Comparison Of SF$_6$ Dissociation Rate Due To Positive and Negative Coronas

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Abstract

Measurements of SF$_6$ dissociation rate due to 75 μA positive and negative coronas have been carried out using a mass spectrometer. The results show that the rates of SF$_6$ degradation and by-product production due to a positive corona are significantly higher than those for a negative corona. The rates of degradation and production of SF$_6$ and gaseous by-products are proportional to the charge transported by the corona. Both positive and negative coronas produce the same major gaseous by-products, SiF$_4$, SO$_2$F$_2$ and SOF$_2$. Besides gaseous by-products, coronas also produce solid by-products, metal fluorides. Due to the impact of high-energy electrons and F$^-$, the positive electrode is always more coated and damaged than the negative electrode.

Keywords: *sulphur hexafluoride (SF$_6$) dissociation, corona discharge, by-products, high-voltage switchgear, dielectric, arc-quenching medium.*

Abstrak

Pengukuran laju disosiasi gas SF$_6$ karena korona positif dan korona negatif telah dilakukan dengan menggunakan spektrometer massa. Hasil menunjukkan bahwa laju degradasi SF$_6$ dan laju produksi hasil sampingan karena korona positif sangat nyata lebih besar dari yang diakibatkan oleh korona negatif. Laju degradasi SF$_6$ dan laju produksi gas hasil sampingan sebanding dengan besarnya muatan yang dibawa oleh korona. Baik korona positif maupun korona negatif menghasilkan gas hasil sampingan utama yang sama, yaitu , SiF$_4$, SO$_2$F$_2$ dan SOF$_2$. Di samping menghasilkan hasil sampingan berupa gas, korona dalam SF$_6$ juga menghasilkan hasil sampingan berupa padatan, yaitu fluorida logam. Hantaman elektron dan ion F$^-$ mengakibatkan elektroda positif selalu mengalami deposit dan kerusakan lebih besar dibanding elektroda negatif.

Kata kunci: *disosiasi sulfur heksafluorida (SF$_6$), pelepasan korona, hasil-sampingan, sistem penghubung listrik tegangan tinggi, dielektrik, media pemadam bunga api listrik.*

1. Introduction

Sulphur hexafluoride (SF$_6$) is an chemically inert gas[1] and has high dielectric strength, three times greater than air[2]. It is widely used in all types of insulating systems including high-voltage switchgear, transformers, and transmission lines[3]. In high-voltage systems, SF$_6$ is used both as a dielectric and an arc-quenching medium.

An electrical breakdown event such as a partial discharge (corona), a glow or an arc will dissociate SF$_6$ into lower order sulphur fluorides, sulphur and fluorine. In the SF$_6$ corona discharge, dissociation of SF$_6$ is caused by electron impact. The chamber of a practical high-voltage system is usually not a contaminant-free environment. Some of the dissociation products will react with contaminants such as water vapour and oxygen, and with the metal surfaces and electrodes of the discharge chamber to form stable gaseous molecular species including gaseous sulphur oxyfluorides, SOF$_2$, SO$_2$F$_2$ and SOF$_4$; sulphur oxide, SO; sulphur dioxide, SO$_2$; and hydrofluoric acid, HF; as well as solid by-products such as sulphur and metal fluorides[4-11]. As a consequence, a reduction in SF$_6$ concentration takes place and the insulating efficiency of the system is degraded. Eventually, the SF$_6$ must be renewed, if failure of the high-voltage system is to be prevented.

Electrical discharges often occur in high-voltage systems either during normal operation or as a result of fault clearances. For example, the switching process in a circuit-breaker generates a transient high-current arc and partial discharges (coronas) tend to be present in high-voltage transformers, transmission lines and switchgear. The work described in this paper focuses on corona discharges since these continuously occur in all high-voltage systems, as a result of local high electric fields around conducting points, fine wires, sharp edges and cavities.

It is difficult to eliminate coronas completely from a practical high-voltage system and the cost of ensuring perfectly-smooth interior surfaces throughout such devices is prohibitive. The presence, magnitude, location and consequences of insidious corona discharges are difficult to monitor. A study of the level of SF_6 or dissociation by-products, is therefore needed, in order to help minimise the negative effects of coronas on high-voltage systems. The information provided by this study allows an early decision to be made regarding SF_6 replacement in order to maintain the desired level of insulating quality. The level of SF_6 and by-product gases can be measured directly using gas analysis equipment, such as mass spectrometry.

There are two types of DC coronas, positive coronas and negative coronas. The types of DC coronas, positive or negative coronas, depend on the polarity of the point electrode. In this paper, both positive and negative coronas are discussed.

2. Experimental Procedure

The SF_6 corona chamber is a chamber of volume 2.9 litres manufactured from a single cylinder of aluminum alloy. Corona discharges were produced between point and plane stainless steel electrodes placed 1.5 cm apart. Steady-state positive and negative coronas were established in the corona chamber using the electrical circuit shown in Figure 1. Here, the power supply was used in fixed-current mode at 75 µA.
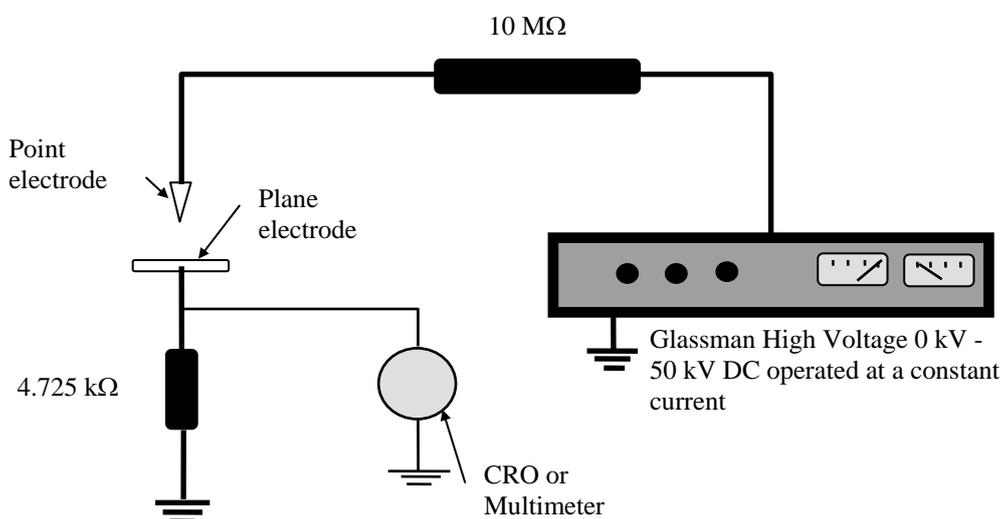
Figure 1. The DC corona discharge circuit.

The mass spectrometer used for this work consists of an analyser tube (an AEI MS10 single-focusing magnetic sector spectrometer having a 180° ion path deflection of 5 cm radius), a controller (VSS RGA10), an electrometer amplifier, an IBM-PC computer associated with an acquisition card CONTEC ADC-10, a voltmeter and a digital storage oscilloscope. The mass spectrometer measures the mass/charge ratio of continuous flow-through gas samples.

Prior to each experiment, the corona chamber, the expansion chamber and the electrodes were cleaned properly. After cleaning, the corona chamber and the expansion chambers were evacuated for a period of 48 hours to a pressure $< 10^{-3}$ Pa. It is likely that vacuum and

purity conditions in the corona chamber are somewhat similar to those in a switchgear unit. After evacuation, the corona chamber was isolated from the rest of the system and filled with pure SF_6 gas to a pressure of 100 kPa. The analyser tube of the mass spectrometer was evacuated and baked to provide a pressure of better than 5×10^{-6} Pa.

The corona discharge was operated at 75 µA for about 145 hours and the gas was analysed every 10 hours discharge. During gas analysis, the corona discharges were switched off. The discharge current was closely monitored and maintained steady at around 75 µA by operating the power supply in fixed-current setting. A

reference mass spectrum was obtained using a fresh SF_6 gas sample at time t = 0.

The procedure for analysing samples from the corona chamber is as follows:

1. Background mass spectrum traces were taken of the residual gas in the mass-spectrometer analyser tube prior to admitting a sample.

2. A sample was leaked into the mass-spectrometer analyser tube through a low volume needle valve to provide a constant pressure of 4 x 10^{-5} Pa. The sample from the chamber was flowed continuously through the mass-spectrometer analyser tube. Sample traces of mass spectra were recorded and plotted by an IBM-PC computer.

3. Results and Discussions

Mass spectra of gas samples were taken from coronas at different times under two different experimental conditions, negative coronas and positive coronas. A commercial SF_6-insulated switchgear chamber is not baked during evacuation, and the cost of the vacuum procedures needed to completely eliminate the presence of water vapour in a system is prohibitive. As a consequence, the chamber normally contains traces of oxygen and water vapour.

Examples of mass spectra for different times and different conditions are shown in Figure 2. The sensitivity of the mass spectrometer is different for different gases, so that the relative peak heights in Figure 2 do not indicate directly the relative concentrations of the gas species. In order to obtain information on the relative concentrations of the gas species from the mass spectra, they need to be adjusted to allow for the different gas sensitivities. A method of analysis has been developed to provide a useful picture of the chemical processes, and SF_6 dissociation and by-product production occurring in SF_6 coronas. Data of mass spectrometer sensitivity for different gases collected by Grey[6] were used to correct the relative peak heights in Figure 2. Figure 2 reveals that both positive and negative coronas reduce the concentration of SF_6 and produce gaseous by-products.

(a)

(b)
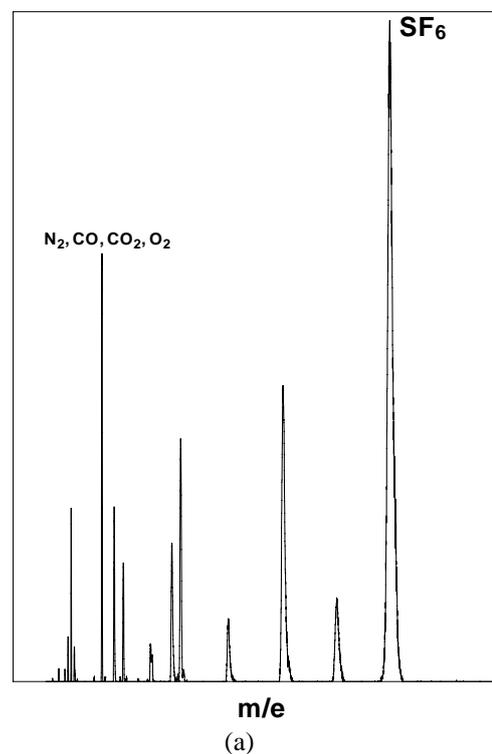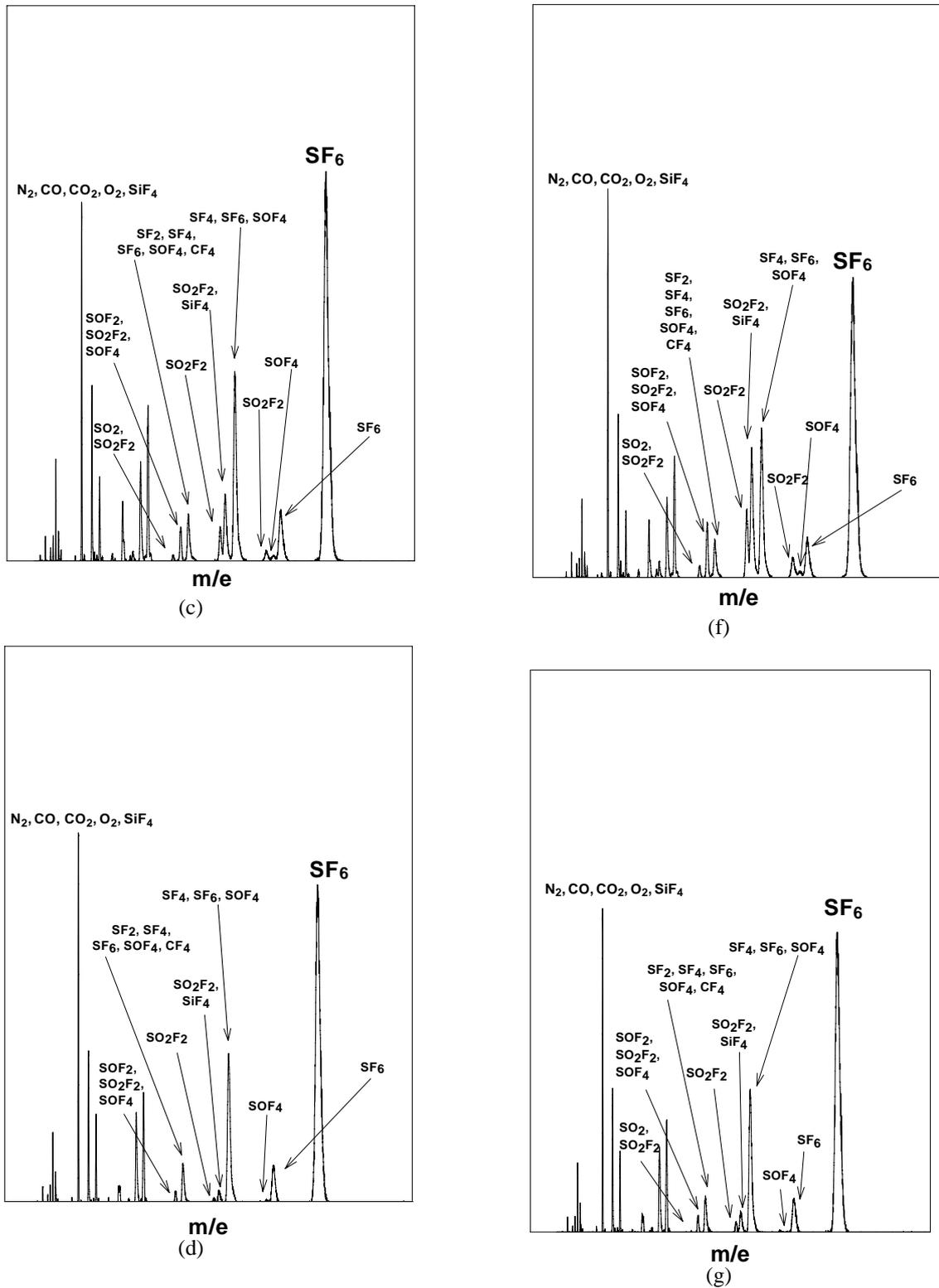
Figure 2. SF_6 mass spectrum taken in (a) positive corona at t = 0; (b) negative corona at t = 0; (c) positive corona at t = 77 hours; (d) negative corona at t = 80 hours; (e) positive corona at t = 146 hours; (f) negative corona at t = 145 hours.

Figures 3 and 4 reveal that both positive and negative coronas degrade or dissociate SF_6 at a rate proportional to the transported charge, which is the product of the discharge time and the average discharge current. The dissociation of SF_6 is accompanied by the production of gaseous by-products as a result of chemical reactions between the products of SF_6 dissociation and contaminants in the chamber. The rates of SF_6 dissociation and gaseous by-product production in positive coronas are higher than in negative coronas. Both coronas produced the same major gaseous by-products, which are SiF_4, SO_2F_2 and SOF_2. The most abundant gaseous by-product for both coronas is SiF_4. SO_2F_2 is the next most abundant by-product in positive coronas, whereas SOF_2 is the next highest in negative coronas. Besides those major by-products, SOF_4, SO_2 and HF were also observed as minor by-products in both types of corona.
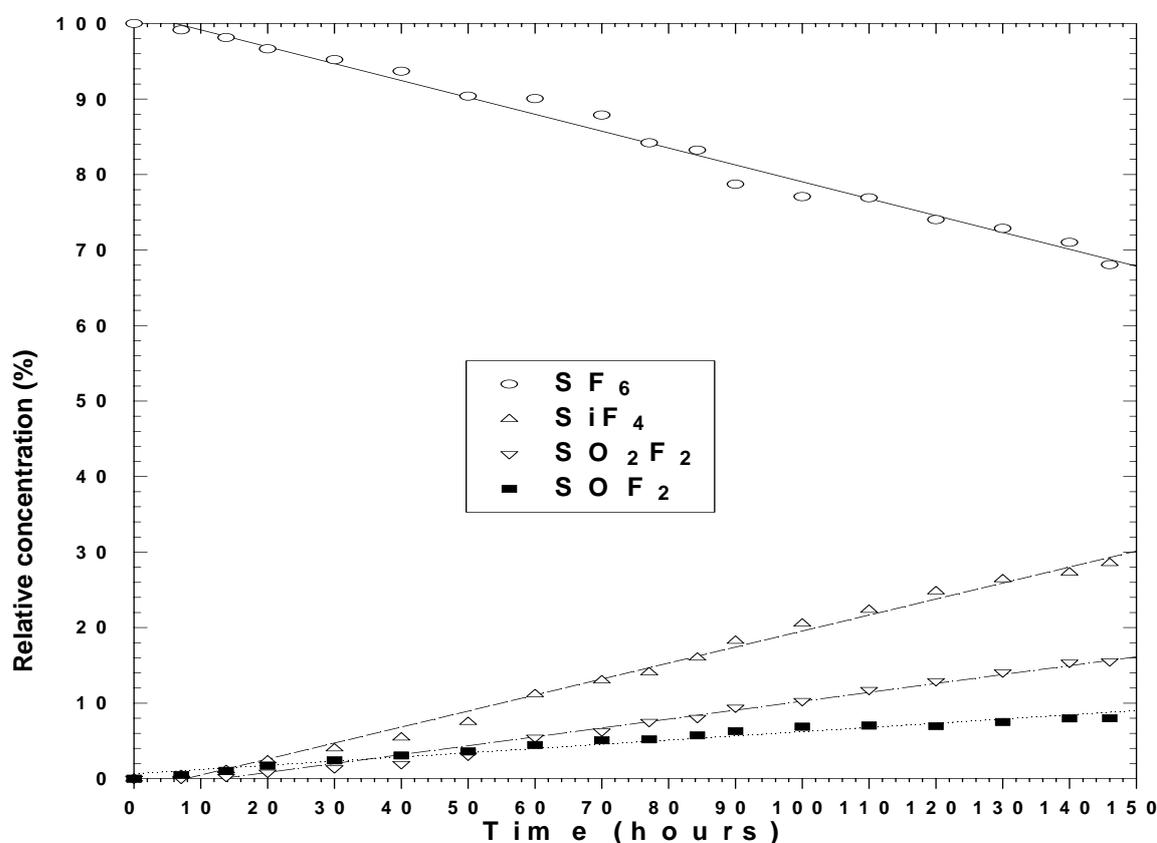
Figure 3. Concentration-time curves for SF_6, SiF_4, SOF_2 and SO_2F_2 during a 100 kPa, 75 µA positive corona discharge.

Besides gaseous by-products, positive and negative coronas also produce solid by-products. Coating and surface modification were observed at both electrodes. For positive coronas, the point electrode was found to be more coated and damaged than for negative coronas, whereas the reverse was the case for the plane electrode. For both positive and negative coronas, the positive electrode showed localised regions of a dark grey-green deposit. The deposits are likely to be metallic fluoride as a result of reaction between the metal electrode and fluorine in the form of negative ions. The positive electrodes also displayed appreciable pitting. The negative electrodes were also coated and pitted, but to a much lesser degree.
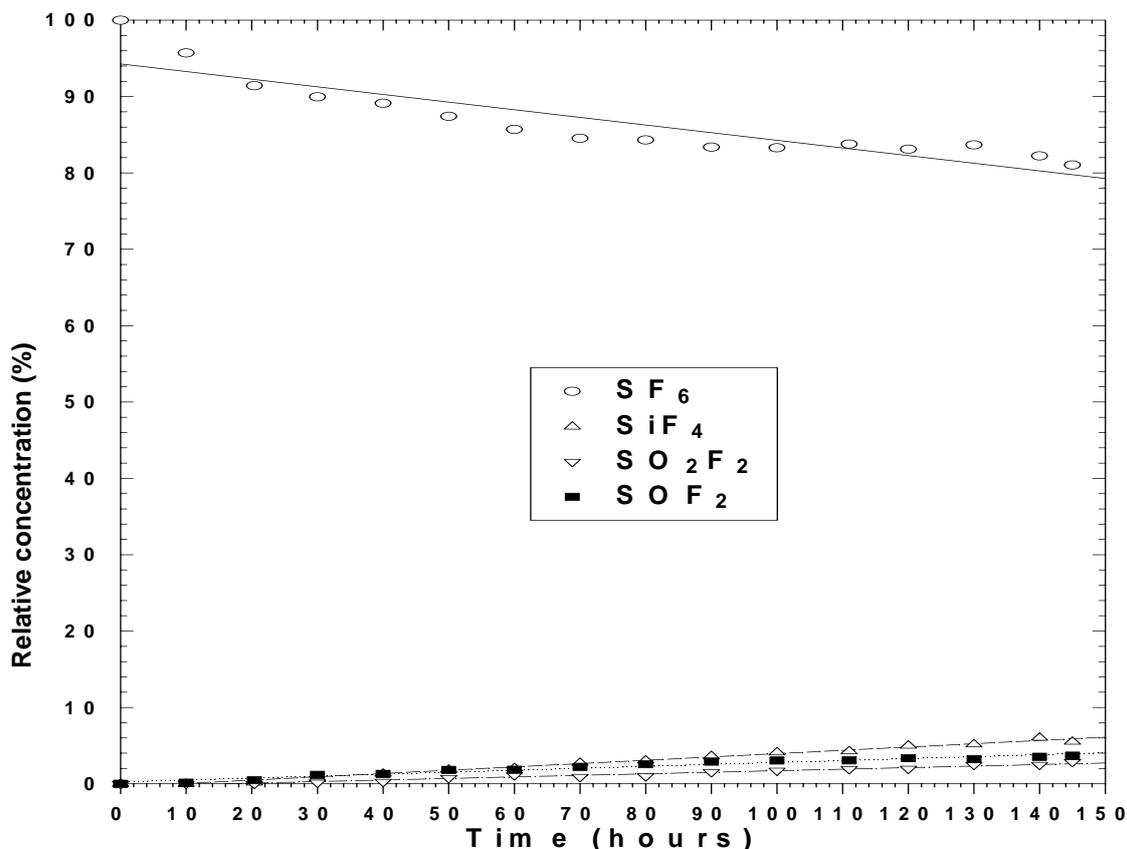
Figure 4. Concentration-time curves for SF_6, SiF_4, SOF_2 and SO_2F_2 during a 100 kPa, 75 μA negative corona discharge.

Figures 2, 3 and 4 reveal that the rate of SF_6 decay and gaseous by-product production are strongly influenced by both the discharge environment and the type of corona. By-products are formed by chemical reactions between contaminants and SF_x fragments. Among the impurities present in the discharge chamber were H_2O, O_2, N_2 and CO_2, existing both in the gas phase and at electrode and chamber surfaces. Among them, H_2O and O_2 have the most significant influence on the discharge chemistry.

SF$_6$ is dissociated in a corona through electron-impact to form F and SF_x (x < 6). These then react with contaminants or with a surface to form by-products, or reformation of SF_6 may occur. Therefore, the rate at which SF_6 degradation occurs depends on a balance between dissociation, reactions between products of SF_6 dissociation and contaminants, and the recombination processes of the lower-order sulphur fluorides and atomic fluorine. Clearly, impurities in the corona environment enhance SF_6 degradation and oxyfluoride production.

Figures 3 and 4 show that the rate of SF_6 degradation in a positive corona is almost double

that of a negative corona, and the by-product production rate in a positive corona is almost five times that for a negative corona. The avalanche-initiating electrons in a positive corona form in the gas, while in a negative corona, they come from the surface of the point electrode. The ionisation region of a corona is confined around the point electrode. In the case of a positive corona, the electrons and negative ions such as F^- move towards the high electric field point electrode. In a negative corona, where positive space charge dominates the ionisation region, positive ions move onto the point electrode and the electrons and negative ions drift into the lower electric field region of the main gap towards the plane electrode. For a positive corona, as the electrons move toward the higher field region, their energy increases, so the electron avalanches grow with very high electron energies resulting in increasing rates of dissociation and ionisation. For a negative corona, as the electrons move out from the point electrode, they move towards a lower field region, and the electron avalanches occur with decreasing electron energies. This leads to a higher rate of electron-impact dissociation of SF_6

in a positive corona than in a negative corona. Thus the higher rate of oxyfluoride production in an SF_6 positive corona than in an SF_6 negative corona indicates that the oxyfluoride production is controlled mainly by the availability of SF_6 fragments as a result of electron-impact-induced SF_6 dissociation. Furthermore, the surface of a positive-point electrode is likely to be hotter than the surface of a negative-point electrode as a result of electron bombardment, and this may cause a higher rate of O_2 and H_2O release from the positive-point electrode into the discharge volume which would also enhance oxyfluoride production[4]. In a positive corona, the point electrode is a target of bombardment by highly energetic negative ions and electrons. The reverse is the case for a negative corona where the point electrode is bombarded by positive ions which are less reactive than negative ions. Hence more severe solid deposition and pitting occurs for a positive point electrode than for a negative point electrode.

SiF$_4$ is the most abundant stable gaseous by-product detected for both positive and negative coronas, when a borosilicate glass window is used in the chamber. The concentration of SiF_4 is proportional to the charge transported, and since there is no deviation from linearity over the range of experiment conditions, it appears that no secondary reactions involving SiF_4 occur. Possible reactions producing SiF_4 at the surface of the glass window are

$$2SF_4 + SiO_2 \rightarrow SiF_4 + 2SOF_2 \qquad (1)$$

$$SF_4 + SiO_2 \rightarrow SiF_4 + SO_2 \qquad (2)$$

$$2SOF_2 + SiO_2 \rightarrow SiF_4 + 2SO_2 \qquad (3)$$

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O \qquad (4)$$

$$4F + SiO_2 \rightarrow SiF_4 + O_2 \qquad (5)$$
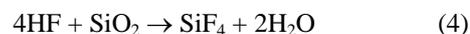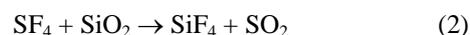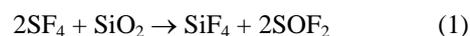
Following analysis of data collected from investigations of glass fibre etching using positive and negative coronas of SF_6 and $SF_6 + H_2$ in unbaked and baked chambers, it is believed that reaction (4) is the major producer of SiF_4 and that reaction (5) makes little contribution to SiF_4 production. Even though only a very small amount of HF was detected using the mass spectrometer, there is nevertheless likely to be a significant amount produced in the corona chamber. Because of its high reactivity, most of the HF reacts with surfaces and does not reach the mass spectrometer. Reactions (1), (2) and (3) are shown later to be unimportant for SiF_4 production.

In general, SOF_2 and SO_2F_2 are the other major stable gaseous by-products generated in both positive and negative coronas. In a positive corona, SO_2F_2 is the second most abundant by-product, whereas in a negative corona SOF_2 is the second most abundant by-product. The concentrations of both increase in proportion to the charge transported. The possible reactions producing SOF_2 and SO_2F_2 in the SF_6 corona are

$$SF_4 + OH \rightarrow SOF_2 + HF + F \qquad \Delta H^0_{298K} = -130 \text{ kJ/mol} \qquad (6)$$

$$SF_3 + OH \rightarrow SOF_2 + HF \qquad k = 8.1 \times 10^{-14} \text{ cm}^3/\text{s} \quad [12] \qquad (7)$$

$$SF_4 + O \rightarrow SOF_2 + 2F \qquad \Delta H^0_{298K} = -124 \text{ kJ/mol} \qquad (8)$$

$$SF_3 + O \rightarrow SOF_2 + F \qquad k = 1.0 \times 10^{-12} \text{ cm}^3/\text{s} \quad [12] \qquad (9)$$

$$SF_2 + O \rightarrow SOF_2 \qquad \Delta H^0_{298K} = -496 \text{ kJ/mol} \qquad (10)$$

$$SF_4 + H_2O \rightarrow SOF_2 + 2HF \qquad k = 1.7 \times 10^{-19} \text{ cm}^3/\text{s} \qquad (11)$$

$$SF_3 + O_2 \rightarrow SO_2F_2 + F \qquad \Delta H^0_{298K} = -260 \text{ kJ/mol} \qquad (12)$$

$$SF_2 + O_2 \rightarrow SO_2F_2 \qquad k \leq 5 \times 10^{-16} \text{ cm}^3/\text{s} \qquad (13)$$

$$SOF_4 + H_2O \rightarrow SO_2F_2 + 2HF \qquad k = 2.0 \times 10^{-21} \text{cm}^3/\text{s} \qquad (14)$$
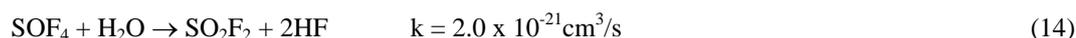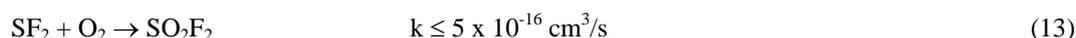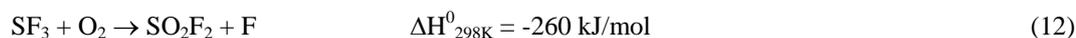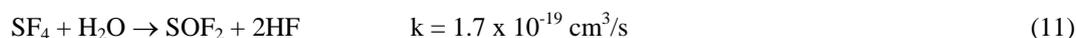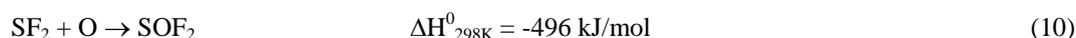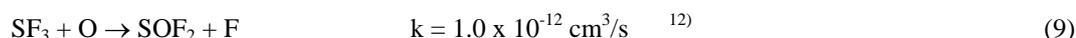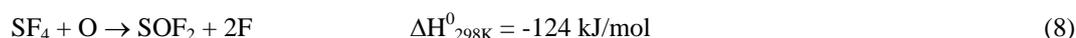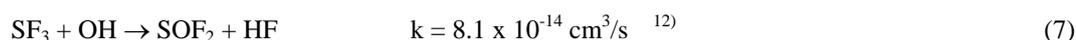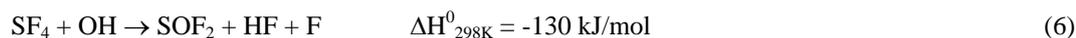
The linearity of the SOF_2 and SO_2F_2 concentrations with time suggests that secondary reactions involving these species are unimportant. Reactions (6) - (11) show that production of SOF_2 is dependent on the presence of SF_x fragments. Reactions (6) - (10) are relatively unimportant for SOF_2 production compared to reaction (11),

which can occur in the main gas volume or at the chamber wall.

In his glow discharge work, Grey observed that the rate of SO_2F_2 production is strongly dependent on O_2 concentration rather than on atomic O concentration[6], so that reactions (12) and (13) may be the important contributors to SO_2F_2 production. The addition of O_2 enhances

the SO_2F_2 yield. Derdouri *et al*. observed the SO_2F_2 level to be independent of the H_2O level[13]. This suggests that the hydrolysis reaction (14) is very slow in the gas-phase. It is believed that this reaction in the gas-phase cannot account for the observed production of SO_2F_2. However, it can be a rapid reaction at the surface of the wall containing adsorbed H_2O[14]. Thus it may account for the low production of SOF_4 in this work.

Early in the positive corona, the relative concentration of SOF_2 was found to be higher than that of SO_2F_2, but after about 50 hours the relative concentration of SO_2F_2 exceeded SOF_2. On the other hand, the production rate of SOF_2 in a negative corona was always higher than that of SO_2F_2. This may be due to energetic electrons and negative ions striking the point electrode in the positive corona and heating the point electrode, thus increasing the rate of oxygen release which has an influence on the production of SO_2F_2 through reactions (12) and (13). Van Brunt and Siddagangappa and Pradayrol *et al*. state that SO_2F_2 is formed preferentially by reactions involving O_2[15,16].

In the present work, the observed uniformity of the SOF_2 production rate with time and the fact that no change in SOF_2 level took place after terminating the discharge over a 10-hour period indicates that secondary reactions involving SOF_2 are not important.

Van Brunt and Pradayrol *et al*. reported that SOF_4 is a major by-product of SF_6 coronas[4,16]. However, in the present work, SOF_4 is found only as a minor by-product. The reason for the low rate of production of SOF_4 in this work is obscure, but it may be due to SOF_4 hydrolysis with water on the surface via reaction (14) to form SO_2F_2.

SO_2 is also a minor by-product. SO_2 can be removed by hydrolysis reactions to produce H_2SO_3 which would condense on the chamber wall[17]. It may cause a small rate of production of SO_2 here.

It is likely that HF has a much higher concentration than that detected by the mass spectrometer. HF is a highly reactive molecular species, which attacks the wall of the chamber and the electrodes. HF is also hydrophobic, and will bind to the chamber wall. Thus, in this work, most of HF has already disappeared before entering the mass spectrometer. Extensive experiments indicate that HF is the major etchant of the glass window and the optical fibre sensor through reaction

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O \qquad (4)$$
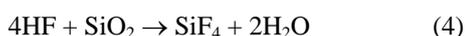
4. Conclusions

Sulphur hexafluoride (SF_6) is widely used as an insulator and an arc quenching medium in high voltage systems. However, the cost of ensuring perfectly-smooth interior surfaces throughout a high-voltage system is prohibitive, with the result that modern, newly-installed circuit-breakers invariably present one or more insidious coronas. Following installation, therefore, the integrity of the insulation of an SF_6 circuit breaker is slowly being impaired as a result of molecular dissociation by the corona and consequent generation of by-products. If the SF_6 is not renewed, failure of the device is likely to eventually occur. To prevent failure of such a system, a monitoring system for SF_6 degradation is required.

The results of the mass spectrometer studies show that the rates of SF_6 degradation and by-product production due to a positive corona are significantly higher than those for a negative corona. This result is consistent with the higher mean electron energies in a positive corona than that in a negative corona[4]. The rates of degradation and production of SF_6 and gaseous by-products are proportional to the charge transported by the corona. Both positive and negative coronas produce the same major gaseous by-products, SO_2F_2 and SOF_2, and these are generated by reactions between the SF_6-dissociation species, SF_x and F, and water-vapour and oxygen impurities. Besides gaseous by-products, coronas also produce solid by-products, particularly on the electrodes. Due to the impact of high-energy electrons and F^- ions, the positive electrode, point or plane depending on corona polarity, is always more coated and damaged than the negative electrode. The deposits on the positive electrode are metal fluorides produced by chemical reaction between hydrogen fluoride or fluorine and the electrode material. Because of their higher rates of chemical reactivity, fluorine and HF could not be detected by the mass spectrometer.

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