TDma 24kV / 16kA	10x
#2	Type B1	N_2, CO_2	24kV / up to 630A	190x
#3	Type B2	N_2, CO_2	TDma 24kV / 21kA	10x
#4	Type B3	N_2, CO_2	TDma 12kV / 25kA	10x
#5	Type A0	N_2, CO_2, O_2	12kV / up to 630A	190x
#6	Type A1	N_2, CO_2, O_2	TDma 10kV / 20kA	10x

Switching Operations

During switching capacity tests sequences of switching

[1] In descending order of volume percentage

operations were applied on the test objects. Relevant for the gas stability in the investigated test setup are electric discharges of the making type. In the voltage range between 10kV and 24kV load making currents up to 630A (all test duties according to IEC 62271-103 except TDma) and short circuit making currents (TDma according to IEC 62271-102/-103) up to 21kA were applied (see Table 1).

Gas samples were taken from the panels before and after the switching capacity tests.

GAS ANALYSIS TECHNIQUES

Gas chromatography-mass spectrometry (GC-MS)

For the analysis of partially decomposed fluorinated gas mixtures gas chromatography-mass spectrometry (GC-MS) is considered most appropriate. The most important advantage of this technique is the separation of the gas mixture on the GC column. This allows detecting pure compounds afterwards with the mass detector and is therefore the preferred method for gas mixtures with many similar gas components. For a good separation of different gas components an appropriate GC column material needs to be selected. Unfortunately there is no single column material which allows good separation of all kind of gas components. Columns allowing a separation of small permanent gas molecules like N_2, O_2, CO, CO_2 do exist, and therefore those gases could be analyzed via GC-MS. However, there mass spectra are less distinct due to their small molecular weights. Reactive molecules like hydrogen fluoride (HF), ozone (O_3) and nitrogen oxides (NO, NO_2) on the other hand can react on the GC column and the latter shows a pressure dependent dimerization reaction ($2\ NO_2 \rightarrow N_2O_4$) which can occur on the GC column. Due to these limitations of GC-MS we decided to use FTIR for the analyses of those molecules.

Fourier-transform infrared spectroscopy (FTIR)

Fourier-transform infrared spectroscopy (FTIR) was applied as the most suitable method for the analysis of ambient air component mixtures. With this analyzing technique numerous infrared active decomposition products of air gases can be well identified, while non infrared active molecules like N_2 and O_2 are not detected. The detection limit and measurement accuracy for a specific gas component very much depends on the instrument configuration (optical path length, spectral resolution, detector noise, …), but also on the overall composition of the gas mixture. However, quantification was focused on the decomposition products considered most relevant.

In order to monitor the actual gas concentrations using FTIR spectroscopy, a Ansyco DX4015 gas analyzer comprising a multi-pass optical cell with a path length of 5m has been used. Spectra have been recorded in the range from 900cm^{-1} to 4200cm^{-1} at a spectral resolution of 8cm^{-1}.

The following figure shows IR spectra recorded for gas samples before and after switching tests compared to reference spectra recorded with defined gas concentrations. From these spectra it can be derived that the gas concentrations are in the range of 29% for CO_2 and 120ppm for CO, respectively.

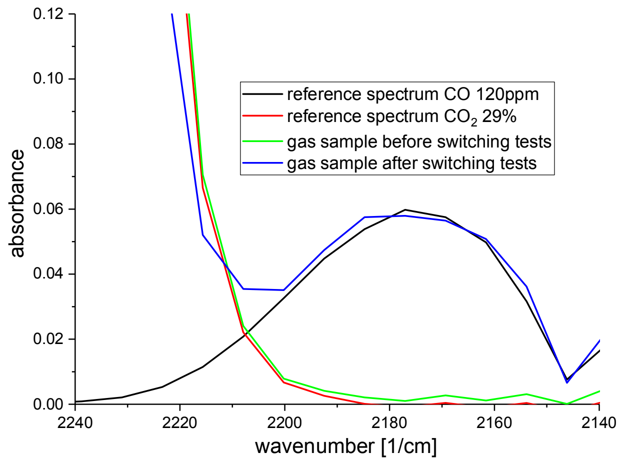

Figure 1: IR spectra recorded for gas samples before and after switching tests compared to reference spectra of known concentrations of CO_2 and CO. Spectral data is presented as absorbance according to the Beer-Lambert law.

Detection limits lower than 1ppm for the respective gas components have been verified using synthetic gas mixtures similar to the gas mixtures used in the switching tests. The resolution of the measurement of concentrations of gas components has been estimated as given in Table 2.

Table 2: Resolution of the applied FTIR gas analysis method for the targeted gas components at a CO_2 background concentration of 35% derived from measurements with synthetic gas mixtures.

gas component	resolution	concentration level
CO	< 1ppm	10ppm
NO	< 0.5ppm	5ppm
NO_2	< 0.5ppm	5ppm
N_2O	< 0.5ppm	5ppm

ANALYSIS RESULTS

The gas samples with and without discharge energy impact were analyzed with FTIR as described.

Table 3: Maximum concentration of gaseous decomposition products after discharge energy impact (background concentrations of the uncharged samples are subtracted[2])

No.	test condition	CO /ppm$_v$	NO /ppm$_v$	NO2 /ppm$_v$	N2O /ppm$_v$
#1	TDma 24kV / 16kA	55	0	15	0
#2	24kV / up to 630A	71	0	0	1.3
#3	TDma 24kV / 21kA	518	9	4.6	0
#4	TDma 12kV / 25kA	180	14	3.7	0
#5	12kV / up to 630A	34	0	0.8	0
#6	TDma 10kV / 20kA	100	7.8	3.9	0

The formation of carbon monoxide could be detected in all charged samples, nitrogen oxides (NO_x) were found in different concentrations. Ozone was not detected. Table 3 shows the concentrations of detected decomposition gases - background concentrations of the corresponding samples before testing are subtracted[2].
The highest concentration of CO is observed for the 24kV sample with the maximum short circuit making current (21kA). All samples from short circuit making tests (TDma) show concentrations of some nitrogen oxides above the detection limit. Only insignificant quantities of NO_x are observed for the samples from load current making tests (#2, #5) however nitrous oxide (N_2O) exceeds the detection threshold in one case, test object #2.
Above certain concentrations the detected substances can be hazardous to health. The gases however are well known, and their physiological effects are comprehensively understood. The acceptable concentration of a hazardous substance in workplace air for a particular material is given by the Occupational Exposure Limit (OEL). Table 4 gives an overview of the 8h OELs of the investigated gases.
In order to evaluate the health and safety risks of the created substances in the switchgear environment the unlikely event of a significant gas leak shall be considered. Therefore, it is assumed that the whole content of the affected panel is distributed inside a closed switchgear room of 30m^3. In such case the resulting

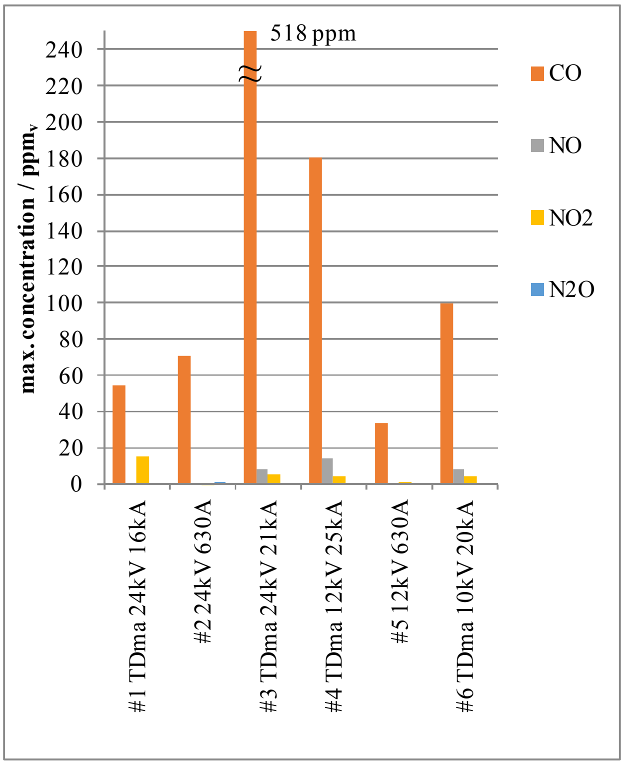

Figure 2: Maximum concentration of gaseous decomposition products after discharge energy impact (background concentrations of the uncharged samples are subtracted[2])

calculated concentrations of the detected decomposition products in the room air are far below the corresponding 8h OELs. This is displayed in Figure 3 where the concentrations are drawn in units of the Occupational Exposure Limits. The highest observed CO concentration (see test object #3) results in a room air concentration of 17% of the OEL of carbon monoxide.

Table 4: Occupational Exposure Limits (8h OELs) of the analyzed gases

Gas		8h OEL /ppm
carbon monoxide [2]	CO	30
nitrogen monoxide [2]	NO	2
nitrogen dioxide [2]	NO_2	0.5
nitrous oxide [2]	N_2O	100
ozone [3]	O_3	0.1

The most significant NO_x concentration that is NO_2 of test device #1 will mean an air concentration of 31% of its OEL in this scenario.

[2] For test objects #1 and #4 no samples were taken before switching capacity tests, so no background concentration was subtracted.

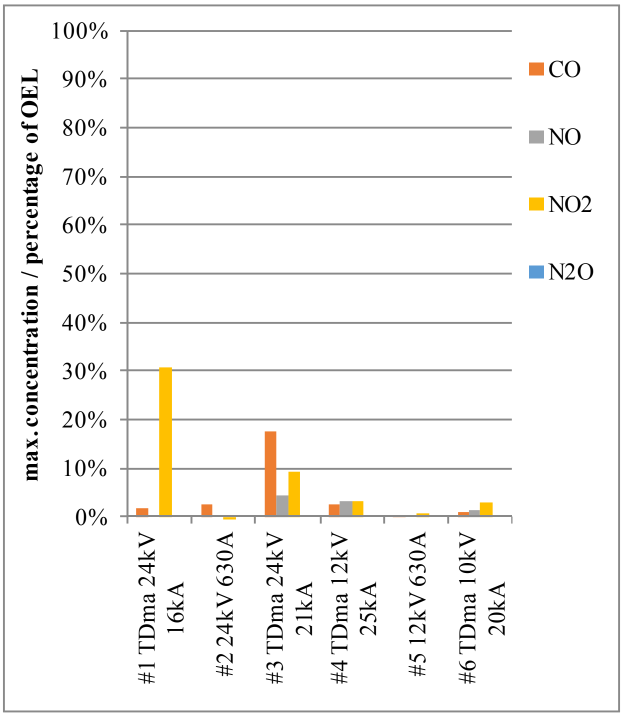

Figure 3: Concentrations in room air in units of the Occupational Exposure Limits (8h OELs) of decomposition products if released to a 30m³ switchgear room

CONCLUSION

The data show a clear correlation between discharge energy impact and decomposition of the gas. This is visible comparing the two samples of 630A load current tests where the 24kV sample (#2) shows twice as much CO than the 12kV one (#5). Also, the CO concentration of 518ppm of sample #3 (24kV/21kA) compared to the CO values of sample #6 indicates the correlation with discharge energy. The latter shows a carbon monoxide concentration of a factor 5 below sample #3. Furthermore 45% less CO is observed in sample #6 with respect to sample #4. Beside the fact that the discharge energy for #6 was lower than in #4 this can also be an indication that the presence of O_2 in the insulation gas mixture can reduce the final concentration of CO. It is well known that also ozone (O_3) is created in gas discharges if oxygen (O_2) is a gas component. In this study signals of O_3 were neither detected nor expected because the time between the switching tests and the FTIR analyses was of the order of several days and any created ozone is expected to decay in this time scale. Several chemical reactions are known to contribute to this decay including also the oxidation of CO to CO_2. Therefore, the presence of pure oxygen in the gas filling is expected to reduce indirectly the final concentration of carbon monoxide. How this reaction can be catalysed by appropriate surface properties of the switchgear may be matter of further investigation.

The health risk from decomposition products due to leakage for people who work or stay in the proximity of a GIS of the considered type can be rated negligible even for unvented switchgear rooms. For the sake of completeness, it should be mentioned that also larger quantities of carbon dioxide in the air can be harmful to health. CO_2 in this case is a component of the insulation gas rather than a decomposition product. But also, CO_2 concentrations in the switchgear's room air will not exceed the corresponding OEL for the described leakage scenario.

SUMMARY

Gas insulated switchgear can be operated with SF_6-free and halogen-free gaseous dielectrics that consist of ambient air components nitrogen (N_2), carbon dioxide (CO_2), and oxygen (O_2). The expected known decomposition products carbon monoxide (CO), nitrous oxide (N_2O), nitric oxide (NO), and nitrogen dioxide (NO_2) have been detected after repeated making arcs of up to 24kV/21kA and 12kV/25kA. The concentrations of these trace gases have been quantified with detection limits less than 1ppm by Fourier-transform infrared spectroscopy (FTIR). The health risk from decomposition products due to leakage is not of concern as its concentrations inside a switchgear room will be significantly below the corresponding Occupational Exposure Limits.

ACKNOWLEDGMENT

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