Compatibility of the $C_4F_7N/O_2/CO_2$ Mixture with Epoxy Resin After Long-Term Thermal and Electro-Thermal Tests

M. Michelarakis, S. Singh, D. Clark, A. Haddad
Advanced High Voltage Engineering Research Centre
School of Engineering, Cardiff University
The Parade, Cardiff, UK

G. Wilson, M. Waldron
National Grid Electricity Transmission PLC
Warwick, UK

***Abstract*- The compatibility between insulating gases and solid materials is an important aspect of the assessment of newly developed eco-friendly replacement candidates of SF_6. During the long-term operation of gas insulated switchgear (GIS) and lines (GIL), the insulation system is subjected to combined thermal and electrical stress. In this study, the compatibility of the 5/13/82% $C_4F_7N/O_2/CO_2$ gas mixture with epoxy resin is investigated using long-duration thermal and electro-thermal tests. Two different experimental set-ups were implemented for the two different types of tests. The solid dielectric samples were extracted from an actual cone-type GIL spacer. The gas samples were analysed by means of gas chromatography mass spectroscopy (GC-MS) and the resulting decomposition products were identified. The solid insulation samples were examined by surface observation. The more noticeable impact on the 5/13/82% $C_4F_7N/O_2/CO_2$ gas mixture was observed at test temperatures close to the glass transition temperature of epoxy resin. Decomposition products such as CO and C_3F_6 were found to be indicators of interaction between the gas and the solid dielectric.**

I. Introduction

Gas insulated switchgear (GIS) are complex assemblies of parts made of different materials. These assemblies are designed for lifetimes of a few decades, service experience reports [1] indicate no end-of-life signs after more than 40 years of operation. For decades, sulphur hexafluoride (SF_6) has been the most common gaseous insulating medium used in GIS. It has been extensively researched for its exceptional dielectric, physical and thermal properties along with its chemical stability and inertness during normal use.

Fluorinated compounds with low global warming potential (GWP) have emerged as promising candidates to replace SF_6 in high-voltage (HV) equipment. Heptafluoroisobutyronitrile (iso-C_3F_7CN, CAS No. 42532-60-5), commonly known as C_4F_7N, is one of the leading SF_6 replacement candidates. According to the Sixth Assessment Report (AR6) of the Intergovernmental Panel on Climate Change (IPCC) [2], C_4F_7N has a 100-year global warming potential (GWP) of 2750 which is significantly lower than that of SF_6 at 24300. In order to reach the minimum allowed temperature rating for the GIS of -25 °C at normal operating conditions [3], it is necessary that the C_4F_7N compound be combined with natural origin gases in binary or ternary mixtures, ultimately resulting in an even lower apparent GWP of the gas mixture.

The compatibility of the low-GWP insulating gas mixtures with known materials used in GIS is an important part of assessing the feasibility of these mixtures to replace SF_6. Dedicated standards related to test procedures for ageing of rubber and plastics are available, although they do not directly address SF_6 or non-SF_6 gases. CIGRE Technical Brochure TB 802 of working group B3.45 [4] provides a comprehensive summary and proposes test protocols for assessing the impact of the materials on the insulating gas and vice versa. The brochure also includes recommendations for the temperature and duration of the gas-material interaction tests. However, selecting the most suitable test parameters remains a challenging task, which can be seen in the relevant published literature.

GIS assemblies comprise a variety of different materials such as metals, polymers, elastomers, greases, coatings, desiccants etc. Epoxy resin post- and cone-type insulators have an important role in providing electrical insulation and mechanical support for the inner high voltage core conductor. Published research works have reported results on the compatibility of epoxy resin with C_4F_7N-based gas mixtures under thermal [5] and electro-thermal stress conditions [6, 7]. In [5], the authors performed thermal stress tests on epoxy resin samples in C_4F_7N/CO_2 for a period of 696 hours and for three test temperatures: 60 °C, 125 °C and 160 °C. Only when the glass transition temperature of the solid dielectric material was significantly exceeded, i.e. at 160 °C, the compound of C_3F_6 was detected in the gas analysis. Analysis performed on the epoxy resin solid samples after testing showed an increased Al_2O_3 content indicating displacement of the filler materials, however no significant degradation was observed. In [6], the authors investigated the exposure of epoxy resin samples in C_4F_7N/CO_2 to combined electro-thermal stress. The test temperature was 70 °C while the duration of the exposure was 1000 hours. No significant decomposition of the insulating gas was observed while higher particle precipitation was noticed for the sample exposed to electro-thermal stress compared to the case where only thermal stress was applied. In another study [7], electro-thermal stress of epoxy resin samples was again investigated. This time, the adopted test temperature was higher, at 112 °C, and the test duration was longer, at 3000 hours. Similarly, no significant degradation of the gas mixture was observed. The surface roughness of the solid samples was

979-8-3315-8902-8/25/$31.00 ©2025 IEEE

shown to have increased and separation of the Al_2O_3 fillers was also observed.

In this work, the compatibility of the 5/13/82% $C_4F_7N/O_2/CO_2$ gas mixture with epoxy resin is investigated. Two different experimental set-ups were implemented. For the first test, only thermal stress was considered where the solid dielectric samples were placed inside sealed containers filled with the gas mixture and then subjected to the test temperature inside an oven. For the second test, combined electrical and thermal (electro-thermal) stress was applied to the test object using an experimental configuration specifically developed for use in this investigation. The extracted gas samples were analysed using a GC-MS device and the detected molecules were identified.

II. Experimental Set-up and Methods

Two different experimental arrangements were used which were run in parallel: one for thermal stress and another for combined electro-thermal stress. For the thermal stress tests, small stainless-steel containers of approximately 120 ml volume were assembled. Inside each container, solid dielectric material samples were enclosed, and the volumes were filled with the 5/13/82% $C_4F_7N/O_2/CO_2$ gas mixture. The containers were placed inside an oven for the application of the required elevated temperature.

The experimental set-up for the application of the electro-thermal stress included the complexity of combining heating the test sample and subjecting the gas mixture to an electric field. The latter test required a new specific design to heat up the test cell and conduct the experiment outside the oven. A sphere-plane electrode arrangement was installed inside a cylindrical 6 L stainless-steel pressure vessel. A silicone rubber bushing with a plated copper conductor was installed for the application of the electrical stress. The applied high voltage waveform was AC-50 Hz with a magnitude 20 kV rms. The diameter of the sphere electrode was 25 mm, and the gap distance was set at 20.6 mm. In this way, the resulting maximum electric field at the surface of the sphere was computed at 3.21 kV/mm. This value is close to the range described in [7] for the maximum electric field on basin and post insulator surfaces. Four epoxy resin samples were placed on the plane electrode, which was at earth potential, and the samples were not in direct contact with the energised sphere electrode. The purpose of this configuration was to avoid any possible discharge process from appearing which might affect the condition of the solid sample and the insulating gas mixture in the long-term. The block diagram of the electro-thermal experimental set-up is shown in Fig. 1. Around the cylindrical pressure vessel, a ceramic heat band was wrapped which was regulated by a PID controller for the control of the temperature.

As described in the relevant standard [3], the maximum allowed temperature for metal parts of GIS ranges from 75 °C to 115 °C depending on whether the surrounding insulating fluid is considered as oxidising (OG) or non-oxidising (NOG). As described in [8], the thermal class of solid materials used as insulation can exceed 115 °C. However, when these materials are in contact with metallic components, their limiting

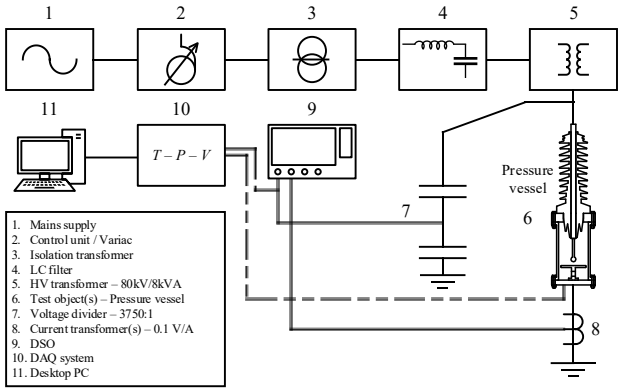


Fig. 1. Block diagram of the combined electro-thermal experimental set-up.

temperature is set by the corresponding limit of the metal part. The first three classes, Y, A and E, refer to minimum temperatures of 90 °C, 105 °C and 120 °C respectively. These three temperatures were considered for the thermal stress tests while, for the combined electro-thermal stress tests, only 90 °C was used at this stage. The duration for both types of tests was 720 hours (30 days ≈ 4 weeks) which, as suggested by CIGRE working group B3.45 [4], is sufficient duration to allow a first differentiation between compatibility tests. The thermal tests were conducted at a pressure of 4.35 bar(a) while the combined electro-thermal tests were conducted at 9 bar(a) of the 5/13/82% $C_4F_7N/O_2/CO_2$ gas mixture.

The analysis of the gas samples was performed using an Agilent 7890B GC/5977A MSD device. The operating parameters of the GC-MS system are listed in Table I. The qualitative identification of the separated products by means of the mass spectra was achieved through the National Institute of Standards and Technology (NIST) library.

III. Results and Discussion

A. Thermal tests

The thermal tests were conducted three times, each time for a different test temperature i.e., 90 °C, 105 °C and 120 °C. The latter temperature level tested is relatively close to the glass transition temperature of epoxy resin which was identified between 117.81-123.99 °C in [7].

The obtained total ion chromatograms (TIC) are summarised in Figs. 2 and 3. Fig. 2 shows the early magnified region of the TICs at the retention time (RT) up to 1.8 minutes. The molecules of O_2 and CO_2 elute faster, thus, they appear relatively early in each TIC. Carbon monoxide (CO), which is a known decomposition product does not separate from O_2 in the current set-up although it is detectable using the dedicated post-processing software. Other known decomposition

TABLE I
GC-MS Parameter Settings

Parameter	Setting
Column	GS-GasPro, 30m×0.32mm
Carrier gas	99.999% He
Column flow	mL/min
Split ratio	8:1
Ionisation method	Electron ionisation (EI)
Scan range	m/z 5 to 350

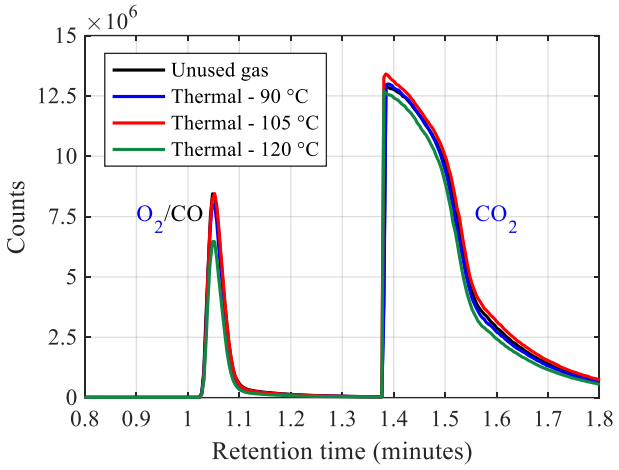


Fig. 2. Magnified region up to RT of 1.8 minutes. The obtained TICs correspond to the three different cases of thermal tests along with the TIC of the unused gas mixture.

products which usually appear early in the TICs such as CF_4, C_2F_6 and C_2F_4, were not detectable here although they are detectable in experiments where the C_4F_7N-based insulating gas mixture is exposed to very high temperature conditions such as arcing plasmas [9]. In the RT region between 3 and 10 minutes, shown in Fig. 3, two peaks are sufficiently distinguishable from the baseline of the TIC obtained for the case of the 120 °C test. The first peak corresponds to C_3F_6, while for the second peak, the best match to the NIST library is CH_3Cl. The C_3F_6 molecule has been detected at the same test conditions i.e., 120 °C for 720 hours, without the epoxy resin sample. It is unlikely that epoxy resin caused that reaction. Regarding the second peak, it has been detected only when epoxy resin with the C_4F_7N-based mixture has been tested. Further validation steps are required to confirm that this is indeed the correct molecule. This compound is listed in [10] with a total lifetime of 0.9 years, GWP of 6 and ozone depletion potential (ODP) of 0.015.

B. Combined electro-thermal tests

The combined electro-thermal test was conducted under a 90 °C test temperature. The pressure vessel was filled with the 5/13/82% $C_4F_7N/O_2/CO_2$ gas mixture to 9 bar(a) at a reference temperature of 20 °C, and the applied test voltage was 20 kV rms. The duration of the test was 720 hours, adopting a temperature similar with the thermal tests described previously. The gas samples were analysed at the start of the test, before the gas mixture had been exposed to any type of stress, at intermediate points of 260 and 500 hours, and again at the end of the test.

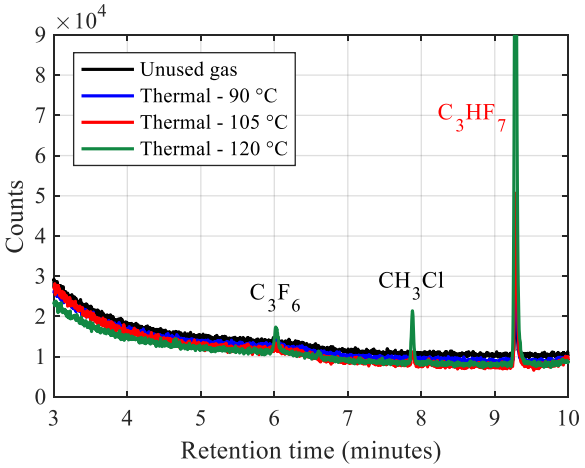


Fig. 3. Magnified region of the TICs between 3 and 10 minutes of the RT.

Fig. 4 shows the early magnified region of the TICs up to an RT of 1.8 minutes, similar to the TICs shown previously in Fig. 2. As before, along with main components of the insulating gas mixture, O_2 and CO_2, CO was also detected. No other compounds indicating decomposition of the C_4F_7N molecule were detected in this RT window. In the RT region between 3 and 10 minutes, shown in Fig. 5, only C_3F_6 was detected. In fact, the peak magnitude and calculated area increased as the electro-thermal test progressed. The same compound has been reported also in earlier published works where results from compatibility and ageing tests were reported [5, 11, 12]. The C_3HF_7 compound is a known impurity of pure C_4F_7N, the peak of which also increased with test time. The peak areas for both C_3F_6 and C_3HF_7 increased linearly with the test time. As was shown previously for the thermal test at 90 °C, there is no indication of decomposition of the C_4F_7N molecule (Fig. 3). For the electro-thermal test, the presence of C_3F_6 is an indicator of decomposition although it needs to be further investigated whether any of the present materials, such as the HV bushing with its conductor, had an impact on the decomposition of the gas mixture.

C. Condition of the solid samples

For all epoxy resin samples, regardless of the type of test and test temperature, a change in their colour was observed, from pale yellow (or beige) to a deep yellow after the test. This visual change was more intense at higher test temperatures. Fig. 6 shows the epoxy resin sample used for the thermal tests at 120 °C. This change might occur due to surface oxidation or thermal degradation or a combination of both. Also, EDX analysis on the surface of the samples before and after testing showed that for the case of the samples used in the electro-thermal tests a

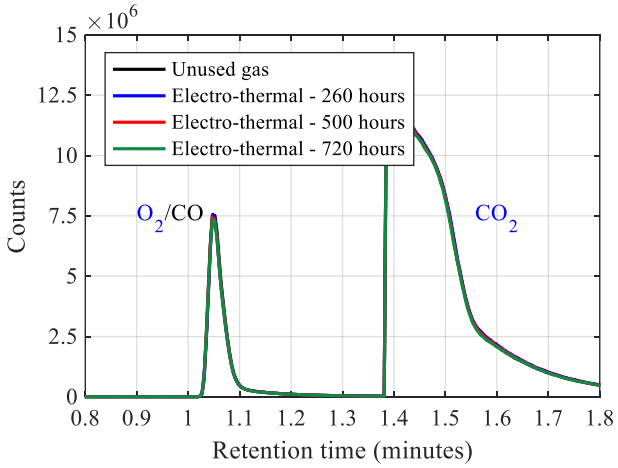


Fig. 4. Magnified region up to RT of 1.8 minutes. The obtained TICs correspond to the three samples analysed in the duration of the electro-thermal test along with the TIC of the unused gas mixture.

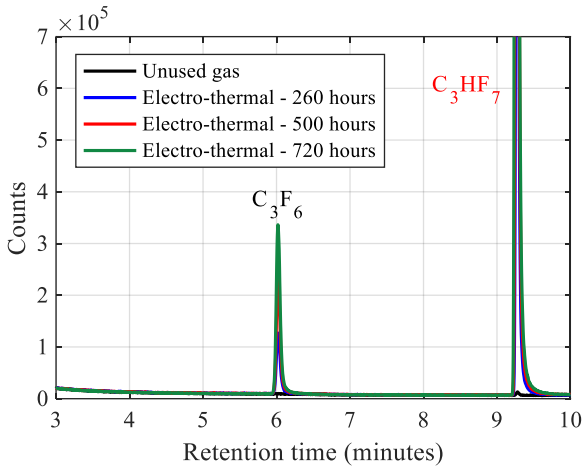
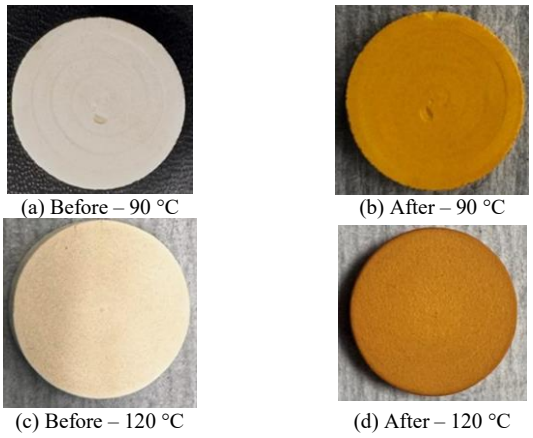


Fig. 5. Magnified region of the TICs between 3 and 10 minutes of the RT.



(a) Before – 90 °C (b) After – 90 °C

(c) Before – 120 °C (d) After – 120 °C

Fig. 6. Epoxy resin samples before and after the thermal tests at 90 °C and 120 °C.

small amount of fluorine (F) was detectable in the range of 2.2-3.5%. This was not detectable in the samples used in only thermal testing. More extended analysis on the condition of the solid samples will be presented in future works.

IV. Conclusion

In this work, the compatibility of the 5/13/82% $C_4F_7N/O_2/CO_2$ gas mixture with epoxy resin was investigated. Two types of tests were conducted: one where only thermal stress was applied and a second where combined electro-thermal stress was examined in a configuration tailored for that type of test. Analysis of the gas samples was performed using a GC-MS device. The key observations that were made are:

(a) Thermal tests showed that there is no noticeable impact on the gas condition at temperatures levels below the ones that are known to have an impact on the solid dielectric.

(b) When the test temperature of thermal tests is 120 °C, which is close to the glass transition temperature of epoxy resin, C_3F_6 and CH_3Cl are detected. These two compounds potentially indicate the impact on the gas mixture and the solid sample respectively.

(c) The electro-thermal tests revealed a more noticeable impact on the gas condition, with the appearance of C_3F_6 clearly distinguishable.

(d) Carbon monoxide (CO) is detected in both thermal and electro-thermal tests, regardless of the applied elevated temperature.

(e) In all cases, after each test, the solid samples showed a change in their colour which might be a sign of oxidation. EDX analysis on the surface of the samples showed a noticeable accumulation of fluorine in the electro-thermal tests.

Acknowledgement

The authors wish to acknowledge National Grid Electricity Transmission for funding and supporting the project titled "Identification and quantification of C_4F_7N gas mixture arcing by-products and their implication for GIS" (NIA project number: NIA2_NGET0028). The authors would also like to thank Christopher Stone for his invaluable support during the experiments.

References

[1] C. Neumann et al., "End of life estimation and optimization of maintenance of HV switchgear and GIS substation", CIGRE, 2012.

[2] IPCC, 2021: Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change [Masson-Delmotte, V., P. Zhai, A. Pirani, S.L. Connors, C. Péan, S. Berger, N. Caud, Y. Chen, L. Goldfarb, M.I. Gomis, M. Huang, K. Leitzell, E. Lonnoy, J.B.R. Matthews, T.K. Maycock, T. Waterfield, O. Yelekçi, R. Yu, and B. Zhou (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

[3] *High-voltage switchgear and controlgear - Common specifications for alternating current switchgear and controlgear*, Standard BS EN 62271-1:2017+A1:2021, Dec. 2021.

[4] CIGRE TB 802 "Application of non-SF_6 gases or gas-mixtures in medium and high voltage gas-insulated switchgear", Cigre W. G. B3.45, 2020.

[5] R. Yuan, H. Li, W. Zhou, Z. Zheng, and J. Yu, "Study of Compatibility Between Epoxy Resin and C_4F_7N/CO_2 Based on Thermal Ageing," *IEEE Access*, vol. 8, pp. 119544-119553, 2020.

[6] R. Yuan et al., "Compatibility between C_4F_7N/CO_2 and Epoxy Resin in Electro-thermal Environment," *Proc. IEEE Int. Conf. High Volt. Eng. App. (ICHVE)*, pp. 1-4., 2020.

[7] C. Wang et al., "Characteristics of C_4F_7N/Epoxy Resin Insulation System Affected by Long-Term Electro-Thermal Accelerated Aging," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 28, no. 6, pp. 1973-1979, 2021.

[8] *Electrical insulation. Thermal evaluation and designation*, Standard BS EN 60085:2008, Mar. 2009.

[9] B. Zhang et al., "Decomposition characteristics of C_4F_7N/CO_2 mixture under AC discharge breakdown," *AIP Adv.*, vol. 9, no. 11, p. 115212, 2019.

[10] World Meteorological Organization (WMO), "Scientific Assessment of Ozone Depletion", GAW Report, No. 278, 509 pp.; 2022.

[11] W. Gao et al., "Materials Compatibility Study of C_4F_7N/CO_2 Gas Mixture for Medium-voltage Switchgear," *IEEE Trans. Dielectr. Electr. Insul*, vol. 29, no. 1, pp. 270-278, 2022.

[12] Y. Li et al., "Study on the thermal interaction mechanism between C_4F_7N-N_2 and copper, aluminum," *Corros. Sci.*, vol. 153, pp. 32-46, 2019.