Experiment Study of Trace Water and Oxygen Impact on SF₆ Decomposition Characteristics Under Partial Discharge

Fuping Zeng*, Ju Tang†, Yanbin Xie**, Qian Zhou*** and Chaohai Zhang§

Abstract – It is common practice to identify the insulation faults of GIS through monitor the contents of SF₆ decomposed components. Partial discharges (PD) could lead to the decomposition of SF₆ dielectric, so new reactions usually occur in the mixture of the newly decomposed components including traces of H₂O and O₂. The new reactions also cause the decomposed components to differ due to the different amounts of H₂O and O₂ even under the same strength of PD. Thus, the accuracy of assessing the insulation faults is definitely influenced when using the concentration and corresponding change of decomposed components. In the present research, a needle-plate electrode was employed to simulate the PD event of a metal protrusion insulation fault for two main characteristic components SO₂F₂ and SOF₂, and to carry out influence analysis of trace H₂O and O₂ on the characteristic components. The research shows that trace H₂O has the capability of catching an F atom, which inhibits low-sulfide SF₆ from recombining into high-sulfide SF₆. Thus, the amount of SOF₂ strongly correlates to the amount of trace H₂O, whereas the amount of SO₂F₂ is weakly related to trace H₂O. Furthermore, the dilution effect of trace O₂ on SOF₂ obviously exceeds that of SO₂F₂.

Keywords: Partial discharge, SF₆, Decomposed component concentration, Trace H₂O and O₂, Influence regularity

1. Introduction

Different patterns and strengths of partial discharge (PD) always occur when SF₆ electrical equipment have some earlier insulation faults. High local electromagnetic energy caused by PD would cause SF₆ to decompose into several kinds of low-fluoride sulfide SFₓ [1-4]. If trace levels of H₂O and O₂ exist in the equipment, the decomposed components would have further reactions with them and produce new characteristic components, such as SO₂F₂, SOF₂, SO₂ and so on [5-11]. The concentration and variation regularity of these characteristic components have close relationship with the patterns of insulation faults, as well as the trace levels of H₂O and O₂ in gaseous SF₆, making it more difficult to recognize the internal insulation deficiency when using them. Although the new gas SF₆ contains few impurities, trace levels of H₂O and O₂ would enter the gas chamber as they are released from internal material or by penetration from the outside air over time [12]. There would be extra-trace levels of H₂O and O₂ inevitably existing in the SF₆ electrical equipment. Hence, when extra-trace levels of H₂O and O₂ exist in SF₆ gas, learning about the decomposition mechanism from both theory and experiment under PD are necessary; obtaining the influence regularity and influence mechanism of trace H₂O and O₂ on decomposed components is urgent. Furthermore, it is imperative to offer an amendment method considering the impacts of trace H₂O and O₂ so that all of the aforementioned methods would lay a solid theoretical foundation for the correct identification and evaluation of the internal insulation faults of SF₆ electrical equipment when making use of the decomposed components.

R. J. Van Brunt from the U.S. National Bureau of Standards conducted a systematic research about the SF₆ decomposition mechanism under PD. He studied the main source [13] of the O atom in SO₂F₂, SOF₂, and SOF₄ using the isotopic tracer technique under the condition of needle-plate electrode of corona discharge. His study pointed out that the O atom of SO₂F₂ mainly comes from O₂, the O atom of SOF₂ mainly comes from H₂O, and the O atom of SOF₄ comes from both O₂ and H₂O. However, the paper also claimed that SO₂F₂ obtains the O atom from H₂O and SOF₂ obtains the O atom from O₂. Nevertheless, the Van Brunt research used the same fixed concentration of H₂O and O₂ without considering their levels of variation. According to Arrhenius’ law of chemical reaction kinetics and mass action law [14], the chemical reaction rate depends on the reaction temperature, reactant concentration, and catalyst. Although Derdouri studied the impact of diverse concentrations of H₂O on SF₆ gas under PD, there is a lack of explanation of the process [15].
In this paper, the authors take advantage of the PD decomposition platform in the laboratory and study the concentration of decomposed SF₆ components and their variation trends under PD when different trace levels of H₂O and O₂ are mixed with SF₆. Moreover, the mechanism of how the various concentrations of trace water and oxygen act on the characteristic decomposed components from the angle of related chemical reaction rate is explained. Considering that random factors may lead to unfavorable results during the experiment, statistical inference using ANOVA is used to investigate the degree of impact of trace H₂O and O₂ on decomposed characteristic components of SF₆.

2. Decomposition Experiment and Quantitative Measurement

2.1 Experiment

This work studies the degree of influence of H₂O and O₂ on decomposed characteristic components of SF₆ under PD from the statistical perspective. Hence, repeating the experiment independently \(n\) (here \(n=4\)) times under the same trace levels of H₂O and O₂ (the level is \(A_i\)) and making sure that each experiment group has only one variable. The procedure suggests that the concentration of O₂ is controlled below 100ppm (the rate of oxygen analyzer is 100ppm) in the experiment gas sample when the experiment on the influence of different trace levels of H₂O was conducted. Likewise, the concentration of H₂O is controlled below 150 ppm when the experiment on the influence of different trace levels of O₂ was conducted. Experimental factors A (H₂O) and B (O₂) were subjected into seven experimental levels, as shown in Table 1.

<table>
<thead>
<tr>
<th>Level</th>
<th>A (H₂O) in ppm</th>
<th>B (O₂) in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>300</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>700</td>
<td>220</td>
</tr>
<tr>
<td>3</td>
<td>1000</td>
<td>460</td>
</tr>
<tr>
<td>4</td>
<td>1300</td>
<td>900</td>
</tr>
<tr>
<td>5</td>
<td>1600</td>
<td>2140</td>
</tr>
<tr>
<td>6</td>
<td>1800</td>
<td>4960</td>
</tr>
<tr>
<td>7</td>
<td>2100</td>
<td>10250</td>
</tr>
</tbody>
</table>

Experiment material: SF₆ (purity: 99.99%, H₂O ≤100 ppm, O₂ ≤100ppm), H₂O, and O₂ were used as experiment materials. The experiment was conducted in the multifunction electrical decomposition of SF₆ equipment designed by our group, which is shown in Fig. 1 [16]. The main body of gas chamber is cylinder and both ends are oval structure to guarantee its air tightness. The volume of the chamber is approximately 10L and the maximum tolerance of air pressure can reach 0.5Mpa. The material of gas chamber is made of stainless steel for its corrosion resistance since the corrosive decomposed compositions of SF₆ may be produced during the experiment. Lead the HV conductor in the gas chamber through HV bushing and the model of insulation faults is positioned in the middle of the gas chamber so that it can connect with bottle of the HV conductor. Gas inlet and gas outlet is equipped to fill in SF₆ required in the experiment and gather the mixed gases sample after PD experiment.

The gas chamber was filled with 0.2 MPa of SF₆. The experimental system diagram is shown in Fig. 2. The needle-plate electrode is needed to simulate the common insulation fault (metal protrusion insulation fault) in the equipment. Moreover, the experiment made use of non-inductive detected impedance to send the pulse current signal to the WavePro 7100XL oscilloscope (Analog band: 1 GHz; sampling rate: 20 GHz; memory depth: 48 MB), which can monitor whether the PD is stable.

2.2 Experiment methods

This experiment uses needle-plate electrode model: spacing \(d\) is 10mm, curvature radius of needle tip is 0.3mm, diameter of ground electrode is 120mm and its thickness is 10mm. All the experiments are conducted at the same condition: the laboratory temperature is controlled at 15°C and relative humidity at 50%, to avoid the impacts of different temperatures and humidity and ensure the experimental results are comparable. The specific experimental requisition and steps are listed as follows:

1. Measurement of the initial voltage \(U_i\) of the intrinsic
PD of the equipment (without putting insulation faults model) and the initial voltage \(U_0\) of the PD of the equipment (after putting the needle-plate electrodes). The respective measurements are \(U_0 = 45\) kV and \(U_0 = 15\) kV.

(2) The gas chamber is vacuumized and then filled with new gas, SF\(_6\), and vacuumized again. This process is repeated two or three times for purification.

(3) For the experimental procedure on the influence of H\(_2\)O on the decomposed characteristic components of SF\(_6\), step (4) is used. Otherwise, for the experiment on the influence of O\(_2\) on the decomposed characteristic components of SF\(_6\), step (5) is used.

(4) The gas chamber is filled with the required amount of H\(_2\)O by gas-syringe when the chamber is in vacuum condition, and subsequently heated in the equipment for 15 minutes. Another 15 minutes is spent to permit the H\(_2\)O to undergo gasification and uniform distribution in the gas chamber. Step (6) follows.

(5) The gas chamber is filled with the required amount of O\(_2\) when the chamber is in vacuum condition. Another 15 minutes is spent to permit the full volume of O\(_2\) to be uniformly distributed in the chamber.

(6) The gas chamber is filled with SF\(_6\) equivalent to a pressure of 0.25 MPa and put aside for 24 hours, so that H\(_2\)O (or O\(_2\)) and SF\(_6\) are fully mixed.

(7) The concentration of H\(_2\)O and O\(_2\) in the mixed gas is measured. If the concentration fails to meet the experimental standards, the procedure goes back to step (2). When the measured concentrations have satisfied the standards, the gas sample is collected and its intrinsic components are analyzed. The respective concentrations of the constituent gases are also measured. Afterward, the mixed gas pressure is adjusted to 0.2 MPa.

(8) The electrical wiring is connected as shown in Fig. 2. The experimental voltage is then gradually raised to 1.5\(U_0\) (22.5 kV) and the PD decomposition experiment is conducted for 10 hours under this voltage. This part of the procedure ensures that the contents of the characteristic components are stable. The oscilloscope is used to monitor the electrical discharge of the needle-plate electrode.

(9) After 10 hours, the concentration of the different decomposed components in the collected gas sample is analyzed using gas chromatograph (GC).

(10) After measuring all the experimental parameters, the gas chamber is vacuumized and put aside for 1 hour to enable absorption of the decomposed components by the surface of the electrode. The time allowance is also aimed to fully extricate the decomposed components attached on the chamber wall and inhibit the impact of the remaining components of the ongoing experiment to the next experiment. The procedure is then repeated from step (2) for the next experiment.

### 2.3 Quantitative measurement of decomposed components

In the aforementioned experiments, the gas chromatograph (Varian CP-3800) was used to quantitatively measure the sample gas components produced by the discharge. The GC used the packed column Porapak QS and special capillary column CP-Sil 5 CB in parallel to separate the components in the mixture. Moreover, the chromatograph used PDHID double detectors (detection precision can reach up to 0.01 ppm) to quantitatively detect each separated component. The chromatographic column was operated in the He (purity: 99.9999%) carrier gas and the working conditions were flow rate, 2 mL/min; constant column...
temperature, 40 °C; sample size, 1 mL; and split ratio, 10:1. Under these conditions, the packed column could separate air, CF₄, and CO₂ effectively, and the special capillary column could separate air, SF₆, SO₂F₂, SOF₂, H₂S, and SO₂ effectively. Fig. 3 shows the standard chromatograph.

This study used the external standard method combined with the standard chromatogram to qualitatively and quantitatively detect the decomposed components of SF₆. Since the SO₂F₂ and SOF₂ are the most important characteristic decomposed components of SF₆ [1, 3, 6–8, 13, 17, 18], the present study conducted intensive research on both. The raw data of each experiment as show in Table 2, Figs. 4 and 5 are the results of production amounts of the SO₂F₂ and SOF₂ yields under PD at different levels of H₂O and O₂ in 10 hours (Each result is the production average value of four times repeated experiments under the same level of trace H₂O or O₂).

3. Influence of H₂O and O₂ on Characteristic Components

Fig. 4 and Fig. 5 show that different levels of H₂O and O₂ contribute to different concentrations of SO₂F₂ and SOF₂ produced by SF₆ even under the same strength and time length of PD. Besides, the inevitable random factors which exert impacts on the experiment results should be considered in the experiment. Hence, the authors used ANOVA to study the impact of the various levels of trace H₂O and O₂ on characteristic components SO₂F₂ and SOF₂ and identify the main influence factors on the production of SO₂F₂ and SOF₂.

3.1 Analysis of variance

ANOVA was introduced by the American statistician Fisher in an agricultural experiment [19]. Subsequently, the method has been widely used in other areas, especially in data analysis of industrial experiments where the method ANOVA shows that the total variance (S_T²) in the sample data can be divided into two parts: variance between groups (S_A²) and variance within groups (S_E²). S_A² is caused by controllable influential factors of different levels and S_E² is caused by all random errors, that is S_T² = S_A² + S_E². The size of the difference between groups and the size of the difference within groups are compared to identify the degree of impact of each level on the experimental results, where S_A², S_E², and S_T² can be achieved from Equ. (1) to (3):

\[ S_T^2 = \sum_{i=1}^{r} \sum_{j=1}^{n} (x_{ij} - \bar{x})^2 \]  
\[ S_A^2 = n \sum_{i=1}^{r} (\bar{x}_i - \bar{x})^2 \]  
\[ S_E^2 = \sum_{i=1}^{r} \sum_{j=1}^{n} (x_{ij} - \bar{x}_i)^2 \]
In the above equations, $x_{ij}$ is the $j$-th independent experimental result under the i-th concentration level of trace H$_2$O and O$_2$ ($A_i$), which means it is the result of the concentration of SOF$_2$ or SOF$_2$ when conducting the $j$-th experiment independently under the i-th concentration level of trace H$_2$O and O$_2$ ($A_i$); $\overline{x}_i$ represents the group mean of the product of SO$_2$F$_2$ or SOF$_2$ under the i-th concentration level of trace H$_2$O and O$_2$ ($A_i$) when conducting experiment $n$ times independently; $\overline{x}$ represents the mean of all the products of SO$_2$F$_2$ or SOF$_2$ under the same influence factor (trace H$_2$O or O$_2$) concentration level. There are seven concentration levels in the present study, hence, $r=7$. $n$ is the number of times the experiment is repeated under the same condition, and in the current study, the experiment is repeated 4 times under the same concentration of trace H$_2$O and O$_2$, thus, $n=4$.

If all the experimental factors (trace H$_2$O and O$_2$) have no significant influence in the experimental results, $S_E^2$ is almost equal to $S_A^2$ and statistics can prove that

$$ F = \frac{S_A^2/(r-1)}{S_E^2/r(n-1)} \sim F(r-1,rn-r) \quad (4) $$

In the equation, $(r-1)$, $rn(n-1)$ are the degrees of freedom of $S_A^2$ and $S_E^2$, respectively. Furthermore, let $S_A^2 = S_A^2/(r-1)$, $S_E^2 = S_E^2/r(n-1)$ and call them mean variance, so that equation (4) can be simplified as

$$ F = \frac{S_A^2/S_E^2}{F(r-1,rn-r)} \quad (5) $$

ANOVA merely makes use of equation (5) to identify the degree of impact of each level (trace H$_2$O or O$_2$) on the experimental results by comparing the differences between groups and the differences within groups. Given the significance level $\alpha$, when the calculated value of $F$ is above the critical value $F_{\alpha}(r-1,rn-r)$, the influence factor (trace H$_2$O or O$_2$) has significant influence on the experimental index (generation amount of SO$_2$F$_2$ and/or SOF$_2$). Furthermore, the bigger the $F$ value of the sample, the more significant the influence the factor has on the experimental index. Hence, specific attention has to be accorded on such influence factor, and additionally such influence factors should be controlled during practical production.

3.2 Analysis of the significance level of influence factors

Significance level $\alpha$ is a critical probable value that represents the possibility to commit the fallacy of refusing the ‘assumption’ in a ‘statistical hypothesis test’ when using the sample information to draw conclusion. The smaller the value of $\alpha$, the lesser the possibility of making the mistake of refusing the ‘assumption’. When analyzing data in the field of general industry, $\alpha = 0.05$; in the field of biology and medicine, $\alpha = 0.01$. In the present study which examines the degree of influence of trace H$_2$O and O$_2$ on the main characteristic components of SF$_6$ (SO$_2$F$_2$ and SOF$_2$) under PD, high precision is required. Hence, a significance level of $\alpha = 0.01$ is adopted. The table of $F$-distribution critical values shows that $F_{0.01}(6,21) = 3.81$. The result is presented in Table 3.

By collating and analyzing the results from Fig. 4, Fig. 5, and Table 3, the findings indicate that both H$_2$O and O$_2$ exert an influence on the main characteristic components SO$_2$F$_2$ and SOF$_2$. However, the products and the degree of influence of H$_2$O and O$_2$ are different. The differences include the fact that H$_2$O has an obvious influence on SOF$_2$ as the $F$ value reaches 87.94, which is much larger than its influence on SO$_2$F$_2$. The formation of SOF$_2$ is linearly proportional to the concentration of H$_2$O, but the formation of SO$_2$F$_2$ has almost no relationship with the concentration of H$_2$O.

Table 3. Analysis of variance result

<table>
<thead>
<tr>
<th>Decomposed component</th>
<th>Influence factor</th>
<th>Error</th>
<th>Degree of freedom</th>
<th>Mean variance</th>
<th>$\alpha$-level</th>
<th>Value of $F$</th>
<th>Is influence significant?</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOF$_2$</td>
<td>H$_2$O</td>
<td>$S_x^2$</td>
<td>6</td>
<td>16.82</td>
<td></td>
<td>3.52</td>
<td>not obvious</td>
</tr>
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<td></td>
<td></td>
<td>$S_x^2$</td>
<td>21</td>
<td>4.44</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>O$_2$</td>
<td>$S_x^2$</td>
<td>6</td>
<td>26.69</td>
<td></td>
<td>4.44</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S_x^2$</td>
<td>21</td>
<td>6.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOF$_2$</td>
<td>H$_2$O</td>
<td>$S_x^2$</td>
<td>6</td>
<td>392.34</td>
<td></td>
<td>87.94</td>
<td>especially</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S_x^2$</td>
<td>21</td>
<td>7.26</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>O$_2$</td>
<td>$S_x^2$</td>
<td>6</td>
<td>140.03</td>
<td></td>
<td>11.98</td>
<td>especially</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S_x^2$</td>
<td>21</td>
<td>11.69</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4. The influence Mechanism of H$_2$O and O$_2$ on the Characteristic Decomposed Components

Under PD, a series of characteristic components are produced by the reaction between the low-fluoride sulfide caused by the decomposition of SF$_6$ and the trace levels of H$_2$O and O$_2$ mixed in the gas. Van Brunt carried out a more detailed study of the SF$_6$ decomposition mechanism under
PD with a needle-plate electrode mode. He proposed using the Plasma Chemical Model to explain the SF₆ decomposition mechanism under PD [8]. He pointed out that under the effect of the high-energy electrons generated by the PD, the following reaction will occur in SF₆:

\[
e + SF₆ \rightarrow SFₓ + (6-x)F + e, \ x = 1 \sim 5
\]  

(6)

The high-energy electrons lead to the decomposition of SF₆ to produce low-fluoride sulfide SFₓ (x = 1 to 5). When no other impurities exist in SF₆, SFₓ will recover quickly with the following reaction:

\[
SFₓ + (6-x)F \rightarrow SF₆, \ x = 1 \sim 5
\]

(7)

\[
k = (1.5 \sim 2.4) \times 10^{11}
\]

Here, k is the rate constants of the reaction. However, during the long-term operation of the SF₆ gas-insulated equipment, it is inevitable that different amounts of ultra-impurity gases, such as H₂O and O₂, will appear in the chamber, released by the internal material of the device and the penetration of external H₂O and O₂ into the equipment. The impurities will lead to a series of more complex chemical reactions with SFₓ and generate SO₂F₂, SOF₂, HF, SO₃, and other compounds. Therefore, trace amounts of H₂O and O₂ play a key role in the production of SO₂F₂ and SOF₂.

### 4.1 Analysis of the characteristic decomposed component with the impact of H₂O

H₂O will undergo the following reaction under PD when H₂O exists:

\[
e + H₂O \rightarrow H + OH + e
\]

(8)

\[
OH + OH \rightarrow O + H₂O
\]

(9)

Meanwhile, the following reactions will occur among H₂O and SF₆ decompositions:

\[
F + H₂O \rightarrow HF + OH, \ k = 9.0 \times 10^{-12} \text{ cm}^3/\text{s}
\]

(10)

\[
F + OH \rightarrow FOH, \ k = 5.0 \times 10^{-13} \text{ cm}^3/\text{s}
\]

(11)

The reaction rate constants k of the reaction (10), (11) and reaction (7), are in the same order of magnitude. On the other hand, the mass action law [14] tells us that the chemical reaction rate r depends on the reactant concentration, Cᵢ, the stoichiometry number, bᵢ, rate and the constant k, and the relationship is as follows:

\[
r = k \prod_i C_i^{b_i}
\]

(12)

Fortunately, under PD, for all of the chemical reactions where SF₆ and H₂O are involved, the stoichiometry number bᵢ is one. This finding suggests that the reaction rate r is proportional to the concentration of the reactants. Therefore, when traces of H₂O exist, H₂O has a capture function of F equivalent to the inhibition of the recovery reaction SFₓ + (6-x)F → SF₆. H₂O inhibits the low-fluoride sulfide SFₓ (x = 1, 2, 3, 4, 5) composite to SF₆, so that the concentration of SFₓ, SF₅, and other components are increased. Additionally, under PD, the trace amount of H₂O has always been small compared with a variety of low-fluoride sulfide SFₓ. Thus, the rates of reaction above are mainly determined by the concentration of H₂O. The higher the concentration of H₂O, the more severe the reaction and the more obvious the inhibition, as explained by the following reactions:

\[
SF₆ + OH \rightarrow SOF₂ + HF, \ k = 1.1 \times 10^{-12} \text{ cm}^3/\text{s}
\]

(13)

\[
SF₆ + O \rightarrow SOF₂ + F, \ k = 2.0 \times 10^{-11} \text{ cm}^3/\text{s}
\]

(14)

\[
SOF₂ + H₂O \rightarrow SO₂F₂ + 2HF, \ k = 2.0 \times 10^{-21} \text{ cm}^3/\text{s}
\]

(15)

Formulas (8) to (11) and (13) to (14) show that when SF₆ is mixed with H₂O, H₂O plays a role in providing OH and O. Hence, the formation of SOF₂ is promoted. Meanwhile, reactions (6) to (11) and (13) to (15) constitute a comprehensive reaction, which is the means by which SO₂F₂ is generated. The generation capacity for SO₂F₂ is determined by trot reaction (15), and with the increasing concentration of H₂O, the amount of SO₂F₂ will slightly increase. However, with nearly 10 orders of magnitude of reaction rate in (15) than the rates of reaction in (10), (11), (13), and (14), and with increased concentration of H₂O, the increase of SO₂F₂ is not obvious, as shown in Fig. 4(a).

On the other hand, the reaction between SF₄ and H₂O will occur as follows [8]:

\[
SF₄ + H₂O \rightarrow SOF₂ + 2HF, \ k = 1.5 \times 10^{-19} \text{ cm}^3/\text{s}
\]

(16)

The reactions in (16) and (12) show that when the concentration of H₂O increases in SF₆, it will promote the production of SOF₂, as shown in Fig. 4(b). However, the reaction rate constant k of reaction (16) is 2 orders of magnitude higher than reaction (15). Therefore, with the increased concentration of H₂O in SF₆, the rate of increase of the SOF₂ produced is significantly higher than that of SO₂F₂, as shown in Fig. 4(b).

The effect of H₂O on SF₆ decomposition characteristics under PD can be summarized as follows:

1. H₂O has a capture function of F which inhibits the low-fluoride sulfide SFₓ (x = 1, 2, 3, 4, 5) composite to recombine with SF₆, leading to the increase in the main low-fluoride sulfide SFₓ, SF₄, and other components. The higher the concentration of H₂O, the more severe the reaction and the more obvious the inhibition.
2. H₂O provides OH and O for the generation of oxygen-containing-sulfur-fluoride compounds, and promotes...
the generation of the intermediate product SOF₄.

(3) H₂O plays a role in promoting the generation of the
final and stable oxygen-containing-sulfur-fluoride
compounds, such as SO₃F₂ and SOF₄. However, because
the hydrolysis reaction rate of SF₄ is nearly two orders
of magnitude higher than SOF₂, the chemical reaction
rate r of SF₂ and H₂O under PD is proportional to the
concentration of H₂O. Thus, with the growth of the
concentration of H₂O in SF₆, the growth rate of SOF₂
is significantly higher than that of SO₂F₂. From the
foregoing generalizations, the impact of H₂O on SOF₂
is significantly higher than the impact of SO₂F₂. Thus,
the formation of SOF₂ has a positive linear association
with the concentration of H₂O.

4.2 Analysis of the impact of O₂ on the characteristic
decomposed component

In the case of SF₆ mixed with O₂, under the impact of
high-energy electrons produced by PD, in addition to
reactions (6) and (7), the following reactions will occur:

\[ O₂ + e → 2O + e \] (17)

Besides the fact that the free state O generated by
reaction (17) will react with SF₃ generated by PD and
generate SOF₄, the action below will happen and generate
SOF₄:

\[ SF₂ + O → SOF₄ \] (18)

Then, both SOF₂ and SF₄ react with the H₂O released by
the electrodes and the internal wall of the decomposition
equipment and generate SO₂F₂ and SOF₂. While O₂ exists,
SF₂ will be involved in the following reaction:

\[ SF₂ + O₂ → SO₂F₂ \] (19)

At present, the reaction rate constant of reaction (19) has
not been found yet. Reference [8] has given the maximum
rate constant \( k = 5.0 \times 10^{-16} \text{ cm}^3/\text{s} \). Similarly, under PD, the
stoichiometric number \( h \) of reaction (14) and the chemical
reactions SF₆ and O₂ are involved in are also equal to one,
and O₂ is always a small amount compared with a variety
of low-fluoride sulfide SFₓ. Thus, the rate of reaction in
(19) is proportional to the concentration of O₂. The higher
the concentration of O₂, the more severe the reaction and
the more SO₂F₂ is generated.

For SO₂F₂, it can be seen from Fig. 5 (a) that when the
concentration of O₂ mixed in SF₆ is less than 460ppm,
the formation of SO₂F₂ decreases with the increase of O₂.
When the concentration of O₂ is higher than 460ppm,
the concentration of SO₂F₂ is positively correlated with
the concentration of O₂ because an increase in the
concentration of O₂ in SF₆ is equivalent to the dilution of
SF₂, SF₄, SF₅, and other low-sulfur and fluorine F. Thus, O₂
plays an inhibitory effect on the reaction:

\[ SF₆ + (6 - x)F → SF₄, x = 1 \sim 5 \]

Although the concentrations of SF₂, SF₃, SF₄, and other
low-sulfur components increase with the discharge and
promote the reaction in (18) ~ (19), with the increase in
the concentration of O₂, the concentration of H₂O released by
the electrodes and the internal wall of the decomposition
equipment is diluted, making the rate of reactions in (8)
to (11) and (15) decrease. Reaction (19) is at lower status
when competing with reaction (14), (15) and (18), thus
leading to the reduction in the amount of SO₂F₂ generated
within 10 hours.

However, when the concentration of O₂ is higher than
460ppm, with a further increase of O₂, the rate of reaction
in (18) undergoes a significant increase, and the rates of
reaction in (8) to (11) and (15) are no longer significantly
reduced. This time, since the concentration of O₂ is high,
reaction (19) plays a dominant role in the generation of
SO₂F₂ when competing with reaction (14), (15), (18). Thus,
when the concentration of O₂ is above 460ppm, the yield
of SO₂F₂ increases with the increase of O₂. Hence, with a
low concentration of O₂ (the concentration of O₂ < 460
ppm), the dilution of the inherent moisture in the device is
the most important factor that affects the formation of
SO₂F₂ and the stability of the decomposition under PD.
Furthermore, the reactions in (8) to (11) and (15), (18)
play leading roles in the formation of SO₂F₂. But at high
concentration of O₂ (the concentration of O₂ > 460ppm),
reaction (19) plays a leading role in the generation of
SO₂F₂, as shown in Fig. 5(a).

For SOF₂, its formation always decreases with the
increase of O₂, but the reduction is not obvious when the
concentration of O₂ is higher than 460ppm. The reason for
the practically unobservable reduction is that with the
increase of O₂ mixed in SF₆, SF₂, SF₃, SF₄, SF₅ and other
low-sulfur, fluorine F undergoes a dilution process, thus playing
an inhibitory effect on the reaction:

\[ SF₆ + (6 - x)F → SF₄, x = 1 \sim 5 \]

Although the concentrations of SF₂, SF₃, SF₄, and other
low-sulfur components increase with the discharge, as the
concentration of O₂ increases, the concentration of H₂O
released by the electrodes and the internal wall of the
chamber is diluted at the same time. The rate of the
reaction which plays a decisive role in the generation of
SO₂F₂ is shown in the following reaction:

\[ SF₆ + H₂O → SOF₂ + 2HF, k = 1.5 \times 10^{-79} \text{ cm}^3/\text{s} \]

will decrease with the decrease in the concentration of
H₂O. This phenomenon is most prominent when H₂O is
diluted (the concentration of O₂ < 460ppm). With further
dilution of H₂O (the concentration of O₂ > 460ppm), the
5. Conclusion

(1) Both H₂O and O₂ influence the main characteristic components SO₂F₂ and SOF₂ during PD, but their by-products and degrees of influence are different. The influence of H₂O on SOF₂ is the most significant and the formation of SO₂F₂ has a positive linear relationship to the concentration of H₂O while its influence on SO₂F₂ is not obvious. The concentration of O₂ influences the formation of both SO₂F₂ and SOF₂ while the influence is much more obvious on SO₂F₂.

(2) H₂O has the ability to catch an F atom and to inhibit the low-fluoride sulfide SF₆ by recombining to SF₅, which increases the concentration of SF₅ and SF₆. H₂O offers OH and O for the formation of oxygenated-sulfur fluoride, which creates a favorable condition for the ultimate formation of SO₂F₂ and SOF₂. However, the hydrolysis rate of SF₅ is much higher than the hydrolysis rate of SO₂F₂ (nearly two orders of magnitude higher), as a result, the increase in the rate of SOF₂ is much higher than that of SO₂F₂ when the concentration of H₂O increases.

(3) When the concentration of O₂ is low, the content of H₂O in the equipment is the main factor which influences the formation of SO₂F₂. When the concentration of O₂ is high, the reaction SF₅ + O₂ → SO₂F₂ contributes mostly to the formation of SO₂F₂. Thus, O₂ is the main factor. As for SOF₂, an increase of concentration would diminish the H₂O concentration, in which case O₂ becomes the most important factor in the decrease of SOF₂.

(4) The trace levels of H₂O and O₂ play key roles on the formation of characteristic decomposed components of SF₆ during PD and have significant influence on the products, so it is necessary to study the decomposition mechanism of SF₆ under different concentrations of H₂O and O₂ under the long run PD, and research on different concentrations will help achieve sufficient knowledge on what influences the regularity in the reactions to propose correction methods accordingly.

Acquiring sufficient knowledge on the decomposition mechanism and the factors that affect variation in the reactions under PD will lay a solid foundation in using decomposed components of SF₆ to assess insulation status and will support related repair guidelines for gas insulated electrical equipment.

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