Plasma-Chemical Decomposition of Gas Mixtures
Applied for Electrical Insulation

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Abstract—In MV and HV energy distribution facilities gas mixtures containing SF₆ are successfully applied for dielectric insulation. Their dielectric strength staying stable over more than 30 years guarantees reliable operation for the complete lifetime of the facility. Because of the global warming potential of SF₆ recently gas insulation with alternative gas mixtures was investigated. We performed experiments simulating the long term exposition of a gas mixture containing 40% N₂O in N₂ to partial discharges. Gas samples filled into a closed vessel were exposed to dielectric barrier discharges. During these tests the electrical properties of the dielectric barrier discharge reactor were monitored. At the end of each test the treated gas sample was analyzed by means of Fourier transform infrared absorption spectroscopy. Applying a specific input energy density of 180 J/l resulted in formation of NO and NO₂ with concentrations as high as 586 ppm and 156 ppm, respectively. The dielectric strength of the gas mixture did not degrade.

Keywords—Dielectric insulation, gas mixture, partial discharge, plasma-chemical degradation

I. INTRODUCTION

The introduction of SF₆ gaseous dielectric in the 1960’s [1] enabled introducing more reliable and compact facilities for electrical energy transmission and distribution such as gas insulated lines (GIL) for high voltage (HV) transmissions and gas insulated switchgears (GIS) [2, 3] both for high voltage and medium voltage (MV). Soon gas mixtures of SF₆ with nitrogen, dry air, or CO₂ aiming on improved dielectric strength and reduced costs of gas insulation were investigated and introduced into the market [4, 5]. On one hand plant geometry, gas mixture, and gas pressure were chosen such that the plant is operated close to dielectric breakdown voltage. Thus at several spots inside of the plant partial discharges (PD) may occur. On the other hand important requirements to such gas mixtures were stability of the dielectric strength for the complete lifetime of the plant (typically 30 years) and - as far as applicable - fulfillment of environmental, health and safety (EHS) regulations. This means that either all the different constituents of the gas mixture are stable enough even in presence of partial discharges or that the products formed by plasma-chemical conversion caused by PD do not compromise the dielectric strength and also fulfill EHS regulations.

Because of the huge global warming potential (GWP) of SF₆ being as high as 23,500 (100-yr time horizon) [6], SF₆ free gas mixtures were considered for application in GIS [7, 8]. Recently N₂O-N₂ mixtures with N₂O volume fractions between 20% and 40% were shown having a dielectric strength as high as 60% of pure SF₆ [9]. The advantage of N₂O based gas mixtures would be that its GWP is just 265. Thus we investigated the application in GIS [7, 8]. Recently N₂ gas mixtures were shown having a dielectric strength as high as 60% of pure SF₆ [9].

II. EXPERIMENTS

A. Experimental Set-up and Procedure

The experimental set-up (Fig. 1) consists of a vacuum tight cross fitting of a MV GIS having a volume of 30 l (reactor vessel), in which a dielectric barrier discharge (DBD) actuator (plasma actuator) is placed. The DBD actuator consists of an HV electrode made of 20 sharp edged, serrated discs, diameter 42 mm, axial distance 5 mm, centered in an alumina tube, inner diameter 46 mm, wall thickness 2 mm (Fig. 2). Its outside wall is covered by metallic coating acting as a ground electrode. The DBD is supplied with repetitively pulsed voltage using an all solid state pulse power supply designed by the Fraunhofer Institute for Laser Techniques [10] (amplitude up to 20 kV, polarity positive, negative, or alternating, pulse duration 1 ms, pulse repetition frequency variable up to 20 kHz). The electrical properties of the DBD actuator were monitored continuously by means of a HV-probe (LeCroy PPE20kV) and a current probe (Stangeness Industries PPE20kV) and a current probe (Stangeness Industries PPE20kV) connected to a digital storage oscilloscope (DSO; LeCroy Waverunner LT224). Using the built-in mathematics of the DSO, power and energy as a function of time t were achieved from current I(t) and voltage U(t) applying

\[ P(t) = U(t) \cdot I(t) \]  

\[ E(t) = \int_0^t P(t) \, dt \]

Traces obtained in a fresh N₂O-N₂ gas mixture at a pressure of 150 kPa are shown in Fig. 3. The average plasma input power is obtained from the pulse energy E_pulse (that is the energy after current and voltage ringing is finished) and the pulse repetition frequency f_rep

\[ P_{av} = f_{rep} E_{pulse} \]
Before each experiment the reactor vessel was evacuated down to a pressure of < 0.3 kPa using a rotary vane pump. Since the history of the MV GIS cross fitting was unknown, during first evacuation the reactor vessel was heated to ~ 60°C. Further for all the tests the same type of drying agent being used in commercial MV GIS was placed inside of the reactor vessel. Gas filling was accomplished by means of a pressurized gas cylinder containing N₂O (Linde, purity 2.5) and N₂ from central gas supply (Linde, purity 5.0) measuring the pressure inside of the reactor vessel using a calibrated piezo-resistive pressure transducer (Keller AG, full range 0.5 MPa, accuracy 0.1% full scale): N₂O was filled into the reactor vessel until the desired partial pressure was reached, then N₂ was added until the desired total pressure being 150 kPa in all tests was achieved. Time was given for mixing of the gases inside of the reactor vessel and for the aluminum walls and epoxy insulators of the reactor vessel to saturate with the gas mixture. Then the reactor vessel was evacuated and filled a second time in order to have stable, reproducible test conditions.

Both the fresh, untreated gas mixture and the gas mixtures exposed to DBD with a well defined specific input energy density were analyzed (Fig. 4) using a Fourier Transform Infrared absorption spectrometer equipped with a 1 m White cell (volume 1 l) heated to 180°C (FTIR; Perkin Elmer System 2000). Gas analysis was performed feeding the gas mixture through the absorption cell of the FTIR with a minimum flow rate of 1 l STP/min. Three minutes after starting gas feed to the absorption cell FTIR spectra were sampled in the wavenumber range from 700 cm⁻¹ to 4000 cm⁻¹ with a resolution of 0.5 cm⁻¹ (sampling interval 0.1 cm⁻¹). For noise reduction averaging over 5 spectra was performed. NO, NO₂, N₂O, HNO₃, HNO₂, H₂O, and O₃ were analyzed quantitatively using sets of calibration spectra for several relevant concentrations and sophisticated statistical methods (Perkin Elmer QuantC software). For other compounds such as NO₂, N₂O₃, and N₂O₅, the FTIR spectra were analyzed qualitatively on a routinely basis.

**B. Low Power Gas Degradation Tests**

The DBD-treatment of a gas mixture for a duration \( \tau \) can be characterized e.g. by the specific energy density

\[
\varepsilon_{vol} = \frac{P_{vo} \tau}{V_{STP}},
\]

where \( V_{STP} \) is the volume of the gas mixture in the reactor vessel normalized to standard temperature and pressure conditions. Gas degradation tests were based on a rough estimation of the specific energy density accumulated by the gas inventory of a GIS due to PD activity over the
plant lifetime resulting in 180 J/STP. Since, however, it was not clear whether long duration treatment with low average plasma power leads to the same results as short duration treatment with high average plasma power, three different test conditions resulting in this specific energy density were applied (Table I). The average plasma input power was varied by keeping the pulse energy (typically 2.2 mJ) constant and varying the pulse repetition frequency. For each of the test conditions at least 3 gas samples were drawn and analyzed by means of FTIR.

C. High Power Gas Degradation Tests

Some more experimental investigations on degradation of the 40% N₂O/N₂ gas mixture applying much higher specific energy densities up to 28 kJ/STP were performed at a gas pressure of 200 kPa. These high power degradation tests having a maximum duration of 240 min were started with an initial pulse energy of 6.7 mJ and constant pulse repetition frequency of 10 kHz. Thus here the initial value of the average plasma input power was 67 W. Gas samples were drawn and analyzed by means of FTIR absorption spectroscopy for several specific energy densities. For each specific energy density investigated an individual experiment was performed.

Since here N₂O₅ was detected, a method for quantitative analysis of N₂O₅ concentration based on integration of the absorbance A as a function of wavenumber ν over the 743 cm⁻¹ and 1246 cm⁻¹ band, respectively, was developed. The gas density in the absorption cell is evaluated from

\[ n_{\text{N}_2\text{O}_5} = \frac{\ln(10)}{S_{\text{band}} A_{\text{max}}} A(\nu) \, dv. \]  

The band strengths of the corresponding N₂O₅ IR bands \( S_{\text{743}} = 4.07 \cdot 10^{-17} \text{ cm} \) and \( S_{\text{1246}} = 4.20 \cdot 10^{-17} \text{ cm} \) were taken from literature [11]. N₂O₅ volume fractions \( X_{\text{N}_2\text{O}_5} \) were obtained dividing the N₂O₅ gas density by the total gas density at atmospheric pressure and 180°C \( n_{\text{tot}} \approx 1.62 \cdot 10^{-5} \text{ m}^3 \text{ mol}^{-1} \)

\[ X_{\text{N}_2\text{O}_5} = \frac{n_{\text{N}_2\text{O}_5}}{n_{\text{tot}}}. \]

III. RESULTS

A. Low Power Gas Degradation Tests

For all test conditions given in Table I DBD treatment of the 40% N₂O/N₂ gas mixture resulted in formation of NO and NO₂, only. Within the statistical error limits no other components could be found in the FTIR absorption spectra. The results of the concentration measurements are summarized in Table II.

The statistical errors of the concentrations were 0.1%, 13 ppm, 0.6 ppm and 3.7 ppm for N₂O, NO, NO₂ and O₃ respectively. No substantial differences in gas degradation can be found between the different test conditions.

In case of high average plasma input power (4.4 W) the concentrations of NO and NO₂ seem to be slightly higher than in case of low average plasma input power, and in case of the medium plasma input power test (2.2 W) the NO₂ concentration seems to be low. However, it is not clear how the drying agent influenced the test results. The electrical properties of the gas mixtures as analyzed from the pulse energy as a function of treatment time turned out to be very stable: The pulse energies stayed constant at 2.2 mJ in all tests.

B. High Power Gas Degradation Tests

In contrast to these experiments in the high power degradation tests an increase of pulse energy over time was observed (Fig. 5). After about 60 min the pulse energy saturated at ~ 12 mJ. A 120 min break of DBD treatment caused a relaxation of the dielectric strength resulting in a decrease of pulse energy to ~ 6 mJ. After another 60 min of DBD treatment the pulse energy saturated again at ~ 12 mJ.

Due to DBD treatment N₂O was decomposed to a substantial degree (Fig. 6). The decrease of N₂O concentration as a function of specific energy density can
be described by an exponential function. The major product of N₂O decomposition is NO₂. However, the concentrations of NO and N₂O₅ as a function of specific energy density (Fig. 7) indicate that NO₂ is neither the primary nor a final product of N₂O decomposition. Instead NO showing a steady decrease in concentration beginning with the first samples drawn from the reactor vessel can be assumed to be a primary reaction product of N₂O decomposition. It is interesting to note that the NO concentration in the reactor vessel decreased as a function of time even when the DBD was not in operation (Fig. 8): The samples for the lowest specific energy density were drawn starting after 30 min of DBD treatment with a time interval of 5 min between the individual gas samples analyzed.

IV. DISCUSSION

Because of the low concentrations of the products found in the low power gas degradation tests substantial gas degradation caused by PD activity in gas insulated MV and HV facilities is not to be expected. NO and NO₂ may exhibit corrosive properties in case of a humid atmosphere. If humidity is kept at low levels, e.g. by utilizing sorbents, corrosion issues can be avoided. Since the dielectric strength of the gas mixture is not compromised by gas degradation as long as the specific energy density is kept below 180 J/lSTP, reliable operation of MV GIS with a 40 % N₂O/N₂ gas mixture should be achieved.

Nevertheless, care has to be taken not to release the gas mixture after degradation uncontrolled to the environment: Both NO and NO₂ for example are highly toxic and etching. Exposure limits (AGW TRGS 900) of NO and NO₂ in Germany e.g. are 25 ppm and 5 ppm, respectively. Thus leakage of GIS, especially in case of installation in buildings, has to be avoided.

From the results of the high power gas degradation tests the following assumptions about the kinetics of NTP-degradation of N₂O/N₂ mixtures can be made:

1. N₂O decomposition may be described by a 1ˢ order reaction. The specific energy of N₂O decomposition evaluated from the high power gas degradation tests based on this assumption is 1321 kJ/mol (13.7 eV/molecule). From the NO- and NO₂-formation rate of the low power gas degradation tests a slightly higher value of 1893 kJ/mol (19.6 eV/molecule) is obtained. Since in the low power experiments the decrease in N₂O concentration was too low for quantitative analysis and not all decomposition products may have been detected (N₂O can e.g. also be decomposed into N₂ and O₂), from the difference between these two

![Fig. 5. Pulse energy as a function of duration of DBD-treatment of the 40% N₂O/N₂ gas mixture in high average plasma input power experiments. After 120 min a 120 min break was made.](image1)

![Fig. 6. Molar fractions of N₂O and NO₂ as a function of specific energy density.](image2)

![Fig. 7. Molar fractions of N₂O₅ and NO as a function of specific energy density.](image3)
specific energy values no significant conclusions can be drawn.

2. NO may be a primary decomposition product. This assumption is supported by glow discharge experiments [12] indicating that primary reactions of N2O decomposition are electron collision dissociation to N2 + O and to NO + N, respectively.

3. The decrease of NO concentration as a function of specific energy density can be explained by reactions with O- and N-radicals. Oxidation of NO results in formation of NO2. The decrease of NO concentration as a function of time without DBD-treatment can only be explained by gas phase thermal reactions, e.g. with molecular oxygen or NO2.

4. The slow increase of N2O3 as a function of specific energy density indicates that this species is formed by a chain of secondary reactions involving e.g. NO, NO2, and N2O. Low concentration N2O3 formation was also observed in experiments treating NO2-air mixtures with a dielectric pellet bed reactor [13].

5. Nitrogen and oxygen balances indicate, that a certain fraction of the products is not detected by the FTIR. Since homonuclear molecules are not infrared active, N2 and O2 could be those products being necessary for fulfilling balances.

V. CONCLUSION

Degradation of N2O/N2 gas mixtures due to partial discharge activity in MV GIS was simulated by dielectric barrier discharge treatment of 40% N2O/N2 in a closed reactor vessel. Applying non-thermal plasma treatment with a specific energy density of 180 J/lSTP to the gas mixture did not compromise its dielectric strength. NO and NO2 were formed with concentrations of 550 ppm and 160 ppm, respectively. Thus N2O/N2 gas mixtures could well be applied for dielectric insulation in MV and HV energy transmission and distribution as long as partial discharge activity is kept at a low level.

Increasing the specific energy density to values up to 28 kJ/lSTP resulted in strong decomposition of N2O and formation of NO2 with molar fractions in the 2% range. The gas degradation observed for such high specific energy densities caused a substantial degradation of the dielectric strength. Since NO2 is highly toxic and etching, N2O/N2 mixtures should not be considered for gas insulation in applications where plasma treatment with high specific energy densities can occur.

REFERENCES


