The impact of decomposition products in SF₆ on the electrical surface strength of epoxy resin

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Introduction

SF₆ is an insulating gas with long-term stability, the electrical volume stability of which is tolerant to the presence of foreign gas admixtures [1]. Spark and arc discharges, and permanent partial discharges may be able to produce stable gaseous SF₆-decomposition products [2,3] but do not result in an anticipated reduction in the electrical volume stability, due to the tolerance to foreign gas admixtures.

If however a reaction occurs between the decomposition products and the solid insulation components integrated into the insulation system, then it is possible in certain circumstances that the electrical surface stability of the insulating spacers may be reduced. Degradation in the dominant epoxy resin as a result of sparks and electric arcs in SF₆ is documented [4]. A practical impact is assumed, since failure tests on existing SF₆ insulated plants have shown a degradation on surfaces of insulating spacers [5].

The concept of the contribution of partial discharges to the surface degradation is in contrast one still under discussion, particularly given the wide range of literature available on the partial discharge ageing of epoxy resin and not the impact of gaseous decomposition products resulting from partial discharges [6]. The following study presents a report on the results of tests in which SF₆-decomposition products are produced through partial discharges, and interactions with electrically stressed epoxy resin surfaces are enabled.

1. Experimental set-up and realisation

The test chamber (Figure 1) is a modified standard pressurised chamber with an insulation cover. The insulating cover is manufactured using Teflon® because this does not react with the anticipated SF₆-decomposition products. Metallic elements are produced using aluminium, because aluminium is also used in SF₆ plants. The partial discharge source is created using a pointed electrode with high voltage potential and a quasi-surface electrode with earth potential. The pointed electrode and its bracket are installed and removed when the test chamber is closed. The position of the partial discharge source is intentionally selected in order that a direct partial discharge impact on the sample surface is unlikely.
The gas volume of the test chamber amounts to 2 L, and the maximum internal pressure to 3 bar. With the test chamber’s external arcing voltage lying at around 100 kV and the pressure-dependant arcing voltage of the epoxy resin samples required to lie below this, a pressure limit of 1.7 bar is in place in order that the test is able to function correctly. The chamber is filled with SF\textsubscript{6} following its evacuation at 1 mbar. The test chamber is integrated into a standard voltage testing set-up, which is located within a shielded test laboratory. The magnetic shielding effectiveness at partial discharge-related frequencies lies at around 30 dB.

The cylindrical test samples are produced from industrial epoxy resin filled with quartz flour. The nominal thickness of the samples is 10 mm. Individual deviations will be accounted for through the conversion of each flash-over voltage to provide a flash-over field strength, which will be obtained using the individual thickness of each sample. Every sample will only be subjected to one flash-over incident. The test voltage will be raised from 4 kV/s to the point of flash-over. Flash-over tests will be carried out in aged and non-aged SF\textsubscript{6}.

2. **SF\textsubscript{6} ageing in the test chamber through partial discharges**

The chemical loading of the samples will take place over 96 hours (4 days) during which they will be subjected to an SF\textsubscript{6} atmosphere and will be aged under stable partial discharge activity. The surfaces of the samples shall be cleared of pollutants with acetone before this process takes place. The SF\textsubscript{6} pressure during the ageing process shall be equal to the pressure during the flash-over test procedure which follows immediately.

Without a partial discharge source, the test set-up shall be guaranteed to be free of partial discharge up to approx. 25 kV. In order to ascertain that there is no partial discharge, the aged samples shall be positioned between the aluminium electrodes. This reflects the fact that, in addition to a possible reduction in the electrical surface strength, it is also necessary to anticipate a reduction in the partial discharge inception voltage on the surfaces of the samples. Depending on the SF\textsubscript{6} pressure, the inception voltage of the partial discharge sources lies somewhere between 6 and 10 kV. In order to maintain stable partial discharge voltage activity, the test voltage must be set at a value from 10 to 14 kV.
Figure 2:  Phase separated pattern of a partial discharge within the test chamber

Figure 2 shows an example of a phase separated partial discharge pattern. There is a clear relationship between the apparent charge and the polarity of the test voltage. The partial discharge activity during the negative voltage phase is instable throughout the test period. The reason for this instability can be found in the ageing of the pointed electrodes and the counter electrode. If, as it is would appear, it is [8] the partial discharge from this alternation period which is responsible for the decomposition of the SF$_6$, then its stabilisation is absolutely essential. This would be achieved through the regular cleaning of the aluminium electrodes and / or the exchanging of the needle.

Figure 3:  IMS analysis of the gas after 96 hours of partial discharge activity

The status of the insulating gas is analysed following the ageing process, using the method known as ion mobility spectrometry (in short: IMS) [9,10]. In parallel to this, the humidity of the insulating medium is also ascertained using a dew-point hygrometer. The humidity during tests lies somewhere between 150..180 ppm.
Figure 3 is a representation of the results of an IMS analysis carried out using two spectra. The reference spectrum provides the status of electrically unstressed SF₆ taken from a supply bottle. The other spectrum shows the status of the SF₆ taken from the test chamber immediately after the exposure to the partial discharges. The amplitude of this spectrum has moved 5.2 ms to the right when compared to the amplitude of the reference spectrum, a situation which would occur in the case of a severe contamination of the gas resulting from decomposition products occurring due to the partial discharge exposure [9,10,11].

The reproduction of partial discharge activity does not inevitably lead to a reproduction of the reactionary process. The reaction kinetics are influenced by the type and quantity of reaction partners [12], the emergence of which is the subject of statical scatterings. Thus scatterings of up to 1 ms may well appear in the results of an IMS analysis.

3. Electrical surface strength of non-aged epoxy resin

The investigation of the impact of decomposition products on the electrical surface strength of epoxy resin also requires guaranteed data on the surface strength of unstressed epoxy resin. Thus, the flash-over voltage of 5 unstressed samples must also be ascertained. The surfaces of the samples shall be cleaned of pollutants using acetone and they shall then be placed in the test chamber.

Figure 4: Flash-over field strength $\tilde{E}/\sqrt{2}$ of unstressed epoxy resin samples and breakdown field strength of the apparatus without samples

Figure 4 depicts the average flash-over field strength figures for the unstressed samples, as well as the average breakdown field strength values for the electrode apparatus without the samples and against the SF₆ pressure. The scatter spread shown presents the confidence belt for a confidence range of 95%. As expected the strength values rise with an increase in the gas pressure. The reduction in strength figures as a result of the introduction of the samples is statistically significant.
4. The electrical surface strength of chemically stressed epoxy resin

4.1 Stressed samples without the application of molecular sieves

Following completion of the ageing process with partial discharges as defined above, the partial discharge source is removed. The chamber is now completely refilled. The gas pressure reflects the pressure during partial discharge loading.

![Graph of flashover field strengths](image)

**Figure 5:** Comparison of the flash-over field strengths of stressed and unstressed samples

The value of the flash-over field strengths of the aged samples are plotted together with the values obtained from the unstressed samples (compare with Figure 4) against the SF$_6$ pressure in Figure 5. It is clear that there is a significant reduction in the flash-over field strengths with the aged samples, which is attributable to a decline in electrical surface strength. In addition, one can also see from the diagram that the mathematical mean figure for the flash-over field strengths of the aged samples increases with an increase in pressure to the same degree as the increase seen in the non-aged samples. The notably greater scattering of measured values in the case of the aged samples shows that a comparable partial discharge load can produce a range of surface degradation results, which can be attributed once again to the stochastic of the reaction kinetics.

4.2 Stressed samples with the application of molecular sieves

The test process is repeated once more with the application of a molecular sieve in order to check the measurement results obtained above. This provides a gas humidity of 15 ppm$_v$. Figure 6 shows that the partial discharge loading of the gas chamber does not result in a change in the position of the peak of the IMS spectrum. Thus, one must assume that there are no decomposition products in the SF$_6$. Appropriately, the flash-over tests do not result in any significant loss in strength following the application of the partial discharge loading. A renewed repetition of the test procedure with an increase in the partial discharge loading over 7 days reproduces the same result.
Figure 6:  IMS analysis following a 96 hour partial discharge stressing of SF₆ with the application of a molecular sieve

5. Surface tests

The 4 day loading of a 2 L test volume with a partial discharge of an average 5 pc results in changes of the SF₆, which are evident through the IMS analysis. The results of this SF₆ ageing are assumed to be reactions between the decomposition products and the surfaces of the epoxy resin samples, which reduce the strength of the surface.

Figure 7 shows a large-area change in the colour of the epoxy resin samples following the partial discharge ageing process. This strengthens the hypothesis that the cause is not the close proximity to the partial discharge source itself, but is instead the gaseous decomposition products produced as a result of the partial discharge activity. An EDAX analysis (Figure 8) provides evidence that the decomposition products could lead to the appearance of SiF-compounds (SiF₄) in the surfaces of the samples. Negative effects on the surface strength become likely [13,14], due to their characteristics of a higher conductivity.

Figure 7:  Comparison of an unstressed sample (left) with a stressed sample with breakdown voltage channel (right)

The weak but evident peak for oxygen in the EDAX spectrum for the non-aged sample results from the quartz flour (SiO₂) and is a potential reaction partner to form further by-products.
This does not appear in the spectrum for the aged sample. According to [4], the cause can be identified as the formation of H$_2$O parallel to the formation of the SiF$_4$. The oxygen in addition to the hydrogen that form the water, access the gas. New reaction partners are created to form the decomposition products, meaning that an end of the reaction kinetics is unlikely in the short term.

![EDAX analysis](image)

**Figure 8:** EDAX analysis of a non-aged sample (above) and an aged sample

The manufacturing of the epoxy resin samples does not require the use of chrome, which means that the detection of chrome traces on their surfaces can be attributed only to deposits from the volume of gas on the surface. The active, partial discharge-producing pointed electrode is the only material with a chrome-plated surface, thus the assumption is that the impact of the direct partial discharge is to deposit chrome particles removed from the tip of the electrode. These arrive on the epoxy resin sample by way of diffusion.

**Summary and outlook**

Decomposition products in SF$_6$, which are a direct consequence of partial discharge activity, react with water and air to some highly corrosive products such as hydrogen fluoride (HF) for example. These react with the surface of epoxy resin insulators. The result is a dramatic reduction in the electrical surface strength, whereby the pressure-related volume resistance of SF$_6$ is no longer dominant. Experiments carried out with the application of molecular sieves show no degradation, which means that ageing without the use of a sieve can be attributed to chemical reactions of the decomposition products with the surfaces of the samples. The visual observation of an extensively aged epoxy resin sample shows a clear chemically enhanced change in the surface. An EDAX analysis shows the formation of substances containing fluorine on the surfaces of the samples.
Literature


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