Research on the long-time operation performance of composite insulator shed hydrophobicity under hydrothermal conditions

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Abstract: Due to excellent anti-pollution flashover performance, a composite insulator has become the most frequently and widely used insulator product in transmission lines. Sheath hydrophobicity is the core factor that determines the anti-pollution flashover performance of the composite insulator. To study the change rule of insulator sheath hydrophobicity under the long-term operation condition, more than 390 samples produced by the same manufacturer that had operated for 3–22 years were extracted from the adjacent lines to eliminate the impact of the running environment and manufacturer formula. To study the reasons for hydrophobic fluctuations, surface energy tests and Fourier transform infrared spectroscopy tests were conducted on the superficial layer materials based on a two-droplet method. The change rule of the material physical and chemical properties with operation time was obtained. Next, the relationship between the surface microstructure of the material and operation time was determined by laser scanning confocal microscopy and scanning electron microscopy. Finally, based on the analysis results of surface energy and surface topography, the physical model of shed material hydrophobic variation in the operation process was obtained.

1 Introduction

Due to excellent anti-pollution flashover performance, a composite insulator is widely applied in transmission lines [1–3]. Based on statistical results, there have been over 7 million 66 kV composite insulators in current transmission lines [4]. Composite insulators, by surpassing the traditional glass and ceramic insulators, become the largest number of insulator products.

Hydrophobicity of silicone rubber shed is directly related to anti-pollution flashover performance, and it is the core index representing the operation characteristic of the composite insulator [5]. Since the hydrophobic change mechanism of materials is unclear, there is no test method for the accelerated aging of material hydrophobicity; the natural aging test is very time-consuming and costly. At the same time, the composite insulator silicone rubber material is greatly influenced by the natural environment factors such as ultraviolet, wind and water in the operation process [6–8]. In addition, the difference of process formulation is also closely related to material performance [9, 10]. Therefore, under the long-term operation condition, the change law of shed hydrophobicity is not clear.

More than 390 samples produced by the same manufacturer that had operated for 3–22 years (excluding 22 years) were extracted from the adjacent lines. Besides, the hydrophobicity of the operation material was measured. The hydrophobic change rule was studied. Furthermore, through micro-chemical analysis and microstructure analysis, the hydrophobic change rule and change mechanism of the composite insulator material in the process of long-term operation under high temperature and high humidity area were explored.

2 Test samples

The composite insulators used were taken from several adjacent alternating current transmission lines in Shenzhen, southern part of China. The region belongs to a typical subtropical maritime monsoon area, with the geographical position of east longitude 113°46′–114°37′, north latitude 22°27′–22°52′; it is situated on the border line in the tropical and subtropical belt. With an average temperature of 23°C, it is hot and has a long summer. In addition to the high temperature, Shenzhen area is also rainy and humid. Its annual average relative humidity reaches 79%, and annual rainfall reaches 2747 mm (2001). As seen from China’s average temperature distribution and average rainfall distribution in 2010 (Fig. 1), Shenzhen is one of the muggiest areas in China [11, 12]. High temperature and moisture can aggravate the ageing of the silicone rubber material. The sample products with the longest operation time had undergone severe cracking, umbrella separation phenomenon, reached the finish line of life. Hence, it could be thought that the selected samples covered the whole life cycle of silicone rubber materials.

The majority of samples selected were produced by representative manufacturer A, where the number of hanging accounted for 51% of the usage amount in the south. The products which operated for 22 years were selected from the samples of manufacturer B. A is one of the largest manufacturers of composite insulator in China. Its formulae are assumed to be representative, and according to the statistical results of China Southern Power Grid, 50% of the composite insulators serving at the site were produced by Manufacturer A. Furthermore, the immature technology and formula of early insulators make the inherent differences of materials inevitable. At the same time, Manufacturer B, as one of the few original composite insulator manufacturers, is a typical representative of the early products.

A total of 391 AC composite insulators with operational time of 3, 5, 6, 7, 9, 10, 11, 14, and 22 years were selected. Among them, three were produced by Manufacturer A; new composite insulators were selected as the control group, and their operation life was defined as 0 year. The basic information is shown in Table 1. The umbrella type of all the 500 kV samples was one large umbrella with two small umbrellas, while the type of sample operated for 22 years was one large umbrella with one small umbrella.
3 Hydrophobicity analysis

The hydrophobic performance of materials was studied by using the static contact angle method. The test system and sample are shown in Fig. 2. In the test, the filth on the silicone rubber surface was first washed with alcohol. Three groups of droplets were placed on the surface of each sample, with three drops in each group of the droplet, and the volume of the droplet is 6 μL. The three groups of droplets presented the radial distribution along the sample edge from inside to outside, labelling the serial number of 1–3. In the end, the average static contact angle of nine test points was determined as the static contact angle measurement value of the umbrella.

The static angle test results for the upper surface and lower surface of the umbrella are shown in Fig. 2. In the test, the filth on the silicone rubber surface was first washed with alcohol. Three groups of droplets were placed on the surface of each sample, with three drops in each group of the droplet, and the volume of the droplet is 6 μL. The three groups of droplets presented the radial distribution along the sample edge from inside to outside, labelling the serial number of 1–3. In the end, the average static contact angle of nine test points was determined as the static contact angle measurement value of the umbrella.

To study the material hydrophobicity migration performance, samples 3, 7, 14 and 22 were selected as the representatives for the hydrophobicity migration test. The method of quantitative painting was adopted for smearing, and kaolin was selected as the filth. Shenzhen area is located in the level c–d dirty area. Therefore, for
the filth, the following parameters were taken: equivalent salt deposit density $= 0.25 \text{ mg/cm}^2$, non-soluble deposit density $= 1.5 \text{ mg/cm}^2$; the mobility was conducted in the constant temperature humidity box, with a temperature of 24°C, and relative humidity of 10% so as to reduce volatility. The rest of the test conditions were the same as hydrophobic analysis.

According to the test results, the hydrophobic angle mobility characteristics of aging samples decreased significantly (Fig. 4). By comparing the hydrophobic angle of products with different operation years $314$ h after mobility, the hydrophobic angle of the products which operated for 3 years recovered to $99.8^\circ$, while that of the products which operated for 22 years recovered to $50.9^\circ$.

4 Micro-chemical analysis

Materials static contact angle (i.e. apparent hydrophobicity) is mainly decided by their own performance (i.e., intrinsic hydrophobicity) and their microstructure [13]. To analyse the change of hydrophobicity appearing in the operation process and exploring the reasons for the significant decline in hydrophobic migration ability, micro-chemical analysis was first conducted on the material.

4.1 Surface energy test

For the material with consistent surface microstructure roughness, the solid surface energy is directly related to hydrophobic properties. Therefore, the surface energy was tested after polishing the material (removing 1 mm thick surface material). The solid surface energy $\gamma_S$ was composed of dispersive component $\gamma_{SD}$ and polarity component $\gamma_{SP}$ [14], and they satisfied the following equation:

$$\gamma_S = \gamma_{SD} + \gamma_{SP}$$  \hspace{1cm} (1)

For solid–liquid infiltration, the solid surface energy $\gamma_S$, liquid surface energy $\gamma_L$, interaction energy $\gamma_{SL}$ and static contact angle $\theta$ satisfied Young's equation

$$\gamma_S - \gamma_{SL} = \gamma_L \cos \theta$$  \hspace{1cm} (2)

Interaction energy $\gamma_{SL}$ satisfied the following condition:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_{SD} + \gamma_{LD})$$  \hspace{1cm} (3)

By combining (2) and (3), the following result was obtained:

$$\gamma_L(1 + \cos \theta) = 2(\sqrt{\gamma_{SD} + \gamma_{LD}})$$

$$+ 2(\sqrt{\gamma_{SP} + \gamma_{LP}})$$  \hspace{1cm} (4)

On the basis of the known $\gamma_L$, $\gamma_{LD}$, and $\gamma_{LP}$, solid surface energy could be determined after measuring the static contact angle $\theta$ on the surface of the same solid material if two different liquids were used. Deionised water and $n$-hexadecane were selected as test liquids. The surface energy, dispersion component and polarity component of water were $72.8$, $21.8$, and $51 \text{ mJ/m}^2$, respectively; the surface energy, dispersion component and polarity component of $n$-hexadecane were $27.6$, $27.6$, and $0 \text{ mJ/m}^2$, respectively. The measurement method was consistent with the above-mentioned measurement method of the static contact angle.

The surface energy result showed that the surface energy of the material increased gradually with the operation year (Fig. 5), which indicates the positive correlation between the operating years and intrinsic contact angles of silicone rubber.

In an air environment, if the solid surface energy was higher, the water droplets tend to spread out on the material surface as far as possible in the process of infiltration to reduce the contact area with solid and air, and reduce energy. Hence, the higher material surface energy means a smaller surface contact angle.

4.2 Fourier transform infrared (FTIR) spectroscopy test

To further analyse the change law of the chemical properties of the materials, FTIR was performed to test the shallow layers of silicone rubber.

For main chain Si–O–Si, the absorption peak height of sample Si–O–Si (1020 cm$^{-1}$) [15] was compared (Fig. 6). For the silicone rubber samples with longer operation time, the absorption peak of the shallow layer dropped significantly because the silicone material was affected by UV, heat and electricity in the process of operation. UV and corona discharge could interrupt the weak spot
of main chain Si–O–Si in silicone rubber, decrease the Si–O–Si absorption peak. At the same time, the morphological changes of characteristic peaks also indicated the change of main chain Si–O–Si. Complete main chain Si–O–Si was longer, and the absorption peak was an obvious double-peak structure; the two absorption peaks at 1020 and 1087 cm⁻¹ were closer in height. After the fracture of main chain Si–O–Si, the integrity of the main chain decreased; the absorption peak at 1020 cm⁻¹ was no longer obvious; the main peak of Si–O–Si became unimodal gradually.

The C–H bond reflects the integrity of an internal silicone rubber material side bond (Fig. 6). Among the insulators with long operation years, C–H bond absorption peaks at 790–840, 1255–1270, and 2960 cm⁻¹ exhibited clear decrease, showing that the side bond peaks connected to the Si–O–Si main chain broke during the operation [16]. The decrease of the side bond weakened the shielding effect and made the material more polarised, thus increasing material's surface, and decreasing the intrinsic hydrophobic performance.

At the same time, the content of strong polar groups –OH increased with the operation years. Being affected by oxidation, the surface temperature of the composite insulator rose in high temperature and high humidity environments; water became an auxiliary catalyst and caused the hydrolysis reaction of the silicone rubber. All kinds of free radicals mutually combined, and formed hydrophilic silanol groups and silane alcohol on the material surface, increasing the material polarity and decreasing hydrophobic properties.

Therefore, the weakened shielding effect caused by side bond fracture and the hydrolysis reaction of surface silicone rubber in high temperature and high humidity environment were the main reasons for the increase in material surface energy and the decline in intrinsic hydrophobic angle.

5 Microstructure analysis

5.1 Laser scanning confocal microscopy (LSCM) test

The preliminary observation was conducted on the surface of the silicone rubber material samples with different operation years by LSCM. Based on the observation results, the samples with shorter operation years had no obvious crack and pulverisation on the surface, so they had a dense structure. In contrast, the samples with longer operation years had an obvious crack on the surface (see Fig. 7c), and were marked with much white powder. To further analyse the surface condition, scanning electron microscopy (SEM) was used for testing.

5.2 SEM test

The surface microstructure of silicone rubber samples with different operation years was observed by SEM (see Fig. 8). According to the observation results, the product with shorter operation time had a relatively smooth surface, while the product with long operation time had a raised surface.

By combining with the analysis results of FTIR in the above section, in the operation process, the main chain structure of the silicone rubber surface material was destroyed; the mechanical properties of the materials decreased; external force, such as sand would more likely cause surface erosion. At the same time, after the main chain was damaged, the originally stable package packing three-dimensional structure was also destroyed; under the influence...
of diffusion, inner packing was precipitated to the surface, further increasing the material surface roughness.

6 Discussion

The hydrophobic angle of water droplets on the solid surface could be described with Cassie model and Wenzel model (Fig. 9). Water droplets filled the grooves on the material surface in the Wenzel model [17]. In contrast, water droplets failed to completely fill the groove, which contained some air in the Cassie model.

In the Wenzel model, the actual contact area of water droplets and silicone rubber materials was higher than the apparent contact area (projection of the contact area), with the ratio between the two areas being \( r \). When the roughness of the material is higher, \( r \) will be higher and there will be more cracks in the material. It was assumed that the Eigen hydrophobic angle of the material was \( \theta_e \). If the material was absolutely smooth, its static contact angle would be \( \theta_e \), which was mainly determined by the chemical properties of the material. When the material roughness is \( r \), the surface contact angle \( \theta \) satisfies

\[
\cos \theta = r \cos \theta_e
\]  
(5)

When the material itself is hydrophobic, \( \theta_e > 90^\circ \); when the material roughness rises, \( r \) increases and the hydrophobic angle \( \theta \) also rises. When the material performance declines in the process of operation, \( \theta_e \) drops, and hydrophobic material angle \( \theta \) also declines.

In the Cassie model, water could not fill the surface, but could partially soak up the bulge. At this time, the hydrophobic ability satisfied the following relations (6), where \( f_s \) is the ratio of the raised area and the apparent contact area. When there is sharp protuberance or deep fracture on the material surface, \( f_s \) will sharply reduce, when the contact angle is closer to 180°, and the material shows very good hydrophobic performance

\[
\cos \theta = f_s (\cos \theta_e + 1) - 1
\]  
(6)

For the surface of the silicone rubber material in the process of actual operation, the contact of water with materials should be the Cassie model combined with the Wenzel model. Since the material itself is hydrophobic, water cannot infiltrate deep cracks, but it can infiltrate some shallow cracks. At the initial stage of the operation, the microstructure change is lesser; infiltration is mainly in the Wenzel model; the decrease of the material performance itself plays a leading role in the process of hydrophobic changes, so the hydrophobic performance reduces with the loss of the operation years. With the passage of the time, the material microstructure further deteriorates; cracks began to gradually deepen; the water cannot fill the microporous structure on the surface; then, the contact of water with materials begins to accord with the Cassie model; the influence of the microstructure on hydrophobic performance plays a leading role, and the hydrophobic performance materials significantly increases. Thus, the surface hydrophobic angle presents an apparent U-shaped distribution with the extension of the operation years.

7 Conclusion

(1) Under long-term operation conditions, the hydrophobic performance and operation year of the composite insulator silicone rubber material show an U relationship (rising after falling), the hydrophobicity was not a convective index for the life time evaluation during the operation.

(2) In the earlier and middle stage of operation, the silicone rubber material surface is compact and smooth; material performance is dominant; weakened side bond block and silicone rubber hydrolysis reaction make the material polarity degree and surface energy increase, being the main reason for the decline in silicone hydrophobic performance.

(3) During the later period of the operation, the inside main chain of the silicone rubber material is broken; external erosion and packing precipitation process make material surface roughness reduce; surface microstructure dominates; uneven micro–nanostructure on the surface is the main reason for the increase of silicone hydrophobic performance.
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